NEW CATALYSTS OF «SYNTHETIC OIL» AND ITS DISTILLATES ENNOBLEMENT

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The process of coal distillates hydrotreatment on Mo–Hu/Ni–Re and So–Hu/Ni–Re catalysts has been studied in the given work. As research results show the maximum exit of liquid products – 51,0–56,0 mass.% is observed on the 5% Mo–Hu, 7% Co–Hu/Ni–Re catalysts. Besides, there is an increase in a portion of gasoline fraction in a liquid product up to 29,5% on the 5% Mo–Hu/Ni–Re catalyst, and up to 21,7 mass.% on the 7% So–Hu/Ni–Re. The exit of liquid products increases up to 60,8 mass.% and exit of gasoline fraction increases up to 32,8 mass.% at simultaneous depositing of these catalysts. The content of paraffin hydrocarbons has decreased from 35,8 to 28,3%. The quantity of isoparaffin hydrocarbons in the synthetic oil hydrogenized on deposited 5%Mo-Humate Ni-Re has increased up to 36,2%. To all appearance, during the hydrogenation there is a process of isomerizating. The olefinic, cyclo-olefinic and diene hydrocarbons are present also at the hydrotreated benzine.

Keywords: coal, hydrotreating, catalyst, coal distillate, gasoline fraction

Along with a continual growth in production of oil and gas all over the world, an intersst towards coal, as an alternative source of motor fuels, oil-chemical material and chemical substances arises. Therefore, one of the important directions in modern biochemistry is the development of industrial means to receive practically important oil-chemical, chenmical products from natural organic materials that allow us to avoid usage of ecologically-dangerous substances.

A development of new technologies of processing solid fuel in order to receive fluids, and also a selection of new types of catalysts that posses a high activity and selectivity level and work in mild conditions is a significant problem of modern days [1].

During the recent years, in accordance to the European standards, the following requirements are placed towards motor fuels: benzol content must not exceed 1% of mass, sulphur – 0,05% of mass, olefines – 20% of mass, polycyclic aromatic hydrocarbonss – 11% of mass. The composition of coal distillate preserves unstable nitrogen, oxigen-full compounds, ans also desaturated hydrocarbons that are able to polymerize, so a selection of new types of catalyst, on which processes of hydic cleaning (hydroprocessing) in mild conditions can take place, becomes urgent.

Bibliographic data [2-3] on hydrocleaning and hydrocracking of coal distillates state that that world practice uses sulphured catalysts that are based on Mo–Co–Ni–W, placed on AI_2O_3, SiO_2 and other carriers.

Catalysts with pore radius of more than 100 nm are more active and stable in ennoblement of hydrocarbon materials.

Based on a rich experience of work with skeleton catalysts, we have suggested to use them in hydric cleaning of hydrocarbon materials. Modified skeleton catalysts, based on alloys of Ni-Al are widely used on enterprises of chemical and oil-processing industry.

This work presents the results of studying process of hydroprocessing coal distillates on Mo, Co–Fy/Ni–Re catalysts. The process of hydration and hydro-cleaning of «synthetic oil-1» that is received after liquefaction of coal on placed Mo–Humate and Co-Humate/Ni–Re catalysts was carried out in the catalyst «duck». The results are provided in Table 1.

Table 1

Hydration of «synthetic oil-1» on Mo–Hu and Co–Nu/Ni–Re catalyst
(T = 293 K, mkat = 1r, P_{H2} – atmosphere)

Output of fluids, mass,%					Remains, mass,%	Losses, mass,%
Catalyst	under 453K	453–523K	523–593K	∑		
Ni-Re	20	17,7	2,9	40,6	53,0	6,4
3% Mo–Hu/Ni–Re	17,5	10,0	17,0	44,5	46,1	9,4
5% Mo–Huy/Ni–Re	29,5	10,2	11,3	51,0	45,7	3,3
7% Mo–Hu/Ni–Re	25,1	10,7	14,3	50,1	45,0	4,9
3% Co–Hu/Ni–Re	16,3	7,2	21,0	44.5	46,1	
5% Co–Hu/Ni–Re	18,8	12,3	12,2	43,3	48,0	8,7
7% Co–Hu/Ni–Re	21,7	12,6	21,7	56,0	37,3	6,7
5%Mo–Hu + 7%Co-Hu/Ni–Re	32,8	13,8	14,2	60,8	34,2	5,0

As the results show, maximum output of fluids, 51,0–56,0 of mass%, is observed on 5% Mo–Hu 7% Co–Hu/Ni–Re catalyst. Besides, an increase in part of benzol fraction in fluid on 5%Mo–Hu, 7%Co-Hu/Ni-Re up to 29,5% take place, and on 7% Co–Hu/Ni–Re – up to 21,7% of mass. Under a simultaneous placements of these catalysts an output of fluids increases up to 60,8% of mass, and benzol fraction – up to 32,8% of mass.

Then, the received fraction after liquefaction (353–593 K) was hydrated on the placed Mo-Hu/Ni-Re. The results are provided in Table 2.

Table 2

Output of fluids after hydrating fraction of 353–593 K «synthetic oil-2» on catalyst Mo–Hu/Ni–Re

Output of fluids, mass,%					Remains, mass,%	Losses, mass,%
Comment	under 453 K	453–523 K	523–593 K	∑		
Zeolyte catalyst	4,8	7,7	35,0	47,5	46,6	5,9
3% Mo–Hu/Ni–Re	44,7	22,0	18,4	85,1	8,2	6,7
5% Mo–Hu/Ni–Re	48,4	28,3	14,8	91,5	4,8	3,7
7% Mo–Hu/Ni–Re	51,6	17,8	19,1	88,5	7,8	3,7

As the results show, an output of fluids increases up to 91,5% of mass, the maximum output is observed on 5% catalyst Mo–Hu/Ni–Re. We should point out that on 7% catalyst Mo–Hu/Ni–Re an output of benzol fraction increased up to 51,6% of mass.

Thus, here a principal possibility of hydrocleaning benzol fraction, received from distillates of Kuminsk coal in mild conditions and skeleton catalysts.

Chromatographic method was used to study group hydrocarbon content of benzol fraction. The results are provided in Table 3.

Table 3

Group hydrocarbon content of benzol fraction

Hydrocarbons	Hydrocarbon content,%					
	Catalyst, zeolite	5% Mo–hu/Ni–Re (Syn. oil-1)	7% Co–Hu/Ni–Re (Syn. oil-1)	5% Mo–Hu + 7% Co–Hu/Ni–Re (Syn. oil-1)	5ml 353-453K + 5% Mo–Hu/Ni–Re, solvent ethanol (Syn. oil-2)	22ml 353-593K + 5% Mo–Hu/Ni–Re (Syn. oil-2)
Paraffines	35,8	23,2	14,7	13,6	28,3	29,4
Iso-paraffines	16,3	28,7	26,0	19,6	19,6	36,2
Aromatics	25,0	21,6	34,1	42,2	23,2	15,2
Naphtenes	14,2	16,2	14,8	16,9	16,4	11,7
Olefines	8,1	4,8	6,8	5,6	11,0	6,4
Cyclic olefines	0,6	5,2	3,5	2,1	1,5	1,0
Dienes	-	0,3	0,07	-	-	0,01
Research method	69,4	72,7	77,3	82,3	71,7	73,6

According to the data of chromatographic analysis, we can see a decrease in paraffine hydrocarbons from 35,8 to 13,6%. We can observe significant changes in the number of isoparaffine hydrocarbons. During the process of hydro-cleaning, the reaction of dealkylation of alkile-aromatic hydrocarbons takes place. As a result, the contents of aromatic hydrocarbons multiplies by two. While contents of aromatic hydrocarbons in benzol, that has been received with zeolite, equaled 25,0% of mass, on the placed Mo, Co–Humate/Ni–Re catalyst it incresed up to 42,2% of mass. The benzol content in placed catalysts has decreased. Whilein content of benzol fraction, received with hydration of coal on zeolite, it equaled 0,479%, on the placed Mo, Co-HumateNi-Re catalyst it equaled 0,243–0,356%. Compared to the oc-

tane number of the initial gasoline (69,4), octane number of the gasoline, cleaned on Mo, Co–Humate/Ni–Re catalyst, increased up to 82,3. The number of olefine hydrocarbons decreased from 8,1 to 4,8%. According to the chromatographicdata, we can see significant changes in contents of benzole fraction that has been hydrated in ethanol. Contents of parffine hydrocarbons has decreased form 35,8 to 28,3%. The amount of iso-paraffine hydrocarbons in the «synthetic oil-2» that has been hydrated with placement of 5% Mo–Humate Ni–Re increased up to 36,2%. Obviously, process of isomerisation takes place during hydrogenation. Olefine, cyclic olefine, and diene hydrocarbons are also present in hydro-cleaned gasoline.

Thus, gasoline, received from the distillates of Kunminsk coal in mild conditionson placed skeleton catalysts, corresponds to the modern requirements towards the quality of motor fuels and ecological standards.

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