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SELF-SUSTAINED FLAMELESS HEAT GENERATOR BASED ON CATALYTIC OXIDATION OF METHANE OR PROPANE-BUTANE MIX FOR HEATING VARIOUS OBJECTS, INCLUDING FOR FIELD HEATING

An effective catalyst based on ceramic block support with honeycomb structure made of synthetic cordierite with a low coefficient of temperature linear expansion has been developed. Flameless heat generator based on oxidation of methane or propane-butane mixture has been designed. Laboratory and bench trials have showed that the effectiveness of the generator is identical to the foreign analogues. The manufacture of self-sustained flameless heat catalytic generators and catalysts have been launched.

Keywords: catalytic heat generator, catalyst for flameless methane or propane-butane mixture oxidation, honeycomb structure cells, and cordierite.

The combustion of solid, liquid, and gaseous fuels in catalytic generators is an effective and environmentally friendly method of heat generation. This is very relevant in the view of modern trends in power engineering sector, which are based on the transition from the centralized to the combined electricity supply, including the self-sustained power plants with different thermal capacity. Catalytic flameless combustion is an effective way for energy- and resource-saving use of solid, liquid, and gaseous fossil fuels. Here are the main advantages of the catalytic flameless combustion as compared with the jet fire listed:

1) Complete fuel combustion that facilitates raising output-input factor up to 97—99%;

2) Reduced combustion temperature from 1000—1200 down to 300—700 °C while keeping a high combustion intensity;

3) Complete combustion of both poor and stoichiometric fuel-air mixes;

4) Reduction of air pollution with poisonous gases, including CO and NO_x, as a result of reduced combustion temperature and complete combustion of the fuel;

5) Use of cheaper construction materials as a result of reduced process temperature.

Catalytic combustion is fundamentally different from the jet (homogeneous) fire, insofar as the fuel on surface of solid catalyst is oxidized without flame. The catalysts in the course of complete oxidation (heterogeneous combustion) of fuel-air mixture are involved in the chemical reaction of fuel components with surface oxygen of the catalyst with further regeneration of reduced catalyst surface by oxygen of the gaseous phase. The gaseous fuel has several advantages over the solid and the liquid ones: it is cheap and quickly mixed with air, which enables burning gas with a lower excessive amount of oxidizer. The presence of a catalyst in the reaction system lowers the temperature of burning gaseous fuel from 1000—1200 to 300—

700 °C while maintaining a high burning intensity and ensures the complete combustion of fuel-air mixtures in wide range of fuel/air proportions, including, stoichiometric mixtures. The most important fact is that the catalyst ensures a complete conversion of fuel into products of deep oxidation and prevents emissions of carbon monoxide and organic compounds that are products of incomplete combustion of hydrocarbons. Deep oxidation catalysts are based on porous oxide carrier to which active ingredients containing precious metals (mainly, platinum and palladium) are applied. Numerous crystalline alumina modifications that determine the final properties (micro-porosity, pore size distribution, and specific surface area) are commonly used as catalyst carriers.

Practically, granular materials in the form of extrudate and balls made of oxide material (e.g., aluminum oxide catalysts for fuel combustion in stationary bulk or in fluidized layer of catalyst) are used. An important aspect of preparing the aggregate media is the so-called «*dual porosity*». For this purpose, oxides with specific effective surface and meso- or microporous structure are applied to the outer surface and into the pores of ceramic material (cell or porous material with a high permeability) having a diameter from 500 nm to several microns [1].

The most common catalysts for flameless combustion of hydrocarbon fuels are composites based on platinum group metals (PGM) and oxides of 3d-metals or those deposited on inert carrier which defines the catalyst macrostructure.

Oxides of transition metals (Cu, Cr, Mn, Co, etc.) are an efficient alternative to precious metals as catalysts for combustion of fuels. However, the simple oxides are prone to being baked at high temperature and to interacting with the carrier material with subsequent formation of new inactive phase. Therefore, often, high-temperature oxide phases such as hexa-aluminates obtained, for example, as a result of the interaction of manganese and aluminum oxides at high temperature, are used. The general disadvantage of the catalysts that do not contain PGM, in particular, those described in patents [2—7] is a high temperature at the start of operation, the need for additional (PGM based) catalyst for «ignition», and incomplete combustion of hydrocarbon fuels. These shortcomings make impossible the indoor use of these catalysts for portable catalytic heat generators based on flameless combustion of hydrocarbon fuels.

The most effective catalysts for flameless combustion of organic fuels, including C1—C4-hydrocarbons, are the systems containing platinum particles having a size of 1—5 nm [8]. The platinum nano-catalysts are matchless in terms of activity, completeness of fuel combustion, thermal and chemical stability. Disadvantages of these catalysts are expansive active component, platinum volatility at temperature over 800 °C, as well as poisonous sulfuric compounds. The use of palladium catalysts is limited with temperature of 700—800 °C [9].

Various crystalline modifications of aluminum oxide that determine structural properties (microporosity, pore size distribution, and specific surface area) are widely used as catalyst carriers [10]. To enhance thermal stability of the catalysts for flameless combustion of combustible gases, modifiers such as oxides of lanthanum, cerium, magnesium, strontium and so on are added to the catalysts.

There is a variety of heat catalytic generators: the fluidized bed reactors with granular catalyst; the fixed bed reactors with granular, cellular, fibrous catalysts [11—14]. Also, there are catalytic heat generators having a capacity of up to 200 kW and more and operating based on fuel combustion in a fluidized bed catalyst. In such catalytic heat generators (KHG), fuel oxidation runs on the surface of special granules of oxide catalysts kept fluidized in the flux of fuel, air, and combustion products. Heat is withdrawn from the bed through heat exchange surfaces inside the bed or by direct contact of the catalyst with the working fluid. Because of their heavy mass and large dimensions these catalytic generators are suitable for use only in stationary conditions.

The common feature of methods for preparation of platinum-based catalysts is platinum used

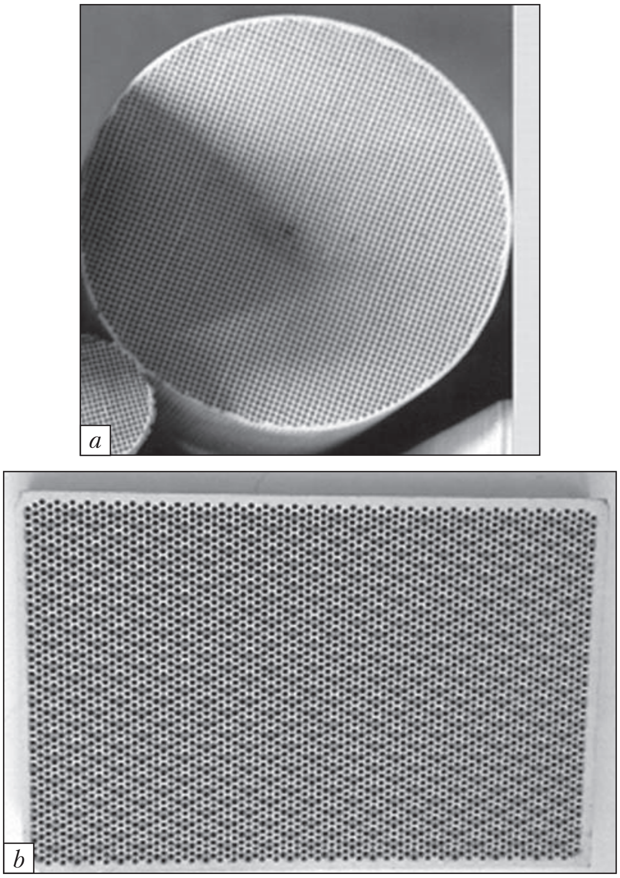

Fig. 1. General view of the case of catalytic block produced by *a* – Frantsevych Institute for Problems of Materials Science, the NAS of Ukraine; *b* – *Technoceram* LLC, Bila Tserkva

as an active component and cell structure used for the application of active components.

It should be noted that widespread application of catalytic combustion of hydrocarbon fuels is hampered by lack of perfectly designed effective catalysts meeting a set of very strict requirements: low temperature at the start of reaction of hydrocarbon fuel oxidation, high thermal and chemical stability, high productivity and selectivity by products of complete oxidation of organic molecules (up to 100%), low content of active component, low GFD resistance, etc.

This research is aimed at designing modular honeycomb-structured catalysts which maximally meet the above mentioned requirements.

DESIGN OF CELL CATALYSTS FOR FLAMELESS COMBUSTION OF GASEOUS HYDROCARBON FUELS (METHANE AND PROPANE-BUTANE MIXES) WITH MINIMUM EXCESSIVE OXYGEN

The main components of modular catalysts are the skeleton, a modular carrier with a system of longitudinal holes, and the catalytic active coating on the block surface [15–19].

The skeleton frame defines its macrostructure, GFD resistance, and mechanical strength. Among various systems that can be used as carrier, the most attractive are honeycomb-structured blocks of synthetic cordierite (synthetic ceramic with general formula $2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$). This material is notable for a low linear expansion and is thermally stable up to 1200 °C, which is very important, insofar as the flameless combustion catalyst always undergoes a heat shock while being ignited. Round- and square-shaped blocks of synthetic cordierite manufactured by Frantsevych Institute for Problems of Materials Science and *Technoceram* LLC (Bila Tserkva) were used as skeletons of modular catalyst. Their general view is given in Fig. 1.

The composition and physical and chemical properties of blocks define their catalytic capacity. Complex oxide composites ($CuCr_2O_4$, Mn_3O_4), including modified oxides of rare earth metals (La_2O_3) and metallic platinum were selected as active components of catalysts that ensure complete combustion of hydrocarbons and have low temperature of ignition. Platinum being very expensive, its content in the catalyst should be as minimum as possible. This can be reached due to dispersion of platinum on the surface and in the pores of secondary carrier.

The presence of secondary carrier in the structured ceramic-based catalysts is caused by several reasons. Firstly, increasing carrier's surface before application of active components. The role of secondary carrier is to tie stably and strongly the catalytically active components with the carrier's material, to enhance thermal stability of the catalyst, to ensure required surface morphology, and to increase dispersion capacity of active components, which contributes to enhancing the interface catalytic activity.

Usually, Al_2O_3, ZrO_2, SiO_2, and aluminum silicates, i.e. thermally stable systems capable of forming porous structures with required properties and high adhesion to the surface of modular carrier, on the surface of ceramic matrix, are used as secondary carrier [20, 21]. For this research, aluminum oxide was chosen for having a sufficient thermal stability, chemical inertness to fuel components and extensive porous structure. The properties of the coating based on aluminum oxide materially depend on the conditions of its application: composition of solution, conditions of coating formation, heat treatment and modifiers.

A technique for the synthesis of fine mesoporous secondary carrier based on Al_2O_3 has been designed. It can be used for forming the secondary carrier layer on the surface of ceramic modular honeycomb-structured matrixes. Upon the results of X-ray phase analysis, the aluminum oxide obtained is a mix of amorphous and γ-modified Al_2O_3. The material crystalizes into γ-Al_2O_3 phase while being heated at 850 °C. Specific surface area of the obtained aluminum oxide is as good as that of the industrial carrier based on γ-Al_2O_3. Thermal stability of the porous structure of synthesized Al_2O_3 reaches 850 °C. As temperature exceeds 850 °C, specific surface area of the carrier decreases sharply.

Enhancing resistance of aluminum oxide porous structure to agglomeration can be reached by its modification with rare earth elements [22, 23]. Effect of mix of La, Ce, Sm and Pr nitrates on thermal stability of secondary carrier layer has been studied. According to Table 1, one could conclude that there is a range of concentration of rare-earth metal oxides (REMO) within which thermal stabilization is reached. An increase in REMO content from 3 to 10% does lead neither to growing specific surface area of Al_2O_3 nor to enhancing thermal stability. According to X-ray-photoelectronic spectroscopy (XPS) data (Fig. 2), this can be caused by the formation of phases of numerous REM aluminates. The mentioned REMO do not have an extensive porous structure, therefore, as a result of their crystallization, specific surface area can decrease. So, it is necessary to use the secondary carrier containing, at most, 3.0—5.0 wt. % REMO.

Fig. 3 shows changes in the specific surface area of block after coating with aluminum oxide taken from solutions of aluminum oxynitrate and mix of aluminum oxynitrate and REM salts. A significant thermal stabilization effect has been reported for secondary carrier at a temperature over 850 °C.

A series of catalysts coated on cordierite matrix of spinel-based oxide systems ($CuCr_2O_4$,

Table 1

Test Results of Modular Catalysts for Flameless Combustion of Propane-Butane Mix

Catalyst	Content of incomplete combustion products in gaseous mix after catalyst, % (in 10 min, 5 hours of operation)	
	CO, %	Hydrocarbons (in conversion to C_3H_8), %
10% $CuCr_2O_4/Al_2O_3$ / cordierite	3.5	0.34
10% $CuCo_2O_4/Al_2O_3$ / cordierite	2.2	0.21
10% Mn_3O_4—BaO—La_2O_3/Al_2O_3 / cordierite	2.6	0.19
0.5% Pt/Al_2O_3 / cordierite	Not found / Not found	0.005% / 0.0045%
0.1% Pt / Al_2O_3 / cordierite	0.002 / 0.0007	0.007% / 0.008%
0.1%Pt/Al_2O_3 + 3%OP3E / cordierite	Not found / Not found	0.0018% / not found
0.1% Pt / Al_2O_3 + 5% OP3E / cordierite	Not found / Not found	0.0015% / not found
0.1% Pt/ Al_2O_3 + 10% OP3E / cordierite	Not found / Not found	0.009% / not found
0.1% Pt / cordierite	0.02 / 0.02	0.01% / 0.01%
Uncoated block (jet fire)	0.023 / 0.028	0.021% / 0.025%

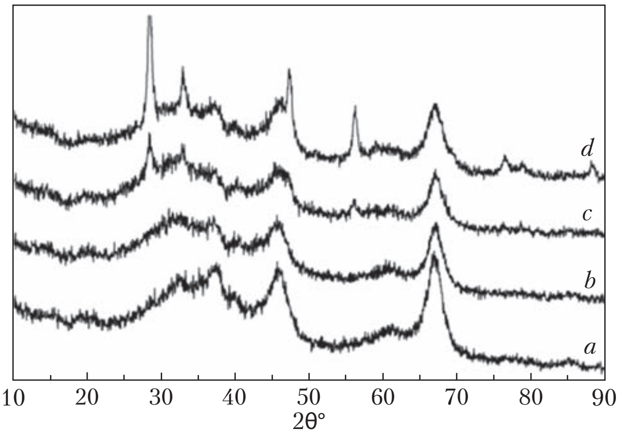

Fig. 2. Diffraction patterns of aluminum oxide obtained by decomposition of aluminum salt blend $(Al(OH)_l(NO_3)_m \times nH_2O$, where l = 1—3; m = 1—2; n = 0—2), including REMO modified, after heat treatment at 850 °C: *a* — Al_2O_3, *b* — Al_2O_3+3.0% REMO, *c* — Al_2O_3+5.0% REMO, *d* — Al_2O_3+ +10.0% REMO

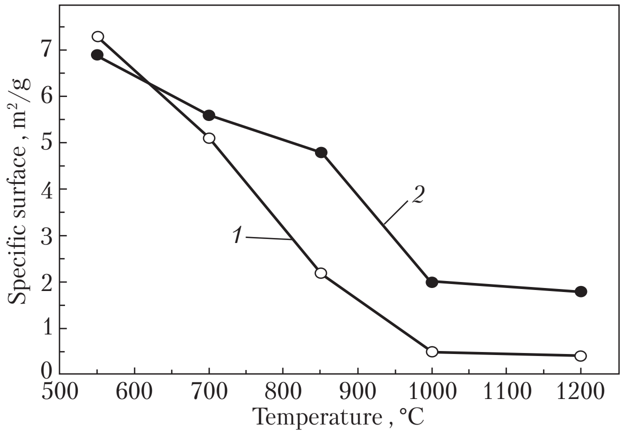

Fig. 3. Temperature dependence of specific surface area of blocks coated with secondary carrier by soaking with solutions of aluminum oxynitrate 5.8 weight % (curve 1) and oxynitrate + REM salts 5.6 weight % (5 weight % of the coating mass in terms of the equivalent amount of REMO). Time of heat treatment at each point is 3 hours

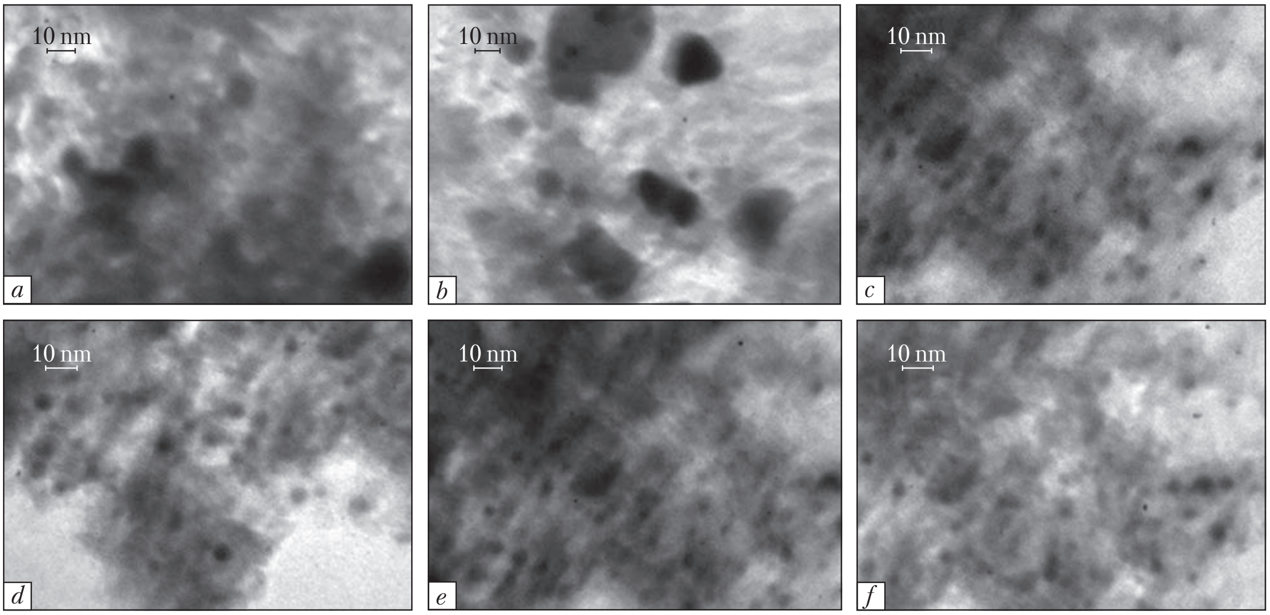

Fig. 4. Micro-picture of catalytically active coating taken from the surface of catalytic block (platinum nanoparticles in the aluminum oxide matrix obtained by decomposition of aluminum nitrate (*a*, *b*); aluminum oxynitrate (*c*, *d*); and aluminum oxynitrate modified with REMO (5%) (*e*, *f*) before (*a*, *c*, *e*) and after (*b*, *d*, *i*) block operation

$CuCo_2O_4$, Mn_3O_4) and platinum has been manufactured and studied.

Fig. 4 features a micro-picture of the surface of metallic platinum as catalytically active coating of the block. The size of platinum nanoparticles of the coating obtained by thermal decomposition of aluminum nitrate ranges 8—15 nm (Fig. 4, *a*). After the catalyst action during several hours (cure in reaction mix or direct use in flameless combustion of hydrocarbon gas) they partially agglomerate (Fig. 4, *b*), as a result of insufficient stabilization of the coating and its ability to compensate excessive charge of the surface of nanoparticles without preventing their agglomeration.

In the blocks with aluminum oxide applied by designed techniques, platinum nanoparticles of 3—6 nm (Fig. 4, *c*) are formed in the carrier matrix. After the catalyst action they partially agglomerate up to 4—8 nm (Fig. 4, *d*).

Tables 2 and 3 show the test results of modular catalysts as elements of heat generators based on flameless combustion.

The test results given in Tables 2 and 3 show that the spinel-based ($CuCr_2O_4$, $CuCo_2O_4$, Mn_3O_4) oxide systems do not ensure complete combustion of fuel, with a material content of CO in the combustion products reported. Among the reasons for such ineffectiveness there can be low activity, insufficient temperature of self-heating and oxygen deficiency. Platinum catalyst ensures complete combustion of propane-butane mix (household gas) at a temperature below 500 °C with no CO being present in the discharge gas (either CO concentration is lower than the permissible one for household appliances (under 200 ppm) or CO is totally absent). Presence of REMO stimulates the creation of oxygen accumulating capacity in the catalyst, which is important for the use of fuel mixes consisting of combustible gas /oxidant close to stoichiometry.

REM compounds (REMO: oxides of La, Ce, Sm, Pr) added assure the coatings with high thermal stability, which stabilizes platinum nanoparticles in the secondary carrier matrix (Fig. 4, *e*, *f*), which, to a certain extent, is a result of stabilization of both the secondary carrier, aluminum oxide, (this could be seen from comparison of Figs. 3 and 4), and nanoparticles themselves, due to their interaction with REMO. In particular, the presence of REMO facilitates keeping the surface of platinum nanoparticles partially oxidized $Pt_n^{\delta+}$, including, due to the creation of surface compounds with REMO (similarly to palladium [23]). Also, acid-base pair required for better absorption and activation of hydrogen before its oxidation appears in the place of contact of charged particles.

CATALYST PRODUCTION PROCESS FLOWCHART

The key stages of flameless combustion catalyst production are the preparation of solution for laying of secondary carrier; the laying of secondary carrier; and the application of active component, platinum, to modified ceramic modular honeycomb-structured matrixes.

Correspondingly, the process chart of flameless combustion catalyst production has the following stages:

- Preparation of solution for laying of secondary carrier;
- laying of secondary carrier;
- application of active component, platinum.

For the preparation of catalyst, a block of synthetic cordierite 132 × 92 × 13 mm with 1 mm channels was used (Fig. 4).

Synthesis of Solutions for the Application of Secondary Carrier

Aluminum nitrate $Al(NO_3)_3 \cdot 9H_2O$ 39H2O is dried in oven at 130—160 °C for 14—20 hours until aluminum oxynitrate $Al(OH)_l(NO_3)_m \cdot nH_2O$. is formed. The ratio of the former to the latter should reach 2.5—2.7 : 1.

The required quantity of mix of aluminum nitrate and aluminum oxynitrate was dissolved with water at ambient temperature and brought to the boil. While stirring up, ammonia nitrate (or 25% ammonia solution) was added and boiled up to complete dissolution of the residue and formation of transparent colloid solution with a density of 1.4 g/cm^3. The solution concentration was adjusted by adding water or$Al(NO_3)_3 \cdot 9H_2O$ and $Al(OH)_2(NO_3) \cdot H_2O$. Aluminum salt content (in conversion to Al_2O_3) was 0.15 g/ml. *pH* of solution is 3.0—3.5.

$La(NO)_3 \cdot 6H_2O$, $Sm(NO)_3 \cdot 6H_2O$, $Ce(NO_3)_3 \times \times 6H_2O$ and $Pr(NO_3)_3 \cdot 6H_2O$ were used to modify aluminum oxide. Their concentration in the secondary carrier (in conversion to oxides) reached 3—10% of Al_2O_3 weight. The calculated quantity of REM salts was added to the solution for applying aluminum oxide. Recommended content of REM salts in the ready element was 3—5% of secondary carrier weight.

Laying of Secondary Carrier

For preparing the catalyst, the ceramic block was submersed into solution of aluminum and REM salts of required concentration. After keeping the block in solution (2—3 min), the residues of solution were blown out from the pores and the block walls by compressed air, and the sample was dried at 100—120 °C, then baked at 500—600 °C, for 3—4 hours. Specific surface area grew from 0.45—0.5 m^2/g to 5.2—6.0 m^2/g.

Introduction of active component (platinum)

The active component to the ceramic modular matrix modified by a layer of secondary carrier and stabilizers was introduced by its soaking with

Table 2

Test Results of Modular Catalysts for Flameless Combustion of Methane

Catalyst	Content of incomplete combustion products in gaseous mix after catalyst, % (in 10 min/ 5 hours of operation)	
	CO, %	Hydrocarbons (in conversion to C_3H_8), %
0.5% Pt / Al_2O_3 / cordierite	Not found / Not found	0.006 / 0.0055
0.1% Pt / Al_2O_3 / cordierite	0.003 / 0.0008	0.008 / 0.009
0.1% Pt/ Al_2O_3 + 3% ОРЗЕ / cordierite	Not found / Not found	0.0021 / Not found
0.1% Pt / Al_2O_3 + 5% ОРЗЕ / cordierite	The same	0.0017 / Not found
0.1% Pt /Al_2O_3 + 10% ОРЗЕ / cordierite	» »	0.0098 / Not found
0.1% Pt / cordierite	0.03 / 0.03	0.012 / 0.012
Block without catalytic coating (jet fire)	0.036 / 0.046	0.023 / 0.028

Table 3

Results of Laboratory Tests of Combustible Gases at the Exit from Heat Generator

Catalyst, Sample №	Combustion of methane		Combustion of propane-butane mix	
	CO / NO_x	Hydrocarbons (in conversion to HC_1), %	CO, NO_x	Hydrocarbons (in conversion to HC_1), %
1	Not found	0.005	Not found	0.004 / 0.0045
2	0.0003% CO / Not found	0.007	» »	0.0036
3	Not found	0.007	» »	0.0028
4	» »	0.009	» »	0.0028
5	» »	0.007	» »	0.0029
6	0.0002% CO / Not found	0.007	» »	0.0026
7	Not found	0.007	» »	0.0029
8	» »	0.007	» »	0.0038
9	0.0003% CO / Not found	0.009	» »	0.0036
10	Not found	0.007	» »	0.0031

aqueous solution of platinum hydrochloric acid H_2PtCl_6 with moisture capacity reaching about 20—22%. Having been soaked, the blocks were blown with air to remove the residues of solution, dried in air flux at 100—120 °C during 3 hours and baked at 550 °C in air during 4 hours. Platinum content in the catalyst should be 0.10%.

To activate platinum, preliminary heat treatment of catalyst in reaction mix containing a reducing and an oxidizing agents (for instance, hydrocarbon, CO or hydrogen in air) is required. The presence of oxygen in the reaction mix enables maintaining the accumulative capacity of REMO in the catalyst.

DESIGN OF CATALYTIC HEAT GENERATOR BASED ON FLAMELESS COMBUSTION OF METHANE OR PROPANE-BUTANE MIX

While configuring the heat generator, various options have been considered:

- Installation of catalytic block directly on the frame of mixing chamber (difficulties while repairing or replacing of the catalytic block can occur) and in the charger (improvement of repairability, quick replacement of charger from the catalytic block);
- Arrangement and shape of upper installation gratings (bent up or down, limitation on sliding of gratings along the face end of radiator, possibility of installation of a standard diameter (up to 100 mm) can on the gratings);
- For the case of heat generator operation in field conditions it was decided to use the catalytic block shaped as standard decorative mesh to protect the punched holes (the mesh protects fragile ceramic tiles both from shocks and from dropping foreign bodies);
- Nipple is fixed with two nuts in the fitment bore of the socket (the fitment bore is made in such a way as to ensure maximally precise axial position of gas jet); 0.5 mm thick adjusting washers are used for positioning the nozzle with respect to the entry to the body of mixing chamber);
- To protect the injector nozzle from contamination (during transportation or in idle mode) a detachable hatch is used.

This configuration is the simplest and most reliable since it ensures both quick disassembly and assembly. The material for heater elements was selected on the basis of following considerations:

- The material should be corrosion- and heat-resistant, resistant to atmospheric corrosion and chemical degradation in gaseous environment at a temperature over 550 °C;
- The material should be kind for treatment and welding.

The elements cannot be made of aluminum-containing alloys because of high temperature inside the mixing chamber (~500 °C). Therefore, corrosion-resistant steel 12X18H10T of various grades was chosen for the main elements of the generator. It has a temperature of 850 °C at the beginning of intensive dross formation. This totally meets the requirements for the product.

The flameless self-sustained heat generator is a prefabricated assembly with option of quick disassembly and reassembly while repairing. The ceramic tiles are replaced simultaneously with the replacement of whole charger. The generator contains a fuel injection nozzle installed in the mixer and a distribution box closed with protective screen. The diffusor outlet is closed with a disperser; the radiator is made of multilayer catalytic material; the protective screen is a metallic mesh ensuring enhanced heat emission with a quiet discharge of working gas-air mix that almost does not contain nitrogen oxides and carbon monoxide (CO).

Gas fire is set by a match or a lighter with the screen removed. The generator is easily repairable due to a simple configuration, use of standard fastenings, and possibility of dirt removal from the screen.

TRIAL RESULTS OF HEAT GENERATOR BASED ON FLAMELESS COMBUSTION OF METHANE OR PROPANE-BUTANE MIX

The generator in various operating modes has been tested on trial bench. The trials of flameless self-sustained heat generator based on catalytic oxidation of methane or propane-butane mix were aimed at verifying safety of its use as additional or basic heater for residential, commercial or mili-

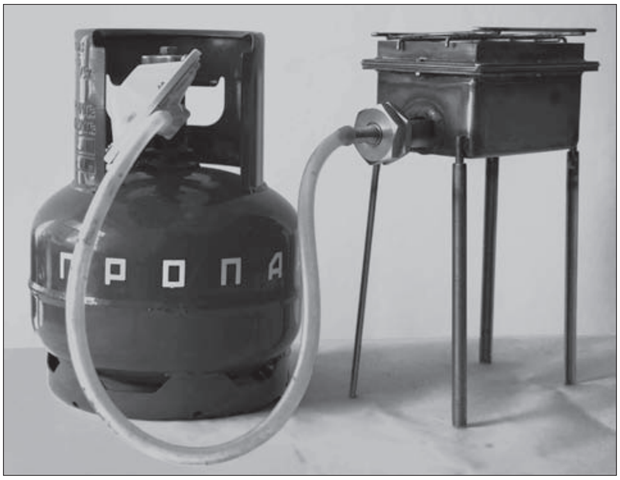

Fig. 5. Catalytic heat generator based on flameless combustion of methane or propane-butane mix

tary facilities (country houses, workshops, warehouses, garages, for field operation, as well as for geological, civil engineering, and agricultural purposes). Trial conditions were maximally approximated to the operating ones: the prototype was tested on gaseous fuels (methane or propane-butane mix) for which it was designed.

During the trials the following parameters have been established:

- Volume flow rate of gas V, m^3/hour;
- Reliability and stability of prototype;
- Absence of hazardous combustion products (CO and NO_x) emitted;
- Completeness of fuel combustion;
- Reproducibility of test results and adjustability of operating modes;
- No flame within visible range.

The samples of catalytic blocks of the flameless generator were tested using the trial bench. General view of self-sustained flameless generator is given in Fig. 5.

TECHNIQUE FOR ANALYSIS OF GAS AT THE DISCHARGE FROM HEAT GENERATOR

The after-burner gas samples were taken after 0.5-hour operation, using a 100 ml gas pump. The mentioned volume was taken at a height of 7—9 cm from the catalyst, by installing a pipe of the same diameter on the working element. The sampling procedure was used level the gas concentration gradient. Gas was supplied to chromatographer by letting the sample (100 ml) through valves with 1 ml loops (for the analysis with the use of heat capacity detector, HCD) and with 0.1 ml loops (for the analysis with the use of flame-ionization detector, FID).

Gas was analyzed using *Crystal-Lux* 4000M chromatographer (*Chromatech*, RF). Analysis for the presence of CO, CO_2, NO_x, and O2 was made using HCD on the columns filled with molecular sieves NaX and *Polysorb-1*. To separate hydrocarbons, a capillary column HP-FFAP, 0.32 mm × 50 m was used with FID. Each sample was tested 5 times for each parameter (with an accuracy of, at least, 5%).

The analysis results for the combustible gases at the discharge of generator are presented in Table 3.

Table 4

Main Physical and Chemical Properties of Combustible Gases

Property	Methane	Propane-butane mix
Low combustion heat, MJ/m^3	37.26	100.65
Estimated quantity of air for combustion V°, m^3	9	27
Density at T = 20 °C and p = 0.101 MPa, kg/m^3	0.68—0.9	2.21
Ignition at normal pressure, mixed with air, %	5.0—15.0	1.5—9.5

Table 5

Results of Laboratory Tests

Parameter	Methane	Propane- butane mix
Combustible gas consumption, l/min	1.5	1.5
Gas/air proportion	1 / 10	1 / 30
Temperature of catalytic block, °C	480	520
Time to catalytic regime, min	1	1
Time to complete use of gaseous fuel in container (5 l), hour	8	15
Heat capacity of generator, kW	0.9	2.5

Table 6

Tests Results of Catalytic Flameless Heat Generator

Combustible gas	Methane	Propane-butane
Nominal heat capacity, kW	0,9	2,5
Time to complete consumption of gas fuel in the container (40 l), hour	67	120
Weight of heat generator, kg	0,5	0,5
Temperature of discharge gases at a distance of 50 mm, °C	140	150
Fuel consumption, l/min	1,5	1,5
Flame	No	No

Note. Gas consumption is given for environment temperature of 0 °C and atmospheric pressure of 101.3 kPa.

Table 3 shows that due to the proposed technology the generator almost does not produce hazardous combustion products (CO and NO_x). The main physical and chemical properties of combustible gases are given in Table 4.

The results of laboratory tests of the catalytic heat generator based on the flameless combustion of methane or propane-butane mix are given in Table 5.

TRIALS OF HEAT GENERATOR BASED ON FLAMELESS COMBUSTION OF METHANE OR PROPANE-BUTANE MIX AT *CheZaRa* PJSC

The operating modes of generator have been tested at *CheZaRa* PJSC, using heat generator based on flameless combustion of methane, having an output capacity of 0.9 kW and on combustion of propane-butane mix, having an output capacity of 2.5 kW (Fig. 6).

The heat generator on liquefied gas was connected to gas container using a flexible hose and pressure controller РДСГ 2-1,2 in the case of propane-butane mix DSTU 21805-94 and РДСГ 1-1,2 DSTU 20448-90, in case of methane. Catalytic panel (a ceramic honeycomb-structured block with a layer of heterogeneous catalyst fixed in metallic frame) was used as heating element. The trial conditions were maximally approximated to the operating ones.

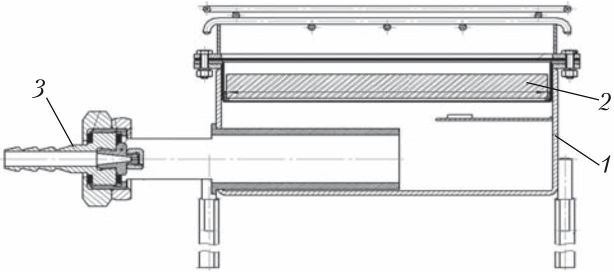

Fig. 6. Chamber of self-sustained flameless heat generator: *1* — body; *2* — catalyst; *3* — nozzle for fuel supply

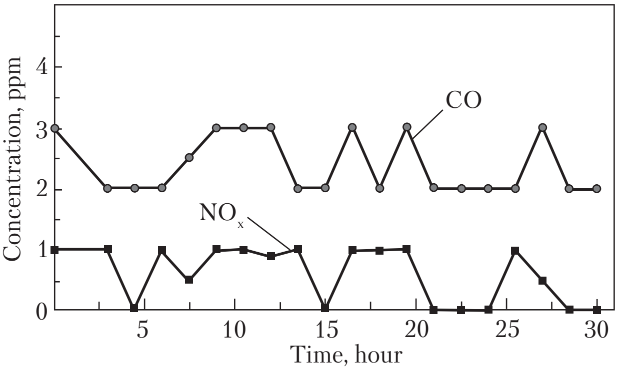

Fig. 7. Change in CO and NO_x content in discharge gas with time

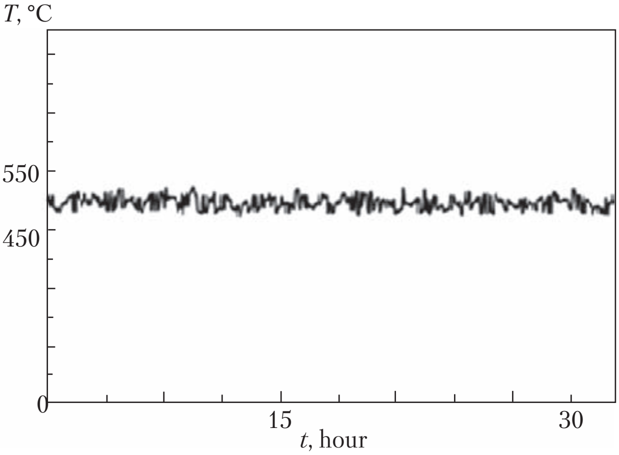

Fig. 8. Endurance tests with time

The following parameters were measured in the trials:

- Temperature of external surface of catalytic layer: 480 °C for methane, and 520 °C for propane-butane mix;

- Concentration of nitrogen and carbon oxides;
- Content of non-reacted methane in oxidation products;
- Hydraulic resistance of heating element.

Control measurements of pressure and gas/air consumption rate have been done. For the combustion of natural gas (wt %: methane — 97.46; ethane — 1.11; propane — 0.37; isobutane — 0.06; butane — 0.06; pentane — 0.02) the ecological indices for 0.9 kW heat generators in the nominal mode by volume share of discharge gases were as follows: CO — 2—3 ppm, traces of NO_x, CH_4 — 10—20 ppm, CO_2 — 10%, the rest were gases (89.5%). Due to the designed technique, the ecological indices for 2.5 kW heat generators in the nominal mode by volume share of discharge gases for the combustion of propane-butane mix were as follows: CO — 1—2 ppm, CH_4 10 — 15 ppm, CO_2 — 5%, the rest was gases (95%).

The tests of combustion of various fuels have showed that the use of this configuration of heat generator with the proposed catalyst enables improving efficiency ratio of combustion up to almost 100%, preventing the formation of incomplete combustion products (carbon dust and hydrocarbons), and reducing significantly the emission of CO, NO_x and toxic oxygen-containing organic compounds. The test results of composition of discharge gases from combustion of fuels are given in Fig. 7. No deviations of ecologic parameters from the initial ones have been reported.

The endurance tests of heat generator have showed that the catalyst remains active during 30 hours (Fig. 8). The test results are summarized and given in Table 6.

The test results have showed that the burner configuration ensures self-sustainable noiseless and flameless combustion of fuel in the catalyst bed. The catalyst stability remained unchanged during 30 hours after the tests.

CONCLUSIONS

Specific features of catalytic flameless combustion of gaseous fuel have enabled designing the heat generator having the following advantages: light weight, mobility, flexibility, high efficiency, low fuel consumption. It generates neither smog emissions nor radiation in the visible range, which enables to prevent detection of device in the field conditions, especially, in the case of military operations. Due to the designed technology, the operating heater does emit neither harmful combustion products (CO, NO_x) nor smog, nor fire, nor smell. The heater works on environment friendly, cheap and quite safe gaseous fuel widely used both in household and industrial sectors. The catalyst stability remains unchanged after the trials.

The self-sustained flameless heat generator on the basis of catalytic oxidation of methane or propane- butane mix for heating varous facilities (including, under field conditions) designed at the Pysarzhevskyi Institute of Physical Chemistry of the NAS of Ukraine and manufactured at *CheZaRa* PJSC has been tested successfully at Chernihiv Radio-Set Plant and commercialized.

The prototype generator based on catalytic flameless combustion of gaseous fuels was presented at *Weapons and Safety* exhibition (September 22—25, 2015, Kyiv). The exhibit has attracted attention of the military men, representatives of the Ministry of Emergency Situations of Ukraine, and civilians. The exhibition embraced an information and communication event *Prospects for R&D Support of the Defense Industry of Ukraine, with a lecture Catalysts of Self-Sustained Flameless Gas Heat Generator for Heating Various Objects, Including, for Field Heating* given within the framework of the event.

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АВТОНОМНИЙ БЕЗПОЛУМ'ЯНИЙ ГЕНЕРАТОР ТЕПЛА НА ОСНОВІ КАТАЛІТИЧНОГО ОКИСНЕННЯ МЕТАНУ АБО ПРОПАН-БУТАНОВОЇ СУМІШІ ДЛЯ ОПАЛЕННЯ РІЗНИХ ОБ'ЄКТІВ, В ТОМУ ЧИСЛІ В ПОЛЬОВИХ УМОВАХ

Створено ефективний каталізатор на базі керамічного блокового носія стільникової структури з синтетичного кордієриту з низьким температурним коефіцієнтом лінійного розширення та розроблено безполум`яний генератор тепла на основі спалювання метану або пропан-бутанової суміші. Результати лабораторних та стендових випробувань показали, що автономні безполум'яні генератори тепла за ефективністю роботи не поступаються зарубіжним аналогам. Налагоджено виробництво автономних безполум'яних каталітичних генераторів тепла та каталізаторів для них.

Ключові слова: каталітичний генератор тепла, каталізатор безполум'яного горіння метану або пропан-бутанової суміші, блоки стільникової структури, кордієрит.

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АВТОНОМНЫЙ БЕСПЛАМЕННЫЙ ГЕНЕРАТОР ТЕПЛА НА ОСНОВЕ КАТАЛИТИЧЕСКОГО ОКИСНЕНИЯ МЕТАНА ИЛИ ПРОПАН-БУТАНОВОЙ СМЕСИ ДЛЯ ОБОГРЕВА РАЗЛИЧНЫХ ОБЪЕКТОВ, В ТОМ ЧИСЛЕ В ПОЛЕВЫХ УСЛОВИЯХ

Создан эффективный катализатор на базе керамического блокового носителя сотовой структуры из синтетического кордиерита с низким температурным коэффициентом линейного расширения и разработан беспламенный генератор тепла на основе сгорания метана или пропан-бутановой смеси. Результаты лабораторных и стендовых испытаний показали, что предлагаемые генераторы тепла по эффективности роботы не уступают зарубежным аналогам. Налажено производство автономных беспламенных каталитических генераторов тепла и катализаторов для них.

Ключевые слова: каталитический генератор тепла, катализатор беспламенного горения метана или пропан-бутановоі смеси, блоки сотовой структуры, кордиерит.

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