In this study, the object of the research is low-rank coal during the process of thermal heating of five types: brown, high moisture brown, long-flame, coke weakly sintering and coke fusinite.

In the research, when conducting thermal and gas analysis in inert media, the problem of using low-rank coal in the thermal heating process to obtain volatile fuel gases was solved by identifying the quantitative and qualitative performance of its behavior. Quantitative indicators are determined as the mass of thermal destruction products: the mass of coal tar and gas products and semi-coke under optimal temperature conditions of their maximum release. Qualitative indicators of coal behavior are components of thermal decomposition products. It is revealed that the behavior of low-rank coals in the process of thermal heating is determined by the degree of metamorphism. In this case, long-flame and brown coals have a lower release of volatile fuel gases than coke weakly sintering and coke fusinite coals due to a lower degree of metamorphism and greater degrees of thermal oxidation and dehydration.

Thermal decomposition component ranges consisting of polyaromatic fragments (HCN, C_6H_{12}, C_4H_5N), greenhouse gases (CH_4 and CO_2), toxic gases (H_2S and NH_3) and synthesis gases (CO and H_2) have the highest share of release. Optimal temperature conditions and ranges for the release of low molecular weight gases used as high calorific volatile fuel gases are obtained.

The results can be used in the design, optimization and construction of thermal heating equipment, correction of gasification and pyrolysis processes. Moreover, they can be applied in localized coal tar spots minimization technologies and for designing targeted gases extraction

Keywords: coal, thermal heating, temperature, decomposition, volatile fuel gases, energy efficiency

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IDENTIFICATION OF THE LOW-RANK COALS THERMAL HEATING BEHAVIOR

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1. Introduction

The trend towards more economical and environmentally friendly solid fuel energy generation equipment leads to the necessity to develop technologies for more efficient use of coal in the development of clean coal technologies. To date, one of the effective methods to create such technologies is thermal heating of coal for the purpose of combustible gases release (preheating, gasification, pyrolysis) and their further use to improve the efficiency of equipment. In addition to releasing combustible gases, thermal heating helps to stabilize flames, increase combustion efficiency and reduce toxic emissions. Thermal heating efficiency can be significantly increased when considering the individual characteristics of coal [1–3]. Moreover, thermal heating of fuel can be applied not only to power generation equipment, but also to installations providing heat generation for utilities and production facilities, where lower temperature ranges and low-rank coals are used. At the same time, each type of coal, especially low-rank, has an individual set of positive and negative characteristics that affect its behavior during the thermal heating process. High-quality coals have a more stable structure and higher density, so today thermal heating treatment such as gasification, pyrolysis and coking has been successfully applied. However, these technologies require high-temperature processing ranges and complex process designs, making the processes energy-intensive and not always environmentally friendly. The use of low-rank coals for thermal heating allows the process to be located in lower temperature areas, which will undoubtedly affect the power capacity and efficiency. At the same time, nowadays, low-quality coal produced worldwide accounts for about 86 % [4] and at the same time, the growth of coal production and consumption is not decreasing. However, the structure of low-rank coal is unstable and therefore the process of thermal heating of low-rank coal depends on its qualitative and quantitative indicators. The quantitative behavior is determined by the mass of thermal decomposition products. Qualitative – the composition of components at optimal temperature ranges of their maximum output in different environments. Taking into account the above indicators, firstly it will be possible to develop and adjust the operation of plants directly for specific types of low-rank coal in the given temperature ranges. Secondary, research on the low-rank coals thermal heating behavior will lead to the development of techniques and installations for producing target gases used in industrial production. In addition, the availability of a set of coal behavior characteristics within the specified temperature ranges will allow optimizing the operation of small boiler equipment operating under the conditions of separation of additional synthesis reducing the release of carbon-containing components and other emissions into the environment. All the above shows that the studies carried out within the framework of the low-rank coals thermal heating behavior are relevant.

2. Literature review and problem statement

The paper [5] presents the results of experimental studies, which proved the link between low-rank coal permeability and temperature rise even in the range from 0 °C to 200 °C, determined by the aromatic bonds in polyaromatic rings. Moreover, the results suggest that the permeability of coal can be increased with temperature. This will definitely affect the thermal destruction process and the rate at which volatile fuel gases and other fragments are released during thermal heating. However, the study did not achieve the objective of releasing volatile fuel gases in low temperature ranges because the experiments were conducted for coal bed methane and heat-carrying gases N_2, CH_4 and CO_2. On the one hand, the research results justify the possibility of releasing combustible gases at low temperatures, but on the other hand, the process of high temperature ranges of fragmentary decomposition products is not defined, which is no less important.

The temperature range approach for the study of thermal heating processes was used in the paper [6], which presents the results of research to improve the quality of low-rank coals using rapid heating technologies at a rate of ~$100–10^{-4}$ °C/min in the temperature range from 350 °C to 550 °C. However, it is known that the heating rate can significantly change the behavior of coal depending on its characteristics during the thermal heating process. To solve this problem, the authors of the work [7] using differential thermal analysis, nuclear magnetic resonance, and electron spin resonance identified three main areas of low-quality coal behavior, taking into account covalent bonds due to activation energy in the simulation of thermal heating processes, and the authors of the paper [8] presents experimental results showing a direct relationship between the coal activation energy at any quality and any temperature. The structural features of coal reflect the interaction of different macromolecules at different temperature and velocity levels. There is no doubt that the results reflect the efficiency of the thermal heating process by determining the coal behavior, but they are imitative, which limits their use directly to the development of thermal coal processing devices.

The papers [9, 10] present the results on pre-heating coal, showing the reduction of NO formation, taking into account the qualitative analysis of the release of volatile fuel gases with various influences in the temperature range up to 1,200 °C. In the presented case, pulverized coal is completely converted to volatile fuel gases, which proves not only the environmental effect but also the efficiency of the coal heating process with the preliminary release of volatile fuel gases. In this case, the authors of the work [11] propose to use pre-heating chambers with partial ignition and burnout of fuel. However, there were no studies of the volatile fuel gases output possibilities and their release conditions, which is undoubtedly important for many energy processes. The paper [12] presents studies that can be used as a basis for the design of thermal heating installations taking into account different media. In particular, the steam thermal heating process is presented, which shows an increase in the efficiency of coal pre-treatment. But in this case, there is also no consideration of the quantitative and qualitative characteristics of coal decomposition processes depending on the type and characteristics. Given the above, the indicators of low-rank coal are presented in the paper [13]. It is shown that volatile fuel gases from special coal heat treatment can be used to replace ignition oil in thermal power plants. The authors demonstrated the results of research on the production of volatile fuel gases of low-rank coals with the determination of their net calorific volume. And even the temperature ranges of the process of obtaining volatile fuel gases for starter fuel have been determined. Undoubtedly, the results prove the effectiveness of low-rank coals for the production of volatile fuel gases during the thermal heating process. However, it is not known whether these studies can be applied to a wider range of technologies, including medium and small power. Ecological aspects of thermal heating of low-rank coal were considered in the papers [14], which showed that heating of low-rank coal in small boilers from 40 kW to 100 kW with oxygen deficiency in the temperature range from 100 °C to 450 °C affects the reduction of CO_2 emissions to 10 % and the increase in operating efficiency range from 10 % to 15 %.

All this assumes the feasibility of studies to determine the low-rank coals thermal heating behavior, taking into account optimal temperature ranges and heating medium.

3. The aim and objectives of the study

The aim of the study is to obtain the behavior parameters of low-rank coals in the thermal heating process. This will allow increasing the efficiency of the coal thermal heating process based on the results of thermal heating behavior evaluation and make it possible to set the energy and cost-effective operating parameters of the low-rank coal thermal heating process for the release of volatile fuel gases and other components of thermal decomposition depending on the purpose of the process or installation with necessary concentration.

To achieve the aim, the following objectives were accomplished:

– to analyze the quantitative behavior indicators of coals depending on the type, taking into account the mass loss during thermal heating with the determination of the main temperature ranges;

– to analyze the qualitative behavior indicators of the component composition of low-rank coke coal thermal heating products with recommendations for temperature ranges for maximum volatile fuel gases output.

4. Materials and methods

The object of the research is low-rank coal during the thermal heating process. The main hypothesis of the study is the determination of the possibility to obtain the required amount of volatile fuel gases taking into account the low-rank coals thermal heating behavior. In the course of the work, it was assumed that coals with low genetic maturity, such as the specimens presented, are analogs of polymers capable of thermal destruction to emit various components, including volatile fuel gases. Experiments were carried out with a sufficient number of measurements, precisely in an amount of for high-moisture brown coal – 136; brown coal – 215; long-flame coal – 637; coke fusinite coal – 359 and coke weakly sintering coal – 853, which simplified the optimal average data. Five samples of low-rank coals were used as materials for the study. According to ASTM D7582-15 "Standard test method for approximate analysis of coal and coke macro-thermogravimetric analysis", coal samples were enriched with flotation in CCl_4 (tetrachloride) and C_6H_6 (benzene) solutions with a density $\rho \leq 1.5$ kg/m^3. Coal types are shown in Table 1.

Table 1

Coal types

No. of sample	Formation	Type
1	Sarykol 3B	Brown
2	Shubarkul LF	Long-flame
3	Maykuben B	High moisture brown
4	Eastern Stratum – 2 CWS	Coke weakly sintering
5	Bogenbai Gila CF	Coke fusinite

Coal type sample specifications are presented in Table 2.

Table 2

Coal specifications

No. of sample	Elementary content, % daf				Technical analysis, % daf			Qr, MJ/kg
	C, %	H, %	S_t, %	(O+N+S), %	W_a, %	A_d, %	V_{daf}, %	
1	70	4.9	0.3	25.1	5.9	14.2	48.0	27.16
2	81.0	5.6	0.7	13.4	9.7	5.5	43.3	33.04
3	72.6	5.1	1.0	22.4	3.3	14.8	44.1	28.59
4	86.4	5.0	0.3	8.6	1.5	15.5	26.1	34.64
5	89.0	5.0	0.9	6.0	0.6	11.3	18.6	35.80

The study used complex coal research methods, including thermogravimetric analysis in a given temperature interval of the carbon organic decomposition kinetics. The analysis was carried out in the inert nitrogen environment of the integrated "Skimmer" system with a Netzch STA 409 quadrupole gas analyzer in the temperature range from 200 °C to 800 °C at a sample heating rate of 100 °C/min. During the experiment, mass loss (TG) and mass loss rate (DTG) were recorded.

To carry out the study of the thermal heating process in an inert environment, the developed installation was used with automatic continuous online control of the output of liquid and gaseous combustion products, the schematic diagram of which is presented in Fig. 1.

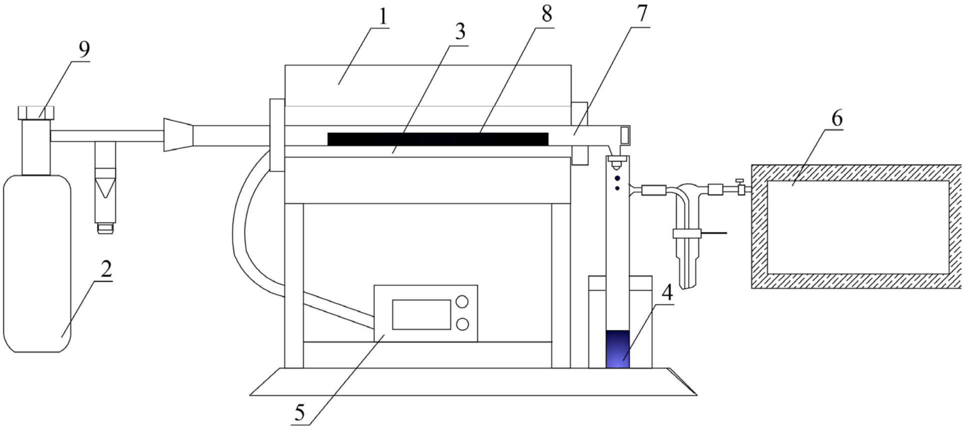


Fig. 1. Installation for the thermal heating process in an inert environment: 1 – heating device; 2 – gas cylinder; 3 – multimeter; 4 – coal tar condensate collection device; 5 – automatic controller; 6 – quadrupole gas analyzer; 7 – coal sample treatment reactor; 8 – coal sample; 9 – fuel pressure regulator

The installation allows carrying out mass and chemical analysis of the thermal destruction products composition of coal samples at temperatures above 600 °C. The composition of gases formed during thermal decomposition was recorded with an SRS QMS – 300 high-pressure gas analyzer, taking into account the release of the mass of hydrocarbons (CH), ammonia (NH_3), hydrogen sulfide (H_2S), carbon oxide and dioxide (CO and CO_2) and hydrogen (H). In addition, liquid products of coal decomposition (coal tar) and solid residue (semicoke) were formed during thermal destruction, the output of which was also recorded during the experiment.

5. Results of research on the behavior pattern parameters of Kazakhstan's coals in the thermal heating process

5. 1. Analysis of the quantitative parameters of coal behavior depending on the type

Thermogravimetric analysis was carried out in the study of the heating rate influence on the thermal decomposition process of the coal organic mass for brown, coke weakly sintering, fusinite and long-flame with identification of quantitative indicators of the behavior by temperature ranges. The initial mass loss results in the temperature range from the beginning of decomposition (T_0) to activation (T_{200}) are shown in Fig. 2.

The bar chart in Fig. 2 compares the percentage of mass losses at the beginning of the thermal destruction process in the temperatures range from the initial temperature of destruction to 200 °C for brown, high moisture brown, coke fusinite, long-flame and coke weakly sintering types of coal.

In general, brown coal was more active in mass losses during thermal destruction than coke weakly sintering coal. The maximum of mass losses was shown by long-flame and high moisture brown coal (accounted for 10.55 % and 9.73 % at the initial temperatures of 92 °C and 98 °C, respectively). It can be seen, that brown coal is less active than others. Its mass losses were twice as less as those of other coal types and accounted for 5.03 % at the initial temperature of 81 °C.

On the other hand, coke weakly sintering types of coal were more passive in the process of thermal decomposition during thermal heating. The minimum of mass losses was shown by coke fusinite coal, which accounted for 0.08 % for the whole initial period although the initial temperature of destruction for the test sample was 94 °C.

Overall, the mass loss process is determined by the desorption of hygroscopic moisture. Definitely, brown and long-flame coals have a higher moisture content, than coke kinds of coal.

Thermogravimetric analysis involves the calculation of the temperature peak of the first derivative indicating the highest mass loss rate (T_{max}) taking into account the decomposition rate V_{max}, %, min for the tested coal samples (elution band).

The temperature values at the maximum decomposition rate at the inflection point for the relevant coal samples are shown in Fig. 3.

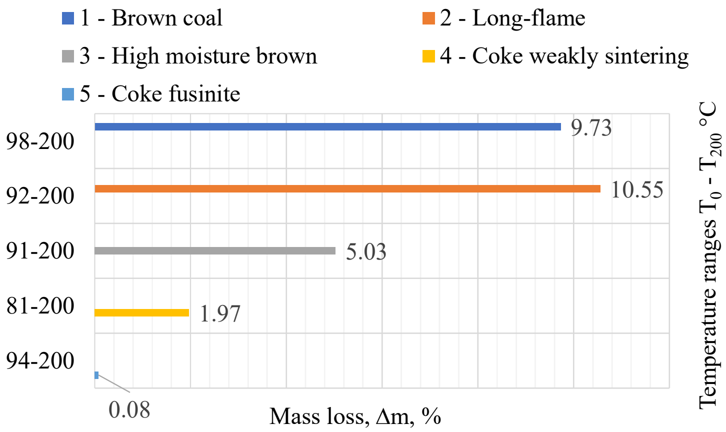


Fig. 2. Mass loss in the initial period of decomposition in the temperature range of $T_0 - T_{200}$

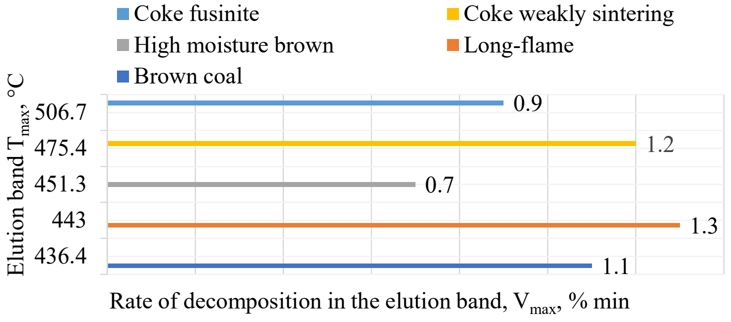


Fig. 3. Temperature at the maximum decomposition rate (elution band)

The rate of decomposition is defined by temperature and for different kinds of coal has different values even for the same types of coal from the same basin.

The bar chart in Fig. 3 provides information about the temperature at the maximum thermal destruction rate (elution band) in °C for the coke fusinite, high moisture brown, coke weakly sintering, brown and long-flame types of coal and about the decomposition rate in minimum percent during the thermogravimetric analysis for each type of coal.

In general, the elution band is within the temperature range from 430 °C to 510 °C and the decomposition rate doesn't have significant differences for the tested types. Looking in more detail, the graph illustrates that for the brown coal sample the majority of decomposition shifted towards the area of lower temperatures and it is equal to 436.4 °C. Similar results were obtained for the samples of high moisture brown and long-flame types of coal represented by 443 % and 451.3 %, respectively.

In comparison, the coke kinds of coal are more thermally stable. Their majority decomposition area is within the temperature range from 451 °C to 507 °C (for coke fusinite and coke weakly sintering coals, respectively).

To summarize, the temperature of the elution band increases with the growth of genetic coal maturity, which is proved by the greater thermal resistance of coke weakly sintering coal.

After comparing the results, the range of thermal destruction with the mass loss of the tested samples during heating can be divided into three main stages as shown in Fig. 4.

The point-by-point diagram in Fig. 4 compares mass losses due to decomposition during the thermal heating process in the temperature range from 25 °C to 1,000 °C for brown, high moisture brown, coke fusinite, long-flame and coke weakly sintering types of coal as a percentage. The process of thermal decomposition was divided into five heating periods with temperature ranges from: 25 °C to 200 °C; 200 °C to 300 °C; 300 °C to 650 °C; 650 °C to 800 °C; 800 °C to 1,000 °C, while there are three clear phases in the mass losses visible range from:

1) 200 °C to 300 °C – minor mass losses;
2) 300 °C to 650 °C – maximum mass losses;
3) 650 °C to 800 °C – drop in mass losses for all types of the tested coal samples.

The highest percentage of 13.9 % was shown by high moisture brown coal at a maximum temperature of 443.0 °C. In contrast, in the same period of raising temperature, coke fusinite coal had the lowest percentage of 5.7 % at a maximum temperature of 506.7 °C for this period. It can be noted that for the other types of coal, a sharp increase in mass losses was also observed in this period of raising temperature. Brown coal had a 13.1 % mass loss, long-flame coal – 11.3 % mass loss and coke weakly sintering coal – 9.9 % mass loss. It can be characteristic of thermal decomposition in the raising temperature range from 25 °C to 300 °C and the range from 650 °C to 1,000 °C as a period of slight mass losses for all types of coal. In this period, each tested sample was characterized by total mass losses:

1) brown coal – 23.5 %;
2) coke fusinite coal – 10.4 %;
3) long-flame coal – 25.3 %;
4) high moisture brown coal – 33 %;
5) coke weakly sintering – 13.5 %.

Overall, all types of the tested samples had the same trend of thermal destruction. During the period of raising the temperature range from 25 °C to about 400 °C–500 °C, an increase in mass losses is commonly observed, and after the temperature above 500 °C, a decrease in mass losses can be seen.

In general, the results are presented in Table 3.

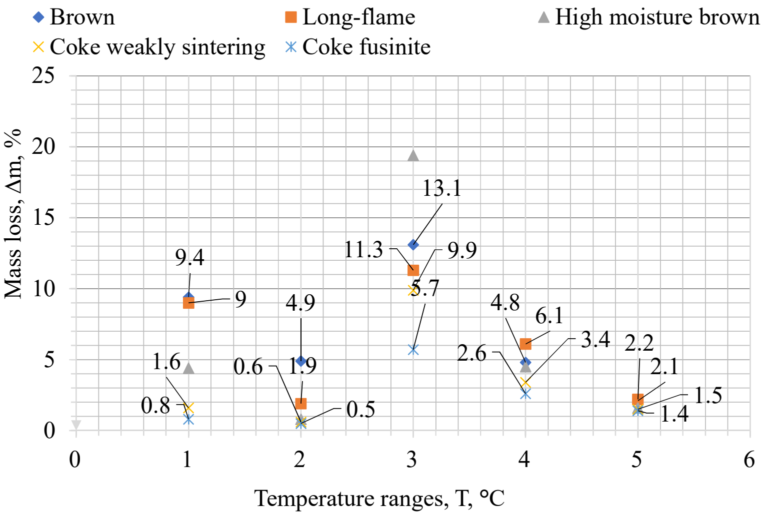


Fig. 4. Mass losses of the tested coal samples in the temperature ranges

Table 3

Results of thermogravimetric analysis

No. of sample	$T_{\max}$, °C	$V_{\max}$, %/min	Δm, mass%, temperature ranges, °C					
			25–200	200–300	300–650	650–800	800–1,000	25–1,000
1	436.4	–1.1	9.4	4.9	13.1	4.8	2.1	46.7
2	451.3	–0.7	9.0	1.9	11.3	6.1	2.2	36.6
3	443.0	–2.2	4.4	0.8	19.4	4.5	1.6	40.5
4	475.4	–1.2	1.6	0.6	9.9	3.4	1.5	23.4
5	506.7	–0.9	0.8	0.5	5.7	2.6	1.4	16.1

For the whole period, the majority of mass losses occurred in the sample of brown coal, the minority of mass losses was shown by the sample of coke fusinite coal represented by 46.7 % and 16.1 %, respectively.

5. 2. Analysis of the qualitative component composition of low-rank coke coal thermal heating products with recommendations for temperature ranges for maximum volatile fuel gases output

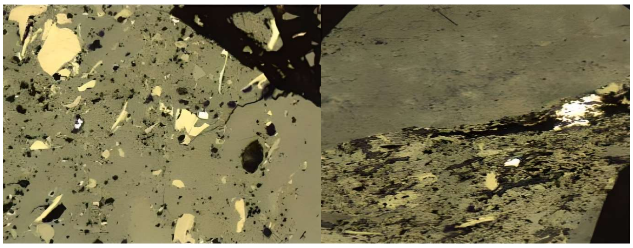
The qualitative composition of liquid and gaseous products of thermal decomposition is determined by the conditions of the thermal heating process of coals at the output of various components, including combustible products.

The study of the qualitative composition during thermal heating of coal samples without oxygen access was carried out in the temperature range up to 610 °C when determining the mixture of hydrocarbons C_1–C_6 output, coal tar products, ammonia, hydrogen sulfide, hydrogen and other chemical compounds under continuous monitoring. The study used samples with the highest metamorphism and lowest mass loss to account for the release of combustible substances without including hygroscopic moisture:

1) coke weakly sintering coal (V^{daf}=26.1 %);

2) coke fusinite coal (V^{daf}=18.6 %).

Microphotographs of coal samples are shown in Fig. 5, *a*, *b*.



a *b*

Fig. 5. Microphotographs of coal samples: *a* – coke fusinite coal; *b* – coke weakly sintering coal

Microphotographs of coal polished section, measuring 20×20×5 mm (weighing about 2–3 grams) are made by the point contact method under a microscope in reflected light according to [15] at a magnification of 300 times with a displacement step of 0.5–0.6 mm. The preassembled coal samples were dried to a constant mass in the temperature range from 25 °C to 103 °C with a size of less than 200 μm (0.02 mm). The composition of thermal destruction gaseous products was determined by a Netzch STA 409 quadrupole gas analyzer. The weight method was used to determine T_{sk} coal tar mass, S_{ka} semi-coke and gaseous compounds.

Liquid compounds were investigated by isolating acid coal tar, oils and asphaltenes as polycyclic compounds. Asphaltenes were determined by deposition to hexane. The determination of the hydrocarbon mixture was carried out by the chromotographic division of liquids into silicogel when using disorbents of hexane and acetone. All samples were preliminary examined for total moisture content according to [16], ash content and volatile discharge according to [17], sulfur according to [18], and carbon and hydrogen content according to [19]. A preliminary analysis of the standard methodologies is presented in Table 2.

The results of the studies on the output of destruction products with the determination of the weight composition are presented in Table 4 and Fig. 6.

Table 4

Weight composition of coal samples during thermal heating

Type of coal	No.	Sample weight before the experiment, m_{sample}^{befor}, gr	Sample weight after the experiment, m_{sample}^{after}		Mass of coal tar, m_{Task}		Mass of semi-coke, m_{Ska}		Mass of gas products, m_G	
			g	%	g	%	g	%	g	%
Coke fusinite	1	12.14	8.95	100	1.35	15	6.59	73.72	1.0	11.2
Coke weakly sintering	2	12.09	10.3	100	1.25	6.53	8.82	85.61	0.23	7.86

The shares of composite compounds released during thermal heating for coke fusinite (sample 1) and coke weakly sintering coals (sample 2) as a percentage (Fig. 6) are presented.

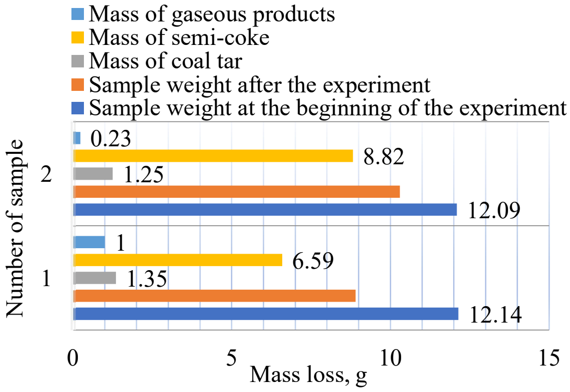


Fig. 6. Proportions of composite compounds mass losses for coal samples during the thermal heating process

It is seen that for both samples, which have approximately the similar mass at the beginning of the experiment (number 1 – 12.14 g and number 2 – 12.09 g), the proportions for coal tar mass have subtle differences, accounting for 1.35 g and 1.25 g, respectively. On the other hand, the mass of semi-coke for sample 2 is greater than for sample 1. Comparing the mass of gas products, it is clear that the mass of gas products for sample 2 is four times less than for sample 1.

To summarize, it is clear that for coke fusinite kinds of coal, the mass of coal tar and gas product as a result of deep thermal heating will be higher than for coke weakly sintering kinds of coal.

The gaseous product composition was recorded with continuous data collection of the full spectrum of gaseous products and their masses. The purity of the experiment was ensured by recording the background mass of the gaseous components in the laboratory chamber before each experiment. Table 5 presents the component composition of the products formed during thermal decomposition.

Table 5

Component composition of volatile fuel gases

Content, %	Sample 1				Sample 2			
	Temperature, °C				Temperature, °C			
	150	300	450	610	150	300	450	610
Greenhous gaseous fragments								
CH_4	–	–	52.38	34.1	–	–	59.2	38.47
CO_2	100	100	21.72	1.49	100	100	14.98	4.16
Polyaromatic gaseous fragments								
HCN	–	–	9.15	0.24	–	–	8.96	0.80
C_6H_{12}	–	–	4.1	0.55	–	–	3.5	0.44
C_4H_5N	–	–	1.1	0.95	–	–	0.46	0.25
Toxic gaseous fragments								
H_2S	–	–	3.15	0.18	–	–	2.8	0.33
NH_3	–	–	0.44	0.38	–	–	0.77	0.55
Synthesis gaseous fragments								
CO	–	–	6.01	42.95	–	–	4.81	34.12
H_2	–	–	1.89	19.1	–	–	4.52	20.88

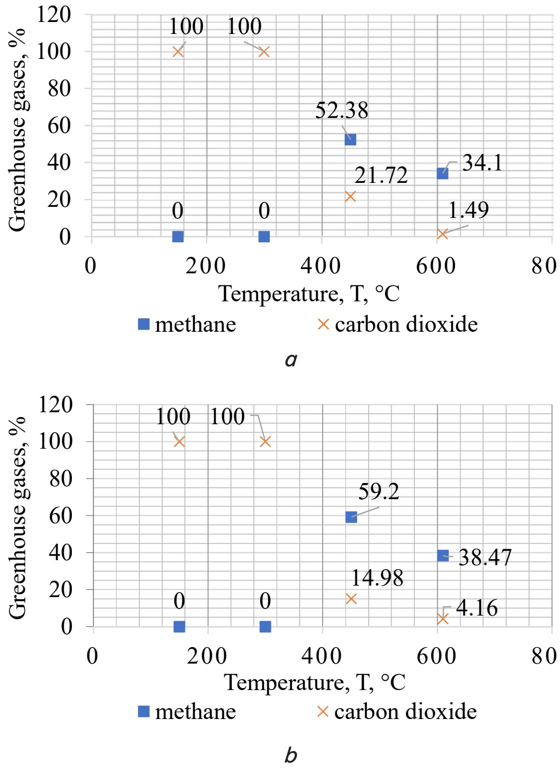
The processes of greenhouse gaseous fragments output for coke fusinite coal (Fig. 7, *a*) and coke weakly sintering coal (Fig. 7, *b*) over the temperature rising period from 150 °C to 610 °C are presented in the point-by-point diagrams.

Generally speaking, the trends in fragments CH_4 and CO_2 output are similar for both samples. CO_2 output already began at the initial stage of the thermal heating process and accounted for 100 % up to 300 °C for both. Then it fell dramatically from about 80 % at 450 °C to 92 % at 610 °C for coke fusinite coal (Fig. 7, *a*) and from about 80 % at 450 °C to 92 % at 610 °C for coke weakly sintering coal (Fig. 7, *b*).

Similarly, gas methane CH_4 output at the initial stage of the thermal heating process was 0 % up to 300 °C for both samples. In the temperature range from 300 °C to 450 °C, it rocketed from 0 % to 52.38 % for coke fusinite coal (Fig. 7, *a*) and 59.2 % for coke weakly sintering coal (Fig. 7, *b*) and by the temperature of 610 °C it dropped to 34.1 % and 38.47 %, respectively, for the first and second samples.

It is clear that the majority of CO_2 output occurs up to 300 °C, most of the methane output is in the temperature range from 300 °C to 450 °C for both coal samples.

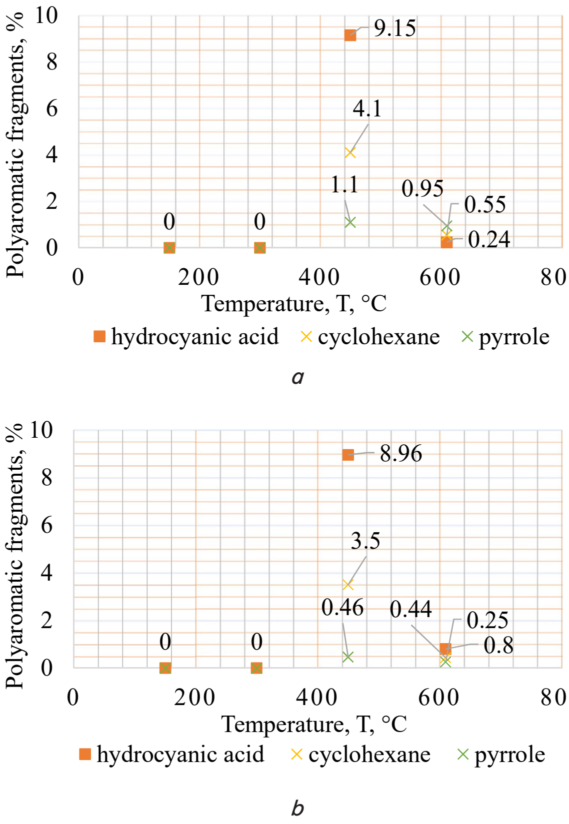
The processes of polyaromatic fragments output over the temperature rising period from 150 °C to 610 °C for coke fusinite coal (Fig. 8, *a*) and weakly sintering coal (Fig. 8, *b*) are presented in the point-by-point diagrams. For both types of coal, the output of polyaromatic fragments averages about 14 % at a temperature of 450 °C and about 2 % at 610 °C. Polyaromatic fragments include hydrocyanic acid (HCN), cyclohexane (C_6H_{12}) and pyrrole (C_4H_5N).



a

b

Fig. 7. Greenhouse gaseous fragments CH_4 and CO_2 output during decomposition in the thermal heating process for two coal samples: *a* — coke fusinite coal; *b* — coke weakly sintering coal



a

b

Fig. 8. Polyaromatic fragments output during decomposition in the thermal heating process for two coal samples: *a* — coke fusinite coal; *b* — coke weakly sintering coal

Overall, the output trends for all polyaromatic fragments are similar. The most noticeable output was obtained for HCN (hydrocyanic acid), which rose dramatically from 0 % to 9.15 % for coke fusinite coal (Fig. 8, *a*) and coke weakly sintering coal to 8.96 % (Fig. 8, *b*) in the temperature range from 300 °C to 450 °C. This provides a nearly nine-fold increase in HCN output over the period of rising temperature range from 150 °C to 450 °C for both samples. It can be seen that by the end of the thermal heating period, when the temperature rose to 610 °C, the HCN output dropped drastically by 0.24 % for coke fusinite coal (Fig. 8, *a*) and 0.8 % for coke weakly sintering coal (Fig. 8, *b*).

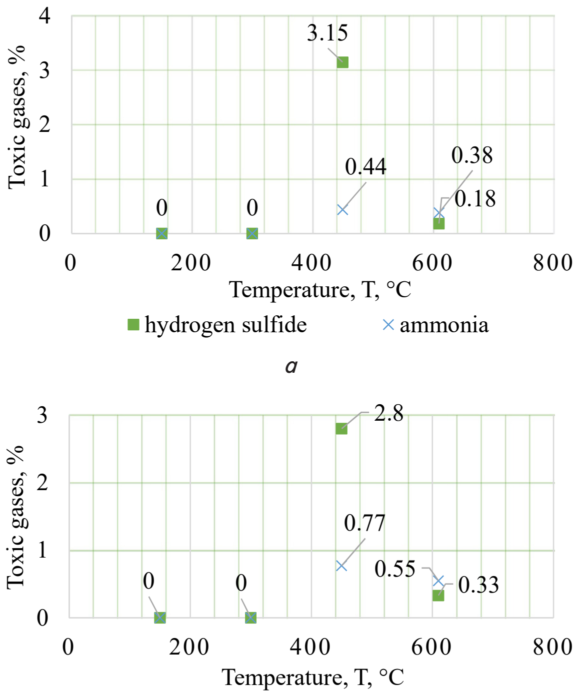
It is noted that the output of C_2H_{12} (cyclohexane) is half as much and C_4H_5N (pyrrole) is about ten times less than the output of HCN for both types of coal. The process of C_2H_{12} and C_4H_5N output occurred in the same way as the output process of HCN but at a slower pace. There was no fragment release in the temperature range from 0 °C to 300 °C for both samples. In the period of rising temperature range from 300 °C to 450 °C, for C_2H_{12} it was about 4.1 % (Fig. 8, *a*) and 3.5 % (Fig. 8, *b*), respectively, for the first and second samples. By the end of thermal heating, the fragments output fell to 0.55 % for coke fusinite coal (Fig. 8, *a*) and 0.44 % for coke weakly sintering coal (Fig. 8, *b*).

The C_4H_5N (pyrrole) output was at an even slower pace but in the same temperature range periods. During the temperature rising from 0 °C to 300 °C, there was no fragment output for both types of coal. In the period from 300 °C to 450 °C, it gradually increased (to 1.1 % and 0.46 % for the first and second samples, respectively). At the end of the process, the fragment C_4H_5N output slightly decreased to 0.95 % for coke fusinite coal (Fig. 8, *a*) and 0.25 % for coke weakly sintering coal (Fig. 8, *b*).

It is clear that the output of the polyaromatic fragments HCN, C_4H_5N and C_2H_1 was in the temperature range from 300 °C to 610 °C and the majority of it was in the temperature range from 300 °C to 450 °C. It can be observed that the proposed thermal heating method provides the possibility of extracting polyaromatic fragments at lower temperatures, whereas during the combustion and other heat treatment these fragments are extracted at a temperature of at least 600 °C.

NH_3 (ammonia) and H_2S (hydrogen sulfide) constituted the minority part of toxic gaseous fragments during thermal heating of low-rank coke coals. On average, they consist of about 3 % H_2S and 0.6 % NH_3. The processes of toxic gaseous fragments output for coke fusinite coal (Fig. 9, *a*) and coke weakly sintering coal (Fig. 9, *b*) over the temperature rising period from 150 °C to 610 °C are shown in the point-by-point diagrams.

Overall, the majority of toxic gases released in the temperature range from 300 °C to 450 °C and accounted for hydrogen sulfide 3.15 % for coke fusinite coal (Fig. 9, *a*) and 2.8 % for coke weakly sintering coal (Fig. 9, *b*). There were peaks of output for all toxic gaseous fragments for both coal samples. After the temperature of 450 °C, the percentage of hydrogen sulfide fell dramatically by the end of the thermal heating process also for both samples. The same can be seen for the fragment NH_3 output, but in a different amount, which was 0.44 % for coke fusinite coal (Fig. 9, *a*) and 0.77 % for coke weakly sintering coal (Fig. 9, *b*) in the temperature range from 300 °C to 450 °C. After the temperature of 450 °C, it gradually fell to 0.18 % and 0.33 % for the first and second coal samples.



a

b

Fig. 9. Toxic gaseous fragments output during decomposition in the thermal heating process for two coal samples: *a* — coke fusinite coal; *b* — coke weakly sintering coal

To summarize, the growth rate of H_2S output was about three times that of NH_3 output. There is no doubt that less ammonia release, as an extremely hazardous waste, will ensure a more environmentally friendly process.

In general, during the thermal heating process, the output of synthesis gases CO (carbon oxide) and H_2 (hydrogen) was about 62 % for coke fusinite coal and 55 % for coke weakly sintering. The processes of synthesis gases output for coke fusinite coal (Fig. 10, *a*) and coke weakly sintering coal (Fig. 10, *b*) over the period of rising temperature from 150 °C to 610 °C are presented in the point-by-point diagrams.

In total, both of synthesis gaseous fragments had an uptrend of output during the process. In the temperature range from 150 °C to 450 °C, it gradually increased to 6.01 % CO output and 4.81 % H_2 output for coke fusinite coal (Fig. 10, *a*) and to 1.89 % CO output and 4.52 % H_2 output for coke weakly sintering coal (Fig. 10, *b*). After the temperature of 450 °C, it was rocketed to 42.95 % CO output and 19.1 % H_2 output for the first sample (Fig. 10, *a*) and 34.12 % CO and 20.88 % H_2 output for the second one (Fig. 10, *b*). It can be noted; that the main part of the synthesis gaseous fragments output occurs in the temperature range from 450 °C to 610 °C, as opposed to the fragments considered above.

The most efficient volatile fuel gases produced by the process of thermal heating of low-rank coke coals are NH_3, CH_4, H_2 and CO. Their share in the thermal heating process is more than 65 % at a temperature of 450 °C, and by the temperature of about 600 °C it reaches an average of 97 %. There is no volatile fuel gases output up to 400 °C, which are recommendations for the selection of temperature ranges and temperature treatment of low-rank coke coals without air access in the temperature range from 400 °C to 650 °C, taking into account the purpose of the coal processing plant.

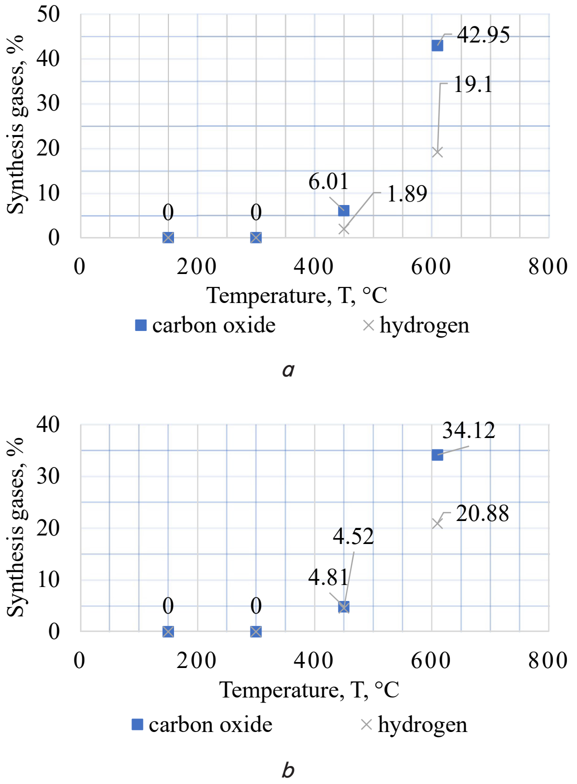


Fig. 10. Synthesis gases output during decomposition in the thermal heating process for two coal samples: *a* – coke fusinite coal; *b* – coke weakly sintering coal

6. Discussion of the quantitative and qualitative parameters of coal behavior depending on the type

Quantitative and quantitative behavior indicators of low-rank brown and coke coals during thermal heating were obtained in the study. These results explain the interaction activity of low-rank coals to the medium temperature effect and show the intensity of thermal decomposition processes with the release of combustible components depending on the structure, coal specifications and genetic maturity. Quantitative behavior indicators defined as thermal decomposition product mass (Fig. 2) showed a significant share of the output in the process of coal decomposition in the proposed method by desorption of hygroscopic moisture and destruction of unstable carbon bonds. This is explained by the weak and atonic structure of coals with a low degree of coalification, which include low-rank coals. The lower peak temperature of the first derivative (inflection point) (Fig. 3), which characterizes brown coals as less metamorphic, also supports this statement. This justifies the choice of complete desorption of hygroscopic moisture stage in the temperature range from 0 °C to 200 °C. There is an alternative to moving the extraction of combustible components of thermal decomposition to a lower temperature range from 300 °C to 610 °C, where the maximum concentration of volatile fuel gases, including synthetic gases, is observed (Fig. 4) at moderate speeds in the presence of nitrogen. The overall picture of mass loss (Table 3) shows that the yield of decay products in low-rank coke coals is determined by the quantitative content of macerals groups, which are also directly related to the genetic maturity of coals for low-rank coals.

Experimental gas analysis (Table 5) showed that the mass fraction of gas components for the tested samples of low-rank coke fusinite and coke weakly sintering coal with particle sizes up to 0.2 mm 450 °C is 11.2 % and 7.86 %, respectively, compared to similar studies of coal with particle sizes of 0.0035 mm at 800 °C with 14.57 % [9]. The nitrogen gas environment had a positive influence on the result, contributing to the development of coal decomposition processes with a low degree of metamorphism. This will certainly affect the cost-effectiveness of the thermal heating process, given the lack of pre-preparation and the choice of off-process drying. Given the output of the gas components from the pilot study and presented in Fig. 7–10, the temperature ranges can be taken as a basis for obtaining the specified fragments with the highest concentration in the low temperature ranges. This will determine the possibility of simplifying the design of coal thermal heating devices, which will also affect the economy of production. In addition, the separation of the exhaust stages of the gas components with the determination of composite composition and improving the environmental friendliness of the coal thermal heating process is ensured. Thus, for low-rank coke coals, the stage of volatile fuel gases release of up to 97 % was obtained, the temperature range of which will allow for the most rational use of the thermal heating process for this type of coal, taking into account its further automation by the temperature of the highest concentration output.

Previous studies have shown how fuel components are produced in high temperature and high-rate flows or for direct use in specific installations [6, 13, 14]. The peculiarity of the proposed method is the possibility of producing combustible components in low-temperature ranges in the presence of an inert medium by producing a ratio between the characteristics of coal, volume of thermal decomposition products and quality of components composition according to temperature. This makes it possible to obtain volatile fuel gases economically from low-rank coals and expands the scope of their application.

The main limitation of this study is the applicability limit due to the instability of coal specifications even for one deposit, which vary for the same types of coal in a sufficient range. As a consequence, the study requires statistical processing of sufficient experimental data to identify the best low-temperature combustion temperature ranges.

The main disadvantage of this research is the difficulty of dealing with intervening factors when applying the technique directly to the real process. Research carried out on pilot plants will undoubtedly make it possible to adjust this drawback to real technology.

The development of this study might be an energy-efficient technology for producing volatile fuel gases from low-rank coals. The results can be used for adjusting the processes of gas generation from coal (pyrolysis and gasification processes), small heating devices (pyrolysis and condensation boilers) in order to improve their efficiency and reduce emissions. In addition, it can be an approach for developing methods for the production of targeted gases, replacement of high-calorific fuels with gases obtained during the boiler start-up at large power generating facilities and minimizing the formation of complex mixtures of organic compounds and their deposition on the surfaces of thermal heating devices. However, for the results to work in real conditions, experimental consideration of the production factors of application is necessary.

7. Conclusions

1. Thermogravimetric analysis of low-rank coals was carried out to determine the quantitative indicators of coal behavior during the thermal heating process. The results of the analysis gave an idea of the main characteristic temperature ranges of coal behavior due to coal specifications, structure and genetic maturity. Temperature ranges can be characterized as the temperature range from 200 °C to 300 °C – minor mass losses; the range from 300 °C to 650 °C – maximum mass losses and the range from 650 °C to 800 °C – a sharp drop in mass loss. At the same time, the mass loss due to the process of desorption of hygroscopic moisture for brown and long-flame coal samples is more intense in the temperature range from 200 °C to 300 °C than for coking coal samples. It is noted that coals with a lower degree of metamorphism are more susceptible to thermal oxidation and dehydration than low-morphized coking coals or fusinite coals. As genetic maturity increases, the temperature of the elution band grows towards the highest temperatures, so that the stage of division into coal organic matter can be represented by the temperature range from 300 °C to 650 °C. The next stage is the mass drop stage due to the destruction of weak carbon bonds and simultaneous structuring of the carbon residue in the temperature range from 650 °C to 800 °C. The mass loss peaks for all coal samples are the peaks of moisture transfer from the phase separation surface when they are degraded to emit volatile fuel gases. It is recommended to take coking coals with a low degree of mesomorphism for the thermal heating process, taking into account their behavior pattern when decomposition products are fragmented.

2. To determine the quality of coal in the thermal heating process, it is efficient to use the temperature range from 150 °C to 650 °C with pre-heating at 103 °C to achieve the minimum output of hygroscopic moisture. The main component composition of thermal decomposition products includes: polyaromatic fragments (HCN, C_6H_{12}, C_4H_5N), greenhouse gaseous fragments (CH_4 and CO_2), toxic gaseous fragments (CH_4 and CO_2) and synthesis gaseous fragments (CO and H_2). It is taken into account that the process of releasing combustible gases for both samples starts at a temperature of 300 °C, where the CO_2 output is almost completely over. Therefore, it is possible to separate the thermal heating phases with the removal of carbon dioxide at the preliminary stage and obtain a process with minimal toxicity. The results on coal tar components output by the type of coal make it possible to minimize the formation of complex mixtures of organic compounds and their deposition on the surfaces of thermal heating devices. The obtained temperature range of the main volatile fuel gases from 300 °C up to 450 °C can serve as a methodological recommendation in technologies for producing targeted gases. For low molecular weight gases, the temperature range was obtained, which is offset towards the largest temperature up to 610 °C with a possible increase in output with rising temperature, which will allow adjusting the technologies of gasification and pyrolysis of coals. The temperature ranges of the maximum concentration volatile fuel gases release period are unified for low-grade coke coals, exactly for coke fusinite and coke weakly sintering. It is recommended to use the temperature range from 400 °C to 650 °C with an output of volatile fuel gases NH_3, CH_4, H_2 and CO up to 97 % in the presence of an inert nitrogen medium. These thermal treatment conditions will reduce energy consumption.

Conflict of interest

The authors declare that they have no conflict of interest in relation to this research, whether financial, personal, authorship or otherwise, that could affect the research and its results presented in this paper.

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Data availability

Data will be made available on reasonable request.

Use of artificial intelligence

The authors confirm that they did not use artificial intelligence technologies when creating the current work.

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