N E W S
OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN
SERIES OF GEOLOGY AND TECHNICAL SCIENCES
ISSN 2224-5278
Volume 3, Number 429 (2018), 189 – 196

UDC 662.67

B. T. Yermagambet, N. U. Nurgaliyev, M. K. Kazankapova, Zh. M. Kasenova

Institute of Coal Chemistry and Technology LLP, Astana, Kazakhstan.
E-mail: coaltech@bk.rubake.yer@mail.ru nurgaliev_nao@mail.ru maira_1986@mail.ru zhanar_k_68@mail.ru

INVESTIGATION OF THE THERMAL DECOMPOSITION PROCESS OF KENDYRLIK DEPOSIT OIL SHALES

Abstract. In the article, experiments on the thermal treatment of Kendyrlik shale by its carbonization and activation were carried out. First, shale was carbonized in an inert argon medium in the temperature range 25-700 °C and then activated by water vapor at a temperature of 850-900 °C. The analysis of the elemental composition of the resulting synthetic gas showed that the highest concentration of combustible gas components (CO, H_2, CH_4) is observed at 900°C (in the absence of H_2S, low CO_2 and a small amount of liquid products - resin). Shale pyrolysis was also carried out in argon medium up to 900 °C. As a result of the analysis of the component composition of liquid products, it was found that mainly isoalkenes, alkanes and isocycloalkanes are formed. However, the elemental composition of the produced gas showed that the volume of gas and its caloric content are significantly lower in comparison with similar parameters for the gas produced during the activation of shale.
Keywords: shale, Kendyrlik, activation, carbonization, pyrolysis, gas.

Introduction. Globally, the significance of shale is its value as a source of energy, an alternative to other types of fossil fuels (for example, oil and coal) [1]. The solution to the problem of the use of oil shale, especially abroad, is mainly considered in the direction of their processing, with the production of shale resin - a substitute for oil and artificial gas (a substitute for natural gas). At the same time, the determining qualitative characteristics are: the content of organic matter and the yield of resin; calorific value (by class); the content of sulfur, rare and dispersed elements in the initial shale, semi-coking resin, gas products and ash residue; composition of the products obtained (resin, gas mixture); the ratio of the yield of the semi-coking resin to the heat of combustion (in groups) [2].

Possessing a high calorific value of combustible mass, shaleis one of the low-grade fuelsdue to the huge amount of ash. The high content of hydrogen (up to 11%) in kerogen and volatile substances (combustible mass), reaching 80%, makes it possible to utilize shale as a raw material for pyrolysis and gasification processes, as well as chemical processing for the production of various oils, motor fuels, phenols, tanning beds, combustible gas, various valuable chemical products for the chemical industry [3]. Liquid hydrocarbons (shale oil-resin), obtained by pyrolysis, are similar in composition to petroleum hydrocarbons and can be considered unconventional (shale) oil [4].

At present, considerable experience in ground processing of oil shale in off-shore retorting technology has been accumulated [5]: Galoter Process (GALOTER, Russia-Estonia), Enefit (modification of Galoter process), Kiviter (Estonia), Alberta-Taciuk Process (ATP) (Australia) , Petrosix (Brazil), ToscoII (USA), Fushun (China), Paraho Process (USA), Lurgi-Ruhrgas (Germany), Chevron STB (USA), etc. Energy efficiency of technologies is provided by technological operations optimizing physical and chemical conditions of the main process - pyrolysis process. The obtained industrial results [5, 6] showed the high efficiency of the use of oil shales.

One of the most effective shale processing technologies is the Galoter Process technology for the production of shale oil, motor fuels. This technology is mastered on a large industrial scale in Estonia (Narva). Using the potential heat of raw materials and economic efficiency, it surpasses all the technologies of thermal processing of oil shale that exist in the world today.

According to the Kazakhstan Research Institute of New Chemical Technologies and Materials, at least 25 deposits of oil shale, related to sediments of the Upper Devonian, Lower Carboniferous, Upper Paleozoic, Middle and Upper Jurassic and Paleogene, have been identified on the territory of Kazakhstan. They differ in the composition of the initial substance and in the conditions of formation, which to a large extent determined their quantitative and technological characteristics. The deposits of oil shale in Kazakhstan are extremely poorly studied [7, 8].

One of the promising and largest coal-shale basins is the Kendyrlyk basin (East Kazakhstan region), whose total reserves are estimated at 4,075 million tons, including balance reserves - 708 million tons [8,9]. It is followed by the Baykhozhinskoye (in Southern Kazakhstan) and the Priuralsky group of deposits in the west of the country [8].

The main advantage of Kendyrlyk resin is a low sulfur content, which is removed by conventional methods used in refining petroleum products. In Kendyrlyk shale, the sulfur content usually does not exceed 1%, and in many other deposits, the sulfur content in shale is 4-7%, and sometimes 9%. The total thickness of the shale horizons is more than 100 m, the thickness of the beds varies from 1 to 12 m, the calorific value is 4-15 MJ/kg, the yield of the resins is 4-20% [10, 11].

Therefore, the aim of this work is to study the processes of thermal processing of Kendyrlyk shale for the production of hydrocarbon products.

Research methods

Humidity, ash content and volatility of oil shales were determined on the Thermogravimetric Analyzer "ThermosterEltra" (according to ASTM D7582-12 "Standard Test Methods for Proximate Analysis of Coal and Coke by Macro Thermogravimetric Analysis"). The bulk density, the pH of the aqueous extract, the adsorption activity by methylorange were determined in accordance with [12, 13].

Elemental shale analysis was performed using energy dispersive X-ray spectroscopy on a SEM (Quanta 3D 200i) instrument with an attachment for energy dispersive analysis from EDAX at a resolution of: 3.0 nm at 30 kV (high vacuum mode); <12 nm at 3 kV (low vacuum mode); with an accelerating voltage from 200 V to 30 kV and with an increase from x50 to x100000. Elemental analysis is determined from Be to U. Samples were attached to a copper holder using conductive adhesive paper. Previously, a thin conducting layer of carbon was deposited on the surface of the samples in a special vacuum installation for better passage of charges. The energy of the exciting electron beam in the analysis was 15 keV, the working distance was 15 mm.

The thermal decomposition of oil shale was carried out as follows. Previously, the shale was crushed on a hammer mill (Molot-200) to a fraction of 0.1 mm and granular samples with a diameter of 0.8 cm were obtained using a tablet press (model 1000). The obtained shale samples were first subjected to heat treatment at a heating rate of 1-2 deg/min in an inert argon medium in the temperature range of 25-700 °C, and then activation of shale with water vapor within 850-900 °C. Also, the process of pyrolysis of shales in an inert argon medium in the temperature range 25-900 °C was carried out at a heating rate of 10-15 deg/min, in order to obtain mainly liquid products (resins).

The elemental composition of the gas (released in the processes of carbonization and activation) and liquid products (after distillation with the selection of hydrocarbon fractions) was determined on a Chromos GC-1000 chromatograph.

Results and discussion

TheKendyrlyk oil shale was selected as a subject for research. The results of analyzes of the technical and chemical composition of shales are presented in tables 1, 2.

Table 3 and figure 1 show the temperature dependences of the gas components obtained as a result of the carbonization and activation of the Kendyrlik shale. The formation of combustible gas components (CO, H_2, CH_4) occurs in accordance with the basic chemical reactions:

$$2H_2O \rightarrow 2H_2 + O_2 - 115\ 700\ kcal \quad (1)$$

$$C + H_2O \rightarrow CO + H_2 - 28\ 150\ kcal \quad (2)$$

$$C + CO_2 \rightarrow 2CO - 38\ 400\ kcal \quad (3)$$

$$C + 2H_2 \rightarrow CH_4 + 18\ 600\ kcal \quad (4)$$

Table 1 – Characteristics of the Kendyrlyk shale

Indicator, wt.%	Value
Total moisture, W^r_t Ash content, A^r Volatile substances outlet, V^{daf}	1-10 63-73 20-23
Element composition, wt.%	
C^{daf} H^{daf} S^d_t N^{daf} O^{daf}	76.88 9.27 0.23 1.25 12.37
Chemical composition of the mineral part, wt.%	
SiO_2 Al_2O_3 Fe_2O_3 CaO MgO K_2O+Na_2O SO_3	58.2 17.2 7.3 2.3 1.0 10.5 3.4

Table 2 – Chemical composition of Kendyrlik shales

Element	Wt. %	Atom. %
C	25.75	37.80
O	37.41	41.23
Na	0.56	0.43
Mg	0.96	0.70
Al	4.74	3.10
Si	20.05	12.59
K	1.44	0.65
Ca	5.10	2.25
Fe	3.99	1.26

Table 3 – Temperature dependence of gas components obtained from Kendyrlik shale

Temperature, °C							Gas composition, %							
							O_2	H_2	CO_2	N_2	CH_4	CO	C_2H_6	C_3H_6,C_3H_8
200	–	–	–	–	–	–	53.9	0.30	35.6	8.31	–	–	1.12	–
–	350	–	–	–	–	–	41.9	11.8	24.5	4.22	4.61	6.93	3.8	2.19
–	–	450	–	–	–	–	19.8	20.7	37.6	4.49	3.75	8.93	3.24	1.47
–	–	–	650	–	–	–	15.2	9.63	40.6	4.96	–	24.4	2.75	2.38
–	–	–	–	750	–	–	10.8	9.57	23.8	4.41	–	48.8	2.24	0.29
–	–	–	–	–	850	–	13.76	38.3	2.62	2.21	–	39.8	3.18	0.13
–	–	–	–	–	–	900	4.02	33.4	1.28	6.65	2.86	49.5	2.24	0.04

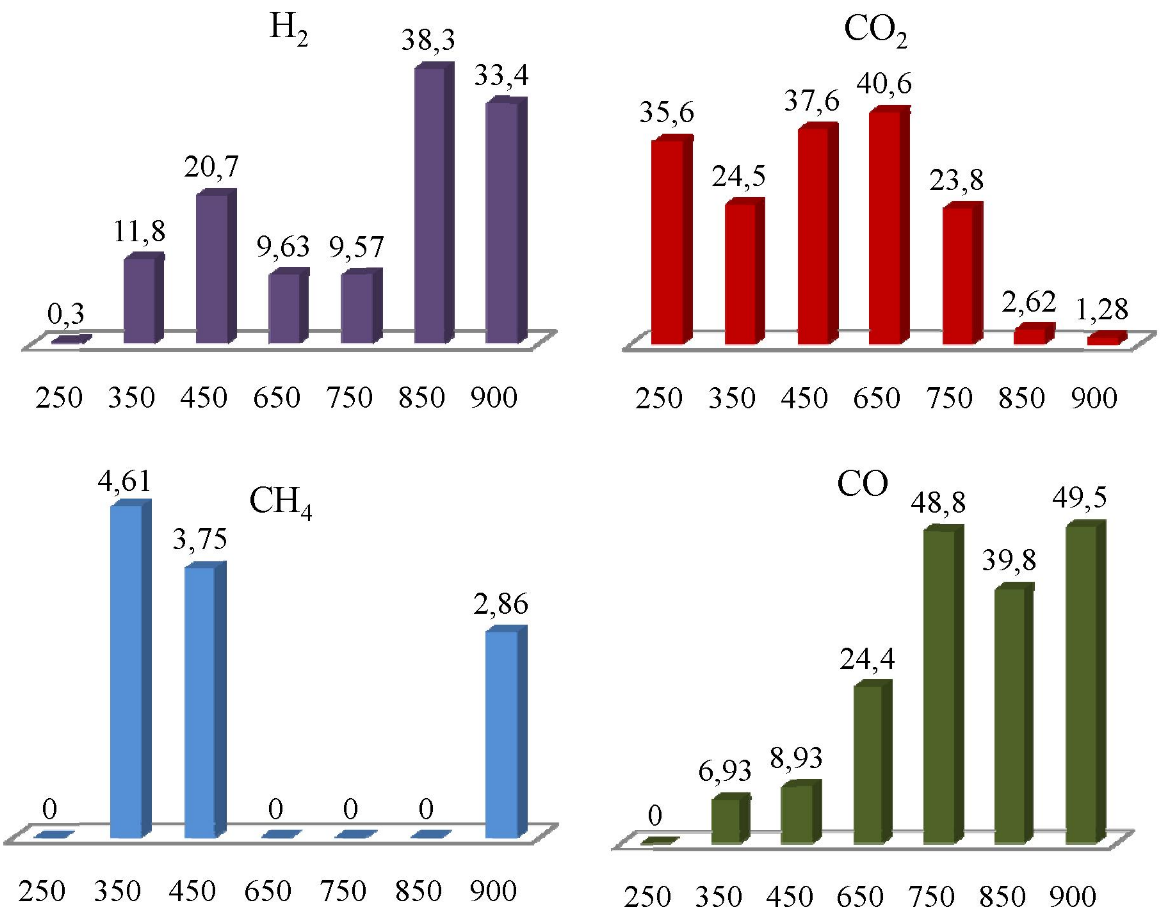

Figure 1 – Temperature dependence of gas components obtained from Kendyrlik shale

The obtained results show that the content of C_2-C_3 hydrocarbons at the whole temperature level is insignificant and is about 2-6%. In the transition from 450 °C to 650 °C, depending on the concentration of H_2 and simultaneously increases the content of CO. Beginning at a temperature of 750 °C, the CO_2 fraction decreases sharply and a significant increase in the caloric value of the gas is observed, due to an increase in CO, which is most likely to occur in accordance with the reaction (3). At a temperature of 850 °C, during the activation process, the H_2 content increases sharply (from 9.57 to 38.3%), due, apparently, to the supply of water vapor. The total fraction of the combustible gas components (CO, H_2, CH_4) in-creases and becomes greatest at the maximum shale activation temperature of 900°C. At the same time, H_2S is virtually absent during the entire process of the thermal deposition of oil shale.

The greatest oxygen content at 200-350 °C is associated with the release of pyrogenic water and oxygen-containing organic compounds, due to the decomposition of the side groups of macromolecules (since the carbon-oxygen bonds are the least stable in the thermal ratio). With further heating at 450-650 °C, oxygen is also observed in sufficient quantities (but to a lesser extent) because of the thermal decomposition reactions of the most thermostable organomineral complexes and the release of the bulk of the resin and gaseous hydrocarbons. In the temperature range 750-900 °C, decomposition of calcite and dolomite takes part in the formation of oxygen, the content of which can reach up to 50% in the mineral shale [14].

Table 4 shows the material balance of the shale activation of the Kendyrlik deposit.

Table 5 shows the elemental composition of the gas obtained as a result of the pyrolysis of the Kendyrlyk shales.

Table 4 – Material Balance of Shale Activation of the Kendyrlik deposit

#	Incoming products	Content			№	Outgoing products	Content		
		g	cm^3	%			g	cm^3	%
1	Shale	500		96.2	1	Solid residue	398.0	306.0	76.5
2	Water (saturated steam)	20	7.8	3.8	2	Generator gas	68.4	59.5	13.2
	Total	520		100	3	Liquid product (resin)	3.6	3	0.7
					4	Water	50	50	9.6
					Total		520		100

Table 5 – Gas composition of pyrolysis of shales of the Kendyrlik deposit

Temperature, °C						Gas composition, vol, %							
						O_2	H_2	CO_2	N_2	CH_4	CO	C_2H_6	C_3H_6,C_3H_8
350	–	–	–	–	–	54.0	3.08	27.5	9.40	0.00	0.15	3.48	2.31
–	400	–	–	–	–	28.2	11.0	28.1	10.7	1.41	16.6	2.75	1.16
–	–	450	–	–	–	52.5	2.32	31.7	9.3	0.01	0.12	1.93	2.07
–	–	–	720	–	–	32.7	4.77	8.75	7.15	–	44.4	1.42	0.78
–	–	–	–	820	–	61.7	6.03	4.12	5.25	0.14	22.4	0.29	0.03
–	–	–	–	–	900	59.5	9.51	1.97	4.93	–	23.9	0.15	–

As it can be seen from the data obtained, the most caloric gas (due to the content of the CO gas generally, 44%) is observed at a temperature of 720 °C, with an insignificant fraction of H_2 (≈5%), the absence of CH_4 and a small concentration of CO_2 (≈9%). A further increase in temperature to 820 °C leads to a significant decrease in the caloric value of the gas due to a significant decrease in CO (from 44.4 to 22.4%). In the course of pyrolysis, when the gas is heated to 900 °C, the C_2-C_3 (up to ≈6%) and CH_4 (up to 1.5%) gas concentrations are insignificant, the CO_2 content is significantly reduced (to ≈2%) and H_2S is practically absent.

In the process of pyrolysis of shales, the vapor-gas mixture was withdrawn to the refrigerator, where the hydrocarbon vapor condenses to form a shale resin. The liquid products obtained in this process in the temperature range 350-500 °C were distilled on a rotary evaporator (at temperatures $T < 55$ °C and T = 55-61 °C under vacuum) with the selection of hydrocarbon fractions. Figures 2 and 3 show the chromatograms of the obtained liquid pyrolysis products of Kendyrlyksk shale.

The component composition of fractions of liquid hydrocarbons formed during pyrolysis of shale is represented by a set of C_6-C_{20} compounds (arenes, alkanes, isoalkanes, isocycloalkanes, alkenes, isoalkenes, isocycloalkenes). According to the results of the analysis (figures 2, 3), the main part of the products consists mainly of isoalkenes, alkanes andisocycloalkanes. Moreover, the hydrocarbon fractions obtained after distillation at T = 55-61 °C (under vacuum) have a much wider set of compounds than whenT <55 °C (under vacuum), mainly due to arenes, isoalkanes, isocycloalkanes.

The material balance of the pyrolysis of the Kendyrlyk oil shale is shown in table 6. The results of the data show that the amount of liquid products obtained is much larger and the volume of synthetic gas is smaller compared to similar parameters for products obtained during the activation of shale with water vapor.

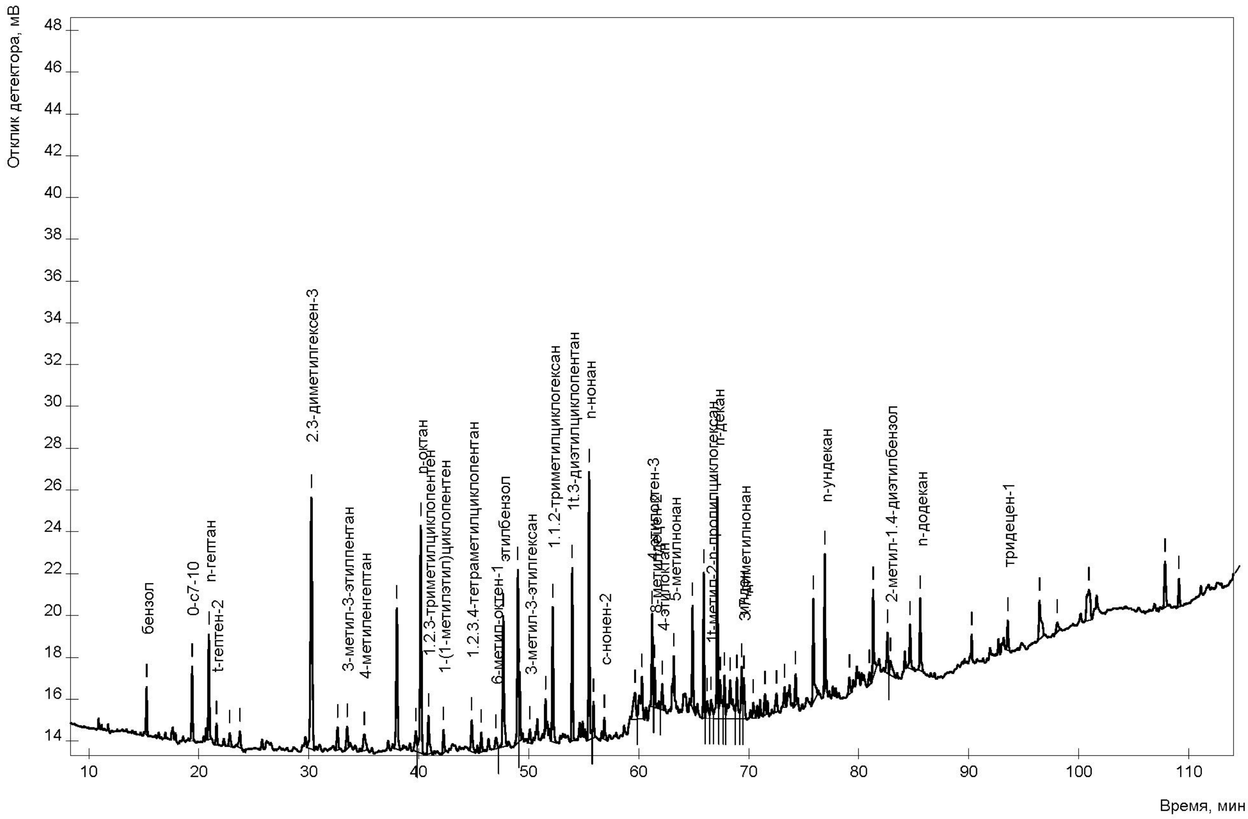

Figure 2 – Chromatogram of liquid pyrolysis products from Kendyrlyksk shale obtained by distillation at T <55 °C (under vacuum)

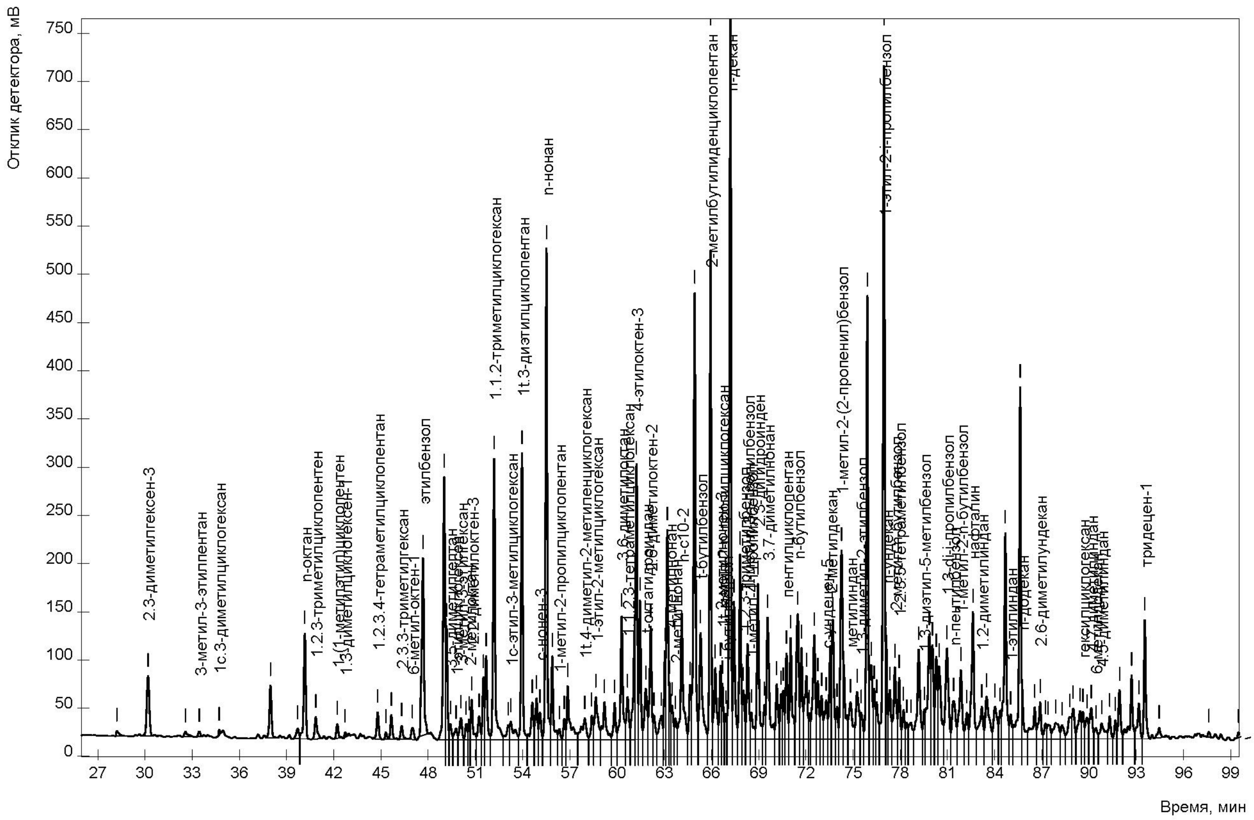

Figure 3 – Chromatogram of liquid pyrolysis products from Kendyrlyksk shale obtained by distillation at T = 55-61 °C (under vacuum)

Table 6 – Material balance of pyrolysis of Kendyrlyk shale

#	Incoming products	Content			№	Outgoing products	Content		
		g	cm^3	%			g	cm^3	%
1	Shale	500		100	1	Solid residue	409.0	371.8	81.8
	Total	500		100	2	Generator gas	40.5	35.2	8.1
					3	Liquid product (resin)	29.0	24.2	5.8
					4	Water	21.5	21.5	4.3
						Total	500		100.0

Conclusions. The experiments on the thermal decomposition of the Kendyrlyksk oil shale have shown that during the activation of the raw material with water vapor at a temperature of 900 °C a high-calorific synthetic gas with a low content of harmful and ballast substances is formed. Such gas may be suitable for use as an energy fuel (for obtaining thermal and electric energy) and as synthesis gas (CO, H_2). This gas, as well as the resin obtained as a result of pyrolysis (in argon), can be a valuable raw material for the production of motor fuels and other chemicals of chemical engineering (phenols, tannins, etc.).

The present work was carried out within the framework of the scientific and technical program No. 0020 / PTF-15 on the topic: "Development of technologies and creation of a pilot complex for deep processing of Kazakh shales with a feedstock capacity of 250 tons per year", funded by the Science Committee of the Ministry of Education and Science of the Republic of Kazakhstan.

REFERENCES

[1] Srtizhakova Yu., Avakyan T., Lapidus A. Proceed-ings of the DGMK-Conference «Catalysis – Innovative Applications in Petro-chemistry and Refining». Dresden, Germany. **2011**, 217. (in Eng.)

[2] Strizhakova Ju.A. M.: Nedra, **2008**, 192. (in Russ.)

[3] Ryzhov A.N., Avakjan T.A., Smolenskij E.A., Lapidus A.L. Doklady Akademii nauk. **2012**, 447, 1: 44-48. (in Russ.)

[4] Golicyn M.V. Moskva: Izd-vo Znanie, **1990**. 48. (in Russ.)

[5] Grushevenko D., Grushevenko E. Centr izuchenija mirovyh jenergeticheskih rynkov INJeI RAN, **2012**, 49. (in Russ.)

[6] Zjuba O.G., Glushhenko O.N. Nacional'nyj mineral'no-syr'evoj universitet «Gornyj», Sankt-Peterburg, **2012**, 7, 4. (in Russ.)

[7] Domnin C. Jekspert Kazahstana. – №8 (400). 04.03.**2013**. (in Russ.)

[8] Kasenov B.K., Ermagambet B.T., Bekturganov N.S., Nabiev M.A., Kasenova Sh.B., Sagintaeva Zh.I., Kuanyshbekov E.E., Seisenova A.A. Solid Fuel Chemistry, **2016**, 3: 149-151. (in Eng.)

[9] Azizov T.M., Vlasov V.I. Spravochnik. Almaty.**1997**, 91-101. (in Russ.)

[10] Kotlukov V.A. SPb.: Znanie, **1987**, 32. (in Russ.)

[11] Ginzburg A.I. Moskva: Nedra, **1991**, 116. (in Russ.)

[12] Smirnov A.D. L.: Himija,**1982**, 168. (in Russ.)

[13] Kabulov A.T., Nechipurenko S.V., Efremov S.A. Trudy Kol'skogo nauchnogo centra RAN, **2015**, 5(31): 527-531. (in Russ.)

[14] Spravochnik slancepererabotchika. L.: Himija, **1988**. 256 p.

Б. Т. Ермағамбет, Н. У. Нургалиев, М. К. Казанкапова, Ж. М. Касенова

ТОО «Институт химии угля и технологии», Астана, Казахстан

ИССЛЕДОВАНИЕ ПРОЦЕССА ТЕРМИЧЕСКОГО РАЗЛОЖЕНИЯ ГОРЮЧИХ СЛАНЦЕВ КЕНДЫРЛЫКСКОГО МЕСТОРОЖДЕНИЯ

Аннотация. В статье проведены эксперименты по термической обработке Кендырлыкского сланца путем его карбонизации и активации. Сначала проводили карбонизацию сланца в инертной среде аргона в интервале температур 25-700 °С и затем активацию сланца водяным паром при температуре 850-900 °С. Проведенный анализ элементного состава полученного синтетического газа показал, что наибольшая концентрация горючих компонентов газа (CO,H_2,CH_4) наблюдается при 900 °С (при отсутствии H_2S, низкого содержания CO_2 и малом количестве жидких продуктов – смолы). Также проводили пиролиз сланца в среде аргона до 900 °С. В результате анализа компонентного состава жидких продуктов выявлено, что образуются преимущественно изоалкены, алканы и изоциклоалканы. Однако элементный состав полученного газа показал, что объем газа и его калорийность существенно ниже по сравнению с аналогичными параметрами для газа, выделяющегося в процессе активации сланца.

Ключевые слова: сланец, Кендырлык, карбонизация, активация, пиролиз, газ.

Б. Т. Ермағамбет, Н. У. Нургалиев, М. К. Казанкапова, Ж. М. Касенова

«Көмір химиясы және технология институты» ЖШС, Астана, Қазақстан

КЕНДІРЛІК КЕНІШІНІҢ ЖАНҒЫШ СЛАНЕЦТІҢ ТЕРМИЯЛЫҚ ЫДЫРАУ ҮРДІСІН ЗЕРТТЕУ

Аннотация. Мақалада Кендірліксланецін термиялық өңдеу нәтижелері келтірілген. Алдымен сланец аргон қатысында, инертті ортада 25-700 °С температура интервалында карбрнизацияланып, 850-900 °С температурада су буымен активация әдісімен өңделді. Түзілген синтетикалық газдың элементтік құрамын талдау нәтижесінде жанғыш газ компоненттірінің (CO, H_2, CH_4) айтарлықтай концентрациясы 900 °С байқалды (H_2S жоқ, CO_2 газы мен сұйық өнім-шайырдың аз мөлшері түзілген). Сонымен қатар аргон қатысында 900 °С-та сланецтің пиролизі жүргізілді. Түзілген сұйық өнімнің компоненттік құрамын талдау нәтижесінде негізінен изоалкендер, алкандар және изоциклоалкандар түзілгені анықталды. Алайда, түзілген газдың элементтік құрамынан анықталғандай газдың көлемі мен оның калориясы сланецті активациялау үдерісі кезінде бөлінетін газдың параметрлерімен салыстырғанда айтарлықтай төмен екені байқалды.

Түйін сөздер: тақтатас, Кендірлік, карбонизация, активация, пиролиз, газ.

Yermagambet Bolat Toleukhanuly – Doctor of Chemical Science, Professor, Director of LLP "Institute of Coal Chemistry and Technology", Astana, Kazakhstan, E-mail:
bake.yer@mail.ru

Nurgaliyev Nurken Uteuovich – Candidate of Chemical Science, Leading Researcher of LLP "Institute of Coal Chemistry and Technology", Astana, Kazakhstan, E-mail:nurgaliev_nao@mail.ru

Kazankapova Maira Kuttybaevna – Phd, Senior Researcher of LLP "Institute of Coal Chemistry and Technology", Astana, Kazakhstan, E-mail:maira_1986@mail.ru

Kassenova Zhanar Muratbekovna – Master of Chemical Sciences and Technology, Deputy Director of LLP "Institute of Coal Chemistry and Technology", Astana, Kazakhstan, E-mail: zhanar_k_68@mail.ru