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TERMAL UTILIZATION OF KENDERLYK FIELD SHALES AND SOLID OIL RESIDUE

Abstract. This work presents the results of studies on the joint hydrogenation of the Kendyrlykoil shale and tar to obtain components of motor fuels and the prospects of using the hydrogenation method under low hydrogen pressure.It has been established that the most optimal technological parameters for the process of thermal cracking of tar with oil shale are 425 °C, the process takes 60 minutes and the oil shale added to the tar is 12.0%. When using the Kenderlyk shale under the accepted conditions of thermal cracking, a high yield of light distillates is obtained, calculated on the tar with low coke formation.

Keywords: thermo-catalytic destruction, shale, tar, yield of light fractions, Kenderlyk, organic mass of shale.

Based on experiments on the thermal dissolution of oil shale in Russia, the fundamental principles of a new process for the thermochemical processing of oil residues have been developed [1-5]. It is based on the unique properties of oil shale - natural hydrogen donors acting as radical generators and cracking catalysts.

The process proceeds at a temperature of 390-440 °C and a pressure of 3-8 MPa. A feature of the Kenderlyk shale used in the process is the high hydrogen content in its organic matter.Other sapropelite fuels may be used in this process.

The process under development is based on well-known ideas about the mechanism of thermal destruction (thermal dissolution) of the organic mass of oil shale [6, 7]. Under the accepted conditions, the processes of decomposition and liquefaction of the organic mass of oil shale occur with the formation of radicals of various molecular weights and liquid products that contain compounds having donor-hydrogen properties: hydro derivatives of condensed aromatic hydrocarbons, nitrogen and oxygen derivatives, as well as cyclic alcohols.These chemically active compounds formed from the organic matter of shale under the conditions of the process of thermochemical processing, cause the destruction of high-boiling hydrocarbons that are part of the tar, according to the radical-chain mechanism. The development of the hydrogenation reactions of the compounds of the feedstock and its decomposition products is significantly affected by the mineral part of oil shale, consisting largely of aluminosilicates and iron salts [8-10].

During the thermochemical processing of tar in the presence of oil shale, along with the deep destruction of high molecular weight hydrocarbon tar, the destruction of the asphaltenes contained in it seems to occur.

The bulk of the organic matter of shale (up to 90 wt.%) goes into liquid and gaseous products [11]. In the process under development, oil shale and the

products of its transformation activate, as noted, tar degradation reactions, and are also a source of components of the liquid process products.

However, the information available about this process is mainly reflected in patents [12-16], and in the literature there is no information about the patterns and technological parameters that affect the yield and quality of the target product obtained.

Thus, from the published literature it can be concluded that, although this technology (joint thermochemical processing of tars and heavy oils with shale) began to be developed back in the late 80's of the last century, however, until now, systematic studies of the laws of this process, its technological features were not identified, there is no information on the quality of the obtained fractions and environmental assessment of this process.

The paper presents the results of studies on the development of thermal cracking of tar in a mixture with crushed oil shale to obtain components of motor fuels and raw materials for catalytic cracking.

Together with the Federal State Unitary Enterprise "Institute of Combustible Minerals - Scientific and Technical Center for the Combustible Processing of Combustible Minerals", we developed a method for the joint thermo-catalytic processing of tar and Kendyrlykoil shale [17-20].

For research, we used the ordinary Kendyrlykoil shale of Quartz JSC with the following characteristics (wt.%): W^a - 0.8; A^d - 64.5; C^{daf} 74-77; H^{daf} - 7.3-9.9; S^d - 0.6-1.3; the conventional organic mass of the shale, which was determined by the formula [OM = 100 - A^d - (CO_2)w], is equal to 33.2 wt.%

Compounds of calcium, silicon and aluminum predominate in the mineral part of the Kenderlyk shale (table 1).

Table 1 – Characterization of the mineral part of the oil shale of the Kenderlyk field

The content of components in the ash, wt.%							
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

As a raw material, tar was used for mixtures of oils of Western Siberia with boiling point (b.p.) >520 °C with the following characteristics: density at 20 °C - 0.948 g/cm^3 ; viscosity - 9.7cST; content, wt.%: C - 85.60; H 10.72; S 2.06; N - 0.30; asphaltenes - 13.6; V and Ni - 180 and 90 g/t, respectively. Thermal cracking was carried out in the Scientific Research Institute for New Chemical Technologies and Materialsin an intensively shaken reactor with a volume of 0.2 L at 400–440 °C and a working pressure of nitrogen of 5–8 MPa.

In the preparation of oil shale paste, shale crushed in a ball mill to a particle size of less than 200 μm was mixed with tar in various proportions.The resulting paste was once dispersed in alaminar dispersantof Pushkin-Khotuntsev with 1.0 mm gaps between the plates at a rotation speed of the movable plate of 1420 rpm.

Table 2 shows the results of experimental studies on optimizing the ratio of oil shale: oil product in oil shale paste.

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

Thermal cracking products, wt.%	The concentration of shale wt. %				
	3.0	6.0	9.0	12.0	15.0
Gas	4.6	4	4.2	5.4	5.7
Water	1.8	1.6	2.0	1.5	1.1
Fraction from b.p. up to 180 °C	8.5	9.9	12.9	12.7	11.4
Fraction at the range b.p.180-360 °C	25.2	34.8	41.6	51.3	49.5
Remainder at the range b.p. above 360 °C	57.9	49.7	39.3	29.1	38.3
Total yield of light distillates	35.7	44.7	54.5	64.0	60.9
Coke content on the mineral part of the shale	7.9	5.6	3.8	3.3	3.4

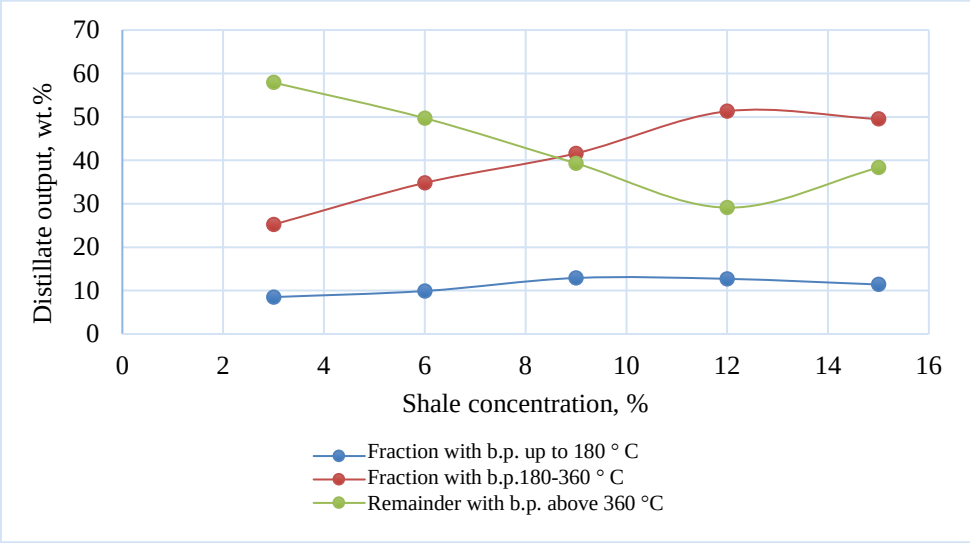

Figure 1 – The dependence of the yield of liquid products on the concentration of shale

From Figure 1 it follows that the optimal amount of oil shale added to the tar is 12.0%.When using the Kendyrlykshale under the accepted conditions of thermal cracking, a high yield of gasoline fraction from b.p. up to 180 ° C - 12.7% based on tar and diesel fraction at the rangeb.p. 180-360 ° C - 51,3%.With a decrease to the additions of Kenderlyk shale to 9.0%, the total yield of light fractions decreases from 64.5 to 54.5 %.A further decrease in the amount of added shale to 6.0 and 3.0% leads to a significant decrease in the yield of

fractions of motor fuels to 44.7 and 35.7%, respectively, increases the yield of heavy residue from b.p. above 360 ° C and coke.

An increase in the content of ordinary shale in oil shale paste above 15.0% is impractical, as this will lead to a complication of the process technology, increased erosion of the equipment by the mineral part of the shale, stratification of the reaction mixture into liquid and solid phases and complication of the hardware design of the unit for separation of solid components from liquid thermal cracking products.

Table 3 shows the results of studying the influence of process temperature on the yield of target products of thermal cracking of tar in a mixture with shale.

Table 3 – Effect of temperature on thermal cracking a mixture of oil shale and oil.
Conditions: 5.0 MPa, reaction time 1.0 h, vigorously shaken reactor

The yield of products, wt. %	Temperature, ° C		
	400	425	440
Gas	6.5	5.4	4.8
Water	1.4	1.5	1.0
Fraction with b.p. up to 180 °C	11.6	12.7	10.4
Fraction with b.p.180-360 °C	46.4	51.3	49.1
Remainder with b.p. above 360 °C	34.1	29.1	34.7
Total yield of light distillates	58.0	64.0	59.5
Coke content on the mineral part of the shale	2.1	3.3	4.0

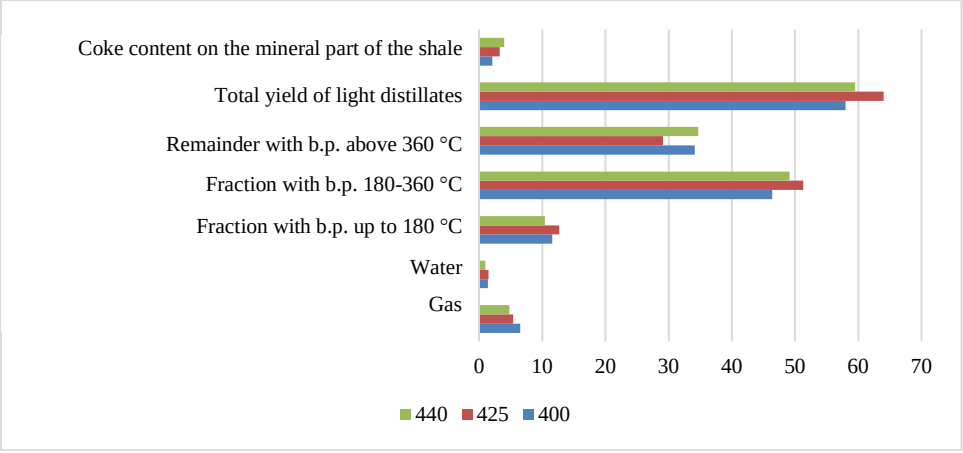

Figure 2 – Dependence of the influence of temperature (°C)
on the thermal cracking of a mixture of oil shale and oil

From figure 2 it follows that at a temperature of 400 C° yield of the gasoline fraction with b.p. up to 180 °C is relatively small and amounts to 11.6% based on tar, while a rather large amount of diesel fraction is formed in the process

(46.4%).With increasing processing temperature above 425 °C to 440 °C is increased to 4.0% coke formation and decreases the total yield of light and medium distillates with 64.0 (425 °C) to 59.5% (440 °C).Thus, as a result of experimental studies, it was found that the optimal process temperature is the interval 425-430 °C.

Table 4 and Figure 3 show the results of studying the effect of the duration of the process on the yield of distillate fuel fractions.

Table 4 – The results of thermal cracking of a mixture of oil shale with oil at different durations of the process.Conditions: 425 ° C, 5.0 MPa, vigorously shaken reactor

Thermal cracking products , wt.%	Response Time, min		
	30	60	120
Gas	4.5	5.4	6.1
Water	1.2	1.5	1.7
Fraction with b.p. up to 180 °C	10.8	12.7	11.6
Fraction with b.p. 180-360 °C	47.4	51.3	48.2
Remainder with b.p. above 360 °C	36.1	29.1	32.4
Coke content on the mineral part of the shale	2.9	3.3	4.3
Total yield of light distillates	58.2	64.0	59.8

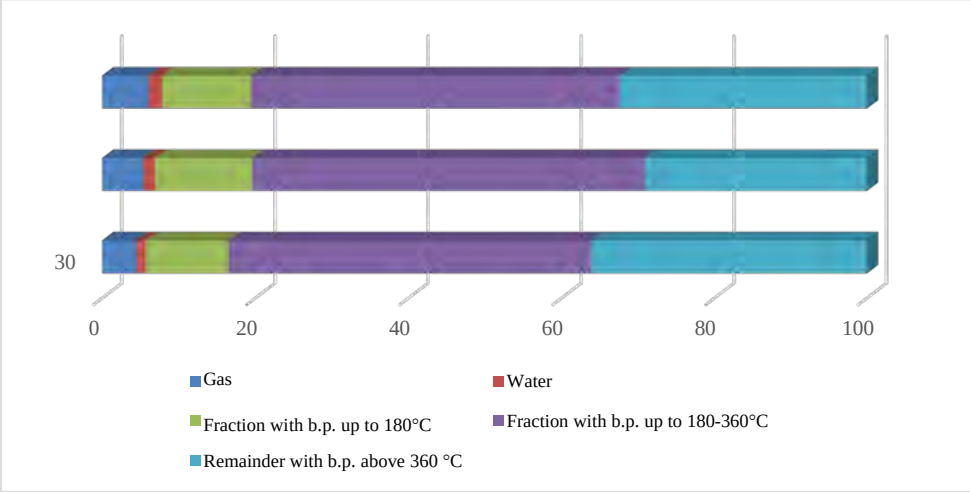

Figure 3 – Dependence of the influence of the duration of the process on the yield of thermal cracking products

It was found that reducing the reaction time from 60 to 30 minutes leads to a decrease in the yield of the gasoline fraction and an increase in the content of middle distillates in thermal cracking products from bales. 180-360 °C. With increasing reaction time up to 120 minutes was an increase in coke formation

(4.3%) and a decrease of the total yield of light fractions of 4.2% compared to the implementation of the process at 60 minutes.

Thus, based on the data obtained it can be stated that the most optimal technological parameters of the process of thermal cracking of tar with slate are temperature 425 °C, time of 60 minutes and the process number of the shale as a dopant 12 wt.%.

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Резюме

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АУЫР МҰНАЙ ҚАЛДЫҚТАРЫ МЕН
КЕНДІРЛІК КЕН ОРНЫНЫҢ ТАҚТАТАСЫН
ТЕРМИЯЛЫҚ ҚАЙТА ӨҢДЕУ

Жұмыста мотор отынының компоненттерін алу үшін Кендірлік жанғыш тақтатасы мен гудронды бірлесіп гидрогенизациялау бойынша зерттеулердің нәтижелері және сутегінің жоғары емес қысымымен гидрогенизациялау әдісін қолдану перспективалары келтірілген. Тақтатас пен гудронның термокрекинг процесін жүзеге асырудың ең оңтайлы технологиялық параметрлері 425°С температура болып табылады, процесті жүзеге асыру уақыты 60 минут және гудронға қосылатын тақтатас мөлшері 12,0% құрайды. Термокрекингтің қабылданған жағдайларында Кендірлік тақтатасын қолданғанда гудронға есептегенде аз мөлшерде кокс түзе отырып, ашық дистилляттардың жоғары шығымы алынады.

Түйін сөздер: термокаталитикалық деструкция, тақтатас, гудрон, ашық фракциялар шығымы, Кендірлік, тақтатастың органикалық массасы.

Резюме

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ТЕРМИЧЕСКАЯ ПЕРЕРАБОТКА СЛАНЦЕВ
И ТВЕРДОГО НЕФТЯНОГО ОСТАТКА
КЕНДЕРЛЫКСКОГО МЕСТОРОЖДЕНИЯ

В работе приведены результаты исследований по совместной гидрогенизации Кендырлыкского горючего сланца и гудрона для получения компонентов моторных топлив, а также перспективы применения метода гидрогенизации под невысоким давлением водорода. Установлено, что наиболее оптимальными технологическими параметрами осуществления процесса термокрекинга гудрона со сланцем являются температура 425 °С, время осуществления процесса 60 мин и сланца, добавляемого к гудрону, составляет 12,0 %. При использовании Кендерлыкского сланца в принятых условиях термокрекинга получается высокий выход светлых дистиллятов в расчёте на гудрон с низким коксообразованием.

Keywords: термокаталитическая деструкция, сланец, гудрон, выход светлых фракций, Кендырлык, органическая масса сланца.