BULLETIN OF NATIONAL ACADEMY OF SCIENCES
OF THE REPUBLIC OF KAZAKHSTAN
ISSN 1991-3494 **https://doi.org/10.32014/2018.2518-1467.5**
Volume 5, Number 375 (2018), 42 – 47

UDC 662.74:552

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THERMAL CRACKING OF FUEL OIL IN SLATE MIXTURE

Abstract. The results of investigation of thermal cracking of fuel oil of Zhanazhol deposit in the mixture with bituminous slate are specified in this article to obtain motor fuels and raw materials for catalytic cracking. The dependence of light distillate fractional yield of slate concentration (3-12 wt. %), temperature (668-708 K) and time of thermal cracking are determined by the method of non-linear regression. According to the light distillate fractional yield, the following can be considered as optimal conditions of reaction: temperature 688 K, time of treatment 60 minutes and quantity if activating agent (slate) 9 wt. %. Total light distillate fractional yield under these conditions reaches 50.8 wt. %. The obtained light distillates of cracking contain moderate quantity of aromatic hydrocarbons (25.5-30.1 %), unsatisfied compounds (iodine value is equal to 1.5-3.9) and very small amount of sulphur (0.01-0.04 wt. %), that ensures compliance with modern requirements for gasoline and diesel fuels according to environmentally hazardous components.

Key words: thermocatalytic cracking, activating agents, slate, fuel oil.

Introduction. Ever-growing demand on motor fuels, which at least pollute environment, stipulates further development of advanced processing of high-molecular oil raw material (boiling temperature exceeds 520-560 ^{0}C), as well as solid combustible minerals (coal, slate, top soil).

Strengthening of requirements for the quality of obtained products leads to significant changes of process diagrams and methods of use of the specified types of raw materials [1-3].

An original process of thermochemical treatment of black oil fuel of native and destructive origin (fuel oil, tar, reduced pyrolysis resin, cracked residual, used oils, etc.) is developed in Russian and Kazakhstan, which includes the use of activating agents, which have no analogues abroad. This process is implemented at a pressure of 0.5-2 MPa, temperature of 400-430 °C without hydrogen [4-6].

Natural agents of sapropelite origin (bituminous slate, top soil, sapropelites, liptobiolites, boghead minerals) are used as activating agents. The effect of their interaction on oil residuals is studied on the example of use of bituminous slate [7-12]. It is established, that organic and mineral parts of bituminous slate have an activating influence on thermal conversion of heavy-oil products. Thus, various compounds, offering properties of hydrogen donators are generated during deconstruction of organic mass of slate (kerogen) within a range of temperatures of 370-420 °C. These compounds actively conduce to the hydrogenation reaction of unsatisfied compound, which are created during cracking of oil residuals and prevent heavy carbon producing.

On the other hand, mineral part of slate, which contains alumosilicates, black iron oxide, molybdenum, cobalt, nickel and other catalytic active metals, also conduces to the intensification of reactions of cracking and hydrogenation. While using bituminous slate as activating agent in the quantity of 5-25 % and containing 15-70 % of kerogen, the process of thermal cracking of oil residuals, implemented within a range of temperature of 390-450 °C can be controlled, with light distillate fractional yield up to 70 % without pellet and carbon producing, not exceeding 5 % [13-20].

Experiment. The results of investigation of development of slate thermal cracking in the mixture with refined bituminous slate are specified in this article to obtain components of motor fuels and raw materials for catalytic cracking.

Samples of bituminous slate of JSC Kvarts (Kenderlyk deposit), additionally enriched by the floatation and liquid centrifugal separation methods, with the following specifications (wt. %) have been used for the investigations: W^a 1.2-1.3; A^d 18-22; C^{daf} 74.2-74.7; H^{daf} 8.9-9.0; S^{daf} 1.2-1.4; N^{daf} 0.4-0.5; Q^{daf} 14.5-15.0. Silicium (58.2 wt. %) and aluminium compounds (17.2 wt. %) prevail in the composition of mineral part of Kenderlyk slate.

Fuel oil of Zhanazhol oil withh a boiling temperature of >520 ^{0}C with the following specifications has been used as raw material: density at a temperature of 20 ^{0}C 0.933 g/cm^3; viscosity 9.8 cSt.; content of asphaltene 1.6 and solids 0.3 wt. %. Thermal cracking has been carried out in rotating autoclave with a volume of 2 l at a temperature of 400-440 ^{0}C and operating pressure of nitrogen of 5-8 MPa.

Slate has been mixed with fuel oil up to 12 wt. % while preparing oil and slate paste refined in ball mill (table 1). The obtained paste has been singly dispersed in laminar dispersant of Pushkin-Khotuntsev with holes between plates of 1.0 mm at a speed of moving plate rotation of 1420 rpm.

Table 1 – Influence of slate concentration
on product yield (wt. %) of catalytic thermal treatment of fuel oil and slate (688 K, 60 min, 5 MPa)

The thermolysis product	The amount of oil shale, wt.%				
	0	3	6	9	12
Gas	8,1	4,9	5,3	5,5	7,8
Fraction up to 180 °C	15,0	7,1	10,8	13,5	20,0
Fraction 180-360 °C	14,0	28,7	31,8	37,3	39,0
Fraction> 360 °C	62,9	59,3	52,1	43,3	33,2
The total yield of light distillates	29,0	35,8	42,6	50,8	59,0

The results of investigation of slate concentration influence on thermal cracking of fuel oil show that the increase in concentration of slate leads to the increase in light distillate fractional yield up to 50 %.

It is worth noting that thermal cracking of fuel oil with slate additives proceeds with insignificant gas production (4.9-8.1 wt. %), ensuring the high yield (more than 90 %) of ash-free hydrotreated feed and components of motor fuels.

According to the data specified in Table 1, the dependence of light distillate fractional yield on the quantity of slate (x) and fractional yield >360 ^{0}C (y) has been determined by the method of non-linear regression.

$$G(x, y) = 4{,}483*x + 0{,}4569*y - 0{,}02491*x*y \quad (1)$$

Data specified in table 2 shows that function G (x, y) satisfactorily present experimental data. The diagram of function G (x, y) is shown on figure 1. It can be seen that the dependence of light distillate yield on the quantity of slate is linear: light distillate yield increases, when the slate weight increases.

The results of investigations under autoclave conditions are specified in tables 3–5. According to the data specified in table 3, it is worth noting that light distillate fractional yield is equal to 37.0-50.8 % depending on the temperature of thermal cracking. Besides, the yield of gasoline fraction increases with a boiling temperature up to 180 ^{0}C increases from 6.2 % at a temperature of 668 K up to 21.2 % and at a temperature of 708 K the yield of diesel fraction with a boiling temperature of 180-360 ^{0}C is equal to 30.8-23.2 %, correspondingly.

Table 2 – Comparison of experimental and design data
on the dependence of total light distillate yield on quantity of slate and fractions >360^{0}C

Total yield of light products		Δ = (exp.-calc.)	100*Δ/exp., %
experiment	calculation		
29,0	28,74	0,26	0,8966
35,8	36,11	-0,31	-0,8659
42,6	42,91	-0,31	-0,7277
50,8	50,42	0,38	0,7480
59,0	59,05	-0,05	-0,0848

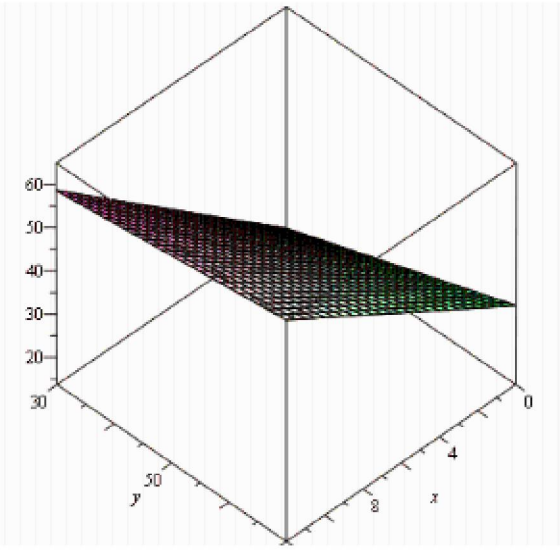

Figure 1 –
The graph of the function G (x, y)

Table 3 – Influence of temperature on thermal cracking of fuel oil mixed with slate (9 % of slate, 60 min, 5 MPa)

The thermolysis product	Temperature, K				
	668	678	688	698	708
Gas	3,0	4,4	5,5	7,1	9,1
Fraction up to 180 °C	6,2	11,9	13,5	17,6	21,2
Fraction 180-360 °C	30,8	34,9	37,3	31,0	23,2
Fraction> 360 °C	60,0	48,8	43,3	44,3	46,5
The total yield of light distillates	37,0	46,8	50,8	48,6	44,4

According to the data specified in table 3, the diagram of dependence of total light distillate yield on the process temperature is constructed (figure 2). It is shown on the figure that light distillate yield has a polynomial dependence on temperature (R=0.9845).

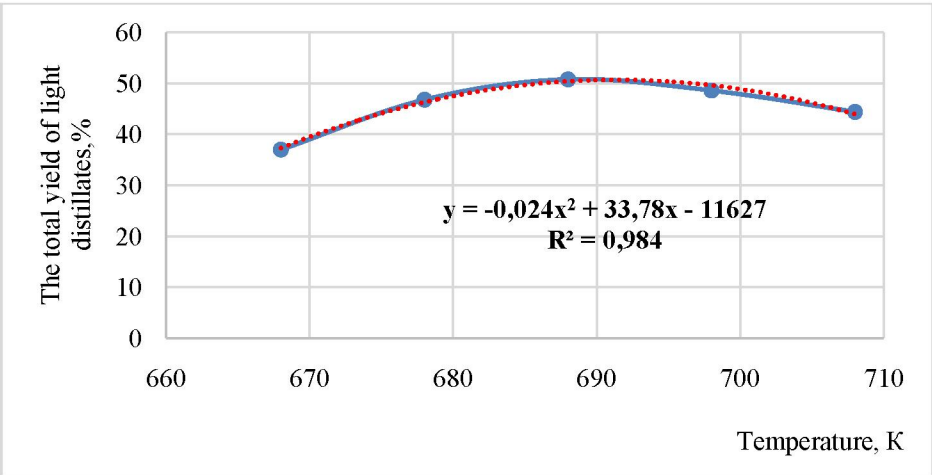

Figure 2 – Dependence of light distillate yield on thermal cracking temperature

The function describing total light distillate yield G (t, n) of *t* temperature and fractional yield 360 ^{0}C *n,* is the following:

$$G(t, n) = 0{,}1492*t + 3{,}663*n - 0{,}007045*t*n \quad (2)$$

Function repeatability is specified in table 4, and its diagram is shown on figure 3 in 3-D coordinates.

Table 4 – Comparison of experimental and design data
on the dependence of total light product yield on temperature and fractions >360^{0}C

Total yield of light products		Δ=(exp.-calc.)	100*Δ/exp., %
experiment	calculation		
37,0	37,1	-0,1	-0,2703
46,8	46,9	-0,1	-0,2137
50,8	51,3	-0,5	-0,9843
48,6	48,6	0	0
44,4	44,0	0,4	0,9009

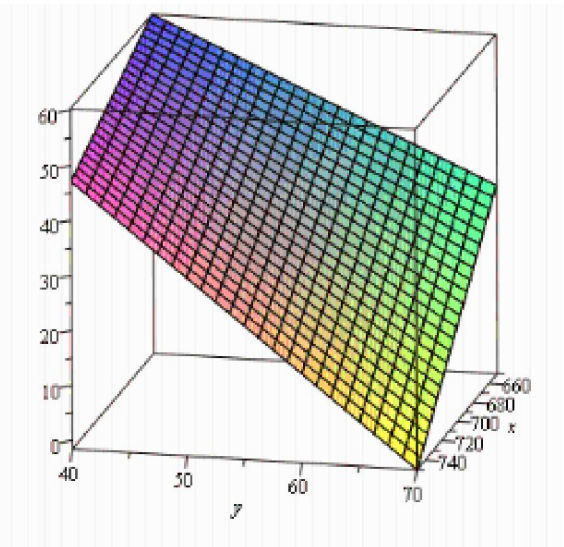

Figure 3 – The graph of the function G (t, n)

The results of investigation of influence of thermal cracking time duration on main results of the process (table 5) show that when the time of reaction changes from 10 to 60 minutes, the yield of gasoline fraction increases (from 7.5 to 13.5 %) and yield of medium distillates increases (from 22.6 to 37.3 %), which are better that indices of industrial process of thermal cracking of such type of raw material.

Table 5 – Results of thermal cracking of fuel oil mixed with slate at a various time duration of the process
(688 K, 9 % slate, 5 MPa)

The thermolysis product	Thermolysis time, min				
	10	15	30	45	60
Gas	2,0	2,8	3,7	5,2	5,5
Fraction up to 180 °C	7,5	8,9	10,5	13,5	13,5
Fraction 180-360 °C	22,6	28,3	33,1	36,9	37,3
Fraction> 360 °C	67,5	60,0	52,7	44,4	43,3
Coke on a solid phase	2,4	2,8	3,7	5,2	5,5
The total yield of light distillates	30,1	37,2	43,6	50,4	50,8

According to tables 1, 3, 5, the yields of gasoline fractions with a boiling temperature up to 180 ^{0}C is equal to 13.5-20.0 % at a temperature of 688 K, and the yield of diesel fractions is equal to 37.3-39 %. Gasoline and diesel fractions of cracking (table 6) contain moderate quantity of aromatic hydrocarbons (25.5 and 30.1%, correspondingly), unsatisfied compounds (iodine value is equal to 1.5 and 3.9) and very small amount of sulphur (0.01-0.04 wt. %), that ensures compliance with modern requirements for gasoline and diesel fuels according to environmentally hazardous components.

Table 6 – Specification of distillate products of thermal cracking of fuel oil mixed with slate

Index	Fractions with b.t., ° C	
	up to 180	180-360
Density at 20 ° C, g/cm^3	0,7460	0,8696
The refractive index, n_D^{20}	1,4200	1,4795
Group hydrocarbon composition, wt.%		
paraffin + naphthenic	74,5	69,6
aromatic	25,5	30,1
Iodine number, g J2 / 100 g of product	1,5	3,9
Element composition, wt.%:		
C	85,50	87,14
H	13,82	12,81
S	0,01	0,04
N	0,08	0,01

Conclusion. Therefore, to optimize the conditions of thermal cracking, the investigation has been carried out using simple slate of Kenderlyk deposit as activating agent. The influence of slate concentration, temperature and time of reaction on thermal cracking product yield has been studied. According to the yield of distillate fractions, the following can be considered as optimal conditions of reaction: temperature 688 K, time of treatment 60 minutes and quantity if activating agent (slate) 9 wt. %. Total light distillate fractional yield under optimal conditions reaches 50.8 wt. %.

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МАЗУТ ПЕН ТАҚТАТАС ҚОСПАСЫН ТЕРМИЯЛЫҚ КРЕКИНГІЛЕУ

Аннотация. Мақалада мотор отындары мен каталитикалық крекингке арналған шикізат алу мақсатында Жаңажол кен орнының мазутын жанғыш тақтатас қоспасында термиялық крекингтеу үрдісінің нәтижелері келтірілген. Сызықтық емес регрессиялық талдау әдісімен жеңіл дистиллят фракцияларының тақтатас концентрациясына (3-12 масс.%), температураға (668-708 К) және термокрекингті жүзеге асыру ұзақтылығына (10-60 мин.) тәуелділіктері анықталды. Жеңіл дистилляттардың шығымына қарайтын болсақ, оңтайлы деп 688 К температураны, 60 минут уақытты және 9 масс. % тақтастас концентрациясын айтуға болады. Осы оңтайлы жағдайларда жеңіл сұйық өнімдер шығымы 50,8 мас. %-ға жететіндігі дәлелденді. Алынған жеңіл крекинг дистиллятарының құрамында орташа мөлшерде ароматты (25,5-30,1%) және қанықпаған көмірсутектер (йод саны 1,5-3,9) анықталған. Сонымен қатар, экологиялық қауіпті компоненттері бойынша бензин мен дизель отындарына қойылатын талапты қанағаттандыратын күкірт мөлшері (0,01-0,04 масс.%) өте аз екендігі анықталды.

Түйін сөздер: термиялық крекинг, белсендіргіш қоспалар, тақтатас, мазут.

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ТЕРМИЧЕСКИЙ КРЕКИНГ МАЗУТА В СМЕСИ СО СЛАНЦЕМ

Аннотация. Приведены результаты исследования термического крекинга нефтяного мазута месторождения «Жанажол» в смеси с горючим сланцем для получения моторных топлив и сырья для каталитического крекинга. Методом нелинейной регрессии определены зависимости выхода светлых дистиллятных фракций от концентраций сланца (3-12 масс.%), температуры (668-708 К) и времени осуществления термокрекинга (10-60 мин.). Судя по выходу светлых дистиллятов оптимальными условиями реакции можно считать: температуру 688 К, время переработки 60 минут и количество активирующей добавки (сланца) 9 масс. %. Суммарный выход светлых дистиллятных фракций при этих условиях достигает 50,8 масс. %. Полученные светлые дистилляты крекинга содержат умеренное количество ароматических углеводородов (25,5-30,1%), непредельных соединений (йодное число равно 1,5-3,9) и очень малое количество серы (0,01-0,04 масс.%), что обеспечивает современные требования на автобензины и дизельные топлива по экологически опасным компонентам.

Ключевые слова: термокаталитический крекинг, активирующие добавки, сланец, мазут.

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