Study of the chemical and technological properties of long-flame, long-flame-gas and gas coals of the Kuznetsk Basin

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Abstract. The results of a study of the chemical and technological properties of low-metamorphosed coals of the Kuznetsk basin of long-flame (L), long-flame-gas (LG) and gas (G) technological grades. Coal samples are low-sulfur, medium-ash with a low ash basicity index, are characterized by a rather significant yield of semi-coking resin, gaseous and volatile substances. According to the established technological indicators, these coals can be recommended for energy and technological use, for example, in the process of semi-coking.

1. Introduction

Coal is a complex organomineral formation with various properties and quality indicators, depending on which the main directions of the energy and technological use of this raw material are determined. The chemical potential of coals characterizes the possibility of obtaining various chemical products during their processing, for example, when obtaining chemical products during pyrolysis, in carbonization processes, when coal is exposed to gas reagents and solvents [1-8].

The extensive available reserves and the high chemical potential of Kuzbass hard coals determine the relevance of the search for rational ways of their integrated use, based on knowledge of their structure, properties of coals and the chemistry of pyrolytic transformations.

The Kuznetsk coal basin has reserves of coal of various grades and, therefore, there is a need to study their chemical and technological properties in order to identify rational directions of their use.

This paper presents the results of a study of the chemical and technological properties of low-metamorphosed coals of the Kuznetsk Basin.

2. Results and discussion

For the study, 3 samples of coals were used, selected at various coal mines of Kuzbass: No. 1 - Aleksievskaya mine, Krasnogorsky seam, No. 2 - Kotinskaya mine, seam 51, No. 3 - mine them. Kirov, Polenovsky reservoir.

The technical and elemental analyzes of coal samples were determined using standard methods. The number of oxygen-containing groups was determined: carbonyl - by reaction with hydroxylamine hydrochloric acid, carboxyl - by the acetate method, total acidity - by ion exchange with sodium hydroxide. The oxygen content in the "active" groups was determined by summing up its percentage in the identified groups, the amount of "inactive" oxygen - by the difference between the total oxygen and oxygen content in the "active" groups.

The ash residue for analysis was obtained by slow ashing of analytical coal samples in a muffle furnace at a temperature of 815 ° C for 3 hours. The microanalysis of ash-forming elements was
carried out using a JEOL JSM-6390 LA scanning electron microscope with a JED-2300 X-ray spectrum analyzer as an analytical attachment.

Petrographic analysis was carried out on an automated complex for assessing the grade composition of coals of the SIAMS-620 system (Russia) in an oil immersion environment. The microcomponents were counted automatically at a magnification of 300 times in reflected light.

The assignment of coal samples to the grade composition was carried out in accordance with the unified classification of coals by genetic and technological parameters based on the values of the reflectance of vitrinite \( \left( R_o, \right) \), the sum of fusainized components \( \left( \Sigma LC \right) \) and the yield of volatile substances \( \left( V_{daf}, \% \right) \).

Thermal analysis was carried out on a Netzsch STA 409 thermal analyzer under the following conditions: sample weight 40 mg; platinum-iridium crucible; heating up to 1000ºC at a rate of 100ºC / min in a helium environment. During the analysis, weight loss (TG) and rate of weight loss (DTG) were recorded. The following parameters were used to characterize the thermal decomposition: \( T_{\text{max}} \) is the temperature of the maximum decomposition rate, \( V_{\text{max}} \) is the rate of decomposition at the inflection point on the DTG curve. Weight loss (\( \Delta m \)) was calculated in the temperature ranges of the most intense sample decomposition.

Determination of the yield of semi-coking products from coals was carried out by the gravimetric method according to GOST 3168-93 (ISO 647: 1974). The essence of the standard method consists in heating a sample of the test fuel in a glass retort (with a capacity of 100 cm\(^3\)) to 550 ºC and determining the yield of primary resin \( (T_{sk}) \) and pyrogenetic water \( (W_{sk}) \) with their subsequent separation, as well as the yield of semi-coke \( (sK) \) and gaseous products \( (G_{sk}) \).

Removal of pyrogenetic water was carried out by the method of Dean and Stark. The essence of the method consists in the formation of an azeotrope consisting of water and a solvent, which is distilled off into the Dean and Stark nozzle, and after cooling, the water and solvent are separated. The content of the primary resin of semi-coking is defined as the difference between the mass of the resulting condensate and pyrogenic water. The char yield was determined by the gravimetric method.

Prior to analytical studies, carbon-containing inclusions of coal dust, soot and other suspended particles insoluble in toluene were separated from the semicoking resin by the method described in [9].

Group analysis of the semi-coking resin included its separation into asphaltenes (high molecular weight high boiling polycyclic heteroatomic compounds), neutral hydrocarbons in the form of oils and oxygen-containing resins \([10-12]\). Asphaltenes were isolated by precipitation of benzene-soluble products with hexane. To separate a mixture of hydrocarbons soluble in hexane, we used the chromatographic adsorption method for separating complex liquid mixtures on porous adsorbents (silica gel). Elution was carried out sequentially with hexane and alcohol-benzene mixture (1: 1 by volume). The content of oils (eluted with hexane) and resins (eluted with an alcohol-benzene mixture) was determined by the gravimetric method after distilling off the solvent.

Characteristics of the main chemical-technological properties and chemical composition of the studied coal samples are given in tables 1-3.

**Table 1. Petrographic composition of the studied coal samples.**

| Coal sample No. | Petrographic parameters,% | Vitrinite reflection index | Coal grade according to GOST 25543-88 |
|----------------|---------------------------|---------------------------|-------------------------------------|
| 1              | 89                        | 2                         | 9                                   | 0.58 | 0.023 | L |
| 2              | 83                        | 4                         | 13                                  | 0.64 | 0.036 | LG |
| 3              | 72                        | 4                         | 24                                  | 0.75 | 0.060 | G |
Table 2. Characteristics of the studied coal samples.

| Coal sample No. | Technical analysis, % | Elemental composition, % per daf | Atomic ratio |
|-----------------|-----------------------|----------------------------------|--------------|
|                 | \( W^a \) | \( A^d \) | \( V^{daf} \) | \( S^d \) | C | H | \((O + N + S)\) | H/C | O/C |
| L               | 1.8 | 9.4 | 44.4 | 0.3 | 79.4 | 5.6 | 15.0 | 0.85 | 0.14 |
| LG              | 2.5 | 2.5 | 41.4 | 0.5 | 81.9 | 5.6 | 12.5 | 0.82 | 0.11 |
| G               | 1.1 | 4.5 | 42.2 | 0.4 | 83.7 | 5.6 | 10.7 | 0.80 | 0.10 |

Table 3. Oxygen distribution by functional groups.

| Coal sample No. | Functional composition, mg-equiv/g per daf | Oxygen in groups, % per daf |
|-----------------|---------------------------------------------|-----------------------------|
|                 | \( >C=O \) | \(-COOH\) | \(-OH\) | «active» | «inactive» |
| L               | 0.37 | 0.02 | 0.07 | 0.4 | 14.6 |
| LG              | 0.14 | 0.01 | 0.05 | 0.2 | 12.3 |
| G               | 0.08 | 0.01 | 0.02 | 0.1 | 10.6 |

The results of petrographic analysis (Table 1) show that coals of low stages of metamorphism of technological grades L, LG and G, whose vitrinite reflectance \( (R_o, r) \) varies from 0.58 to 0.75%, were selected for the study. The studied samples contain a rather significant amount of vitrinite components, the largest amount of which is contained in the coal sample of grade L (up to 89%). The maximum amount of lean components \( (\Sigma LC) \) up to 26% is contained in a coal sample of grade G.

The results of technical analysis and the elemental composition of coals are shown in Table 2. It can be seen that the studied samples of coals have different ash content, the value of which varies from 2.5% in a sample of grade LG to 9.4% in a sample of grade L coal. low-sulfur, since the sulfur content \( (Std) \) in them is less than 1.5%. With an increase in the genetic maturity of the samples (an increase in the \( R_o, r \) index), the atomic ratio of H/C and O/C decreases. The largest amount of oxygen and heteroatoms is contained in the organic mass of the grade L coal sample (Tables 2 and 3).

Any use of coals in various technological processes necessitates the determination of the inorganic components contained in them [13-15]. The chemical composition of the ash samples of the studied coals is shown in Table 4. In its composition, a relatively high content of silicon and aluminum oxides should be noted. It should be noted that the ash residues are characterized by low basicity, since the value of the \( I_0 \) ratio calculated by the formula: \( Fe_2O_3 + CaO + MgO + Na_2O + K_2O / SiO_2 + Al_2O_3 \) [15] is less than unity for all samples.

To study the features of thermal decomposition of coal samples, thermogravimetric analysis was carried out (Table 5). According to the presented results, thermal destruction of all coal samples is characterized by at least three stages of decomposition.
### Table 4. Chemical composition of the ash of the studied coal samples (wt%).

| Coal sample No. | SiO₂  | Al₂O₃ | Fe₂O₃ | CaO  | MgO  | TiO₂ | Na₂O | K₂O  | P₂O₅ | SO₃ | I₀  |
|----------------|-------|-------|-------|------|------|------|------|------|------|-----|-----|
| L              | 41.0  | 30.5  | 6.9   | 5.4  | 4.1  | 1.1  | 2.2  | 2.1  | 3.8  | 2.9 | 0.29|
| LG             | 40.2  | 33.4  | 6.3   | 4.5  | 3.8  | 1.5  | 1.6  | 1.6  | 2.8  | 4.3 | 0.24|
| G              | 24.7  | 40.8  | 5.4   | 7.5  | 4.3  | 1.0  | 1.8  | 1.1  | 8.0  | 5.4 | 0.31|

### Table 5. Results of thermogravimetric analysis of coal samples

| Coal sample No. | Tₘₐₓ, °C | Vₘₐₓ, % /min | Δm, wt. %, at temperatures, °C | 20-160 | 160-300 | 300 - Tₘₐₓ | Tₘₐₓ - 600 | 600-800 | 20-1000 |
|----------------|----------|--------------|-------------------------------|--------|----------|-------------|------------|--------|---------|
| L              | 444      | 2,11         | 2,0                          | 1,3    | 10,1     | 14,9        | 6,3        | 37,3   |         |
| LG             | 448      | 2,67         | 2,4                          | 0,7    | 11,2     | 15,6        | 6,0        | 37,6   |         |
| G              | 458      | 2,67         | 1,0                          | 0,4    | 11,8     | 14,6        | 5,7        | 36,4   |         |

The first stage - up to a temperature of 160 °C - is mainly due to the desorption of hygroscopic moisture. The data on the amount of moisture, calculated from the results of thermogravimetric analysis, generally agree with the values determined by the standard method (Table 2).

In the temperature range of 160-300 °C in all coal samples, there is an insignificant weight loss due to the processes of dehydration and decarboxylation of oxygen-containing functional groups. The largest weight loss in this temperature range is possessed by the sample of grade L, which is characterized by the highest content of heteroatoms (Table 2) and oxygen-containing functional groups (Table 3) in its organic matter.

The second stage in the temperature range of 300-600 °C is determined by the decomposition of fragments that form the basis of the organic mass of coals, due to the destruction of carbon-carbon bonds with the release of volatile products and the formation of semi-coke. The sample of long-flame coal is characterized by a lower thermal resistance - the maximum of the main decomposition of organic matter is shifted to the region of lower temperatures. With an increase in the genetic maturity of coals, the temperature at the inflection point (Tₘₐₓ) increases from 444 to 458 °C.

The third decomposition interval, located in the zone of higher temperatures (600-800 °C), is obviously associated with the structuring of the carbon residue, proceeding with the release of low-molecular gases (CO, H₂, CH₄, etc.).

To assess the chemical-technological potential of coals, the yield of semi-coking products was determined, the results of which are shown in Table 6.

### Table 6. The yield of semi-coking products of the studied coal samples

| Coal sample No. | Semi-coke sK | Resina Tₖ | pyrogenic water Wₖ | Gas and losses Gₖ |
|----------------|--------------|------------|-------------------|-------------------|
| L              | 67,2         | 10,1       | 7,7               | 15,0              |
| LG             | 70,0         | 12,1       | 7,3               | 10,7              |
| G              | 70,3         | 13,4       | 7,0               | 9,3               |

The above analytical data show that when using grade D coal, the least amount of semi-coke and tar is formed, but the highest yield of pyrogenic water and gaseous substances is noted. The release of a more significant amount of vapor-gas products is explained by the presence in the organic mass of
this sample of a larger number of heteroatoms (table 2) and oxygen-containing functional groups (table 3).

The characteristics of the semi-coking resins are given in Table 7. It can be seen that, in addition to the C and H atoms, the organic mass of the resins contains heteroatoms O, N, and S. The resin obtained from a coal sample of grade D has the highest atomic ratio H/C and O/C. The semi-coking resin obtained from a sample of G grade coal is characterized by a slightly lower content of heteroatoms (O + N + S) in its composition. When determining the component composition, it was found that this pyrolysate contains the largest amount of high molecular weight hydrocarbons in the form of asphaltenes and resinous substances. The semi-coking resin obtained from a coal sample of grade L contains the largest amount of oil fraction (Table 7).

### Table 7. Characteristics of semi-coke resins from the studied coal samples.

| Resin sample code | Elemental composition, % per daf | Atomic ratio | Component composition of resin, % |
|-------------------|---------------------------------|--------------|----------------------------------|
|                   | C  | H  | (O + N + S) | H/C | O/C | oils | resins | asphaltenes |
| L                 | 80.2 | 8.9 | 10.9 | 1.33 | 0.10 | 29.3 | 59.1 | 11.6 |
| LG                | 82.4 | 8.9 | 8.7  | 1.30 | 0.08 | 25.8 | 62.4 | 11.8 |
| G                 | 84.0 | 8.8 | 7.2  | 1.26 | 0.06 | 20.2 | 67.3 | 12.5 |

### 3. Conclusion

Using a complex of chemical and physicochemical methods of analysis, three samples of low-metamorphosed coals have been characterized. The coals are low-sulfur, medium ash with a low ash basicity. Petrographic analysis showed that the studied coal samples are predominantly vitrinite (vitrinite components contain more than 70%). The investigated samples are characterized by a rather significant yield of semi-coking resin, gaseous and highly volatile substances. According to the established technological indicators, these coals can be recommended for energy and technological use, for example, in the process of semi-coking in order to obtain solid and liquid hydrocarbon products.

### 4. References

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