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INFLUENCE OF VARIOUS FACTORS ON HYDROGENOLYSIS OF THE SHALE OF THE KENDYRLYK DEPOSIT

Abstract. The present work represents the results of studies on the hydrogenation of Kendyrlyk oil shale for the production of motor fuel components, assessment of the state and prospects of hydrogenation under low hydrogen pressure. According to the experimental data, the dependence of the yield of liquid products (YLP) on the temperature, pressure and duration of the experiment was determined by the method of nonlinear regression. It is shown that an increase in the temperature and duration of the experiment does not exert a noticeable effect on the shale hydrogenolysis indicators. And with increasing of hydrogen pressure in the range from 4.0 to 8.0 MPa, the degree of transformation of the organic mass of shale (OMS) increases by 20% and the amount of shale in the reaction of hydrogen is doubled, the yield of liquid products, gas and water is increasing.

Key words: hydrogenolysis of shale, the yield of liquid products, Kendyrlyk, bauxite, the organic mass of shale, the degree of conversion.

Introduction. Oil shale is one of the promising types of organic raw materials, which can largely compensate, and in the future replace oil products and gas. Unlike other types of solid fossil fuels (SFF), oil shales contain significant amounts of hydrogen in organic matter. The possibility of obtaining liquid and gaseous hydrocarbons from oil shales, similar in composition and properties to petroleum products and natural gas, makes it possible to consider them as important strategic resources [1].

World reserves of oil shale in the equivalent of shale resin are approximately 2.9 trillion barrels, but the industrial processing of oil shale is carried out only in a few countries. At the same time, research begun in the first half of the twentieth century in the field of the processing of oil shale in synthetic motor fuels and chemical products did not cease, and have again become relevant by now.

About 25 deposits and shows of oil shales dated to the Upper Devonian, Lower Carboniferous, Upper Paleozoic, Middle and Upper Jurassic and Paleogene deposits have been identified on the territory of Kazakhstan to date. They differ in the composition of the initial substance and the conditions of formation, which, largely, determined their qualitative and technological characteristics.

The shales of the Kendyrlyk Formation (the Kalynkar and Best layers) have been most thoroughly studied, the shales of the Saikansk Formation are the least studied. High-quality schists of the "Best" layer. The average content of resin exceeds 10%, reaching in some samples up to 27%. The distillation of the resin showed the possibility of using shale to produce artificial fuel. Earlier, we studied the thermodynamic analysis of gasification and the thermocatalytic processing of the Kenderlyk oil shale [2-5]. In the present work, the influence of various factors on the hydrogenolysis of the shale of the Kenderlyk field was studied.

Experiment. The work was carried out by researchers from the Research Institute of New Chemical Technologies and Materials and the Moscow State Mining University

As a raw material for hydrogenation, samples of oil shale of Kvarts JSC were applied, additionally enriched by flotation and centrifugal separation in heavy liquids. Shale concentrates had a particle size of less than 0,1-0,2 mm, contained (wt. %): W^a – 1,2-1,3; A^d – 18-22 (including carbon dioxide 2,4-2,5); S^d – 1,7-1,8. The elemental composition of the samples was the following (% on daf): C – 74,2-74,7; H – 8,9-9,0; S – 1,2-1,4; N – 0,4-0,5; O – 14,5-15,0. Heat of combustion of oil shale Q^{daf} was 31,5-33,4 kJ/kg.

Shale paste consisting of 40 wt.% shale and 60 wt.% liquid shale product with a boiling point above 300-320 °C, obtained in the process itself and during the pyrolysis of liquefaction residues was subject to hydrogenation. 0.5-3.0% catalysts were added to the paste, the corresponding polymetallic ores containing Fe, Ni, and Ti were used.

Hydrogenation was carried out at the Research Institute of New Chemical Technologies and Materials in an intensively shaken reactor with a volume of 0.2 liters and at Moscow State Mining University in a bench-type flow-through unit with a reactor volume of 0.8 liters, and the processing of slurry (the remainder of shale liquefaction) by pyrolysis in a flow unit with a moving downward layer of a solid coolant. The capacity of the unit was 3-10 kg of raw materials/h [9-14].

The results of the thermocatalytic hydrogenation of Kenderlyk shale in the intensively shaken reactor are shown in table 1.

Table 1 – Characterization of the process of thermocatalytic hydrogenation of Kendyrlyk shale. Ratio shale : pasteurizer – 1 : 1,5; Pressure, MPa – 8,0; Duration, min. – 15; Catalyst - Bauxite -094, wt.% – 2,0; A^d – 15,0

Process indicators	Temperature, °C		
	410	420	440
Degree of transformation of OMS, wt. %	83,2	84,5	82,2
Hydrogen in the reaction, wt. %	0,8	1,2	1,5
The yield of liquid products, wt. %	50,3	49,7	46,2
With boiling point higher 320 °C	27,2	28,4	29,5
The remainder with boiling point higher 320 °C	23,1	21,3	16,7
Gas, wt. %	10,3	11,4	12,1
Water, wt. %	7,6	7,8	8,0
Coke on the mineral part, wt. %	2,5	2,9	3,6

According to table 1, the nonlinear regression method was used to determine the dependence of the yield of liquid products during the hydrogenation of shale on the temperature T and the degree of transformation of the OMS W:

$$YLP\ (T,W) = 0{,}18T + 0{,}49W - 0{,}0019 \cdot T \cdot W \quad (1)$$

It was shown (figure 1) that the temperature dependence of YLP to the temperature is extreme, and the data in table 2 indicate that the function of YLP (T, W) satisfactorily reproduces the experimental data.

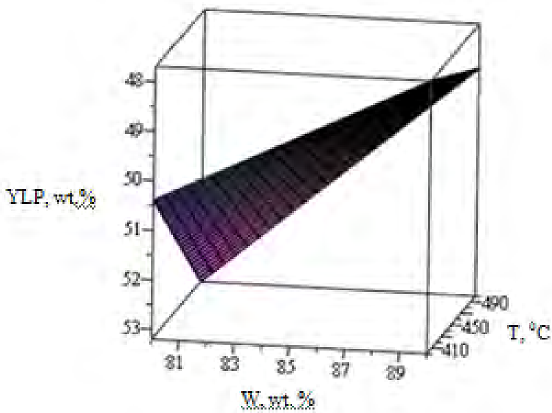

Figure 1 – Influence of temperature and the degree of transformation of OMS on the yield of liquid hydrogenation products

Table 2 – Comparison of experimental and calculated data on the yield of liquid products as a function of temperature and degree of transformation (shale: pasteurizer = 1: 1.5, τ = 15 min, P = 8.0 MPa, catalyst - bauxite No. 094)

Tempe-rature, °C	W, wt. %	The yield of total liquid products, %		Δ = (exp.–calc.)	100·Δ/exp., %
		experiment	calculation		
410	83,2	50,3	55,0	-5	-10
420	84,5	49,7	54,0	-4	-8,0
440	82,2	46,2	52,0	-6	-13,0

The obtained results indicate that the temperature has a significant effect on the indices of the hydrogenolysis of oil shale. In the temperature range 410-440 ºC, the degree of transformation of the organic mass of shale reaches 82.2-84.5%, with increasing temperature, an increase in gas production and hydrogen consumption is observed from 0.8 to 1.5 wt. % as a result of the destruction of the fraction with a boiling point above 320 ºC, the content of which in hydrogenate decreases from 23.1 to 16.7 and the content of gasoline and diesel fuel increases. The content of coke on the mineral part is insignificant, but increases in the studied temperature range from 2.5 to 3.6 wt.%.

A similar effect on the process of hydrogenolysis of shale has an increase in the reaction time to 30-45 minutes. The data characterizing this fact are summarized in table 3.

Table 3 – Hydrogenolysis of Kendyrlyk shale. Ratio shale : pasteurizer 1 : 1,5; Pressure, MPa – 8,0; Temperature – 410 ºC; Catalyst - Bauxite -094, wt. %. – 2,0; A^d – 15,0

Process indicators	Duration of experience, min		
	15	30	45
Degree of transformation of OMS, wt. %	83,2	84,7	87,2
Hydrogen in the reaction, wt. %	0,8	1,35	1,7
The yield of liquid products, wt. %	50,3	49,8	49,4
With boiling point higher 320 ºC	27,2	29,6	30,1
The remainder with boiling point higher 320 ºC	23,1	20,2	19,3
Gas, wt. %	10,3	11,5	12,6
Water, wt. %	7,6	7,9	8,2
Coke on the mineral part, wt. %	2,5	2,8	3,9

The function describing the total YLP G (*t,W*) as a function of the duration of the experiment *t* and the degree of OMS conversion W, is as follows:

$$G(t, W) = -0{,}27t + 0{,}59W + 0{,}0030 \cdot t \cdot W \quad (2)$$

The reproducibility of the function is given in table 4, and its graph in the three-dimensional coordinate system is shown in figure 2.

We have studied the effect of pressure on the indices of hydrogenolysis in the interval 4-8 MPa. The results are shown in table 5.

With increasing hydrogen pressure in the range from 4.0 to 8.0 MPa, the degree of transformation of the organic mass of shale increases by almost 20%, and the amount of hydrogen involved in the reaction doubles, the yield of liquid products, gas, water increases, i.e. the process of hydrogenolysis of Kendyrlyk shale intensifies, the content of gasoline and diesel fuel increases. The hydrogen pressure above 8 MPa does not have a significant effect on the process indicators.

Table 4 – Comparison of the experimental and calculated data on the yield of liquid products as a function of the duration of the experiment and the degree of transformation (T = 410 ° C, P = 8.0 MPa, shale: pasteurizer = 1: 1.5, bauxite catalyst No. 094)

Duration of experience, min	W, wt. %	The yield of total liquid products, %		Δ = (exp.–calc.)	100·Δ/exp., %
		experiment	calculation		
15	83,2	50,3	49,0	1	2,0
30	84,7	49,8	50,0	0	0
45	87,2	49,4	51,0	-2	-4,1

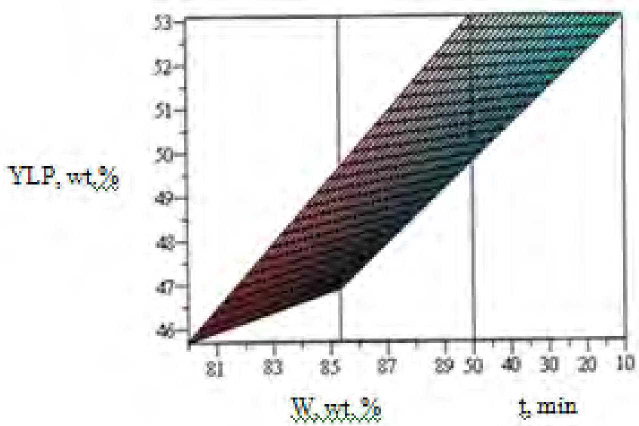

Figure 2 – The graph of the dependence of YLP on the duration of the experiment and the degree of transformation of OMS

Table 5 – Characteristics of hydrogenolysis of Kendyrlyk shale depending on the pressure of the process. Ratio shale : pasteurizer 1 : 1,5; Temperature – 420 ºC; Experiment duration – 15 min; Catalyst - Bauxite -094, wt. %. – 2,0; A^d – 15,0

Process indicators	The hydrogen pressure in the reactor volume, MPa				
	4,0	6,0	8,0	9,0	10,0
Degree of transformation of OMS, wt. %	64,1	76,3	83,2	84,1	83,1
Hydrogen in the reaction, wt. %	0,4	0,6	0,8	1,1	1,0
The yield of liquid products, wt. %	40,2	47,1	50,3	50,3	49,9
With boiling point higher 320 ºC	18,4	19,3	27,2	27,4	26,9
The remainder with boiling point higher 320 ºC	21,8	27,8	23,1	22,9	23,0
Gas, wt. %	6,8	8,9	10,3	11,0	10,5
Water, wt. %	5,7	6,8	7,6	7,8	7,8
Coke on the mineral part, wt. %	1,8	2,1	2,5	2,5	2,5

According to the data in table 5, hydrogen in the series of experiments varies insignificantly (from 0.4 to 1.1), so the total YLP can be represented as a function of *G (P, W)* from two variables: pressure (P) and degree of OMS transformation (W). Mathematical processing of the data of table 5 by the method of nonlinear regression showed the following relationship:

$$G(P, W) = 4{,}876 \cdot P + 0{,}5408W - 0{,}05184 \cdot P \cdot W \quad (3)$$

Table 6 shows the data showing the reproducibility of the experimental data G (P, W), and figure 3 shows its graph, which clearly shows the dependence of the YLP in the hydrogenolysis of the Kenderlyk meteorite shale on the pressure and the degree of OMS transformation.

Table 6 – Comparison of the experimental and calculated data on the yield of liquid products as a function of the pressure of the process and the degree of conversion (T = 420°C; t = 15 min; shale : pasteurizer = 1:1,5; Catalyst - Bauxite № 094)

Process pressure, MPa	W, wt. %	The yield of total liquid products, %		Δ = (exp.–calc.)	100·Δ/exp., %
		experiment	calculation		
4,0	64,1	40,2	40,88	-0,68	-1,692
6,0	76,3	47,1	46,79	0,31	0,6582
8,0	83,2	50,3	49,50	0,80	1,5900
9,0	84,1	50,3	50,12	0,18	0,3579
10,0	83,1	49,9	50,62	-0,72	-1,443

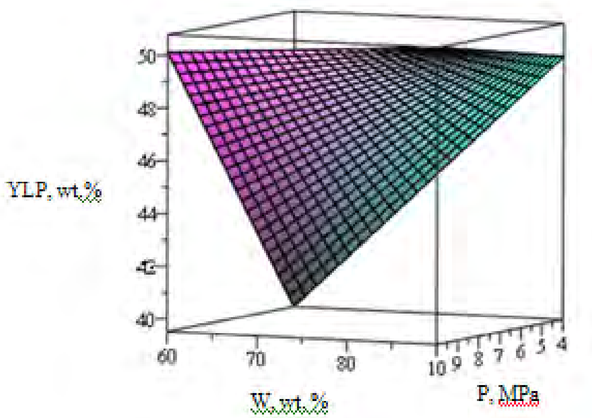

Figure 3 – Graph of the YLP function (P, W)

Conclusion. Thus, the analysis shows that during the hydrogenolysis of shale of Kenderlyk deposit, the temperature and duration of the experiment do not have a significant effect on the yield of liquid products, and increasing the hydrogen pressure in the interval from 4.0 to 8.0 MPa leads to an increase in YLP from 40.2 to 50.3 by weight %. The hydrogen pressure above 8 MPa does not have a significant effect on the process indicators.

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Резюме

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ВЛИЯНИЕ РАЗЛИЧНЫХ ФАКТОРОВ НА ГИДРОГЕНОЛИЗ СЛАНЦА МЕСТОРОЖДЕНИЯ «КЕНДЕРЛЫК»

В настоящей работе приведены результаты исследований по гидрогенизации Кендырлыкского горючего сланца для получения компонентов моторных топлив, оценка состояния и перспективы применения метода гидрогенизации под невысоким давлением водорода. По экспериментальным данным, методом нелинейной регрессии определены зависимости выхода жидких продуктов (ВЖП) от температуры, давления и продолжительности опыта. Показано, что увеличение температуры и продолжительности времени эксперимента не оказывают заметного влияние на показатели гидрогенолиза сланца, а с повышением давления водорода в интервале от 4,0 до 8,0 МПа на 20% увеличивается степень превращения органической массы сланца (ОМС) и количество вовлеченного в реакцию водорода увеличивается в два раза, нарастает выход жидких продуктов, газа и воды.

Ключевые слова: гидрогенолиз сланца, выход жидких продуктов, Кендерлык, боксит, органическая масса сланца, степень превращения.

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«КЕНДЕРЛІК» КЕН ОРНЫ ТАҚТАСЫН ГИДРОГЕНДЕУГЕ ӘРТҮРЛІ ФАКТОРЛАРДЫҢ ӘСЕРІ

Берілген жұмыста Кендерлік кен орнының жанғыш тақтатасын гидрогендеу арқылы мотор отындарының компоненттерін алу нәтижелері, күйді бағалау мен сутегінің төмен қысымында гидрогендеу әдістерін қолдану болашағы көрсетілген. Зерттеу нәтижелері бойынша сызықтық емес регрессия әдісі арқылы сұйық өнімдердің шығымының (СӨШ) температураға, қысымға және тәжірибенің ұзақтылығына тәуелділіктері анықталған. Нәтижесінде температура мен тәжірибенің ұзақтылығын жоғарылату тақтасты гидрогендеу көрсеткіштеріне айтарлықтай әсер етпейді, ал сутектің қысымы 4,0-тен 8,0 МПа аралығында жоғаралаған сайын тақтастың органикалық салмағының (ТОС) айналу дәрежесі 20 % жоғарылайды және судың, газдың, сұйық өнімдердің шығымы, реакцияға кіріскен сутектің мөлшері 2 есе жоғарылайды.

Түйін сөздер: тақтатасты гидрогендеу, сұйық өнімдердің шығымы, Кендерлік, боксит, тақтатастың органикалық салмағы, айналу дәрежесі.