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The New Methods of Deep Processing of Oil Residues in Conjunction with Shales

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Abstract. The results of studies on the development of a new process of thermal cracking of tar oil as a slurry with crushed oil shale to obtain components of motor fuels. The results suggest doubtless advantages of the process before the industrial of thermo cracking, since the single-stage processing of raw materials in relatively in the mild conditions (5 MPa, 425 °C, volumetric feed rate 1.0 h^{-1}) is achieved deep destruction of tar oil (the yield petrol fraction with a bp amounts to up to 180 °C – ~12 mass % of middle distillates with a bp 180-360 °C – 43-44 mass %, of raw material for catalytic cracking of a bp 360-520 °C – ~15-16 %, based on the initial tar oil). Formed like coke products and raw materials contained in V and Ni is postponed on the mineral part of slate and removed from the reaction zone with the liquid products of the process.

Introduction

In the impossibility of increasing oil production and continued growth in demand for conventional power processing of heavy residues and high-viscosity oil, natural bitumen, coal and oil shale is becoming a strategic direction in the development of oil processing industry of Kazakhstan, Russia and the CIS countries.

New trends in Russian development of the technology is the development of oil refining catalytic cracking and catalysts of process viscosity breaking, delayed coking and hydroconversion tar. Of this set technologies promising can be recognized a process of hydroconversion of tar, which has, according to the foreign analogues, is costly and technically difficult [1].

The process of catalytic cracking is constantly improving, and the expense of new technological solutions and catalysts can reach the data described in the article: the yield of gasoline with a boiling point 205 °C – 51 mass % the total yield C_3-C_4 of gases – 16 mass %; the octane number MI – 94.2; sulfur content in petrol – 0.005 mass %. Indicators of the quality of new gasoline catalytic cracking catalysts (in particular the "Lyuks-2") outperforming the best foreign catalysts «Brilliant Grace» and «LS-60P» of the firm «Engelhard». However, the question remains open of energy saving new technologies, as this will determine the feasibility of new projects number.

Without doubt residue hydroconversion process deserves serious attention, because it allows different oils from tars get 81-86 % of synthetic oil. However, the above results in the literature do not provide any information about the technical possibility of implementing and the most importantly, the material and energy consumption.

Institute GrozNRI through the process of hydroconversion of heavy oil feedstock in the lungs and middle distillates at 6-10 MPa using nanosize catalyst. In the radically of new catalytic system provided better access to the active centers of reagents. Composition is not disclosed but, according to the literature, it is – Mo catalyst developed at the Institute of Fossil Energy to process coal liquefaction and hydroprocessing of petroleum residues. A distinctive feature of this catalyst – emulsion condition with a particle size 118.6-460.3 nm which is reached in the preparation of when entering predecessors in the feedstock.

During the processing of raw materials in pilot plants is achieved yield of synthetic oil from 63.4 (raw-bitumen) to 81-86 % (raw materials, oil or tar). A synthetic oil density 857-890 kg/m^3 does not contain metals, but contains 1.2-2 mass % Sulfur. By the proposed flow sheet such oil is sent for further processing known techniques to produce commercial products.

Discussion

We jointly with FSUE "Institute of Fossil Fuels (FSUE IFF) – Technology Center on complex processing of combustible minerals" developed a method of the joint processing of catalytic thermal Kenderlyk tar and oil shale.

The article contains results studies on the development of the process of thermal cracking of tar mixed with crushed combustible slate for components of motor fuels and raw materials for catalytic cracking. To study used ordinary Kenderlyk shale JSC "Quartz" with the following characteristics (mass %) – W^a – 0.8; A^d – 64.5; C^{daf} – 74-77; H^{daf} – 7.3-9.9; S^d – 0.6-1.3; conventional organic weight shale, which was determined according to the [$OM = 100 - A^d - (CO_2)_M$] is equal to 33.2 mass %.

As part of the mineral Kenderlyk shale prevail compounds of calcium, silicon and aluminum (Table 1).

Table 1 – Characteristics of the mineral oil shale deposits of Kenderlyk

Content of the components in the ash, [mass %]							
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O
58.2	17.2	7.3	2.3	1.0	3.4	-	10.6

Experimental part

As a raw material used of tar mixtures with oils of West Siberia bp. > 520 °C with the following characteristics: the density at 20 °C – 0.948 g/cm^3, viscosity 9.7 C; the content, mass %: C – 85.60, H – 10.72; S – 2.06; N – 0.30; the asphaltenes – 13.6; V and Ni – 180 and 90 g/t. The thermal cracking performed in RINCT&M shaken vigorously in a reactor volume of 0.2 L at 400-440 °C and an operating pressure of nitrogen 5-8 MPa and in a flow bench setup FSUE IFF reactor with a volume of 3L at 425-435 °C, 5 MPa, volumetric feed rate 1-2 h^{-1} and a flow rate of the mixing of reagent (nitrogen) 400-500 liters per 1 kg of the reaction mixture.

In the preparation of pasta oil shale shredded in a ball mill to a particle size less than 200 microns slate mixed with tar in various ratios. The resulting paste was dispersed in a single plate dispersant of Pushkin-Hotuntseva with a gap between the plates of 1.0 mm at a speed of rotation of the movable plate 1420 revs/min.

Table 2 presents the results of experimental studies on the optimization of the shale: Oil product in oil shale paste.

Data in the Table 2 that the optimal number of shale added to the tar is 15.0 %. When using Kenderlyk shale thermal cracking in the assumed conditions (experiment 1), we obtain a high yield of gasoline fraction with bp. to 200 °C – 12.5 % based on the tar and diesel fraction with bp. 200-370 °C – 53.6 %. When reducing additives Kenderlyk shale to 10.0 % total yield of gasoline and diesel fraction decreased from 66.1 to 55.0 %. Further reduction in the amount of added oil shale up to 8.0 and 5.2 %, resulting in a significant decrease in the yield fraction of motor fuels to 43.2 and 26.8 %, respectively, increases the output of heavy residue, bp. 370 °C and coke.

Increase in the content raw pasta in petroleum shale above 15.0 % is impractical because it would lead to complication of process technologies, increased erosion of apparatus mineral part of shale, the stratification of the reaction mixture on the liquid and solid phases and complexity of hardware registration node separation of the solid components from the liquid products thermal cracking.

Use in instead of thermocracking Kenderlyk raw shale sulfur shale practically does not affect the yield of the desired product of the process. The yield of gasoline and diesel fractions a total is 66.9 %.

Table 2 – The results of thermal cracking of tar with different contents of shale (425 °C, 5.0 MPa, reaction time 1.0 h, shaken vigorously reactor)

The yield of products	№ of experiments				
	1	2	3	4	5
	Is taken, mass %:				
1. Tar	100.0	100.0	100.0	100.0	100.0
2. Private of Kenderlyk shale, including:	15.0	10.0	8.0	5.2	15.0
Organic mass of shale (OMS)	5.9	3.9	3.1	2.2	7.2
The mineral part	9.1	6.1	4.9	3.0	7.8
	Obtained in the calculation of the tar mass %:				
1. Gaz	5.7	4.2	4.0	3.7	5.7
2. Water	2.0	0.8	0.8	0.9	1.1
3. The fraction with bp. 200 °C	12.5	13.0	8.8	8.6	12.4
4. The fraction with bp. 200-370 °C	53.6	42.0	34.4	18.2	54.5
5. Residue with bp. above 370 °C	28.8	40.1	49.5	62.9	30.1
The coke content on the mineral oil shale mass %	3.3	3.8	5.6	7.9	3.4

Table 3 shows the results on the effect of the process temperature on the yield of the desired products thermal cracking of tar mixed with shale. At a temperature of 400 °C output of gasoline fraction bp. to 200 °C with a relatively small and is 9.1 % based on the tar, while in the process, a sufficiently large amount of the diesel fraction (53.2 %). As the temperature of the process above 425 to 440 °C increases coke production up to 4.0 % and is reduced the total yield of the readily boiling and middle distillates from 66.1 (425 °C) to 61.5 % (440 °C). Thus, the results of experimental studies showed that the optimum temperature of the process is the interval 425-430 °C (maximum).

Table 3 – Temperature effect on the thermal cracking mixture of shale with petroleum products. Conditions: 5.0 MPa, reaction time 1.0 h shaken vigorously reactor

The yield of products	Temperature, °C		
	400	425	440
1. Tar	100.0	100.0	100.0
2. Private of kenderlyk shale	15.0	15.0	15.0
The yield of products, mass. % On tar oil			
1. Gaz	4.5	5.7	7.5
2. Water	1.0	2.0	0.4
3. The fraction with bp. 200 °C	9.1	12.5	14.3
4. The fraction with bp. 200-370 °C	53.2	53.6	47.2
5. Residue with bp.above 370 °C	36.0	28.8	32.5
The coke content on the mineral oil shale mass %	2.1	3.3	4.0

Table 4 shows the results on the effect of the duration of the process on the yield of distillate fuel fractions. Found that the reduction in response time from 60 to 30 min leads to decrease in the yield of gasoline fraction and an increase in the content of middle distillate products thermal cracking with bp. 200-370 °C. On the increase response time to 120 min was an increase in coke formation (up to 4.3%) and reduced the total yield of gasoline and diesel fractions of 3.1 % compared with the implementation process for 30 minutes.

Table 4 – Results of the thermal cracking of oil shale with a mixture of petroleum product at different duration of the process. Conditions: 425 °C, 5.0 MPa, shaken vigorously reactor

Data	Response time, min		
	30	60	120*
1. Tar	100.0	100.0	100.0
2. Private of Kenderlyk shale	15.0	15.0	15.0
The yield of products, mass % on tar oil			
1. Gaz	4.5	5.7	7.5
2. Water	1.2	2.0	2.4
3. The fraction with bp.200 °C	10.0	12.5	16.0
4. The fraction with bp. 200-370 °C	57.3	53.6	48.21
5. Residue with bp. above 370 °C	30.0	28.8	27.5
The coke content on the mineral oil shale wt. %	2.9	3.3	4.3
* – working pressure of process 8.0 MPa			

The results obtained in the reactor were shaken vigorously reflected in the implementation of the process in a Metal display with running the installation FSUE IFF (Tables 5-7).

Table 5 – Material balance (mass %) of contact thermal cracking of tar mixed with fuel of Kenderlyk shale (5 MPa nitrogen supply 400-500 l/l raw bench flow setting)

Indicators	The conditions of process	
	425-435 °C, 1.0 h^{-1}	425-435 °C, 2.0 h^{-1}
Obtained by		
1.Tar	100.0	100.0
2. Shale, including:	15.0	15.0
OMS*	5.9	5.9
ash	9.1	9.1
TOTAL:	115.0	115.0
Received		
1. Dehydrated and ashless products of hydrogenation, including fractions with bp. (°C):	90.7	93.2
Up to 180	12.6	10.8
180-360	44.3	32.3
360-520	14.4	15.8
above 520	19.4	34.3
2. The solid residue, including:	14.9	14.2
The mineral part of oil shale	9.1	9.1
Undissolved part of OMS	0.4	0.5
coke	5.4	4.6
3.Gaz, including:	7.7	6.0
C_1-C_4	1.6	1.2
CO CO_2	0.1	0.1
N_2	5.8	4.5
H_2	0.2	0.2
4. Water + loss	1.7	1.6
TOTAL:	115.0	115.0
*OMS – Organic mass of shale		

The table shows that at 425-435 °C and a space velocity of feed 1-2 h^{-1} output gasoline fractions bp. to 180 °C is 10.8-12.6 %. Gasoline cracking (Table 6) contains a moderate amount of aromatic hydrocarbons (~27.0 %) and unsaturated compounds (iodine number is 26.4), which provides the modern requirements for gasoline on environmentally dangerous component. However, the use of the gasoline as a motor gasoline component standard EURO (GOST R 52368-2005) very difficult because of the content in it 2.5 vol. % phenol and 1.2 % vol. nitrogenous base. Therefore, shale gasoline should be subjected to hydro purification in a separate step of the process, and then subjected to catalytic reforming to increase the octane number. Output of diesel fractions bp. 180-360 °C is 32.3-44.3 %, which is 2.2-3 times higher. Than in industrial thermal cracking fuel oil, gas oil and coker tars. Aromatic hydrocarbons in the fractions with bp.180-360 °C with 53.8 %, but due to the high sulfur content (1.42 %) and unsaturated compounds (iodine number is 33.9) middle distillates derived from shale must also expose hydro cleaning, and for diesel fuel with a cetane number of 47-51 items require partial hydrogenation of aromatic hydrocarbons.

Table 6 – Characteristics of distillate of products thermal cracking of tar mixed with shale

Indicators	The fractions with bp., °C		
	to 180	180-360	360-520
Density at 20 °C, g/cm^3	0.7666	0.8696	0.9295
Content,%:			
Phenols	2.5	1.5	-
Nitrogenous bases	1.2	4.2	-
Of hydrocarbon sucking mass %:			
Paraffin + naphthenic	72.7	46.2	22.2
Aromatic	27.3	53.8	61.1
Silicagel resin	-	-	16.7
Asphaltenes	-	-	3.4
Iodine number, g I_2/100 g	26.4	33.9	12.5
The elemental composition, wt. %:			
C	85.50	86.20	86.57
H	13.82	12.20	11.19
S	0.60	1.42	1.97
N	0.08	0.18	0.27
Content,%:			
V	-	-	5.0
Ni	-	-	20.0

In the developed a new process of thermal cracking of tar with slate remains unturned to 34 % of the heavy residue from bp. above 520 °C. This residue is not very different in their physical and chemical properties (Table 7) from the original tar and can be returned for processing in the form of a mixture with the starting material.

Table 7 – Characteristics of tar residue hydrocracking mixed with shale

The index	Heavy residue bp. > 520 °C	Solid residue of Process
The density at 20 °C, g/cm^3		
Asphaltene content, mass %:	1.0361	-
Elemental composition, mass %:	16.3	-
C	83.80	-
H	9.46	-
S	1.68	1.0
N	0.64	-
O	4.42	-
The content, g/t		
V	125.0	1017.0
Ni	103.0	766.0