Fuels Desulphurisation by Adsorbtion on Fe / Bentonite

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Desulfurisation of atmospheric distillation gasoline and gas oil was performed by adsorption process on Fe/ bentonite. The adsorbant was characterized by determining the adsorption isotherms, specific surface area, pore volume and average pore diameter. Adsorption experiments of atmospheric distillation gasoline and gas oil were performed in continuous system at 280…320°C, 5 atm and volume hourly space velocities of 1…2 h^{-1}. The efficiency of adsorption on Fe / bentonite was better at desulphurisation of gasoline versus gas oil.

Keywords: *adsorptive desulphurization, gasoline, gas oil, sulphur*

Crude oil/ petroleum and implicitly the petroleum products contain a chain of hydrocarbons but also sulfur, nitrogen and oxygen compounds. The sulfur content in the crude oil/petroleum varies between 0.1 and 15%, and occurs in different forms: sulfides, disulfides, mercaptans, thiophenes, benzothiophenes, dibenzothiophenes, benzonaphthothiophenes and dinaphthothiophene.

Currently, desulphurisation of refined petroleum products is performed by catalytic hydrodesulfurization (HDS) in fixed bed reactors. Sulfur bound in various organic species is then converted to H_2S which is removed and then transformed into elemental sulfur by the Clauss process [1].

The decrease of sulfur content involves reducing of productivity and leads to higher consumption of energy. It is known that the usual desulphurization processes shows some disadvantages, such as: they are energy intensive, they use expensive catalysts and large amounts of hydrogen.

In conclusion it is necessary to develop alternative technologies and catalyst /support systems adequate which reduce energy costs in the hydrotreating process. [2] Thus it was imposed a new concept for hydrodesulfurization, respectively an advanced technology which proposes a two-phase reactor, based on a new concept, that proposes pre-saturation of the oil product [1].

The hydrodesulfurization process depends on the structure of the sulfur compounds. Such, direct hydrodesulfurization are made harder to aromatic sulfur compounds and hydrodesulfurization resistance increases with the degree of substitution of the aromatic ring. For example dibenzo-thiophene hydrodesulfurization (DBT) arises easier than for 4-methyl-dibenzo-4,6-dimethyl thiophene and -dibenzo-thiophene. By adding phosphorus at the catalyst the desulfurization increased in the following order: DBT <4-MDBT <4.6-DMDBT [3].

Improving the performance of hydrodesulfurization catalysts is difficult to achieve due to the interaction of sulfur with components of catalysts. For example the catalysts containing zeolites, although have a higher acidity than those on alumina, were strongly inhibited by sulfur or nitrogen impurities due to their sensitivity to these substances. If the acidity is relatively weak, nitrogen compounds can significantly affect hydrodesulfurization activity, inhibiting active centers [4].

In such cases, the most promising desulfurization process can be the adsorption process. Several types of adsorbents, such as zeolites, activated carbon, nickel, copper adsorbents based on noble metals (gold, silver, platinum, palladium), oxides of metals, have been investigated regarding their efficiency in the desulfurization of hydrocarbon liquids [5].

Although there are many studies that address the processing of bioresources towards obtaining fuels [6, 7], the number of publications that address the desulfurization by chemical adsorption is relatively low. In this paper we studied obtaining of a adsorbent for desulfurization to reduce the load of hydrodesulfurization stage.

Experimental part

Chemicals

The raw materials used in experiments were metallic iron powder e ≥ 99%, reduced Sigma-Aldrich, powdered bentonite (Sigma-Aldrich), nitrogen purity from Linde Company and atmospheric distillation (DA) gasoline and gas oil. The main characteristics of the atmospheric distillation gasoline and gas oil used in the experiment are shown in table 1.

Table 1
CHARACTERISTICS OF RAW MATERIALS USED IN EXPERIMENT

Characteristic	DA GASOLINE	GAS OIL
Density d^{15}, g/ cm^3	0.728	0.857
Sulfur, ppm	2005	2256
Initial boiling point, °C	32	204
Final boiling point, °C	177	324
Total aromatics, %vol	10.44	24.41
Olefin, %vol	3.29	-

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Adsorbent preparation

The granulated adsorbent was prepared by kneading metallic iron powder and bentonite powder with water at *p*H 6.5 and at a weight ratio solution / powder: 1/1. The kneading was achieved at temperature of 25°C during 3 h. Drying of the granulated adsorbent was carried out at 120°C for a period of 6 h.

Adsorbent characterization

Chemical composition of adsorbent used in the experimental program was determined by atomic absorption (Varian AA240FS). Adsorbent characterization was performed by determining the particle size of the iron and the textural characteristics. The iron particle size has been determined by dynamic light scattering (DLS) using Nano ZS (Red badge). 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 on fixed bed reactor in a continuous system. The process was carried out in isothermal conditions and the temperature was adjusted 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.

Reaction conditions were:

-pressure: 5 bar;

-temperature: 280...320°C;

-volume hourly space velocities (VHSV): 1...2h^{-1};

-nitrogen/ raw material ratio: 400Nm^3/m^3.

The sulfur content of atmospheric distillation gasoline and gas oil were determined by standard method EN ISO 2084-2004.

Results and discussions

Textural data of bentonite used at kneading in the experimental program are presented in table 2.

The specific surface area and the pores volume of the adsorbent was relatively small compared to other adsorbents used in such processes.

Table 3 shows the metal iron particles characteristics. The high density of iron particles hampers the homogenization of bentonite during the extrusion process.

The mass ratio absorbent/ bentonite in extrudates, determined by atomic absorption, was 1/6. Data of granulated adsorbent have been obtained by the automatic recording and processing of adsorption-desorption isotherms of nitrogen. Isotherms of adsorption-desorption are shown in figure 1.

Textural characteristics of adsorbent are presented in table 4. The specific surface area of the adsorbent has a typical value for bentonite-based adsorbents.

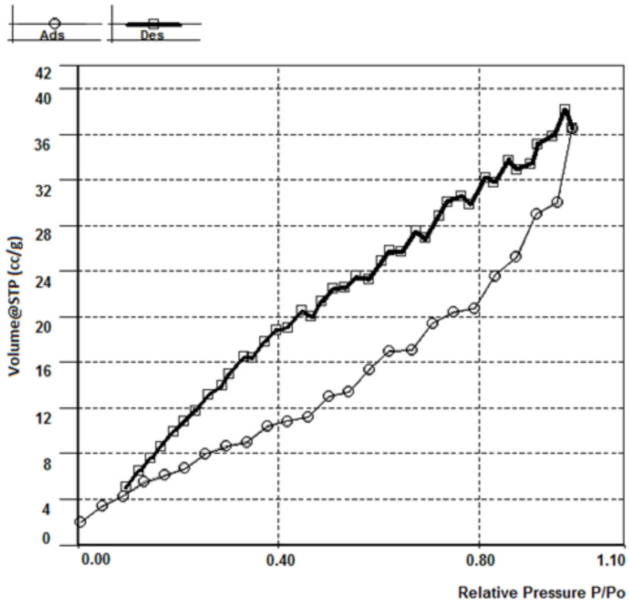

Fig.1. The isotherm of adsorption-desorption of Fe / bentonite

Table 2
CHARACTERISTICS OF BENTONITE

Characteristics	Values
Specific surface area, m^2/g	51.04
The pores volume with a diameter greater than 566.6 (mezo and macropores) Å, cm^3/g	0.315

Table 3
THE IRON PARTICLES CHARACTERISTICS

Characteristics	Values
Aspect/ appearance	gray powder
Resistivity, μΩ-cm	9.71
Impurities (insoluble in HCl)	≤0.5%
Density at 25 °C, g/cm^3	7.86

Table 4
TEXTURAL CHARACTERISTICS OF ADSORBENT

Adsorbent	Pore Volume, cm^3/g	Pore Diameter, nm	Specific Surface Area, m^2/g
Fe / bentonite	0.055	3.816	35.013

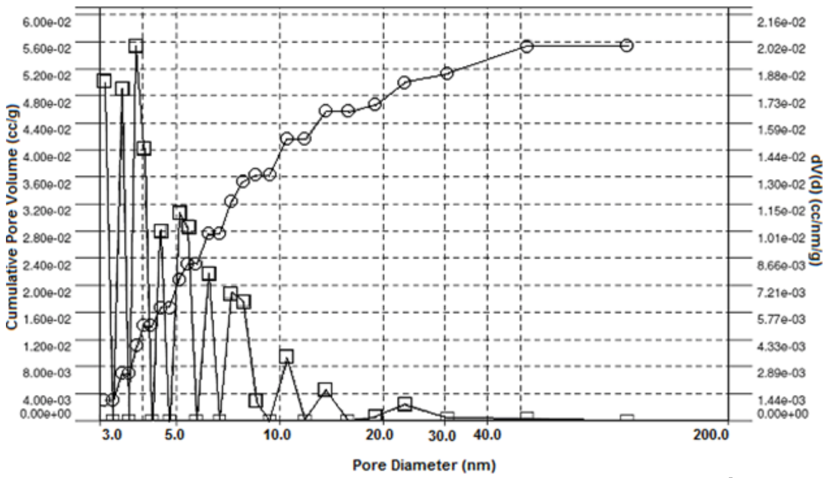

Fig.2. The pore size distribution of the adsorbent Fe / bentonite by BJH method desorbtion

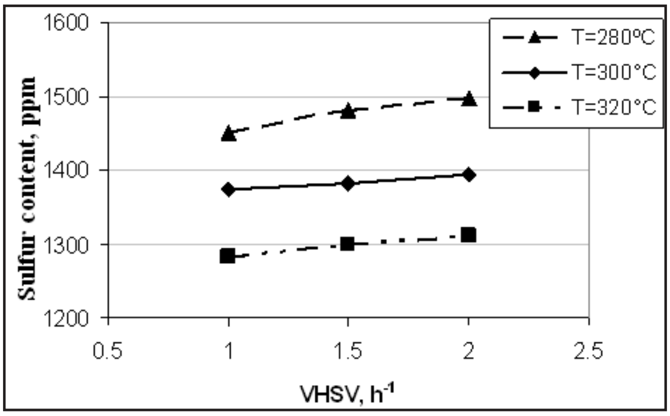

Fig.3. Sulfur content of DA gasoline variation with volume hourly space velocitie

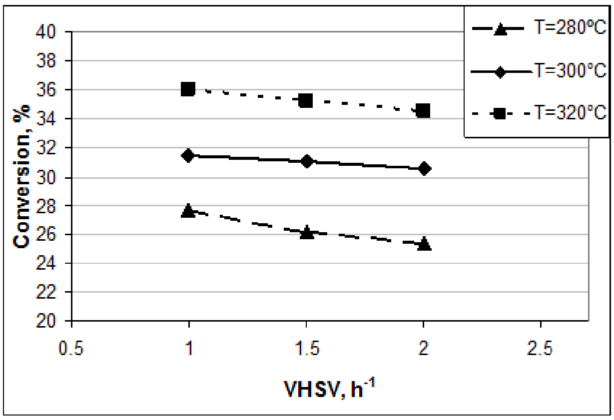

Fig. 4. Conversion of sulfur compounds in DA gasoline with volume hourly space velocities, at a pressure of 5 bar

Figure 2 shows that the Fe / bentonite adsorbent possesses a well-defined large pore size and a maximum distribution centered around 38Å. The textural characteristics of Fe /bentonite indicate a decreasing of specific surface up to 35 m^2/g by kneading, while the pore size distribution value (38.16 Å), calculated using the Barrett–Joyner–Halenda (BJH) algorithm, suggest obtaining of pores in the mesopore range.

The sulfur content of DA gasoline decreases after desulphurization process up to approx. 36%. Figure 3 shows the sulfur content variation with the volume hourly space velocities of DA gasoline at three temperatures. At higher temperatures (320°C) and lower volume hourly space velocities (1 h^{-1}), the sulfur content in gasoline is lower (1280 ppm). It observed an slight increase of the sulfur content with the increase of volume hourly space velocities. At lower temperatures (280°C), the variation of sulfur content of DA gasoline with volume hourly space velocities increase with the same slope like at higher temperatures (300 and respectively 320°C).

The variation of the conversion of sulfur compounds in DA gasoline with volume hourly space velocities at a pressure of 5 bar is shown in figure 4. Observe that conversion of sulfur compounds decreases with increasing of volume hourly space velocities by a similar slope with variation sulfur of DA gasoline content with volume hourly space velocities.

The variation in the sulfur content of the DA gasoline with temperature, at the three values of the volume hourly space velocities, is shown in figure 5. The sulfur concentration decreases with the increase of temperature, with a similar slope for the three values of the volume hourly space velocities. At relatively low temperature (280°C) and high volume hourly space velocities (2h^{-1}) it shows a decrease of the sulfur content with approx. 25% reported at raw material.

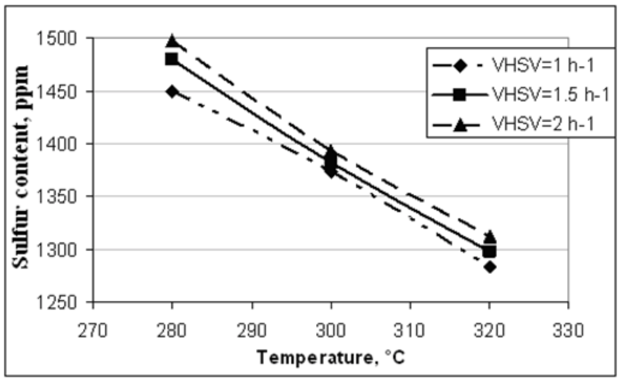

Fig. 5. Variation of sulfur content of DA gasoline with temperature, at a pressure of 5 bar

The variation of the conversion of sulfur compounds in DA gasoline with temperature at a pressure of 5 bar is shown in figure 6. Is an increase of the conversion of sulfur compounds with temperature by a gradient similar to the curves of lowering the sulfur content with temperature.

The sulfur content of gas oil decreases after desulphurization with up to approx. 20% on temperature range studied. Figure 7 presents the variation of the sulfur concentration in gas oil desulfurized with volume hourly space velocities at three temperatures. It is observed an increase in the sulfur concentration with increasing volume hourly space velocities for the three temperatures, the slope of the variation being similar.

The variation of the conversion of sulfur compounds in gas oil with volume hourly space velocities at a pressure of 5 bar is shown in figure 8. The conversion of sulfur compounds decreases with volume hourly space velocities by a similar slope in the range of temperature studied.

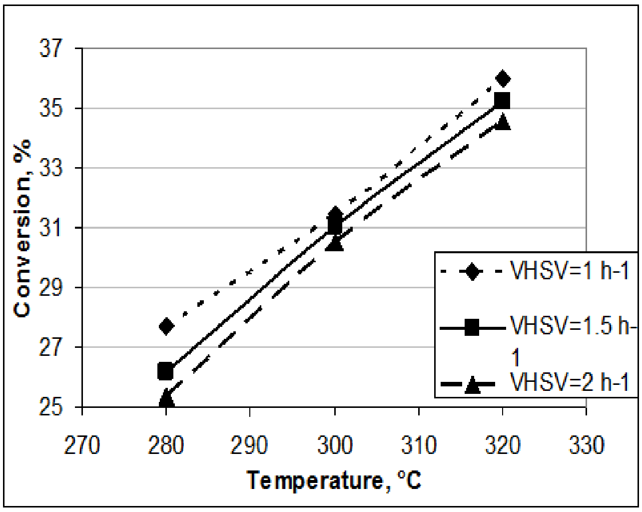

Fig. 6. Conversion of sulfur compounds in DA gasoline with temperature, at a pressure of 5 bar

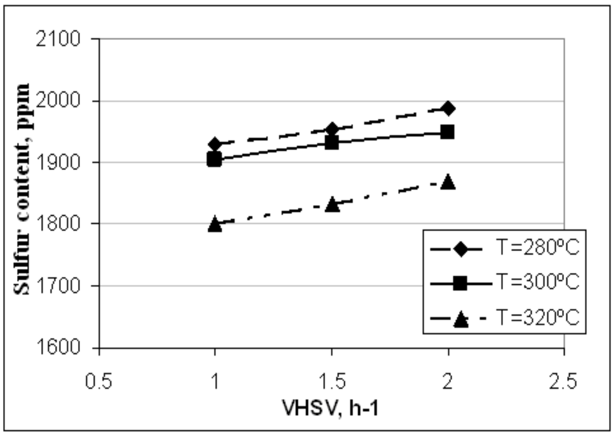

Fig. 7. Sulfur content of gas oil variation with volume hourly space velocities, at a pressure of 5 bar

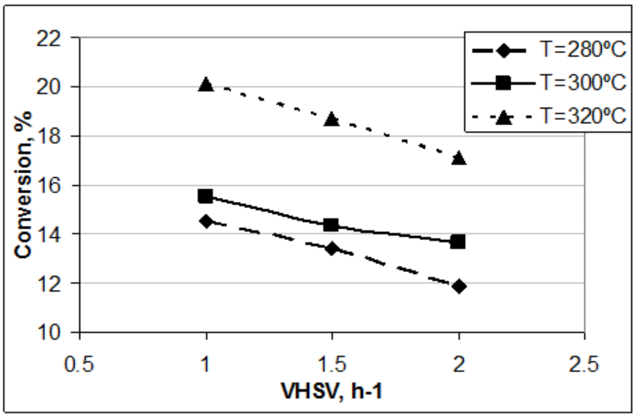

Fig. 8. Conversion of sulfur compounds in DA gasoline with volume hourly space velocities, at a pressure of 5 bar

The sulfur content of gas oil decrease with temperature after a slower slope in the temperature range 280-300°C than in the range 300-320°C for all three volume hourly space velocities (fig. 9). It is observed a low decrease of the sulfur content (with approx. 11.88%) reported to the raw material at relatively lower temperature (280°C) and higher volume hourly space velocities (2 h^{-1}).

The variation of the conversion of sulfur compounds in gas oil with temperature at a pressure of 5 bar is shown in figure 10. Slope of the variation of sulfur compounds conversion increases with temperature on volume hourly space velocities range studied.

Comparing the results obtained in the same conditions it can be mentioned a better efficiency of metallic iron –

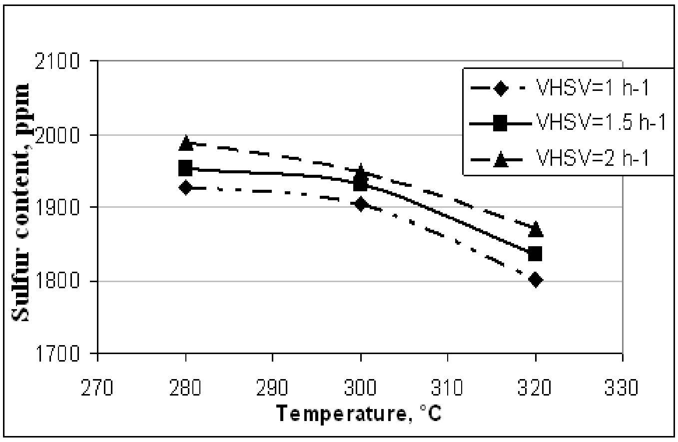

Fig. 9. Sulfur content variation of gas oil with temperature, at a pressure of 5 bar

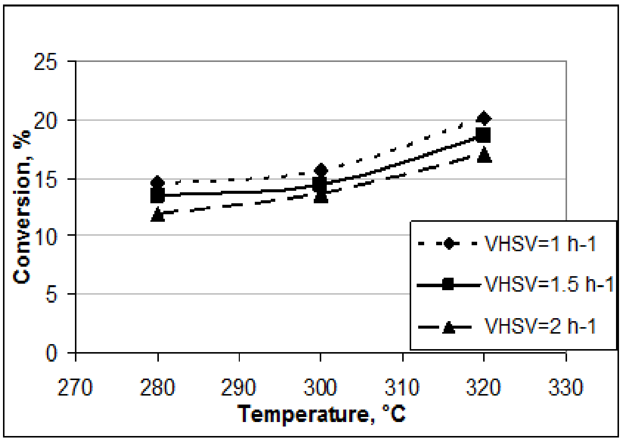

Fig. 10. Conversion of sulfur compounds of gas oil with temperature, at a pressure of 5 bar

bentonite adsorbent for desulfurisation of DA gasoline versus gas oil.

Conclusions

Desulfurisation of atmospheric distillation gasoline and gas oil was performed by adsorption process on Fe / bentonite.

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

Adsorption experiments of atmospheric distillation gasoline and gas oil were performed in continuous system at 280…320°C, 5 atm and volume hourly space velocities of 1…2 h^{-1}.

The efficiency of adsorption on Fe / bentonite was better at desulphurisation of gasoline versus gas oil.

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