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Desulfurization of diesel by oxidation/extraction scheme: influence of the extraction solvent

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Abstract

Due to the future specifications for sulfur content in middle distillate like diesel, a lot of research work has been done to develop alternative methods for desulfurization. This work presents the results for the desulfurization of diesel by an oxidation and extraction (O/E) scheme. This process can be considered like a post-treatment to the traditional hydrodesulfurization. A diesel with 320 ppmw of total sulfur was employed to evaluate the elimination of sulfur compounds. The oxidation reaction was carried out with hydrogen peroxide at 30 wt.%, in a heterogeneous system with a WO_x/ZrO_2 catalyst at 15 wt.% of W; the extraction was performed with four polar solvents. The experiments were done in a batch reactor at 333 K and atmospheric pressure. As an average, the sulfur content in the diesel after treatment was 90 ppmw. A speciation of the sulfur compounds before and after O/E scheme was also included. Additionally, solubility data of dibenzothiophene sulfone in the polar solvents as a function of temperature were obtained.

Keywords: Oxidation; Extraction; Diesel; Sulfone

1. Introduction

The new regulations in sulfur content in fuels have motivated the search of alternative methods for desulfurization [1]. Technologies employed nowadays for reducing sulfur content in diesel fuel currently reaches down to 150–500 ppmw, the goal of the upcoming regulations is to achieve 15 ppmw. The main problem of traditional technologies, like hydrotreatment process, to fulfill this target is related with the type and quantity of polyaromatic sulfur compounds such as dibenzothiophene (DBT) and its derivatives, especially 4,6-AlkylDBT's. These compounds have a steric hindrance and their reactivity with catalysts is very slow. An alternative to avoid it is the oxidation and removal of sulfur compounds [2–4].

Hulea et al. [5], reported in 2001 the oxidation of tetrahydrothiophene (THT), diphenyl sulfide (PhSPh), thiophene (T), 2-acetylthiophene (2-AcTh), 2,5-dimethylthiophene (2,5-DMT), benzothiophene (BT) and dibenzothiophene (DBT) with H_2O_2 over molecular sieves such as TS-1, Ti-beta and Ti-HMS. Palomeque et al. [6], studied in 2002 the oxidation of DBT with H_2O_2 over a hydrotalcite and MgLa mixed oxide. On the other hand, Petrostar announced a commercial oxidation process for desulfurization based on a peroxyacetic acid catalyst [7]. Also, UNIPURE showed a commercial oxidative process based in the O/E scheme [8]. More recently, Lyondell Chemical Company described how it is possible to eliminate the sulfur compounds with an oxidation process [9]. The main advantages of this new technology are low costs, moderate operational conditions, and short residence time, there is no need of additional hydrogen consumption, as known from the open literature [7–9].

In this work, new data of the (O/E) scheme of sulfur compounds present in diesel were obtained using hydrogen peroxide (H_2O_2) at 30 wt.% in a heterogeneous system with a tungsten/zirconia (WO_x/ZrO_2) catalyst. The extraction of

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the oxidized sulfur compounds was done with four polar solvents. A speciation of the sulfur compounds before and after O/E was also included. Additionally, measurement data of the solid–liquid equilibrium (SLE) of dibenzothiophene sulfone ($DBTO_2$) in four polar solvents were obtained as a function of temperature.

From these results, it was possible to establish the role that plays the type of solvent during the extraction of sulfur compounds present in diesel before and after the oxidation step.

2. Experimental

2.1. Synthesis of WO_x/ZrO_2 catalyst

$ZrO_{2-x}(OH)_{2x}$ was prepared by hydrolysis of a 0.5 M $ZrOCl_2$ solution (Aldrich, 98% $ZrOCl_2{\cdot}8H_2O$) using dropwise addition of NH_4OH (Baker, 28% NH_3) until a final pH value of 10 [10,11]. WO_x/ZrO_2 sample was prepared by impregnation of $ZrO_{2-x}(OH)_{2x}$ with an ammonium metatungstate $[(NH_4)_6(H_2W_{12}O_{40}){\cdot}nH_2O]$ solution (Strem Chemicals, 99.9%) maintaining the pH = 10 (tungsten content was 15 wt.%). The whole mixture was stirred and heated to evaporate the water content followed by calcination in air for 3 h at 773 K.

The material was characterized by X-ray diffraction (Siemens D500) using a Cu Kα radiation at a scanning rate of 0.003° s^{-1} and a Ni filter. The generator conditions were 30 kV and 20 mA in the angular range of 5–70° (2θ). The surface area (BET) was estimated from the adsorption–desorption isotherm of N_2 determined at its boiling temperature (Micromeritics ASAP-2000).

2.2. Oxidation/extraction experiments

The experiments were carried out in a glass batch reactor under stirring at 1000 rpm at atmospheric pressure. A heated circulating bath (PolyScience) was used to control the temperature (±0.1 K). The reaction temperature was set at 333 K and measured with a Fluke digital thermometer calibrated periodically against the triple point of water with a resolution of ±0.1 K.

50 ml of diesel with 320 ppmw of total sulfur obtained from hydrotreating of Mexican Straight Run Gas Oil (SRGO, Table 1) were mixed with 50 ml of γ-butyrolactone ($C_4H_6O_2$, 99.0 mol% Aldrich, boiling point bp = 477 K), *N*,*N*-dimethylformamide (DMF, 99.9 mol% HPLC Aldrich, bp = 426 K), 2-ethoxyethanol ($C_4H_{10}O_2$, 99.0 mol% Aldrich, bp = 409 K) or acetonitrile (MeCN, 99.93 mol% HPLC Tecsiquim, bp = 355 K) in the presence of 0.2 g of WO_x/ZrO_2 catalyst containing 15 wt.% of W. The system was heated to 333 K under stirring where 0.4 ml of H_2O_2 at 30 wt.% (J.T. Baker) were added. Samples were taken every 2, 5, 15, 30 and 60 min. The diesel rich phase was analyzed with different techniques described afterwards.

2.3. Non-oxidative extraction experiments

Samples with 150 ml of solvent and 150 ml of diesel were mixed in a batch container for 3 h at 298 K. After stirring, the sample remained static for 12 h at the same temperature.

Table 1
Properties of diesel before and after solvent extraction

Property	Diesel feedstock	Diesel after extraction with			
		$C_4H_6O_2$	DMF	$C_4H_{10}O_2$	MeCN
Total sulfur (ppmw)	320	180	130	180	220
Total nitrogen (ppmw)	55	17	5831	14	4093
Cetane index	55.3	57.7	57.9	54.3	57.4
Total aromatics (wt.%)	26.6	24.0	23.7	23.3	24.0
Monoaromatics (wt.%)	17.4	16.2	16.1	16.1	16.3
Diaromatics (wt.%)	7.4	6.6	6.5	6.4	6.8
Polyaromatics (wt.%)	1.8	1.2	1.1	0.8	0.9
Density at 288 K (kg m^{-3})	843.5	837.3	835.9	846.6	837.4
D-86 IBP (K)	501	473	427	406	353
5%	527	525	508	524	528
10%	538	541	547	538	539
15%	545	548	549	542	545
20%	550	552	552	546	551
30%	558	561	559	554	559
40%	566	568	566	564	566
50%	573	575	573	573	573
60%	580	581	580	582	580
70%	587	588	588	589	588
80%	596	597	596	597	596
85%	601	602	601	604	602
90%	607	608	607	609	608
95%	618	619	618	615	619
D-86 FBP (K)	628	631	631	628	630

Phase separation was done with a Pyrex brand squibb separatory funnel. Again, the diesel rich phase was analyzed as follows.

2.4. Analysis procedures

Energy-dispersive X-ray fluorescence spectrometry was used to determine the total sulfur in samples by Horiba SFLA 1800. The test method is based on the ASTM D-4294 standards. The total nitrogen content was measured with the ASTM D-4629 method.

The ASTM D-5186 method was used for the determination of monoaromatic, polynuclear aromatic hydrocarbon and total aromatic compounds in diesel by supercritical fluid chromatography.

To establish the (O/E) effect in the content and type of organic sulfur compounds, a speciation of diesel was done for samples that have been taken at 60 min of reaction according with the ASTM D-5326 method, the sample was analyzed by gas chromatography with an appropriate sulfur selective detector.

The cetane index was calculated using the following equation (ASTM D-976):

$$\mathrm{CI} = 454.74 - 1641.416D + 774.74D^2 - 0.554B + 97.803(\log_{10} B)^2 \quad (1)$$

where CI is the cetane index, D the density at 15 °C (g/cm^3), B the mid-boiling temperature (°C), determined by the test method ASTM D-86 and corrected to standard barometric pressure.

2.5. Solubility of dibenzothiophene sulfone in solvents

To study the solubility of the sulfones in the solvents or diesel, an experimental cell of 10 cm^3 was designed at our institution (Fig. 1). Degassing was carried out in situ by freezing–evacuating–thawing cycles. Afterwards, the cell was placed in a bath with a temperature control. To help the contact between solid and liquid phases, the samples were mixed with a magnetic stirrer at 600 rpm (Fig. 2). A mixture of a known overall concentration of dibenzothiophene sulfone (DBTO$_2$, 97 mol%, Aldrich) with one of the polar solvents or diesel was prepared and placed inside the cell to find out the solubility data. The experiment consisted of determining the temperature at which the last trace of the solid solute disappeared while being slowly heated [12]. The temperature obtained represents the liquid saturation, and it was reported from the mean of at least six measurements on each one of the binary samples. The technique was fast and highly accurate. The estimated error in composition is ±0.0060 in solute weight fraction and ±0.1 K in temperature.

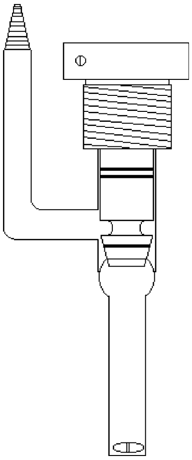

Fig. 1. Experimental cell to determine the SLE.

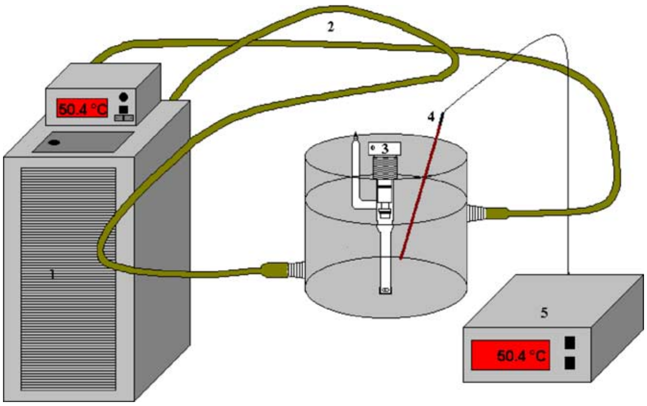

Fig. 2. Experimental equipment used to determine the SLE. (1) Heated circulating bath; (2) hoses; (3) cell; (4) platinum resistance probe; (5) thermometer.

3. Results and discussions

The XRD pattern of WO$_x$/ZrO$_2$ calcined at 773 K shows only two wide bands in the 18–40 and 40–70° ranges in angular displacement (2θ), indicating an amorphous structure and/or a small crystallite size (<4 nm), in agreement with a previous work of Barton et al. [13]. These authors reported that the crystallization temperature in the WO$_x$/ZrO$_2$ system was strongly dependant of the tungsten surface concentration and dispersion.

The presence of tungsten oxide strongly influences the surface area in comparison with pure ZrO$_2$ [14]. The surface area of pure ZrO$_2$ and WO$_x$/ZrO$_2$ was 90 and 125 m^2/g, respectively, as can be seen, the specific surface area of the WO$_x$/ZrO$_2$ catalyst is much larger than that of pure ZrO$_2$ calcined at the same temperature. Sohn and Park [15], showed in 1998 that surface area increases gradually with increasing tungsten oxide content up to 20 wt.% of WO$_3$, what is associated with the interaction between WO$_x$ species and ZrO$_2$ that protects catalysts from sintering. A more detailed characterization of the WO$_x$/ZrO$_2$ system was reported previously [11,16].

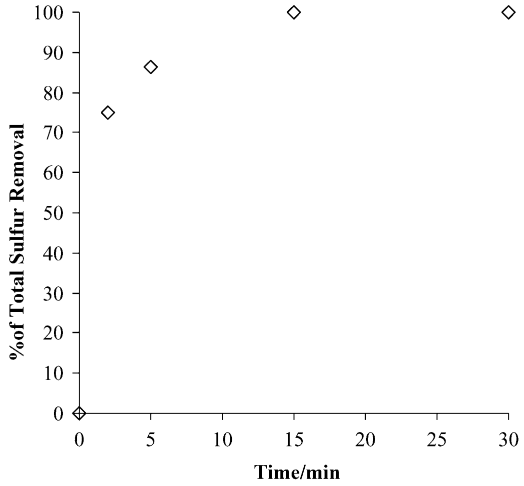

Fig. 3. Percentage of total sulfur removal after the (O/E) scheme. The reaction conditions were 0.2 g of WO_x/ZrO_2 catalyst containing 15 wt.% of W, 50 ml of model solution (DBT + *n*-heptane with 500 ppmw of total sulfur), 50 ml of MeCN, 0.2 ml of H_2O_2 at 30 wt.%, 1000 rpm and 333 K.

As a reference system, the (O/E) of DBT in *n*-heptane (J.T. Baker 99.5 mol%) at 333 K was selected. After the extraction of the $DBTO_2$ with acetonitrile, it can be noticed in Fig. 3 that the sulfur removal after 15 min of reaction was almost 100%. Hulea et al. [5] worked with similar reaction conditions but with a catalyst based upon Ti-beta. After 300 min of reaction, the authors got 60% of DBT conversion. By the other hand, Palomeque et al. [6] worked at similar reaction conditions using a Mg–La hydrotalcite catalyst. After 60 min of reaction, the DBT conversion was almost 100%. Although Palomeque's experiments and ours are in good agreement, our results demonstrate that not only the DBT conversion is high but also the sulfone extraction is good.

After working with a model solution, the (O/E) of a Mexican diesel was done. The cetane index of every test was calculated using Eq. (1), considering the mid-boiling temperature and the density at 288 K (Table 1). These values are higher in comparison with the diesel feedstock except for the case of $C_4H_{10}O_2$.

The total aromatics content has a decrease when the polar solvent was used during the extraction.

The IBP is very close to the boiling point of pure solvents because of a small amount of solvent remains in the diesel rich phase after extraction.

In Table 2, the results of the speciation of AlkylDBT's compounds are shown. This analysis was done before and after the desulfurization of diesel with the (O/E) scheme. It could be observed that the remaining sulfur compounds are mainly compounds with steric hindrance, 4,6-dimethyl-DBT is the most abundant compound found. The results showed that after (O/E) scheme, the removal of 4,6-dimethyl-DBT is 81.3% for the best case ($C_4H_{10}O_2$), this result is very important since it shows that for real feedstock like diesel there is a synergism between the catalyst and the extraction solvent that could be improved in the achievement of 15 ppmw of sulfur through (O/E) scheme.

In Table 3 is showed a comparison between the results of sulfur, nitrogen and aromatics removal of the feedstock using the (O/E) scheme after 60 min of reaction and the non-oxidation extraction method. The total sulfur content was

Table 2
Effect in the polyaromatic sulfur compounds content before and after the (O/E) scheme

Compound	Sulfur before (O/E) scheme (ppmw)	Sulfur after (O/E) scheme (ppmw)			
	Feedstock	$C_4H_6O_2$	DMF	$C_4H_{10}O_2$	MeCN
4,6-Dimethyl-DBT	96	25	30	18	30
2,4,6-Trimethyl-DBT	21	4	5	5	6
3,4,6-Trimethyl-DBT	6	4	5	5	6
4-Ethyl,6-methyl-DBT	29	10	14	9	11
1,4,6-Trimethyl-DBT	5	3	4	4	5
4,6,8-Trimethyl-DBT	14	11	14	11	11
4,6,9-Trimethyl-DBT	9	6	8	7	9
Others	140	27	44	71	62
Total	320	90	124	130	140

Table 3
Comparison between oxidation/extraction scheme vs. non-oxidative extraction scheme

	$C_4H_6O_2$	DMF	$C_4H_{10}O_2$	MeCN
Percentage of total sulfur removal with the (O/E) scheme	72	61	59	56
Percentage of total aromatics removal with the (O/E) scheme	25	30	28	20
Percentage of total nitrogen removal with the (O/E) scheme	90	–	83	–
Percentage of total sulfur removal with only the extraction scheme	45	53	40	27
Percentage of total aromatics removal with only the extraction scheme	10	10	12	10
Percentage of total nitrogen removal with only the extraction scheme	69	–	75	–
Dipole moment (Debye)	4.12	3.86	2.08	3.44

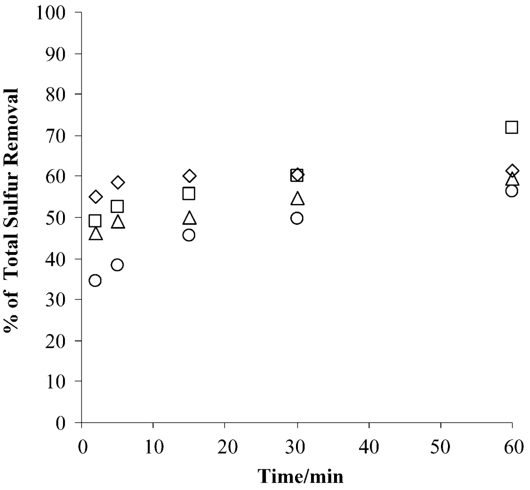

Fig. 4. Influence of solvents in the O/E scheme desulfurization. (□) $C_4H_6O_2$(1) + $DBTO_2$(2); (◇) DMF(1) + $DBTO_2$(2); (△) $C_4H_{10}O_2$(1) + $DBTO_2$(2); (○) MeCN(1) + $DBTO_2$(2).

reduced up to 72%. It is clear that the performance in the removal of sulfur compounds depends on the type of solvent used during the extraction step. Fig. 4 shows the percentage of total sulfur removal versus time for the solvents used in this work; the best result is obtained when $C_4H_6O_2$ is used. Regarding with the removal of total aromatics, higher values were obtained through (O/E) method.

The total nitrogen content decreases significantly during the reaction, but it is quite sensitive when the (O/E) method is applied. For the cases of DMF and MeCN, it was not possible to quantify the total nitrogen content because the solvent itself contributes to the measurement. It cannot be discard the fact that this high removal of nitrogen compound from the feedstock contributes to the sulfur removal.

A relationship between the dipole moment for each solvent and the sulfur and nitrogen removal was observed. As the dipole moment of the extraction solvent decreased, the total sulfur and nitrogen contents increased. However, the results obtained suggest that the dipole moment is not the only important factor in the (O/E) scheme, the anomalous behavior in the MeCN indicated that the electronegative difference between the heteroatom of oxygen and nitrogen could be a very important aspect to improve the efficiency in the sulfur removal. This demonstrated the importance of the thermophysical properties of the solvent used during the sulfone extraction, but also should be considered that there is a synergism between the catalyst, the solvent and the oxidant. It is well known that aprotic solvents, like $C_4H_6O_2$, DMF, $C_4H_{10}O_2$, and MeCN, enhance water and hydrogen peroxide dissociations to obtain OH^- and HO_2^-, respectively. The perhydroxyl ion (HO_2^-) is quite stable in these solvents, and interacts with the hydroxyl groups formed during water dissociation to produce the superoxide radical O_2^-. This radical reacts with the WO_x species present at the catalyst surface to generate a highly oxidant system [17–19].

In Fig. 5, the results of the solubility of $DBTO_2$ in the four solvents and diesel are showed. The $DBTO_2$ is barely soluble in diesel at all the temperatures plotted, and it suggests that the $DBTO_2$ could be removed easily even with simple physical methods. The curves indicate that solubility decreases according with the following sequence: DMF > $C_4H_6O_2$ > MeCN > $C_4H_{10}O_2$. At the left side of each curve we will have a totally miscible system. These curves could also help us to establish the amount of solvent require to remove a certain amount of $DBTO_2$. This information is useful to select a solvent for the extraction step in the (O/E) scheme. After analyzing the results of Tables 1 and 2, it could be expected that the $C_4H_6O_2$ should be the best solvent for the sulfone extraction, but it was not that way as was demonstrated in Fig. 5. These results confirm that there is a synergism between the catalyst and the extraction solvent, which participates during the chemical reaction.

Finally, some industrial aspects for the application of the system reported in this work have been previously published by Ramírez-Verduzco et al. [3].

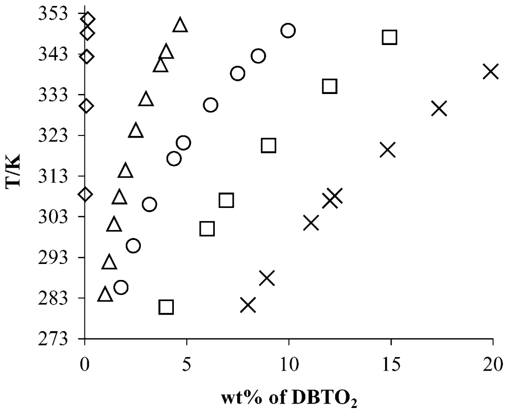

Fig. 5. Solubility of $DBTO_2$ in four polar solvents and diesel: (◇) diesel(1) + $DBTO_2$(2); (□) $C_4H_6O_2$(1) + $DBTO_2$(2); (×) DMF(1) + $DBTO_2$(2); (△) $C_4H_{10}O_2$(1) + $DBTO_2$(2); (○) MeCN(1) + $DBTO_2$(2).

4. Conclusions

A WO_x/ZrO_2 catalyst was tested for the (O/E) scheme desulfurization on a diesel with 320 ppmw of total sulfur obtained from hydrotreating of Mexican Straight Run Gas Oil (SRGO). The above results therefore suggest that this simple approach can be the basis for obtaining ultra-low sulfur-containing diesel oil with up to 90 ppmw at mild conditions (333 K and 101.3 kPa) after 60 min of reaction.

In general, the aprotic solvents with a high dipole moment are better to remove of corresponding oxide sulfur compounds.

The extraction of sulfur compounds was more effective when it is carried out along with the oxidation procedure.

In all cases, the total sulfur content is so far of 15 ppmw, however, the effect of the type of solvent used during the extraction step was established as well as its synergism with the catalyst. The information obtained in this work will be used to generate a better understanding to evaluate the potential of the (O/E) scheme for the production of ultra low sulfur diesel (ULSD). Efforts are being done to establish a detail mechanism of the (O/E) scheme considering the effects of the catalyst, the solvent and the oxidant.

Acknowledgements

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