Fuels Desulphurisation by Adsorption on Fe / Bentonite

CONSTANTIN SORIN ION1, MIHAELA BOMBOS2, GABRIEL VASILIEVICI2, DORIN BOMBOS1

1 Petroleum-Gas University of Ploiesti, 39 Bucuresti Blvd.,100680, Ploiesti, Romania
2 National Research Institute for Chemistry and Petrochemistry, ICECHIM, 202 Splaiul Independentei, 060021, Bucharest, Romania

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, benzanthiophenones and dinaphthothiophene.

Currently desulfurisation of refined petroleum products is performed by catalytic hydrodesulfurization (HDS) in fixed bed reactors. Sulfur bound in various organic species is then converted to H₂S which is removed and then transformed into elemental sulfur by the Claus 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 [1].

Experimental part

Table 1

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>DA GASOLINE</th>
<th>GAS OIL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density d³, g/cm³</td>
<td>0.728</td>
<td>0.837</td>
</tr>
<tr>
<td>Sulfur, ppm</td>
<td>2005</td>
<td>2256</td>
</tr>
<tr>
<td>Initial boiling point, °C</td>
<td>32</td>
<td>204</td>
</tr>
<tr>
<td>Final boiling point, °C</td>
<td>177</td>
<td>324</td>
</tr>
<tr>
<td>Total aromatics, %vol</td>
<td>10.44</td>
<td>24.41</td>
</tr>
<tr>
<td>Olefin, %vol</td>
<td>3.29</td>
<td>-</td>
</tr>
</tbody>
</table>

* email: gabi.vasilievici@gmail.com

REV.CHIM.(Bucharest) ● 68 ● No. 3 ● 2017 http://www.revistadechimie.ro 483
Adsorbent preparation
The granulated adsorbent was prepared by kneading metallic iron powder and bentonite powder with water at pH 6.5 and at a weight ratio solution/powder: 1/1. The kneading was achieved at temperature of 25°C during 3h. Drying of the granulated adsorbent was carried out at 120°C for a period of 6h.

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.

### 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.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific surface area, m(^2)/g</td>
<td>51.04</td>
</tr>
<tr>
<td>The pores volume with a diameter greater than 566.6 (mezo and macropores) Å, cm(^3)/g</td>
<td>0.315</td>
</tr>
</tbody>
</table>

Table 2 CHARACTERISTICS OF BENTONITE

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aspect/ appearance</td>
<td>gray powder</td>
</tr>
<tr>
<td>Resistivity, µΩ·cm</td>
<td>9.71</td>
</tr>
<tr>
<td>Impurities (insoluble in HCl)</td>
<td>≤0.5%</td>
</tr>
<tr>
<td>Density at 25 °C, g/cm(^2)</td>
<td>1.86</td>
</tr>
</tbody>
</table>

Table 3 THE IRON PARTICLES CHARACTERISTICS

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Pore Volume, cm(^3)/g</th>
<th>Pore Diameter, nm</th>
<th>Specific Surface Area, m(^2)/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe / bentonite</td>
<td>0.055</td>
<td>3.816</td>
<td>35.013</td>
</tr>
</tbody>
</table>

Table 4 TEXTURAL CHARACTERISTICS OF ADSORBENT
Figure 2 shows that the Fe/bentonite adsorbent possesses a well-defined large pore size and a maximum distribution centered around 38 Å. The textural characteristics of Fe/bentonite indicate a decreasing of specific surface up to 35 m²/g by kneading, while the pore size distribution value (38.16 Å), calculated using the Barrett-Joyner-Halenda (BJH) algorithm, suggests obtaining 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 (2 h⁻¹) it shows a decrease of the sulfur content by approx. 25% reported at raw material.

The variation of 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 (2 h⁻¹) it shows a decrease of the sulfur content by approx. 25% reported at raw material.

The variation of the conversion of sulfur compounds in DA gasoline with temperature at a pressure of 5 bar is shown in figure 6. It 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 process 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.
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 - 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 adsorbent 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.

**References**

2. WACHE, W., DATESEVICH, L., JESS, A., NEUMANN, G., Fuel, 85, 2006, p. 1483;

Manuscript received: 21.04.2016