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EVALUATING POSSIBLE INDUSTRIAL APPLICATIONS OF COMBUSTIBLE SHALES AND SHALE ASH WASTES

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Today energy consumption is constantly growing while explored reserves of easily accessible oil are depleting, which is a reason why most countries tend to diversify their energy mix, develop non-hydrocarbon energy sources and use domestic types of fuel, including the low grade ones. Thereby interest is raised to such a source of hydrocarbons as combustible shales. Combustible shales appear to be one of the highest-potential types of organic raw materials, which may offset and in future even substitute oil products and gas. The paper is investigating behavior and structure of combustible shales during heat treatment in order to identify their possible industrial applications. A synchronous thermal analysis has been held, chemical composition of combustible shales' mineral fraction and optimal conditions for shale fines briquetting have been determined.

Key words: combustible shales, synchronous thermal analysis, specific surface area, briquetting, low grade fuel.

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Introduction. One of the greatest global challenges of the 21st century is a rapid depletion of easily accessible and high quality non-renewable energy sources – oil and natural gas. All Russian largest oil fields were commissioned as far back as in the Soviet times, in recent years the major focus is on intensification of production rates. The current resources have been extracted by more than 50 %, the share of hard-to-access resources, the water cut of oil and the share of sulfur-bearing oil are increasing. As forecasted by experts oil production will be relocating to hard-to-reach and remote areas. This will increase the cost of extraction and the ultimate cost of refined products [5]. The present-day economic environment calls for diversification of energy mix, development of non-hydrocarbon energy sources and use of local types of fuel, including non-traditional and low grade ones, such as combustible shales [2].

Reserves of combustible shales in shale tar and gas equivalent are significantly higher than reserves of oil and natural gas [2, 4]. Russia is among the countries with the largest reserves of combustible shales, it's outpaced only by USA and Brasil. Reserves of combustible shales and shale tar in Russia are shown in Table 1. As you can see, considerable reserves of combustible shales are concentrated in Baltic, Oleneksk and Sinsk-Botomsk basins.

Table 1

Combustible shale fields in Russia [2, 4]

Basin	Reserves of combustible shales, mln tones	Reserves of shale tar, mln tones
Baltic (Leningrad field)	10,246.7	1,386.2
Timano-Pechorsk	4,888.0	351.4
Vychegodsk	58,105.8	4,590.0
Central	59.6	5.4
Volzhsky	25,822.4	2,805.5
South Ural	47.55	2.8
Oleneksk	380,000.0	19,000.0
Sinsk-Botomsk	220,000.0	5,500.0
Irkutsk region and Transbaikal	111.7	60.5
Total	700,288.85	33,701.8

As opposed to other types of solid fossil fuels combustible shales contain a considerable amount of hydrogen in organic matter and have a high concentration of mineral components (up to 50 %) [6]. That's why in order to identify rational industrial applications of combustible shales information is needed on their chemical and mineral composition, organic structure and changes in basic substance at different stages of heat or chemical treatment [7-10].

The purpose of this study is to investigate behavior of combustible shales during heat treatment and their composition in order to identify their possible industrial applications. In order to accomplish this purpose the following tasks have been solved:

1) synchronous thermal analysis of combustible shales was conducted;
2) chemical composition of combustible shales' mineral fraction was determined;
3) specific surface areas of combustible shales and of shale ash were compared;
4) optimal conditions for shale fines briquetting have been identified.

Experiment Method. Research target - combustible shales from Leningrad field of Baltic basin.

Synchronous thermal analysis (thermogravimetric and differential thermal analysis) was conducted in modular thermal analyzer SetsysEvo 1750SETERAM under the following conditions:

1. In the dynamic high purity nitrogen atmosphere (consumption 40 ml/min). In order to avoid air oxygen residuals in the furnace chamber it was vacuumed twice and then filled with nitrogen. A heating rate was 10°C per minute up to 1000 °C.

2. In dynamic air atmosphere. In the course of experiment a mixture of oxygen and nitrogen in proportions as contained in the air was fed into the furnace chamber. A heating rate was 10°C per minute up to 1000 °C.

A chemical composition of combustible shales was studied using energy dispersive X-ray fluorescent instrument Epsilon3 PANalitical, measurements were made with Omnian program, making it a semi-quantitative analysis.

Specific surface area of combustible shales and ash was analyzed with automatic gas sorption analyzer Autosorb^{iQ}. Gas used in the course of analysis - nitrogen, analysis duration – 700 min. The area and micropore values were determined using the following methods: MultiPointBET, BJHmethod (adsorption) and BJHmethod (desorption).

The shale fines were briquetted on laboratory hydraulic press PGL-20 under pressure 10 and 15 MPa both with preliminary material humidification and without it. The strength properties of the produced shale briquettes were determined based on the standard method 'Coal briquettes. Methods for the determination of mechanical strength' (GOST 2189-75). Mechanical strength of the briquettes was determined by briquette dropping onto the metal plate. As mineral content in combustible shales may reach 50 %, thus enhancing the briquette strength, the number of drops was increased from 4 up until the briquette was fully destructed. A heat resistance of shale briquettes (when heat treatment does not cause their destruction) was tested at temperature 800-1000°C in muffle furnace SNOL-8.2/1100.

Results and Discussion Figure 1 shows a general view of the thermogram obtained upon combustible shales heating in an inert atmosphere (condition 1), where X axis is the experiment duration; Y_1 axis (highlighted in red) is the temperature in the furnace chamber (°C.); Y_2 axis (highlighted in green) is a change in the sample mass during the experiment (% rel.); Y_3 axis (highlighted in blue) is a dependency revealed by differential thermal analysis (DTA dependency), reflecting changes in heat flow inside the furnace chamber (differential temperature difference).

As it appears from the graph when heated a sample goes through dissociation registered at two distinct stages of mass change. Dissociation processes are also accompanied with endothermic effects registrable through DSC dependency. Total loss in sample mass during the experiment comprised 43.5 % [10, 11].

Fig.2 shows the thermogravimetric (TG) dependency with a more detailed analysis of the mass loss during the heating process. For correct determination of mass loss temperature ranges a DTG dependency have been identified representing the first derivative of the weight loss over time (highlighted in pink). It is shown that during the first stage, recordable in the range between 331-520 °C, mass loss was 24.6 % due to the release and subsequent evaporation of shale tar. The second stage of mass loss recordable in the range between 679-806 °C comprises 12.2 % and can be explained by decomposition of minerals contained in the combustible shales (calcite, dolomite). The total loss in sample mass in the process of heating from the room temperature up to 1000 °C comprises 42.6 %.

Fig.3 shows the DTA dependency of combustible shale in a nitrogen atmosphere. It is demonstrated that sample dissociation and release of volatiles contained in the combustible shales are accompanied with three endothermic effects in the temperature ranges between 364-489 °C (bituminization), between 507-527 °C (shale tar evaporation) and between 674-808 °C (decomposition of mineral component) respectively. The highest heat absorption intensity is observed during high-temperature treatment.

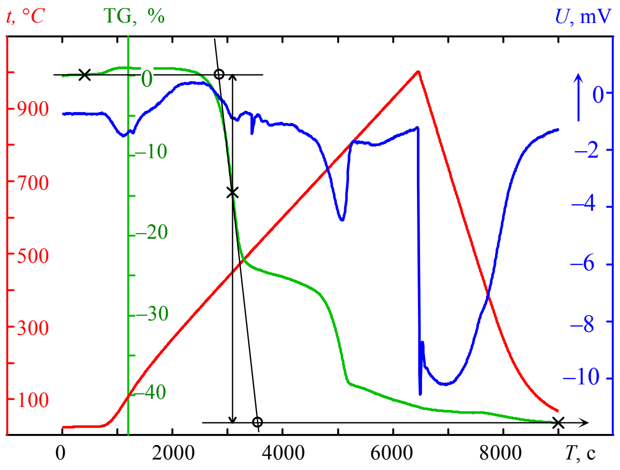

Fig. 1. General view of thermogram in nitrogen atmosphere

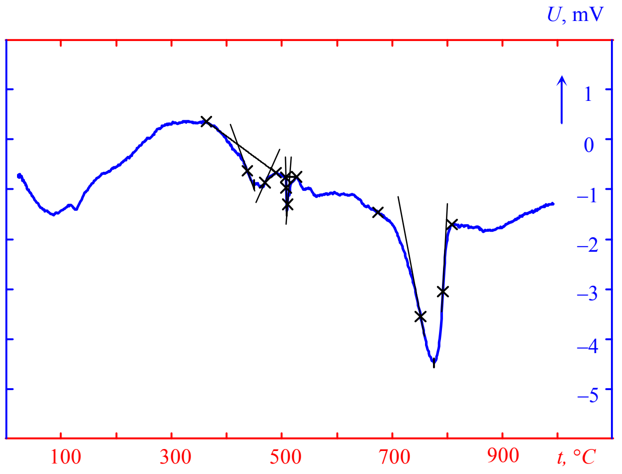

Fig. 3. DTA dependency of combustible shales in inert atmosphere

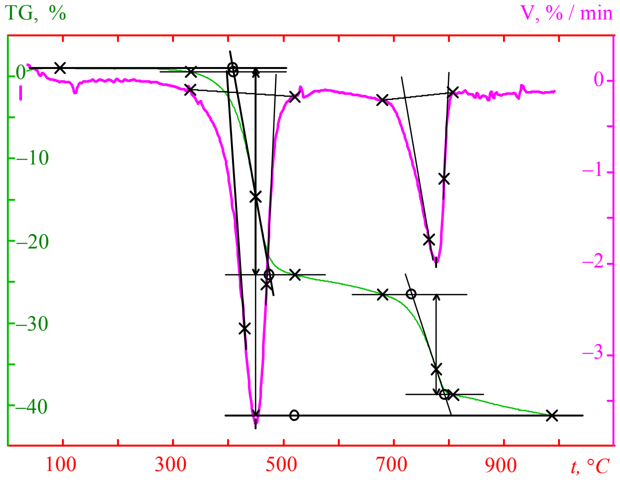

Fig. 2. TG and DTG dependencies of combustible shales in nitrogen atmosphere

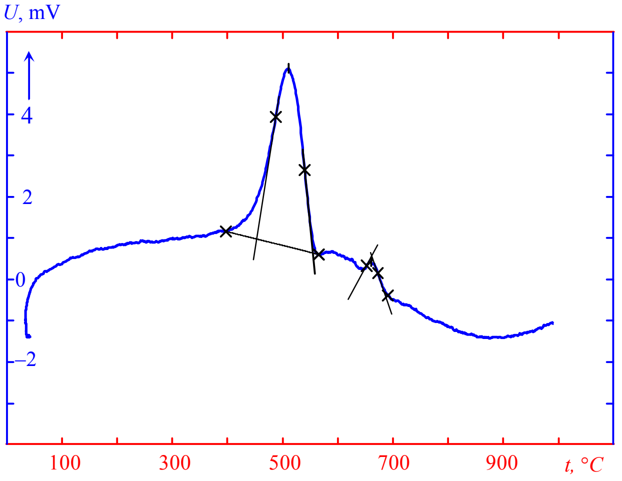

Fig. 4. DTA dependency of combustible shales in air atmosphere

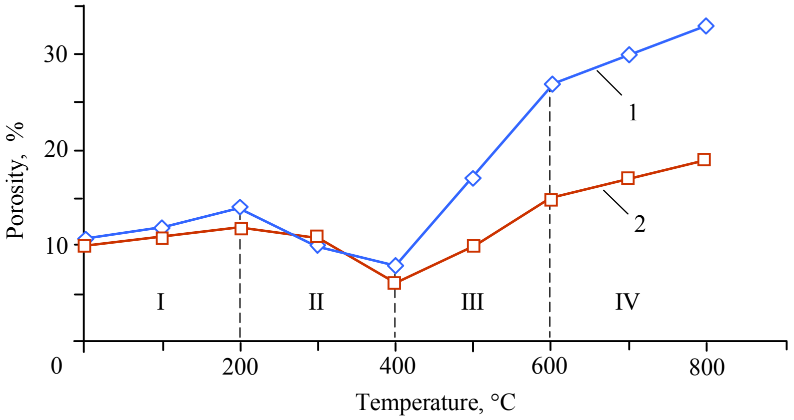

Fig. 5. Changes in macroporosity of combustible shales in air (1) and nitrogen (2) atmospheres [1]

Fig.4 shows combustible shale DTA dependency identified in dynamic air atmosphere (condition 2). The main exothermic effect associated with shale combustion is observed in a range between 397-566 °C (shale tar evaporation). Besides exothermic effects of weaker intensity are observed at higher temperatures in a range between 566-691 °C.

Chemical composition of mineral fraction of combustible shales, % is as follows:

Component	Composition	Component	Composition
Al_2O_3	7.7	MnO	0.1
SiO_2	33.2	Fe_2O_3	4.6
P_2O_5	0.5	MgO	0.9
SO_3	4.4	CaO	39.9
K_2O	7.1	TiO_2	1.3

As evidenced by chemical analysis of mineral fraction contained in combustible shales from Leningrad field (Table 2), almost all minerals are present in shales in the form of oxides: SiO_2, Al_2O_3, CaO, Fe_2O_3, MgO, etc. Mineral fraction of the shales mostly consists of calcium oxide (CaO – 39.9 %) and silicon oxide (SiO_2 -33.2 %).

Measurement of specific surface area and distribution of micropores of combustible shales and shale ash with fractions less than 125 μm (Table 2) revealed that the specific surface area of combustible shales is higher than that of shale ash.

Table 2

Specific surface area of combustible shales and shale ash

Parameter	Method	Unit of measurement	Combustible shales	Shale ash
S_y	MultiPointBET	cm^2/g	12.93	2.29
S_y	BJHmethod (adsorption)	cm^2/g	11.57	1.24
S_y	BJHmethod (desorption)	cm^2/g	12.32	2.24
Total volume of micropores	BJHmethod (adsorption)	cm^3/g	0.190	0.037
Total volume of micropores	BJHmethod (desorption)	cm^3/g	0.190	0.037
Average micropore diameter		nm	15.9	25.4
Volume of micropores with diameter less than 227 nm		cm^3/g	0.051	0.00459

Table 3

Impact of composition and pressure on strength properties of briquettes

Material characteristics			Physical properties		
Briquette composition	Material humidity, %	Pressure, MPa	Mechanical strength		Heat resistance (800-1000°C)
			Resistance to		
			shock, number of falls	compression, kg/cm^2	
Fraction from 2 mm to 125 μm					
Combustible shales	11.6	10-15	1	0.5	Destruction
Combustible shales and water	37	10-15	2	0.5	« «
Fraction less than 125 μm					
Combustible shales	11.6	10	1	0.5	Destructed
		15	2	0.7	Was not destructed
Combustible shales and water	37	10	5	4.0	« «
		15	6	5.0	« «

As a result of heat treatment fine-pored structure gets compacted (total volume of micropores and specific surface area decrease). Along with decrease in micropores the volume of macropores increase (Fig. 5) [1].

Total volume of micropores of combustible shales (measured using BJHmethod (desorption)) is equal to 0.190 cm^3/g, and of ash – 0.037 cm^3/g (Table 2). Macroporosity is increased due to coarsening of mineral aggregates contained in combustible shales. The study revealed that the shale ash is composed of silicates.

Table 3 shows results of experiments investigating the impact of composition and pressure on the strength properties of the briquettes. The shale fines with fraction sizes from 2 mm to 125 µm and less than 125 µm were used, the larger fractions cause excessive wear of the press and higher energy consumption for crushing.

When the humidity of briquetted material with fractions less than 125 µm is increased from 11.6 to 37 % and briquetting pressure is increased from 10 to 15 MPa the mechanical (strength) properties of shale briquettes are improved (Table 3).

The experiment results proved that the most optimum material for briquetting is the consumable shales with fractions less than 125 µm and humidity of 37 %, briquetting pressure 15 MPa. The produced briquette has the following mechanical properties:

- shock resistance - briquette withstands six falls;
- compression resistance $\delta_{compr} = 5$ kg/cm^2;
- heat resistance at temperature 800-1000 °C.

For efficient use of shale fines of varying size additional researches were pursued to study briquetting material with the following fractional composition: 50 % fractions with sizes from 2 mm to 125 µm and 50 % - less than 125 µm. If the fraction size is larger the pressure and briquetting time shall be increased, that's why for the study maximum fraction size was from 2 mm to 125 µm. Experiment results are presented in Table 4.

Table 4

Briquetting research results (pressure 15 MPa)

Material characteristics		Physical properties		
		Mechanical strength		Heat resistance (800-1000°C)
		Resistance to		
Briquette composition	Material humidity, %	shock, number of falls	compression, kg/cm^2	
Combustible shales	8	1	0.5	Destructed
	11.6	2	1.0	« «
Combustible shales and water	23	4	3.0	Was not destructed
	37	2	1.0	« «
	40	2	1.0	« «

With rational fractional composition with particle sizes less than 125 µm and from 2 mm to 125 µm (in 1:1 proportion), the optimum humidity is 23 %. The produced briquette has the following mechanical properties:

- shock resistance – briquette withstands four falls;
- compression resistance $\delta_{compr} = 3$ kg/cm^2;
- heat resistance at temperature 800-1000°C.

Conclusion

1. The heat treatment of combustible shales in inert atmosphere leads to dissociation registrable at two distinct stages of mass change: 331-520 °C (mass loss of 24.6 % due to release and subsequent evaporation of shale tar) and 679-806 °C (mass loss of 12.2 % due to decomposition of minerals contained in the combustible shales – calcite, dolomite). The total loss in sample mass in the process of heating from the room temperature up to 1000°C comprises 42.6 %.
2. Sample dissociation and release of volatiles contained in the combustible shales (in inert atmosphere) are accompanied with three endothermic effects in the temperature ranges between 364-489 °C (bituminization), between 507-527 °C (shale tar evaporation) and between 674-808 °C (decomposition of mineral component) respectively.
3. Total volume of micropores of combustible shales (measured using BJHmethod (desorption)) is equal to 0.190 cm^3/g, and of ash– 0.037 cm^3/g.

4. During extraction and processing of combustible shales the shale fines of varying fractional composition are produced, which are almost not used for further processing and are stored in the dumps. The research helped to identify optimal conditions for briquetting of shale fines, which are as follows:

- fraction size of less than 125 μm, material humidity 37 %, briquetting pressure 15 MPa; briquette mechanical properties: shock resistance – briquette withstands six falls, compression resistance – $\delta_{compr} = 5$ kg/cm^2, heat resistant at temperature 800-1000 °C;
- fraction size equal to 2 mm – 125 μm and less than 125 μm (1:1), material optimal humidity 23 %, briquetting pressure 15 MPa; briquette mechanical properties: shock resistance - briquette withstands four falls, compression resistance - $\delta_{compr} = 3$ kg/cm^2, heat resistant at temperature 800-1000 °C.

Findings:

- Shale fines can be briquetted without binding agents, which reduces the cost of final product;
- Increase in briquetting pressure (from 10 to 15 MPa) and humidity (from 11.6 % to 37 %) improves strength properties of shale briquettes;
- Shale fines can be briquetted without preliminary material drying, as capillary strength of adsorbed liquid creates necessary adhesion between material particles.

5. Based on the studies of chemical composition of combustible shales it was determined that mineral fraction of combustible shales mainly consists of the following oxides: Si_2O, Al_2O, CaO, Fe_2O_3. Based on analysis of minerals contained in the combustible shales complex applications can be proposed both for mineral and organic fractions of combustible shales, such as:

- use combustible shales and shale ash as a natural mineral filtering and sorption material for water purification from organic contaminations (oil and oil products) and heavy metals;
- use mineral components of combustible shales (SiO_2, CaO, Al_2O_3, Fe_2O_3) as fluxing additives for metal reduction in the metallurgical industry.

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