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HIGH GRADE PETROLEUM RESIDUE RECYCLING WITH SHALE ADDITIVE

Abstract. This work covers thermal cracking of tar in a mixture with milled oil shale for production of components of motor oils and feedstock for catalytic cracking. It contains the results of optimization of technological parameters (shale concentration, temperature and timing) and material balance (mass %) of the process. It has been determined that one-stage processing under the relatively mild conditions (5 MPa, 425°C, feed space velocity of 1.0 h^{-1}) results in a deep destruction of tar (gasoline yield with boiling point up to 180°C is approx. 12 mass %; middle distillate yield with boiling point of 180-360°C is 43-44 mass %; yield of feed for catalytic cracking with boiling point of over 360°C is approx. 15-16 mass % in terms of initial tar). The formed coke-like products including V and Ni contained in the feedstock are deposited on the mineral part of shale and removed from the reaction zone along with liquid process products.

Keywords: thermal cracking, solid oil residual, tar, shale, motor oils, Kenderlyk, coking.

Introduction. Processing of heavy oil residues and high-viscosity oil, natural bitumen, coal and shale becomes a strategic direction of development of oil refining industry of Kazakhstan, Russia and CIS countries under the condition of impossible increase of production of oil and permanent growth of need in conventional sources of energy [1-3].

The new trends in development of oil refining technology include development of catalytic cracking processes and catalysts of viscosity breaking process, delayed coking and tar hydro-conversion. The latter one is most promising, however, according to foreign analogues, it is very expensive and technologically difficult.

The catalytic cracking process is being constantly improved, and the following parameters can be achieved due to the use of new technological solutions and catalysts: gasoline yield with boiling point of 250°C is 51 mass %; total C3-C4 gas yield is 16 mass %; research octane number is 94.2; and petrol sulfur content is 0.005 mas. %. Quality parameters of new catalysts of catalytic cracking of gasoline exceed parameters of best foreign catalysts Brilliant Grace and LS-60P of Engelhard. However, the issue of energy saving of new technologies is still open, because this predetermines feasibility of new projects.

It is obvious that the process of hydro-conversion of residues deserves paying a close attention to it, because it allows producing 81-86% of synthetic oil from tars of various oils. However, the results given in the literature provide no information

about technical feasibility and, what is most important, required materials and energy.

Processing of feedstock using pilot plants results in output of synthetic oil from 63.4% (feedstock – bitumen) to 81-86% (feedstock – oil fuel or tar). Synthetic oil with its density of 857-890 kg/m^3 contains no metals, however, it contains 1.2-2 mas. % of sulfur. According to the proposed technology, such oil is forwarded for further refining using the known technologies to produce commercial products.

EXPERIMENTAL PART

The work contains the results of researches on development of the process of thermal cracking of tar in a mixture with milled oil shale for production of components of motor oils and feedstock for catalytic cracking.

Together with the Federal State Unitary Enterprise Fossil Fuel Institute – Research and Development Center of Integrated Processing of Fossil Fuels we developed a method of combined thermal-catalytic processing of tar and Kenderlyk oil shale [4-7].

Ordinary Kenderlyk oil shale of Quartz JSC was used for research purposes. The oil shale parameters are as follows (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; conditional organic matter of shale determined using the formula [OM = 100 – A^d – (CO_2)m] is equal to 33.2 mass %. Calcium, silica and aluminum compounds prevail in mineral composition of Kenderlyk oil shale: SiO_2 – 58.2; Al_2O_3 – 17.2; Fe_2O_3 – 7.3; CaO – 2.3; MgO – 1.0; SO_3 – 3.4; and K_2O – 10.6 mass %.

Tar with boiling point of > 520°C was used as feedstock. The tar had the following parameters: density at 20°C – 0.948 g/cm^3; viscosity– 9.7 cS; content, mass %: C – 85.60; H – 10.72; S – 2.06; N – 0.30; asphaltene – 13.6; V and Ni – 180 and 90 g/t, respectively. Thermal cracking was carried out in the Research Institute of New Chemical Technologies and Materials in intensively shaken 0.2 l reactor at 400-440°C, and nitrogen working pressure of 5-8 MPa.

Shale was mixed with tar in various ratios when making oil shale paste milled in ball mill to particle size of less than 200 μm. The produced paste was dispersed one time in Pushkin-Khotuntsev plate disperser with 1.0 mm clearances between plates at movable plate rotation speed of 1420 rpm.

RESULTS AND DISCUSSIONS

According to experiments carried out previously [8] for optimization of technological parameters (shale concentration, temperature and timing) of the process of thermal cracking of shale in a mixture with solid oil residue, the optimum quantity of shale added to tar is 15.0%, temperature of the tar thermal cracking process is 425°C and process time is 30-60 minutes.

The results obtained in intensively shaken reactor were accounted for when running the process in a bench flow unit of the Federal State Unitary Enterprise Institute of Fuel Fossils (table 1–3).

Table 1 – Material balance (mass %) of thermal contact cracking of tar in a mixture with Kenderlyk oil shale (5 MPa, supply of nitrogen – 400-500 l/l of feedstock, bench flow unit)

Parameter	Conditions of process	
	425-435°C, 1.0 h^{-1}	425-435°C, 2.0 h^{-1}
Materials used		
1. Tar	100	100
2. Shale, including:	15	15
organic-mineral structure	5.9	5.9
ash	9.1	9.1
TOTAL:	100.0	100.0
Produced		
1. Dehydrated and ash-free hydrogenation product,	90.7	93.2
including fraction with boiling point (°C):		
up to 180	12.6	10.8
180-360	44.3	32.3
above 360	33.8	50.1
2. Solid residue, including:	14.9	14.2
mineral part of shale	9.1	9.1
undissolved part of organic-mineral structure	0.4	0.5
coke	5.4	4.6
3. Gas, 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 + losses	1.7	1.6
TOTAL:	115.0	115.0

According to Table 1, the gasoline yield with boiling point up to 180°C at 425-435°C and feed space velocity of 1-2 h^{-1} is 10.8-12.6%. Cracking gasoline (table 2) contains a moderate quantity of aromatic hydrocarbons (~ 27.0%) and unsaturated compounds (iodine number is 26.4), which satisfies the current gasoline requirements in terms of environmentally hazardous components. However, the use of such gasoline as a component of EURO standard gasolines (GOST R 52368-2005) is pretty complicated due to the presence of phenols (2.5 vol. %) and nitrogenous bases (1.2 vol. %). Therefore, shale oil must be exposed to a separate hydrotreating, and then to catalytic reforming to increase the octane number. The diesel yield with the boiling point of 180-360°C is 32.3-44.3%, which is 2.2-3 times higher than that in case of industrial thermal cracking of fuel oil, tar and gasoil of coking. The content of aromatic hydrocarbons in fractions with boiling point of 180-360°C is

53.8%; however, middle distillates produced from shale must be exposed to hydrotreating due to a high content of sulfur (1.42%) and unsaturated compounds (iodine number is 33.9), and production of diesel fuel with cetane number of 47-51 requires a partial hydration of aromatic hydrocarbons.

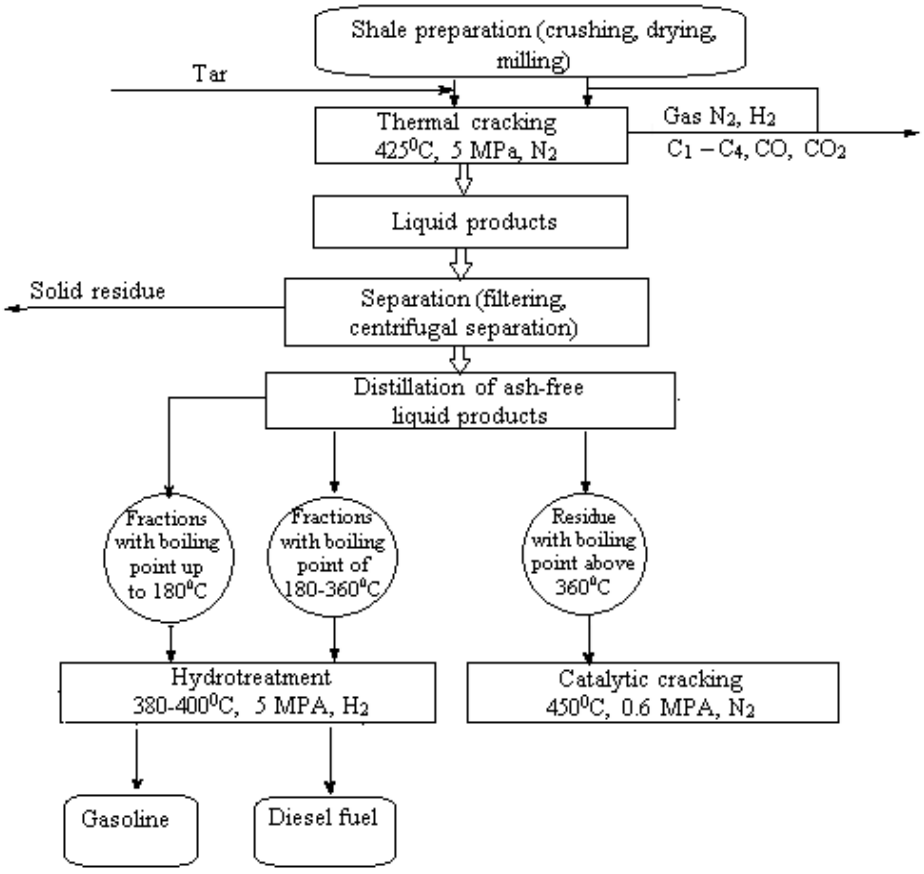
Table 2 – Characteristics of distillate products of tar thermal cracking in a mixture with shale

Parameter	Fractions with boiling point, °C		
	up to 180	180-360	above 360
Density at 20°C, g/cm^3	0.7666	0.8696	0.9295
Content, vol. %:			
phenols	2.5	1.5	–
nitrogenous bases	1.2	4.2	–
Hydrocarbon-type content, mass %			
paraffin + naphthene	72.7	46.2	22.2
aromatic	27.3	53.8	61.1
silica gel resins	–	–	16.7
asphaltenes	–	–	3.4
Iodine number, g J_2/100 g of product	26.4	33.9	12.5
Elemental composition, mass %:			
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, g/t			
V	–	–	5
Ni	–	–	20

Table 3 – Characteristics of residues of tar thermal cracking in a mixture with shale

Parameter	Heavy residue with boiling point > 360°C	Solid residue of process
Density at 20°C, g/cm^3	1,0361	–
Content of asphaltenes, mass %	16.3	–
Elemental composition, mass %:		
C	83.80	–
H	9.46	–
S	1.68	1.0
N	0.64	–
O (by variety)	4.42	–
Content, g/t		
V	125	1017
Ni	103	766

The heavy residue with boiling point above 360 °C remains unconverted in the developed new process of thermal cracking of tar (figure). This residue is little differ in its physical and chemical properties from the original tar (table 3) and then goes into the process of catalytic cracking or can be returned to processing as a mixture with the original raw material.



Principal diagram of thermal cracking of tar in a mixture with oil shale

It should be noted that thermal cracking of tar with addition of shale produces a small amount of gas (6.0-7.7 mass %), which results in high yield (above 90%) of ash-free hydrotreated feed and components of motor fuels (above 55%). The produced gas mainly consists of hydrocarbons C_1-C_4 (Table 2) that can be used for own needs during the technological process. It is worth mentioning that the process gas contains almost no hydrogen, which is formed in huge amounts during industrial thermal-contact cracking (TCC) and burned down.

Conclusion. The results of experimental researches clearly evidence the advantages of the new process of thermal cracking of tar with a mixture of shale as

compared to the industrial thermal cracking, because the single-step processing under relatively mild conditions (5 MPa, 425°C, feed space velocity of 1.0 h^{-1}) results in a deep destruction of tar (gasoline yield with boiling point up to 180°C is approx. 12 mass %; middle distillate yield with boiling point of 180-360°C is 43-44 mass %; yield of feed for catalytic cracking with boiling point of over 360°C is approx. 15-16 mass % in terms of initial tar). The formed coke-like products including V and Ni contained in the feedstock are deposited on the mineral part of shale and removed from the reaction zone along with liquid process products.

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Резюме

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ТАҚТАТАС ҚОСЫЛҒАН МҰНАЙ ҚАЛДЫҚТАРЫН ЖОҒАРЫТЕМПЕРАТУРАЛЫҚ ӨҢДЕУ

Жұмыста мотор отындарының компоненттерін және каталитикалық крекинг шикізатты алу үшін ұсақталған жанғыш тақтатаспен қоспадағы гудронның термиялық крекинг үрдісі зерттелінді. Үрдістің материалдық балансы (масс. %) мен технологиялық параметрлерін (сланец концентрациясы, температура және уақыты) оңтайландыру нәтижелері келтірілген. Бір сатылы қайта өңдеу кезінде салыстырмалы жұмсақ жағдайларда (5 МПа, 425 °С, шикізатты берудің көлемдік жылдамдығы 1,0 сағ.$^{-1}$) гудронның терең деструкциясына (қайнау темп. 180 ^{0}С дейінгі бензин фракцияның шығымы ~12 масс. %; қайн.темп. 180-360 ^{0}С болатын орташа дистилляттар 43-44 масс. %; каталитикалық крекинг шикізаты болып табылатын қайн.темп. 360 ^{0}С

жоғары дистиллят бастапқы гудронға есептегенде ~ 15-16 масс.%) қол жеткізілгені анықталды. Үрдіс нәтижесінде түзілген кокстәрізді өнімдер мен шикізат құрамындағы V және Ni тақтатастың минералдық бөлігіне жиналады және реакциялық аймақтан үрдістің сұйық өнімдерімен бірге шығарылады.

Түйін сөздер: термиялық крекинг, ауыр мұнай қалдығы, гудрон, тақтатас, мотор отындары, Кендерлік, коксүзілу.

Резюме

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ВЫСОКОТЕМПЕРАТУРНАЯ ПЕРЕРАБОТКА НЕФТЯНОГО ОСТАТКА С ДОБАВКАМИ СЛАНЦА

В работе исследован процесс термического крекинга гудрона в смеси с измельчённым горючим сланцем для получения компонентов моторных топлив и сырья для каталитического крекинга. Приведены результаты оптимизации технологических параметров (концентрация сланца, температуры и продолжительности) и составлен материальный баланс (масс. %) процесса. Установлено, что при одноступенчатой переработке в относительно мягких условиях (5 МПа, 425 °С, объёмная скорость подачи сырья 1,0 $ч^{-1}$) достигается глубокая деструкция гудрона (выход бензиновой фракции с т. кип. до 180 °С составляет ~ 12 масс. %; средних дистиллятов с т. кип. 180-360 °С – 43-44 масс. %; сырья для каталитического крекинга с т. кип. Выше 360 °С ~ 15-16 масс. % в расчёте на исходный гудрон). Образующиеся коксообразные продукты и содержащиеся в сырье V и Ni откладываются на минеральной части сланца и выводятся из реакционной зоны с жидкими продуктами процесса.

Ключевые слова: термический крекинг, твердый нефтяной остаток, гудрон, сланец, моторные топлива, Кендерлык, коксообразование.