Hydrocracking of Delayed Coker Gas Oil by Cobalt Catalysts

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Hydrocraking of heavy delayed cooking gas oil was performed on two particulate catalyst based on Co, Ni-Co / Al_2O_3 respectively Co-Mo / Al_2O_3. The catalysts were prepared by sequential impregnation. The distribution of the acid strength of the prepared catalysts was determined by thermic desorption of diethyl amine in the temperature range from 20 to 600°C. Textural properties of the catalysts, consisting of large specific surface, high pore volume and mesopore size distribution with a single maximum pore show a good accessibility of catalysts. Experiments were carried out on a laboratory echipament using a fixed bed catalytic reactor at a temperature of 400°C, pressure of 100 atm with a gas oil volume flow rate (VHSV) of 1.0 h^{-1} and a volume ratio hydrogen/gas oil of $900 Ncm^3/cm^3$. The organic compounds evaluated were total aromatic hydrocarbons, polyaromatic hydrocarbons and unsaturated hydrocarbons. The activity of prepared catalysts was similar, total aromatics content being greater in the case of the catalyst Co-Mo / Al_2O_3.

Keywords: catalyst, hydrotreating, support acidity, heavy delayed cooking gas oil, aromatics hydrocarbons

Oil prices has had the initial effect, orientation of oil refining companies for processing heavy oil fractions with features unsuitable for manufacturing automotive fuels, such as heavy diesel oil and diesel catalytic cracker. Hydrotreating is a preliminary step in the processing of heavy oil fractions regardless of sulfur content, especially for fractions that have a higher content of sulfur, protecting catalyst system used in the final stages of the refining process. Improving the properties of the final product of refining process (such as color, odor, stability) and reducing emissions of NOx and SO_2, which may derive from the combustion of heavy petroleum fractions distilled, constitutes the main arguments for hydrotreating heavy residues. Correcting the distillation range and flash temperature is usually achieved by hydrocracking, and reducing the content of aromatics such as monocyclic and di-, tri-, and multicyclic aromatic hydrocarbons is achieved by nucleus saturation. Thus, hydrogenation of aromatic hydrocarbons, a process extensively documented, is a topic addressed in several studies, both because of the negative impact on the environmental conditions of increasingly severe and increasing demand for fuel interest [2].

Removing sulfur from the reaction mixture prior to catalytic hydrogenation process of the aromatic ring, facilitates the carrying out of this catalytic process [3], [4]. The high aromatic content is associated with a poor quality product, causing a low cetanic number for diesel fuel [5], [6] and an increased polluting emission of exhaust gases. Consequently, in terms of environmental protection, fuel fabrication with less harmful aromatics by saturation is the main solution to reduce exhaust gas content in such organic compounds [7]. Although the presence of polycyclic aromatics in heavy oil fractions such as heavy diesel oil was seen long before, on the scientific field did not paid sufficient attention to reducing content in such compounds [8].

Compared to studies of literature that approach the hydrodesulfurization [9] and hydrodenitrogenation [10], the number of publications that address the hydrogenation of aromatics is relatively low, priority concerns being directed towards processing of bioresources [11-14.]

In this paper is studied the influence of two catalysts based on Co, like Ni-Co / γ-Al_2O_3 and Co-Mo /γ-Al_2O_3 on the main features of a heavy coking diesel oil.

Experimental part

The raw materials used in experiments were heavy delayed cooking gas oil, cobalt (II) nitrate hexahydrate puriss p.a.(Sigma-Aldrich), nickel(II) nitrate hexahydrate puriss p.a.(Sigma-Aldrich), ammonium heptamolybdate tetrahydrate (Sigma-Aldrich), γ-alumina granulated and electrolytic hydrogen purity from Linde Company. The main characteristics of the coking gas oil used in the experiment are shown in table 1.

Table 1
CHARACTERISTICS OF HEAVY DELAYED COOKING GAS OIL USED IN EXPERIMENTS

Characteristic	**Value**
Density d^{20}, g/ cm^3	0.8374
Total aromatics, %vol	37
Polyaromatics, %	13.3
Sulfur, %gr.	0.4610
Bromine index, mg/100g m.p	10.95
Aniline point,°C	52
Freezing point, °C	-44
Flash point, °C	58
Average molar mass, kg/kmol	200

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The synthesis of catalysts where achieved by successive impregnation with aqueous solutions of the precursors of catalysts, applying the method of filling the pores. The precursors of the catalyst are cobalt nitrate, nickel nitrate and ammonium heptamolybdate tetrahydrate. Concentration of catalyst precursor of the impregnation solution is calculated according to the proposed metal content (6% Ni and 3% Co/Al_2O_3 for Ni - Co/ γ-Al_2O_3; 4% Co and 10% Mo for Co-Mo/ γ-Al_2O_3). Conditioning of the catalyst between impregnation was achieved by drying at 160°C for 4 hours and the final conditioning was performed by drying at 160°C for 6 hours, calcination at 450°C for 6 h and two-stage reduction by treatment with sodium borohydride in aqueous solution at a temperature of 80°C, followed by activation in a stream of hydrogen at 450°C for 6 h.

Chemical composition of catalyst used in the experimental program was determined by atomic absorption (Varian AA240FS). Catalyst characterization was performed by determining the acid strength and textural characteristics. The acid strength distribution of the active center has been determined by the method of thermal desorption of diethyl-amine on a DuPont Instruments “Thermal Analyst 2000/2100” coupled with a module “951 ThermogravimetricAnalizer”[15,16]. Textural characteristics of the catalysts (surface area, pore volume, average pore diameter, pore-size-distribution) were determined on a Autosorb 1 Quantacrome.

The experimental program was performed in a continuous system and fixed bed catalytic reactor. The process was carried out in isothermal conditions. 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.

Reaction conditions were:

-pressure: 100 atm;

-temperature: 400^{0}C;

-volume hourly space velocities of coking gas oil (VHSV): 1.0 h^{-1};

-volume ratio hydrogen/coking gas oil (R): 900Ncm^3/cm^3.

Characteristics of coking gas oil were determined by standard methods as follows: density (EN ISO 12185), total aromatics and polyaromatics (ASTM D5186), unsaturated hydrocarbons (STAS 315-74), freezing point (ASTM D 5972), flash point (SR 5489), sulfur content (EN ISO 2084-2004) cetane number (ASTM D796) and cetane index ASTM-D4737.

Results and discussions

For the first catalyst the concentration of Ni on catalyst support was 6% and of Co was 3%, and for the second catalyst the concentration of Co on catalyst support was

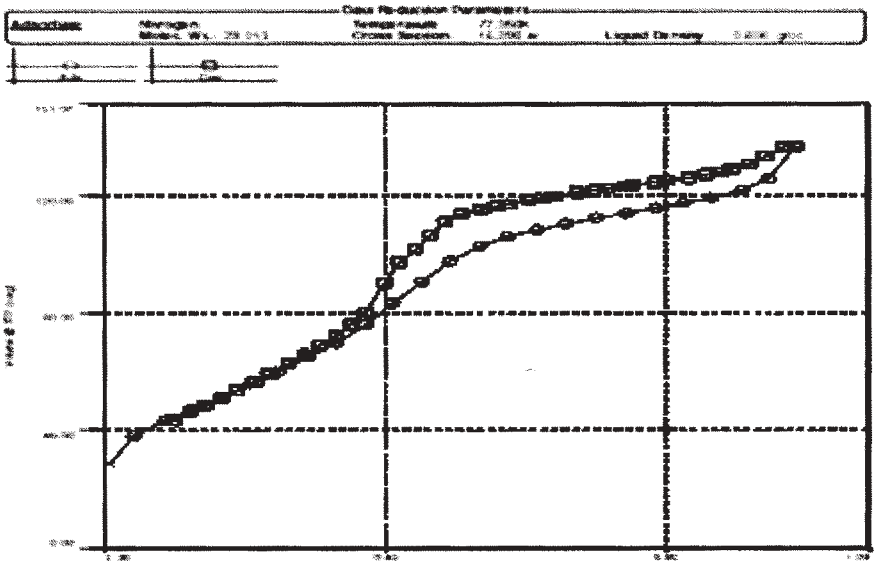

Fig. 1. The isotherm of adsorption for catalyst Ni-Co / γ-Al_2O_3

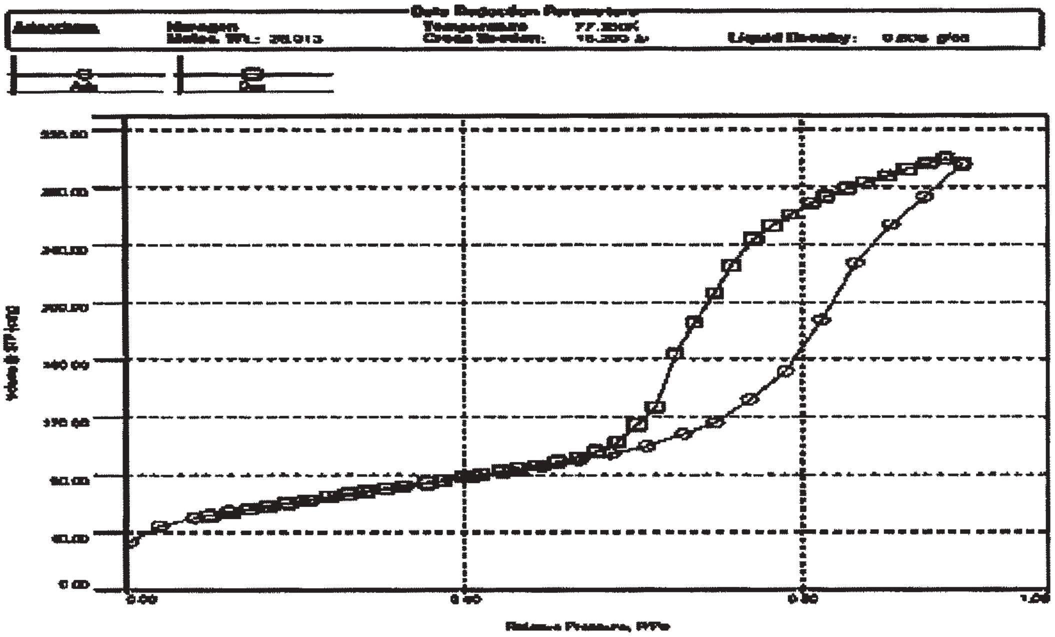

Fig.2. The isotherm of adsorption for Co-Mo / γ-Al_2O_3 catalyst

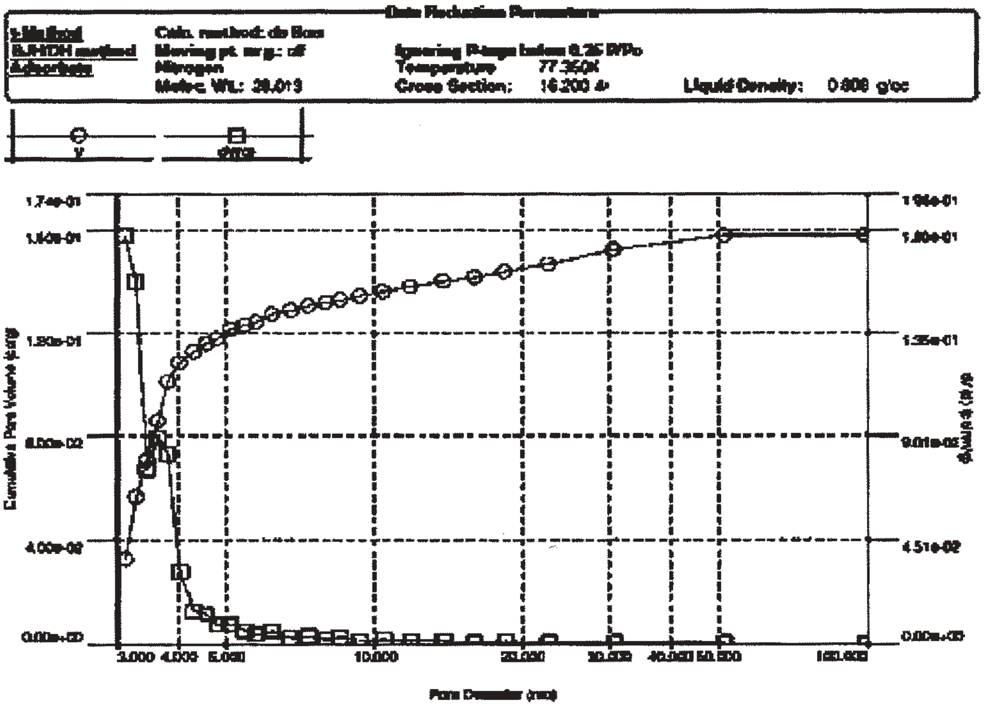

Fig.3. Textural characteristics of Ni-Co / γ-Al_2O_3 catalyst

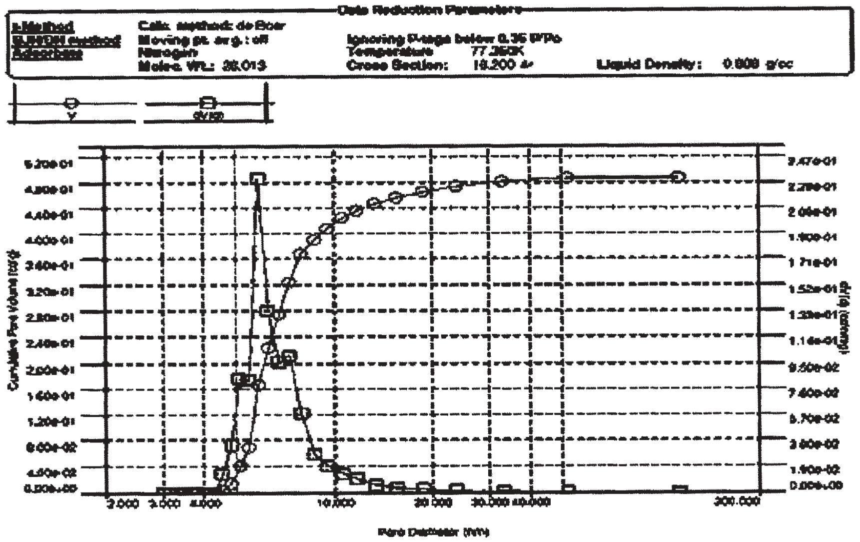

Fig.4. Textural characteristics of Co-Mo/ γ-Al_2O_3 catalyst

Table 2
TEXTURAL PROPERTIES OF THE TWO CATALYSTS

Catalysts	Pore Volume cm^3/g	Pore Diameter nm	Specific Surface Area m^2/g
Ni-Co / γ-Al_2O_3	0.158	3.119	150,695
Co-Mo/ γ-Al_2O_3	0.486	5.840	274.145

6% and of Mo was 10%. Texture data have been obtained by the automatic recording and processing of adsorption-desorption isotherms of nitrogen. Isotherms of adsorption-desorption are shown in figures 1 and 2.

To assess the pore size and distribution of pores was used desorption branch of isotherms with hysteresis, applying BJH method. Pore size distribution is shown in figures 3 and 4.

Experimental determination of the specific surface has been determined by the BJH method of cumulative desorption from volume of pores. The specific surface area was calculated using the equation in the linear part of the BET adsorption isotherm. Textural analysis of the two catalysts is presented in table 2.

The acid strength distribution of catalytic center for the two catalysts is shown in figures 5 and 6 (A-concentration of centers with weakly acidic, B- concentration of centers with the medium acidity, C-concentration of centers with high acidity)

From figure 5 is seen that Ni-Co / γ-Al_2O_3 catalyst shows a high content of weak acids centers (2.44 mEq./g), a concentration much lower of medium acidic centers(0.27meq. /g) and of strong acidic centers (0.42 mEq./g).From figure 6 is seen that CoMo / γ-Al_2O_3catalyst shows a higher content of weak acids centers (0.48 mEq./g) and a lower concentration of medium acidic centers (0.28 mEq./g) and of strong acidic centers (0.33 mEq./g).

Hydrocracked product characteristics on NiCo/γ-Al_2O_3 and Co-Mo/γ -Al_2O_3 catalysts are shown in below figures. The figure 7 shows that the heavy delayed cooking gas oil density decreases after hydrocracking with the two

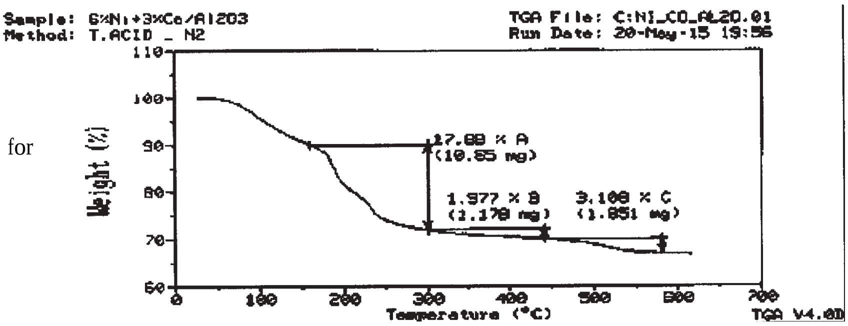

Fig.5. The distribution of the acid strength for Ni-Co / γ-Al_2O_3 catalyst

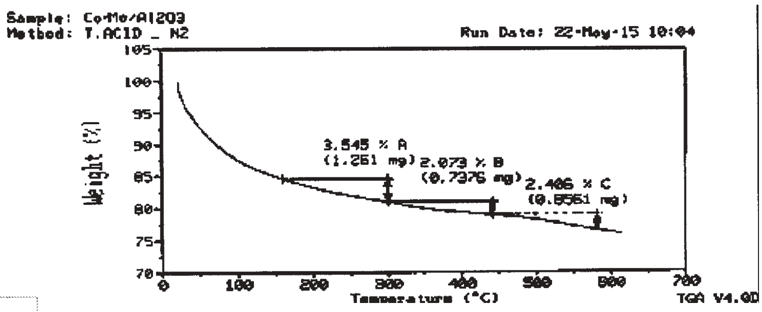

Fig.6. The distribution of the acid strength for Co-Mo/ γ-Al_2O_3 catalyst

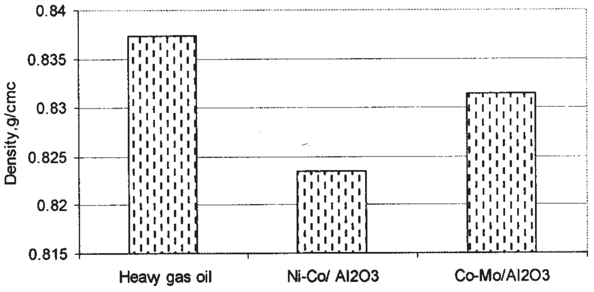

Fig.7. Influence of catalysts on density of hydrocrackates gas oil (400^0C, 100 atm, VHSV 1.0 h^{-1}, volume ratio hydrogen / coking gas oil 900Ncm^3/cm^3)

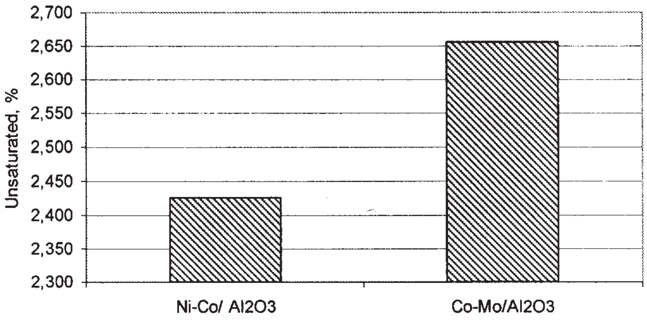

Fig. 10. Influence of catalysts on unsaturated hydrocarbons

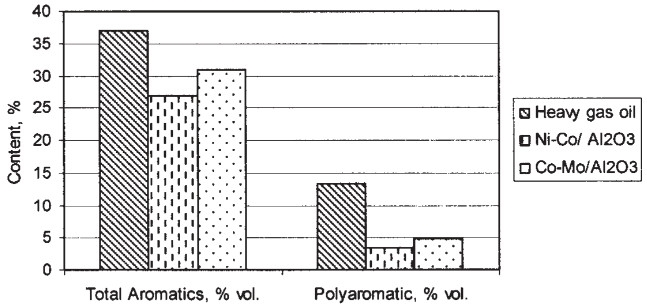

Fig.8. Influence of catalysts on total aromatic hydrocarbons and polyaromatic hydrocarbons

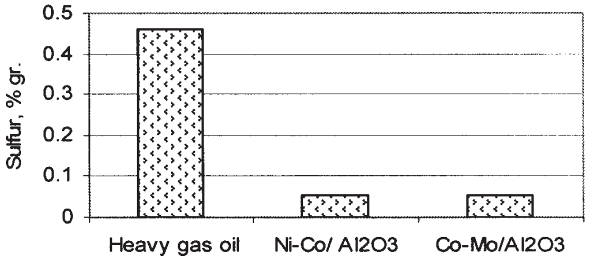

Fig.11. Influence of catalysts on sulphur content of hydrocrackates gas oil

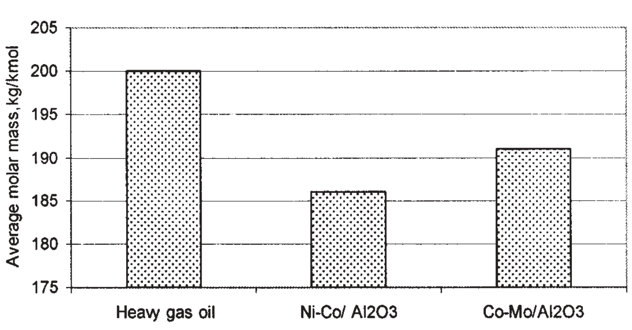

Fig.9. Influence of catalysts on average molar mass of hydrocrackates gas oil

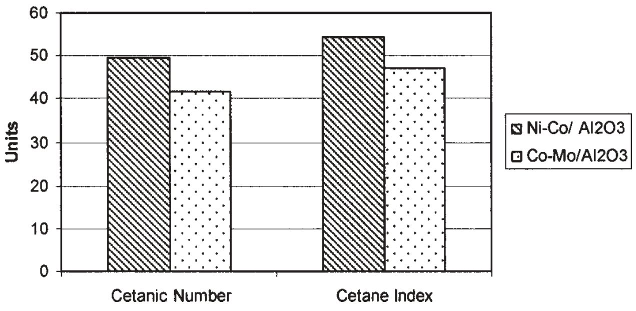

Fig.12. Influence of catalysts on cetane number and cetane index.

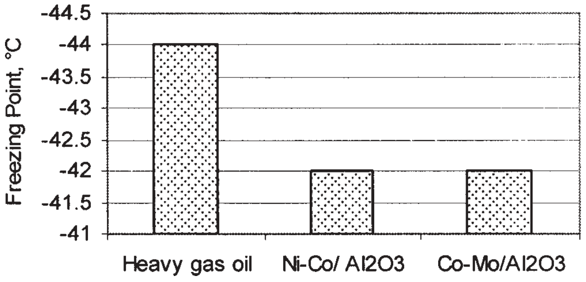

Fig.13. Influence of catalysts on freezing point

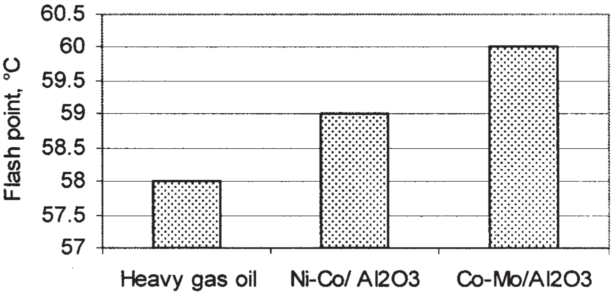

Fig.14. Influence of catalysts on flash point

catalysts, the decrease being more pronounced on Ni-Co/ γ-Al_2O_3 catalyst. This variation of density is correlate with variation of total aromatic hydrocarbons and polyaromatic hydrocarbons (fig. 8). Thus the higher activity in the reaction of aromatic ring saturation on Ni based catalyst is reflected in the sharp decrease of aromatic and polyaromatic hydrocarbon content on Ni-Co / γ-Al_2O_3 catalyst.

The average molecular weight of coker gas oil declines on the two catalysts, the decrease being more pronounced on the hydrocracking Ni-Co/γ-Al_2O_3 catalyst (fig. 9). This behavior is due to the higher activity of Ni-Co/γ-Al_2O_3 catalyst in the cracking process of hydrocarbons.

The content of unsaturated hydrocarbons in heavy delayed cooking gas oil decrease more pronounced after hydrocracking on Ni-Co/γ-Al_2O_3 catalyst, higher activity of Ni in the hydrogenation reaction of olefins being responsible for reducing the content in unsaturated hydrocarbons (fig. 10).

The sulfur content decreases after hydrocracking of coking gas oil on the two catalyst, the decrease beind at similar values for both catalyst (fig. 11).

Cetane number and cetane index of hydrocrackate gas oil coking have high values for both catalysts tested, higher values being obtained on Ni-Co/γ-Al_2O_3 catalyst, higher activity of Ni in the hydrogenation reaction of aromatic hydrocarbons and polyaromatics being responsible for this difference (fig. 12)

The freezing point decreases after hydrocracking of heavy delayed cooking gas oil on the two catalysts, the decrease being at similar values for both catalysts (fig. 13). This decrease is due by partial saturation of aromatics and by cracking reactions with formation of lower molecular weight hydrocarbons.

The flash point decreases after hydrocracking of heavy delayed cooking gas oil on two catalysts, the decrease being at similar values for each catalyst (fig. 14). This decrease is due to cracking reactions that favor the formation of lower molecular weight hydrocarbons.

Conclusions

Two catalysts were prepared by pore filling method, in order to test in hydrocracking process of heavy delayed cooking gas oil.

Catalysts were characterized by determining the adsorption isotherms, specific surface area, pore volume, average pore diameter and the acid strength.

The adsorption isotherms of nitrogen on the catalysts prepared shows the hysteresis loop characteristic of mesoporous solids.

The specific surface area was calculated using the linear part of the BET equation from the adsorption isotherm, the Co-Mo/γ-Al_2O_3 catalyst presenting a greater surface area than Ni-Co/γ-Al_2O_3 catalyst.

Pore volume, pore size distribution and average pore diameter were evaluated automatically from desorption branch of isotherms with hysteresis by applying the BJH, the largest pore volume of the Ni-Co / Al_2O_3 catalyst.

The Ni-Co / γ-Al_2O_3 catalyst has a total acidity greater than the Co-Mo/γ-Al_2O_3 catalyst, acidity due to a high concentration of weak acids centers.

Hydrocracking experiments of heavy delayed cooking gas oil were performed on the two catalysts in continuous system at 400^{0}C, 100 atm pressure, volume flow rate of 1.0 h^{-1}, volume ratio hydrogen/coking gas oil from 900Ncm^3 / cm^3.

The addition of Ni was responsable for higher performance obtained on Ni-Co / γ-Al_2O_3 catalyst namely a lower content of total aromatic hydrocarbons, polyaromatic hydrocarbons and unsaturated hydrocarbons, characteristics that reflect other important properties such as cetane number or cetane index.

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