Assessment of the Effect of Oxygen and Carbon Dioxide Concentrations on Gas Evolution During Heat Treatment of Thermoanthracite Carbon Material

Yevgen Panov[1], Nikolai Gomelia[1], Olena Ivanenko[1*], Andrii Vahin[2], Serhii Leleka[1]

[1] Department of Ecology and Technology of Plant Polymers, Faculty of Chemical Engineering, Igor Sikorsky Kyiv Polytechnic Institute, Peremogy Avenu, 37/4, 03056 Kyiv, Ukraine

[2] Private Joint Stock Company «Ukrainian Graphite», Pivnichne shose str., 20, 69600 Zaporizhzhia, Ukraine

* Corresponding author's e-mail: olenka.vasaynovich@gmail.com

ABSTRACT

The processes of the interaction of carbon material (thermoanthracite pouring) with a gas-air mixture in a heat chamber were studied while heating to 800–850°C. The influence of temperature, oxygen and carbon dioxide concentration on the formation efficiency of carbon monoxide, carbon dioxide, hydrogen and methane was determined. A pilot plant was created, which provided heating of the carbon material at the indicated temperatures and regulating the supply of air and carbon dioxide. It was found that a noticeable oxidation of the carbon material in the heat chamber in the presence of oxygen or carbon dioxide occurs at the temperatures above 500°C. Significant concentrations of carbon monoxide were formed at temperatures of 600–800°C. It was shown that when using gas mixtures with an oxygen content of 7–21% minimum concentrations of carbon monoxide are formed at an oxygen content of 14%. At temperatures above 500°C, the formation of hydrogen and methane in gas flows was noted. The methane yield increased with the decreasing oxygen content.

Keywords: carbon monoxide, flue gases, thermoanthracite pouring, graphitization, oxidation, pyrolysis

INTRODUCTION

The technological processes in which carbon materials are heat treated, such as coking, graphitization, synthesis gas production, coal burning, are always accompanied by the formation of carbon dioxide and toxic carbon monoxide.

Carbon monoxide is one of the most harmful components of flue gases in industry and in transport emissions [Rattan et al., 2014]. Particularly significant and dangerous is the air pollution by carbon monoxide in the production of electrodes by graphitization [Karvatskii et al., 2016; Panov et al., 2012]. At the same time, a significant amount of flue gas enters the atmosphere through leaks in the electrode kilns. Often the carbon monoxide formation process is useful. For example, in the production and processing of synthesis gas from solid fuels [Matkovskij et al., 2011; Kovalev et al., 2010].

If the volumes of anthropogenic emissions of toxic gases into the atmosphere are estimated generally, then, of course, carbon monoxide ranks first in terms of this indicator and its volumes grow annually by 20–30% due to the human activity [Tsyganova et al., 2002].

A lot of attention is paid to increasing the efficiency of carbon monoxide oxidation to reduce its content in emissions [Kašpar et al., 2003]. To a large extent, the problem of the carbon monoxide oxidation [Ivanova et al., 2002; Sokolskyi et al., 2012] or its synthesis [Matkovskij et al., 2011; Kovalev et al., 2010] is solved using catalysts. The most commonly used catalysts are based on manganese dioxide [Sokolskyi et al., 2012], oxides of cerium, silver, gold [Dey et al., 2017], cobalt, lithium, copper, manganese [Sokolskyi et al., 2007].

However, while its oxidation is quite convenient and widespread in the purification of the gas

emissions of internal combustion engines from carbon monoxide using catalysts, , the widespread use of catalysts at large industrial enterprises is problematic. This is due to the specificity of the production technologies, large volumes of emissions and the high price of catalysts. Often, the use of catalysts casts doubt on the feasibility of production due to the exorbitant increase in the cost of neutralizing the carbon monoxide emissions. Therefore, it is important to determine the parameters of heat treatment of carbon materials in the presence of oxygen, which ensure a decrease in the total yield of carbon monoxide under these conditions.

The aim of this research is studying the processes of gas evolution during the heat treatment of carbon material by the example of thermoanthracite pouring at temperatures up to 850°C in a mixture of air with carbon dioxide to determine the conditions for reducing the concentration of carbon monoxide in gas streams.

MATERIALS AND METHODS

Thermal anthracite pouring with a particle size of 2.8–6.0 mm is used as the carbon material during the research. In order to study the processes of gas evolution during the heat

treatment of the material, a laboratory unit was created, the scheme of which is shown in Figure 1 [Panov et al., 2019].

The created unit includes a heat chamber 4, consisting of a ceramic tube 6 with a heating element 8, in which, with the help of thermocouples 5 and thermal relay 9, a predetermined temperature level is maintained using element 8. A sample of dried and suspended carbon material in a stainless steel glass 7 is placed in a ceramic tube 6 in a heat chamber. The temperature is raised from room temperature to 850°C for 7 hours. A mixture of gases is passed through a ceramic tube 6 and a pipe for removing the gas mixture 3. At room temperature, by controlling the air and carbon dioxide supply, a predetermined oxygen concentration is established using the gas analyzer 1. When heated, the flow rate of CO_2 and air does not change. In the process of heating, the composition of the gas mixture at the exit from the heat chamber is constantly monitored. After heating and cooling, the mass of carbon material is determined. In separate experiments, at given air and CO_2 flow rates, the temperature is raised to a predetermined level (400, 500, 600, 700, 800 °C) and at specified temperatures, the sample is held for 3–4 hours, constantly analyzing the composition of the gas stream.
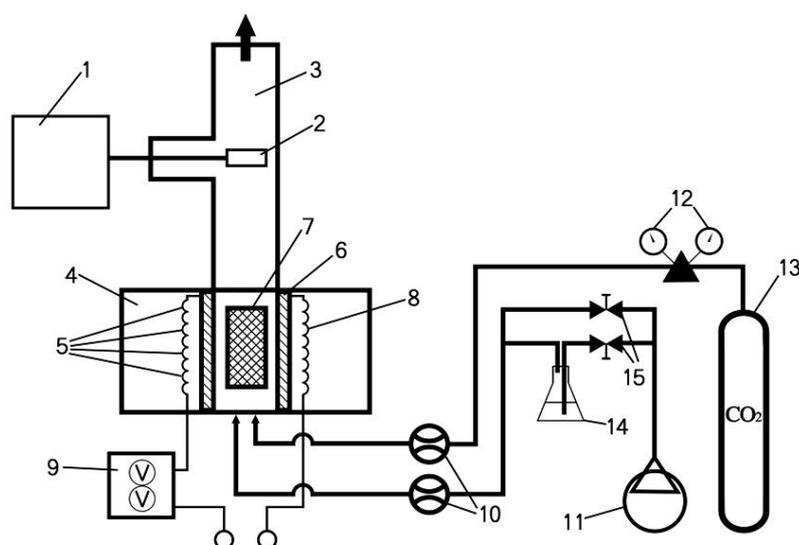
Fig. 1. Scheme of a laboratory unit for studying gas evolution during heat treatment of carbon material: 1 – gas analyzer VARIO PLUS industrial analyzer MRU air fair; 2 – gas analyzer gas sampler; 3 – pipe for removal of the gas mixture; 4 – heat chamber; 5 – thermocouples; 6 – ceramic tube; 7 – glass made from stainless steel mesh; 8 – heating element; 9 – temperature relay TENSE PC-96; 10 – rotameters of the RF-RFM LGFI.407142.002 EF series; 11 – compressor; 12 – gear; 13 – carbon dioxide cylinder; 14 – flask filled with water; 15 – cranes

The mass loss of the sample (ΔM) is determined using massmetry by the formula (g):

$$\Delta M = M_{in} - M_{fin},$$

where: M_{in} is the initial mass of the sample of carbon material before heat treatment, g;

M_{fin} is the final mass of the sample of carbon material after the heat treatment, g

The amount of carbon dioxide (V_{CO2}) formed due to the oxidation of carbon is calculated by the formula (dm^3):

$$V_{CO2} = (\Delta M/12) \cdot 22,4.$$

The specific amount of carbon monoxide (Q_{CO}) formed per 1 g of loaded carbon is determined by the formula (mg/g):

$$Q_{CO} = \frac{C \cdot V \cdot t}{Min},$$

where: C is the CO concentration, mg/m^3; V is the flow rate of the gas mixture, m^3/h; t is the heating time, h; Min is the mass of the loaded thermoanthracite pouring, g.

RESULTS AND DISCUSSION

At the first stage of the research, the gas evolution processes were studied by gradually heating the heat chamber from room temperature to 800–850°C while blowing the gas mixture through it with constant monitoring of the temperature and composition of the gas-air mixture. The flow rate of the gas-air mixture was maintained at a constant level within each experiment at a given ratio of air flow and carbon dioxide.

As can be seen from Table 1, until the temperature reached 490°C, the content of oxygen an carbon dioxide in the gas mixture remained relatively stable. The formation and accumulation of carbon monoxide in the mixture was recorded at a temperature > 300°C. At the same temperature, the presence of hydrogen in the gas mixture at a concentration level of ~ 40 mg/m³ was noted. With a further increase in temperature, the concentration of hydrogen in the mixture ranged from 26–35 mg/m³. At 850°C, it decreased to 8.9 mg/m³. In addition to hydrogen, methane was observed in a gas mixture at concentrations of 106–426 mg/m³ at a temperature of 265–850°C. The concentration of carbon monoxide at 490°C increased to 812 mg/m³, and at 644 °C – to 2800 mg/m³. The concentration of carbon monoxide reached the maximum values of ~ 8000 mg/m³ at 850°C.

The main reactions that lead to the formation of carbon monoxide are the interaction of carbon with oxygen [Panov et al., 2012], carbon with carbon dioxide and water vapor [Molina et al.,1998]. In this case, oxygen and water vapor are present in the air. The water vapor content reaches 4%. In addition, carbon dioxide is introduced into the gas mixture. Therefore, it is likely that reactions will occur in the following way:

$$3C + 2O_2 = C_3O_4 \tag{1}$$

$$C_3O_4 = 2CO + CO_2 \tag{2}$$

$$C_3O_4 + C + O_2 = 2CO + 2CO_2 \tag{3}$$

$$C + CO_2 = 2CO \tag{5}$$
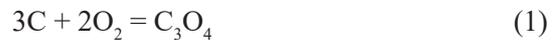
Table 1. Change in the concentration of oxygen, oxide and carbon dioxide, hydrogen and methane in a mixture of air and CO2 when it is purged through a carbon-filled heat chamber (thermoanthracite pouring) (m=445 g) at a gas mixture flow rate of 376 dm3/h with temperature, depending from heating time

No.	t, h	T, °C	[O$_2$], %	[CO$_2$], %	[CO], mg/m³	[H$_2$], mg/m³	[CH$_4$], mg/m³	Q$_{CO}$, mg/g
1	0	21	14.44	34.92	0.0	0.0	0.0	0.0000
2	1	265	14.46	34.89	0.0	0.0	106.5	0.0000
3	2	339	14.45	34.92	187.5	40.1	142.0	0.1580
4	3	394	14.45	35.31	187.5	31.2	319.5	0.1580
5	4	490	14.76	35.61	812.5	35.6	284.0	0.6865
6	5	644	14.65	35.26	2812.5	35.6	284.0	2.3764
7	6	795	14.00	35.20	4250.0	26.7	355.0	3.5910
8	7	890	13.21	39.48	8125.0	8.9	426.0	6.8652

Reactions (4) and (5) are endothermic, but under the conditions of heating the mixture with a heating element, their implementation is quite possible. The passage of reaction (4) can be judged by the formation of hydrogen and methane. The only source of hydrogen entering the gas mixture is water; at high temperatures it interacts with carbon (reaction 4) or carbon monoxide [Molina et al.,1998] (reaction 6):

$$CO + H_2O = CO_2 + H_2. \tag{6}$$
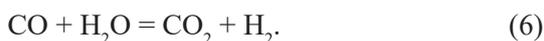
In turn, methane can be formed due to the interaction of hydrogen with carbon and carbon monoxide [Matkovskij et al., 2011; Kovalev et al., 2010]:

$$C + H_2 = CH_4 \tag{7}$$

$$CO + 3H_2 = CH_4 + H_2O \tag{8}$$

At the same time, the concentrations of all given components of the gas mixture, including carbon dioxide and carbon monoxide, hydrogen and methane, as well as water, are formed as a result of dynamic equilibrium between the reactions of their formation and conversion.

Carbon monoxide mainly binds upon interaction with oxygen [Panov et al., 2019] in the presence of water vapor:

$$CO + \frac{1}{2}O_2 \xrightarrow{H_2O} CO_2. \tag{9}$$
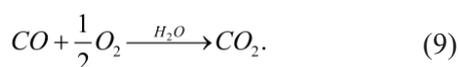
Although the reaction (6) is quite possible, hydrogen can also be oxidized by oxygen to form water:

$$H_2 + \frac{1}{2}O_2 = H_2O \tag{10}$$

It is also likely that reactions (7) and (8) will occur. In turn, methane can be oxidized to carbon dioxide, and can provide the formation of carbon monoxide and hydrogen [Molina et al.,1998]:

$$CH_4 + 2O_2 = CO_2 + 2H_2O \tag{11}$$

$$CH_4 + H_2O = CO + 3H_2 \tag{12}$$

$$CH_4 + \frac{1}{2}O_2 = CO + 2H_2 \tag{13}$$

$$CH_4 + CO_2 = 2CO + 2H_2. \tag{14}$$

Judging by the results shown in Table 1, it can be said that at temperatures up to 500°C, when the mixture does not contain significant concentrations of carbon monoxide, hydrogen, and subsequently methane, are formed during the interaction of water with carbon (reaction 4) and hydrogen with carbon (reaction 7), respectively. Carbon monoxide can be formed both due to the interaction of oxygen with carbon, and due to the oxidation of carbon by its dioxide.

If the reactions associated with the conversion of carbon monoxide are singled out, then it is possible to say that it mainly reacts with oxygen (reaction 9) and water (reaction 6). Under ordinary conditions, given the high oxygen concentration, reaction (9) predominates. The acceleration of this reaction contributes to an increase in the oxygen concentration. However, at the same time, reactions (1–3) are accelerated, which leads to an increase in the content of carbon monoxide in the gas mixture.

With an increase in the oxygen concentration in the initial gas mixture to ~ 15.5%, there is an increase in the concentration of CO in the gas

Table 2. Dependence of the concentration of oxygen, oxide and carbon dioxide, hydrogen and methane in a mixture of air and CO_2 when blowing it through a carbon-filled heat chamber (thermoanthracite pouring) (m=431 g) at a gas mixture flow rate of 350 dm³/h on temperature and time stay in cell

No.	t, h	T, °C	[O_2], %	[CO_2], %	[CO], mg/m³	[H_2], mg/m³	[CH_4], mg/m³	Q_{CO}, mg/ g
1	0	20	15.65	28.09	0.0	0.0	0.0	0.0000
2	1	270	15.66	28.11	0.0	0.0	142.0	0.0000
3	2	335	15.44	28.12	125.0	0.0	213.0	0.1015
4	3	393	15.62	28.50	187.5	0.0	213.0	0.1523
5	4	476	15.25	28.18	250.0	0.0	284.0	0.2030
6	5	634	15.04	28.41	1375.0	0.0	390.5	1.1166
7	6	785	15.00	29.12	8687.5	0.0	355.0	7.0548
8	7	850	14.70	30.22	15875.0	0.0	639.0	12.8915

stream to 1375 mg/m³ at a temperature of 634 ° C (Table 2). The concentration of carbon monoxide increases along with temperature. At a temperature of 795–850°C, the CO concentration reaches 8687–15875 mg/m³.

The specific amount of CO formed reaches 7.1–12.9 mg/g. In the previous case (Table 1), the maximum Q_{CO} values are 3.6–6.9 mg/g.

In this case, the presence of hydrogen in the gas mixture was not noted. Obviously, this is due to its interaction with carbon with the formation of methane and oxygen with the formation of water. It is possible that at temperatures> 650°C, when a significant amount of carbon monoxide is formed, part of the hydrogen reacts with it to form methane. In any case, in this process, the hydrogen binding reactions are more likely to occur during its formation. The concentration of methane in this experiment, as in the previous case (table 1), is at a level of 200–400 mg/m³ at temperatures up to 785°C. At a temperature of ~ 850°C, the concentration of methane increased to 639 mg/m³, which is possible and associated with an increase in the concentration of carbon monoxide as well as its transformation in the presence of water vapor (reaction 6.8) into methane.

When air is blown through a heat chamber without adding CO_2, an increase in the concentration of formed carbon monoxide with temperature is observed as well (Table 3). At a temperature of 546°C, the CO concentration reached 2333 mg/m³ (QCO = 3.44 mg/g), and at a temperature of 869°C it increased to 7213 mg/m³ (Q_{CO} = 11.10 mg/g). Under these conditions, judging by the increase in the concentration of CO_2, it is possible to say that a significant part of the oxygen is spent on carbon oxidation. At the same time, the amount of carbon monoxide formed increases to

a certain extent. At temperatures of 546–661°C, the amount of carbon monoxide formed is higher than when the oxygen concentration in the gas mixture is 15.5%. In addition, with an increase in the oxygen concentration, as a rule, an increase in the mass loss of carbon material due to its oxidation is observed. At $[O_2]$ = 14% ΔM = 15.0 g, and at $[O_2]$ = 20.95% ΔM = 58.8 g at a heat treatment time of the carbon material of 7 hours. Despite the fact that in this case the hydrogen concentration in the gas mixture reached 41–53 mg/m³ at a temperature of 218–869°C, the methane content is low. Only at 546°C did the methane content reach 141 mg/m³, and at a temperature of 869°C, its concentration increased to 453 mg/m³.

It should be noted that when using air saturated with water vapor, due to its bubbling through a layer of water in front of the heat chamber, a significant decrease in the concentration of carbon monoxide (up to 1085–1133 mg/m³) is achieved at high temperatures (~ 847–885℃). Obviously, this is due to the acceleration of reaction (6) due to an increase in the concentration of water vapor in the gas mixture. Since reaction (6) significantly affects the process at temperatures> 700℃, then at a temperature of 630℃ in this case, it did not contribute to a decrease in the content of carbon monoxide in the gas mixture.

A decrease in the concentration of oxygen in a mixture of air and CO_2 does not always lead to a decrease in the concentration of CO in the gas stream after the heat chamber. Thus, when using a mixture containing ~ 7.63% oxygen and 62.20% CO_2 (Fig. 2, Table 4) at 615℃, the CO concentration reached

1193 mg/m³. At 720℃, it grows to 7318 mg/m³. Under these conditions, the specific amount of CO forms reach 1.92 mg/g at 615℃

Table 3. Change in the concentration of oxygen, oxide and carbon dioxide, hydrogen and methane in the air stream when it is purged through a carbon-loaded heat chamber (thermoanthracite pouring) (m=382 g (I) m=377 g (II)) without saturation with water vapor (I) and when saturated with water vapor (II) with temperature depending on the purge time at an air flow rate of 588 dm³/h

t, h	T, °C		[O₂], %		[CO₂], %		[CO], mg/m³		[H₂], mg/m³		[CH₄], mg/m³		Q_CO, mg/g	
	I	II	I	II	I	II	I	II	I	II	I	II	I	II
0	21	19	20.95	20.95	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.0000	0.0000
1	218	207	20.59	20.94	0.04	0.04	0.00	0.00	47.17	37.65	0.00	0.00	0.0000	0.0000
2	336	324	20.90	20.93	0.07	0.09	2.08	0.00	52.23	48.96	2.38	19.05	0.0031	0.0000
3	422	415	20.76	20.89	0.15	0.22	128.16	520.61	53.65	58.16	18.28	35.28	0.1970	0.8004
4	546	532	20.03	19.53	0.77	1.21	2233.13	3275.85	53.07	56.83	141.67	319.44	3.4371	5.0411
5	661	630	18.02	18.31	2.52	2.48	3893.75	4553.69	41.80	53.56	318.85	331.58	5.9924	7.0082
6	851	847	17.11	18.20	3.74	2.37	4738.71	1133.33	41.52	52.38	289.29	263.10	7.2930	1.7440
7	869	885	16.71	18.13	4.38	2.65	7213.24	1085.42	53.57	57.11	453.78	280.95	11.1027	1.6701
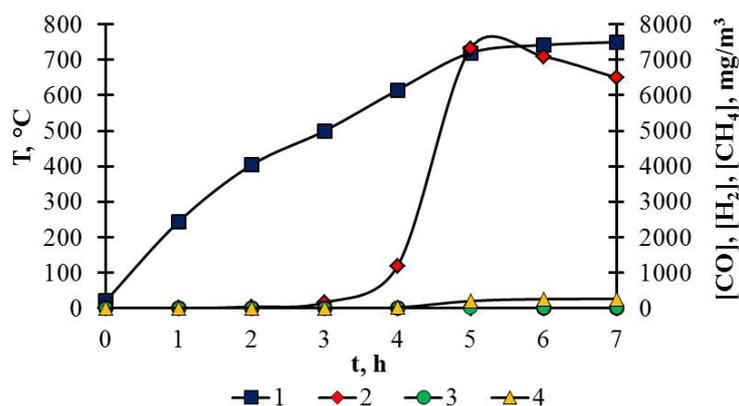
Fig. 2. Change in temperature in a heat chamber (1), concentration of carbon monoxide (2), hydrogen (3) and methane (4) over time in a mixture of air and CO_2 ($[O_2]$=7.63 %, $[CO_2]$=62.20 %, $[N_2]$=30.17 %) when blowing it through a heat chamber with thermoanthracite carbon material (M=359 g) with a flow rate of 579 dm^3/h

Table 4. Changes in the temperature of the gas mixture, the concentration of oxygen, dioxide and carbon monoxide in it, the specific amount of carbon monoxide formed with heating time while blowing the mixture of air and CO_2 through a heat chamber (gas mixture flow rate 579 dm^3/h) with a mass of carbon material 359 g

t, h	T, °C	$[O_2]$, %	$[CO_2]$, %	$[CO]$, mg/m^3	Qco, mg/g
0	21	7.63	62.20	0.00	0.0000
1	244	7.64	62.20	0.00	0.0000
2	404	7.74	62.31	37.50	0.0597
3	500	7.73	62.44	160.12	0.2581
4	615	8.05	61.85	1193.75	1.9241
5	720	8.15	61.74	7318.70	11.8042
6	742	8.13	61.57	7097.92	11.4476
7	750	8.21	61.55	6500.00	10.4833

and 10.48–11.80 mg/ at 720–750°C. These are significantly higher Q_{co} values, as at an oxygen concentration of 20.95%. Obviously, in this case, the formation of CO occurs largely due to the interaction of carbon dioxide with carbon through reaction (5). At the same time, the oxygen in the mixture is clearly not enough for the oxidation of CO to CO_2.

This should be taken into account when optimizing the manufacturing conditions of graphite electrodes [Karvackiy et al., 2011; Bogacki et al., 2012].

The disadvantage of previous experiments is that over time the temperature in the heat chamber constantly increased, which led to a constant change in the composition of the gas-air mixture. Subsequently, a series of experiments was carried out in which a mixture of air and CO_2 was passed through a heat chamber at fixed temperatures. Thus, Figures 3 and 4 show how the composition of the air (the content of O_2 and CO_2) changes when it is passed for 4 hours at fixed temperatures

– 495, 615, 700, and 800°C. It can be seen from the figure that at given temperatures the content of CO_2 and O_2 is practically unchanged. However, since the carbon material oxidized faster at high temperatures, the CO_2 content is also higher at higher temperatures. Accordingly, the oxygen concentration decreases with increasing temperature.

The concentrations of carbon monoxide in this series of experiments at certain temperatures are relatively stable (Fig. 5). At 495°C, the CO concentration is at the level of 1011–1081 mg/m^3 for 4 hours. However, at 615°C, the concentration of carbon monoxide gradually decreased over 4 hours from 1667 to 979 mg/m^3. This means that under these conditions, the rate of carbon monoxide conversion prevailed over the rate its formation. The same is observed at 700 and 800°C. At the same time, if at 700°C the CO concentration decreases from 5958 mg/m^3 to 3867 mg/m^3, then at 800°C it decreased from 8125 to 3609 mg/m^3. This indicates that during the heat treatment of
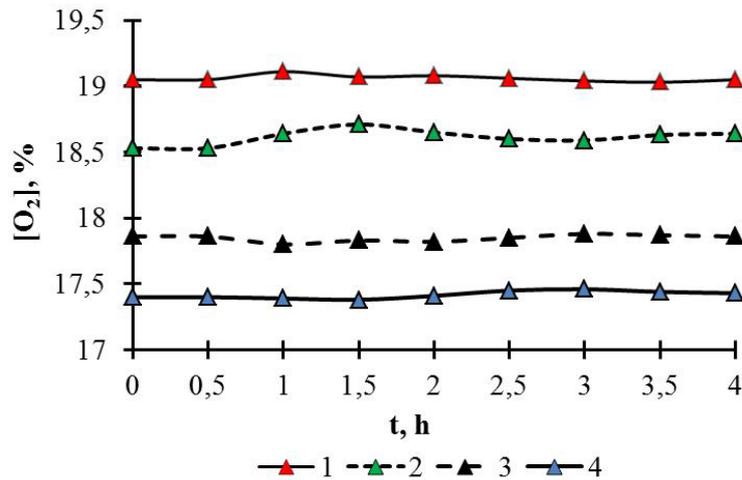
Fig. 3. Change in oxygen concentration (1, 2, 3, 4) in the gas mixture with the time of air purging through the heat chamber at an air flow rate of 650 dm³/h at an average temperature in the heat chamber, °C: 495 (1); 615 (2) 700 (3); 800 (4) with a mass of carbon material in the sample 393–400 g
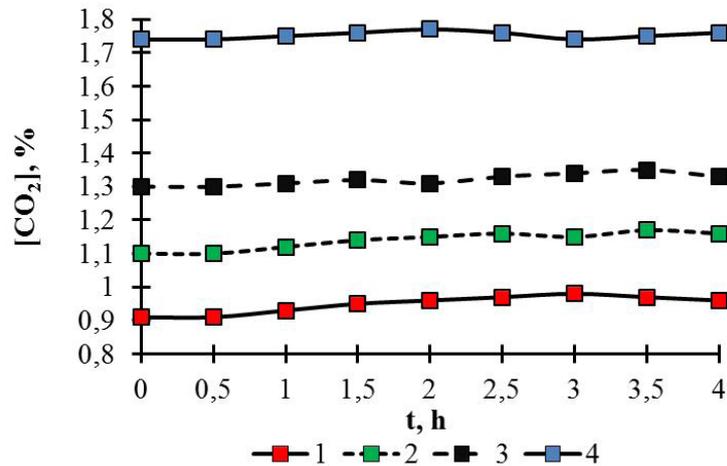
Fig. 4. Change in the concentration of carbon dioxide (1, 2, 3, 4) in the gas mixture with the time of air purging through the heat chamber at an air flow of 650 dm³/h at an average temperature in the heat chamber, °C: 495 (1); 615 (2) 700 (3); 800 (4) with a mass of carbon material in the sample 393–400 g

carbon materials for a long time [Karvatskii et al., 2013], the bulk of carbon monoxide can accumulate not at high temperatures (T> 700°C), but in a relatively low temperature zone (400 <T<500 °C), where the reactions of carbon monoxide formation are faster, as are the processes of its conversion. Since the flue gases pass through chambers with electrode material from a zone with a high temperature (1200°C) to a zone with a low temperature (T≈150–200°C), it is the formation of carbon monoxide at 400–500°C that can cause an increase in its concentration in the flue gas exhaust.

It is interesting to note that when the carbon material is heated in thermal chambers for

relatively constant temperatures for several hours, the level of hydrogen concentrations at 495, 615 and 700°C reaches 20–40 mg/m³, and methane at concentrations of 120–140 mg/m³ is formed only at 700°C (Table 5).

It is possible that at temperatures up to 700°C, the accumulation of hydrogen occurs due to the low rate of its conversion with the formation of methane. At 800°C, hydrogen is likely to turn into both methane and water. However, the methane accumulation is not observed both due to the rapid oxidation of the formed hydrogen in the presence of oxygen, and due to the conversion of methane due to reaction (11), possibly partially due to reaction (13).

In the next series of experiments, a mixture of air and carbon dioxide is passed through a heat chamber loaded with carbon material and heated in accordance with a temperature to 400, 500, 600, and 700 at oxygen concentrations of 13.80% (400, 500 °C) and 14.28% (600, 700°C). Purge of the heat chamber at the set temperature – 4 hours. As can be seen from Fig. 6, in this case, small amounts of carbon monoxide are formed at temperatures of 400 and 500°C, which is associated with a relatively low reaction rate (1–5). At 600°C, the CO concentration decreased from 2750 mg/m³ to 1113 mg/m³, and at 700°C, from 3375 to 2421 mg/m³.

This indicates that – at given temperatures – the rates of carbon monoxide formation processes increase. However, at a given oxygen concentration, the rate of the process of its oxidation to CO_2 increases as well (Fig. 7).

If the data in Fig. 5 and Fig. 6 are compared, it can be said that at 600°C the level of CO concentration in the gas mixture is slightly lower at an initial oxygen concentration of 20.95%, but because in 4 hours, the CO concentration both at an oxygen content of 20.95% and at 13.80% approaches ~ 1000 mg/m³. At 700°C, the CO concentration is significantly lower at an oxygen concentration of 13.80% compared with air, where $[O_2] = 20.95\%$.

Obviously, the oxygen content in the gas mixture allows to control the concentration of the formed carbon monoxide to a certain extent. However, for a more significant reduction, it is advisable to use catalysts [Panov et al.,
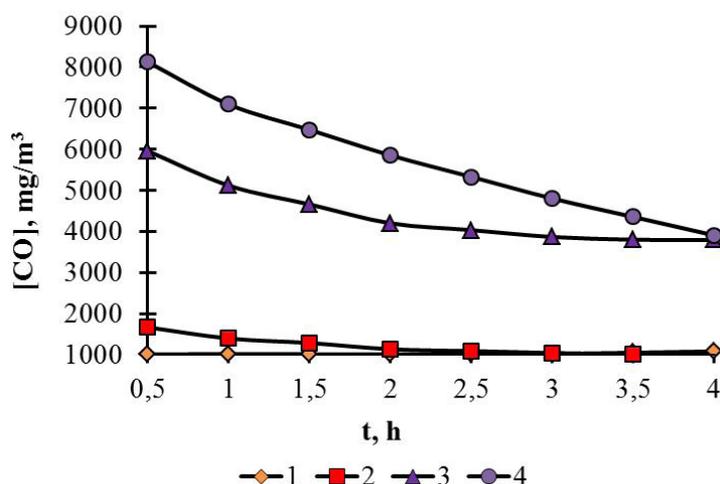
Fig. 5. The dependence of the concentration of carbon monoxide (1, 2, 3, 4) in the gas mixture on the time of air purging through the heat chamber at a flow rate of 650 dm³/h at an average temperature, °C; 495 (1); 615 (2) 700 (3); 800 (4) with the mass of carbon material in the sample 393–400 g ($\Delta M_1 = 16.5$ g $\Delta M_2 = 20.1$ g $\Delta M_3 = 23.0$ g $\Delta M_4 = 30.8$ g)

Table 5. The dependence of the concentration of hydrogen (1, 2, 3, 4) and methane (5, 6, 7, 8) in the gas mixture on the time of air purging through the heat chamber at a flow rate of 650 dm³/h at temperature, °C: 495 (1; 5); 615 (2, 6); 700 (3, 7); 800 (4, 8) with the mass of carbon material in the sample 393–400 g ($\Delta M_1 = 16.52$ g $\Delta M_2 = 20.1$ g $\Delta M_3 = 23.0$ g $\Delta M_4 = 30.8$ g)

t, h	$[H_2]$, mg/m³				$[CH_4]$, mg/m³			
	1	2	3	4	5	6	7	8
0.5	27	51	25	12	0	0.00	122.51	0.00
1	28	47	26	14	0	0.00	123.81	1.19
1.5	28	44	26	15	0	0.19	128.51	1.19
2	28	41	27	15	0	7.14	134.52	1.19
2.5	28	36	28	16	0	10.14	135.01	1.56
3	29	30	29	16	0	15.48	135.71	2.05
3.5	29	27	26	17	0	12.6	138.73	2.15
4	30	24	23	17	0	8.33	145.24	2.38
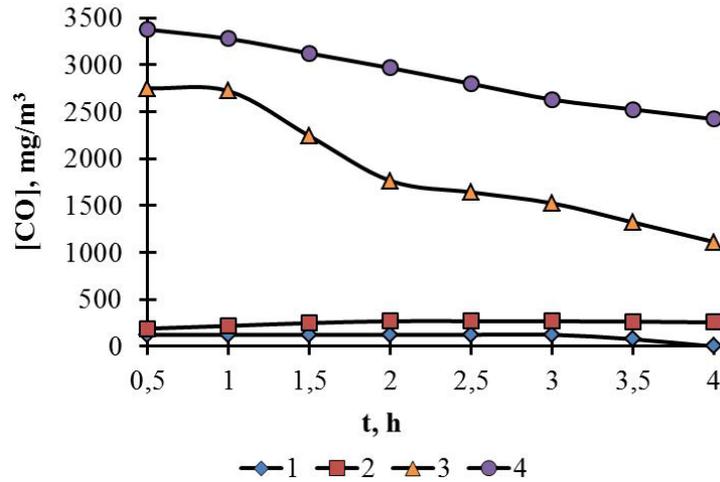
Fig. 6. Dependence of the concentration of carbon monoxide (1, 2, 3, 4) on the time of blowing a mixture of air and CO_2 through a heat chamber at a temperature, ℃; 400 (1); 500 (2) 600 (3); 700 (4) at a gas mixture flow rate; dm³/h: 470 (1); 609 (2) 389 (3); 383 (4)

2019] or installations for its additional oxidation [Karvatskii et al., 2013].

Somewhat unexpected are the results of observing changes in the concentrations of hydrogen and methane when heating a carbon material while blowing a mixture of air and CO_2. Thus, with a decrease in the oxygen concentration in the gas mixture (Table 6), the hydrogen concentrations are very low. It is practically absent in the gas mixture. However, the methane concentrations reached 900–1000 mg/m³ at 400℃ and 150–200 mg/m³ at 700℃. The decrease in the hydrogen concentration can be explained by the acceleration of its conversion with the formation

of methane and, possibly, a decrease in the rate of formation due to a decrease in the water vapor content when air is diluted with a stream of CO_2. The accumulation of methane concentration at 400 and 500℃ can be explained by the predominance of the rate of reactions of its formation over the reactions of its conversion. Moreover, this effect is much more noticeable at lower temperatures.

The oxidation rate of the formed methane increases along with temperature, which leads to a decrease in its concentration to 257 mg/m³at 600℃ and to 204 mg/m³at 700℃. However, at an oxygen concentration of 20.95%, its concentration is even lower (Table 5).
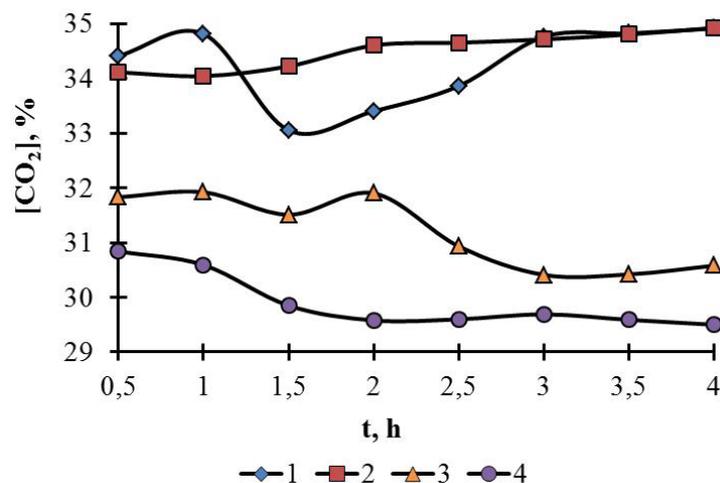
Fig. 7. The dependence of the concentration of carbon dioxide (1, 2, 3, 4) on the time of blowing a mixture of air and CO_2 through a heat chamber at a temperature, ℃; 400 (1); 500 (2) 600 (3); 700 (4) at a gas mixture flow rate; dm³/h: 470 (1); 609 (2) 389 (3); 383 (4)

Table 6. Change in the concentration of hydrogen (1, 2, 3, 4) and methane (5, 6, 7, 8) with the passage of a mixture of carbon dioxide with air through a heat chamber at a temperature; ℃ 400 (1, 5); 500 (2, 6); 600 (3, 7) and 700 (4, 8) at a gas mixture flow rate, dm³/h: 470 (1, 5); 609 (2, 6); 389 (3, 7); 383 (4, 8)

t, h	$[H_2]$, mg/m³				$[CH_4]$, mg/m³			
	1	2	3	4	5	6	7	8
0.5	13.24	0.00	4.32	0.00	921	208	250	150
1	7.29	0.00	3.57	0.00	932	259	308	158
1.5	6.21	0.00	3.32	0.00	935	284	295	166
2	5.51	0.00	3.27	0.00	939	294	276	173
2.5	3.58	0.00	3.23	0.00	989	297	274	178
3	2.08	0.00	3.20	0.00	1017	301	272	183
3.5	0.85	0.00	2.98	0.00	1015	308	263	195
4	0.00	0.00	2.68	0.00	1010	316	257	204

CONCLUSIONS

While studying the processes of gas formation during the heating of thermoanthracite pouring in a heat chamber at a temperature of 19–869℃ when passing a mixture of air and CO_2 through the chamber:

1. It is shown that during the heat treatment of carbon material, the formation of mono- and dioxide of carbon, hydrogen and methane occurs. The rate of carbon oxidation increases along with the oxygen concentration in the gas mixture at temperatures above 500℃. The formation of hydrogen and methane is noted at temperatures above 300℃.

2. The effect of the concentration of oxygen and CO_2 on the content of CO, H_2 and CH_4 in the gas mixture is established when air and CO_2 are introduced into the chamber. The minimum CO concentrations are observed at an oxygen concentration of ~ 14% and CO_2 ~ 31%. With a further increase in the concentration of oxygen or CO_2, the CO content in the gas mixture increases as well. At these concentrations of O_2 and CO_2 in the gas mixture, an increase in methane concentration of 250–1000 mg/m³ is noted.

3. The nature of the change in the concentration of carbon monoxide in the gas flows of a mixture of air and CO_2 at constant temperatures (400–800℃) in a heat chamber with carbon materials on the change in the concentration of carbon monoxide from the time of heat treatment was determined. It was shown that at the oxygen concentrations from 14.00 to 20.95% at temperatures > 600℃, the CO concentration decreases with the heat treatment time, which indicates that its oxidation under these conditions is more likely to occur during its formation.

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