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ENERGY BALANCE FOR A THREE-WAY CATALYTIC REACTOR

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Summary. The paper presents the methodology of energy balance determination for a three-way catalytic reactor of exhaust gases. Calculations results and the results of experimental simulation investigations into the temperature change in exhaust gases flowing through the converter are also provided. It was demonstrated that the change in exhaust gases temperature, measured as the difference between exhaust gases temperature as they flow out of the converter and into it, could be used as a diagnostic signal. It may help to evaluate the effectiveness of an exhaust gases three-way catalytic reactor.

Key words: exhaust gases catalytic reactor, energy balance, diagnostics

INTRODUCTION

The number of automotive vehicles in use leads to a rise in fuel consumption on a global scale and, as a result, increase in the emission of exhaust gases harmful components into the environment.

The most important atmosphere pollutants emitted from piston internal combustion engines are: carbon monoxide CO, hydrocarbons HC, nitrogen oxides NO_x, particulate matter PM and aldehydes RCHO, sulphur and lead compounds. Presently, the most effective method of reducing the emission of the above-mentioned noxious substances is the neutralisation and filtration of exhaust gases. Simultaneous chemical change of carbon monoxide CO, hydrocarbons HC, nitrogen oxides NO_x into substances that are not harmful is possible due to widely applied three-way catalysts (TWC).

Long lasting, extreme service conditions of catalytic converters, the use of fuels of different, sometimes low, qualities make converters get deactivated, which deteriorates a vehicle's ecological performance. Therefore, continuous evaluation of a converter's operative effectiveness and its technical state is a vital issue.

One of the methods of an assessment of a TWC operation's effectiveness is the measurement of the temperature of exhaust gases at the converter inflow and outflow. Exhaust gases temperature difference measured in such a way is treated as a catalytic converter's diagnostic signal. It is caused by internal exothermic chemical reactions and heat transfer. The determination of the above-mentioned exhaust gases temperature difference and its application to the evaluation of a catalytic reactor's effectiveness is possible, owing to a proper determination of a converter's energy balance.

ENERGY BALANCE FOR A THREE-WAY CATALYTIC REACTOR

The equation of energy balance for a three-way catalytic reactor is necessary to determine the temperature of exhaust gases flowing out of the converter. It also accounts for thermal effects of chemical reactions proceeding inside the reactor and for heat transfer between the flowing exhaust gases and the converter bed. The temperature of exhaust gases flowing into the converter can be determined on the basis of the engine heat calculations and the heat balance equation made for the exhaust gases outlet system located between the exhaust gases outflow from the cylinder and their inflow to the converter. The exhaust gases temperature can also be measured experimentally.

While making the energy balance for the exhaust gases catalytic reactor the following assumptions are made:

- the reactor operates at the set conditions of internal combustion engine work,
- exhaust gases flow through the catalytic converter is a stationary one-dimensional flow,
- exhaust gases flow through a single reactor channel takes place at convection heat transfer between exhaust gases and the channel walls,
- four basic reactions proceed inside the reactor: the oxidation of carbon monoxide, hydrocarbons and hydrogen and the reduction of nitrogen oxides, for which thermal effects are determined,
- values of thermal effects of chemical reactions taking place in the reactor depend on temperature and are calculated on the basis of Kirchoff law.

The functional diagram of a three-way catalytic reactor is shown in Fig. 1.

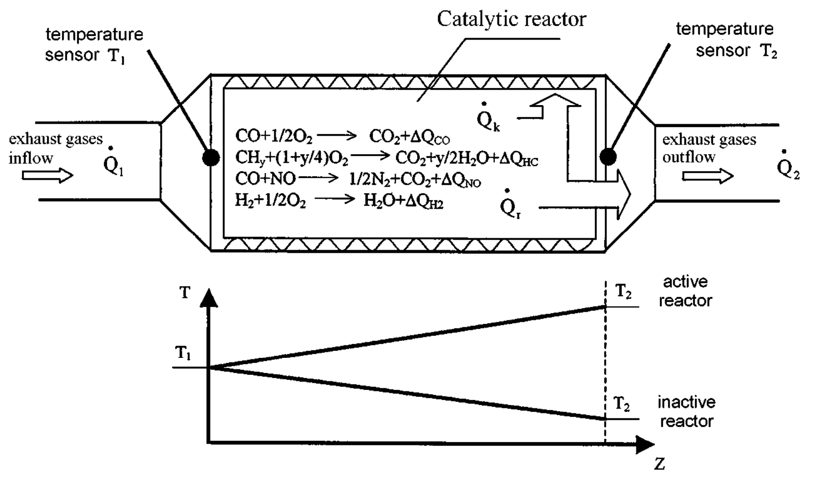

Fig. 1. The functional diagram of a three-way exhaust gases catalytic reactor [Ambrozik A. *et al.*]

The equation of the heat expenditure balance in the reactor has the form:

$$\dot{Q}_1 + \dot{Q}_r - \dot{Q}_k - \dot{Q}_2 = 0 \tag{1}$$

where:

$\dot{Q}_1$ – expenditure of the heat supplied with exhaust gases flowing into the reactor;
$\dot{Q}_r$ – expenditure of the internal source of heat emitted in the reactor;
$\dot{Q}_k$ – expenditure of heat transferred by convection between exhaust gases and the catalytic reactor monolith;
$\dot{Q}_2$ – expenditure of heat convected with exhaust gases flowing out of the converter.

The values of the components of the reactor energy balance (1) is calculated from the dependence: heat expenditure of exhaust gases $\dot{Q}_1$ flowing into the converter is calculated from the formula:

$$\dot{Q}_1 = \dot{M}_s \mu \cdot c_{p1} \int_{T_0}^{T_1} (T_1 - T_o), \ \mathrm{W} \tag{2}$$

where:

$\dot{M}_s$ – kilo-molar expenditure of exhaust gases flowing out of cylinders and passing through the engine outlet (reactor),
$\mu \cdot c_{p1}$ – kilo-molar specific heat of exhaust gases,
T_1 – temperature of exhaust gases at the converter inflow,
T_o – ambient temperature.

The values of the quantity $\dot{M}_s$ are calculated in accordance with the formula:

$$\dot{M}_s = \beta_r \cdot \frac{n}{2} \cdot V_s \cdot \eta_v \cdot c \cdot \frac{\rho_s}{M_{\mu s}}, \ \frac{kmol}{s} \tag{3}$$

where:

β_r – real coefficient of molar changes,
n – crankshaft rotational speed,
V_s – cylinder swept capacity,
η_v – degree of the cylinder filling,
c – number of engine cylinders,
ρ_s – exhaust gases density,
$M_{\mu s}$ – kilo-molar exhaust gases mass.

The mean kilo-molar specific heat of exhaust gases at constant pressure is calculated on the basis of the formula:

$$\mu \cdot c_p = a + b \cdot \frac{T_1 + T_2}{2}, \frac{J}{kmol \cdot K} \tag{4}$$

The expenditure of the heat emitted in the reactor due to the chemical reactions taking place in it (Fig. 1):

$$\dot{Q}_r = \Delta \dot{M}_{co} \cdot Q_{pCO} + \Delta \dot{M}_{HC} \cdot Q_{pHC} + \Delta \dot{M}_{H_2} \cdot Q_{pH_2} + \Delta \dot{M}_{NO_x} \cdot Q_{pNO_x} \tag{5}$$

In the dependence above, the quantities $\Delta \dot{M}_{co}, \Delta \dot{M}_{HC}, \Delta \dot{M}_{H_2}$ and $\Delta \dot{M}_{NO_x}$ denote the values of kilo-molar expenditures of the reactions of respective exhaust gases components, which reacted in the converter in accordance with Fig.1, whereas the quantities $Q_{pCO}, Q_{pHC}, Q_{pH_2}$ and Q_{pNO_x} are the values of kilo-molar thermal effects of oxidation and reduction reactions in the converter.

The values of $\Delta \dot{M}_i$ are calculated from the dependence:

$$\Delta \dot{M}_i = \dot{M}_{wi} - \dot{M}_{di} \tag{6}$$

where:

$\dot{M}_{wi}$ – kilo-molar expenditure of the i-th component flowing out of the converter, whereas

$\dot{M}_{di}$ – kilo-molar expenditure of the i-th component flowing into the converter.

The values of the quantities of thermal effects of chemical reactions of the exhaust gases i-th component in the catalytic reactor are calculated from the formula:

$$Q_{pi} = Q_i^o + \alpha_i \frac{T_1 + T_2}{2} + \beta_i \left(\frac{T_1 + T_2}{2} \right)^2, \frac{J}{kmol} \tag{7}$$

In the formula (7), the quantities Q_i^o denote the values of thermal effects of the exhaust gases i-th component under standard conditions; the quantities α_i and β_i are summary specific heats calculated in accordance with [Ambrozik 2003], whereas T_1 and T_2 are exhaust gases temperatures at the converter inflow and outflow, respectively.

The expenditure of the heat transferred by convection to the reactor monolith is calculated in accordance with Newton formula:

$$\dot{Q}_k = \pi D_z L \alpha_p \left(\frac{T_1 + T_2}{2} - T_{sc} \right), \text{W} \tag{8}$$

where:

D_z – the substitute (hydraulic) reactor diameter,

L – the reactor length,

α_p – the heat transfer coefficient,

T_1 and T_2 – exhaust gases temperatures at the converter inflow and outflow, respectively,

T_{sc} – the reactor wall temperature.

Expenditure of the heat $\dot{Q}_2$ convected with exhaust gases flowing out of the converter is calculated from the formula:

$$\dot{Q}_2 = \dot{M}_s \mu \cdot c_{p2} \int_{T_0}^{T_2} (T_2 - T_o), \text{ W} \tag{9}$$

Inserting dependences (2)÷(9) into the equation (1), a quadratic equation is obtained, whose solution is the value of exhaust gases temperature T_2 at the converter outflow. The value of the difference of exhaust gases temperatures ΔT, being a diagnostic signal for the catalytic converter is calculated from the formula:

$$\Delta T = T_2 - T_1 \tag{10}$$

OBJECT OF INVESTIGATIONS AND THE RESEARCH STAND

The investigations focused on a three-way catalytic reactor Pt-Rh/ AL_2O_3-CeO_2 , whose monolith volume was V_m = 1.2 dm^3 , installed in the engine Rover 1.4 outlet system. The converter, manufactured by Lindo – Gobex company of Gorzów Wielokopolski, Poland, has the form of a metal monolith covered with the support structure γ-Al_2O_3 – CeO_2 with platinum and rhodium crystallites deposited on it at the ratio 5:1. Platinum and rhodium amount to 2.0 g/dm^3 of the monolith volume. It has a cylindrical shape, 100mm in diameter D and 150mm in length L. The possibility of installing the catalytic reactor monolith without an intermediate layer or the catalytic layer of noble metals makes it possible to experimentally simulate the operation of a three-way catalytic reactor in the range from 0 to 100% of its activity, with the step every 12.5%. In the simulation experiment, in the converter front part, the segments of the active monolith are substituted with inactive ones. The activity of catalytic reactor is defined as the ratio of the volume of active segments V_a to the volume of the whole reactor V_k.

$$A = \frac{V_a}{V_k} \tag{11}$$

The efficiency of the catalytic reactor being investigated is assessed with the value of the conversion coefficient determined in accordance with the formula:

$$k_x = \frac{C_{x1} - C_{x2}}{C_{x1}} \tag{12}$$

where:

C_{x1} and C_{x2} – denote respective concentrations of the i-th component at the reactor inlet and outlet.

Engine Rover 1.4, in the outlet system of which the catalytic reactor is installed, is characterised by the following technical data:

– Cylinder diameter D_c	0.075 m
– Piston stroke S	0.079 m
– Displacement volume V_{ss}	1394 cm^3
– Cylinder system and number	R4
– Compression ratio ε	10.5
– Power rating N_{eN}	76 kW
– Rated rotational velocity of the crankshaft n_N	6500 r.p.m
– Maximum torque M_{eM}	145 N·m
– Rotational velocity of the torque n_M	3000 r.p.m

While investigated, the engine was fuelled with unleaded petrol Eurosuper 95, which complies with the standard PN/EN-228.

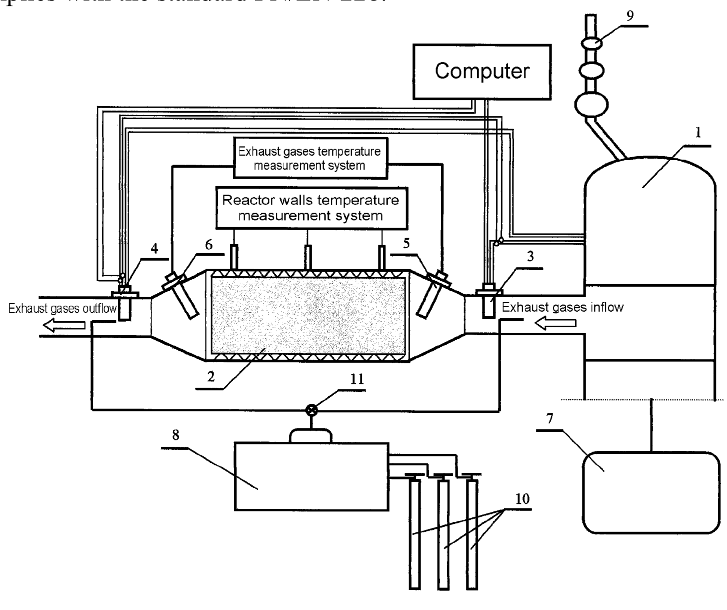

Fig. 2. Diagram of the research stand: 1 – magneto ignition Rover engine; 2 – three-way catalyst; 3 – oxygen sensor used to control air-fuel mixture composition; 4 – oxygen sensor used to evaluate the reactor technical state; 5 – exhaust gases temperature sensor at the reactor inflow T_1; *Leszek Mościcki,* Lublin, Poland 6 – exhaust gases temperature sensor at the reactor outflow T_2; 7 – eddy-current brake HEW150; 8 – exhaust gases analyser; 9 – system for fuel consumption measurement; 10 – set of standard gases; 11 – three-way valve

The research stand presented in Fig. 2. was additionally equipped with:

1. The system for the measurement of fuel consumption, which complies with the standard PN – 88/S-02005.
2. Computerised exhaust gases analyser called Multigas Analytical System Dual Purpose manufactured by Richard Olivier Ltd, which enables us to takes measurements of the concentration of the following components of exhaust gases:
   - carbon monoxide and carbon dioxide with NDIR method;
   - summary amount of hydrocarbons with FID method (converted into propane);
   - summary amount of nitrogen oxides with CLD method (converted into nitric oxide).

   Apart from the above-mentioned exhaust gases components, with the analyser one is capable of taking measurements of oxygen contained in exhaust gases with the paramagnetic method.
3. A set of standard and auxiliary gases necessary for the calibration of the systems for measuring the concentration of exhaust gases poisonous components.
4. Multichannel system for temperature measurements, which comprises: EMT – 100 indicator by Czaki Thermo company with channel selector and temperature detector NiCr – NiAl(K) of TP – 371K – W1 – M8×1 type.
5. Computerised system for recording signals from oxygen concentration sensors using the measurement card PCL – 818 and notebook class PC by HELIKAN company.

RESULTS OF INVESTIGATIONS AND CALCULATIONS

The results of experimental investigations and the obtained calculations results are presented in Tables 1 and 2 and in Fig. 3.

Table 1. Values of parameters and work indexes based on thermal calculations for the engine and the catalytic reactor when the activity of its operation equals 100%

Experiment no.	n r.p.m	M_e N·m	N_e kW	λ	η_v	M_{czr} kmol	G_e $\frac{kg}{h}$	g_e $\frac{g}{kW \cdot h}$	q_c $\frac{kg}{cycle}$	$\dot{M}_S$ $\frac{kmol}{s}$
	1	2	3	4	5	6	7	8	9	10
1.	2000	36	7.54	1.023	0.71	$5.28\cdot10^{-6}$	2.40	$3.04\cdot10^{2}$	$1.00\cdot10^{-5}$	$4.84\cdot10^{-4}$
2.		48	12.14	1.019	0.87	$6.47\cdot10^{-6}$	2.95	$2.81\cdot10^{2}$	$1.23\cdot10^{-5}$	$4.81\cdot10^{-4}$
3.		58	14.21	1.021	0.91	$7.61\cdot10^{-6}$	3.47	$2.73\cdot10^{2}$	$1.44\cdot10^{-5}$	$4.84\cdot10^{-4}$
4.	3000	32	10.05	1.018	0.78	$4.72\cdot10^{-6}$	3.24	$3.07\cdot10^{2}$	$8.99\cdot10^{-6}$	$4.86\cdot10^{-4}$
5.		45	13.19	1.013	0.85	$5.93\cdot10^{-6}$	4.08	$2.76\cdot10^{2}$	$1.13\cdot10^{-5}$	$4.90\cdot10^{-4}$
6.		60	18.85	1.009	0.93	$7.09\cdot10^{-6}$	4.90	$2.48\cdot10^{2}$	$1.36\cdot10^{-5}$	$4.92\cdot10^{-4}$
7.	4000	32	13.40	1.008	0.62	$2.81\cdot10^{-6}$	2.59	$1.85\cdot10^{2}$	$5.40\cdot10^{-6}$	$4.90\cdot10^{-4}$
8.		45	18.85	1.004	0.74	$3.26\cdot10^{-6}$	3.02	$1.53\cdot10^{2}$	$6.29\cdot10^{-6}$	$4.92\cdot10^{-4}$
9.		62	25.97	1.004	0.92	$4.11\cdot10^{-6}$	3.81	$1.40\cdot10^{2}$	$7.95\cdot10^{-6}$	$4.98\cdot10^{-4}$

Table 1. continued

$\Delta \dot{M}_{CO}$ $\frac{\text{kmol}}{\text{s}}$	$\Delta \dot{M}_{HC}$ $\frac{\text{kmol}}{\text{s}}$	$\Delta \dot{M}_{NO}$ $\frac{\text{kmol}}{\text{s}}$	$\Delta \dot{M}_{H2}$ $\frac{\text{kmol}}{\text{s}}$	k_{CO} %	K_{HC} %	K_{NO} %	Q_{pCO} $\frac{\text{J}}{\text{kmol}}$	Q_{pHC} $\frac{\text{J}}{\text{kmol}}$
11	12	13	14	15	16	17	18	19
$-3.34 \cdot 10^{-6}$	$-2.68 \cdot 10^{-7}$	$-5.68 \cdot 10^{-7}$	$-1.10 \cdot 10^{-7}$	98.6	94.5	78.2	$-283.8 \cdot 10^{6}$	$-1994.1 \cdot 10^{6}$
$-3.41 \cdot 10^{-6}$	$-2.98 \cdot 10^{-7}$	$-6.31 \cdot 10^{-7}$	$-1.17 \cdot 10^{-6}$	98.8	94.3	83.3	$-279.0 \cdot 10^{6}$	$-1981.2 \cdot 10^{6}$
$-3.70 \cdot 10^{-6}$	$-3.38 \cdot 10^{-7}$	$-7.48 \cdot 10^{-7}$	$-1.22 \cdot 10^{-6}$	98.7	94.6	75.9	$-278.1 \cdot 10^{6}$	$-1975.5 \cdot 10^{6}$
$-3.35 \cdot 10^{-6}$	$-3.08 \cdot 10^{-7}$	$-5.37 \cdot 10^{-7}$	$-1.10 \cdot 10^{-6}$	98.6	94.7	73.1	$-281.1 \cdot 10^{6}$	$-1982.7 \cdot 10^{6}$
$-3.45 \cdot 10^{-6}$	$-2.72 \cdot 10^{-7}$	$-1.33 \cdot 10^{-6}$	$-1.31 \cdot 10^{-6}$	98.6	94.9	85.3	$-279.1 \cdot 10^{6}$	$-1978.2 \cdot 10^{6}$
$-3.98 \cdot 10^{-6}$	$-2.38 \cdot 10^{-7}$	$-1.23 \cdot 10^{-6}$	$-1.19 \cdot 10^{-6}$	98.8	94.5	91.5	$-278.5 \cdot 10^{6}$	$-1974.7 \cdot 10^{6}$
$-3.09 \cdot 10^{-6}$	$-2.94 \cdot 10^{-7}$	$-1.28 \cdot 10^{-6}$	$-1.02 \cdot 10^{-6}$	98.8	93.6	94.1	$-280.1 \cdot 10^{6}$	$-1983.2 \cdot 10^{6}$
$-4.24 \cdot 10^{-6}$	$-2.75 \cdot 10^{-7}$	$-1.56 \cdot 10^{-7}$	$-1.38 \cdot 10^{-6}$	99.0	87.3	97.9	$-278.5 \cdot 10^{6}$	$-1978.0 \cdot 10^{6}$
$-4.53 \cdot 10^{-6}$	$-2.52 \cdot 10^{-7}$	$-1.74 \cdot 10^{-7}$	$-1.49 \cdot 10^{-6}$	98.9	86.1	91.8	$-277.4 \cdot 10^{6}$	$-1973.2 \cdot 10^{6}$

Q_{pNO} $\frac{\text{J}}{\text{kmol}}$	Q_{pH_2} $\frac{\text{J}}{\text{kmol}}$	$\dot{Q}_{pCO}$ W	$\dot{Q}_{pHC}$ W	$\dot{Q}_{pNO}$ W	$\dot{Q}_{pH_2}$ W	$\sum \dot{Q}$ W	T_1 K	T_2 K	ΔT K
20	21	22	23	24	25	26	27	28	29
$-373.7 \cdot 10^{6}$	$-250.2 \cdot 10^{6}$	935.35	725.58	209.82	272.05	2143	1176	1274	98
$-372.3 \cdot 10^{6}$	$-246.3 \cdot 10^{6}$	965.21	669.54	194.31	277.51	2106	1180	1281	101
$-370.9 \cdot 10^{6}$	$-244.4 \cdot 10^{6}$	1040.1	666.75	277.56	298.83	2279	1198	1296	98
$-371.0 \cdot 10^{6}$	$-247.6 \cdot 10^{6}$	940.29	609.04	311.42	270.79	2132	1181	1278	97
$-370.8 \cdot 10^{6}$	$-245.2 \cdot 10^{6}$	992.41	588.19	383.11	351.21	2335	1191	1285	94
$-370.1 \cdot 10^{6}$	$-242.5 \cdot 10^{6}$	1110.2	537.34	493.95	320.36	2461	1205	1294	89
$-371.0 \cdot 10^{6}$	$-246.1 \cdot 10^{6}$	863.68	579.37	476.48	249.31	2169	1188	1281	93
$-370.2 \cdot 10^{6}$	$-244.5 \cdot 10^{6}$	991.62	464.13	568.25	271.32	2295	1191	1291	96
$-369.3 \cdot 10^{6}$	$-242.1 \cdot 10^{6}$	1261.1	496.72	643.63	363.27	2763	1199	1301	102

Table 2. Measurement results obtained in experimental investigations into three-way catalytic converter at the reactor activity 100% [Łączyński 2004]

Experiment no.	n r.p.m	M_e Nm	t_p s	CO_2 %	O_2 %	CO %	HC ppm	NO_x ppm	T_{sc} K	T_1 K	T_2 K	ΔT K
	1	2	3	4	5	6	7	8	12	13	14	15
1.	2000	36	56.6	12.78 14.09	1.01 0.00	0.70 0.01	806 44	1503 327	685	664	746	82
2.		48	46.0	12.75 14.20	0.99 0.04	0.82 0.01	772 44	1747 291	715	703	777	74
3.		58	39.2	12.78 14.17	1.03 0.05	0.78 0.01	743 40	2049 494	763	741	817	76
4.	3000	32	42.0	12.96 14.30	0.96 0.04	0.72 0.01	732 39	2354 633	710	703	777	74
5.		45	33.3	12.95 14.41	0.89 0.05	0.74 0.01	666 34	3062 449	784	759	831	72
6.		60	27.2	12.99 14.44	0.86 0.04	0.84 0.01	635 35	3376 287	831	814	885	71
7.	4000	32	30.2	13.12 14.73	0.82 0.04	0.82 0.01	671 43	3173 186	822	803	862	59
8.		45	24.3	12.86 14.14	0.81 0.00	0.99 0.01	621 79	3419 73	884	861	922	61
9.		62	18.2	12.42 14.04	0.79 0.00	0.92 0.01	588 82	3805 311	924	912	977	65

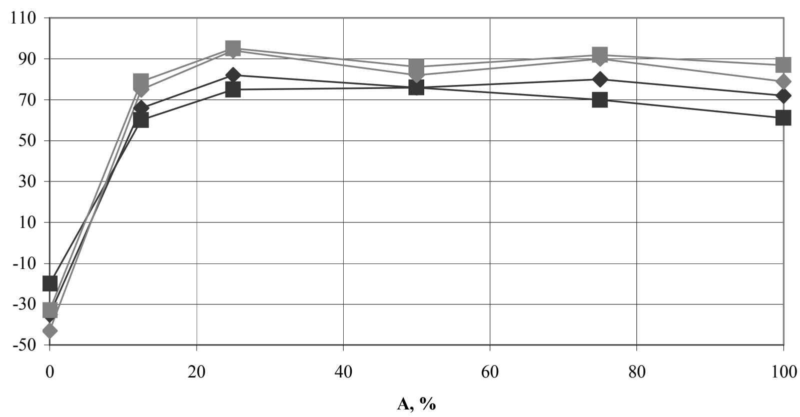

Fig. 3. Comparison of experimental ΔT_b and calculated ΔT_o exhaust gases temperature difference depending on the simulated operation of the catalytic reactor A

$\Delta T_b = f(A)$ at n = 2000 r.p.m

$\Delta T_b = f(A)$ at n = 3000 r.p.m

$\Delta T_o = f(A)$ at n = 2000 r.p.m

$\Delta T_o = \mathrm{f}(A)$ at n = 3000 r.p.m

CONCLUSIONS

The methodology of energy balance determination for a three-way exhaust converter worked out by the authors confirms it is possible and justifiable to adopt the difference in exhaust gases temperature at the converter inflow and outflow as a diagnostic signal used to evaluate the catalytic reactor efficiency. The values of the above-mentioned temperature differences determined experimentally and on the basis of the energy balance proposed in the article do not differ by more than 12%.

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