Study of the kinetic dependences of the glow and determination of the threshold characteristics of ignition of coals with different stages of metamorphism under the action of microsecond laser pulses

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Abstract. In this work, the study of the kinetic dependences of the glow and determination of the threshold characteristics of the ignition of coal of grades long-flame, semi-lean caking, weakly caking, lean and anthracite under the action of microsecond laser pulses was carried out. For the aforementioned coals, three successive stages of ignition were found with characteristic $H_{cr}$ thresholds. The first stage of ignition is associated with the heating of the surface of coal particles and the ignition of microprotrusions; the duration of the glow practically repeats the duration of the laser pulse. The second stage of ignition is associated with the release and ignition of volatiles in a millisecond time interval; the third - with the ignition of a non-volatile residue, the glow duration reaches 120 ms. With an increase in the degree of coalification, almost constant values of the first ignition threshold $H_{cr}^{(1)}$ are found. For the studied coals, with an increase in the degree of coalification, a decrease in the second threshold $H_{cr}^{(2)}$ and an increase in the third ignition threshold $H_{cr}^{(3)}$ are observed.

1. Introduction
The study of the processes occurring at the initial stages of coal ignition is an important direction for improving technologies for intensifying the combustion of solid mineral fuels.

When studying the initial mechanisms of coal ignition, laser radiation can be used as an energy source [1-5]. The use of laser radiation to initiate thermochemical processes of coal ignition has a number of advantages over traditional methods: the simplicity of the differentiated supply of energy to the surface of the coal sample and the ease of controlling the duration of exposure. However, a detailed study of the initial mechanisms of coal ignition under laser action has practically not been carried out. Such investigations began in our previous works: the kinetic dependences of the glow were investigated and the threshold characteristics of laser ignition of coals of grades brown (B), long-flame gas (LFG), gas (G), Fat (F), coking (C) were determined [6-8]. This work is a continuation of earlier studies devoted to the study of the initial ignition mechanisms of coals using other grades of coals.

2. Objects and techniques
The objects of study were coals of the Kuznetsk coal basin of various stages of metamorphism: long-flame (LF), semi-lean caking (SLC), weakly caking (WC), lean (L), and anthracite (A).

The results of technical and elemental analysis of coals are shown in Tables 1 and 2.

**Table 1. Results of technical analysis of coals**

| No  | Sample, coal grade                                           | Technical analysis |
|-----|-------------------------------------------------------------|--------------------|
|     |                                                             | $W_a$, % | $A^d$, % | $V_{daf}$, % |
| 1   | Sample No. 72, grade LF, mine "Kamyshansky" Severo-Taldinskoye deposit, seam 73 | 7.6      | 6.2      | 44.5        |
| 2   | Sample No. 34, grade SLC, mine "Tomusinsky"                 | 0.1      | 6.7      | 19.8        |
| 3   | Sample No. 45, grade WC, mine "Bachatsky"                   | 1.3      | 4.7      | 19.0        |
| 4   | Sample No. 81, grade L, Kuznetskinveststroy JSC, seam 19a    | 0.5      | 6.2      | 14.4        |
| 5   | Sample number 33, grade A, mine "Bungurskiy"                | 0.4      | 3.6      | 7.7         |

$W_a$ is analytical moisture content; $A^d$ is ash content; $V_{daf}$ is yield of volatiles.

**Table 2. Results of elemental analysis of coals**

| No  | Sample, coal grade                                           | Elemental analysis |
|-----|-------------------------------------------------------------|--------------------|
|     |                                                             | N, %   | C, %   | H, %   | S, %   | O, %   |
| 1   | Sample No. 72, grade LF, mine "Kamyshansky" Severo-Taldinskoye deposit, seam 73 | 2.3    | 74.4   | 5.3    | 0.5    | 17.5   |
| 2   | Sample No. 34, grade SLC, mine "Tomusinsky"                 | 2.0    | 84.2   | 4.2    | 0.3    | 8.7    |
| 3   | Sample No. 45, grade WC, mine "Bachatsky"                   | 2.1    | 83.8   | 4.0    | 0.1    | 10.0   |
| 4   | Sample No. 81, grade L, Kuznetskinveststroy JSC, seam 19a    | 2.0    | 89.7   | 4.1    | 0.4    | 3.8    |
| 5   | Sample number 33, grade A, mine "Bungurskiy"                | 1.8    | 89.6   | 3.3    | 0.4    | 4.9    |

The coals were ground in a ball mill, then sieved through a vibrating sieve with a mesh size of 63 μm. The experimental samples were a 10 mg sample placed in a copper capsule 5 mm in diameter and 2 mm deep.

A schematic of the experimental setup and a detailed description of the procedure for studying the kinetic dependences of the glow and determining the threshold characteristics of coal ignition are given in [6, 8]. The coals were ignited using single pulses of the first harmonic ($\lambda = 1064$ nm) of a YAG: Nd$^{3+}$ laser operating in the free-running mode. The laser pulse duration was 120 μs, the pulse energy was up to 1.5 J. Using a photomultiplier tube, the glow of the coal sample was converted into an electrical signal and recorded with an oscilloscope.

3. Experimental results

As in our previous works [6-8], according to the nature of the registered kinetic dependences for the studied coal grades, three stages of ignition were distinguished, which have a threshold character. The energy density corresponding to 50% of the probability of registering a flash at different stages of coal ignition was taken as the ignition threshold for coals at the corresponding stage $H_{cr}^{i}$.

As an example, Figure 1 shows the kinetic dependences of the luminescence of grade LF coal corresponding to three
stages of ignition at energy density values corresponding to $H_{cr}^{(1)}$, $H_{cr}^{(2)}$ and $H_{cr}^{(3)}$. Qualitatively similar kinetic dependences were recorded for all the studied coals.

Figure 1. Kinetic dependences of the glow of grade D coal corresponding to three stages of ignition: (a) the first stage of ignition, $H_{cr}^{(1)} = 0.51$ J/cm$^2$; (b) second stage of ignition $H_{cr}^{(2)} = 2.41$ J/cm$^2$; (c) third stage of ignition $H_{cr}^{(3)} = 3.08$ J/cm$^2$.

The kinetic dependences of the glow at the first stage of ignition for the studied coals have a similar character, the glow duration slightly exceeds the duration of the laser pulse and reaches 150 μs. At the second stage of ignition, the kinetic dependence includes the glow of the first stage and the glow in the time interval from 2 to 14 ms, while the glow duration decreases with an increase in the degree of coalification of the studied coals. At the third stage of ignition, the kinetic dependence includes the glow of the first two stages and the glow that appears in $\sim$ 10-30 ms after exposure to a laser pulse for grade LF coal and after $\sim$ 2-4 ms for coal grades SLC, WC, L and A. Glow in the third the ignition stage takes a time interval of $\sim$ 70-120 ms for coal grade LF and $\sim$ 6-15 ms for coal grades SLC, WC, L and A.

To determine the ignition thresholds, the coal samples were successively irradiated with a single laser pulse with a certain energy, and the kinetic dependence of the glow was recorded. Then the pulse energy increased and the experiment was repeated. The ignition probability $p$ was determined as the ratio of the recorded kinetic dependences to the total number of coal samples. A detailed description of the technique is given in the previous work [6].

Figure 2 shows the dependences of the probability of ignition of grade LF coal on the energy density of the laser pulse, which were used to determine the thresholds $H_{cr}$ at different stages of ignition (probability curves).
Figure 2. Dependence of the probability of ignition of grade LF coal on energy density of laser radiation.
1 – probability curve corresponding to the first stage of ignition;
2 – probability curve corresponding to the second stage of ignition;
3 – probability curve corresponding to the third stage of ignition.

Qualitatively similar dependences were obtained for all studied coals.

Table 3 shows the values of the ignition thresholds of the studied coals.

Table 3. The values of the ignition thresholds of the studied coals.

| No | Sample, coal grade | $H_{cr}^{(1)}$ J/cm$^2$ | $H_{cr}^{(2)}$ J/cm$^2$ | $H_{cr}^{(3)}$ J/cm$^2$ |
|----|-------------------|--------------------------|--------------------------|--------------------------|
| 1  | Sample No. 72, grade LF, mine "Kamyshansky" Severo-Taldinskoje deposit, seam 73 | 0.51 | 2.41 | 3.08 |
| 2  | Sample No. 34, grade SLC, mine "Tomusinsky" | 0.49 | 1.13 | 7.55 |
| 3  | Sample No. 45, grade WC, mine "Bachatsky" | 0.46 | 1.00 | 7.95 |
| 4  | Sample No. 81, grade L, Kuznetskinveststroy JSC, seam 19a | 0.38 | 0.94 | 8.48 |
| 5  | Sample number 33, grade A, mine "Bungurskiy" | 0.41 | 1.10 | 9.32 |

Figure 3 shows the dependences of the ignition thresholds on the degree of coalification of the studied coals.
Figure 3. Dependences of ignition thresholds on the degree of coalification of the studied coals: (a) for the first stage of ignition, $H_{cr(1)}$; (b) for the second stage of ignition $H_{cr(2)}$; (c) for the third stage of ignition $H_{cr(3)}$.

Figure 3 shows that with an increase in the degree of coalification, almost constant values of the first ignition threshold $H_{cr(1)} = 0.38-0.51$ J/cm$^2$ with a large statistical spread are observed. For bituminous coals, with an increase in the degree of coalification, a decrease in the second ignition threshold $H_{cr(2)}$ and an increase in the third ignition threshold $H_{cr(3)}$ are observed. For anthracite, the second and third ignition thresholds differ insignificantly from the values of $H_{cr(2)}$ and $H_{cr(3)}$ for bituminous coal of a high degree of coalification, grade L. Qualitatively similar dependences were observed using coals of grades LFG, G, F and C [7].

In our previous work [8], the staging of ignition is associated with the occurrence of the following thermochemical processes in coals. The first stage of ignition is associated with heating the surface of coal particles and igniting microprotrusions. The second stage of ignition is associated with the release and ignition of volatile substances in the gas phase, and the third stage is associated with the ignition of the non-volatile residue of coal particles. These conclusions are supported by the literature data [9] and the results of our experiments [6-8].

The authors of [9] have shown that the ignition of a coal particle when exposed to laser radiation is initiated at microprotrusions. The dependence of the ignition time of a coal particle and the minimum intensity of laser radiation required for its ignition on the number of inhomogeneities on the surface of a coal particle was found [9]. Thus, the process of ignition of microprotrusions is associated with the sizes of particles and the geometry of their surfaces, which have a significant statistical spread and, as a result, give the experimentally measured values of $H_{cr(1)}$. Recall that in this work we used coal samples with a particle size of <63 μm. Probably, it is the process of ignition of microprotrusions that
makes a decisive contribution to $H_{cr}(1)$ and leads to a weak dependence (or its absence) on the degree of coalification of the studied coals. To explain the dependences of the second $H_{cr}(2)$ and third $H_{cr}(3)$ coal ignition thresholds on the degree of coalification, at this stage of research, as in [6-8], the following model is proposed.

The initiation of chemical reactions is associated with the absorption of laser radiation energy. With an increase in the degree of coalification, the absorption index of coal $k$ increases [10]. The temperature of laser ignition of coals $T_{Li}$ remains almost unchanged in the metamorphism series [11]. The heat capacity of the studied coals changes insignificantly, for example, the true heat capacity of LF grade coal is $c_{300K} \approx 1.11 \text{kJ/kg K}$, the true density of the studied coals also changes insignificantly, for LF coal the true density is $\rho_{true} \approx 1.40 \text{g/cm}^3$, and for A grade coal $\rho_{true} \approx 1.32 \text{g/cm}^3$ [13]. Therefore, when various coals are ignited to achieve $T_{Li}$, the bulk density of the absorbed energy $Q_v$ changes only slightly.

$$c \rho \Delta T = Q_v$$  \hspace{1cm} (1)

On the other hand

$$Q_v \propto H \cdot k$$  \hspace{1cm} (2)

Hence, it follows that with an increase in the degree of coalification and an increase in $k$, $H_{cr}(2)$ decreases. At the third stage of ignition, with an increase in the degree of coalification, an increase in the third ignition threshold is observed. Thus, a qualitatively opposite dependence is observed with that observed at the second stage of ignition. At the third stage of ignition, the coal particles are heated to the ignition temperature as a result of the action of two factors: heating due to the absorption of the laser pulse energy; heating of coal particles as a result of combustion of the gas phase. With an increase in the degree of coalification, the mass of burnt volatiles decreases, which, accordingly, leads to a relatively less heating of coal particles. To reach the ignition temperature, an increase in the laser pulse energy is required, which leads to the observed dependence of $H_{cr}(3)$ on the degree of coalification.

4. Conclusion

During laser ignition of coals of grades LF, SLC, WC, L, A, three stages of ignition are distinguished, which have a threshold character. The first stage is associated with heating the surface of coal particles and the ignition of microprotrusions. The second stage is associated with the release and ignition of volatile substances, the third - with the ignition of a non-volatile residue.

The glow duration at the first stage of ignition slightly exceeds the duration of the laser pulse and reaches 150 $\mu$s. The glow duration at the second stage of ignition at $H = H_{cr}(2)$ is in the time interval from 2 to 14 ms; at the third stage of ignition takes a time interval of $\approx 70$-120 ms for LF grade coal and $\approx 6$-15 ms for SLC, WC, L and A coal grades.

With an increase in the degree of coalification, almost constant values of the first ignition threshold $H_{cr}(1)$ are observed. For the studied coals, with an increase in the degree of coalification, a decrease in the second threshold $H_{cr}(2)$ and an increase in the third ignition threshold $H_{cr}(3)$ are observed.

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