Physicochemical properties of microcomponents of the Kuznetsk Basin coals

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Abstract. Coals are heterogeneous in nature, and they most often combine different amounts of three macerals - vitrinite, liptinite and inerinite. Vitrinite, which is responsible for the caking capacity of coal, solubility in organic solvents, mechanical properties, etc., is of decisive importance for the technological properties of coal raw materials. This paper presents the results of a study of vitrinite concentrates isolated from coal of the Kuznetsk coal basin. Using chemical and physicochemical methods of analysis (technical and elemental analyses, IR and 13C NMR spectroscopy, etc.), analytical data were obtained reflecting the change in the composition of their organic mass from the degree of coalification. It was found that with an increase in the stage of metamorphism in vitrinite concentrates, the yield of volatile substances (Vdaf) decreases, the carbon content increases from 82.2 to 88.5% and, accordingly, the content of oxygen and heteroatoms in the organic mass decreases from 11.8 to 6.2%.

1. Introduction
The variety of properties of fossil coals is largely determined by their microcomponent (maceral) composition and stage of metamorphism. Of the four groups of microcomponents (vitrinite, semivitrinite, inerinite and liptinite) that compose the organic matter of coal, vitrinite and inerinite are of decisive importance for the technological properties. Vitrinite is a gelificated component responsible for the caking capacity of coals, solubility in organic solvents, moisture content, ash content, mechanical properties, etc. Inerinite is a substance with a clearly distinguishable woody cellular structure, a sooty or fibrous structure. The organic matter of inerinite is more aromatized, has an increased (relative to vitrinite) degree of condensation of carbon nets, does not pass into a plastic state and does not produce liquid products of thermal destruction [1-3].

To study the chemical, physical and chemical-technological properties of coals and individual components, concentrates of macerals are isolated, using separation methods in heavy liquids. As a rule, in the general case, when coal is stratified, the organic part of the lightest fractions is enriched with macerals of the liptinite group and the vitrinite group, while in the organic part of the heavy coal fractions, macerals of the inerinite group are mainly concentrated [4-6]. It should be noted that the chemical and technological properties of coals are mainly determined by the properties of the vitrified components of their organic mass.

The purpose of this work is to study the material composition and physicochemical properties of coal fractions with a density of less than 1.30 g / cm³.
2. Results and discussion

Eight coal samples of various stages of metamorphism were used as objects of study, from which fractions with a density of less than 1.30 g/cm³ were isolated. To isolate them, we used the method of fractional analysis of coals (GOST 4790-80), the essence of which is the stratification of the fuel under study into fractions in liquids of different densities. The separation was carried out in a mixture of carbon tetrachloride and benzene at a decreasing solution density: 1.40 and 1.30 g/cm³. The choice of solution densities was determined by the fact that the maximum content of vitrinitized inclusions is concentrated in fractions floating up in liquids with a density of <1.30 g/cm³ [5-9].

Coal fractions with a density <1.30 g/cm³ with a particle size of less than 0.2 mm were subjected to analytical studies. Technical analysis was carried out using standard methods. The composition of organic matter was determined by elemental analysis.

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.

IR spectra were recorded on an Infralum-FT-801 Fourier spectrometer in the range of 400-4000 cm⁻¹ [10]. When determining the optical density of the bands, a straight line drawn between the transmission maxima in the region of 650 cm⁻¹ and 1800 cm⁻¹ was taken as the baseline. Then the optical density was normalized to the optical density of the band in the region of 1450 cm⁻¹ [11, 12].

High-resolution solid-state ¹³C NMR spectra were recorded on a Bruker Avance III 300 WB instrument using standard proton decoupling magic angle spinning cross polarization (CPMAS) at 75 MHz with contact time 1500 μs, accumulation of 4096 scans, delay between scans 2 s, sample rotation frequency 5 kHz. To obtain quantitative data, the spectra were modeled using the Dmfit program. Ranges corresponding to the resonance absorption of the following groups of carbon atoms, ppm, were distinguished on the spectra: 187-171 - carbon atoms of carboxyl groups and their derivatives (СООН); 171-148 - carbon atoms of aromatic systems associated with an oxygen atom (СаrО); 148-93 - carbon atoms of aromatic systems with a substituted and unsubstituted hydrogen atom (Саr + СНар); 67-51 - carbon atoms of methoxyl groups (OCH₃); 51-0 - carbon atoms of alkyl fragments (Сₐлk). The degree of aromaticity is \( f_0 = \frac{С_аr + С_Наr}{С_аr + С_Наr + С_ₐлk} \).

| Sample code | Petrographic parameters, % | Vitrinite reflection index | Stage of metamorphism |
|-------------|-----------------------------|----------------------------|-----------------------|
| 1           | 96                          | 1                          | I                     |
| 2           | 92                          | 1                          | I-II                  |
| 3           | 95                          | 1                          | II                    |
| 4           | 92                          | 2                          | II                    |
| 5           | 78                          | 2                          | II-III                |
| 6           | 79                          | 6                          | III-IV                |
| 7           | 75                          | 15                         | IV                    |
| 8           | 81                          | 7                          | IV                    |

The characteristics of coal samples are given in Tables 1 and 2. Analytical data show that samples of different stages of metamorphism from I to IV were studied, the vitrinite reflectance \( R_{о,r} \) varies from 0.63 to 1.41%. All studied objects are low-ash \( (A^d <5\%) \). With an increase in the value of the vitrinite reflectance in coal samples, the yield of volatiles \( (V_{daf}) \) decreases, the carbon content increases from 82.2 to 88.5% and, accordingly, the content of oxygen and heteroatoms in the organic mass decreases from 11.8 to 6.2%. Against the background of an increase in the carbon content in coal samples, the \( Q_{daf} \) value increases from 34.12 to 36.08 MJ/kg.
Table 2. Characteristics of the studied samples.

| Sample code | Technical analysis, % | Elemental composition, % per daf (dry, ash-free) | Atomic ratio | Higher caloric value, $Q_{sdaf}$, MJ/kg |
|-------------|-----------------------|-------------------------------------------------|--------------|---------------------------------------|
|             | $W^0$ | $A^d$ | $V^d$ | $C$ | $H$ | $(O+N+S)$ | $H/C$ | $O/C$ | |
| 1           | 1.9   | 3.6   | 43.0 | 82.2 | 6.0 | 11.8 | 0.88 | 0.11 | 34.12 |
| 2           | 1.1   | 2.8   | 42.2 | 83.2 | 6.0 | 10.8 | 0.87 | 0.10 | 34.57 |
| 3           | 0.9   | 4.9   | 39.1 | 85.3 | 6.0 | 8.7  | 0.84 | 0.08 | 35.51 |
| 4           | 0.9   | 4.6   | 36.2 | 85.7 | 5.9 | 8.4  | 0.83 | 0.07 | 35.55 |
| 5           | 0.8   | 4.4   | 35.7 | 86.3 | 5.8 | 7.9  | 0.81 | 0.07 | 35.69 |
| 6           | 0.5   | 1.4   | 22.5 | 88.7 | 5.3 | 6.0  | 0.72 | 0.05 | 36.08 |
| 7           | 0.5   | 1.7   | 22.6 | 88.6 | 5.3 | 6.1  | 0.72 | 0.05 | 36.03 |
| 8           | 0.8   | 1.5   | 21.5 | 88.5 | 5.3 | 6.2  | 0.72 | 0.05 | 36.00 |

The dependences of technological parameters (volatile matter yield $V^d$ and higher heat of combustion $Q_{sdaf}$) on the vitrinite reflectance are shown in Figures 1 and 2. As expected, the volatile matter yield is closely related to the stage of coal metamorphism, and this relationship is described by a first-order regression equation (Figure 1). The relationship of the highest calorific value of vitrinite concentrates is described by the second degree regression equation (Figure 2).

![Figure 1](image1.png)  
**Figure 1.** Relationship between the vitrinite reflectance index ($R_o$, $r$) and the volatile matter yield ($V^d$) of coal fractions with a density less than 1.30 g/cm$^3$.

![Figure 2](image2.png)  
**Figure 2.** Relationship between the vitrinite reflectance index ($R_o$, $r$) and the higher calorific value ($Q_{sdaf}$) of coal fractions with a density less than 1.30 g/cm$^3$.

By the method of IR-spectral analysis, the peculiarities of the molecular composition of vitrinite fractions have been established, which are characterized by the following frequency absorption regions: oxygen $-$OH (band 3400 cm$^{-1}$) and C-O (bands in the region of 1260-1050 cm$^{-1}$); aromatic $-$C= C (bands 3040, 1600, 900-700 cm$^{-1}$); aliphatic - CH$_2$ and CH$_3$ (bands 2920, 2860, 1450, 1380 cm$^{-1}$). However, the intensity of the bands in the IR spectra is different. The highest content of aliphatic groups - CH$_2$ and CH$_3$ (bands 2920, 2860 cm$^{-1}$) is contained in samples of the middle stage of metamorphism with vitrinite reflectance ($R_o$, $r$) from 0.82 to 0.98%. The highest content of aromatic structures is contained in samples with $R_o$, $r$ $> 1.27%$.

The ratio of optical densities at 2920 and 3040 cm$^{-1}$ (parameter $D_{2920}/D_{3040}$) is often used as a characteristic of the degree of aromaticity of coals [13–15]. Figure 3 shows that this indicator changes for the studied samples in direct proportion to the vitrinite reflectance $R_o$, $r$, the correlation coefficient is 0.947. Coal sample No. 8 has the highest degree of aromaticity, which is consistent with its chemical and technological parameters - the lowest yield of volatile substances ($V^d$) and atomic ratio (H/C)
It should be noted that the release of volatiles from the studied coals correlates with the structural parameter \(D_{3040}/D_{2920}\) (Figure 4).

Figure 3. Change in the intensity ratio of the \(D_{3040}/D_{2920}\) bands in IR spectra of vitrinite concentrates versus their vitrinite reflectance \((R_o, r)\).

Figure 4. Relationship between the yield of volatile substances \((V_{daf})\) of vitrinite concentrates and changes in the intensity ratio of the \(D_{2920}/D_{3040}\) bands in their IR spectra.

The change in the degree of aromaticity of the investigated fractions, determined on the basis of the analysis of the intensity of the bands in their IR spectra, is confirmed by the data of \(^{13}\text{C}\) NMR spectroscopy, the results of which are shown in Table 3.

Table 3. Parameters of the fragmentary composition of coal samples according to \(^{13}\text{C}\) NMR spectra.

| Sample code | Distribution of carbon atoms by structural groups, rel. % |
|-------------|----------------------------------------------------------|
|             | CH1 CH2 CH1O C\text{alk}O C\text{al}H + C\text{ar} | C\text{ar}O COOH | \(f_o\) |
|             | ppm ppm ppm ppm ppm ppm ppm ppm ppm ppm ppm ppm ppm ppm |
| 1           | 5.12 23.48 2.96 0.84 63.17 3.49 0.76 0.69 |
| 2           | 5.31 24.36 1.99 0.54 62.51 4.96 0.33 0.68 |
| 3           | 6.72 23.73 0 0 65.12 3.96 0.48 0.68 |
| 4           | 7.06 21.48 0 0.01 67.04 4.13 0.28 0.70 |
| 5           | 7.52 21.35 0 0.16 67.46 3.24 0.26 0.70 |
| 6           | 5.00 12.83 0 0.16 79.07 2.56 0.38 0.82 |
| 7           | 5.55 11.60 0 0.41 80.03 2.19 0.21 0.84 |
| 8           | 4.91 10.62 0 0.21 81.91 2.21 0.14 0.86 |

Analysis of the data obtained showed that with an increase in the stage of metamorphism (an increase in the \(R_o, r\) index, Table 2), the aromaticity index \(f_o\) of the studied samples increases from 0.69 for sample No. 1 to 0.86 for sample No. 8. The increase in the aromaticity index is associated with a decrease in the amount of aliphatic carbon in the structural fragments in the range of 0-51 ppm, while the decrease in the proportion of aliphatic carbon occurs mainly due to \(\text{CH}_2\) fragments in the range of 25-51 ppm. (Table 3).

3. Conclusion

The density fractionation method was used to assess the material composition of 8 coal samples of various stages of metamorphism. Petrographic analysis has shown that the maximum content of vitrinite gelificated substances is concentrated in coal fractions with a density of less than 1.30 g/cm\(^3\).

Using chemical and physicochemical methods of analysis (technical and elemental analyzes, IR and \(^{13}\text{C}\) NMR spectroscopy, etc.), analytical data were obtained reflecting the change in the composition of the organic mass of the lightest coal fractions from the degree of their coalification, expressed by the vitrinite reflectance index.
It has been established that with an increase in the stage of metamorphism of coal fractions, the yield of volatiles \((V_{\text{daf}})\) decreases, the carbon content increases from 82.2 to 88.5\% and, accordingly, the content of oxygen and heteroatoms in the organic mass decreases from 11.8 to 6.2\%. Against the background of an increase in the carbon content in coal samples, the \(Q_{s,\text{daf}}\) value increases from 34.12 to 36.08 MJ/kg.

The IR and \(^{13}\text{NMR}\) spectroscopy data show that with an increase in the vitrinite reflectance value, the aromaticity index \(\alpha\) of the studied samples increases from 0.69 for sample No. 1 \((R_o, r = 0.63\%)\) to 0.86 for sample No. 8 \((R_o, r = 1.41\%)\). The increase in the aromaticity index is associated with a decrease in the amount of aliphatic carbon in the structural fragments in the range of 0-51 ppm, while the decrease in the proportion of aliphatic carbon occurs mainly due to \(\text{CH}_2\) fragments in the range of 25-51 ppm.

4. References

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