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Intensification of Coal Liquefaction Process with the Help of Mechanical Activation

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Abstract

The results of investigation of the effect of mechanochemical treatment of coal under the shock-shear action on coal liquefaction process in a hydrogen-donor solvent are presented. In order to explain the choice of coal raw material most easily subjected to mechanical activation and thermal dissolution, the investigation was carried out with vitrinite concentrates of brown and black coal samples with different degree of metamorphism of technological grades D, G, Zh, K (R_0 = 0.4–1.25 %). It was shown that liquefaction of mechanochemically activated coal not only results in an increase in the yield of liquid products of the transformation of the organic matter of coal samples but also in substantial changes in their qualitative composition.

INTRODUCTION

Coal remains the main organic fuel in modern world because its resources are much larger than those of oil and natural gas. Intense consumption of oil and natural gas, with their limited resources, provide inevitable increase in the scale of coal consumption, among other purposes, as one of the alternative sources for the production of liquid petrol and various chemicals.

The Kuznetsk coal basin is the largest and the most unique basin of Russia in resources and grade composition of mined coal kinds; they vary from brown and candle coal to anthracite. The major part of mined coal is used for power engineering and for coking; however, at present an increasing interest to the search for effective coal-chemical technologies aimed at obtaining liquid hydrocarbons appears.

One of the alternative methods of coal liquefaction is thermal dissolution in hydrogen-donor solvents allowing one to obtain a wide range of oil-like products under relatively mild conditions. However, due to the absence of catalysts and gaseous hydrogen, as a rule, the characteristics of this process are not competitive with some other processes, for example hydrogenation [1, 2]. Because of this, one of the possible methods to increase the efficiency of thermal dissolution of coal may be preliminary low-temperature activation. Among the known methods of coal modification [2] (mechanical activation, alkylation, halogenation, oxidation, *etc.*) the most suitable one from the economical and technological viewpoints is likely to be mechanical activation. The mechanical activation of coal brings substantial changes in its composition and properties [2–5]. The direction and degree of structural and chemical transformations of the organic mass of coal depend both on the kind and intensity of mechanical energy transferred, and on the characteristics of coal itself. At present, the design of highly productive high-energy activator mills (tens *g*) has been developed and their production has been established; these mills are intended not only for grinding but also for rendering new properties increasing the reactivity of a material to be dispersed [6, 7].

EXPERIMENTAL

In order to explain the choice of coal raw material most easily prone to mechanochemical activation and thermal dissolution, and in order to eliminate the effect of petrographic heterogeneity, the investigation was carried out with vitrinite concentrates of brown and black coal of the Kuznetsk basin, grades D, G, Zh, K. The concentrates were isolated sequentially by hand and by separation on the basis of density in a mixture of carbon tetrachloride and benzene. The characteristics of vitrinite concentrates (95–98 % of the major component) are listed in Table 1.

Mechanochemical treatment of coal was carried out for 10 min in AGO-2 activator mill of planetary centrifugal type in the medium of tetralin. Tetralin was chosen as a paste-former because it is widely used as a model hydrogen-donor solvent of oil or coal origin. The mass fraction of the solid phase in the mixture was 50 %. Steel balls 8 mm in diameter were used as the activating bodies; centrifugal acceleration was 60 *g*. A cylinder 100 cm^3 in volume was used; 1/3 of its volume was filled with the balls and 1/3 with the sample to be treated. Such a charge corresponds to the shock-abrasive mode of operation and provides the maximal effect of the milling bodies on the sample under investigation. The cylinders were cooled with water during operation to exclude substantial heating of the material under treatment.

After mechanical treatment, coal samples were subjected to deep extraction with benzene, dried, then mixed with a fresh portion of tetralin and exposed to thermal dissolution. Thermal dissolution of the initial and modified coal samples was carried out in micro-autoclaves with a volume of 10 ml using non-isothermal procedure [8]: temperature range, 300–450 °C; coal mass, 2 g; coal to tetralin ratio, 1 : 2; medium, inert gas; heating rate, 2.5 °C/min. When the required temperature was achieved, the process was interrupted by sharp cooling of the micro-autoclave with cold water. The analysed parameters were: the degree of conversion of the organic coal mass (OCM), determined from the ash content of the initial sample and the solid residue after liquefaction, and the yield of asphaltenes in the liquid product [9]. Deviations between determinations of the same type did not exceed 3 abs. %.

RESULTS AND DISCUSSION

It was established that mechanochemical treatment in tetralin medium promotes an increased yield of extractable substances from all the coal samples investigated. The yield of the additional amount of soluble products was 8–12.5 % as a mean; it was much higher than the amount of substances extracted from the initial coal samples. These data are in good agreement with the results obtained by other authors [3, 4] and confirm high efficiency of mechanochemical treatment under the selected conditions.

The results of thermal dissolution of the initial and modified coal samples are shown in Fig. 1. It should be noted that the dependence of conversion degree on temperature exhibits an identical S-shaped behaviour for all the coal samples; such a shape is characteristic of non-isothermal method. Up to 300 °C the degree of

TABLE 1

Characteristics of vitrinite concentrates

Coal grade	R_0, %	Technical analysis, %		Elemental composition, % daf					Atomic ratio	
		A^d	V^{daf}	C	H	O	N	S	H/C	O/C
B	0.41	11.8	48.6	71.8	5.5	21.8	0.9	0.3	0.91	0.23
D	0.63	2.2	41.6	77.2	5.4	14.6	2.6	0.2	0.85	0.14
G	0.73	1.9	40.8	79.5	5.5	11.8	3.0	0.2	0.83	0.11
Zh	0.98	4.1	34.6	86.2	5.7	4.3	3.3	0.5	0.80	0.04
K	1.25	1.8	24.4	88.1	5.1	4.1	2.5	0.2	0.69	0.03

Note. R_0 is reflection index of vitrinite (an optical parameter characterizing the degree of metamorphism of coal); A^d, V^{daf} are ash content and the yield of volatiles, calculated per dry (d) and dry ash-free (daf) mass, respectively.

conversion is insignificant; as a rule, it does not exceed the yield of alcohol-benzene extracts form the initial coal samples [10]; this means that mainly extraction of the soluble substances with tetralin occurs within this temperature range; no noticeable depolymerization of the macromolecular part of the OCM occurs. Further temperature rise causes a sharp increase in the conversion degree; at a temperature of 350–400 °C, corresponding to the start of intensive decomposition of OCM, the rate of thermal dissolution (an increase in conversion rate) reaches the maximal value. At 425–450 °C, an increase in conversion degree becomes minimal due to exhausted reactive part of the organic coal mass.

In comparison with the results of thermal dissolution of initial coal, the degree of conversion of mechanically activated samples increases in the high-temperature range by 4–12 % as a mean. However, within the low-temperature region (300–350 °C) we observe only insignificant changes in conversion degree (see Fig. 1). It should be noted that the maximal increase in conversion degree is observed for the coal of grades B, D and G; an increase in conversion rate is smaller for coal samples with increased metamorphism stage (Fig. 2). This is likely to be caused by the presence of a large amount of macromolecular fragments prone to mechanical destruction in the structure of low-metamorphized coal samples.

Minimal changes of the conversion degree of mechanically activated samples in the low-temperature range are explained by the removal of soluble coal components during preliminary extraction; both the components present in the initial samples (bitumoids) and those newly formed during mechanical destruction are removed by extraction. The macromolecular part of the OCM remaining after mechanical treatment and complete extraction with benzene is likely to contain stronger bonds; therefore, thermolysis of these bonds occurs at higher temperature.

At the same time, a new supramolecular and molecular structure of OCM is likely to be formed during mechanical activation in tetralin medium due to the rupture of the weakest carbon-carbon and carbon-oxygen bonds]2, 3] and stabilization of the formed coal radicals by

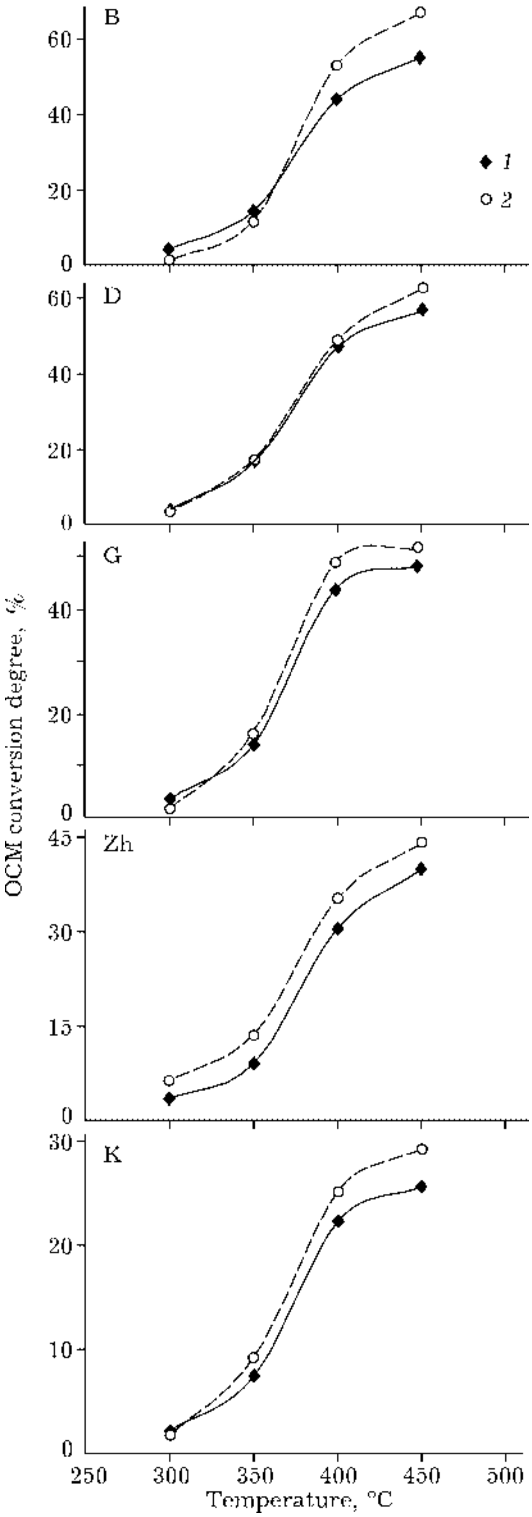

Fig. 1. Dependence of conversion degree of the OCM on temperature of thermal dissolution process for the coal samples of different metamorphism degree values: *1* – initial coal, *2* – mechanically activated sample.

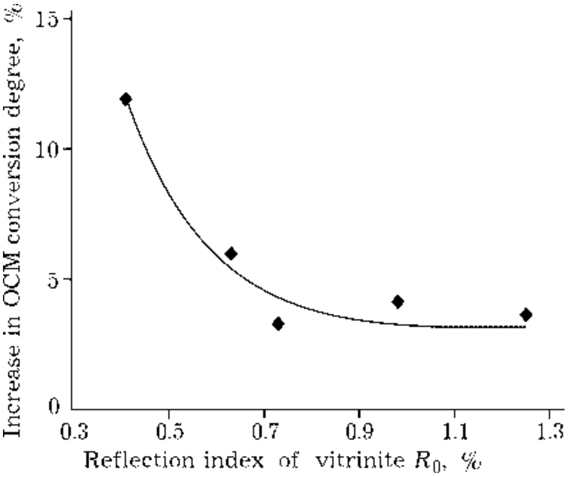

Fig. 2. Increase in the OCM conversion degree during thermal dissolution (450 °C) of mechanically activated carbon.

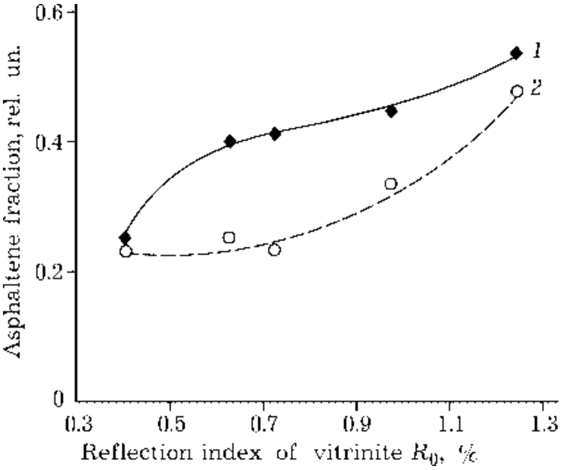

Fig. 3. The fraction of asphaltenes in the products of thermal dissolution of the initial (*1*) and mechanically activated (*2*) coal.

hydrogen of the solvent; this structure prevents polycondensation processes during thermal dissolution. As a result, the final degree of conversion into liquid products at 450 °C increases in comparison with the initial samples.

Together with an increase in the final coal conversion degree during thermal dissolution after mechanical activation in tetralin, we observe changes in the group composition of the formed liquid products. For all the coal samples, the fraction of asphaltenes in the liquid products of thermal dissolution decreases (Fig. 3), which is the evidence of deep destruction of coal macromolecules under intense mechanical action.

CONCLUSIONS

Thus, a principal possibility to intensify liquefaction processes in coal samples of different metamorphism degree from the Kuznetsk Basin by means of preliminary mechanochemical activation in tetralin is demonstrated. The highest effect of mechanical activation is exhibited during thermal dissolution of low-metamorphized coal samples. With an increase in metamorphism degree ($R_0 > 1.0$ %), the effect of mechanical treatment weakens, which is likely to be due to the strengthening of the structure of initial coal samples within the metamorphism sequence.

The data obtained in the investigation are of practical interest for the development of conditions of mechanochemical action and for choosing the coal raw material in order to increase its reactivity and obtain the products of the required composition. The formation of an additional amount of liquid products after mechanical activation of coal in the medium of hydrogen-donor solvent can be used to develop the processes aimed at an increase in the quality of combined fuel oil – mixtures of coal and heavy petroleum residue. By subjecting coal to intense mechanochemical treatment one may increase the content of liquid hydrocarbon fractions in the suspension ready for combustion.

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