Mechanochemical brown coal destructuring to produce humic species

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Abstract. The research data on the mechanical destruction of brown coal in the presence of an oxidizing agent are reported in the present paper. The study object is brown coal specimens with high (more than 30%) and low (less than 10%) initial contents of humic acids. The mechanochemical oxidation efficiency was evaluated by a change in the inorganic component content and in the yield of humic acids as the organic component in the ash composition. Hydrochloric acid solutions of 1-5% concentration were used as an oxidizing agent. Oxidation was considered and carried out as a raw material pretreatment with its subsequent processing to produce humic species, mechanical activation was introduced into the flowsheet for brown coal processing in view to foster interaction between solid particles and the reagent. The data obtained indicate the effectiveness of this process in terms of both increasing the yield of humic acids, and reducing the ash content in the prepared coal.

1. Introduction

Coals are the conventional natural resource of prime importance in the fuel-and-energy industry, but their unique properties make them of great scientific interest as a valuable natural raw material for chemical industry.

Nowadays challenge in investigation into coal properties deals with development of novel processing techniques and intensification of traditional ones in fuel and not fuel coal utilization trends. One of recent research trends in this field is application of physical fields at both raw coal processing and direct production of coal-based products. The Federal Special-Purpose Program “Economic and Social Development of the Far East and Baikal Regions for the period till 2025 ” makes provision for special orientation of investment projects, including the comprehensive processing of primary resources along with modernization and development of up-to-date processing plants [1], just confirming the actuality of research projects dealing with the search for highly efficient processing techniques enabling to involve local natural resources into profitable industrial utilization.

Mechanical destructuring of solid anthracides in view to improve efficiency of their processing is reposed on formation of new surfaces of a solid substance in the grinding process. Realization of the mechanical effect in the presence of chemical agents capable to react with new-formed solid surface stimulates higher rates of chemical reactions.

Mechanochemical activation is one of advanced mineral processing trends, intended to improve the yield of a target product from natural organic materials and to commercialize the comprehensive processing technologies.
It is known that the mechanical activation of solid fuels leads to global alterations in structure of their organic substance, viz., formation of uncompensated links, radicals, dynamic active centers and specific orientation of destructured molecules of the coal substance.

In particular, mechanoactivation of turfs allows modification of their molecular structure owning to reduction in molecular mass, increase in content of functional groups and higher bio-accessibility. Mechanoactivation of turfs is widely used to produce humic acids [2]. Mechanoactivation of brown coals is practiced to higher the humic acids yield [3], as well as an effective coal preparation for thermal hydrogenation to produce toluene-soluble products [4]. Mechanical activation of coal in a fine grinding operation is good in coal-burning process, as it increases the reactive power of the fuel [5].

The mechanochemical modification based on the solid-phase transformations of species with the application of special agents is one of efficient methods for on-target alteration of the fragment composition of humic acids. Therefore, efficiency of alterations, resulted from the mechanochemical activation can be assessed by a change in the yield of humic acids.

2. Laboratory experiment results

Investigation into alteration of brown coal properties under mechanoactivation was carried on two specimens. The first brown coal specimen of 2B brand, originated from Kangalass deposit, Republic of Sakha, Yakutia, is characterized by the high initial yield of humic acids. Its specifications are humidity being $W^d = 13.8\%$, ash content being $A^d = 7.4\%$, yield of volatiles being $V^d = 46.2\%$, yield of free humic acids $(HA)_{gf}^d$ under GOST 9517-94 amounting to 32.3 %. The second brown coal specimen of 2B brand from Kharanor deposit, Transbaikal Region, is specified with low initial yield of humic acids. Its specifications are $W^d = 14.4\%$, $A^d = 9.2\%$, $V^d = 45.6\%$, $(HA)_{gf}^d = 7.4\%$.

According to the experimental procedure the coal specimens were mixed with a chemical oxidizing agent and then subjected to wet grinding. The test coal specimen was preliminarily ground down to less than 2 mm in size. The test coal amount was 50 g in each experiment. Volume of chlorohydric acid addition was 30, 45, 60, 75 or 90 ml at acid concentration within 1–5 % (with 1 % step). Mechanoactivation was realized in FRITSCH planetary mill at rotation speed of 300 rpm. Mechanoactivation time was 10 min. After the mechanical activation coal was washed with water down to neutral reaction of washing water ($\text{pH} = 6$). Next the coal specimen was dried in the air, ground down to analytical coarseness and assayed.

Earlier we reported the detailed analysis of experimental mechanical activation results on Kangalass brown coal [3]. We followed the same procedure in the present research with certain variations, namely, the mechanoactivation time of 4, 10, and 16 min were added to above cited variable parameters. The results of the experiments reveal that:

– good correlation of reduction in ash content with volume, as well as concentration of an oxidizing agent. Factorial analysis and mathematical modeling of the process [3] made it possible to derive the regression equations of both linear two-factors and multi-factors types, which are capable to describe more than 80 % of the results on variations in ash content in coal under oxidation in the mechanical activation process.

– higher yield of humic acids indicates low consistency of the obtained results with the study parameters, but the general tendency to parameter growth is observed. Thereto, the second-order equation provides the most reliable description of the increase in the yield of humic acids in oxidation under mechanical activation is the most reliable factor according to the results of factorial analysis and mathematical modeling [3]. This equation considers all the acting factors with correlation factor $R = 0.626$ and reliably describes only 40 % of obtained experimental data.

Let neglect the effect of water volume, used for an oxidizing agent to obtain solution concentrations required for the mechanical activation process and consider correlation between the humic acid yield and a mass of an oxidizing agent in a test specimen. Therewith we average the experimental results on this factor. For example, such data smoothing collects a group of the results
involving: 90 ml of the oxidizer of 1 % concentration; 45 ml of the oxidizer of 2 % concentration; 30 ml of the oxidizer of 3 % concentration, because all these solutions contain the same HCl oxidizer mass amounting to 0.9g per 50 g of coal (or 18 g per 1 kg of coal). In the earlier analytical generalization of the research results these experiments fell in different groups [3].

The results of such experimental data processing show that the reduction in ash content in the specimens (Figure 1) is observed for oxidizer values up to 2.25 g per 50 g of coal specimen (or 45 g per 1 kg of coal). Moreover, sharp reduction in ash content takes place at values up to 0.75 g of НCl in a specimen (or 15 g per 1 kg of coal), the ash content runs down smoothly within the range from 0.75 to 2.25 g (or within 15–45 g per 1 kg of coal). Henceforth the reduction of ash content is not observed for both Kharanor and Kangalass coals.

![Figure 1. Variations in ash content with the use of mechanochemical activation of brown coal (□—Kangalass brown coal; ○—Kharanor brown coal).](image1)

The parameter of humic acid yield also has zones with different character of variations in specimens (Figure 2). In the case with Kangalass brown coal the zone of rather sharp reduction in humic acid yield is traced at up to 2.25 g of the oxidizer in the specimen (or 45 g per 1 kg of coal), further growth of oxidizer mass leads to reduction in humic acid amount. In the case with Kharanor brown coal the humic coal yield ascends at values up to 0.75 g (or 15 g per 1 kg of coal), hereafter the values of humic acid yield remain stable (neither reduction nor rise).

![Figure 2. Variations in the yield of humic acid with the use of mechanochemical activation of brown coal (□—Kangalass brown coal; ○—Kharanor brown coal).](image2)
The mathematical processing of experimental data enables to construct the following models of relationship between ash content and yield of volatile components versus oxidizer mass with the use of mechanochemical destructuring of brown coals:

1) in the presence of HCl of 0–2.25 g in mass per 50 g of coal specimen:
   — Kangalass brown coal:
   \[ A^d = -2.5587m + 12.7 ; \quad R = 0.837 \]
   \[ (HA)_{def}^f = 7.4863m + 32.3 ; \quad R = 0.876 \]
   — Kharanor brown coal:
   \[ A^d = -2.1709m + 9.2 ; \quad R = 0.785 \]
   \[ (HA)_{def}^f = 3.8098m + 7.4 ; \quad R = 0.718 \]

2) in presence of HCl of 0–45g per 1 kg of coal:
   — Kangalass brown coal:
   \[ A^d = -0.1279m + 12.7 ; \quad R = 0.837 \]
   \[ (HA)_{def}^f = 0.3743m + 32.3 ; \quad R = 0.876 \]
   — Kharanor brown coal:
   \[ A^d = -0.1085m + 9.2 ; \quad R = 0.785 \]
   \[ (HA)_{def}^f = 0.1945m + 7.4 ; \quad R = 0.718 \]

3. Conclusions

The processing of experimental data made it possible to determine the critical amount of the oxidizer providing the maximum reduction in ash content and the increased yield of humic acids. The relationships derived within the established oxidizer mass intervals are capable to describe minimum 50 % of experimental data \( (R > 0.71) \). The reported data justify the efficiency of mechanochemical destructuring process and feasibility of its application to prepare brown coals.

References

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