

The object of research is a low-temperature gasification technology of weakly grade metamorphized coals. One of the outstanding issues of the low-temperature gasification technology of weakly grade metamorphized coals remains the long processing period due to the coal weak energy activation directly dependent on the release of volatile gases, which depend on isotropic state of coal. The problem that was solved is to scale up coal activation energy through the sudden heat during thermal processing. The results obtained show a shift of the volatile gases release beginning to a temperature of 410°C in the same quantity as with the step-by-step heating to a temperature of 500°C. In addition, the sudden heat contributes to a reduction of CO₂ emissions by 12%, indicating an improvement in environmental performance. These results are explained by the fact that a sharp difference in temperatures of 20°C and 400°C creates conditions for the appearance of energy distortion in the isotropic zones of the coal body heating. This energy weakens and destroys the internal bonds between the coal particles and creates conditions for the release of new volatile elements at lower temperatures.

The main features of the results obtained, which made it possible to solve the problem studied are the results on transformation of thermal stresses into energy of distortion at the sudden heat in the relationship between the mechanics and physics of anisotropic coal. The scope and conditions of practical use of the results obtained is will allow for the adjustment of gasification techniques for coals with low degree of metamorphism and the establishment of gasification regimes, taking into account the design and capacity of the gasifiers

Keywords: weakly grade metamorphized coal, sudden heat, distortion energy, thermogravimetric analysis, thermal stress

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EVALUATING OF THE SUDDEN HEAT IMPACT ON VOLATILE GASES RELEASE DURING THE GASIFICATION PROCESS OF WEAKLY GRADE METAMORPHIZED COAL

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1. Introduction

Thermal processing of coal for the generation of the volatile gases is an alternative and clean technology to direct combustion [1, 2]. The target product of thermal processing is the volatile gases produced and by-products in the form of semi-coke and liquid polycyclic compounds, which are influenced by the genetic and physical characteristics of the coal as being unstable in their properties.

Nowadays, the thermal processing process requires additional refinements, use of associated reagents and may have significant disadvantages in the development of a quality of the process, primarily determined by high heating costs in the temperature ranges from 700°C to 1100°C due to the unstable and complicated weakly grade metamorphized coals structures [3, 4]. This trend in the development of coal

gasification technologies has no significant prospects, as it is associated with high costs for its implementation. This is especially related with weakly grade metamorphized coals, which are anisotropic materials which properties change unpredictably during thermal heating. An approach to identify the energy that can be activated from within an anisotropic substance undergoing sudden heat is the most right appropriate for weakly grade metamorphized coals gasification process. Because this energy is expended on the activation of internal elemental bonds with transition into weakening and distortion of bonds will be reduced gasification temperature levels for coals with weakly grade degree of metamorphism. All above mentioned show the usefulness and relevance of the studies conducted in the context of the identification of the sudden heat effects in gasification process of weakly metamorphized coals.

2. Literature review and problem statement

The paper [5] presents the results of low-temperature gasification technology of low-rank coals research. It is shown that it is possible to reduce the temperature range from 500°C to 700°C with the output of the CH₄, CO and H₂ volatile gases up to 80% due to the energy coal particles activation in the presence of a steam phase. But there were unresolved issues related to limit the moisture due to the fusing particles of ash and coal and concomitant reduction of the kinetics energy activation development in the system «coal-air». The reason for this may be the weakening of thermodynamic processes due to the mechanics of the particles when they collide, as a result of which the activation of energy in the coal mass, not able to release volatile gases is reduced. A way to overcome these difficulties can be the presence of products – neighbors with high activation energy and weak connections or moisture content, which also affects the states of bonds in the coal. The trend of activation of energy in coal particles is represented by the presence of moisture in paper [6]. It is shown that the change of coal particles permeability in the presence of electrostatic manifestations also directly affects the activation of energy bonds in ash and coal. In addition, the ratio of the emitted volatile carbon increases. However, the above papers did not take into account the distribution of activation energy when changing the kinetic release process of volatile substances. Two-parameter energy distribution was obtained in the paper [7] for wood fuel over an 8-hour period, proving that new volatile substances can be generated in a temperature range from 400°C to 1000°C at a rate of the temperature rise of 20 K/min. Nevertheless, results are only available for light organic fuel, not for low – rank coals. The positive effect on the activation of low-quality coal energy in relation to H₂ yield, as well as reduce CO₂ emissions was presented in paper [8], taking into account the conduct of copulation at a sharp rise in temperature up to 700°C in the presence of moisture. However, the relevance of the technology is reduced due to the process instability in the presence of young organic with weak connections and the strict need for careful preparation. Furthermore, it causes instability of the gasification process, due to the strict necessity for requirements on fractionation size and composition of coal, with a specified permeability that will exclude the composting and particle compaction in the presence of moisture [9, 10]. The composition fractionation measures can be carried out by including a technological separation reflux when using high-voltage electrodes. But the use of high-voltage electrodes not only makes the technology more expensive, but also reduces its safety. This question the authors [11] tried to solve by using active additives at a rapid heating of 100–104°C/min for energetic activation in coking coal particles. However, this thermal heating method of the low-temperature gasification has contributed to the depolymerization and microcellular degradation of coal due to the resulting fluidity in the thermoplastic stage [12]. Simultaneously this fact may indicate that a sudden change in temperature even at low temperatures can affect the behavior of coal, especially when the structure is weak, which characterizes genetically immature coal. All this suggests that it is advisable to conduct a study on the effect of sudden thermodynamic effects on resilient plastic macrostructure, taking into account the degradation processes required for the release of volatile fuels from weakly metamorphized coals. Furthermore, it is clear that

improving technology to reduce carbon-based emissions, including CO₂, and increase volatile gases output, including CO and H₂, requires forcing temperature action in the range from 300°C to 450°C, where high-calorific gases can be released [13, 14]. The temperature range from 300°C to 650°C for low-grade metamorphosed coals is the starting zone of significant mass loss, whereas the temperature threshold of 400°C is the point of departure for deformation processes due to temperature. At the same time the highest output growth of gaseous products is observed in the temperature range 450–550°C, taking into account the increase of hydrogen output at the starting point 400°C. Taking into account all above mentioned, it is proposed to evaluate the effects of sudden heat action on the degree of coal energy activation due to emerging thermodynamic and elastic stresses taking into account the thermophysical and mechanical properties of coals with a weak degree metamorphism.

3. The aim and objectives of the study

The aim of the study is evaluating of the sudden heat effect at a temperature threshold 400°C, accepted as a point of inflection on the volatile gases release during the gasification process of weakly grade metamorphized coals through the activation coal energy due to the thermal stress. This will reduce the energy costs of the gasification process and establish economically viable gasification regimes with reduced CO₂ output.

To achieve this aim, the following objectives are being solved:

- to investigate the weakly grade coal energy activation;
- to analyze of the generation obtaining volatile fuel gases in the gasifier and compare with standard method.

4. Materials and methods

4.1. Object and hypothesis of the study

The object of the study is the process of low-temperature gasification for weakly grade metamorphized coals with implementation of the sudden heating effect technology. The main hypothesis of the study is that sudden heat increases the efficiency of the process to generate volatile gases by the activation energy strengthen required for the formation of new volatile elements. The assumption is made in the study that the implementation of the sudden heat creates additional energy, which distorts and breaks internal connections between coal elements and increases process efficiency. Simplification adopted in the study – application of sudden heat at a threshold temperature level of volatile gas release for weakly grade metamorphized coals. The influence of temperatures above or below threshold temperature level has not been taken into account. Standardized research and data processing methods were used in the work.

4.2. Coal samples

Coke weakly sintering coal samples were used for thermal processing under sudden heat conditions. All coal samples were previously analyzed following rules of the National Standards for testing solid mineral fuels. Elementary content, technical analysis and physical-mechanical properties are represented in Tables 1, 2.

Coal samples elementary and technical content

N	Elementary content, (% _{daf})				Technical analysis, (% _{daf})				Q_r , (MJ/kg)
	C	H	S_t	(O + N + S)	$W_a^{initial}$	$W_a^{dehumidity}$	A_d	V_{daf}	
S1	81.0	5.6	0.7	13.4	2.2	1.2	5.5	43.3	33.04
S2	87.4	5.0	0.3	11.6	2.4	1.5	17.1	26.4	34.64
S3	89.0	5.0	0.9	6.0	1.9	0.6	13.5	18.6	35.80

Moisture content in the studies is not assumed to be absolute value and determined by the coal preparation conditions standardized and interlinked with required methods of coal selection and preparation, according to which, samples of coal were dried in a nitrogen tank at 105–110°C.

Moisture mass fraction of the analysis sample

$$W_a = \frac{m_2 - m_3}{m_2 - m_1} \cdot 100\%, \quad (1)$$

where m_1 , m_2 , m_3 – mass of the tank, mass of the tank with coal before and after dehumidify process, respectively, in gram. The result of determining the mass percentage of analytical moisture is taken as the arithmetic mean value of the results of two parallel definitions. The result is calculated to an accuracy of 0.01% and rounded to 0.1%.

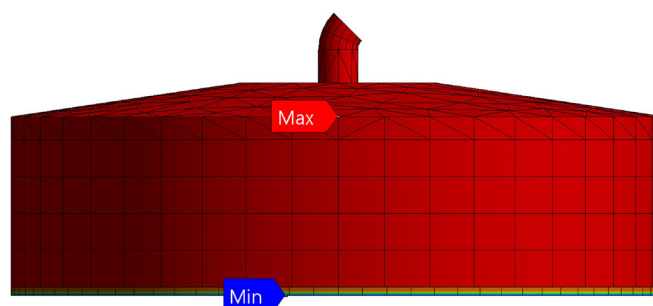
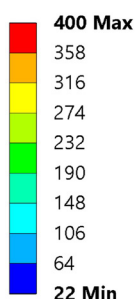


Fig. 1. Physical model coal thermal processing chamber using sudden heat at temperature 400°C

Table 2

Coal samples physical-mechanical properties

N	Density, (kg/m ³)	Thermal capacity, (J/kg°C)	Thermal conductivity, (W/m C)	Transmissivity, (Ms)	Pore volume, (sm ³ /g)
S1	1400	1400	0.33	75.1	0.036
S2	1400	1400	0.33	74.2	0.038
S3	1250	1400	0.22	78.1	0.030

The study used complex methods, which included analysis of the coal energy activation due to the occurrence of stresses at sudden thermal heat in the Ansys CFX software environment and laboratory analysis of volatile gases output for samples at coal sudden placing to the stationary temperature field 400°C. The research was conducted in the «Specialized Research Laboratory on Energy Problems» of the S. Seifullin's Kazakh Agrotechnical University (Republic of Kazakhstan).

4. 3. Experimental methods of the sudden heat effect during the coal thermal processing

The purpose of coal thermal processing for the volatile gases release is to ensure the conditions produced by the thermal destruction of coal at specified temperature zones during the formation of semi-coke, coal separation and structure. An important part of this process is to create conditions for the activation of bond energy, ensuring the difference between the energies of normal, deformed and broken bonds within coal, taking into account the work of internal forces aimed at distorting the bonds. This can be achieved by a sharp increase in internal energy at the moment when there is no

change in volume. This can be achieved by the stress generated by the action of a pressure and temperature gradient as a result of thermal strain in the thermodynamic system under variation of free energy [15]. It seems that such conditions can be provided in the thermal heating chamber at sudden temperature rise. Fig. 1 represented a physical model of the thermal processing chamber using sudden heat at temperature 400°C with a sudden heat effect by the thermodynamic process of radiation and convection. The chamber contains coal of mass from 24.18 to 78.4 kg, depending on density, with an even layer height, not more than 0.2 m. Surface area of the heating chamber surface area 0.85 m², with a heating chamber volume of 0.056 m³.

Simulation of the thermal processing process with sudden heat was performed using the Steady State Thermal and Static Structural Mechanical APDL modules of the Ansys CFX software environment. Simulation of the thermal processing process is a part of the experimental design in the Design of products based on Engineering thermal-structural calculations Methodology. Simulation performed by thermal analysis based on the finite element method using APDL ANSYS (ANSYS Parametric Design Language). Determination of the statistical dependence of the average values was evaluated using the Student's t-test taking into account the normal distribution of temperature, total heat flux, thermal strain and equivalent thermal stress quantitative data.

The purpose of the simulation is to determine the degree of coal energy activation in the coal decomposition system under the influence of the active medium of thermal radiation and convection caused by the transformation of thermal stresses into energy of distortion at sudden heat. All experiments were carried out under the process conditions presented in Table 3, with constant heat flow direction in a single volume, taking into account the mechanical, elemental and thermal characteristics of the coal samples presented in Table 4 [16].

Based on the heat radiation and convection processes that occur during thermal processing under the conditions of sudden heat the change in the value of the heat flux can be represented as follows, Q

$$Q = K_1 \varepsilon_1 \delta T_1^4 - K_2 \varepsilon_2 \delta T_2^4, \quad (2)$$

where Q – an intensity of the heat exchange, (T_1 , T_2) – the absolute thermodynamic temperatures of the heat source and coal respectively, (K_1 , K_2) – the coefficients of the geometry proportions. Heat exchange coefficient determines the temperature increase in dependence of time in form

$$t_c^0 = t_b^0 + 10^{-2} (0.002Q - 4) \tau - 10^{-4} (0.0127Q - 19) \tau^2, \quad (3)$$

where (t_c^0, t_b^0) – top and initial top coal layer temperature;
 τ – a time of sudden heat process.

Process conditions

Sample no	Process variables					
	Initial temperature, (°C)	Radiation ambient temperature, (°C)	Convection ambient temperature, (°C)	Film coefficient (W/m ² ·°C)	Total heat flux (W/m ²)	Mass (kg)
S1	20	400	300	1.2	251.0	79.168
S2	20	400	300	1.2	153.9	79.168
S3	20	400	300	1.2	253.1	28.274

Coal elastic-plastic properties

Sample no	Temperature (°C)	Young's modulus (GPa)	Poisson's ratio	Bulk modulus (GPa)	Shear modulus (Pa)
S1	20	3.30	0.44	2.16	1.14
	100	3.20	0.46	3.34	1.09
	200	2.10	0.46	2.90	0.71
	500	2.10	0.41	1.60	0.72
S2	20	2.00	0.40	2.33	0.71
	100	1.90	0.38	2.53	0.68
	200	1.88	0.37	2.60	0.68
	500	1.59	0.29	1.36	0.61
S3	20	3.50	0.30	3.91	1.34
	100	3.10	0.28	3.50	1.24
	200	3.05	0.22	4.06	1.25
	500	2.80	0.21	3.60	1.15

When considering collisions in element-to-element relationships, model gas mixture formation with account of energy balance due to sudden heat impact in a unit of unchanging volume

$$Kn^{cb} T^{cb} = 3Kn^{cb} \cdot t_c^0 + Kn^{cb} \frac{7-5\gamma^c}{2(\gamma^c-1)} (t_b^0) + Kn^{cb} \frac{7-5\gamma^b}{2(\gamma^b-1)} (t_c^0), \quad (4)$$

where n – the element concentrations; cb – the interelement collisions (c – properties of element under consideration; b – properties of background element); γ – an adiabatic constant.

The development of the stress kinetics process accompanied by the distortion of bonds and activation of energy coal as a function of temperature can be presented by the mathematical model of the equation

$$\frac{A}{KT} = \frac{E}{4 \ln a}, \quad (5)$$

where K – Stefan-Boltzmann constant; E – an apparent activation energy.

In this case, the kinetics of coal body activation energy can be determined by the dependence of the stress energy generated by the heat flux at the process of sudden heat. Thermal and mechanical stresses at sudden heat conditions cause equivalent stress in the coal body spring in the direction of the heat flow under the effect of temperature and

pressure gradients in the normal direction to the temperature increasing isotherm according to [17–20]:

$$\varepsilon_x = \frac{1}{E} [\sigma_x - \mu(\sigma_y + \sigma_z)] + \alpha \Delta T, \quad (6)$$

$$\varepsilon_y = \frac{1}{E} [\sigma_y - \mu(\sigma_x + \sigma_z)] + \alpha \Delta T, \quad (7)$$

$$\varepsilon_z = \frac{1}{E} [\sigma_z - \mu(\sigma_x + \sigma_y)] + \alpha \Delta T, \quad (8)$$

Table 3

Table 4

where $(\sigma_x, \sigma_y, \sigma_z)$ – the distortional stresses in direction x, y, z , μ – Poisson's ratio; E – the elastic modulus; α – a thermal expansion factor; ΔT – the difference between the temperatures at the moment of stress and at the moment when the deformation is zero.

In this case mathematical model of thermodynamic process in adiabatic chamber with sudden heat effect can be presented for zones without change of volume

$$\frac{dT}{t} = \frac{1}{\tau} \times \left[T_1 - T_2 + \frac{(U_{f1} \cdot k_c \cdot C_c + U_{f2} \cdot k_b \cdot C_b) \cdot R \cdot \frac{T_2}{p}}{C_p} \right], \quad (9)$$

where $k_{c;b}$ – the constants at the interelement collisions; U_{f1} and U_{f2} – the heat effect of the collisions with account of the pressure due to distortional stresses in a zones without deformation.

It is known that the energy of a distortion, defined as a potential energy, is equal like a negative work of internal forces [21, 22]

$$U_f = \frac{1+\mu}{6E} \left[(\sigma_x - \sigma_y)^2 + (\sigma_y - \sigma_z)^2 + (\sigma_x - \sigma_z)^2 \right], \quad (10)$$

where U_f – the distortion energy, $(\sigma_x, \sigma_y, \sigma_z)$ – the stresses, which appear in the body of coal in x, y, z directions respectively.

The main conditions for the sudden heat process to ensure the heat radiation flux and the resulting stresses are in one direction, which is necessary to provide the conditions for the growth of element-bond distortions in the coal.

4. 4. Experimental method of the generation obtaining volatile fuel gases in the gasifier

According to the ASTM D7582-15 «Standard test method for the approximate analysis of macro-thermographic analysis of coal and coke» samples of low-temperature, coke weakly sintering samples of coal (S1, S2, S3) that have undergone thermal processing under the use of sudden heat in laboratory the experimental pilot unit shown in Fig. 2 and heat-treated at a temperature of 10°C/min.

The analysis was carried out in an inert nitrogen medium with a Netzch STA 409 quadruple gas spectrometer and continuous data recording according to the National Standard «Gas analysis and gas analyzers». During the analysis, volatile gases CH₄, CO, H₂ and carbon dioxide gas were recorded [23].

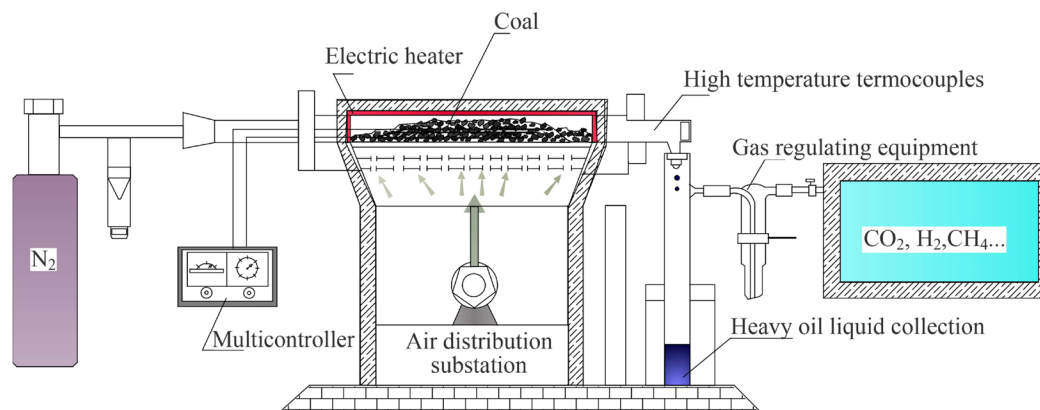


Fig. 2. Pilot unit

5. Research results on the influence of the sudden heat in gasification of weakly grade metamorphized coal on energy activation of coal and output of H_2 , CH_4 , CO and CO_2

5.1. Analysis results of the weakly grade coal energy activation

From the foundation of thermodynamics, a sharp increase in temperature in the adiabatic system is an intensive parameter that changes the pressure, phase and chemical potentials of components. The sudden thermal heat contributes to the effect of energy accumulation in the formation in the isothermal zones of coal without change of volume. Distortion is manifested in the phase changes of the microstructure, ensuring the transformation of stresses into energy when temperature and pressure gradients occur [24]. In these zones, the distortion energy is not spent to overcome external forces related to the change of shape. In these zones, the growth of activation energy was investigated at consecutive coinciding points for three different coal samples while determining the minimum and maximum growth of energy accumulation taking into account the non-linear behavior of the finite elements with loss of stability as a result of thermal stress due to the sudden heat. The solution of the problem was carried out by selecting the optimal solution for the sudden heating at the point of departure for deformation processes through the analysis of the end elements.

Distortion energy is converted into negative work of internal forces, aimed at distorting and weakening elemental bonds of structural units of coal. Alkan chains and aromatic rings are disturbed, the distortion of which violates stability and facilitates the release of the born units [25]. The distortion energy arising from thermal stresses on isotherms without change in volume was estimated by the Equivalent stress (von Mises), expressed as energy accumulation per unit volume of coal.

Thus, the growth of activation energy is a function of the stresses arising in all directions of the thermal stress applied in the coal body at a given point, depends on elastic-plastic, physical and technical properties, taking into account Fig. 3 shows the minimum and maximum increase of distortion energy under sudden heat by thermal radiation at a tem-

perature of 300°C , created by the heat active medium in the coinciding sequent points without changing in volume on the isotherm 300°C for S1 and S2.

Fig. 4 illustrates that the trend of energy accumulation is the same in the isosurface areas at about 300°C . Both coal samples in the range of 63 kPa to 68 kPa show approximately the same increase in the activation energy distortion, corresponding to values from 17 to 21 kJ/kmol-s (Fig. 3, 4). With the increase of the thermal stress value to values from 70 to 79 kPa at an isotherm of 300°C , the behavior of coal S2 shows an unstable sinusoidal kinetics of the energy distortion accumulation up to 30 kJ/kmol-s with the entire isothermal region.

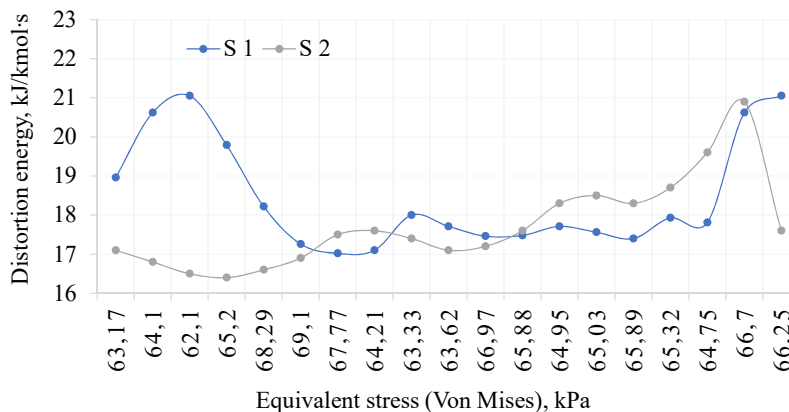


Fig. 3. Line graph of the distortion energy minimum growth from the Equivalent stress (von Mises) value in the coinciding sequent points without changing in volume on the isotherm 300°C

The S1 have a smooth kinetics of the energy change up to 22 kJ/kmol-s (Fig. 4). The coal S3, on a 300°C isotherm do not have isochoric regions and therefore do not have an increase in energy distortion activation on the isotherm 300°C . For these samples, the energy activation starts at a temperature 400°C (Fig. 5).

Fig. 5 shows that S3 have the highest amount of the distortion energy, but its accumulation area is shifted towards higher values of thermal stress. The value of the distortion energy growth reaches values up to 55 kJ/kmol-s at equivalent stress (von-Mises) is equal to 198 kPa. It seems that this is due to the high elasticity, lower thermal conductivity in a given temperature range and greater permeability of the micro-components of coal.

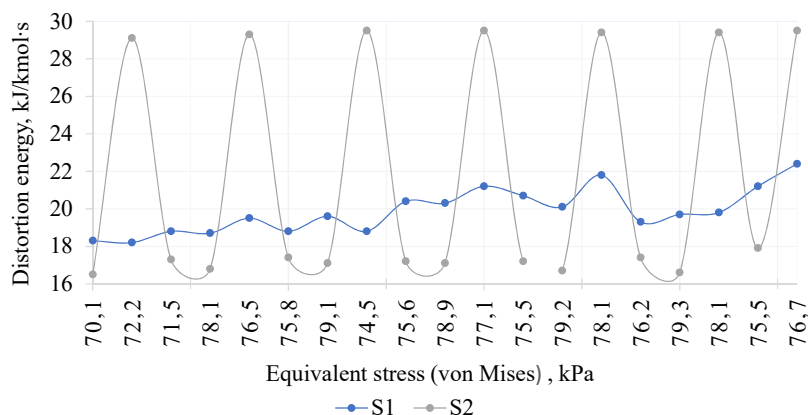


Fig. 4. Line graph of the distortion energy maximum growth from the Equivalent stress (von Mises) value in the coinciding sequent points without changing in volume on the isotherm 300°C

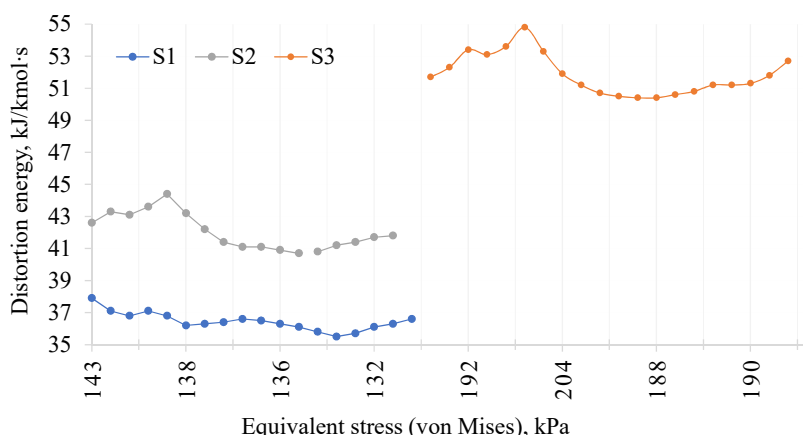


Fig. 5. Line graph of the distortion energy maximum growth from the Equivalent stress (von Mises) value in the coinciding sequent points without changing in volume on the isotherm 300°C for the coal samples

In order to identify the possibility of determining a coal sample with the maximum capacity of energy accumulation, the energy accumulation intensity kinetics of the investigated samples (Fig. 6) is identified.

As shown in Fig. 6, two samples are having the capacity to accumulate distortion energy changing at the temperature 300°C S1 and S2, but the maximum growth has sample S1. It is possible that this is determined by its higher bulk modulus characteristics in a given range of temperature values.

Fig. 7 shows that all the coal samples have an accumulation intensity of the distortion energy in the isochoric areas at the isotherm 400°C. However, S3 more active in energy accumulation growth than S2 and S1 and it shows maximum result approximately for about 55 kJ/kmol·s. For samples S1 and S2 the maximum distortion energy is 39 kJ/kmol·s and 45 kJ/kmol·s respectively.

Fig. 8–10, *a, b* show that the thermal stresses arising in equivalent stress (von-Mises) in the isochoric areas are spent on the accumulation of activation energy of coal. The minimum value of equivalent stress is observed for samples S1 and is in the region for about 0.1 GPa. For sample S1, the area of accumulation of thermal stresses that transfer into energy ac-

tivation has an even distribution nature and is about half of the total volume. For samples S2, the magnitude of the stresses in the region of no change in volume has large differences and has a random distribution from 0.04 to 0.17 GPa. However, the energy accumulation area of for samples S2 takes up more than half of the coal volume. The greatest value of the energy accumulation is the S3 samples. In this case, over the same period of time, the potential for expansion of the energy storage area for S3 samples is also more intense. The maximum equivalent stress for S3 samples in the no volume change zones is almost 0.2 GPa. In addition, the magnitude of the occurrence of stresses is closer to the center with a greater significance than for the above-described samples. The convergence error consists of -0.0000001 , taking into account in experiments and determined due to convergence of absolute deviations.

The value of the specific energy distortion has shown the thermal behavior of coal, which directly affects the change in internal structure and activation of energy.

This energy is necessary for the release of volatile gases in the full amount of coal that has undergone sudden heat (Table 5).

Table 5

Coal samples specific energy distortion on the isotherm 300°C and 400°C

Sample No.	U_{f300}^{\min} (kJ/kg·s)	U_{f300}^{\max} (kJ/kg·s)	U_{f400}^{\min} (kJ/kg·s)	U_{f400}^{\max} (kJ/kg·s)
S1	38.124	136.133	16.510	27.220
S2	42.440	148.440	48.340	32.240
S3	–	–	105.260	571.824

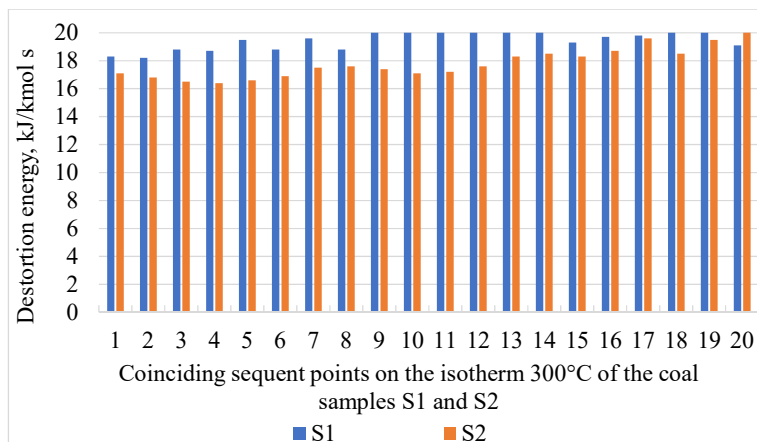


Fig. 6. Bar chart of the minimum distortion energy for the coal samples on the isotherm 300°C without volume changing

Table 5 shows that the minimum value of the specific energy distortion, expended on the change and weakening of the bonds within in the S1 is 16.510 kJ/kg·s at on the isotherm 400°C. The maximum value of S3 is 571.824 kJ/kg·s also at 400°C isotherm. Research has shown that the effect of the energy distortion accumulation converted into activation of coal energy,

depends not only on the physical properties of the coal but also on the mechanical. S3 is having the highest value of energy accumulation distortion, they are more transmissivity with amount 78.1 Ms and more elastic in a given temperature range, Young's Modulus 3.5 GPa. In this case, the region of the energy distortion accumulation is shifted for these samples towards

the isotherms 400°C. Samples with lower transmittivity (range from 74 Ms to 75 Ms) and less elasticity (Young's Modulus range from 1.8 GPa to 3.3 GPa) have an area of energy distortion accumulation on the both isotherms 400°C and 300°C. However, quantitatively the distortion energy for them is significantly less and is not more than 148.44 kJ/kg.s.

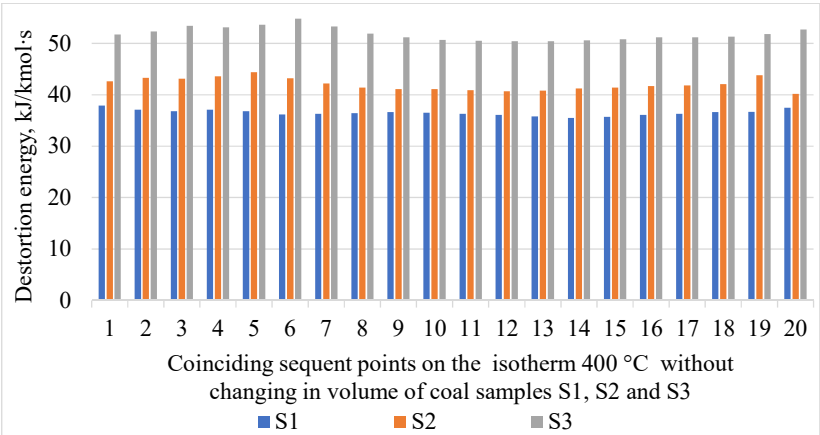


Fig. 7. Bar chart of the maximum distortion energy for the coal samples on the isotherm 400°C without volume changing

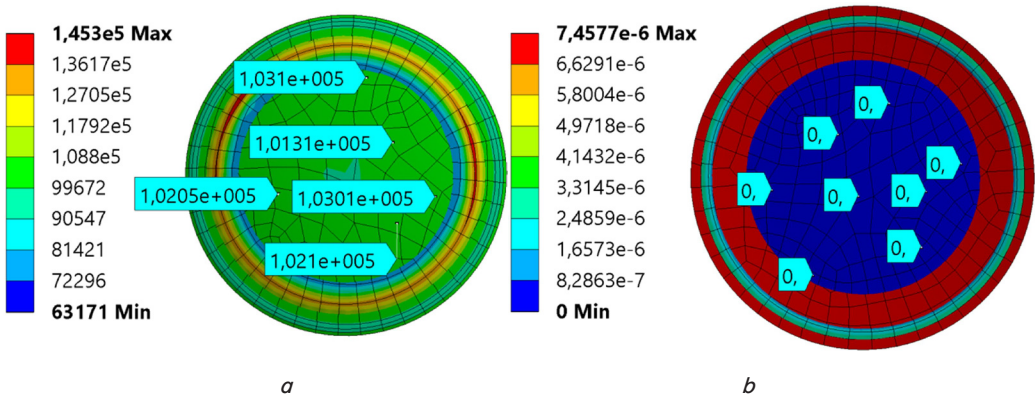


Fig. 8. Occurrence of stresses on the isotherms 300°C and 400°C in the isochoric regions of the S1 coal samples: *a* – equivalent stress; *b* – total deformation

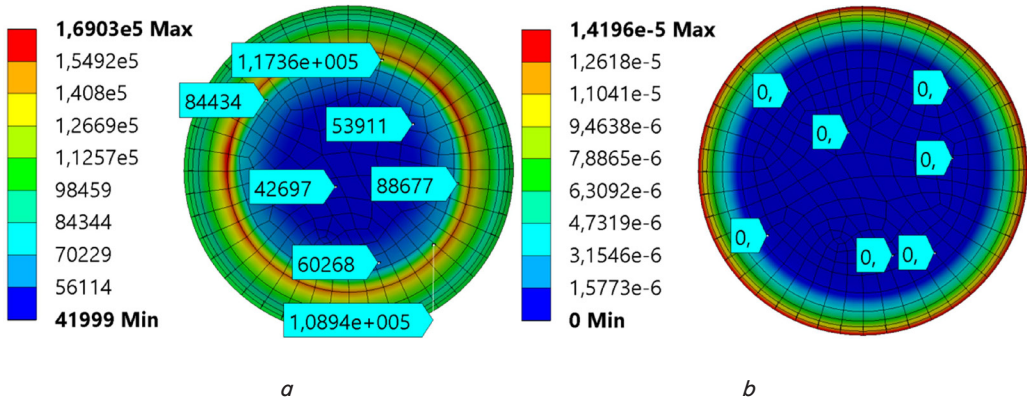


Fig. 9. Occurrence of stresses on the isotherms 300°C and 400°C in the isochoric regions of the S2 coal samples: *a* – amount of the equivalent stress; *b* – total deformation

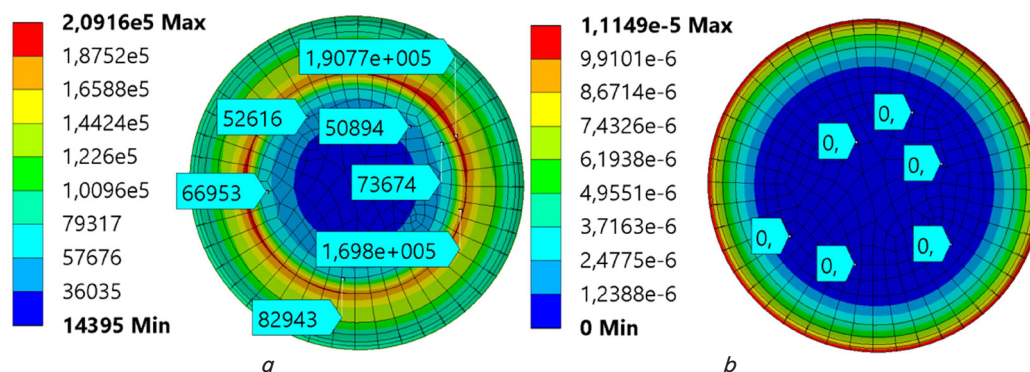


Fig. 10. Occurrence of stresses on the isotherms 300°C and 400°C in the isochoric regions of the S3 coal samples:
a – amount of the equivalent stress; *b* – total deformation

5.2. Research results on the generation CH₄, CO, H₂ and CO₂ in the gasifier after sudden heat and heated by standard method

Determination of the sudden heat effect on the release of volatile gases CH_4 , CO , H_2 and CO_2 was determined by comparing the gas output of test samples after sudden heat with a further rise in temperature $10^\circ\text{C}/\text{min}$ and according to ASTM D7582-15 «Standard test method for approximate analysis of coal and coke macro-thermogravimetric analysis» under standard heating with similar lifting velocity. Gases content represented in the Fig.11–13. Working standard error to gas analyzer error ratio is no more than 0.2, which corresponds to the ASTM.

The graphs (Fig. 11–13) above compare volatile gases H_2 , CO and CH_4 output for three weakly grade metamorphized coal samples. It is clear that the area of volatile gases release has already started at a temperature of $410^\circ C$. The highest yield after sudden heat has CH_4 (Fig. 11) in amount of 33% at $500^\circ C$ for S2 and the lowest consist of approximately 21% at $400^\circ C$ for S3. Compared to the ASTM D7582-15 test samples (TGA), the maximum CH_4 yield of the S1, S2, S3 samples that have been suddenly heated for about 63% is lower. However, positive fact is the shift of CH_4 release into the lower temperature region and the upward trend of CH_4 release. This indicates a positive trend in the gases release in comparing of coal samples tested according to standard methodology. It appears that the higher CH_4 release can be explained by favorable conditions for hydrogen content and lower tensile mechanical properties of sample S2.

Fig. 12, 13 illustrates fragments CO and H₂ output at the decomposition process during the thermal heating for three coal samples after process of sudden heat and testing according ASTM D7582-15 «Standard test method for approximate analysis of coal and coke macro-thermogravimetric analysis». According to the Fig. 12, 13, the CO and H₂ areas has shifted from the start of the process at 10°C and started at 410°C. The highest release of the both CO and H₂ gases is observed for S3 after sudden heat with a maximum output of CO and H₂ in amount of 17.61% and 12.54 respectively at a temperature 500°C.

The minimum CO and H₂ gases release also has a S3 in amount of 9.09% for CO and 4.55% for H₂ at 410°C respectively. In compare of the standard method of heating coal samples in this value area have less CO and H₂ yield, but the positive effect is also seen in the tendency to increase in further heating, which causes further thermal decomposition with release of volatile gases. The graphs of the distortion energy growth due to the equivalent stress (von Mises) for S3 (Fig. 4, 10) also points to this trend. Fragments of CO₂ output at the decomposition during the process of thermal heating for three coal samples after the sudden heat and testing according ASTM D7582-15 «Standard test method for approximate analysis of coal and coke macro-thermogravimetric analysis» are represented in the Fig. 14.

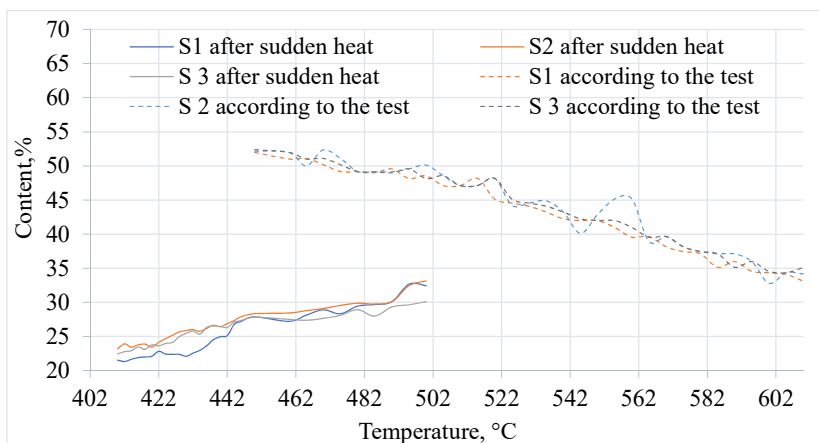


Fig. 11. Fragments of CH₄ output at the decomposition during the process of thermal heating for three coal samples: after the sudden heat and testing according ASTM D7582-15 «Standard test method for approximate analysis of coal and coke macro-thermogravimetric analysis»

It is noticeable that the CO₂ release (Fig. 14) for all samples which have sudden heat is significantly lower than for samples which have standard thermal processing (TGA) with a gradual heating of 10°/min. The CO₂ release for all samples started at a temperature of 402°C in amount of 30%. The maximum yield of the S1 coal samples consist of for about 31.22% and at a temperature of 500°C the CO₂ release for this type of coal have already in amount of 10.01%.

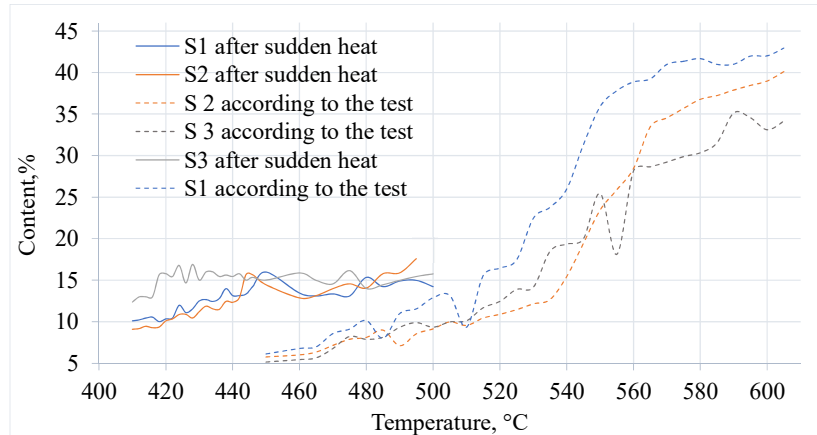


Fig. 12. Fragments of CO output at the decomposition during the process of thermal heating for three coal samples after the sudden heat and testing according ASTM D7582-15 «Standard test method for approximate analysis of coal and coke macro-thermogravimetric analysis»

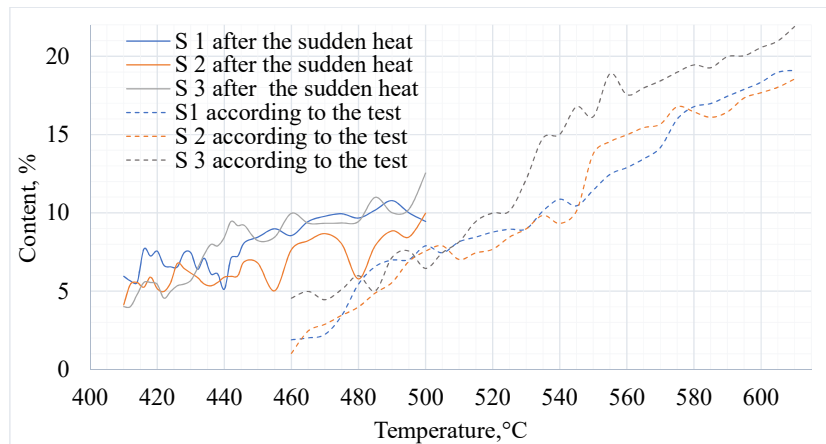


Fig. 13. Fragments of H₂ output at the decomposition during the process of thermal heating for three coal samples after the sudden heat process and testing according ASTM D7582-15 «Standard test method for approximate analysis of coal and coke macro-thermogravimetric analysis»

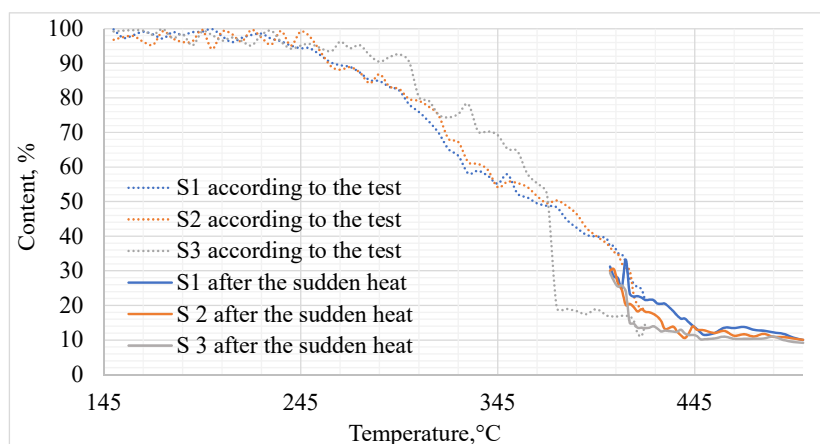


Fig. 14. Fragments of CO₂ output at the decomposition during the process of thermal heating for three coal samples after the sudden heat and testing according ASTM D7582-15 «Standard test method for approximate analysis of coal and coke macro-thermogravimetric analysis»

The minimum CO₂ release was shown by S3 samples at an initial temperature of 402°C with in amount of 29.45% and after further heated by 500°C the CO₂ level decreased to 9.15%. On the other hand, standard heating of coal

samples showed a significant CO₂ release for all samples starting at 150°C with an average amount approximately 97%. By the temperature 450°C, the CO₂ release was reduced by almost 10 times, but the release time was more

and consist of approximately 30 minutes. Reduction of CO₂ release for all samples that have been suddenly heated to the same values occurred within 5 minutes with reduction in CO₂ of almost 12% over the thermal processing period.

To confirm the physical experiment, the data was determined and compared based on an analytical kinetic model of CO₂, CH₄, CO, H₂ gas mixture formation in the sudden heating chamber. Kinetic model of gas mixture formation based on equation (4) and (9) like approximal model [26] taking into account Grum-Grzhimaylo's Standard Method and represented like system of equations:

$$C_{\text{CO}_2} = C_{\text{CO}_2}^0 \exp\left(\frac{k_{\text{CO}_2} F}{V} \tau\right) + \frac{\exp\left(\frac{k_{\text{CO}_2} F}{V} \tau\right) - \exp\left(-\frac{k_{\text{O}_2} F}{V} \tau\right)}{k_{\text{O}_2} - k_{\text{CO}_2}} \cdot 100\%, \quad (11)$$

$$C_{\text{CH}_4} = C_{\text{CH}_4}^0 \exp\left(\frac{k_{\text{CH}_4} F}{V} \tau\right) + \frac{\exp\left(\frac{k_{\text{CH}_4} F}{V} \tau\right) - \exp\left(-\frac{k_{\text{CO}_2} F}{V} \tau\right)}{k_{\text{CH}_4} + k_{\text{CO}_2}} \cdot 100\%, \quad (12)$$

$$C_{\text{H}_2} = C_{\text{H}_2}^0 \exp\left(-\frac{k_{\text{O}_2} F}{V} - \exp\left(-\frac{k_{\text{H}_2} F}{V} \tau\right)\right) \cdot 100\%, \quad (13)$$

$$C_{\text{CO}} = C_{\text{CO}}^0 \exp\left(\frac{k_{\text{CO}} F}{V} \tau\right) - \frac{\exp\left(\frac{k_{\text{CO}} F}{V} \tau\right) - \exp\left(-\frac{k_{\text{O}_2} F}{V} \tau\right)}{k_{\text{O}_2} - k_{\text{CO}}} \cdot 100\%, \quad (14)$$

where $C_{\text{CO};\text{CO}_2;\text{CH}_4;\text{H}_2}$ – the fragments of gas content in the gasification process, respectively; $C_{\text{H}_2;\text{CH}_4;\text{CO};\text{CO}_2}^0$ – the fragments of gas content in equilibrium gasification process, respectively; τ – the gas host time in the isothermal zone; F – the area of the isothermal zone; V – the volume of the isothermal zone; $k_{\text{O}_2;\text{H}_2;\text{CO};\text{CO}_2;\text{CH}_4}$ (k_i) – the velocity reaction constant for fragments gas respectively; λ – the heat exchange coefficient

$$k_i = \frac{1}{\frac{1}{\beta} + \frac{\exp\left(\frac{U_f}{RT}\right)}{P_E}}, \quad (15)$$

where β – an external mass exchange factor; P_E – a preexponential factor; U_f – the distortion activation energy in isothermal areas.

Correlation for thermal conductivity of coal to temperature

$$\lambda_i = \frac{\rho}{(4511)^{3.5}} \sqrt{T}. \quad (16)$$

The data of the sample gasification coke weakly sintering coals kinetic constant and fragments gas content in

equilibrium process taken in accordance with taking into account thermogravimetric analyses [27].

Comparison of analytical results for CH₄, CO, H₂, CO₂ fragments analytical gas content kinetic model and physical experiment is represented in Tables 6–9. Comparison are shown taking in the temperature range from 410°C to 444°C as a starting threshold of the sudden heat impact.

Table 6

Comparison of the analytical and experimental results of the CH₄ fragments gas content in the gasification process with sudden heat effect

Temperature (°C)	CH ₄ analytical fragments gas content (%)			CH ₄ experimental fragments gas content (%)		
	S1	S2	S3	S1	S2	S3
410	21.02	22.11	21.05	21.90	22.88	21.67
412	21.45	22.34	21.10	22.10	22.22	21.63
414	21.87	22.67	21.18	22.53	22.12	22.02
416	21.15	22.78	21.34	22.45	22.34	22.56
418	21.55	23.19	22.35	22.98	23.80	22.15
420	21.34	22.91	22.35	22.85	22.56	22.21
422	21.67	23.12	22.39	22.90	23.68	23.24
424	21.91	23.48	22.45	23.45	23.90	23.26
426	22.01	23.89	22.78	23.54	23.16	23.56
428	22.11	23.45	22.91	23.68	23.02	23.78
430	22.83	24.15	23.47	24.01	24.89	24.22
432	22.43	25.67	23.12	23.56	25.23	25.16
434	22.39	25.89	23.78	23.10	25.89	25.65
436	22.39	26.01	23.64	23.16	26.87	26.46
438	22.11	25.78	23.98	22.94	25.14	25.51
440	22.56	25.98	24.15	23.20	25.37	25.07
442	22.98	26.01	24.98	23.73	26.89	26.76
444	23.65	26.19	26.45	24.28	26.54	26.88

Table 7

Comparison of the analytical and experimental results of the CO fragments gas content in the process of the gasification with sudden heat effect

Temperature (°C)	CO analytical fragments gas content (%)			CO experimental fragments gas content (%)		
	S1	S2	S3	S1	S2	S3
410	10.11	9.09	12.38	10.34	9.67	12.93
412	10.22	9.18	12.44	10.89	9.85	13.42
414	10.44	9.45	12.56	11.15	10.10	13.56
416	10.55	9.28	13.02	11.78	10.18	13.98
418	10.01	9.37	13.44	11.56	10.22	14.12
420	10.34	10.10	13.98	11.90	10.89	14.14
422	10.45	10.34	13.45	11.98	11.55	14.55
424	11.98	10.87	13.45	12.12	11.14	14.90
426	11.10	10.90	14.44	12.78	11.72	15.12
428	11.55	11.81	14.78	12.25	12.64	15.56
430	12.05	11.87	13.06	12.94	12.39	15.67
432	12.77	11.55	14.84	13.18	12.26	16.78
434	12.44	11.56	14.88	13.78	12.49	16.88
436	12.59	11.49	14.90	13.16	12.33	16.90
438	13.98	12.55	14.34	14.33	13.56	16.94
440	13.15	12.68	14.51	14.23	12.68	16.98
442	13.15	13.66	14.98	13.90	14.48	16.98
444	13.33	15.67	15.01	13.55	16.91	17.01

Table 8

Comparison of the analytical and experimental results of the H₂ fragments gas content in the process of the gasification with sudden heat effect

Temperature (°C)	H ₂ analytical fragments gas content (%)			H ₂ experimental fragments gas content (%)		
	S1	S2	S3	S1	S2	S3
410	1.35	1.22	1.2	1.48	1.56	1.22
412	1.88	4.45	2.04	1.05	4.13	2.01
414	4.22	4.45	3.44	4.78	4.33	3.34
416	5.11	4.45	4.76	5.45	4.64	4.55
418	5.95	4.12	4.01	5.16	4.47	4.37
420	5.65	5.44	4.01	5.65	5.30	3.91
422	5.78	5.55	3.78	5.12	5.78	3.45
424	5.98	6.77	5.55	5.67	6.55	5.02
426	7.68	6.45	5.55	7.14	6.65	5.25
428	7.24	6.16	5.43	7.89	6.25	5.85
430	7.55	5.87	4.55	7.15	5.70	4.22
432	6.55	5.45	5.48	6.45	5.67	5.78
434	6.55	6.90	5.34	6.18	6.80	5.23
436	6.55	6.95	5.45	6.23	6.85	5.34
438	7.45	6.98	5.69	7.01	6.87	5.42
440	7.45	7.01	6.45	7.34	7.12	6.02
442	7.39	7.14	7.34	7.23	7.45	7.35
444	7.10	7.01	7.98	7.55	7.27	7.75

Table 9

Comparison of the analytical and experimental results of the CO₂ fragments gas content in the process of the gasification with sudden heat effect

Temperature (°C)	CO ₂ analytical fragments gas content (%)			CO ₂ experimental fragments gas content (%)		
	S1	S2	S3	S1	S2	S3
410	31.22	30.01	29.45	31.11	30.14	29.22
412	28.44	29.45	27.04	28.12	29.01	27.44
414	27.91	29.18	25.44	27.44	29.14	25.34
416	25.11	28.15	25.76	25.23	28.44	25.22
418	33.21	24.45	24.01	33.14	24.11	24.14
420	23.45	23.55	21.01	23.34	23.41	21.01
422	22.55	17.55	14.78	22.68	17.75	14.44
424	22.68	16.77	13.55	22.44	16.18	13.01
426	22.34	15.45	13.55	22.01	15.44	13.01
428	21.55	13.15	13.43	21.15	13.98	13.05
430	20.45	13.47	13.55	20.23	13.01	13.98
432	20.55	12.45	13.98	20.14	12.03	13.61
434	20.45	11.34	13.34	20.98	11.11	13.56
436	18.23	10.18	12.45	18.44	10.45	12.67
438	16.13	10.11	12.15	16.15	10.34	12.45
440	15.34	9.54	12.01	15.33	10.01	12.81
442	14.34	11.89	11.99	14.11	11.14	12.05
444	13.55	11.05	11.45	13.23	10.23	12.34

The relative error of the physical measurements in relation to the analytical kinetic model for the formation of CH₄, CO, H₂, CO₂ fragments gas content no more than 5%. According to the National Standards for measurement error the results are satisfactory.

6. Discussion of the sudden heat impact results on volatile gas release from coal gasification with weakly grade of metamorphism

Sudden heat, which was in the temperature range from 20°C to 400°C, for weakly grade metamorphized coals has shown a change in the value approximately 65% lower. There is no doubt that this CO₂ release trend is positive for the environmental effect of coal thermal processing taking into account a thermal processing process for the release of volatile gases. First of all, it was found that all three coal samples (S1, S2, S3) have the ability to accumulate energy distortion in the isochoric regions, aimed at activating coal energy at temperatures 300°C and 400°C. At the 300°C isotherm, under sudden heat conditions, the coal samples S1 and S2 reach energy distortion in amount of 21.5 kJ/Kmol·s and 20.09 kJ/Kmol·s respectively (Fig. 4, 5). Coal samples S3 does not have the ability to accumulate energy distortion at a temperature of 300°C. With the increase of the thermal stress on the 400°C isotherm, all three samples show sufficient capacity for accumulation of energy distortion affecting activation of coal energy. Coal samples S2 show on the 400°C isotherm a sudden sinusoidal kinetics change in the energy distortion with peak up to 30 kJ/mol with all over isotherm in the isochoric areas. The S3 coal samples (Fig. 5, 7) show the maximum kinetics of the energy distortion of the change-over in the isothermal regions at 400°C, but the isothermal regions in the S3 sample are offset towards large amount of the stress magnitude. It appears that this trend of energy accumulation in S3 coal samples is determined by the large elastic characteristics, large value of thermal conductivity factor and greater transmissivity of the micro-components contained in the coal. To confirm the activity of the coal behavior taking into account the capacity for accumulation of energy distortion, which disturbs stability and facilitates the release and birth of units, the magnitude of the occurrence of stresses in the isochoric areas was evaluated (Fig. 8, a, b)) and the specific distortion energy of coal samples at temperatures 300°C and 400°C in the same areas (Table 5). The results showed that the minimum stress value observed for sample S1 in amount of 0.1 GPa, as well as the relative energy distortion for this sample does not exceed 136.133 kJ/kg·s. The stress growth kinetics in the isochoric areas on 400°C isotherm for coal sample S3 shows the highest amount of the energy distortion (Fig. 10, a, b, Table 5) reaching 571.824 kJ/kg·s.

The results of the CH₄ analysis release showed that the total percentage of its output in the range from 400°C to 500°C is in 63% lower than in standard processing. However, the discharge temperature region is offset towards lower temperatures, which supports the assumption that the effect of the distortion energy on the activation of energy within the coal (Fig. 11). This is positive from the standpoint that, gasification of methane from weakly grade metamorphized coals with a release rate of at least 45–95% requires temperatures from 600°C to 1000°C, or careful preparation of coal [13, 28].

The CO output results for all three weakly grade metamorphized coal samples (S1, S2, S3) also show a shift in the region of release and the start of the process already at 410°C. Both the minimum and maximum CO release in amount of 9.09% and 17.61% respectively observed for S3 samples (Fig. 12). Coal samples S3 have a higher carbon content, greater transmissivity with the lowest pore volume, which affects CO. For this temperature period range from 410°C to 500°C all samples after sudden heat have a smaller

CO output, but as with CH₄ their temperature range is shifted towards lower temperatures not typical of conventional coal and biomass gasifiers [13, 28, 29]. No doubt that it is positive moment. The same trend has been observed in the study of hydrogen release. The S3 samples showed both the lowest and highest output H₂ in amount of 1.2% and 12.54% at a temperature 410°C and 500°C respectively. This can be explained by the fact that S3 coal samples have the smallest modulus of elasticity, whereby the effect of the influence of energy distortion on the energy activation taking into account to transmissivity determines the greatest increase in the output of CO and H₂ in a short time. For all samples that have been suddenly heated, the average CO₂ release content is in amount for about 65% lower at the beginning of the process and is in amount for about 12% lower than calculated per unit time. Maximum release content is shown by S1 samples in amount approximately 13.22% at the beginning of the process. However, at a temperature 500°C the CO₂ level release for sample S1 has already in amount for about 10.01%, indicating a trend towards its possible decrease with further heating. Unlike CO and H₂ release, the minimum CO₂ output in a share of sample S3, which by the end of 500°C was in amount approximately 9.15%. It seems that this is due to the presence in carbon dioxide of a significant number of intermolecular forces, which are disturbed by the effect of temperature.

7. Conclusion

1. The results of the thermal stress activation show the ability more than 40% of thermal treated weakly grade metamorphized coal to accumulate and convert the energy of tension during sudden heat and transform this energy into the energy of distortion, which weakening bonds inside coal in a minimum amount of 38.24 kJ/kg·s and maximum amount 571.824 kJ/kg·s. Coal samples with high carbon content, low elasticity and greater transmission at the 400°C isotherm demonstrate a higher energy storage capacity, weakening and distorting the connection when there is no energy accumulation at the 300 isotherm.

2. The results of the effect of the active energy at sudden heat on the quantity and volatile gases produced by anisotropic elastic coal during a sudden heat shows that

it is possible to shift the output period of H₂, CO and CH₄ and CO₂ to 410°C. This indicates that the thermal heating period during gasification process can be reduced. The most favorable sudden heat affects on the CH₄ output, not less, than 33% for samples with the highest hydrogen content and lower elasticity properties. The introduction of sudden heat shows results in 30% reduction of CO₂ already at 402°C with a drop of total CO₂ output during the process in a temperature range from 400°C to 500°C to about 12%. This indicates an improvement in the environmental characteristics of gasification weakly grade metamorphized coal.

Conflicts of interest

The authors declare no conflicts of interest.

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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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