

Розглянуто вплив температури, концентрації кисню та витрати газоповітряної суміші на ефективність окислення термоантрацитного вуглецевого зернистого матеріалу з утворенням монооксиду та діоксиду вуглецю. Змодельована установка передбачала нагрівання в термокамері зразку вуглецевого матеріалу при постійному пропусканні через зону нагрівання газоповітряної суміші, отриманої при регулюванні подачі повітря та вуглекислого газу. Температурний діапазон становив 20–850 °С.

Встановлено, що помітне окислення вуглецевого матеріалу в термокамері при продуванні газоповітряних сумішей із вмістом кисню 8–21 % починається при температурах вищих 500 °С, а значні концентрації монооксиду вуглецю утворюються при температурах 600–800 °С. Визначено, що за концентрації кисню 14 % вміст монооксиду карбону у димових газах мінімальний у вибраному діапазоні концентрацій кисню 8–21 %.

Показано, що при використанні газової суміші, насиченої водяними парами, ефективність доокислення монооксиду карбону зростає при температурах 650–850 °С, проте при використанні марганцевого каталізатору каталітичної дії парів води не спостерігається.

Запропоновано використання марганцевого каталізатора, нанесеного у вигляді мікрочастин на поверхню вуглецевого матеріалу, що забезпечує суттєве зниження концентрації СО при температурах 500–850 °С. Недоліком процесу є збільшення втрат вуглецевого матеріалу в 1,6–2,0 рази за рахунок прискорення процесів окислення вугілля до СО та СО₂.

Представлено можливість створення визначених умов для проведення технологічного процесу окислення термоантрацитного вуглецевого зернистого матеріалу на підприємствах для забезпечення зниження вмісту монооксиду карбону в продуктах окислення

Ключові слова: монооксид вуглецю, димові гази, термоантрацитна пересітка, графітація, вуглецевий матеріал, діоксид марганцю, окислення, екологічний каталіз

ESTIMATION OF THE EFFECT OF TEMPERATURE, THE CONCENTRATION OF OXYGEN AND CATALYSTS ON THE OXIDATION OF THE THERMOANTHRACITE CARBON MATERIAL

Ye. Panov

Doctor of Technical Sciences, Professor
Department of Chemical, Polymer
and Silicate Engineering**
E-mail: panov@rst.kpi.ua

N. Gomelia

Doctor of Technical Sciences,
Professor, Head of Department*
E-mail: m.gomelya@kpi.ua

O. Ivanenko

PhD, Associate Professor*
E-mail: olenka.vasaynovich@gmail.com

A. Vahin

PhD, Deputy Director General for Ecology
Private Joint-Stock Company «Ukrainky Grafit»
Pivnichne shose str., 20, Zaporizhia, Ukraine, 69600
E-mail: vagin@ukrgrafit.com.ua

S. Leleka

PhD, Senior Researcher
Scientific Research Center «Resource-saving
Technologies»**
E-mail: sleleka@rst.kpi.ua

*Department of Ecology and

Technology of Plant Polymers**

**National Technical University of Ukraine
«Igor Sikorsky Kyiv Polytechnic Institute»
Peremohy ave., 37, Kyiv, Ukraine, 03056

1. Introduction

In the technological processes with heat treatment of carbon, such as coking, graphitization, coal combustion, carbon oxides are always formed if gas mixtures contain oxygen at higher or lower concentrations. Typically, these processes are accompanied by the formation of carbon dioxide and toxic carbon monoxide.

Despite the considerable number of methods of carbon monoxide reoxidation before flue gases are released into the atmosphere, creating conditions for effective oxidation at

the production stage is an important problem that has not been sufficiently studied.

There has been an acute problem of protecting the population from carbon monoxide poisoning since the 1950s. No less acute problem is greenhouse gas emission. But in recent years there has been no decrease, but an increase in carbon oxide emissions to the atmosphere due to a significant reduction in volumes of natural gas used and growth of solid fuel combustion. Atmospheric pollution with carbon monoxide in electrode production by graphitization is particularly significant [1, 2].

2. Literature review and problem statement

It is known that carbon monoxide, one of the most harmful components of flue gases of industrial enterprises and vehicles, is also called the «silent killer» [3]. This gas has no smell, color, taste and irritating effect, so it cannot be felt by the sensory organs. Lighter than air by about 3 %, carbon monoxide rises up and freely spreads. It is known that at present the atmosphere contains $5 \cdot 10^{11}$ kg of carbon monoxide and 20–30 % more are added annually as a result of human activity [4].

Despite numerous studies in this area, the problem of converting carbon monoxide into carbon dioxide does not lose relevance. The paper [5] presents the results of studies, which note that CO oxidation to CO₂ without a catalyst at temperatures below 650 °C is very limited. As available active catalysts for CO oxidation, it is proposed to use MnO₂, Co₃O₄, CuO oxides, which allows reducing the process temperature to 120–150 °C. However, catalytic oxidation of carbon monoxide has been most studied when used in the automotive industry, since the catalyst efficiency particularly depends on the temperature of exhaust gases during cold engine start [6].

As for production, recent studies have focused on the use of manganese compounds for catalytic purposes. The possibility of using CuMnO_x hopcalite as a promising catalyst for low-temperature CO oxidation, obtained by KMnO₄ co-precipitation is noted [7]. Doping with metal oxides (CeO_x, AgO_x, AuO_x) increases the ability of hopcalite catalysts to adsorb CO [8].

According to the authors of [5], electrochemical manganese dioxide, obtained from fluorine electrolytes, is a more active catalyst for CO oxidation compared with chemical MnO₂. That is, the catalytic properties of manganese dioxide can be significantly improved by changing the method of production. At the same time, high efficiency of cobalt-, copper- and lithium-doped manganese dioxide obtained by the electrochemical method for the catalytic conversion of CO into CO₂ is noted [9]. However, despite the high efficiency and stability of the considered catalysts, there is no hope for large-scale introduction of them in the coming years for various reasons, among which the most significant are high price and complicated methods of production. In general, known catalytic exhaust systems at enterprises in the form of carrier applied noble metals, metal oxides and high-temperature superconductors require a significant amount of active components [4].

Separately, for combustion or oxidation of carbon materials, a number of technical solutions have been developed to reduce carbon monoxide emissions. Thus, in [10], modernization of the rules of electrode products firing is proposed, which can be applied only if the firing duration and the maximum process temperature are increased. The use of the CO local afterburning plant in the form of a heat exchanger-utilizer [11] will be associated with excessive consumption of natural gas which will be spent for heating the gas-air flow. Radical replacement of Riedgammer's multi-chamber annular furnaces with tunnel furnaces [12] will also face significant capital expenditures on re-equipment of production. The introduction of catalytic exhaust systems in particular in the process of electrode graphitization is also impossible due to the high content of resinous substances in flue gases [13].

As a result, the introduction of the proposed solutions at enterprises is limited or impossible at all. Thus, the issue

of reducing the carbon monoxide content in flue gases in an economically feasible way without reducing the quality of the resulting products remains unresolved.

One of the ways to overcome the above obstacles in the process of catalytic conversion of CO into CO₂ can be the use of manganese dioxide film coatings, whose high efficiency for the catalytic oxidation of organic compounds in aqueous solutions is confirmed in [14, 15]. In this case, the stability of carrier applied coatings is easily provided by adjusting the process parameters of the medium [14]. Also, this catalyst is proposed to be used instead of expensive noble metals, because the surface of the platinum catalyst is poisoned in the oxidation process with adsorbed carbon monoxide particles [15].

At the same time, the works [14, 15] deal with the processes of neutralizing organic compounds in aqueous solutions. Therefore, it was interesting to study the oxidation efficiency of carbon monoxide by catalytic oxidation of CO using the manganese dioxide film coating in a gas environment at enterprises where heat treatment of carbon occurs. In addition, the possibility of easy application of this catalyst to the components of the technological process, in particular, to the thermoanthracite charge in electrode production by graphitization, should cause minimum capital costs for the catalytic conversion of CO into CO₂.

3. The aim and objectives of the study

The aim of the work is to determine conditions for reducing the carbon monoxide content in carbon material oxidation products.

To achieve the aim, the following objectives were accomplished:

- to study the processes of carbon material oxidation, depending on the temperature, composition and flow rate of the gas mixture;
- to determine the effect of water vapor on the processes of carbon material oxidation during heat treatment;
- to estimate the effect of manganese oxide (IV) applied on carbon material on the carbon oxidation intensity and the ratio of carbon monoxide and dioxide in oxidation products;
- to determine conditions for effective reoxidation of carbon monoxide.

4. Materials and methods of study of carbon material oxidation processes in a heat chamber

Thermoanthracite charge with a particle size of 2.8–6.0 mm was used as carbon material in the studies.

To study gas emission processes during the heat treatment of the material, a laboratory installation was created, the scheme of which is presented in Fig. 1.

The installation includes a heat chamber 4 consisting of a ceramic tube 6 with a heating element 8, where by means of thermocouples 5 and temperature relay 9, the set temperature level is maintained by a heating element 8. The sample of dried and weighed carbon material in a stainless steel cup 7 was placed in a ceramic tube 6 in a heat chamber. The temperature was raised from room temperature to 850 °C for 7 hours. The gas mixture was passed through a ceramic tube 6 and gas mixture discharge tube 3. At room temperature, by adjusting the supply of air and carbon dioxide using a gas analyzer 1, a given oxygen concentration was set. During

heating, the flow rate of CO₂ and air was not changed. In the process of heating, the composition of the gas mixture at the heat chamber output was constantly monitored. After heating and cooling, the mass of carbon material was determined.

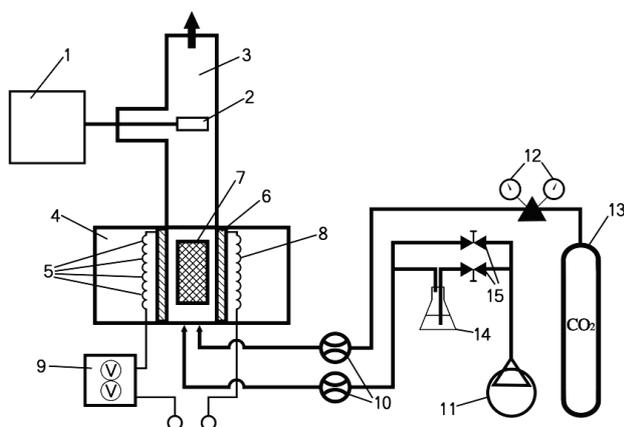


Fig. 1. Scheme of a laboratory installation for the study of gas emission processes in the heat treatment of carbon material: 1 – VARIO PLUS industrial analyzer MRU air fair; 2 – gas analyzer sampler; 3 – gas mixture discharge tube; 4 – heat chamber; 5 – thermocouples; 6 – ceramic tube; 7 – stainless steel mesh cup; 8 – heating element; 9 – TENSE PC-96 temperature relay; 10 – RF-RFM LGFI.407142.002 EF rotameters; 11 – compressor; 12 – reducer; 13 – cylinder with carbon dioxide; 14 – water-filled flask; 15 – cranes

The change in the carbon dioxide concentration was determined by the difference between the final concentration at the given temperature and the initial concentration at room temperature. At the same time, the data on the concentration of oxygen, which is mainly spent on the formation of carbon dioxide and monoxide were refined.

The change in the concentration of carbon monoxide, methane and nitrogen was determined from the data obtained with the gas analyzer.

The specific amount of carbon monoxide (Q_{CO}) produced per 1 g of carbon charge was determined by the formula (mg/(g·h)):

$$Q_{CO} = \frac{C \cdot V}{M}, \quad (1)$$

where C is CO concentration, mg/m³; V is gas mixture flow rate, m³/h; M is the mass of loaded thermoanthracite charge, g.

The practical mass loss of the carbon material sample (ΔM_p) during heat treatment was determined by the formula (g):

$$\Delta M_p = M_{in} - M_{fin}, \quad (2)$$

where M_{in} is the initial mass of the carbon material sample before heat treatment, g; M_{fin} is the final mass of the carbon material sample after heat treatment, g.

The practical mass loss as a percentage (ΔM) was found by the formula (%):

$$\Delta M = \frac{M_{in} - M_{fin}}{M_{in}} \cdot 100\%. \quad (3)$$

Theoretical mass loss of the carbon material sample (ΔMt) during heat treatment was calculated based on the chemical reactions (g):



Considering the recorded concentrations of CO₂ and CO, the theoretically calculated mass of oxidized carbon was determined by equation (1) and (2).

The amount of manganese oxide was determined from a decrease in the potassium permanganate content in a solution per unit mass of carbon material. When using a 1% potassium permanganate solution during treatment for a day, the content of precipitated MnO₂ in the carbon material is 0.5%. When using a 5% potassium permanganate solution during contact for a day, the MnO₂ content in the carbon material is 1.5%.

5. Results of studies of carbon material oxidation during heat treatment

5.1. Effect of temperature, composition and flow rate of gas-air mixture, water vapor on carbon material oxidation processes

According to the results of determining changes in the carbon material temperature over heating time (Table 1), the temperature in the heat chamber increased for 7 hours from 18.6–21.0 °C to 790–860 °C. At the same time, at different oxygen concentrations, the temperature of the processes varies insignificantly. If within the first two hours the temperature increase is accidental, for the last five hours the temperature rises faster with increasing oxygen concentration in the gas mixture. Perhaps this is due to an increase in heat emission during carbon oxidation intensification.

Table 1

Change in temperature (T) in the heat chamber, CO concentration (C_{CO}) and amount of formed carbon monoxide (Q_{CO}) over heating time (t)*

t, h	$T, ^\circ C$				$C_{CO} \cdot 10^2, \% / Q_{CO}, mg/(g \cdot h)$			
	1	2	3	4	1	2	3	4
0	21	20	20	18,6	0/0	0/0	0/0	0/0
1	265	270	258	219	0.54/0.05	0/0	0/0	0/0
2	339	335	320	335	1.61/0.16	1.07/0.10	0.54/0.05	0.54/0.06
3	394	393	396	421	2.15/0.21	1.61/0.15	2.15/0.19	4.29/0.46
4	490	476	513	541	9.66/0.95	3.76/0.36	2.69/0.23	40.25/4.35
5	644	634	653	665	43.99/4.33	25.75/2.44	45.60/3.98	35.41/3.83
6	795	785	731	847	61.71/6.07	138.43/13.09	96.05/8.38	54.73/5.91
7	850	850	850	860	41.85/4.12	112.67/10.66	84.77/7.39	63.31/6.85
$\Sigma Q_{CO}, mg/(g \cdot h)$					15.9	26.8	20.2	21.5

Note: * – conditions at an oxygen concentration in the gas mixture, %: 14.06 (1), 15.50 (2), 17.50 (3), 20.95 (4) at a flow rate of the gas mixture, dm³/h: 376 (1); 350 (2); 323 (3); 350 (4)

It should be noted that the change in the concentration of carbon monoxide formed was not so clear. First of all, it should be pointed out that a significant increase in carbon monoxide concentration occurs at temperatures close to 500 °C and CO concentration increases significantly at temperatures of 650–800 °C. The lowest carbon monoxide concentrations in gas mixtures are noted at an oxygen concentration of 14 %. With an increase in oxygen concentration to 15.5 %, the maximum CO content (at the level of 13,125–16,125 mg/m³) is observed. With a further increase in oxygen concentration in the gas mixture, carbon monoxide content in the gases at the heat chamber outlet is slightly reduced. Similarly, along with oxygen concentration, the specific amount of carbon monoxide formed changes with temperature. The maximum amount of carbon monoxide per 1 g of carbon charge is formed at an oxygen concentration of 15.5 % at temperatures of 785–850 °C.

The change in carbon dioxide concentration during the heat treatment of carbon material can be judged from the results in Fig. 2. At an oxygen concentration of 14.06 %, the increase in CO₂ concentration in the mixture after heat treatment ranges from 0.183 mol/m³ to 2.036 mol/m³. As for CO, the concentration varies from 0.0089 to 0.2567 mol/m³ (Table 1). At an oxygen concentration in the gas mixture of 15.5 %, the maximum increase in CO₂ concentration reaches 0.9107 mol/m³, while the maximum increase in CO reaches 0.5759 mol/m³, which is close enough to the change in CO₂ concentration.

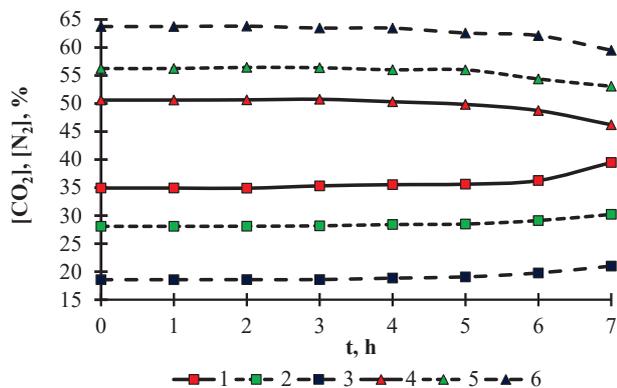


Fig. 2. Change in the concentration of carbon dioxide (1; 2; 3) and nitrogen (4; 5; 6) over time when passing the gas-air mixture at an oxygen concentration of 14.06 % (1; 4); 15.5 % (2; 5); 17.5 % (3; 6) at a flow rate, dm³/h: 376 (1; 4); 350 (2; 5); 323 (3; 6) (ΔM_{p1} =15.00 g; ΔM_{p2} =9.90 g; ΔM_{p3} =8.40 g; ΔM_{t1} =14.37 g; ΔM_{t2} =9.30 g; ΔM_{t3} =8.35 g)

The largest decrease in the mass of the carbon material sample during heat treatment at an oxygen concentrations of 14.0–17.5 % was observed at oxygen concentrations of 14.0 %, and the lowest mass decrease at concentrations of 17.5 % (Fig. 2, Table 2). The theoretically calculated mass loss in terms of the amount of formed carbon monoxide and

dioxide is close to the mass loss, determined by massometry. The increase in the mass loss of samples 1, 2, 3 (Fig. 2) is more likely due to the higher flow rate of the gas mixture than the decrease in oxygen concentration.

It should be noted that in the process of heat treatment of carbon material with the gas mixture containing oxygen at a concentration of 14.06–17.5 %, an increase in methane concentration (Fig. 3) is observed already at temperatures of 258–270 °C.

This can be explained by the fact that methane is released mainly due to the degassing of hydrocarbons from the carbon material.

Table 2

Change in the mass (ΔM) of carbon material for 7 hours, depending on oxygen content ([O₂]), temperature (T) and flow rate of the gas mixture (V)

T, °C		[O ₂], %	V, dm ³ /h	C _{KMnO₄} , %	M _{in} , g	M _{fin} , g	ΔM_p , g	ΔM_t , g	ΔM , %
min	max								
21.0	860	20.95	588	–	376.5	340.1	36.4	36.4	9.668
18.5	885	20.95*	588	–	382.3	340.2	42.1	41.8	11.012
17.7	860	20.95	588	1	362.4	303.6	58.8	58.6	16.251
19.4	855	20.95	588	5	329.5	258.0	71.5	70.9	21.700
20.7	860	20.95*	588	5	385.1	325.0	60.1	59.3	15.606
20.0	800	17.5	323	–	431.4	423.0	8.5	8.4	1.970
21.0	820	15.5	350	–	431.4	421.5	9.9	9.5	2.29
21.0	822	14.0	376	–	445.0	430.0	15.0	14.4	3.37
18.31	747	7.63	338	5	359.1	347.0	12.1	10.9	3.36

Note: * – Conditions with air saturation with water vapor

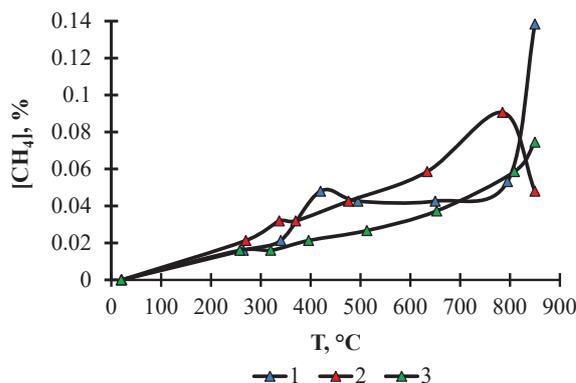


Fig. 3. Dependence of methane concentration of (1; 2; 3) on the heat chamber temperature at a flow rate of oxygen in the gas-air mixture, dm³/h: 52.60 (1), 54.25 (2), 56.53 (3)

As for the intensity of carbon oxidation by the mixture of air and carbon dioxide, according to the results in Fig. 4, 5 and Table 2, it can be said that oxidation intensity increases with increasing temperature and with increasing flow rate of the gas-air mixture. In this case, at an oxygen concentration of more than 14 %, the increase in the content of this gas has little effect on carbon oxidation intensity. The main parameters are the temperature and flow rate of the mixture. So, at oxygen concentrations of 14.0, 15.5 and 17.5 % at the gas flow rate of 376.0, 350.0 and 323.0 dm³/h, respectively, 52.60,

54.25 and 56.53 dm³ of oxygen respectively per hour were supplied in the heat chamber. Therefore, this had little effect on the intensity of carbon monoxide and dioxide formation.

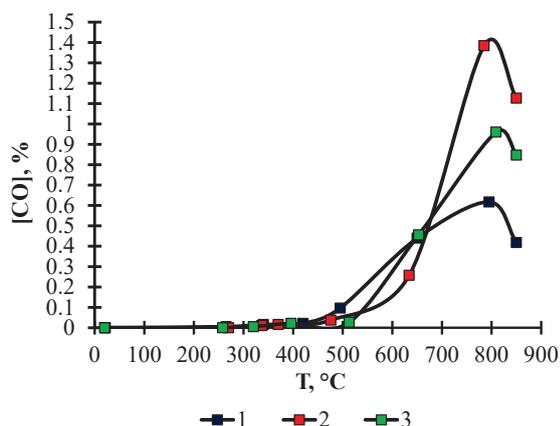


Fig. 4. Dependence of carbon monoxide concentration (1; 2; 3) on the heat chamber temperature at a flow rate of oxygen in the gas-air mixture, dm³/h: 52.60 (1), 54.25 (2), 56.53 (3)

On the other hand, when air, saturated with water vapor is fed into the heat chamber, during the preliminary air bubbling through the water layer, the results of gas emission differ substantially (Fig. 5). If at temperatures of 546–660 °C carbon monoxide concentrations were close when supplying dry and moist air (5,875 and 6,062 mg/m³ at 546 °C and 4,313 and 5,378 mg/m³ at 660 °C, respectively), then at temperatures of 660–850 °C, CO concentration reached 6,375 mg/m³ when supplying dry and 1,125 mg/m³ when supplying moist air. The difference in carbon monoxide concentrations reached 6,000 mg/m³ in the temperature range of 850–870 °C. Obviously, this is due to the catalytic effect of water vapor on high-temperature carbon monoxide oxidation. At the same time, when supplying air saturated with water, the mass of carbon material decreased by 42.1 g,

whereas when supplying unsaturated air, the mass of carbon material reached 36.4 g.

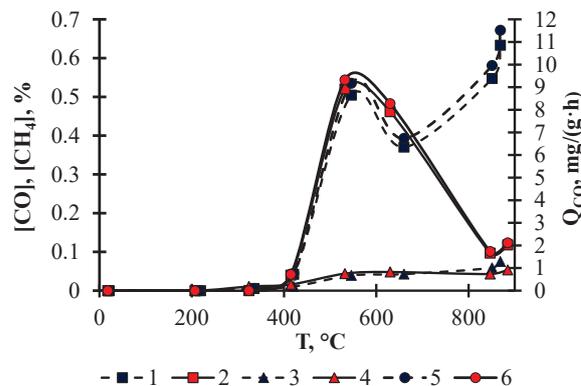


Fig. 5. Effect of the heat chamber temperature on the concentration of carbon monoxide (1; 2), methane (3; 4) and specific amount of carbon monoxide formed (5; 6) when passing air (1; 3; 5) and moist air (2; 4; 6) through the thermoanthracite carbon material at a flow rate of 588 dm³/h

5. 2. Effect of manganese oxide (IV) applied on carbon material on carbon oxidation intensity and ratio of carbon monoxide and dioxide in oxidation products

To intensify the processes of reoxidation of carbon oxide during the heat treatment of carbon material, it was modified by 1 % and 5 % potassium permanganate solutions by the method [14]. At the same time, when interacting with coal, permanganate is reduced to MnO₂ and remains on its surface in the form of microcrystals.

The results of using carbon material, modified with a 1 % potassium permanganate solution, are given in Table 3. When passing clean air, an increase in carbon dioxide concentration reached 5.59 % at a temperature of 674–847 °C, and carbon monoxide concentration decreased from 5,875–7,375 mg/m³ to 2,400–2,875 mg/m³.

Table 3

Change in temperature (T), concentration of O₂, CO₂, CO, CH₄ and Q_{CO} over heating time of carbon material, modified with a 1 % KMnO₄ solution *

t, h	T, °C			CO ₂ , %/C _{CO2} , %			C _{CO} ·10 ² , %/C _{CH4} ·10 ² , %			Q _{CO} , mg/(g·h)		
	1	2	3	1	2	3	1	2	3	1	2	3
0	16.7	19.8	26.0	20.95/0.03	18.45/15.30	16.15/28.81	0/0	0/0	0/0	0.0	0.0	0.0
1	288	315	216	20.95/0.04	18.46/15.35	16.12/28.82	1.07/18.09	0/1.06	0/1.06	0.21	0.0	0.0
2	372	335	320	20.95/0.08	17.89/15.39	16.14/28.78	1.07/11.71	0/0.53	0/3.72	0.21	0.0	0.0
3	465	427	384	18.84/1.89	17.28/15.93	16.12/28.85	1.07/11.18	0.54/1.06	0.54/3.75	0.21	0.07	0.08
4	528	484	470	18.03/2.66	16.51/16.57	15.44/28.90	4.29/12.77	2.69/1.60	1.07/3.75	0.84	0.35	0.17
5	674	591	593	16.51/4.41	15.57/17.38	12.77/29.65	20.92/15.44	24.68/4.78	25.22/4.26	4.11	3.22	3.90
6	847	838	793	14.81/5.59	13.73/17.48	12.77/32.18	24.68/19.16	25.75/4.78	37.03/7.98	4.85	3.36	5.72
7	–	868	826	–	12.99/18.35	10.47/34.46	–	8.59/4.26	52.58/9.06	–	1.12	8.12
ΣQ _{CO} , mg/(g·h)										10.4	8.1	18.0

Note: * – conditions during purging through the heat chamber: 1 – air (V=590 dm³/h), ΔM_{p1}=46.0 g; 2 – air and CO₂ mixture (2:3) at CO₂ flow rate of 60 dm³/h (V=392 dm³/h), ΔM_{p2}=35.3 g; 3 – air and CO₂ mixture (2:3) at CO₂ flow rate of 130 dm³/h (V=464 dm³/h), ΔM_{p3}=24.2 g

In the case of passing the mixture of air and CO₂ through the thermoanthracite carbon material, a decrease in CO reoxidation efficiency was observed. Thus, at an oxygen concentration of 18.45 %, the maximum CO concentration reached 3,000 mg/m³, and at an oxygen concentration of 16.15 %, the maximum CO content was the level of 6,125 mg/m³. The maximum increase in CO₂ concentrations reached 3.05 and 5.64 %, respectively. As oxygen concentration decreased, the mass loss was 46.02, 35.50 and 24.20 g, respectively.

The results obtained at the air flow rate of 588 dm³/h using the carbon material modified with a 5 % potassium permanganate solution are shown in Fig. 6, 7 and Table 4.

Table 4
Change in temperature (T), concentration of CO₂, O₂ over heating time (t) during purging air (1; 3; 4) and moist air (2; 5)* through the chamber

t, h	T, °C					C _{CO₂} , %/C _{O₂} , %				
	1	2	3	4	5	1	2	3	4	5
0	21.0	18.5	17.7	19.4	20.7	0.03/20.95	0.03/20.95	0.03/20.95	0.03/20.95	0.03/20.95
1	219	207	288	315	212	0.04/20.95	0.04/20.95	0.04/20.95	0.82/19.53	0.14/19.39
2	335	316	368	390	360	0.07/20.76	0.14/20.94	0.09/20.90	2.58/18.08	1.61/18.13
3	421	414	464	460	436	0.15/20.59	0.34/20.85	1.06/20.88	3.91/17.48	1.95/17.60
4	541	535	528	520	510	0.77/20.03	1.86/18.76	1.74/17.74	3.27/17.43	2.07/17.51
5	665	627	658	640	643	2.52/18.02	3.22/16.71	3.00/15.74	3.35/16.57	2.72/17.00
6	847	845	838	832	832	3.74/17.11	3.81/16.61	5.60/14.08	4.13/16.54	4.57/15.31
7	860	885	860	855	860	4.38/16.71	4.08/13.57	7.30/11.63	4.65/15.92	6.18/13.82

Note: * – conditions for the modification of the thermoanthracite carbon material: 1, 2 – unmodified; 3 – modified with 1 % potassium permanganate solution; 4, 5 – modified with 5 % potassium permanganate solution

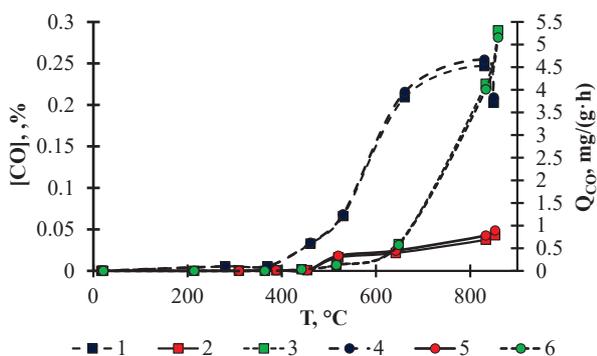


Fig. 6. Dependence of carbon monoxide concentration (1; 2; 3), specific amount of carbon monoxide formed (4; 5; 6) on the heat chamber temperature when passing air (1; 2; 4; 5) and moist air (3; 6) through the thermoanthracite carbon material modified with a 1 % (1; 4) and 5 % potassium permanganate solution (2; 3; 5; 6) at the air flow rate of 588 dm³/h

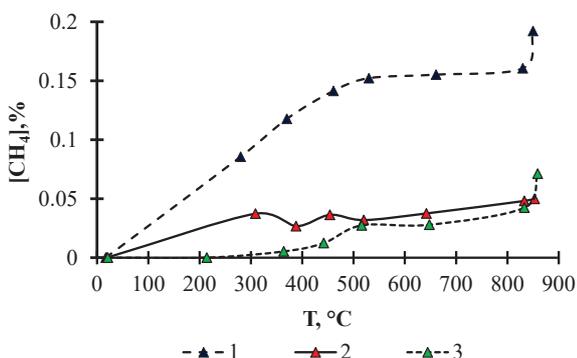


Fig. 7. Dependence of methane (concentration 1; 2; 3) on the heat chamber temperature when passing air (1; 2) and moist air (3) through the thermoanthracite carbon material, modified with 1 % (1) and 5 % potassium permanganate solution (2; 3) at the air flow rate of 588 dm³/h

As can be seen from Fig. 6, when using the material modified with a 5 % potassium permanganate solution, CO concentration in the gas mixture did not exceed 500 mg/m³. The use of this moist air has led to an increase in carbon monoxide concentration within 2,625–3,375 mg/m³ at temperatures of 800–850 °C. In this case, the application of moist air has led to a significant increase in CO₂ concentration in the gas mixture (Table 4).

It is obvious that manganese dioxide acts as a catalyst for CO reoxidation in the presence of oxygen. In the presence of water vapor, its efficiency at high temperatures (~850 °C) decreases. The efficiency of CO reoxidation by manganese dioxide also decreases dramatically when the oxygen concentration in the air mixture decreases to 8.31 % (Fig. 8).

As can be seen from Fig. 8, CO concentration in the gas mixture after the heat chamber reaches 3,250–7,875 mg/m³ at temperatures of 618–749 °C.

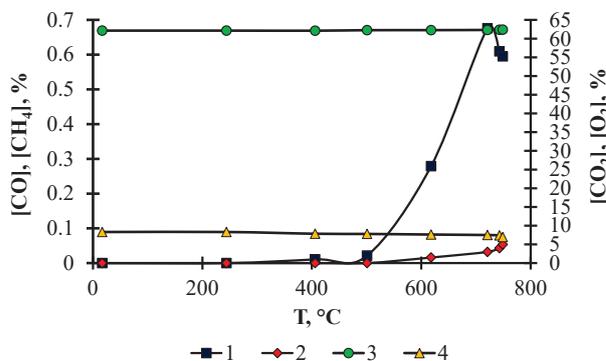
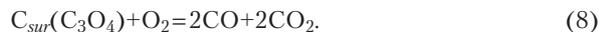


Fig. 8. Dependence of carbon monoxide (1), methane (2), carbon dioxide (3) and oxygen (4) concentration on the heat chamber temperature when passing the gas mixture through the thermoanthracite carbon material, modified with a 5 % potassium permanganate solution at a flow rate of 337 dm³/h

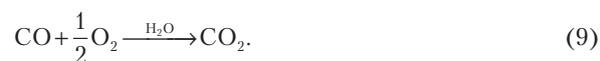
6. Discussion of the results on the processes of high-temperature oxidation of carbon material

According to the literature, carbon interacts with oxygen at high temperatures according to reactions [2]:



It is therefore clear that at the first stage of oxidation, the molar ratios of carbon monoxide and dioxide are 2:1 or 1:1. However, the results give a somewhat different relationship (Table 1, Fig. 2). The maximum carbon monoxide concentration reaches 126 mmol/m³, while under similar conditions carbon dioxide concentration was 455 mmol/m³. In other cases, CO₂ concentration even more exceeded the CO concentration. This is due to the fact that carbon monoxide in the presence of water vapor traces interacts with oxygen to form carbon dioxide. If we consider that the maximum carbon monoxide concentrations were reached within 500–700 °C, then we can say that in this temperature range a significant part of carbon monoxide is not reoxidized completely.

If we consider the process as a whole, then, in addition to reactions (6)–(8), the following reaction takes place:



In most cases, the reaction rate (9) is insufficient for complete reoxidation of carbon monoxide. The speed of this process can be described by the equation:

$$U_{(9)}=K_{(9)}\cdot[\text{CO}]^1\cdot[\text{O}_2]^{1/2}. \quad (10)$$

In fact, this reaction takes place in several stages, the most probable of which are the following:



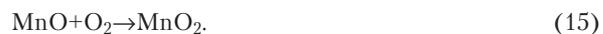
Of the reaction stages (11)–(13), the reaction rate (11) is the highest. The rate constant in the temperature range of 400–600 °C reaches 1.9·10¹²–2.57·10¹² cm³/mole·s [2]. Obviously, the limiting stage of the process is the reaction (12) whose rate constant in the same temperature range varies within 1.03·10²–6.89·10⁴ cm³/mol·s. It is obvious that the process of carbon monoxide reoxidation mainly depends on the oxygen concentration in the gas mixture. However, the rate of its formation also depends on oxygen concentration with a constant amount of carbon material. Therefore, its concentration in the gas mixture (Table 1) depends on both the oxidation rate of carbon material and the rate of CO reoxidation to CO₂. On the other hand, the degree of carbon material oxidation to CO and CO₂ within oxygen concentrations of 14.0–17.5 % is less dependent on oxygen concentration than the flow rate of the gas-air mixture (Tables 1, 2, Fig. 2). During heating of carbon material, the total loss of its mass at an oxygen concentration of 14.0, 15.5 and 17.5 %, respectively, amounted to 15.0, 9.9 and 8.4 g.

It is known that without the formation of hydroxyl radicals, oxidation of carbon monoxide to dioxide is impossible. Therefore, one should expect a decrease in the concentration of carbon monoxide in the mixture with an increase in water vapor concentration. As can be seen from Fig. 5, when passing air saturated with water vapor through the heat chamber during bubbling through water, there was a decrease in car-

bon monoxide concentration at temperatures of 630–885 °C. Obviously, this is due to an increase in the rate of hydroxyl radicals formation and the whole process of CO reoxidation to CO₂. Though in general, carbon material loss when passing ordinary air compared with moist air is slightly smaller and is 36.4 g compared with 42.1 g. Relatively significant loss of carbon material compared with the experiments presented in Table 1 and Fig. 2, 3 (previously 15.0–8.5 g) is due to higher air flow rate and higher heating temperatures at the final stage.

A certain decrease in carbon monoxide concentration was achieved using the carbon material modified with a 1 % potassium permanganate solution (Table 3). CO concentration was reduced to 1,000–3,000 mg/m³. With a decrease in oxygen concentration, the effect is slightly lower. With the use of carbon material modified with a 5 % permanganate solution, the maximum CO concentration was reduced by more than an order to 500 mg/m³.

Obviously, this is due to the catalytic action of MnO₂ acting by the reaction:



On the other hand, if we consider that in all cases, using potassium permanganate-modified carbon material at the same air flow rate, the carbon mass loss increases 1.6–2.0 times, then this cannot be explained simply by the growth of the oxidation rate of carbon monoxide. On the one hand, the acceleration of the second stage of carbon oxidation at the expense of the catalyst leads to the acceleration of the first stage due to a reduction in the rate of the reverse process. This is also noted when using moist air, where water played a catalyst role. On the other hand, at high temperatures, the possibility of interaction between manganese dioxide and coal is not excluded, which is precisely the reason for a significant acceleration of the process of carbon material oxidation. Therefore, in the case when carbon oxidation is undesirable, manganese dioxide should be applied to an inert material.

As can be seen from Fig. 8, when the oxygen concentration in the gas mixture decreases, the efficiency of the manganese catalyst is sharply reduced. This can be explained by the lack of oxygen to convert MnO to MnO₂. In this case, MnO practically does not interact with either CO, or carbon. Therefore, the carbon material consumption is only 12.1 g, the concentration of CO₂ formed decreases, but the concentration of carbon monoxide increases.

Such conclusions may be considered appropriate from the practical point of view, but there is a need for a more detailed study of the effect of oxygen concentration on the formation of carbon monoxide, as well as on the catalytic reoxidation of CO at an oxygen concentration of 4 to 16 %. This will allow determining which of the two parameters – oxygen concentration or gas-air mixture flow rate has a decisive influence on the formation and reoxidation of carbon monoxide. From the theoretical point of view, the conclusions made suggest the determination of the mechanism of reducing the carbon monoxide concentration, which is a certain advantage of this study. However, it should be noted that the results of the mechanism of high-temperature carbon material oxidation indicate the indispensable effect of the time of heating carbon material samples at a constant temperature, which clearly has a direct relation to the technological processes in real production. Such uncertainty imposes certain limitations on the use of the results, which

can be interpreted as disadvantages of this study. Failure to remove these restrictions within this study generates a potentially interesting direction for further research. It can, in particular, be focused on identification of the time point of establishing the maximum constant concentration of CO formation. Therefore, there is a need to study the processes of formation of carbon monoxide over a long time of heating of carbon material samples at a constant temperature within 500–800 °C.

7. Conclusions

1. It is found that noticeable oxidation of carbon material in a heat chamber during purging of gas-air mixtures with an oxygen content of 8–21 % begins at temperatures above 500 °C, and significant concentrations of carbon monoxide are formed at temperatures of 600–800 °C.

2. The effect of oxygen in the gas-air mixture and its flow rate during purging it through a heat chamber at temperatures up to 850 °C on carbon monoxide and dioxide concentrations, amount of oxidized carbon is determined. It is shown that, at

an oxygen concentration of 14 %, the content of carbon monoxide is minimal in the chosen range of oxygen concentrations. The amount of oxidized carbon in the range of oxygen concentrations of 8–21 % more depends on the temperature and flow rate of the gas mixture than on oxygen concentration.

3. It is shown that when using the gas mixture saturated with water vapor, the efficiency of carbon monoxide reoxidation increases at temperatures of 650–850 °C. When using the manganese catalyst, the catalytic effect of water vapor is not observed.

4. It is found that when applying manganese dioxide to the carbon material, the rate of carbon monoxide reoxidation to dioxide significantly increases with decreasing concentrations from 13,000–16,000 mg/m³ to 500 mg/m³ at temperatures of 500–850 °C. The disadvantage of the process is a 1.6–2.0 times increase in carbon material losses due to accelerated CO oxidation to CO₂ and coal to CO and CO₂. The efficiency of the catalyst is reduced when the oxygen concentration in the gas mixture is reduced to ~8 %. In this case, carbon losses due to oxidation are reduced almost 3 times compared with the process at 21 % oxygen concentration without the catalyst.

References

1. Numerical analysis of the physical fields in the process of electrode blanks graphitization in the castner furnace / Karvatskii A., Leleka S., Pedchenko A., Lazarev T. // *Eastern-European Journal of Enterprise Technologies*. 2016. Vol. 6, Issue 5 (84). P. 19–25. doi: <https://doi.org/10.15587/1729-4061.2016.83191>
2. Thermal and chemical aspects of formation co in the process of baking of electrodes / Panov E. N., Shilovich I. L., Ivanenko E. I., Buryak V. V. // *Eastern-European Journal of Enterprise Technologies*. 2012. Vol. 4, Issue 6 (58). P. 15–18. URL: <http://journals.uran.ua/eejet/article/view/5586/5026>
3. Rattan G., Kumar M. Carbon Monoxide Oxidation Using Cobalt Catalysts: A Short Review // *Chemistry & Chemical Technology*. 2014. Vol. 8, Issue 3. P. 249–260. doi: <https://doi.org/10.23939/chcht08.03.249>
4. Development of new catalysts for heterogenic catalytic CO to CO₂ oxidation on the basis of β-diketonate metals on a synthetic foamed ceramic / Tsyganova E. I., Didenkulova I. I., Shekunova V. M., Aleksandrov Yu. A. // *Vestnik Nizhegorodskogo universiteta im. N. I. Lobachevskogo*. 2007. Issue 2. P. 95–101.
5. Vysokoeffektivnye oksidno-margancevy katalizatory reakcii okisleniya SO / Ivanova N. D., Ivanov S. V., Boldyrev E. I., Sokol'skiy G. V., Makeeva I. S. // *Zhurnal prikladnoy himii*. 2002. Vol. 75, Issue 9. P. 1452–1455.
6. Kašpar J., Fornasiero P., Hickey N. Automotive catalytic converters: current status and some perspectives // *Catalysis Today*. 2003. Vol. 77, Issue 4. P. 419–449. doi: [https://doi.org/10.1016/s0920-5861\(02\)00384-x](https://doi.org/10.1016/s0920-5861(02)00384-x)
7. Study of Hopcalite (CuMnOx) Catalysts Prepared Through A Novel Route for the Oxidation of Carbon Monoxide at Low Temperature / Dey S., Dhal G. C., Mohan D., Prasad R. // *Bulletin of Chemical Reaction Engineering & Catalysis*. 2017. Vol. 12, Issue 3. P. 393–407. doi: <https://doi.org/10.9767/bcrec.12.3.882.393-407>
8. Effects of Doping on the Performance of CuMnOx Catalyst for CO Oxidation / Dey S., Dhal G. C., Prasad R., Mohan D. // *Bulletin of Chemical Reaction Engineering & Catalysis*. 2017. Vol. 12, Issue 3. P. 370–383. doi: <https://doi.org/10.9767/bcrec.12.3.901.370-383>
9. Spriamuvannia defektnoho poriadku v produktakh anodnoho okyslennia z bahatokomponentnykh za ionamy metaliv elektrolitiv dlia ekolohichnoho katalizu / Sokolskyi H. V., Ivanov S. V., Ivanova N. D., Boldyriev Ye. I., Kobylanska O. V. // *AVIA-2007: materialy Mizhnarodnoi nauko-tekhnichnoi konferentsiyi*. Vol. 3. Kyiv, 2007. P. 41.77–41.80.
10. Development of burning regulations take into account the dynamics of gas emission of burning blanks / Karvackiy A. Ya., Leleka S. V., Pulinec I. V., Lazarev T. V. // *Eastern-European Journal of Enterprise Technologies*. 2011. Vol. 6, Issue 5 (54). P. 42–45. URL: <http://journals.uran.ua/eejet/article/view/2281/2085>
11. Decrease of CO concentration using installation for carbon mono oxide convesion / Karvatskyi A. Ya., Shylovykh I. L., Krutous L. V., Kutuzov S. V. // *Eastern-European Journal of Enterprise Technologies*. 2013. Vol. 2, Issue 11 (62). P. 38–41. URL: <http://journals.uran.ua/eejet/article/view/11730/9872>
12. Air pollution emissions during baking of semi-finished graphite products in a tunnel furnace / Bogacki M., Oleniacz R., Mazur M., Szczygłowski P. // *Environment Protection Engineering*. 2012. Vol. 38, Issue 1. P. 15–23.
13. Emission of polycyclic aromatic hydrocarbons (PAHs) during the production of carbon and graphite electrodes / Mazur M., Oleniacz R., Bogacki M., Szczygłowski P. // *Environmental Engineering III*. 2010. P. 59–66. doi: <https://doi.org/10.1201/b10566-12>
14. Hohotva A. P., Mel'nikova N. V. Ochistka fenolsoderzhashchih vod okisleniem na suspenzii MnO₂ // *Energotekhnologii i resursoberezhenie*. 2008. Issue 5. P. 59–61.
15. Doped manganese (IV) oxide in organic compounds destruction and elimination processes from aqueous solutions / Sokolsky G. V., Ivanov S. V., Ivanova N. D., Boldyrev Ye. I., Lobunets T. P., Tomila T. V. // *Himiya i tekhnologiya vody*. 2012. Vol. 34, Issue 5. P. 386–397.