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Production of nanoporous sorbents by partial steam-air conversion of charcoal

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Abstract. An effective sorbent is activated carbon having a developed nanoporous structure with an average pore diameter about 2-4 nm. Perspective method of activated carbon production is the partial steam conversion of the coal bed in boiler furnaces of power plants. The additional thermal energy is produced by burning the syngas. The aim of this work is to study the co-production of activated carbon and syngas by partial steam-air conversion of charcoal. Due to the presence of oxygen in the flow, intensification of conversion occurs. In the laboratory bed reactor, the mass loss curves and the syngas composition were obtained at temperatures of 800°C and 900°C. Two zones with different reaction mechanisms were identified on the height of the bed. The reactions between carbon and steam shift toward hydrogen formation in the oxygen zone. The dependence of the porous structure of the activated carbon on the conversion degree of the raw material is obtained. The maximum of micropores is formed at a conversion degree of 0.5. The material and energy balance of the partial conversion in the laboratory reactor was estimated.

1. Introduction

One of the global problems of our time is the increase in anthropogenic pollution of the environment. In this regard, there is a continuous tightening of environmental legislation. The development of technologies for purification of industrial emissions is actual. An effective sorbent is activated carbon having a large surface area due to numerous nanopores of less than 100 nm in size. In addition to the developed fields of activated carbon (AC) application – water purification, desulfurization of natural and industrial gases, heavy metal compounds capture [1, 2] , new technologies are being developed: mercury removal from flue gases in power plants [3-5] and CO_2 capture [6].

The main method of activated carbon producing is the steam conversion of the prepared raw material (coal) in horizontal rotary kiln at a temperature of 800-1000°C [7]. The steam conversion in the bed is more simple, but less productive. The producing activated carbon in boiler furnaces of power plants is a perspective method. It is partial steam conversion of the coal bed due to heating from the burning of the main fuel with afterburning of the exuding syngas that is used to receive additional thermal energy [8, 9].

Co-production of activated carbon and syngas requires additional research. In the studies of steam gasification under similar conditions [10, 11], the char characteristics are not considered. In studies [12, 13] dealing on the production of activated carbon, much attention is paid to the properties of solid residue, but syngas is not considered. Only completely investigation of steam conversion allows to estimate energy balance which is necessary for the designing industrial equipment.

Co-production in the presence of a K_2CO_3 catalyst was investigated in [14]. However, instead of a chemical catalyst, it is possible to use air oxygen. Oxygen volume concentration of 1-3% in the steam flow has a positive effect on the energy balance of the process and accelerates the pores formation in the char residue without significant changes in their size compared with pure steam conversion [7]. The aim of this work is to study the effect of operation mode at partial steam-air conversion of charcoal on the activated carbon characteristics and the syngas composition.

2. Materials and method

2.1. Raw material
The used raw material is industrial charcoal produced by pyrolysis of birch in a retort with external heating for 2 hours at an average temperature of 550°C. The size of coal is in the range from 5 to 30 mm. The raw material characteristics are shown in table 1.

Table 1. Proximate and ultimate analysis of the raw material (% mass).

W	A^d	V^d	FC^d	C^{daf}	H^{daf}	O^{daf}	N^{daf}
2.3	2.7	6.2	91.1	97.4	0.9	1.1	0.6

2.2. Conversion process

2.2.1. Experimental reactor
The steam conversion process was carried out in a laboratory fixed-bed reactor. The reactor is made of refractory bricks. It is a vertical cylindrical channel with an internal diameter of 60 mm and a height of 600 mm, heated by a resistance heater to the temperature up to 1000°C. The temperature at the wall and in the center of the reactor is controlled by chromel-alumel thermocouples. The heating power is regulated by an autotransformer. Superheated to 650-750°C steam is blown in the bottom of the channel, at a rate of 1 kg/h. Along with steam, air is supplied in the amount of 20% of the steam flow. The syngas formed during conversion is burning at the reactor outlet. The gas composition is measured by a Gamma-100 gas analyzer with a concentration measurements range, % vol.: O_2 0-100, H_2 0-100, CO 0-70, CO_2 0-30, CH_4 0-20.

2.2.2. Operating mode
The initial coal part weighing 200 g is loaded into the reactor and forms a 400 mm high bed on the grate. The coal is discharged into a tank filled with water after maintaining for a predetermined time. The produced AC is dried and weighed. The weight loss values and conversion degree are determined. The composition of the syngas is measured in 5 minutes during the entire time of each experiment.

Experiments were carried out for 20, 30, 45, 70 and 90 minutes at two temperatures: 800°C and 900°C to obtain the dependence of the mass loss on time. The particular experiment was carried out to measure the dependence of the syngas composition on the height of the bed. The sampling probe was placed on the grate of the reactor before the coal was loaded. The probe was gradually raised, and the gas composition was measured for 2 minutes at each stage.

3. Results and discussion

3.1. Conversion modes
The mass loss curves of the initial material are shown in figure 1. The mass loss rate at 900°C is twice as much at 800°C. The equilibrium composition of the syngas is calculated according to [15]. The experimental and equilibrium syngas compositions are shown in figure 2. The average compositions of the syngas remained constant throughout each experiment and practically coincided at temperatures of

800°C and 900°C. According to the calculation results, the difference in the syngas composition at 800°C and 900°C is less than 2%. Such small difference is comparable with the fluctuations in the gas composition recorded during the experiments, and explains the coincidence of the experimental results.
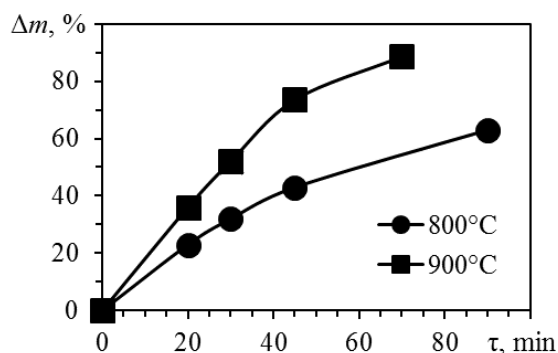

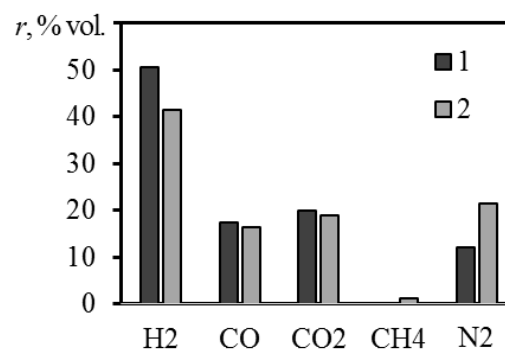**Figure 1.** The mass loss curves of the raw material at temperatures 800°C and 900°C.

Figure 2. Syngas composition at 900°C: 1 – calculated, 2 – experimental.

3.2. Porous structure of char

The surface area and volume of micro-, meso-, and macropores were determined by the Brunauer-Emmett-Teller method (BET) using nitrogen adsorption-desorption isotherms at 77 K, obtained with the Quantachrome Nova 1200e. The results of the analysis of samples are given in table 2.

Table 2. Characteristics of the char samples.

Sample number	Temperature, °C	Time, min	Conversion degree	Pores surface area, m^2/g	Pores volume, cm^3/g
1	-	-	0	97	1.05
2	800	30	0.30	528	1.49
3	800	45	0.43	715	1.61
4	800	90	0.63	785	1.72
5	900	20	0.35	641	1.52
6	900	45	0.74	854	1.80
7	900	70	0.89	928	1.96

Figure 3 demonstrates the obtained nitrogen desorption isotherms at 77 K for samples given in table 2. The dependence of the total volume and surface area of the micro- meso- and macropores on the degree of conversion at 800°C and 900°C calculated from the isotherms are presented in figure 4. If the conversion degree reaches values higher then 0.5, the intensity of combining micropores process increases, that reduces the micropores area and the growth rate of the total pores surface area.
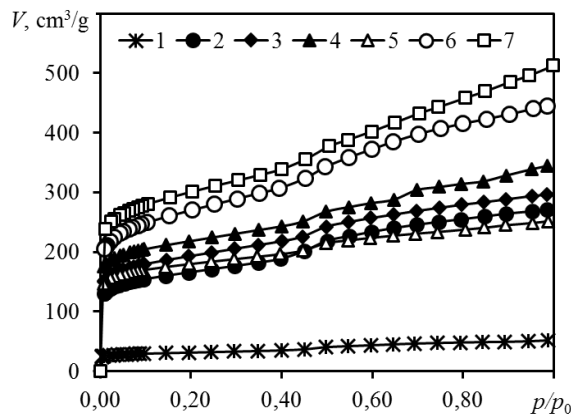
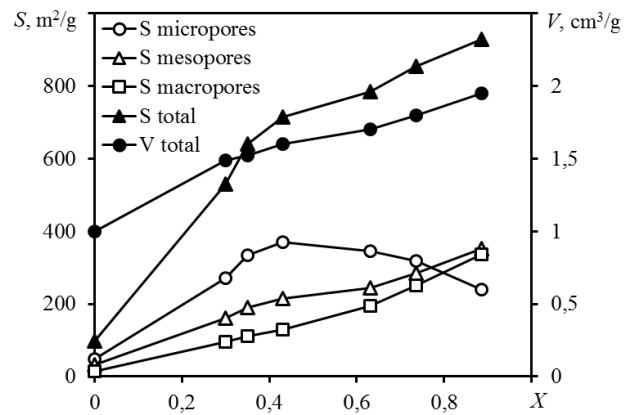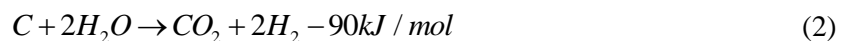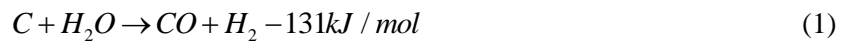**Figure 3.** Desorption isotherms for N_2 at 77 K for char samples.

Figure 4. The porous structure dependence on the conversion degree.

3.3. Material and energy balance estimation

The following reactions occur in the bed during the conversion process:

$$C + H_2O \rightarrow CO + H_2 - 131 kJ / mol \qquad (1)$$

$$C + 2H_2O \rightarrow CO_2 + 2H_2 - 90 kJ / mol \qquad (2)$$

$$C + 2H_2 \rightarrow CH_4 + 75 kJ / mol \qquad (3)$$

$$C + CO_2 \rightarrow 2CO - 172 kJ / mol \qquad (4)$$

$$C + O_2 \rightarrow CO_2 + 394 kJ / mol \qquad (5)$$

Reaction (2) occurs due to steam excess in the reactor.

The dependence of the syngas composition on the height of the bed obtained in the experiments (figure 5) shows that there are two zones with different reaction mechanisms. The boundary between the zones is at a level of about 10 cm. Reactions (1), (2) and (5) occur in the first zone (oxygen); if their products are summed up, then the ratio of $CO:CO_2:H_2$ is equal to 1:2:3, which is equal to the experimental data. In the second zone (reducing), reaction (1) takes place, the ratio of reaction products of which $CO:H_2$ is 1:1, since the experimental concentrations of H_2 and CO increase at the equal rate. The concentration of CO_2 is practically stable, indicating that there is no reaction (2) in the second reaction zone. The reaction (4) in this temperature range is an order of magnitude lower in comparison with the others reactions [7] and has no significant effect on the syngas composition.
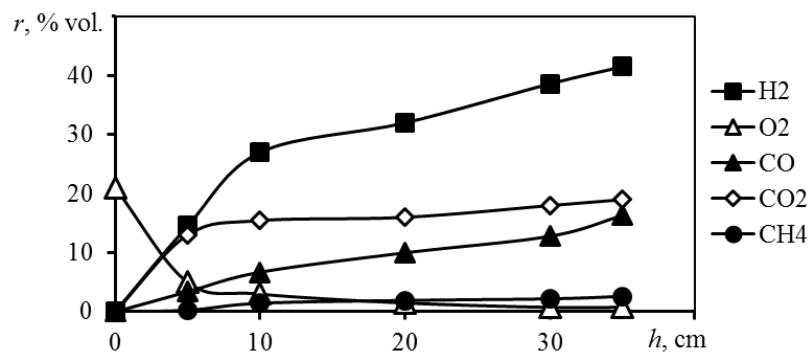

Figure 5. Changes in the syngas composition at the bed height at temperature of 900°C.

The proportions of the initial material taking part in each reaction are calculated from the final syngas composition. Taking into account the elemental composition of the initial material, it may be assumed with simplified estimation that the initial material contains only carbon. The fraction of carbon interacting in reaction (1) is equal to the fraction of CO in the syngas.

The oxygen content at the reactor inlet r_{O2}' is determined by the volume fraction of N_2 r_{N2}'' in dry syngas, and the ratio between nitrogen and oxygen in air:

$$r_{O2}' = 0.269 \cdot r_{N2}'' \tag{6}$$

All oxygen interacts with the carbon of the fuel on reaction (5), resulting in the formation of CO_2. The carbon fraction interacting in reaction (2) is as follows:

$$C_2 = r_{CO2}'' - r_{O2}' \tag{7}$$

The fraction of carbon interacting in reaction (3) is determined by the H_2 balance:

$$C_3 = 0.5 \cdot (C_1 + 2 \cdot C_2 - r_{H2}'') \tag{8}$$

The distribution of carbon on reactions (1)–(5), calculated by equations (6)–(8), is shown in figure 6. The syngas yield is determined by the amount of reacted fuel:

$$V_g = (r_{CO} + r_{CO2} + r_{CH4}) / C_{fuel} \tag{9}$$

The amount of unreacted steam is determined by the amount of incoming steam and dry syngas:

$$v_{H2O}'' = v_{H2O}' - (r_{H2} + 2 \cdot r_{CH4}) \cdot V_g \tag{10}$$

An amount of incoming air is calculated by:

$$v_{air} = V_g \cdot r_{N2} / 0,78 \tag{11}$$

In the energy balance calculation, all values are given per kilogram of fuel carbon. The heat of syngas combustion is used to compensate for the total thermal effect of chemical reactions and to heat the steam, air and fuel to the temperature in the reactor. The remaining energy represents the maximum possible heat loss.

The energy balance was evaluated for conversion case at a temperature of 900°C for 30 minutes. In this mode, the largest area of micropores in the activated carbon was obtained. Calculated by equations (9)–(11) syngas yield was 5.13 nm^3/kg of fuel, the share of transit steam was 65.8%, and the air blast ratio was 21.4%. The energy balance is shown in figure 7.
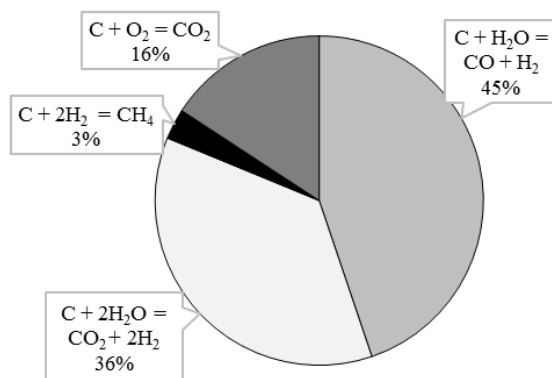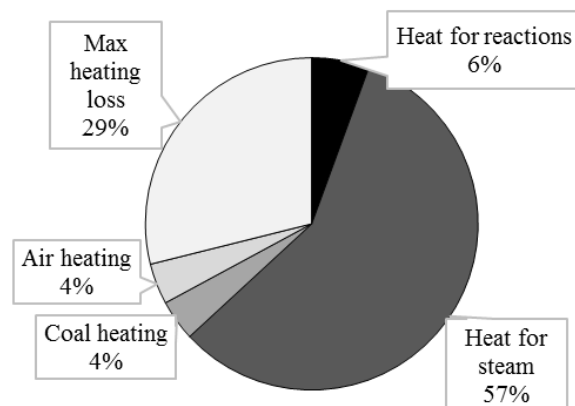

Figure 6. Fuel distribution on reactions.

Figure 7. Energy balance at 900°C for 30 min conversion.

4. Conclusion

The process of co-production of activated carbon and syngas in the course of partial steam-air conversion in a bed reactor has been studied. The conversion rate at 900°C is twice as much at 800°C. Presence of oxygen in the steam flow produce two zones with different reaction mechanisms in the fixed bed reactor. Carbon-water interaction in the oxygen zone is shifting toward of increasing the hydrogen formation. As a result, at the boundary between the zones, the ratio of $CO:CO_2:H_2$ is 1:2:3.

The dependence of the porous structure of activated carbon on the conversion degree has been obtained. Despite the oxygen presence in the amount of up to 15% required for complete combustion of the fuel, the proportion of macropores is not large. Most of the pores are micropores that are formed by interaction with steam. A maximum of micropores smaller than 4 nm is formed at conversion degree of 0.5. The material and energy balance of partial conversion has been estimated. Even taking into account the imperfection of the laboratory bed reactor mode, which consists in more than two-fold excess of steam supply, the heat balance is positive, so the conversion will be self-sustaining in industrial reactors.

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