Fuels Desulphurization by Adsorption on Blasting Grit

CONSTANTIN SORIN ION[1], MIHAELA BOMBOS[2]*, GABRIEL VASILIEVICI[2], CASEN PANAITESCU[1], RALUCA DRAGOMIR[1]

[1] Petroleum-Gas University of Ploiesti, Bucuresti 39, Ploiesti 100680, Romania

[2] National Research Institute for Chemistry and Petrochemistry, ICECHIM, 202 Spl. Independentei, 060021, Bucharest, Romania

Desulphurization by reactive adsorption was studied on sand abrasive blasting grit/ bentonite. The adsorbent was characterized by determining the composition, adsorption isotherms, specific surface area, pore volume and average pore diameter. Adsorption experiments were performed in continuous system at 260…300°C, 25 atm and volume hourly space velocities of 1-2 h^{-1}. The efficiency of adsorption was evaluated at desulphurization of a synthetic reaction mixture and a catalytic cracking gas oil.

Keywords: adsorptive desulphurization, gas oil, blasting grit

To minimize the adverse effects on health and on environment, it have adopted new regulations to reduce sulfur emissions by imposing low concentrations of sulfur fuels, for example in gasoline the sulfur content was restricted in several countries at 10 ppm [1]. In 2005, the sulfur concentration limit in diesel in Europe has been reduced from 350 to 50 ppm, and in 2009 was set at 10 ppm [2]. The most used technology which can convert organic sulfur compounds to hydrogen sulfide, and other inorganic sulfur is the catalytic hydrodesulphurization. These technologies include conventional hydrotreating, the use of advanced catalysts and/or designing a reactor more efficiently but also a combination of hydrotreating processes with other additional processes such as distillation, extraction, etc. to achieve fuel quality specifications.

Advanced hydrodesulphurization of distillates require high expenses costs due of classic hydrotreating process and additional reactors for hydrodesulphurization advanced. The feed ratio with fresh H_2 is about 40 m^3/m^3 petroleum product and the rate of recirculation is about 3. Thus, for a typically pressure of 6 MPa, the pressure decreases by about 1MPa, which must be compensated with a compressor of recirculating. Disadvantages of hydrodesulphurization process it would be the high cost, but also the decrease of fuel efficiency by decreasing the octane level as a result of olefin and aromatic groups saturation.

Desulphurization by adsorption can remove sulfur compounds by physical adsorption or chemisorption. Adsorption process using the porous charcoal and modified adsorbents can be an excellent technique that combined with hydrodesulphurization technique can favor the obtaining of diesel and of other fuels with a decreased sulfur content. A advantage of the desulfurization method by adsorption consists in that the fuel composition remains essentially the same.

Availability for commercial use of many adsorbing substances with different adsorption capacities and different porous structures, makes it necessary to a careful selection of the best options. Sulfur compounds recognized as being weakly polar, can be successfully used for intensive desulphurization of fuels such as diesel. Selection of adsorbents was made considering the polar interactions in order to obtain improvements in performance desulphurization [3].

Reactive adsorption is a mixed method of desulphurization which combines desulphurization process with the chemical adsorption. In this process it was used metals, such as nickel on alumina or other metal oxides. Metallic compound reacts with sulfur to form metal sulfides and thus, the sulfur is fixed on internal surface by chemisorption. In the case of this reaction only the sulfur atoms are adsorbed on the adsorbent surface while the hydrocarbon molecules remaining in fuel [4].

The adsorbents impregnated with transition metals such as nickel, iron, copper, zinc, palladium [5], are considered effective in the sulfur compounds removal. In studies conducted for numerous separation or purification processes, including industrial applications, have used solid adsorbent substances, namely: activated carbon, zeolites, impregnated membranes with silver, polymeric adsorbents etc. These substances have been used due to their high surface and a good adsorption capacity [4].

It has been demonstrated experimentally that by using active carbon as adsorbent in a 10% proportion, initial sulfur content of gas oil is reduced by more than 54%. Another adsorbent material which has been tested was palm kernel carbonized. Using the same concentration like to activated carbon to removal of sulfur from gas oil it was obtained better results. This removal of sulfur has a positive impacts on the environment, by reducing to the half the emissions of sulfur dioxide into the atmosphere [6].

In order to obtain a gas oil with a low sulfur content was tested by hydrodesulphurization a new catalyst of zinc oxide / alumina support impregnated with nickel (Ni) as the active phase. Based on the concept of reactive adsorption, it was hypothesized to improve interactions between metal and support that could lead to improved activity and capacity to absorb sulfur [7]. Other reactive adsorption studies were performed as well as by Fe/ bentonite adsorbent [8]. In this paper we studied obtaining of a new adsorbents based on sand abrasive blasting grit for desulphurization of oil fractions.

Experimental part

The raw materials used in experiments were sand abrasive blasting grit with a particle size of less than 1 mm, powdered bentonite, dimethyl disulfide **(**DMDS**),** isooctane from (Sigma-Aldrich), nitrogen purity from Linde Company and catalytic cracking gas oil.

Chemical composition of blasting grit and powdered bentonite used in the experimental program was

* email: bombos.mm@gmail.com

determined by non-destructive multi-element analysis of materials is energy dispersive X-ray fluorescence (EDXRF) technique on spectrometer PW 4025. - MiniPal - Panalytical. The granulated adsorbent was prepared by kneading blasting grit and powdered bentonite with water at *p*H 6.5 and at a weight ratio solution / powder: 1/1. The kneading was achieved at temperature of 20°C during two hours. Drying of the granulated adsorbent was carried out at 160°C for a period of 6 h.

Textural characteristics of the adsorbent (surface area, pore volume, average pore diameter, pore-size-distribution) were determined on Autosorb 1 Quantacrome. Texture data have been obtained by the automatic recording and processing of adsorption-desorption isotherms of nitrogen. The specific surface area was calculated using the equation in the linear part of the BET desorption isotherm. In order to assess the distribution of pores and the pore size was used desorption branch of isotherms with hysteresis, by applying the BJH method.

The experimental program was performed in a continuous system on fixed bed catalytic reactor. The process was carried out in isothermal conditions and the temperature was regulated with an automatic system coupled with two thermocouples fixed, placed in the reactor jacket. A metallic jacket for the mobile thermocouple was also placed in the axis of the reactor in order to measure the reaction temperature.

Desulphurization experiments were performed on the following types of raw materials:

- synthetic reaction mixtures containing 28.7% dimethyldisulfide in isooctane;
- catalytic cracking gas oil with a sulfur content of 1600 ppm.

Table 1
CHARACTERISTICS OF GAS OIL USED IN EXPERIMENT

Characteristic	Value
Density (d^{15}), g/ cm^3	0.825
Sulfur, ppm	1600
Initial boiling point, °C	226
Final boiling point , °C	354
Total aromatics, %vol	29.53
Polyaromatics, %	10.1
Bromine index, mg/100g	7.3
Flash point, °C	59

Reaction conditions of the gas oil and of the synthetic reaction mixture on blasting grit were:

-pressure: 25 atm;
-temperature: 260...300°C;
-volume hourly space velocities (VHSV): 1-2h^{-1};
-nitrogen/ raw material ratio: 400Nm^3/m^3.

The sulfur content of gas oil was determined by standard method EN ISO 2084-2004. The composition of the synthetic reaction mixture was performed by the method of gas chromatography coupled with mass spectrometry, equipped with capillary column with a length of 30 m having a diameter of 0.250 mm, whose fixed phase was polyethylene glycol (PEG) and He as mobile phase.

Results and discussions

The main characteristics of the catalytic cracking gas oil used in the experiment are shown in table 1.

The metal content of bentonite is shown in figure 1 and in table 2 is shown the content of the oxides.

From the analysis of bentonite composition used in the preparation of the adsorbent can see relevant content in oxides of sodium, potassium and calcium which contribute to increasing the adsorption capacity of the adsorbent.

The metal content of grit blasting is shown in figure 2 and in table 3 is shown the content of the oxides.

The isotherm of adsorption/desorption is shown in figure 3, and the pore size distribution in figure 4. The isotherm is type IV with a H3 hysteresis loop, specific for capillary condensation process on mesoporous solid materials with low affinity for molecules adsorbed and a narrow distribution of pore sizes. In the area of low relative pressure p/po, the nitrogen volume adsorbed by the catalyst is

Table 2
THE OXIDES CONTENT IN THE BENTONITE

Compound	Concentration, %
Na_2O	5.40
Al_2O_3	16.20
SiO_2	68.80
P_2O_5	0.43
SO_3	0.42
Cl	1.90
K_2O	2.87
CaO	1.92
TiO_2	0.25
V_2O_5	0.01
MnO	0.05
Fe_2O_3	1.74
CuO	0.01

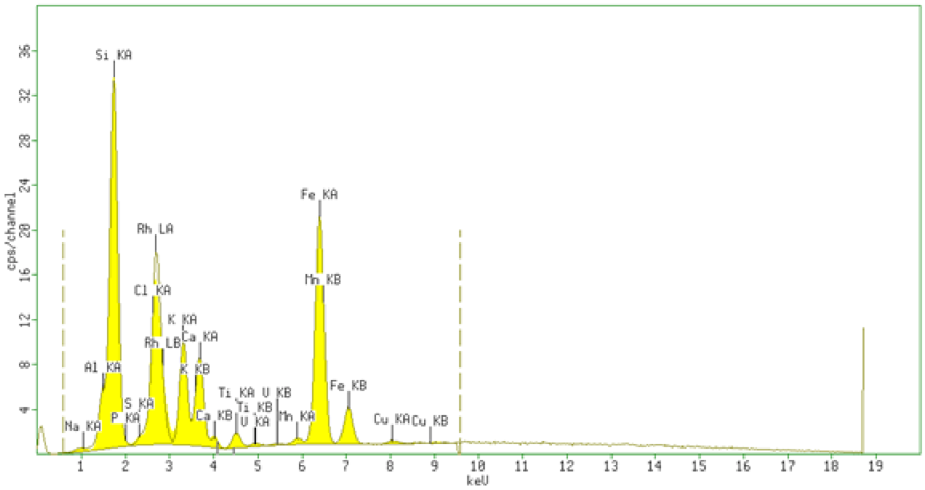

Fig. 1. The elemental composition of bentonite

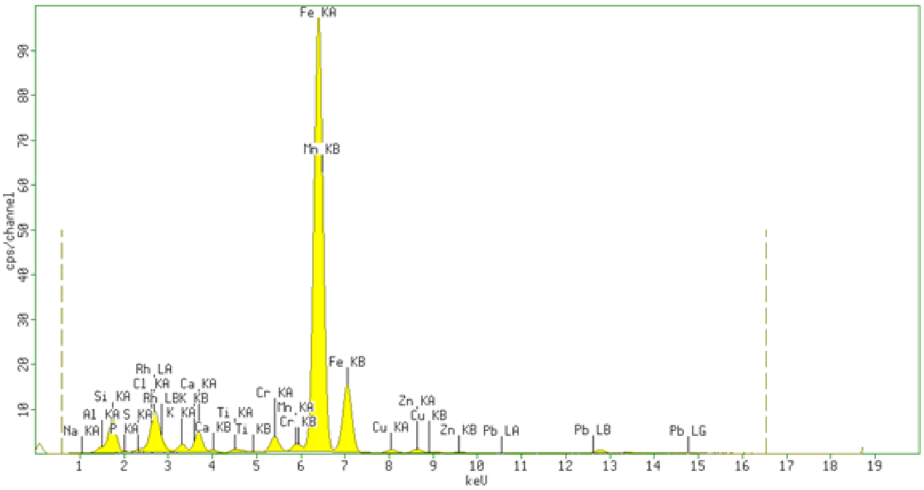

Fig. 2. The elemental composition of blasting grit

Table 3
THE OXIDES CONTENT OF THE BLASTING GRIT

Compound	Concentration, %
Na_2O	7.20
Al_2O_3	13.00
SiO_2	41.90
P_2O_5	0.76
SO_3	0.92
Cl	2.40
K_2O	1.20
CaO	2.57
TiO_2	0.26
Cr_2O_3	0.87
MnO	0.31
Fe_2O_3	28.10
CuO	0.21
ZnO	0.26
PbO	0.04

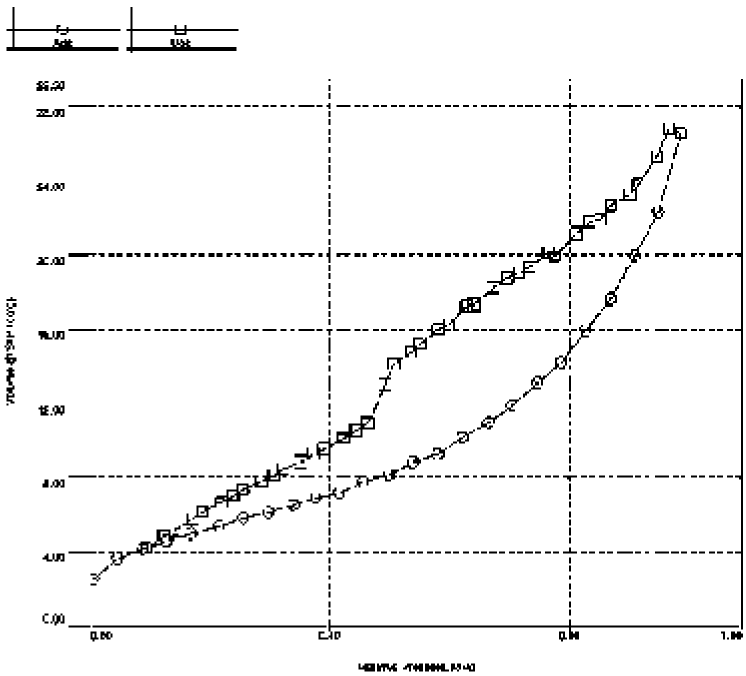

Fig. 3. The adsorption /desorption isotherm for adsorbent

Table 4
TEXTURAL CHARACTERISTICS OF ADSORBENT

Adsorbent	Specific Surface Area, m^2/g	Pore Diameter Dv(d), nm	Total pore volume, cm^3/g
blasting grit	27.877	3.848	0.041

associated with a monolayer adsorption of nitrogen on the surface. At relative pressure close to 1.0 it can be noted an increase in the volume adsorbed and the presence of small hysteresis loops, specific for multilayer condensation of nitrogen in the catalyst pores.

Textural characteristics of the catalyst were determined by the BJH method on the desorption zone and are shown in table 4. The specific surface area of adsorbent is specific to the macroporous product.

Textural properties of the adsorbent consist in large surface area, pore volume relatively large and in single-mode mesopore size distribution, indicating good accessibility of the catalytic center. Thus figure 4 shows that the adsorbent has a distribution with a maximum pore diameter of about 38 Å.

From the analysis of composition of blasting grit used in the preparation of the adsorbent can be seen a high content of iron oxide but a important content in sodium oxide and in potassium and calcium oxide. Also, the presence of other metals such as Mn, Cu, Zn and Pb contributes at the increase of the adsorption capacity.

It is observed the decrease of the raw material sulfur content with the increasing of the temperature. Thus, for the same residence time of feedstock, at 300°C, the sulfur content decrease practically by half for VHSV 1 h^{-1}. Also the increase of residence time results in the decrease of the sulfur content in gas oil. For both values of volume hourly space velocities, slope variation is similar and relatively constant throughout the temperature range studied Working at relatively low temperatures (260°C) , the performance on grit-bentonite sorbent are modest. At VHSV 2h^{-1} and 260°C sulfur content decreases by 12.5%, and a VHSV 1h^{-1} and 260°C, sulfur content decreases by 18.75%.

The variation of sulfur compounds conversion for catalytic cracking gas oil desulphurized is shown in figure 6. Is an increase of the conversion of sulfur compounds

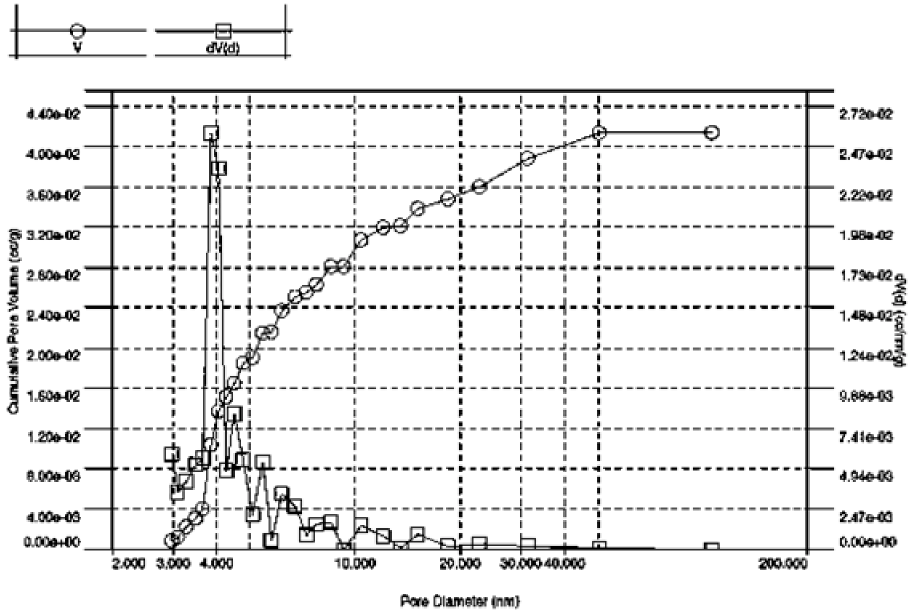

Fig.4. Pore volume distribution based on size, for adsorbent

Table 5
DESULPHURISATION OF DIMETHYL DISULFIDE SYNTHETIC MIXTURE

Nr. crt.	Operating parameters			Content of dimethyl disulphide, %
	Pressure, bar	Temperature, °C	VHSV, h^{-1}	
1	25	260	1	0
2	25	280	1	0
3	25	300	1	0
4	25	300	2	0

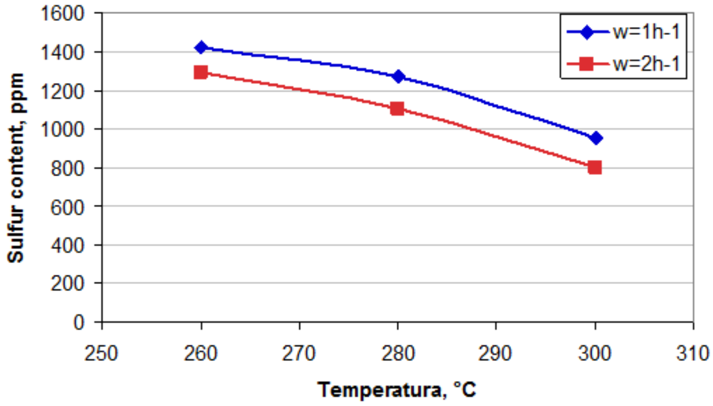

Fig.5. The influence of temperature on sulfur content of catalytic cracked gas oil

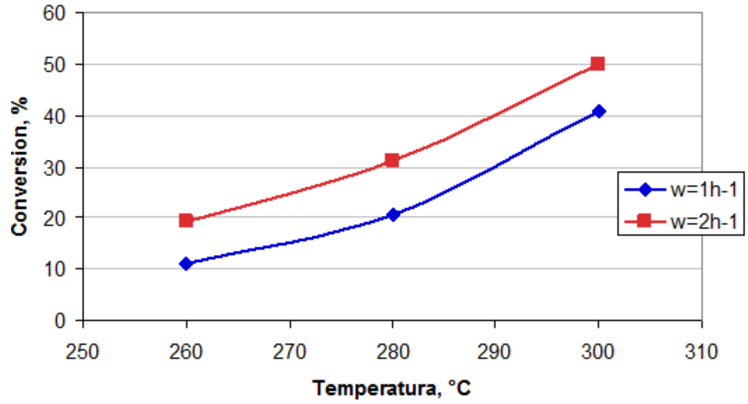

Fig. 6. Conversion of sulfur compounds for catalytic cracking gas oil desulfurized with temperature

with temperature by a gradient similar to the curves of lowering the sulfur content with temperature.

Conclusions

Desulphurization of gas oil was performed by adsorption process on sand abrasive blasting grit/ bentonite.

The adsorbent was characterized by determining the composition, the adsorption isotherms, specific surface area, pore volume and average pore diameter.

Adsorption experiments were performed in continuous system at 260-300^{o}C, 25 atm and volume hourly space velocities of 1-2 h^{-1}.

The efficiency of adsorption on blasting grit/bentonite was evaluated at desulphurization of a synthetic reaction mixture and a catalytic cracking gas oil.

Efficiency of grit adsorbent was higher for desulphurization of aliphatic sulfide and lower in case of a catalytic cracking gas oil.

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