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Laser Pyrolysis of High-Grade Metamorphic Coals

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Abstract

Gaseous products formed in the pyrolysis of samples composed of the tableted K (coking) and A (anthracite) coal microparticles under the action of pulse-periodic laser radiation (with the parameters: 532 nm, 10 ns, 6 Hz, 0.2–0.6 J/cm^2) in the argon environment have been studied. It is shown that the concentration of gaseous products increases exponentially with an increase in the laser radiation energy density. Exceeding the critical radiation energy density values (H_{cr} = 0.18 and 0.26 J/cm^2 for K and A coal ranks, respectively) leads to ablation of coal samples.

Keywords: coal, pyrolysis, laser radiation, mass spectrometry, synthesis gas

INTRODUCTION

Coal pyrolysis is a complex set of chemical and physical processes during which coal is subjected to thermal decomposition in oxygen-free environment [1]. The products of coal pyrolysis are valuable solids (coke, semi-coke), fluids (resins), and gases (synthesis gas, acetylene) [2–4].

A large amount of data on the studies of coal pyrolysis processes has been accumulated by present [5–7]. The works dealing with the studies of gaseous products of coal pyrolysis deserve special attention [8, 9].

Laser pyrolysis is one of the technologies of thermochemical coal conversion involving the use of laser radiation for rapid heating. Laser pyrolysis makes it possible to simplify experimental studies due to sample size reduction, due to which an experiment can be readily reproduced. In addition, rapid heating can reduce the probability of secondary reactions in pyrolysis products [10–16].

The formation of gaseous products under the action of laser radiation on coal was investigated [10–12]. The source of laser radiation involved in the works was a ruby laser with pulse duration of τ = 1 ms, radiation wavelength λ = 694.3 nm and pulse energy E = 1.5–10 J. The molecules detected in gaseous products were H_2, CO, C_2H_2, CO_2, CH_4 and various hydrocarbons. The distribution of gaseous products was concluded to depend on laser pulse energy and on the medium of laser action.

The authors of [13] used mass spectrometry to analyse the gaseous products formed as a result of pyrolysis of coal at different metamorphism stages in vacuum. The samples were affected by five focused millisecond laser pulses with E = 1.5 J. Among gaseous products, H_2, CH_4, CO, C_2H_2, CO_2 were detected. The concentration of gaseous pyrolysis products increases for lower stages of coal metamorphism.

The composition of gaseous products of laser pyrolysis under the action of a pulsed ruby laser (55 kW/cm^2, 694.3 nm) and a continuous CO_2-laser (140 W/cm^2, 10.6 μm) was investigated [14]. The composition of gaseous products was analysed by mass spectrometry. Irradiation with the high energy of a pulsed ruby laser produces a mixture of gases with the high concentrations of H_2 and C_2H_2. Low-energy irradiation with a continuous CO_2-laser gives a complex mixture of H_2, CO and hydrocarbon gases.

The low-energy treatment of coal with CO_2-laser (wavelength 10.6 μm, power up to 130 W, irradiation time 5 s) was carried out in [15]. The major products of the laser pyrolysis of coal were low-molecular hydrocarbons (C_2H_6, C_2H_2, C_2H_4, CH_4), as well as CO_2, CO and H_2, as recorded by gas chromatography. Experiments have shown that the yield of gaseous products increases with an increase in the power and duration of laser radiation within a limited range. Coal characteristics were determined as the main factors affecting the yield of gaseous products.

The composition of the gaseous products of laser pyrolysis of coal at different stages of metamorphism in argon and in a water-coal suspension was studied in [16]. Radiation source was a Nd:YAG-laser (5 ns, 532 nm, 10 Hz, 90–700 mJ/cm^2). The major gaseous products determined by gas chromatography were H_2, CO, CO_2 and various hydrocarbons.

In our works, we studied the effect of pulsed-periodic nanosecond radiation at the second harmonics of the YAG:Nd^{3+}-laser (532 nm, 10 ns, 0.2–0.6 J/cm^2) on the coal samples of B, DG, G, and Zh ranks [17–19]. The formation of H_2, CH_4, C_2H_2, CO and CO_2 was recorded. The concentrations of gaseous products increased linearly with an increase in the density of laser radiation energy. Further on, it is interesting to study the effect of the coal metamorphism stage on the yield of gaseous products.

The present work is a continuation of experiments described in [17–19]. The goal of the work was to study the gaseous products of laser pyrolysis of coal microparticles at high metamorphism stages: K (coking) and A (anthracite) ranks, under the action of the second harmonics of the neodymium laser.

EXPERIMENTAL

The objects of investigation were coal samples of K (coking) and A (anthracite) ranks. The results of proximate and ultimate analysis are presented in Table 1. The procedures used to prepare tableted samples of coal microparticles and to perform the experiments were similar to the approaches described in [17–19].

The source of laser radiation was a Nd^{3+}:YAG-laser LQ929 (SOLAR Laser Systems, the Republic of Belarus), operating in the Q-switching mode at the wavelength of 532 nm. Pulse duration was 10 ns. The diameter of the laser beam was the same as the sample diameter. The laser pulse repetition rate was 6 Hz. The time of laser beam action on coal samples was 25 min. So, the total number of pulses within a series was $N = 9000$. The density of laser radiation energy (H) varied within the range of 0.2–0.6 J/cm^2 in 0.1 J/cm^2 increments.

The gaseous products of pyrolysis were studied using gas analyser QMS 300 (Stanford Research Systems, USA). Recalculation of gas ions of definite masses recorded by the gas analyser into pressure units (P) was performed automatically with the coefficients linking the number of ions and pressure as determined by the manufacturer.

The concentrations of gaseous products (n_i) were calculated using the equation:

$$n_i = \frac{P_i}{kT} \quad (1)$$

where P_i is the partial pressure of the recorded gaseous products, Pa; k is Boltzmann's constant, J/K; T is temperature, K (measured with a resistance thermometer (RT)).

The mass (m_i) of each of the gaseous products was calculated using the Mendeleev–Clapeyron equation:

TABLE 1

Results of the analysis of the coal samples of K and A ranks

Coal rank	Proximate analysis, wt%			Ultimate analysis, wt%				
	W^a	A^d	V^{daf}	C^{daf}	H^{daf}	N^{daf}	S^{daf}	O^{daf}
K	0.6	4.9	21.3	87.7	4.6	2.2	0.4	5.1
A	0.4	3.6	7.7	89.6	3.3	1.8	0.4	4.9

Note. W^a is analytical moisture; A^d is ash content; V^{daf} is the yield of volatile susbtances; a is the analytical state of coal; d is the dry state of coal; daf is the dry ash-free state of coal.

$$m_i = M_i \frac{P_i V_0}{RT} = M_i \frac{n_i V_0}{N_a} \quad (2)$$

where V_0 is the volume of the experimental chamber ($7.5 \cdot 10^{-7}$ m^3), R is the universal gas constant, J/(mol · K); M_i is the molar mass of the i^{th} gas, kg/mol; N_a is Avogadro constant, mol^{-1}.

The proportion of molecules of the i^{th} gas (φ_i) in pyrolysis products was determined as

$$\varphi_i = \frac{n_i}{\sum n_i} \cdot 100\ \% \quad (3)$$

Before experiment and after laser action, sample masses m_1 and m_2, respectively, were determined by weighing using the analytical balance VIBRA HT-84RCE (Shinko Denshi, Japan) with a precision up to 0.1 mg. The sample mass loss was determined using the equation

$$\Delta m = m_1 - m_2 \quad (4)$$

The dependence of the yield of gaseous products on the number of laser pulses (N) affecting the sample was measured at different densities of laser pulse energy (H) using three samples for each H value, and then the average yield was determined for the products involved in calculations. Measurement error was calculated according to Student's (t-test) method with the confidential probability equal to 0.9.

RESULTS AND DISCUSSION

The composition of gaseous products formed in the pyrolysis of coal samples of K and A ranks under the action of nanosecond laser radiation was investigated. In the mass spectra of the gas phase over K and A rank coal samples, the groups of peaks were recorded with mass numbers m/z = 1, 2; m/z = 16, 15, 14; m/z = 25, 26; m/z = 28, 12, 16, 29, 14; m/z = 44, 28, 16, 12. Comparison of the relative intensities of these peaks with the catalogued data for the gas analyser allows us to conclude that they correspond to molecules H_2, C_2H_2, CH_4, CO, CO_2. The dependences of partial pressures and calculated concentrations of H_2 and CO on the number of pulses in the gaseous products of laser pyrolysis of K and A rank coal samples under the action of laser radiation with H = 0.2–0.6 J/cm^3 are shown as an example in Fig. 1.

The dependences of the proportions of gaseous products φ_i, calculated using equation (3), on H at the moment when laser action is completed (N = 9000) for coal samples of K and A ranks are shown in Fig. 2.

The total calculated masses of gaseous products (m_g) and mass losses by samples (Δm) determined by weighing with the analytical balance, depending on H at the moment of laser action termination (N = 9000) for K and A rank coal samples are presented in Table 2.

One can see that Δm exceeds m_g (see Table 2). It follows from this fact that sample ablation in addition to gas evolution takes place during the action of laser pulses. The mass of ablation products (m_{abl}) was calculated using the equation

$$m_{abl} = \Delta m - m_g \quad (5)$$

The products of K and A rank coal pyrolysis under the action of nanosecond laser radiation are H_2, CH_4, C_2H_2, CO and CO_2. The same gaseous pyrolysis products were detected by us previously for coal samples of B, DG, G, and Zh ranks [17–19]. The results of experiments show (see Fig. 1) that the concentration of gaseous pyrolysis products increases at a fixed H with an increase in N of laser action, while at fixed N it increases with an increase in H.

Analysis of the composition of gaseous pyrolysis products depending on H (see Fig. 2) shows that the proportions of CO and CO_2 in the gaseous products of K and A rank coal pyrolysis decrease with an increase in energy density within the range of 0.2–0.6 J/cm^2, while the proportion of H_2, increases, on the contrary. The proportion of C_2H_2 in the gaseous products of K rank coal pyrolysis is nearly constant within the studied laser radiation energy density range. In view of the small CH_4 concentration in the products of K and A rank coal pyrolysis, and C_2H_2 in the products of A rank coal pyrolysis, it is difficult to assess changes in their proportions in the gaseous products.

The proportion of combustible gases (H_2, CH_4, C_2H_2, CO) in the gaseous pyrolysis products at H within the range of 0.3–0.6 J/cm^2 increases from 90±2 to 94±2 % for K rank coal and from 74±2 to 90±3 % for A rank coal (see Fig. 2).

It is demonstrated in [19] that the action of nanosecond laser pulses on the samples of brown coal involves their ablation with the escape of dispersed microparticles 10–50 μm in size, and evaporation of carbon atoms from breakdown paths. Studies of K and A rank coal samples under the conditions similar to those described in [19] gave the same results.

The dependences of ablation product masses on H for K and A rank samples, plotted using the

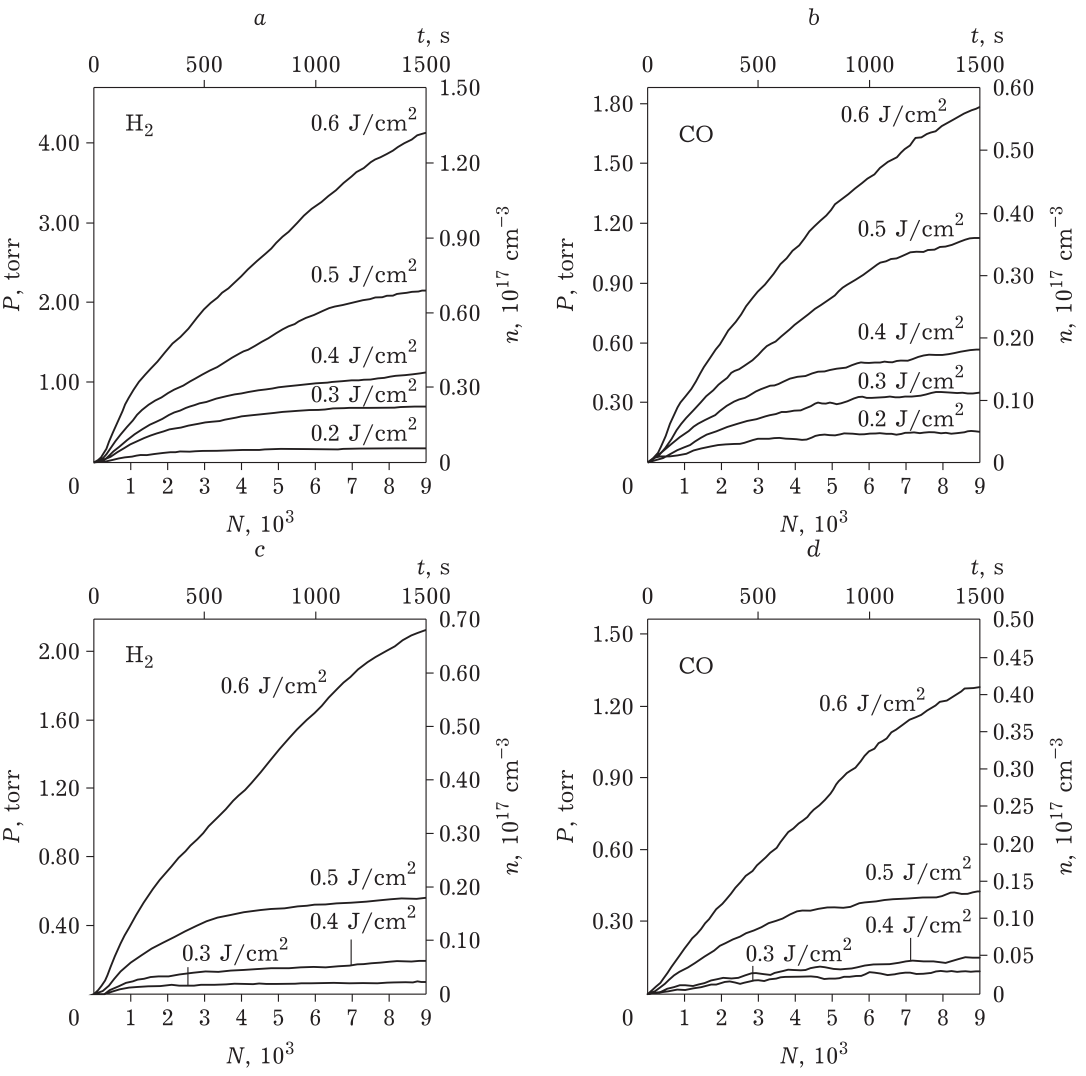

Fig. 1. Dependence of the partial pressure (P) and concentration of H_2 and CO (n) in the gaseous products of laser pyrolysis of coal samples of rank K (a, b) and A (c, d) on the number of laser pulses (N) and the duration of experiment (t).

data presented above (see Table 2), are presented in Fig. 3.

The experimental points are described by the linear law (see Fig. 3), which is in agreement with theoretical calculations for the laser ablation of graphite within the used energy density range [20]. The linear approximation of experimental points can be used to estimate the minimal values of critical energy density (H_{cr}) above which coal sample ablation is observed. The values determined for K and A rank coal samples are $H_{cr} \approx 0.18$ and 0.26 J/cm^2, respectively.

The calculated dependences of the concentrations of gaseous pyrolysis products H_2 and CO for coal samples of K and A ranks on the density of laser pulse energy are shown in Fig. 4. The dependences were obtained using the experimental data in the form of P values recalculated into n according to equation (1). The concentrations increase with an increase in H value following a non-linear law.

To explain the nonlinear dependence of the yield of gaseous pyrolysis products on H, it is necessary to consider a model based on the nonlinear dependence of the optical breakdown and the formation of laser-induced plasma on the density of laser pulse energy. As demonstrated in [21], under the action of laser pulses with energy density above the critical value (H_{cr} = 0.2 J/cm^2), the electron avalanche and optical breakdown are initiated in coal samples in the regions of microdefects. The dependence of electron concentra-

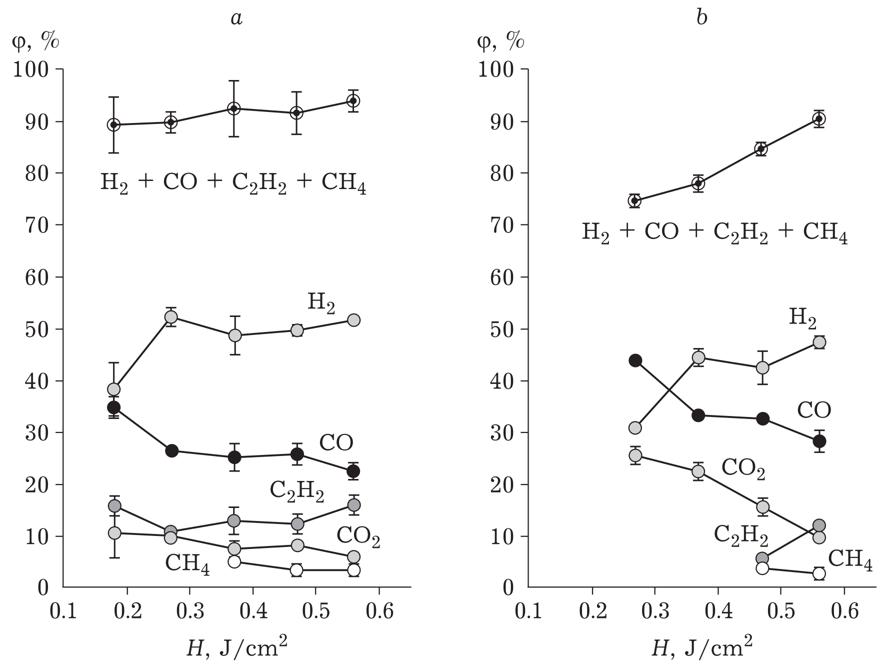

Fig. 2. Dependence of the proportions of gaseous products and combustible gases from pyrolysis (φ) of the coal samples of ranks K (*a*) and A (*b*) on the laser pulse energy density (*H*).

tion (*n*) in the avalanche on the density of laser pulse energy can be described by the equation

$$n = C[\exp(aH) - 1] \quad (6)$$

where *a* is the energy constant of electron avalanche evolvement, cm^2/J; *C* is a constant, cm^{-3}, independent of *H*. In addition, with an increase in *H*, the number of optical breakdown channels is likely to increase. Temperature in these breakdown channels can reach very high values ($T \sim 10^3$–10^4 K) [22, 23]. For this reason, in these breakdown regions intense evaporation of coal matter occurs, along with the formation of coal plasma carrying excited C, H, O atoms and ions, and molecules like CN and C_2, which were observed by different authors in experiments involving laser-induced breakdown spectroscopy (LIBS) [24].

After ionisation of coal molecules, molecular radicals are formed as a consequence of electron avalanche evolvement in the optical breakdown channels, and the number of these radicals correlates with the number of electrons released from coal molecules into the avalanche. In the present work, we suppose that at high temperatures in the optical breakthrough channels, these radicals are primary centres from which thermochemical reactions evolve. As a result of these thermochemical reactions, gaseous products are formed during the laser pyrolysis of coal. We assume that the concentration of the gaseous products of laser pyrolysis is proportional to the concentration of primary radicals. The dependence of the concentration of primary radicals should be described by the same law as that describing the concentration of electrons liberated into the avalanche, that is, by an equation similar to (6).

Judging from the above considerations, the dependence of the concentration of an i^{th} gaseous product (n_i) on *H* should be described by equation

$$n_i = C_i[\exp(a_i H) - 1] \quad (7)$$

TABLE 2

Caluclated mass depending on energy density (*H*) at the moment of completed laser action (the number of laser pulses is 9000) for coal samples of K and A ranks

Coal rank	*H*, J/cm²	m_g, mg	Δ*m*, mg	m_{abl}, mg
K	0.2	0.4±0.1	3.1±0.5	2.7±0.5
	0.3	0.9±0.2	6.8±0.9	5.9±0.9
	0.4	1.4±0.3	13±2	11±2
	0.5	2.9±0.4	21±1	18±2
	0.6	5.0±0.7	34±4	29±4
A	0.3	0.22±0.03	1.4±0.2	1.2±0.2
	0.4	0.38±0.06	4.1±0.7	3.8±0.7
	0.5	0.8±0.3	9±1	9±2
	0.6	3.2±0.5	18.2±0.7	15.0±0.9

Note. m_g is the mass of gaseous products; Δ*m* is mass loss by samples; m_{abl} is the mass of ablation product.

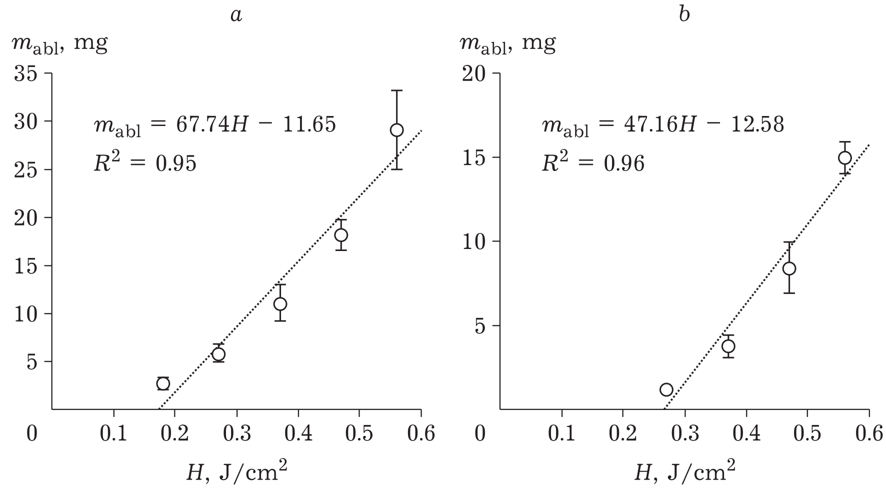

Fig. 3. Dependence of the mass of ablation products (m_{abl}) formed during laser pyrolysis of the coal of ranks K (*a*) and A (*b*) on energy density (H) after 9000 laser pulses. R^2 is approximation confidence.

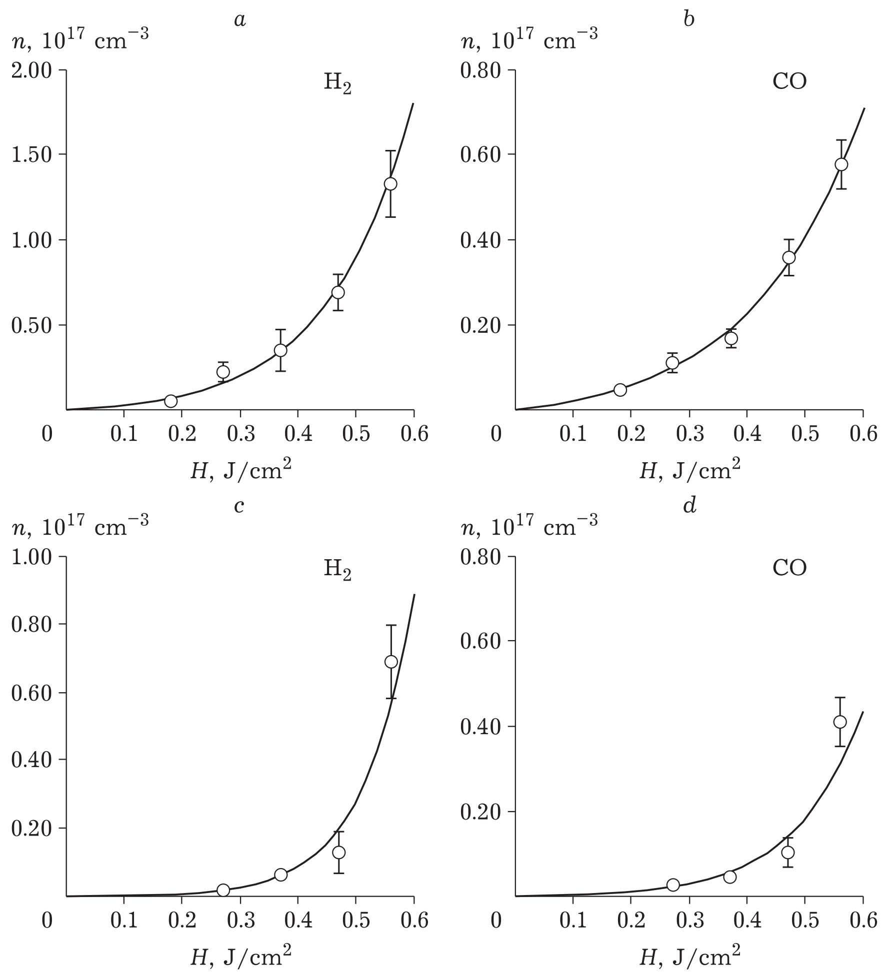

Fig. 4. Dependence of the concentration of gaseous products H_2 and CO (n) at the moment of laser pyrolysis completion for coal of ranks K (*a*, *b*) and A (*c*, *d*) on the density of laser pulse energy (H).

TABLE 3

Approximation parameters to calculate the concentrations of the gaseous products H_2 and CO from laser pyrolysis of coal samples of K and A ranks according to equation (7)

Coal rank	Parameters	Product	
		H_2	CO
K	C, 10^{17} cm^{-3}	0.029	0.033
	a, cm^2/J	6.930	5.228
A	C, 10^{17} cm^{-3}	0.001	0.002
	a, cm^2/J	11.417	8.653

Note. a is the energy constant of electron avalanche development; C is a constant independent of energy density.

where a_i is the energy constant of the thermochemical reaction leading to the formation of the i^{th} gaseous pyrolysis product, and C_i is a constant independent of H.

The continuous curves (see Fig. 4) were plotted with the help of equation (7) with C_i and a_i values listed in Table 3. The calculated curves provide a satisfactory approximation of the points depicting the experimental results.

In addition to the explanation of the observed phenomena by thermochemical reactions developing in breakthrough channels, pyrolysis of the outgoing particles inside the laser beam as a result of ablation can be assumed. However, development of this model requires a number of additional experimental data related to the dependences of the yield of gaseous products on laser beam diameter and particle sizes, which goes out of the framework of the present investigation.

CONCLUSION

1. The gaseous products of pyrolysis of the tableted samples prepared from coal microparticles of K and A ranks in argon under the action of laser pulses (532 nm, 10 ns, 6 Hz, 0.2–0.6 J/cm^2) were determined to contain H_2, C_2H_2, CH_4, CO and CO_2 molecules.

2. The proportion of combustible gases (H_2, CH_4, C_2H_2 and CO) in the mixture of gaseous products of the pyrolysis of coals under investigation increases with an increase in the density of laser radiation energy from 0.3 to 0.6 J/cm^2: for coal of K rank – from 90±2 to 94±2 %, for coal of A rank – from 74±2 to 90±3 %.

3. The action of nanosecond laser radiation exceeding the critical energy density (H_{cr} = 0.18 and 0.26 J/cm^2 for K and A rank coal, respectively) causes ablation of coal samples. The mass of ablation products increases linearly with an increase in the laser pulse energy density.

4. The yield of gaseous products from the pyrolysis of K and A rank coal samples increases non-linearly with an increase in the laser pulse energy density. To explain this phenomenon, a model is proposed, based on the non-linear dependence of the concentration of primary radical centres formed during the optical breakdown of samples on the laser pulse energy density. Thermochemical reactions develop from the primary centres and lead to the formation of the observed gaseous products of laser pyrolysis.

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