Hydrotreating of Coker Gas Oil in Single and Double Catalytic Layer

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Hydrotreating of heavy delayed cooking gas oil was performed in single catalytic layer on Pt-Pd/Zn-ZSM-5 (SCL) and in double catalytic layer on Co-Mo / γ -Al₂O₃ and Pt-Pd/Zn-ZSM-5 (DCL). 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 900Ncm³/ cm³. The organic compounds evaluated were total aromatic hydrocarbons, polyaromatic hydrocarbons and unsaturated hydrocarbons. The activity of double catalytic layer was higher that of single catalytic layer.

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

The hydrotreating process usually is considered a preliminary step in the processing of heavy oil fractions, regardless of sulfur content, aimed to protect catalytic systems used in the final stages of the refining process. Progress made during last years in improving resistance of processing catalytic systems, in the final stages of refining favors combining hydrodesulfurization stage with hydrocracking step.

Data from the literature on light cyclic hydrocarbons hydrocracking (LOC) in a single step, without prior removal of sulfur and nitrogen, highlights the role of acid properties (acidity and distribution of acid strength) on the stabilization and activity of catalyst. This explains the increasing resistance of catalysts based on Pt and Pd when they are deposited on zeolite support. This behaviour can be explained by reduction of sulfur-metal bonds strength in the presence of Bronsted acidic centers. In a recent paper [1] is shown the influence of metal composition and acid function on hydrocracking process of LOC in temperature range of 350-400°C.

In a recent paper [2] were prepared Pd-Rh metal catalysts supported on mesoporous alumina silicates with a molar ratio Pd / Rh = 2/1. The catalysts were prepared by three different methods: *i)*direct incorporation in the gel in the synthesis process of the catalyst support, *ii)*catalyst support impregnation and *iii)*ion exchange. Aluminosilicate support was synthesized in the presence of a fatty alcohol ethoxylate surfactant type $[C_{12}-C_{25}(EO)_4]$ at a Si/Al ratio of 20. The metal content of the catalysts in all experiments was 2% total weight at a molar ratio Pd / Rh of 2/1. The selection of the catalyst was aimed to combine hydrogenation-hydrogenolysis process with cycle opening in the presence of a thiol resistant metal. The dispersion of the metal particles and their size depends on the method of synthesis applied in the catalyst preparation process. Co-impregnation is the preferred approach for preparing the catalyst used in hydrogenation processes and polycyclic aromatic hydrocarbons hidrodearomatization.

Natural and synthetic zeolites have been used in some applications for the conversion of heavy petroleum residues. In a recent paper [3] are presented the results of research on the conversion of heavy oil residue from a vacuum bottoms after they have undergone initial on pyrolysis process.

The four catalysts based on the Pd-Rh [4] activity was tested in the naphthalene and tetraline hydrogenation at 6 MPa, inclusive in the presence of sulfur-containing compounds. The activity of one of these catalysts for the hydrogenation of light cyclic hydrocarbons containing 50 ppm sulfur was assessed in a pilot plant.

Hydrogenation of aromatic hydrocarbons with more cycles was studied by customizing the compounds such as naphthalene, whose dearomatization is done in two stages, with the formation of tetraline in the first stage and decaline in the second, processes that can be accompanied by a cycle opening process through hydrocracking. Such processes were investigated using different types of catalysts: a conventional Ni-Mo catalyst, catalysts Ni - Ru supported on γ-alumina, Rh, Pd / Pt on various supports, presenting various approaches related to the nature of the active phase of catalysts [5-7].

These catalysts consist of finely nanocrystalline particles dispersed on support, being most often promoted. The hydrogenation reaction is seen as an important reaction for efficient production of environmentally friendly fuel. Kinetic considerations relating to liquid phase hydrogenation of aromatic can be studied using naphthalene as a model and selection of kinetic model was done by statistical analysis of results. Catalysts deactivation is a problem that required attention, it is usually caused by deposition of coke, a quick process, touching a pseudo state being the result [8].

Hydrogenation of aromatic compounds is much less addressed compared with the concerns for hydrodesulfurization of petroleum products or for the direction of bio-resources or mixtures of oil fractions and biomass processing [9-11]. In this paper were proposed two versions of heavy oil hydrotreating in the monolayer system on the catalyst Pt-Pd/ Zn- ZSM 5 (SCL) and in the bilayer system of two catalysts Co-Mo /γ-Al₂O₃ — Pt-Pd/ Zn- ZSM 5 (DCL).

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Characteristic	Value
Density d^{20}, g/ cm³	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

Experimental part

The raw materials used in experiments were heavy delayed cooking gas oil, cobalt (II) nitrate hexahydrate puriss p.a.(Sigma-Aldrich), ammonium heptamolybdate tetrahydrate (Sigma-Aldrich), chloroplatinic acid hexahydrate ACS reagent (Sigma-Aldrich), palladium(II) chloride, ReagentPlus (Sigma-Aldrich), γ-alumina granulated, ZSM 5 zeolite in the form H⁺ modified with zinc during the crystallization, granulated with alumina hydrate in a proportion of Zn-ZSM 5/ alumina of 40/60 wt. and electrolytic hydrogen purity from Linde Company. The main characteristics of the coking gas oil used in the experiment are shown in table 1[12].

The synthesis of catalysts where achieved by successive impregnation with aqueous solutions of the precursors of catalysts, applying the method of filling the pores. Concentration of catalyst precursor of the impregnation solution is calculated according to the proposed metal content (1% Pd-0.25% Pt for Pt-Pd/Zn-ZSM 5 and 4% Co-10% Mo for Co-Mo/ γ-Al$_2$O$_3$). Conditioning of the catalyst between impregnation was achieved by drying at 160°C for 4 h and the final conditioning was performed by drying at 160°C for 6 h, calcination at 450°C for 6 h and 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 catalysts 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 Thermogravimetric Analizer". Textural characteristics of the catalysts (surface area, pore volume, average pore diameter, pore-size-distribution) were determined on a Autosorb 1 Quantacrome [12].

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: 400⁰C;
-volume hourly space velocities of coking gas oil (VHSV): 1.0 h⁻¹;
-volume ratio hydrogen/coking gas oil (R): 900Ncm³/cm³.

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

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.
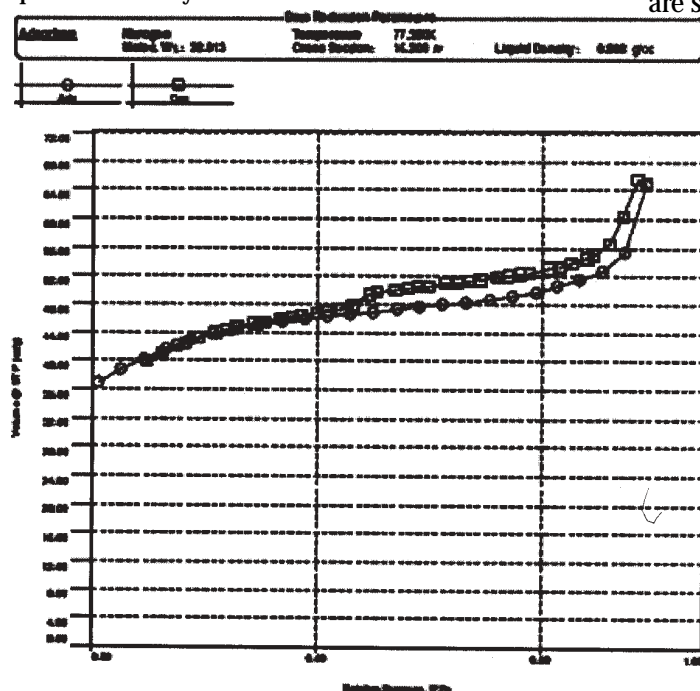

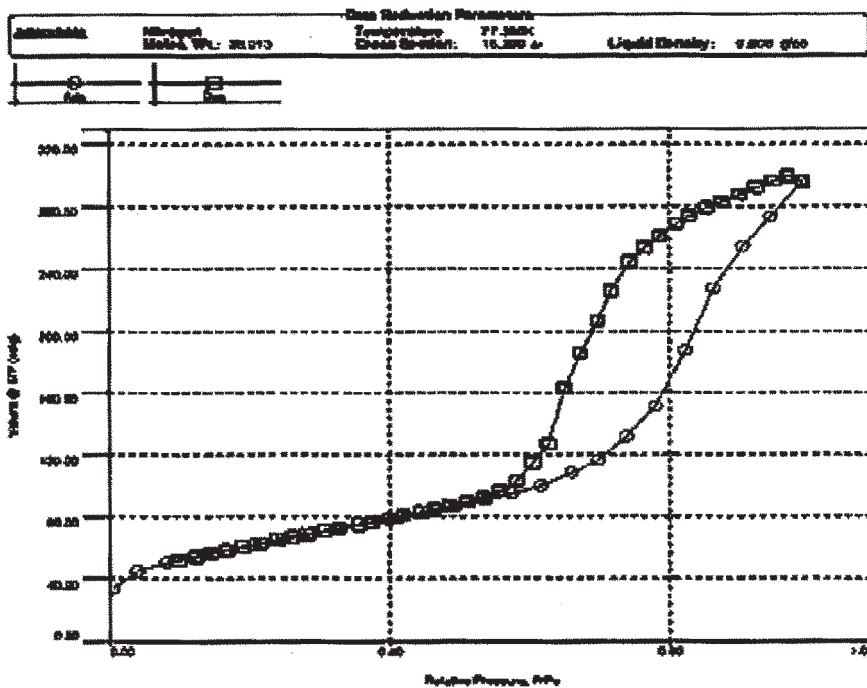Fig. 1. The isotherm of adsorption of Pt-Pd/Zn- ZSM 5 catalyst

Fig.2. The isotherm of adsorption of
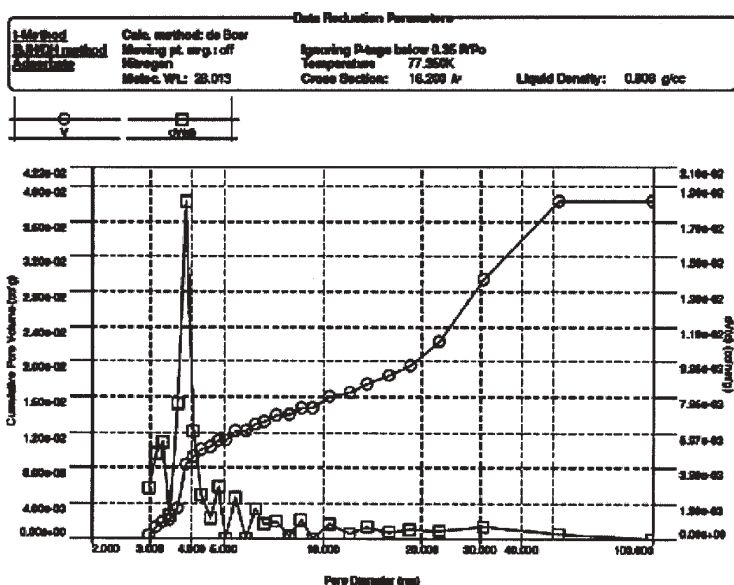Co-Mo/ γ-Al$_2$O$_3$ catalyst [12]

Fig.3. Textural characteristics of Pt-Pd/ Zn- ZSM
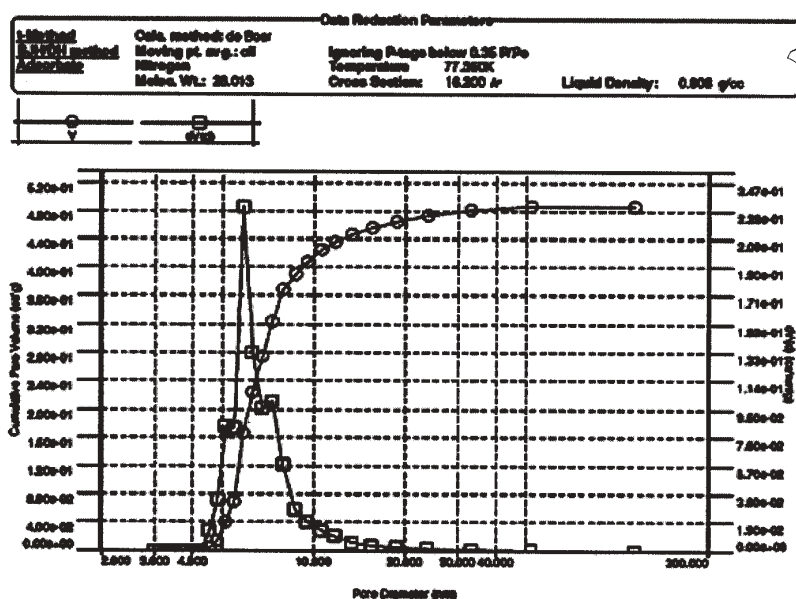5 catalyst

Fig.4. Textural characteristics of Co-Mo/ γ-Al$_2$O$_3$
catalyst [12]

The pore size and distribution of pores were determined on the basis of desorption branch of isotherms with hysteresis, applying BJH method. Pore size distribution is shown in figures 3 and 4.

The BJH method of cumulative desorption from volume of pores have been determined by experimental determination of the specific surface. The specific surface area was calculated using the equation in the linear part of

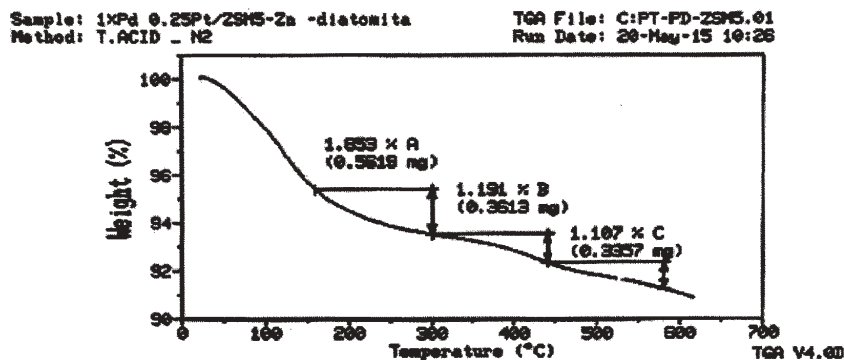| Catalysts	Pore Volume cm³/g	Pore Diameter nm	Specific Surface Area m²/g
Pt-Pd/Zn-ZSM-5	0.318	3.834	217.53
Co-Mo/ γ-Al₂O₃	0.486	5.840	274.145

Table 2
TEXTURAL PROPERTIES OF THE TWO
CATALYSTS [12]

Sample: 1xPd 0.25Pt/ZSM5-Zn -diatomita
Method: T.ACID _ N2
TGA File: C:PT-PD-ZSM5.01
Run Date: 20-May-15 10:26

Fig.5. The distribution of the acid strength
of Pt-Pd/ Zn- ZSM 5 catalyst

Sample: Co-Mo/Al2O3
Method: T.ACID _ N2
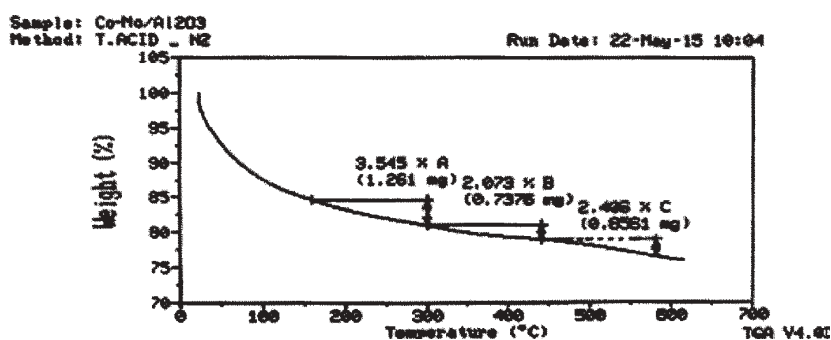Run Date: 22-May-15 10:04

Fig.6. The distribution of the acid strength of
Co-Mo/ γ-Al$_2$O$_3$ catalyst [12]

the BET adsorption isotherm. Textural analysis of the two catalysts is presented in table 2. The median pore diameter was smaller in the case of zeolitic catalyst than with catalysts based on γ-Al$_2$O$_3$.

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 Pt-Pd/ Zn- ZSM 5 catalyst shows a high content of weak acids centers (0.253 mEq./ g), a lower concentration of medium acidic centers (0.163 meq./g) and of strong acidic centers (0.151 mEq./g).

From figure 6 is seen that CoMo/γ-Al$_2$O$_3$ catalyst 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).

Characteristics of hydrotreated product on mono-catalytic system Pt-Pd/ Zn- ZSM 5 and bicatalytic system Co-Mo/γ-Al$_2$O$_3$ — Pt-Pd/ Zn- ZSM 5 are shown in below

figures. Thus the figure 7 shows that the heavy delayed cooking gas oil density decreases after hydrotreating, the decrease being more pronounced on double catalytic layer. This variation of density is correlate with variation of total aromatic hydrocarbons and polyaromatic hydrocarbons (fig. 8). Thus the decrease is more pronounced on double catalytic layer.
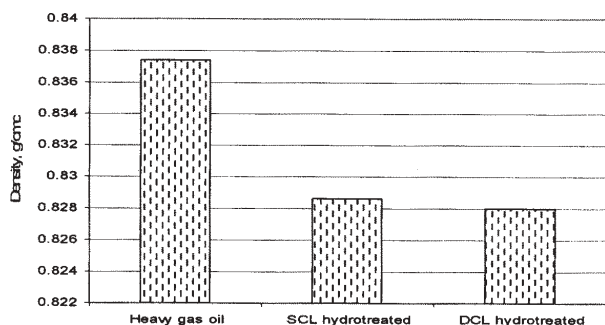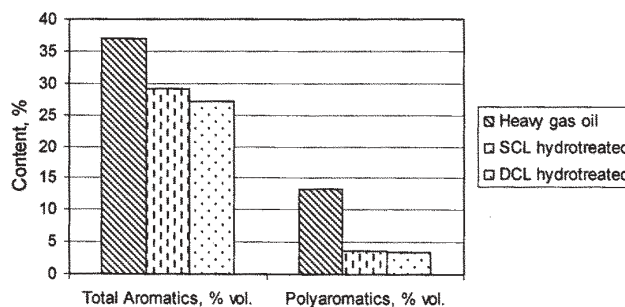
Fig.8. Influence of catalysts on total aromatic hydrocarbons and polyaromatic hydrocarbons

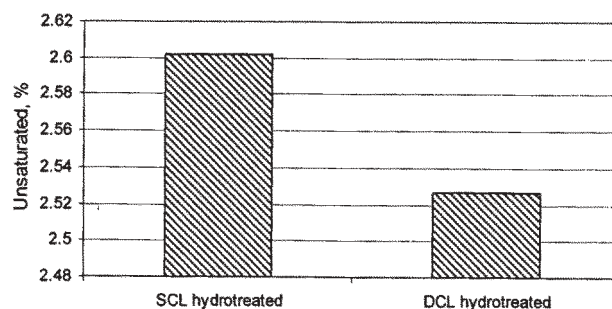Fig.7. Influence of catalysts on density

Fig.9. Influence of catalysts on unsaturated hydrocarbons

The content of unsaturated hydrocarbons in heavy delayed cooking gas oil decrease more pronounced after hydrotreating on double catalytic layer, higher activity of metals Pt-Pd in the hydrogenation reaction of olefins being favored by the presence of catalytic layer of Co-Mo/ γ - Al$_2$O$_3$ (fig. 9).

The sulfur content decreases after hydrotreating of coking gas oil on the two catalyst, the decrease being at similar values for both catalyst systems (fig. 10).

Cetane number and cetane index of hydrocrackate gas oil coking have high values for both catalysts tested, higher values being obtained on double catalytic layer, higher activity of metals Co-Mo in the hydrocraking reaction of alkyl-aromatic hydrocarbons and alkyl-polyaromatics being responsible for this difference (fig. 11)

The freezing point decreases after hydrotreating of heavy delayed cooking gas oil on the two catalysts, the decrease being better for double catalytic layer (fig. 12). This better decrease for double catalytic layer is due by cracking reactions with formation of lower molecular weight hydrocarbons on Co-Mo/ γ-Al$_2$O$_3$.

The flash point decreases after hydrotreating of heavy delayed cooking gas oil on double catalytic layer (fig.13). This decrease is due to cracking reactions on Co-Mo/γ-Al$_2$O$_3$ that favor the formation of lower molecular weight hydrocarbons.

The main characteristics of fractions of gasoline, jet fuel and diesel product obtained by distillation of hydrotreated product on double catalytic layer are shown in table 3. It shows a concentration of unsaturated hydrocarbons, aromatics and polyaromatic in heavier petroleum fractions.
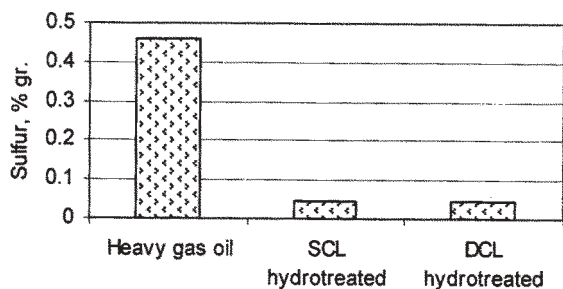

Fig.10. Influence of catalysts on sulfur content of hydrotreated gas oil
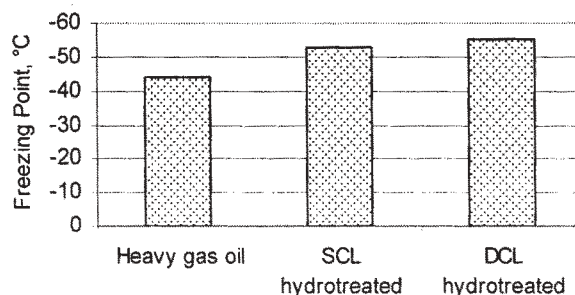

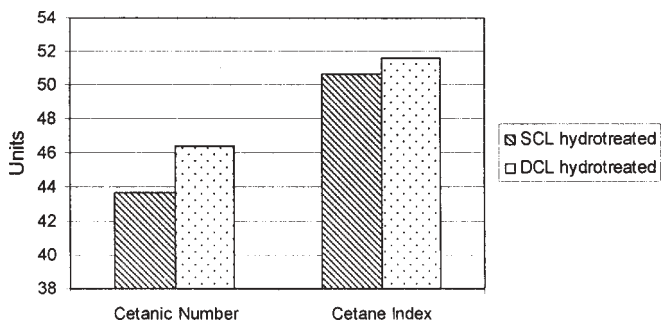Fig.12. Influence of catalysts on freezing point

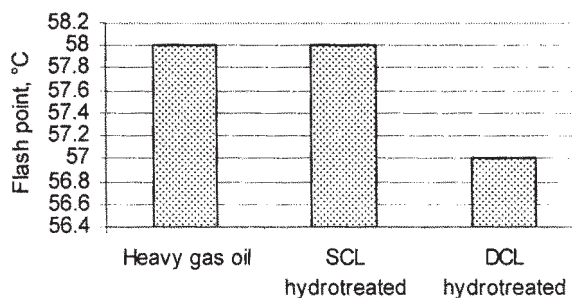Fig.11. Influence of catalysts on cetane number and cetane index

Fig.13. Influence of catalysts on flash point

Characteristics	Gasoline	Jet Fuel	Diesel Fuel
Distillate, %vol.	23.5	41	34
Density, g/ cm^3	0.7221	0.8221	0.9081
Average molar mass, kg/kmol	148	187	198
Total aromatic hydrocarbons, % vol.	8.2	20.1	49.6
Polyaromatic hydrocarbons, % vol.	0	2.4	7.1
Unsaturate, % vol.	0.42	1.58	5.23
The distillation curve			
Initial boiling point, °C	53	180	260
10 %vol., °C	68	195	268
50 %vol., °C	117	225	288
70 %vol., °C	139	238	295
90 %vol., °C	165	255	302

Table 3
CHARACTERISTICS OF DISTILLATE FRACTIONS OBTAINED ON DOUBLE LAYER CATALYTIC SYSTEM Co-Mo/γ-Al$_2$O$_3$ AND Pt-Pd/ZSM-5

Conclusions

Hydrotreating process of heavy delayed cooking gas oil was performed in single catalytic layer on Pt-Pd/Zn-ZSM-5 and in double catalytic layer on Co-Mo /γ-Al_2O_3 and Pt-Pd/Zn-ZSM-5

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

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

Coker gas oil characteristics were more improved when hydrotreating process was conducted in a double layer catalyst.

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