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EFFECTIVE USE OF OIL SHALE FROM THE KENDYRLYK FIELD

Abstract. The chemical composition of the oil shales of the Kendyrlyk field (for comparison, the coals of both the Oi-Karagai and Kendyrlyk fields), and the physical and chemical properties (moisture, ash content, volatile-matter yield) are studied in this article, and the results of the study on hydrogenation of shale and coal for the production of motor fuels components, assessment of the state and prospects for application of the method of joint hydrogenation of oil shale and coal under low pressure. Samples of oil shale from the Kendyrlyk field and coals of both the Kendyrlyk and Oi-Karagai fields were used as raw materials for hydrogenation. It is shown that oil shales differ from coal by high ash content (60.5%), and high hydrogen content (9%). The results of the conducted experimental studies definitely show undoubted advantages of thermal coal liquefaction in a mixture with shale.

Key words: oil shale, Kenderlyk, hydrogenation, coal, Oi-Karagay.

Introduction. Possibility of efficient use of low-grade hydrocarbons not only increases the general resources of energy carriers, but also drastically changes the geopolitical situation in the world [1-3]. It increases the interest in such a source of hydrocarbons as oil shale.

Having considered the variety of historically formed definitions of oil shales, it is possible to suggest the following on the basis of developing modern representations: "Oil shale is a complex fuel organomineral mineral deposit, for its nature being a dispersed mixture of a high-polymeric heteroatomic organic formation based on a sapropelic composition, an admixture of humic substance and mineral mass of different chemical content" [4].

The organic matter of shale is called kerogen, its chemical composition includes: carbon, hydrogen, oxygen, nitrogen and sulfur. Carbon is the main element determining heat of combustion of fossil fuels. Its content in the organic matter of combustible shales can vary from 55 to 85%. Hydrogen is the second most important heat-producing element, which plays an important role in the energy potential of kerogen, since its heat of combustion (129.8 MJ/kg) is almost 4 times higher than that of carbon (34 MJ/kg). The hydrogen content varies between 7-12%. Compared to other solid fossil fuels, the organic matter of oil shales is distinguished by an increased (2-3 times more than for coal) hydrogen content and the best ability to transfer to liquid and gaseous products during thermo-catalytic destruction. Strengthening of requirements for the quality of the resulting products lead to significant changes in flow sheets and methods of using these types of raw materials [5, 11-13].

To date about 25 fields and manifestations 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. They differ in the composition of the initial substance and the conditions of formation, which to a large extent determined their qualitative and processing characteristics. All these fields, except for both Kendyrlyk and Chernozatonsky, have been studied extremely poorly [6].

Oil shale deposits are concentrated in three regions – Eastern Kazakhstan (Kendyrlyk, etc.), Kyzylorda Region (Baykhozha), and Western Kazakhstan (Priuralskaya and Aktobe groups). The explored reserves of oil shale are about 800 million tons. Within the limits of Western Kazakhstan, where the Upper Jurassic schistose deposits are widely developed, five promising areas have been identified (Barbartinskaya, Zapadno-Chaganskaya, Irtyepskaya, Novoemenovskaya and Ozinskaya) with estimated reserves of oil shales exceeding 13 billion tons or about 2 billion tons of shale oil (with an average yield of primary resin of about 15%). Oil shales of Kazakhstan are characterized by a high yield of primary resins (up to 13-23%, sometimes more than given numbers). The most valuable in quality are the oil shales of the Kendyrlyk field [6-10].

On the basis of oil shale, it is necessary to create a new branch of industry in the republic – shale oil refining. With the integrated industrial use of oil shale, it is possible to obtain numerous chemical, fuel-energy products, extraction of associated valuable metals, etc. In Sweden, the production of uranium and alloying metals, heat energy and sulfuric acid, aluminum and iron oxides, potassium and magnesium sulfates [10] are provided in the processing of 1 million tons of shale per year on the basis of clay shales in Ranstad. Among the complex of fuel and energy products, raw materials for which is resin and shale gas, various oils (fuel, carburetor, and diesel ones), bitumen, fuel oil, gasoline, kerosene, etc. should be noted. The heat of gas combustion at a reactor temperature of 900°C is 6415 kcal/m^3, 1000 °C – 4500, and 1100 °C – 6045 kcal/m^3. While low-temperature carbonization, the resin yield was 16-18% on dry shale with a high content of hydrocarbons in shale. Distillation of resin showed the possibility of using shale to produce artificial fuel [11-14].

The chemical composition of the oil shales of the Kendyrlyk field (for comparison, the coals of both the Oi-Karagai and Kendyrlyk fields) and the physical and chemical properties (moisture, ash content, volatile-matter yield) are studied in this article, and the results of the study on hydrogenation of shale, and coal for the production of motor fuels components.

EXPERIMENTAL PART

The classification of shale fines was carried out using the AS Control 200 particle size analyzer with a set of screens from 4 mm to less than 125 μm. Sample weight is 1 kg, amplitude is 2 mm/g, and classification time is 15 minutes.

In order to determine the chemical composition, material samples were used, which were fine granular powders. The physical and chemical properties of the oil shales of the Kendyrlyk field and coals of both the Kedyrlyk and Oi-Karagai fields were studied using the following methods:

Determination of total moisture was carried out according to GOST 11014-2001 Brown coals, bituminous coals, anthracite and oil shales. Shortened methods of moisture determination. A subsample of 2 g mass, taken from shales of 2 mm - 125 μm in size, was dried in the BINDER drying cabinet at a temperature of (105±5) ºC, the mass fraction of moisture was calculated from the mass loss.

Ash content of oil shale was determined in accordance with GOST 11022-95 Solid mineral fuels. Methods for determination of ash. A shale sample of 2 g mass was burned in the SNOL-8.2/1100 muffle furnace at a temperature of (815±10) ºC, and held at a given temperature until a constant mass. Ash content was calculated by mass of residue after calcination.

Volatile-matter yield was determined by heating a sample of 1 g mass in a porcelain crucible with a ground lid in the SNOL-8.2/1100 muffle furnace at 850 °C for 7 minutes.

RESULTS AND THEIR DISCUSSION

The results of the determination of the chemical composition of solid fossil fuels are presented in tables 1 and 2.

Table 1 – Physical and chemical properties and elemental composition of fossil fuels

Characteristics	Bituminous coal from the Kendyrlyk field	Brown coal of the Oi-Karagai field	Oil shale of the Kendyrlyk field
Moisture of the analytical sample (W^A, %)	8,0	7,8	9,6
Ash in a dry state (A^d, %)	15,2	12,0	60,5
Volatile matters (V^{daf}, %)	38,2	35,8	40,2
Total carbon in a dry state (C^{daf}, %)	65,2	74,1	65,2
Hydrogen in a dry state (H^{daf}, %)	3,9	4,7	9,0
Total sulfur in a dry state (S^{daf}, %)	1,3	0,1	1,2
Total oxygen in a dry state (O^{daf},%)	27,9	20,1	23,6
Total nitrogen in a dry state (N^{daf},%)	1,7	1,0	1,7

Table 2 – Chemical composition of the mineral part of solid fossil fuels

Component	Content of components in ash, wt. %						
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O+K_2O
Oil shale of the Kendyrlyk field	58.2	17.2	7.6	2.3	1.0	3.4	10.3
Brown coal of the Oi-Karagai field	35.2	25.8	13.5	19.6	2.9	2	1
Bituminous coal from the Kendyrlyk field	64.7	21.6	3.6	7.5	1.0	0.6	1

According to the studies of the chemical composition of oil shales, it is established that oxygen (23.6%) contained in the organic part prevails in the organic part of the oil shales, while oxides such as SiO_2 (58.2% by weight), Al_2O_3 (17.2 % wt.), and Na_2O + K_2O (10.3 % wt.) prevail in the mineral part of the oil shale.

According to the results presented in Table 1, it is seen that oil shales differ from coal by high ash content (up to 60.5%), and high hydrogen content (9%). Analyzing the data presented above, it is possible to draw conclusions on the possibility of using the mineral part of oil shales as a fluxing addition in the processes of recovery and use of oil shale and shale-ash waste as a sorption material for water purification from organic pollutants (oil and petroleum products).

Further, the results of studies on hydrogenation of Kendyrlyk oil shale and coals for obtaining components of motor fuels, an estimation of a state and prospects of application of a method of hydrogenation under low pressure of hydrogen are presented in the work.

Samples of oil shale and coal from the Kendyrlyk field were used as raw materials for hydrogenation. Heavy residue of Karazhambas oil boiling at a temperature above 500 °C was used as a pasting agent. Hydrogenation was carried out in an intensively shaken reactor with a volume of 0.2 liters. Physical and chemical characteristics and elemental composition of oil shale and coal are presented in tables 1, 2.

The results of the thermocatalytic hydrogenation of the Kendyrlyk oil shale and coal of the Kendyrlyk field are presented in table 3.

Table 3 – Characteristics of the process of thermocatalytic hydrogenation of shale and coal from the Kendyrlyk field (Ratio of coal, shale : pasting agent – 1.0 : 1.0, pressure, MPa – 5.0, temperature, ºC – 420, duration, minutes – 15, catalyst - Bauxite-094, wt.% – 2.0)

Indicator	Bituminous coal from the Kendyrlyk field	Oil shale of the Kendyrlyk field	Coal 35% + shale 15% + 50% pasting agent
Liquid yield, wt. %:	51.3	43.5	70.1
with a boiling point up to 320 ºC	23.4	23.3	29.9
with a boiling point above 320 °C	27.9	20.2	41.0
Gas yield, wt. %:	6.0	20.1	4.1
Sludge yield + losses, wt. %	42.7	36.4	25.9

As can be seen from the Table, during thermocatalytic hydrogenation of solid fossil fuels under the accepted conditions, liquid yield of products is: from coal of the Kendyrlyk field – 51.3%, and from shale – 43.5%. Thermocatalytic cracking of shale proceeds with significant gas formation (20.1 wt. %).

During hydrogenation of coal with the addition of 15% shale, the process proceeds with a slight gas formation (4.1%), which ensures a high liquid yield (70.1%). The resulting gas consists mainly of C_1-C_4 hydrocarbons.

The results of the conducted experimental studies definitely show undoubted advantages of a new process of thermal coal liquefaction in a mixture with shale.

The results of the studies showed that the catalytic properties of oil shales make it possible under optimal conditions to carry out the process of hydrogenolysis of the organic mass of coal with a high degree of conversion into liquid distillates without coke formation. The degree of conversion of a mixture of the organic mass of shale and coal and shale is much higher than that of coal.

Thus, creation of a shale-refining industry in the Republic can be considered an immutable business, which can ease tensions in providing consumers with gasoline, kerosene and other motor fuel, etc. It should be noted that some of epy oil shales in Kazakhstan are enriched with such a rare element as rhenium.

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Резюме

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КЕНДЕРЛІК КЕН ОРНЫ ТАҚТАСЫН ТИІМДІ ПАЙДАЛАНУ

Берілген жұмыста Кендерлік кен орнының жанғыш тақтатасының химиялық құрамы (салыстырмалы түрде Ой-Қарағай және Кендерлік кен орны көмірлері алынды) мен физико-химиялық қасиеттері (ылғалдылығы, күлділігі, ұшқыш заттар шығымы), сонымен қатар мотор отындарының компонентерін алу үшін тақтатас пен көмірді гидрогендеу үрдісін зерттеу нәтижелері, төмен қысымда тақтатас пен көмірді бірегей гидрогендеу әдісін қолдану болашағы мен күйін бағалау келтірілген. Гидрогендеу үрдісінің шикізаты ретінде «Кендерлік» кен орнының жанғыш тақтасы мен Кендерлік және Ой-Қарағай кен орны көмірлері пайдаланылды. Көмірден жанғыш тақтас жоғары күлділігімен (60,5%) және сутегінің жоғары құрамымен (9%) ерекшеленетіні көрсетілген. Жүргізілген тәжірибелік зерттеулердің нәтижелері көмірді сланецтің қоспасымен термиялық сұйылтудың күмәнсіз артықшылықтарын дәлелдейді.

Түйін сөздер: жанғыш тақтатас, Кендерлік, гидрогендеу, көмір, Ой-Қарағай.

Резюме

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ЭФФЕКТИВНОЕ ИСПОЛЬЗОВАНИЕ ГОРЮЧЕГО СЛАНЦА МЕСТОРОЖДЕНИЯ КЕНДЫРЛЫК

В статье изучены химический состав горючих сланцев Кендырлыкского месторождения (для сравнения угли Ой-Карагайского и Кендырлыкского месторождений) и физико-химические свойства (влажность, зольность, выход летучих веществ), а также приведены результаты исследования по гидрогенизации сланца и угля для получения компонентов моторных топлив, оценка состояния и перспективы применения метода совместной гидрогенизации сланца и угля под невысоким давлением. В качестве сырья для гидрогенизации применяли образцы горючего сланца месторождения «Кендырлык» и углей месторождений «Кендырлык» и «Ой-Карагай». Показано, что горючие сланцы отличаются от углей высокой зольностью (60,5%) и высоким содержанием водорода (9%). Результаты проведенных экспериментальных исследований однозначно свидетельствуют о несомненных преимуществах термического ожижения угля в смеси со сланцем.

Ключевые слова: горючий сланец, Кендерлык, гидрогенизация, уголь, Ой-Карагай.