

## New Gas-Phase Catalytic Oxidative Processes for Desulfurization of Diesel Fuel

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### Abstract

An effective gas-phase oxidative desulfurization (ODS) process was proposed. The process was studied in a laboratory reactor with a proprietary catalyst at 300–400 °C and ambient pressure with model fuels represented by thiophene, dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (DMDBT) dissolved in octane, isooctane or toluene. The reactivity of different sulfur containing molecules in ODS was shown to increase in the sequence: thiophene < DBT < DMDBT. The main sulfur containing product of oxidation of these compounds was SO<sub>2</sub>. During the gas-phase ODS both processes of sulfur species oxidation and processes of their adsorption were observed and studied. Based on the conducted studies, different ODS process designs comprising its integration with adsorption and regeneration processes and with conventional hydrodesulfurization (HDS) process were proposed. One scheme is based on alternating regimes of ODS and catalyst regeneration in two reactors: sulfur is removed from organic feedstock by oxidation and adsorption in one reactor while simultaneous regeneration of the catalyst that has accumulated sulfur compounds takes place in another reactor. Two other schemes are based on joint use of ODS and HDS. The conventional HDS process is most effective for removal of low-boiling sulfur containing compounds reactive with respect to hydrogen, while removal of refractory sulfur compounds, such as DMDBT is more easily achieved by gas phase ODS. Thus the combination of these processes is expected to be most efficient for deep desulfurization of diesel fuel.

### 1. Introduction

The specifications and quality changes of transportation fuels represent the most challenging problems for the refiners in the new millennium. The worldwide tendency is towards more severe specifications. New diesel fuel specification, particularly for the industrialized nations, such as Europe, U.S., and Japan, requires drastic reduction in the sulfur contents [1] (Table 1). Other countries are following the footsteps of the industrialized nations to increase the fuel quality to meet the stringent specifications.

For example, in the Clean Air Act Amendments of 1990, the EPA imposed a reduction of the sulfur content in road diesel to 500 ppmw, effective in 1993. In October 2002, the EPA completed its Tier II program, reducing the sulfur content in diesel to

15 ppmw of sulfur, effective June 2010. The “Ultra Low Sulfur Diesel Fuel” (ULSDF) represented 80% of the market in 2006. The cetane number and aromatics content of the diesel remained unchanged at 40 and 35 vol.%, respectively.

The European diesel fuel specifications have been more stringent than the U.S. specification. The European sulfur specification was lowered from 350 ppmw (2000 specification) to <50 ppmw in 2005 and now is <10 ppmw. In addition, European parliament is considering increasing the cetane number higher than the current specification of 51. To meet these stringent specifications, refineries must make substantial investments.

New requirements for ultra-low sulfur content (10 ppmw) in liquid motor fuels (Table 1) demand novel approaches in reactor and process design for

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ultra-deep desulfurization. The gas phase oxidative desulfurization (ODS) was initially proposed for desulfurizing petroleum fractions [2]. Then in a series of papers Yong Lu and coauthors [3, 4] have showed that the aerobic oxidative removal of gasoline-range organosulfur compounds is feasible at atmospheric pressure and moderate temperatures: 300–400 °C on Cu-CeO<sub>2</sub>, Pt-CeO<sub>2</sub> and Cu-Zn-Al catalysts. So, the gas phase oxidative desulfurization of refractory sulfur compounds of motor fuels with air may become a new promising technology for removal of refractory sulfur compounds [5] and offer better economic solutions and incentives in fuel desulfurization than HDS.

**Table 1**

Changes of sulfur specifications of motor diesel fuels in Europe and U.S. over time

Country/Property	Europe 2000	Europe Since 2009	US 1993	US Since 2006
Sulfur, ppmw	350	10	500	15
Cetane Number	51	51	40	40
Aromatics, vol.%	-	-	35	35
Poly Aromatics, wt.%	11	11	-	-

The publications [3, 4] have demonstrated a fundamentally new possibility of selective oxidation of sulfur containing compounds to SO<sub>2</sub> in the presence of air at 300 °C and atmospheric pressure. The authors found Cu-Zn-Al catalyst demonstrated the highest oxidative activity in the ODS of diesel fuels although they did not study its high sorption properties that also should be taken into account. So, we selected an oxide catalyst with Cu-Zn-Al composition for testing gas-phase ODS process and catalyst sorption capacity with a series of thiophene derivatives with a purpose of further development of different ODS process designs. Here we discuss promising ODS process designs, such as ODS integration with adsorption and regeneration processes and with the conventional HDS process.

## 2. Experimental

### 2.1. Catalyst preparation

A new Cu-Zn-Al catalyst used in this study was prepared by precipitation from metal nitrates solution with a solution containing sodium carbonate and sodium hydroxide with appropriate concentrations and subsequent thermal treatment. The detailed procedure of the catalyst preparation is described in [6]. Its chemical composition was Cu – 43 wt.%, Zn – 25 wt.%, Al – 7 wt.%. According to XRD data, the catalyst contains CuO and ZnO phases and high-

ly dispersed (Cu, Zn)Al<sub>2</sub>O<sub>4</sub> spinel phase. The specific surface area (S<sub>BET</sub>) of the catalyst calcined at 500 °C was 95 m<sup>2</sup>/g, the pore volume (V<sub>pore</sub>) was equal to 0.25 cm<sup>3</sup>/g and the average pore diameter (D<sub>pore</sub>) was 9.5 nm.

### 2.2. Characterization of feedstocks and catalysts

The chemical composition of the prepared catalyst was determined by the inductively coupled plasma – atomic emission spectrometry (ICP-AES) method using the Baird Plasma Spectrovac instrument.

The thermogravimetric and differential thermal analysis was carried out in a NETZSCH STA 449 C apparatus. Experiments were conducted over the temperature range from room temperature up to 1000 °C at the heating rate of 5 °C/min in oxygen (15 mL/min) and He (50 mL/min) mixture. Mass-spectra of the products of thermal destruction were registered using MS QMS 403 Aeolos in the range of m/z 1–300 amu.

Sulfur content in feedstocks and products after ODS tests was measured with an X-ray Fluorescence Energy Dispersive Sulfur Analyzer “ASE-2”.

Analysis of hydrocarbon composition of feedstocks and products after ODS tests was conducted using chromat-mass spectrometer SATURN-2000 equipped with a quartz capillary column (l = 30 m, ID = 0.25 mm) packed with NZHF HP-5 sorbent (detection limit – 100 ppm), gas chromatograph Kristal-2000 M, equipped with FID and a quartz capillary column (l = 30 m, ID = 0.25 mm) packed with NZHF HP-5 sorbent (detection limit – 10 ppm) and gas chromatograph Agilent 6890N equipped with JAS AED on a quartz capillary column 19091J-413 HP-5, 30.0 m × 0.32 mm × 0.25 mm (detection limit – 5 ppm).

### 2.3. ODS tests

ODS process was tested with model fuels containing mixtures of thiophene, DBT or 4,6-DMDBT in n-octane, iso-octane or toluene. Sulfur content used was 0.1 or 0.5 wt.%. The experiments were conducted in a fixed bed reactor placed into a furnace. The catalyst loading of 0.5–1.0 mm fraction was 2 g.

## 3. Results and Discussion

### 3.1. Reactivity of different sulfur containing compounds in gas-phase ODS

Three different sulfur containing compounds including thiophene, dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (DMDBT) were selected for ODS experiments. The experiments were

conducted using a solution of sulfur containing compounds in toluene (0.1 wt.% S) at variation of the temperature and O<sub>2</sub>/S ratio.

The results of comparative testing of model fuels containing thiophene, DBT or DMDBT in toluene (0.1% S) are presented in Table 2. The results show that reactivity of 4,6-DMDBT in toluene is two times higher than that of DBT in toluene and 2.5 times higher in comparison with that thiophene in toluene. The sulfur removal from model fuel is increased from 22 to 53% at O<sub>2</sub>/S = 60 and from 27 to 70% at O<sub>2</sub>/S = 140 at change of sulfur containing compound nature from thiophene to DMDBT. It means that reactivity of 4,6-DMDBT is higher than that of DBT and thiophene, which is in agreement with literature data [3, 7, 8].

In case of DMDBT the conversion of sulfur to SO<sub>2</sub> attains 90% at 380-435 °C, and sulfur removal from liquid phase analysis is ca. 80% at 380 °C.

### 3.2. Influence of solvent nature on the efficiency of the ODS process

To study the effect of solvent nature on the efficiency of the gas-phase ODS process two types of solvents were selected (octane as saturated and toluene as aromatic hydrocarbon). The results of these studies are given in Table 3.

Experiments with a model octane-based fuel with sulfur content 0.5 wt.% on the Cu-Zn-Al cata-

lyst shows that the conversion of thiophene into SO<sub>2</sub> is 88-89%, while the measured conversion in liquid phase is 82-83% at 300-320 °C.

The results of study of ODS of thiophene in toluene solution (Table 3) show that the use of aromatic solvent leads to a significant decrease of the sulfur removal efficiency. The thiophene conversion at similar conditions found from the composition of gas phase products and by liquid phase analyses decreases to ca. 20-30%. This decrease of the thiophene conversion is possibly due to higher reactivity of toluene in catalytic oxidation in comparison with octane. Therefore, more oxygen is consumed for the oxidation of the hydrocarbon and less is consumed for the oxidation of thiophene.

### 3.3. Analysis of feedstocks and products

#### 3.3.1. DBT and thiophene in isooctane and octane

To understand general pathways of sulfurorganic conversion in the ODS process, the composition of condensed products was studied and compared with the feedstock initial composition. Taking into account that sulfur dioxide evolved into the gas phase may be partly dissolved in the hydrocarbon part of the fuel, we studied the solubility of SO<sub>2</sub> in octane and toluene. It was shown that the SO<sub>2</sub> solubility in octane and toluene at room temperature did not exceed 15 and 80 ppm, respectively.

**Table 2**

Thiophene, DBT and 4,6-DMDBT transformation in their solutions (0.1 wt.% S) in toluene during gas phase ODS process over Cu-Zn-Al catalyst

S compound	T, °C	O <sub>2</sub> /S	GHSV, h <sup>-1</sup>	C <sub>CO<sub>2</sub></sub> , vol.%	C <sub>SO<sub>2</sub></sub> , vol.%	Sulfur conversion to SO <sub>2</sub> , %	Sulfur removal, % (liquid phase analysis)
Thiophene	340	60	1500	15.0	0.093	18	22
DBT	340	60	1500	15.5	0.082	24	27
DMDBT	340	60	1500	15.0	0.141	42	53
Thiophene	370	140	3000	12.1	0.60	25	27
DBT	370	140	3000	12.9	0.059	39	36
DMDBT	370	140	3000	14.1	0.079	52	78

**Table 3**

Influence of hydrocarbon environment on the efficiency of gas-phase ODS of thiophene. Process conditions: 0.5 wt.% S, O<sub>2</sub>/S = 12, GHSV = 25000 h<sup>-1</sup>.

Solvent	T, °C	C <sub>CO<sub>2</sub></sub> , vol.%	C <sub>SO<sub>2</sub></sub> , vol.%	Sulfur conversion to SO <sub>2</sub> , %	Sulfur removal, % (liquid phase analysis)	Hydrocarbon conversion, %	O <sub>2</sub> consumption by thiophene, %
Octane	300	4.3	0.33	89	83	1.3	46
	320	4.4	0.33	88	82	1.3	46
Toluene	300	15.1	0.10	24	16	3.6	13
	320	15.3	0.12	31	33	3.6	17

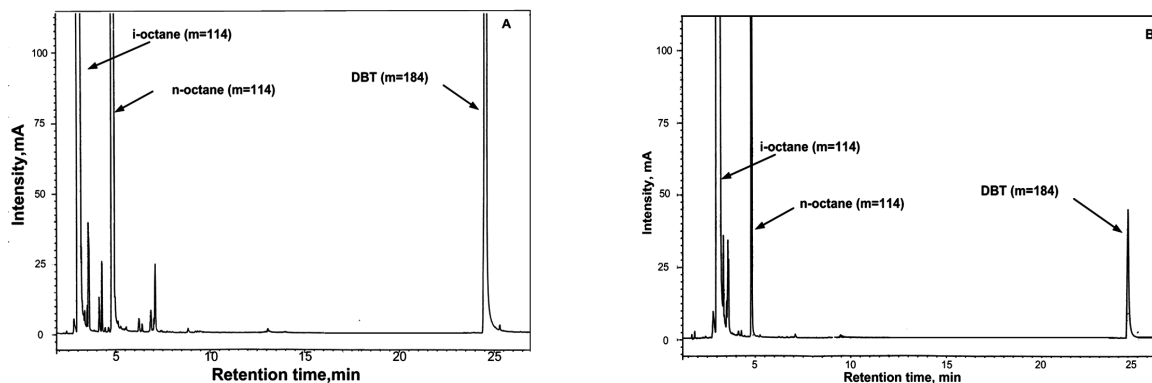


Fig. 1. Chromatogram of initial solution of DBT in isooctane (0.1 wt.% S) (A) and solution after ODS (B) by GC with MS. The ODS conditions:  $T = 260\text{--}280\text{ }^{\circ}\text{C}$ ,  $\text{WHSV} = 6\text{ h}^{-1}$ ,  $\text{GHSV} = 2500\text{ h}^{-1}$ ,  $\text{O}_2/\text{S} = 50$ . Sulfur content determined by GC with MS in initial and treated fuels was 1050 and 160 ppm, respectively.

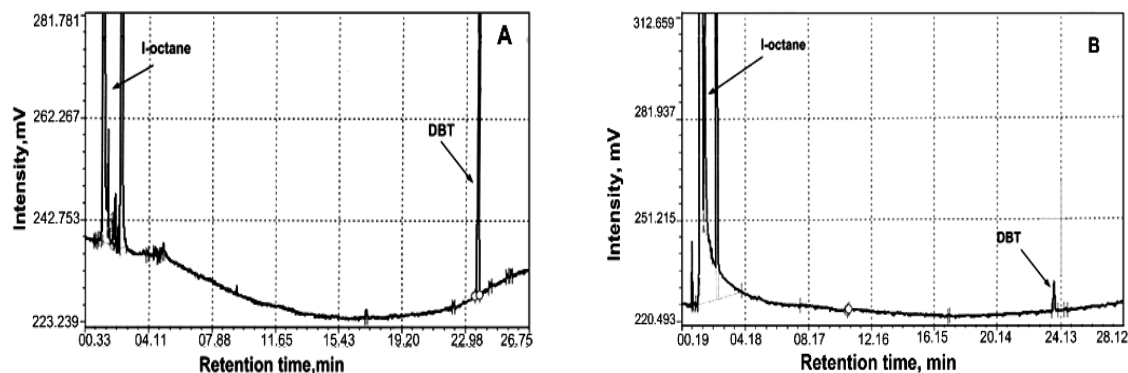


Fig. 2. Chromatogram of initial solution of DBT in isooctane (0.1 wt.% S) (A) and solution after ODS (B) by GC with FID. The ODS conditions:  $T = 260\text{--}280\text{ }^{\circ}\text{C}$ ,  $\text{WHSV} = 6\text{ h}^{-1}$ ,  $\text{GHSV} = 2500\text{ h}^{-1}$ ,  $\text{O}_2/\text{S} = 50$ . Sulfur content determined by GC with FID in initial and treated fuels was 1050 and 160 ppm, respectively.

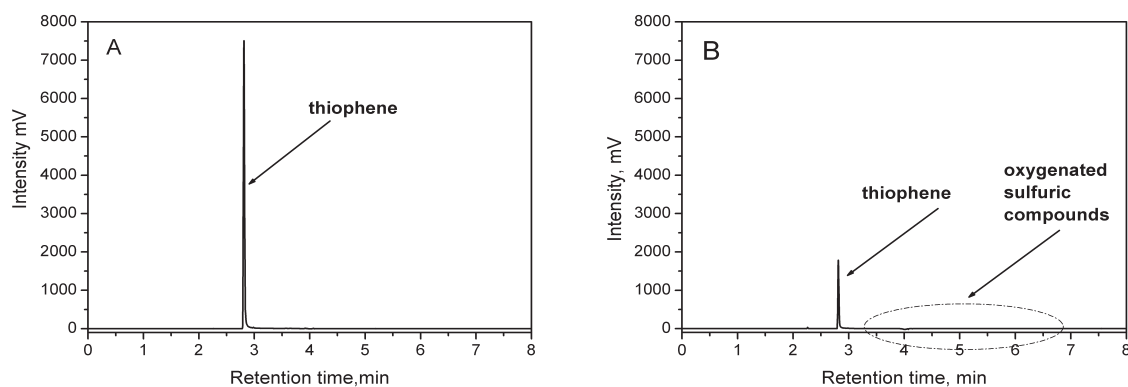


Fig. 3. Chromatogram of initial solution of thiophene in octane (0.1 wt.% S) (A) and solution after ODS (B) by GC with AED. The ODS conditions:  $T = 300\text{--}310\text{ }^{\circ}\text{C}$ ,  $\text{GHSV} = 25300\text{ h}^{-1}$ ,  $\text{WHSV} = 28\text{ h}^{-1}$ ,  $\text{O}_2/\text{S} = 24$ . Sulfur content determined by GC with AED in initial and treated fuels was 4813 and 868 ppm, respectively.

The results of the analyses of the composition of the feedstocks and treated fuels after the ODS process are given in Figs. 1-3. Figure 1a shows the chromatogram of the initial DBT – isooctane mixture. The main peaks observed are those of isooctane, octane admixture and DBT. The spectrum of the condensate after the ODS process shows the same peaks with the DBT decreased by 85% due to its oxidation and removal from the mixture. No peaks of oxygenated compounds, e.g., dibenzothio-

tane, octane admixture and DBT. The spectrum of the condensate after the ODS process shows the same peaks with the DBT decreased by 85% due to its oxidation and removal from the mixture. No peaks of oxygenated compounds, e.g., dibenzothio-

phene sulfone (with well-defined mass peaks 160, 180, 222 [9]) possible side products of dibenzothiophene selective oxidation were detected.

The same results were obtained by analyses of the samples, initial DBT in isooctane and treated at ODS, with GC instrument Kristall 2000 M equipped with FID (Fig. 2). No traces of oxygenated sulfuric compounds (above the sensitivity limit of 10 ppm) in the expected retention time region of 23-28 min were found. It should be noted that conversion of DBT calculated from GC results (ca.90%) is close to that calculated from ASE-2 sulfur analyzer measurements (85%).

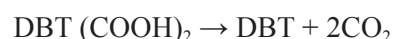
Similar results were obtained with octane – thiophene mixture taken as a model fuel (Fig. 3). No traces of oxygenated sulfuric compounds, such as, e.g., thiophene, tetrahydro-1,1-dioxide or thiophene, tetrahydro-,1-oxide (above the GC sensitivity limit of 5 ppm) in the expected retention time region of 3-7 min were found.

### 3.3.2. DBT and 4,6-DMDBT in toluene

The results of the liquid phase analysis after tests of ODS process of DBT in toluene are given in Table 4. It can be seen that during DBT oxidation in some cases certain amounts of dibenzothiophene sulfoxide were detected in the liquid phase. Possibly, the sulfoxide is an intermediate product of DBT oxidation to SO<sub>2</sub> on the catalyst surface and some of it is desorbed and found in the liquid phase. Another possibility is sulfoxide formation due to the gas phase interaction of oxygen and DBT vapor, therefore, it is observed in reaction products formed at

temperatures higher than the boiling point of DBT.

The results of the liquid phase analysis after tests of ODS process of 4,6-DMDBT in toluene are given in Table 5. It can be seen that during 4,6-DMDBT simultaneously with the oxidation to SO<sub>2</sub> the formation of DBT and 4,6-DMDBT sulfoxide takes place. It should be noted that the formation of oxygen containing products by the oxidation of 4,6-DMDBT is observed at temperatures lower than its boiling point. The formation of 4,6-DMDBT sulfoxide can be explained in the same way as for the formation of DBT sulfoxide. The formation of DBT probably proceeds via oxidation of methyl groups (-CH<sub>3</sub>) to carboxylate groups (-COOH) with their following decomposition on the catalyst surface with formation of CO<sub>2</sub> and DBT:



Then subsequent oxidation of part of DBT to DBT sulfoxide and deep oxidation of DBT to SO<sub>2</sub>, CO<sub>2</sub> and H<sub>2</sub>O take place.

### 3.4. Adsorption of sulfur compounds on the surface. Formation of surface intermediates.

In the composition of spent catalyst, sulfur is detected by CHNS analysis. Its content is determined primarily by the content of sulfur in the model feedstock, the experiment duration and temperature. The sulfur content in catalysts used for ODS of feedstocks containing 0.1 wt.% sulfur as DBT was usually in the range of 0.8-1.2 wt.%.

**Table 4**

Results of the liquid phase analysis after tests of gas phase ODS process of DBT in toluene

Description of the sample	DBT, ppm	DBT conversion from GC analysis, %	DBT sulfoxide, ppm	DBT conversion to DBT sulfoxide, %	Sulfur removal, %
Initial solution of DBT in toluene (862 ppmw S)	862	-	0	-	
Condensate after ODS reaction of DBT in toluene T = 320 °C, O <sub>2</sub> /S = 138, GHSV = 2610 h <sup>-1</sup>	183	78.8	0	0	78.8
Condensate after ODS reaction of DBT in toluene, T = 356 °C, O <sub>2</sub> /S = 139, GHSV = 2900 h <sup>-1</sup>	452	47.6	27	3.1	44.5
Condensate after ODS reaction of DBT in toluene, T = 360 °C, O <sub>2</sub> /S = 139, GHSV = 2900 h <sup>-1</sup>	436	49.4	11	1.2	48.2
Condensate after ODS reaction of DBT in toluene, T = 350 °C, O <sub>2</sub> /S = 139, GHSV = 2900 h <sup>-1</sup>	215	75.1	3	0.3	74.8



**Table 5**

Results of the liquid phase analysis after tests of ODS process with 4,6-DMDBT in toluene

Description of the sample	DMDBT, ppm	DMDBT conversion, %	DBT, ppm	DMDBT conversion to DBT %	DBT sulfoxide, ppm	DMDBT conversion to DBT sulfoxide, %	Sulfur removal, %
Initial solution of 4,6-DMDBT in toluene (1093 ppmw S)	1093		-		-		
Condensate after ODS reaction of 4,6-DMDBT in toluene T = 312 °C, O <sub>2</sub> /S = 139, GHSV = 2084 h <sup>-1</sup>	377	65.5	56	5.1	94	8.6	51.8
Condensate after ODS reaction of 4,6-DMDBT in toluene T = 352 °C, O <sub>2</sub> /S = 139, GHSV = 2084 h <sup>-1</sup>	121	88.9	50	4.6	70	6.4	77.9

The analysis of XRD data and DTA with mass spectrometry (Fig. 4) showed that under the process conditions three types of the processes took place:

- 1) reduction of copper oxide to metal copper;
- 2) formation of surface copper sulfides followed by the formation of bulk sulfides;
- 3) in addition surface sulfates on the surface of spent catalysts are formed.

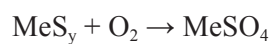
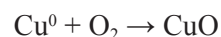


In accordance with literature data, sulfates of copper, zinc and aluminum decompose at temperature higher than 650, 930 and 770-860 °C, respectively. The decomposition of these sulfates should be accompanied by mass loss on DTG curves. For majority of used samples of Cu-Zn-Al catalysts, the mass losses at temperatures 736-750 °C and 815-822 °C accompanied by endothermic effects were observed. The effects at 750 °C and 820 °C are characteristic for all samples independently on the presence of mass gain effects in the low temperature region. It should be noted that the as-prepared Cu-Zn-Al sample does not exhibit these effects; therefore they can be attributed to phase transformations of sulfates of copper, zinc and aluminum. The mass loss in the region of 750-850 °C was ca. 3.4-3.7 wt.% for Cu-Zn-Al samples.

Assumption of formation of surface sulfates is confirmed by studies with other physicochemical methods: FTIR, DTA-TG with mass spectrometry. For instance, the mass loss in samples observed in high temperature region observed on TG curves is accompanied by the evolution of sulfur dioxide

observed by mass spectrometry method (Fig. 4).

The mass increase in the range of 200-500 °C accompanied by an exothermic effect is a superposition of two processes registered by DTA. The first is oxidation of Cu<sup>0</sup> to CuO or oxidation of surface sulfide species to sulfates:



The second is a removal of hydrocarbon fragments from the surface, accompanied by mass loss at 400-550 °C and an exothermic effect. It should be noted that the observed SO<sub>2</sub> evolution accompanied by CO<sub>2</sub> formation is an evidence of the sulfur presence in the condensation products and the adsorbed CSH compound may be adsorbed DBT or the product of its incomplete oxidation:



The formation of surface sulfur containing species during adsorption and the oxidation is confirmed by estimation of material balance of feedstocks and products.

As an example, the material balance of the experiment on oxidation of thiophene in octane is presented further. A total amount of octane passed through the reactor was 178,1 g. The amount of fuel burned off to CO<sub>2</sub> was about 1.2%. (2.1 g) Actually it was observed that 98.8% (176 g) of initial octane amount was condensed after the reactor, which was confirmed by weighting the condensate. The amount of carbon in the catalyst 0.01 g is quite low, therefore the mass balance of carbon was found to be satisfactory. Table 6 summarizes the calculation of sulfur material balance. The deviation between input and

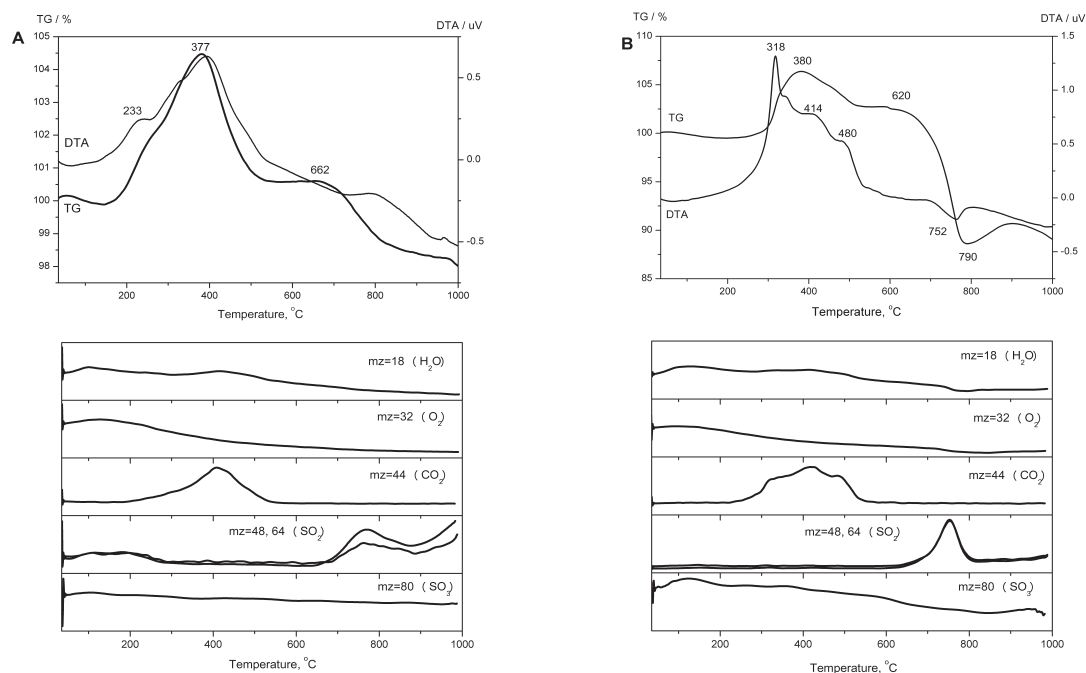


Fig. 4. TG and DTA curves obtained for the Cu-Zn-Al catalyst tested in ODS of DBT in toluene: A – 0.1 wt.% S; B – 0.5 wt.% S.

output of sulfur in this case is 9.2%, which is within the experimental error. Thus, the conducted experiments show that the Cu-Zn-Al catalyst can act both as an adsorbent and as an oxidative catalyst in the ODS process.

**Table 6**

Material sulfur balance calculation for the experiment on ODS of thiophene on Cu-Zn-Al catalyst

Parameter	Value
Input	
1. Total sulfur content in the initial fuel, %	0.0913
2. Rate of fuel input, g/min	0.667
3. Total time on stream, min	267
Total sulfur amount introduced into the reactor ( $1 \times 2 \times 3 / 100$ ), g	0.163
Output	
1. Total sulfur amount in gas phase after the reactor, g	0.112
2. Total sulfur amount in liquid phase after the reactor, g	0.020
3. Sulfur content in the spent catalyst, wt. %	1.096
4. Catalyst weight, g	1.440
5. Total sulfur amount in the catalyst after the reaction ( $3 \times 4 / 100$ ), g	0.016
Total sulfur output from the reactor (1+2+5), g	0.148
Deviation of sulfur content between Input and Output, rel. %	9.2

### 3.5. Prospective ways of implementation of the developed ODS process

#### 3.5.1. ODS combined with adsorption

The desulfurization of the hydrocarbon stream may occur via one of two reaction routes. In a first route, the so-called “oxidative process”, the sulfur compounds are oxidized, and at least a portion of them are oxidized to  $\text{SO}_2$ . In a second route, the so-called “adsorptive process,” the compounds are converted to one or more of sulfates, sulfites, and sulfides. Which route is chosen depends upon process conditions as well as the type and amount of sulfur compounds in the hydrocarbon fuel stream. When the adsorptive route is used, it is necessary to regenerate the catalysts at some point, so as to remove the sulfur compounds adsorbed.

In [10] we described the combination of adsorption and ODS processes. During ODS, sulfur compounds such as surface sulfites, sulfates, etc. are accumulated on the catalyst together with carbon deposits and the catalyst loses its activity, therefore the regeneration stage is required.

The developed scheme (Fig. 5) is based on alternating regimes of ODS and catalysts regeneration in two reactors: sulfur is removed from organic feedstock by oxidation and adsorption in one reactor while simultaneous regeneration of the catalyst that has accumulated sulfur compounds takes place in another reactor.

The regeneration of the catalyst can be conducted in the flow of oxygen containing gas at 350-500 °C (see Fig. 4) or under reduction/oxidation cycles ( $H_2$ -350 °C/ $O_2$ -350 °C).

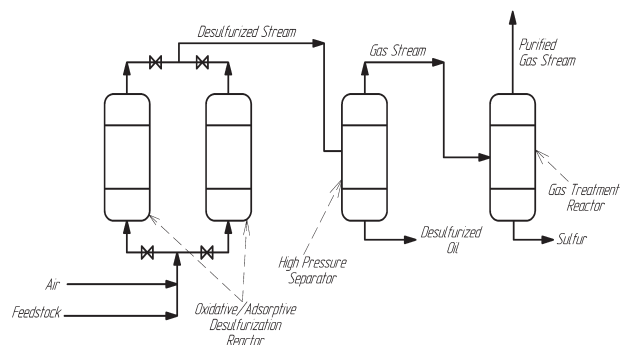


Fig. 5. Reactor system proposed for combined ODS and adsorption process and catalyst regeneration.

### 3.5.2. ODS combined with HDS

As was shown before, the developed ODS process is more efficient for sulfur removal from refractory high boiling alkyl substituted dibenzothiophene derivatives, such as e.g. DMDBT, that are very difficult to desulfurize using conventional HDS.

The combination of ODS and HDS in one catalytic unit is a promising way to desulfurize fuels to ultra-low sulfur levels [11, 12].

In Fig. 6 analyzing sulfur content of light and heavy gas oils, the cumulative sulfur concentrations are plotted against the boiling points of the sulfur-containing compounds to observe concentration variations and trends. Note that the boiling points depicted are those of detected sulfur-containing compounds, rather than the boiling point of the total hydrocarbon mixture. The boiling point of the key sulfur containing compounds consisting of dibenzothiophenes, 4-methyldibenzothiophenes and 4,6-dimethyldibenzothiophenes are also shown in Fig. 6 for convenience. The cumulative sulfur speciation curves show that the heavy gas oil fraction contains a higher content of heavier sulfur-containing compounds and lower content of lighter sulfur-containing compounds as compared to the light gas oil fraction. For example, it is found that 5370 ppmw of C3-dibenzothiophene, and bulkier molecules such as benzonaphthothiophenes, are present in the heavy gas oil fraction, compared to 1104 ppmw in the light gas oil fraction. In contrast, the light gas oil fraction contains a higher content of light sulfur-containing compounds compared to heavy gas oil. Light sulfur-containing compounds are structurally less bulky than dibenzothiophenes and boil at less than 310 °C.

Also, twice as much C1 and C2 alkyl-substituted dibenzothiophenes exist in the heavy gas oil fraction as compared to the light gas oil fraction.

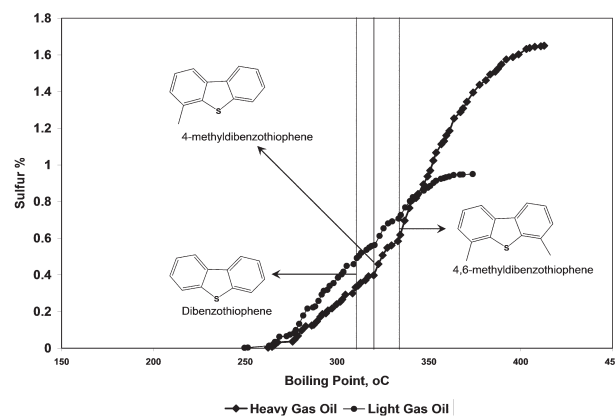


Fig. 6. Predominating sulfur containing compounds in heavy and light oil fractions [11, 12].

Aliphatic sulfur-containing compounds are more easily desulfurized (labile) using conventional hydrodesulfurization methods. However, certain highly branched aliphatic molecules can hinder the sulfur atom removal and are moderately more difficult to desulfurize (refractory) using conventional hydrodesulfurization methods.

The economical removal of refractory sulfur-containing compounds is therefore exceedingly difficult to achieve, and accordingly removal of sulfur-containing compounds in hydrocarbon fuels to an ultra-low sulfur level is very costly by current hydrotreating techniques. When previous regulations permitted sulfur levels up to 500 ppmw, there was little need or incentive to desulfurize beyond the capabilities of conventional hydrodesulfurization, and hence the refractory sulfur-containing compounds were not targeted. However, in order to meet the more stringent sulfur specifications, these refractory sulfur-containing compounds must be substantially removed from hydrocarbon fuels streams.

Oxidative desulfurization (ODS) as applied to middle distillates is attractive for several reasons. First, mild process conditions, temperature up to 400 °C and ambient pressure are normally used, thereby resulting a priori in reasonable investment and operational costs, especially as hydrogen consumption excluded, which is usually expensive. Another attractive aspect is related to the reactivity of high aromatic sulfur containing species. This is evident since the high electron density at the sulfur atom caused by the attached electron-rich aromatic rings, which is further increased with the presence of additional alkyl groups on the aromatic rings, will



favor its electrophilic attack. However, the intrinsic reactivity of molecules such as 4,6-DMDBT should be substantially higher than that of dibenzothio-*phene* (DBT), which is much easier to desulfurize by hydrodesulfurization.

The desulfurization process can be made more efficient if the feedstock is initially fractionized to low boiling and high boiling fractions [11], and each fraction is treated by the most efficient method: the low boiling fraction using conventional HDS and the high boiling one is desulfurized using ODS. The diagram of the process is shown in Fig. 7.

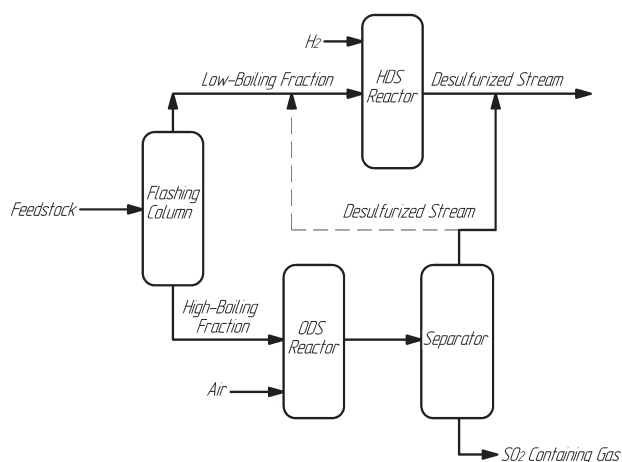


Fig. 7. Schematic diagram of integrated desulfurization system and process.

In this process desulfurization of hydrocarbon feeds is achieved by flashing the feed at a target cut point temperature to obtain two fractions. A first fraction contains refractory organosulfur compounds, which boils at or above the target cut point temperature. A second fraction boiling below the target cut point temperature is substantially free of refractory sulfur-containing compounds. The second fraction is contacted with an HDS catalyst in a hydrodesulfurization reaction zone operating under mild conditions to reduce the quantity of organosulfur compounds to an ultra-low level. The first fraction is contacted with gaseous oxidation agent over an oxidation catalyst having a formula  $Cu_xZn_{1-x}Al_2O_4$  in a gas phase catalytic oxidation reaction zone to convert the refractory organosulfur compounds to  $SO_x$  and low sulfur hydrocarbons. The by-product  $SO_x$  is subsequently removed, producing a stream containing a reduced level of organosulfur compounds.

Another efficient way to integrate ODS and HDS processes [12] is to subject a feedstock to HDS under mild conditions and on the second stage to separate the hydrocarbon stream into 2 fractions: low boiling with most of organosulfur compounds re-

moved by HDS and high boiling fraction which is directed to ODS reactor. The diagram of the process is shown in Fig. 8.

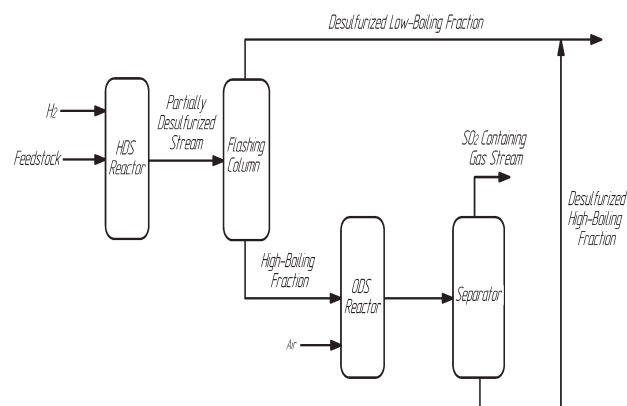


Fig. 8. Schematic diagram of consecutive integration of HDS and ODS.

Desulfurization of hydrocarbon feeds is achieved by first contacting the entire feed with a hydrodesulfurization catalyst in a hydrodesulfurization reaction zone operating under mild conditions; a flashing column downstream of the hydrodesulfurization reaction zone fractionates the effluent to obtain a first fraction which contains refractory organosulfur compounds and a second fraction that is substantially free of organosulfur compounds, since the organosulfur compounds boiling in the range of this fraction were the labile organosulfur compounds which were initially removed by mild hydrodesulfurization. The first fraction is contacted with a gaseous oxidizing agent over an oxidation catalyst having a formula  $Cu_xZn_{1-x}Al_2O_4$  in a gas phase catalytic oxidation reaction zone to convert the refractory organosulfur compounds to  $SO_x$  and low sulfur hydrocarbons.

#### 4. Conclusions

For the study of the influence of hydrocarbon environment on sulfur removal efficiency, tests of gas-phase ODS of thiophene in toluene or octane solutions on the Cu-Zn-Al catalyst were conducted. The thiophene conversion at similar conditions decreased from 60-90% (in octane) to ca. 20-30% (in toluene). This decrease is possibly due to higher reactivity of toluene in oxidation. Therefore, more oxygen is consumed for the oxidation of the hydrocarbon and less is consumed for the oxidation of thiophene.

The gas-phase ODS of thiophene, DBT and 4,6-DMDBT in toluene showed that the 4,6-DMDBT conversion is higher than that of DBT and thiophene.

Therefore, the presence of two methyl groups in 4,6-DMDBT does not have the inhibiting effect in the ODS process by contrast to the HDS process, but on the contrary promotes 4,6-DMDBT oxidation. The reactivity of different sulfur containing molecules in gas phase catalytic ODS increased in the sequence: thiophene<DBT<DMDBT.

For the practical application different ODS process designs comprising its integration with adsorption and regeneration processes and with conventional HDS process were developed and patented. One design is based on alternating regimes of ODS and catalyst regeneration in two reactors: sulfur is removed from organic feedstock by oxidation and adsorption in one reactor while simultaneous regeneration of the catalyst that has accumulated sulfur compounds takes place in another reactor. Two other designs are based on joint use of ODS and HDS. The conventional HDS process is most effective for removal of low-boiling sulfur containing compounds reactive with respect to hydrogen, while removal of refractory sulfur compounds, such as DMDBT is more easily achieved by gas phase ODS. Thus the combination of these processes is expected to be most efficient for deep desulfurization of diesel fuel.

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