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Abstract

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ON THE PROCESS OF HALOGENATION OF COALS UNDER THE ACTION OF ULTRASONIC WAVES

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Questions of the halogenation of coals have recently become topical in connection with the fact that the extraction of rare elements from coals is carried out primarily by halogenating the latter. However, not only is precise information on the mechanism of halogenation lacking, but the methods proposed for carrying it out still remain rather ineffective. Thus, for example, the halogenation reaction of coals proceeds extremely slowly at atmospheric pressure and room temperature. A low percentage of bound chlorine or bromine is also given by methods providing for the halogenation process to be carried out under pressure and at a high temperature of the reaction mixture.

The process of halogenation of coals is heterogeneous. It occurs at the interface of two phases: solid coal—liquid or gaseous halogen. Naturally, more favorable conditions for halogenation can be ensured by methods of obtaining the solid phase in a state of greater dispersion—by increasing its total surface area. Along with this, the rate of the halogenation reaction should be affected by an increase in the chemical activity of the reacting halogen. These requirements are met to a considerable extent by the new method of coal halogenation that we have applied—the use of ultrasonic waves. Under the action of ultrasonic waves, the reaction of combination of halogens with coal is accelerated many times over, and the reaction yield is increased significantly.

In the present communication it will be shown that the bromination process proceeds under relatively mild conditions of insonation, i.e., at a comparatively low intensity of the ultrasonic waves. In addition, observations showed that under the action of ultrasonic waves the reaction with coal is accelerated not only for liquid bromine, but also for gaseous chlorine.

We used a piezoquartz ultrasonic generator. The source of the ultrasonic waves was a round piezoquartz plate; the diameter of the plate was 50 mm; the frequency of oscillations of the ultrasonic waves was 380 kc; their intensity was 8 W per 1 cm^2 of radiating surface. The contact liquid between the radiator and the object of insonation was water. The propagation of the ultrasonic waves was accompanied by the appearance of boiling or of a small fountain on the surface

of the water. A flask with the reaction mixture was immersed in the “ultrasonic” fountain. The penetration of ultrasonic waves into the vessel was evidenced by the rapid (almost instantaneous) degassing of the liquid being insonated and by ripples appearing on the surface of the liquid inside the flask. The distance of the reaction vessel from the radiator was 15–16 cm.

In the case of bromination, the reaction vessel contained 7 g of coal and 21 g of Br in 50 ml of distilled water. After insonation, the coal was filtered off on a Büchner funnel and washed with distilled water until the wash waters gave a negative reaction for bromine content. The quantity of ad-

the bromine bound to the coal was determined by a micromethod developed at the Institute of Fossil Fuels of the Academy of Sciences of the USSR: a coal sample of 6–12 mg is burned in a quartz tube in a stream of oxygen; the combustion products are trapped with a solution of KOH and H_2O_2, in which the bromine content is then determined by titration according to Folgard’ s method.

Table 1

Bromination of long-flame coal under the action of ultrasonic waves*

	Experimental conditions	Duration of bromination	Temp. in °C	W^a	A^c	C^r	H^r	Br_2
Initial coal	—	—	—	3.04	12.50	81.56	6.63	—
2 g coal and 27 g Br_2 in 50 ml water	Without sound	20 hr	0	1.78	3.82	42.3	2.75	50.84
Same	» »	7 min	20	2.91	11.68	73.7	5.79	2.68
» »	With sound	7 min	20	2.87	7.01	43.41	2.85	47.3

* W^a—moisture in coal, wt. %; A^c—ash of dry coal, wt. %; C^r—carbon in the combustible mass of coal, wt. %; H^r—hydrogen in the combustible mass of coal, wt. %; Br_2—bromine, wt. %, calculated on dry coal.

From the results of the study presented in Table 1 it is evident that in 7 min of bromination at room temperature 2.68 wt. % bromine is added to the coal

(calculated on dry coal), whereas with the same duration of bromination in the field of ultrasonic waves, 47.3 wt. % bromine is added. In 7 min of bromination at the indicated intensity of the ultrasonic waves, as much bromine is added to the coal as is added over 20 hr at 0° without sonication. In other words, the bromination process under the action of ultrasonic waves proceeds 160 times faster than under ordinary conditions.

Table 2

Chlorination of long-flame coal under the action of ultrasonic waves

Experimental conditions	Duration of chlorination, min	Amount of chlorine, wt. % (on dry coal)
Without sound	20	2.98
With sound	10	3.48
»	20	6.91

We carried out the chlorination of coals by slowly introducing gaseous chlorine into the reaction vessel—2 gas bubbles per second. With this method of passing the gas through the reaction mixture (7 g of long-flame coal in 50 ml of distilled water), 2.98 wt. % chlorine was added (on dry coal) (the amount of chlorine was determined by the micromethod described above). However, this percentage increases significantly if chlorination is carried out in the field of ultrasonic waves (Table 2).

As the table shows, with increasing duration of sonication the amount of chlorine that has reacted with the coal increases. In 20 min in the field of ultrasonic waves, almost 2.5 times more chlorine reacted than in the same interval of time without sonication.

What is the mechanism of the acceleration, established by us, of the processes of coal halogenation in the field of ultrasonic waves? It is known that ultrasonic waves have a dispersing action, caused most probably by mechanical forces arising during the formation and collapse of cavitation bubbles. Considerable mechanical forces also apparently develop when the frequency of pulsation of the gas bubbles formed coincides with the frequency of the ultrasonic oscillations (the phenomenon of resonance). However, long exposures to ultrasound are required for a noticeable dispersing effect to appear. In analyzing the facts described, it is necessary to take into account the possibility of the occurrence, according to the cavitation electrochemical theory of ultrasonic chemical

reactions—the possible appearance of activated halogen as a result of the dissociation of molecules in cavitation cavities. The possibility of dissociation of iodine molecules with their subsequent recombination in the field of ultrasonic waves was established as early as 1950 ([3]). It must also be borne in mind that in a cavitation cavity, as a result of the splitting of "activated" water molecules, products possessing an oxidizing action appear ([4,5]).

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Note: Figure translations are in progress. See original paper for figures.