

## Catalytic Combustion for Heat Production and Environmental Protection

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### Abstract

Processes and apparatuses for catalytic combustion of fuels for heat production and for treatment of wastes for environment protection are described. Special attention is paid to processes of treatment of mixed radioactive organic waste in a fluidized catalyst bed and for environmentally safe catalytic technology for the utilization of liquid rocket fuel unsymmetrical dimethylhydrazine (UDMH) and wastes, containing it.

### Introduction

Conventional energy producing facilities are based on high temperature ( $\geq 1200^\circ\text{C}$ ) fuel combustion in flame, and they represent one of the main sources of atmosphere pollution with noxious substances and heat. All conventional heating systems with flame fuel combustion have common drawbacks, namely: high toxic emissions (oxides of nitrogen and sulfur, carbon monoxide, benzopyrenes, etc) considerably exceeding the existing sanitary standards, thus impeding the use of these systems in urban areas; high capital costs due to the large dimensions, caused by low heat transfer coefficients from gas to heat exchanging surfaces; fire and explosion risks; strict requirements to construction materials that must be heat resistant and durable.

Flameless catalytic combustion is a promising method for the increase of combustion efficiency and abatement of toxic emissions [1-4]. In this process the reactions of fuel oxidation proceed on the catalyst surface at low temperatures ( $300\text{-}750^\circ\text{C}$ ), providing total fuel conversion to the products of deep oxidation and preventing the formation of nitrogen oxides.

Catalytic combustion is used both for heat production and processing and utilization of different types of wastes. In this paper our results in application of catalytic combustion in following areas are presented:

1. Environmentally friendly catalytic space heaters and water-heating boilers;
2. Technology of treatment of mixed radioactive

organic waste in a fluidized catalyst bed.

3. Environmentally safe catalytic technology for the utilization of liquid rocket fuel UDMH and wastes, containing UDMH.

### Environmentally friendly catalytic space heaters and water-heating boiler

#### *Household catalytic space heaters*

Two versions of household catalytic space heaters have been developed for environmentally safe catalytic combustion of propane-butane from cylinders and natural gas. The active component comprising transition metal oxides is supported on silica-alumina fiber mat (Termocat-1; Fig. 1), or on the multichannel ceramic plate (Termocat-2, 3; Fig. 2). The original construction and use of high performance catalytic materials provide complete burning of fuel and the reduction of concentrations of pollutants ( $\text{CO}$ ,  $\text{NO}_x$ ,  $\text{C}_x\text{H}_y$ ) in the exhaust gas below sanitary norms. The thermal capacity of serially produced heaters is 2.5-3 kW.

#### *Two stage combustion*

The catalytic heat generator based on two stage combustion has been designed and tested, Fig. 3. At the first stage, the flame combustion of natural gas in conditions of fuel-rich mixture at  $\alpha \leq 0,95$  proceeds providing minimal formation of «thermal» nitrogen oxides, then the hot combustion products are diluted by addition of secondary air and pass to the

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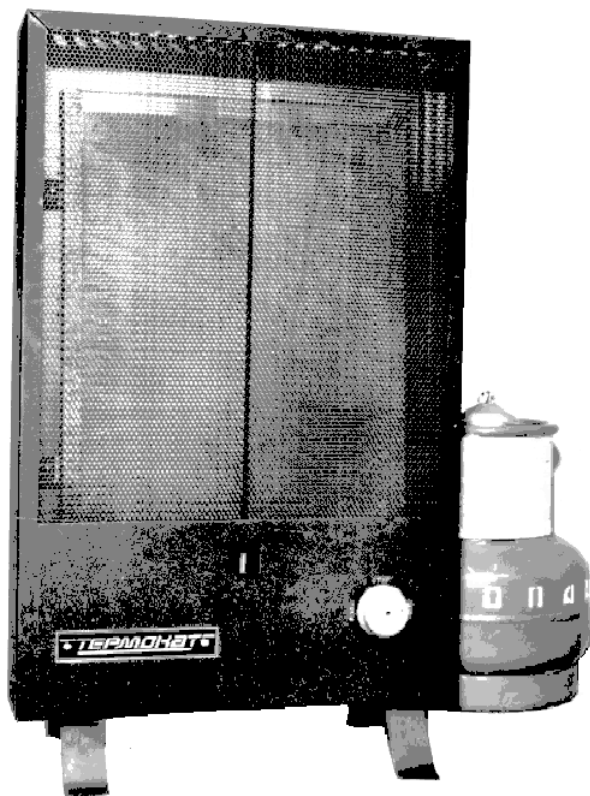


Fig. 1. Photo of Termocat-1.



Fig. 2. Photo of Termocat-2, 3.

second camera, where the catalytic cartridge composed of hexagonal honeycomb monolithic catalysts is placed. Temperature of gases in front of the catalytic cartridge (500-700°C) is sufficient for catalytic oxidation of impurities remaining after flame combustion of fuel. After the cartridge the hot scrubbed gas

is diluted with air. Apparently, the most important part of this type of heat generator is the catalytic cartridge. Our studies of monolithic catalysts have revealed a number of rigid requirements both to material and geometrical parameters of the carrier, and to composition of the active component. In particular, the catalyst should be stable against sharp temperature variations, usual for fuel combustion processes. Investigation of a nature of the active components, genesis of phase composition of both monolithic carrier and active components, and their chemical and thermal stability has allowed to choose the cordierite as optimal carrier (BET surface area 2-10 m<sup>2</sup>/g, crushing strength 10-12 MPa) and combination of oxides of cobalt, copper, magnesium and iron as active components.

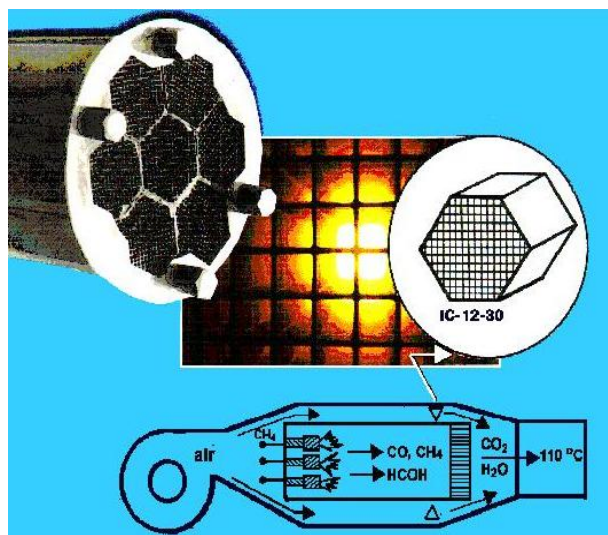


Fig. 3. The two stage combustion catalytic heat generator.

Several modifications of these heat generators have been designed (10 – 500 kW) and tested for heating green houses.

### Catalytic boiler

The boiler developed by Federal State Unitary Enterprise “Irtysk” and Boreskov Institute of Catalysis is equipped with a catalytic burner for flameless catalytic fuel combustion. Two types of burners are developed: 1) the burner in the form of foam ceramic plate; 2) the burner in the form of catalytic heat exchanger consisting of tubes placed into a block of highly porous reticulated foam metal. On the surface of metal or foam ceramic materials

catalytic coating based on oxide composition is deposited. The designs of the boiler and the heat exchanger provide high specific heat productivity and good heat transfer, thus reducing the dimensions and the weight of the boiler.

The catalytic section of the boiler uses modified manganese-aluminum oxide catalyst supported on surface of highly porous reticulated foam materials.

Alumina supported manganese-containing catalysts have high efficiency in deep oxidation of hydrocarbons. Modification of Mn-Al-O-catalyst by additives of rare-earth metal oxides results in an increase

of thermal stability up to 1100-1300°C and, consequently, allows enlarging the temperature range of catalyst operation [5-6]. The high catalytic activity and thermal stability of modified Mn-Al-O-catalysts can be explained by the formation of solid solutions at 500-900°C or hexaaluminates at 1100-1300°C due to interaction of manganese oxide with catalyst support [5]. Catalytic activity data for the modified Mn-Al-O-catalyst in model reaction of deep methane oxidation are presented in Table 1: for initial catalyst, the catalyst after calcination at 900°C as well as after treatment in reaction mixture at 1100°C.

**Table 1**

Catalytic activity of Mn-Al-O-catalyst in model reaction of methane oxidation  
(GHSV - 1000 hrs<sup>-1</sup>, CH<sub>4</sub> concentration – 1 vol.% in air).

Temperature of 50%-conversion of CH <sub>4</sub> , °C					
Initial	After calcination at 900°C/4hrs	After treatment in reaction mixture (9 vol.% CH <sub>4</sub> +air) at 1100°C during			
		3 hrs	10 hrs	20 hrs	50 hrs
490	525	550	595	600	650

Catalytic manganese-containing coating was supported on surface of ceramic foam from the suspension with subsequent calcination at 500°C, as described in [6].

The three-dimensional reticulated foam structure catalyst support (ceramic foam) was developed by Republican Engineering Center "Powder Metallurgy". Ceramic foam is prepared by duplicating the open-cellular polyurethane foam structure using suspensions on the basis of mixed ceramic powders (alumina, kaolin, talc, feldspar, pegmatite *etc.*). The variation of initial powder compositions and high temperature synthesis conditions allows preparing of ceramic foam with high mechanical strength, heat resistance and chemical durability. Independence of pore diameter on porosity and, accordingly on structural and frame properties of the ceramics, provides favourable conditions for heat and mass transfer and high rate of external diffusion catalytic processes in ceramic foam.

For operation in extreme conditions a catalytic heat exchanger was designed in the form of a number of tubes situated in highly porous reticulated matrix of Ni-Cr alloy with deposited catalytic washcoating based on manganese oxides. The principle of preparation of this catalytic heat exchanger consists in du-

plicating the structure of open-cellular polyurethane foam over metal tubes using suspension-electrochemical method with subsequent thermal destruction of organic component and agglomeration. Conditions of deposition of powder, chemical and electrolytic coatings on metal-polymeric model as well as conditions of subsequent low- and high temperature treatment were optimized to provide low thermal resistance between heat exchanging highly porous reticulated foam material and metal tubes. The developed catalytic heat exchanger has high heat-release capability providing thermal stability of catalyst operation and minimization of useful heat losses upon natural gas combustion in water-heating boilers.

The catalytic water-heating boiler is a welded apparatus based on vertical 'firetube' design with lower disposition of catalytic burner with premixed fuel-air feed (Fig. 4). A cylindrical water-filled tank with mineral thermal insulation and 'fire-tubes' placed into tank as well as combustion chamber with ignition device are main units of boiler. The boiler load-carrying structure combines the water-filled tank, the catalytic burner, the igniter, automatic control and safety devices and the flue gas collector into a single construction covered by removable metal sheets.



Fig. 4. Photo of the prototype catalytic boiler.

*Technical characteristics of the prototype catalytic boiler:*

Heat power - 16 kW

Fuel – natural gas with pressure 130 mm water column

Heat efficiency  $\geq 88$  -94%

Pressure of circulating water – 0.065 MPa

Water temperature - 50-90°C

Dimensions - 890×440×440 mm

Weight – 90 kg.

Natural gas is introduced through the automatic control and safety device into nozzles of injectors of mixing block (Fig. 5). Air is drawn through the injectors due to the energy of the gas jet and the underpressure formed. The prepared air-fuel mixture is fed to the catalytic block (Fig. 6). The catalytic block comprises two ceramic foam plates with different pore parameters placed in a drum and sealed over perimeter by thermostable mineral insulation. The upper foam plate with a deposited catalytic coating acts a catalytic reactor in which the gas deep oxida-



Fig. 5. Air-gas mixing block.



Fig. 6. Catalytic block in the metal drum.

tion takes place. The function of the lower foam plate is to prevent the ignition of fuel-air mixture in the mixing block.

The heat energy of the hot ceramic foam plate is used for the thermal radiation that is absorbed by water through the furnace wall and warming-up of incoming fuel-air mixture. The heat energy of combustion products is used for water heating through the walls of convective heat exchanger and, partly, through the furnace wall. The volume of the furnace is small (about 10 L), because the flame fuel combustion takes place only at the starting of the boiler. After heating the catalyst the furnace acts only as heat absorbing

surface. The starting of the boiler is accomplished by means of the ignition torch of 200 W power with the control thermocouple and piezoelectric sparking plug.

The combustion products pass from the furnace into convective heat exchanger consisting of the tubes with turbulators increasing heat-transfer coefficient from combustion products to water. The combustion products cooled below 150°C are directed into the flue gas collector and further into the flue. The water circulation is supported by natural convection.

The testing of the prototype catalytic boiler under

variation of different regime parameters (air excess coefficient, heat power, *etc.*) was carried out.

The testing data (Table 2) show that practically total oxidation of natural gas occurs in the boiler over the range of the heat power 8.3-16.1 kW at the excess air coefficient  $\alpha=1.4-2.3$  and catalyst temperature 700-800°C. As can be seen from the table, the concentration of toxic compounds in the flue gas recalculated to stoichiometric gas mixture ( $\alpha=1$ ) are very low: nitrogen oxides 2-8 ppm and carbon monoxide 0-60 ppm.

**Table 2**

Testing data for the prototype catalytic heat exchanger boiler.

Heat power, kW	Heat efficiency, %	Air excess coefficient ( $\alpha$ )	Concentrations of toxic compounds in flue gas calculated for $\alpha=1$ , ppm			Catalyst temperature, °C
			CO	NO <sub>x</sub>	SO <sub>2</sub>	
16.1	85.4	2.2	59.4	4.4	0	800-850
16.1	88.5	1.8	53.4	5.3	0	800-850
15.0	90.9	1.4	0	7.0	2.8	830-870
13.8	90.9	1.6	14.0	7.8	3.1	830-870
12.7	91.8	1.6	0	7.8	3.1	860-880
12.6	91.6	1.6	1.6	6.2	0	880-920
12.5	89.3	1.7	0	3.4	0	850-860
12.5	92.0	1.6	1.6	6.4	0	530-860
12.5	92.0	1.4	27.2	5.4	0	530-860
12.5	92.0	1.4	1.4	5.8	0	530-860
11.1	88.4	2.0	0	4.1	0	750-850
11.1	87.4	2.3	46.0	2.3	2.3	750-850
8.3	94.0	2.0	0	4.0	0	750-800

### Technology of mixed radioactive organic waste treatment in a fluidized catalyst bed

One of the most urgent problems in the field of nuclear waste management is environmentally safe treatment and disposal of mixed organic wastes containing U, Pu and their fission products [7-9]. These wastes represent a threat to the environment upon their storage and disposal because of the combination of flammability, explosiveness, toxicity and radioactivity, and they need to be treated prior to disposal. They comprise lubricating and hydraulic flu-

ids, extractants, solvents and dilutants, filters, ion-exchange resins, packages, plastic containers, work clothing and other organic materials [8,9]. The development of environmentally clean technology for destruction of these wastes is of great importance. The method of high-temperature flame (or plasma) incineration is hazardous for the environment because it leads to secondary waste streams, e.g., deteriorated refractories, and generation of air pollutants, such as nitrogen oxides CO, polyaromatic hydrocarbons and sub-micron radioactive particles emitted into the atmosphere [8-10].

We have proposed a new technology for the environmentally clean treatment of mixed organic radioactive wastes, which is based on the catalytic combustion of organic wastes [11-16]. In catalytic combustion the fuel is totally oxidized by surface catalytic reactions at low temperatures without a flame, and this process is principally different from conventional flame combustion proceeding at high temperatures via radical-chain reactions. This results in complete conversion of fuel on the catalyst surface to products of total oxidation: CO<sub>2</sub> and H<sub>2</sub>O and precludes the formation of nitrogen oxides.

In recent years catalytic combustion processes have been developed most intensively mainly because of the possibility to substantially reduce toxic emissions of CO, unburned hydrocarbons and nitrogen oxides [11,17-24].

For the treatment of mixed organic wastes, a method of flameless combustion of organic fuels and wastes in a fluidized catalyst bed developed in BIC was chosen [11,24-26]. The unique feature of this method of fuel and waste combustion is the possibility of total oxidation of organic compounds at nearly the stoichiometric ratio with oxygen at low temperatures (600-750°C) with elimination of secondary pollutants, such as NO<sub>x</sub>, CO, polyaromatic hydrocarbons, dioxins, *etc.* This is achieved by the use of highly active catalysts in a fluidized bed, which also allows the efficient removal and possible use of reaction heat. This environmentally safe technology was successfully tested in pilot and industrial plants upon combustion of various fuels and wastes [24-28] including spent scintillation fluids [28].

The project for development of the technology of fluidized bed catalytic destruction of mixed organic waste containing radionuclides was carried out in 1994-1998 by the Boreskov Institute of Catalysis in cooperation with the Novosibirsk Plant of Chemical Concentrates (PCC) and other Siberian Institutions and nuclear weapons materials processing plants (in Novosibirsk, Tomsk-7, Krasnoyarsk-26,-45, Angarsk) and with foreign collaborators: LLNL in the U.S.A., Louis Pasteur University in France, GEC Alsthom and BNFL in UK under the ISTC project No 110. The process is based on total oxidation of waste organic components in a fluidized catalyst bed and transition of radionuclides to a compact solid phase for further processing or disposal.

In the development of this technology the following tasks were accomplished:

- Selection of a suitable active, thermally stable and

mechanically strong catalysts

- Study of the combustion efficiency for waste organic components and exhaust gas composition after catalytic reactor and off-gas treatment units
- Study of the composition and size of the particulates after the catalytic reactor and after off-gas treatment units
- Study of the fate of radionuclides
- Study of the influence of accumulation of radionuclides in the catalyst on its properties
- Optimization of parameters of processes of catalytic combustion and off-gas treatment

The final goal of this work is the demonstration of the technology in the prototype industrial plant at Novosibirsk Plant of Chemical Concentrates where fuel rods are produced. The plant is intended for the treatment of the annual amount of 50 tons of liquid organic mixed wastes represented mainly by lubricants and vacuum pump oils contaminated by uranium isotopes.

For study of mixed organic waste catalytic destruction two pilot installations of 1 kg/h capacity were designed, manufactured and assembled.

The first installation was specially designed for the study of processes of catalytic combustion of simulated waste and processes of exhaust gas purification from particles of surrogate non-radioactive metal oxides and acid gases. It includes a fluidized bed catalytic reactor, cyclone, jet scrubber, two absorber-condensers and an aerosol filter (Fig. 7). The installation operates as follows. The compressed air is supplied to the reactor by compressor (12) in the quantity sufficient for fluidization and total waste combustion at the bed temperature 600-780°C. The wastes from the tank (10) are fed into the reactor by the pump (8) and sprayed in the catalyst bed through the nozzle. The heat of the reaction of waste oxidation is removed by the heat exchanger (2) immersed in the catalyst bed, and the exhaust gas temperature can be decreased to 250-300°C. The exhaust gas from the reactor enters the cyclone (3) where large-sized particles are separated and the gas temperature is decreased to 200-250°C. Traces of unburned organics and CO are removed in the catalytic converter (4) containing a monolithic honeycomb oxidation catalyst. Then the gas passes through a foam jet scrubber (5) which acts both as a gas and particulates trap, and as a regenerative heat exchanger. It removes medium-sized particles (>5 μ) and the major part of acidic admixtures, such as oxides of sulfur and phosphorous. The temperature of the gas

decreases to 70-90°C. After the jet-scrubber, the gas saturated with water vapor enters the absorber-condensers (6) where its purification from low-sized particles takes place with final removal of trace amounts of acid gases and gas cooling to 20-25°C.

Final purification of the gas is carried out in the aerosol filter (7). To exclude the condensation of water on the filter, the gas is heated to 35-40°C by the water heat exchanger (13) using the heat generated from the combustion of wastes.

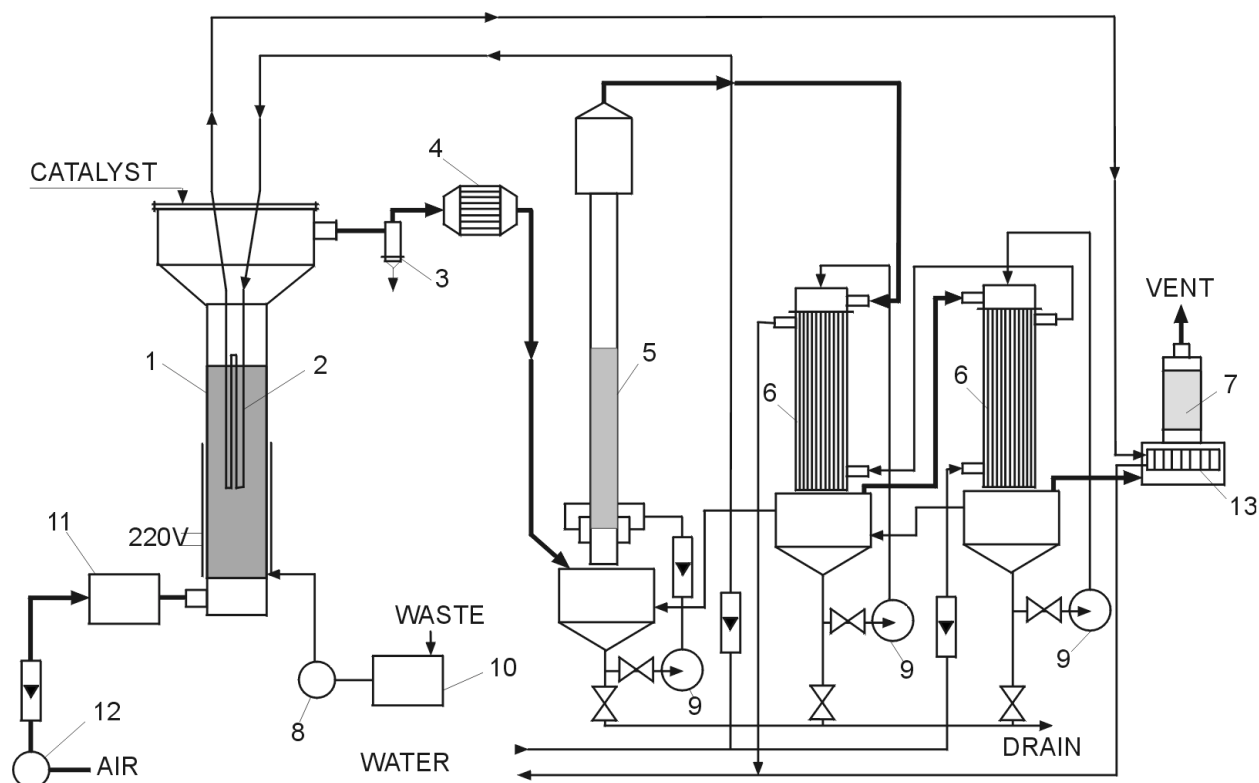


Fig. 7. Schematic diagram of the pilot installation No 1: 1 - fluidized bed reactor, 2 - heat exchanger, 3-cyclone, 4 - CO catalytic converter, 5 - jet scrubber, 6 - absorber-condensers, 7 - aerosol filter, 8 - waste pump, 9 - water pumps, 10 - tank with wastes, 11 - electric heater, 12 - compressor, 13 - heat exchanger.

The second installation was constructed at PCC for the experiments with radioactive wastes of the Plant to study catalyst performance in destruction of real radioactive materials. It includes a catalytic reactor of 120 mm diameter and a cyclone. The exhaust gas from this installation is directed to the centralized off-gas treatment system of the Plant.

At BIC, efficient catalysts for application in fluidized bed combustion of organic wastes were developed and batches of catalyst were prepared for testing in the pilot installations.

In a fluidized bed reactor, the catalyst is subjected to the following combined severe effects: mechanical shocks and attrition; high temperature; chemical action of stoichiometric fuel/air mixtures; poisoning effects of sulfur, alkaline metals and other elements

for the case of combustion of crude fuels and organic wastes.

One of the most important problems encountered in the use of fluidized bed combustion is catalyst attrition. To solve this problem, special mechanically strong (crushing strength up to 50 MPa) catalysts were developed. The catalysts are prepared by supporting oxides of Fe, Cr, Mg, Cu and other metals on strong spherical  $\gamma$ -alumina beads with a high specific surface area. The catalysts that were shown to have the most optimum operational properties in mixed waste treatment are those based on magnesium chromite: IC-12-72 (20%  $\text{MgCr}_2\text{O}_4/\gamma\text{-Al}_2\text{O}_3$ ) and IC-12-73 (20%  $\text{Cu}_x\text{Mg}_{1-x}\text{Cr}_2\text{O}_4/\gamma\text{-Al}_2\text{O}_3$ ) with granule diameter of 1.4-2.0 mm. These catalysts retain high activity during long operation at 600-780°C, are resistant to

sulfur poisoning, and have high mechanical strength providing low catalyst attrition - less than 0.5% per day.

The experiments on catalytic combustion of the mixed waste organic components were carried out in both of the pilot installations with a variety of oils and solvents supplied from nuclear materials plants participating in the project. The experiments showed that in all cases a high efficiency of organics conversion is achieved. The analysis of the total organic content performed with chromatographic FID detector showed the content of organic compounds to be below 10 mg/m<sup>3</sup>. The typical composition of the exhaust gas after the catalytic fluidized bed reactor is: combustion products CO<sub>2</sub> and H<sub>2</sub>O, small amounts of CO (30-400 ppm), NO<sub>x</sub> (10-60 ppm), SO<sub>2</sub> (3-30 ppm), and particulate matter (50-200 mg/m<sup>3</sup>) formed from the ash residue of wastes and due to catalyst attrition.

In order to remove from the exhaust gas of the fluidized bed catalytic reactor traces of organics and CO, it was proposed to install a platinum monolithic catalyst (CO converter) after the cyclone [29]. Platinum containing catalysts on monolithic honeycomb aluminosilica supports were specially designed to remove CO from dust loaded gases. The catalyst is a rectangular monolith (72×72×75 mm) with a large number of parallel channels (2×2 mm) separated by thin walls on which the active component is supported.

The concentration of CO in the flue gas upon catalytic combustion of oils was 50-400 ppm for the catalyst MgCr<sub>2</sub>O<sub>4</sub>/Al<sub>2</sub>O<sub>3</sub> and 30-40 ppm for the catalyst Cu-MgCr<sub>2</sub>O<sub>4</sub>/Al<sub>2</sub>O<sub>3</sub>. CO converter provides CO removal over 95%, thus decreasing CO concentration below 16 ppm – the maximum allowable value in air according to Russian Standard for production areas.

The various regimes of the processes of catalytic combustion and off gas purification in the pilot installations were examined. Under optimum regimes, the concentration of NO<sub>x</sub> was 5-30 ppm, that of CO was 0-15 ppm, SO<sub>2</sub> 1-10 ppm, and concentrations of particulates were less than detection limit of 1 mg/m<sup>3</sup>. Table 3 shows how harmful emissions can be controlled by catalytic incineration of oil sludge. The three-fold decrease of NO<sub>x</sub> emission can be attained by the decrease of temperature from 780 to 710°C. The resulting increase of CO concentration after the fluidized bed reactor is not a problem, as CO is almost totally oxidized in CO converter.

The particulates in the gas stream after the fluid-

**Table 3**

Results of analysis (ppm) of CO and nitrogen oxides in off-gas upon catalytic combustion of oil sludge over catalyst MgCr<sub>2</sub>O<sub>4</sub>/Al<sub>2</sub>O<sub>3</sub>.

Temperature in catalytic reactor	Units where gas probes are taken	CO	NO	NO <sub>2</sub>
780°C	Cyclone	24	58	1
	CO converter	0	54	4
	Jet scrubber	0	55	2
	Absorber-condenser-1	0	56	1
	Absorber-condenser-2	0	49	0
710 °C	Cyclone	98	18	1
	CO converter	0	17	4
	Jet scrubber	0	17	3
	Absorber-condenser-1	0	16	1
	Absorber-condenser-2	0	16	0

ized bed catalytic reactor are formed from inorganic admixtures (ash) of the wastes and also from the catalyst attrition. The values of dust concentration in the gas stream are usually in the range of 50-200 mg/m<sup>3</sup>. The data on dust concentration and its removal by various gas cleaning units are presented in Table 4. The results show that gas cleaning units efficiently remove particulates from the gas stream. After the absorber-condensers, the dust is practically absent in the gas within the sensitivity of the analytical method used (< 1mg/m<sup>3</sup>).

The experiments in pilot installations revealed a phenomenon of radionuclide accumulation in the catalyst. A series of experiments were carried out with model wastes containing additions of W and Th compounds simulating admixtures of uranium in real wastes. First, the catalytic combustion of an individual waste component (lubricating oil) was studied, then the oil was doped with sodium tungstate to W concentrations of 112 and 1673 mg/L, or with thorium nitrate to Th concentrations of 40 and 200 mg/L, and the resulting suspension was fed into the fluidized bed reactor.

The analysis of the results obtained in the study of catalytic combustion of simulated waste showed gradual accumulation of the metal in the catalyst granules, in the catalyst dust captured by the cyclone and the scrubbing liquids in the gas cleaning units (Fig. 8), the major part (over 50%) of the metal being retained



**Table 4**

Results of the study of dust removal by gas cleaning units upon catalytic combustion of industrial oil I-50A.

No	Apparatus	Dust conc. at the outlet, mg/m <sup>3</sup>	Dust removal by each unit, % of initial conc.	Size of removed particles, m	Total dust removal efficiency by the units chain, %
1	Reactor	165	-	-	-
2	Cyclone	36.4	77.9	28-160	77.9
3	Jet scrubber	8.5	16.9	3-28	94.8
4	Absorber-condenser-1	2.2	3.8	< 3	98.6
5	Absorber-condenser-2	< 1	≥ 0.8	< 3	> 99.4

in catalyst granules. The gas cleaning units efficiently remove the remaining part of the W or Th from the gas stream. The distribution of the metal oxide over gas cleaning units show that over 80-90% of the metal is removed from the gas stream in the jet scrubber and the remaining part is captured in the absorber-condensers.

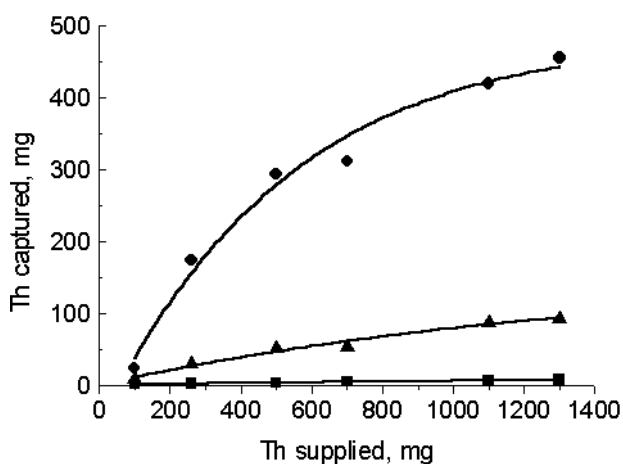


Fig. 8. Accumulation of Th in catalyst granules (●), gas cleaning units (▲) and catalyst dust in cyclone (■).

The distribution of the metal from waste in catalyst granules was studied by the X-ray microprobe technique. The granule, held in epoxy resin, was cut stepwise and each section was scanned by the X-ray microprobe analyzer providing data on the local concentration of the metal. The results obtained (Fig. 9) show that the metals are mostly concentrated at the outside surface of the catalyst beads. This accounts for larger concentrations of the metals in the catalyst dust captured by the cyclone, formed as a result of catalyst attrition.

The main catalyst characteristics: mechanical strength, specific surface area and activity during experiments were maintained at the level sufficient

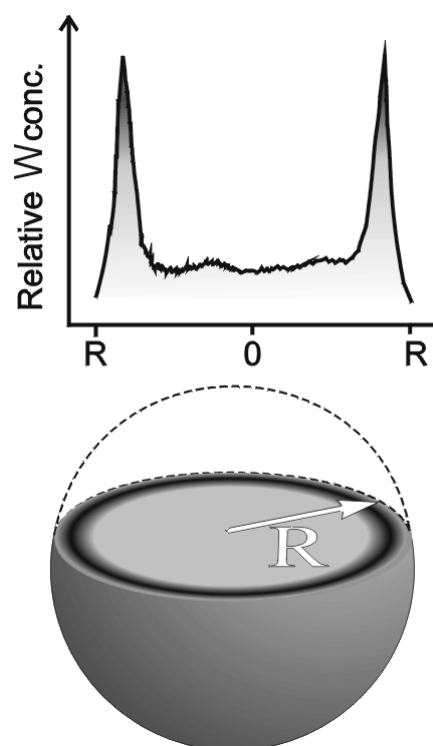


Fig. 9. Distribution of W over spherical catalyst granule.

for stable and efficient waste catalytic destruction.

The accumulation of U in catalyst granules upon catalytic treatment of spent oils and extractants of fuel rods production with uranium content 120 mg/L and 10 g/L, respectively was studied in the pilot installation at PCC. The experiments confirmed high efficiency of the proposed method for the treatment of the industrial mixed wastes containing uranium. The results show that the ratio between uranium captured in the catalyst bed and removed from the bed by the flow of the reaction products is dependent on the type of the wastes and uranium content, and up to 70% of uranium is retained in catalyst granules. This allows for reduction of the load on the off-gas treatment system and an increase of its efficiency.

The radionuclides can be recovered from the spent catalyst by conventional methods, e.g. by dissolving of the spent catalyst in nitric acid and the subsequent extraction by tributyl phosphate.

The experimental results obtained in pilot-scale experiments showed the technology of fluidized bed catalytic combustion to be efficient for environmentally safe treatment of liquid organic wastes

containing radionuclides. Based on these studies, a technological scheme and design documentation of the prototype demonstration plant for treatment of PCC mixed liquid organic wastes formed in fuel rods production with a capacity of 50 t/year were prepared. The block diagram of the demonstration plant with expected emission characteristics is given in Fig. 10.

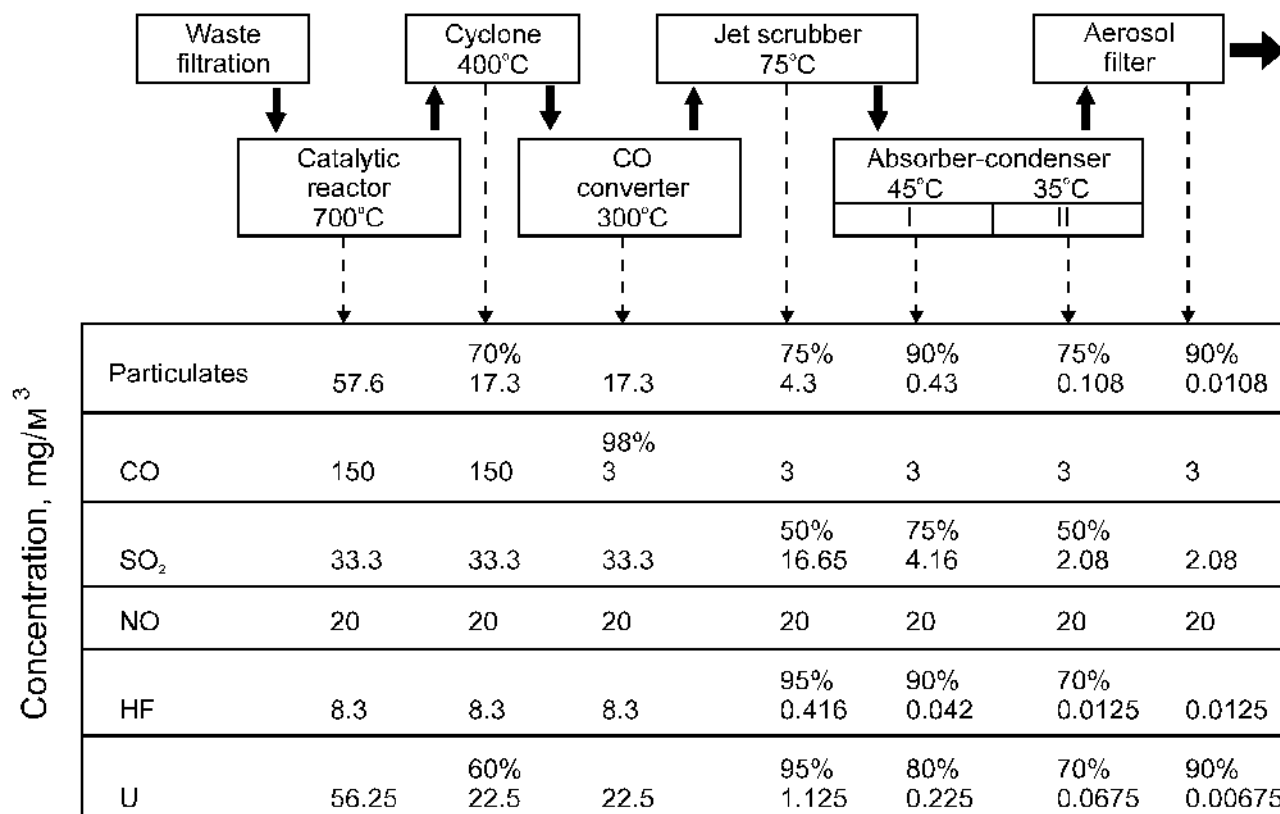


Fig. 10. Prototype Demonstration Plant Design and Emission Characteristics.

At present the fabrication of all apparatuses of the plant is finished, the assembly of the plant is completed and the tests of the plant are planned. The plant is intended to solve one of the urgent environmental problems of Novosibirsk Region by reducing the volume of mixed waste by 100 times and transition it to less hazardous forms, which are safely disposed by existing technologies.

### Environmentally safe catalytic technology for the utilization of liquid rocket fuel UDMH and wastes, containing UDMH

Reduction and conversion of defense industries in

Russia have made extremely important the issues of development and implementation of environmentally safe and efficient processes for liquid rocket fuel utilization. One of the most topical problems is development of the process for utilization of 1,1-dimethylhydrazine (CH<sub>3</sub>)<sub>2</sub>N-NH<sub>2</sub> (or unsymmetrical dimethylhydrazine – UDMH, technical name – «heptyl»), by itself representing a highly toxic and explosive substance.

In the frame of ISTC Project No 959, Boreskov Institute of Catalysis (BIC) in collaboration with State Rocket Center «Academician V.P. Makeyev Design Bureau» (SRC) and other institutions has developed a new environmentally safe method for UDMH de-

struction by means of the complete catalytic oxidation to harmless products ( $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{N}_2$ ). In order to destroy UDMH, it is suggested to use a combination of methods of oxidation in the reactor with fluidized catalyst bed and liquid-phase catalytic oxidation of UDMH traces in the scrubber fluids of gas purification units [30-34].

A study of UDMH vapor oxidation by air has been conducted at BIC in the laboratory kinetic setup on different solid catalysts, including  $\text{Cu}_x\text{Mg}_{1-x}\text{Cr}_2\text{O}_4/\gamma\text{-Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ , 0,64% Pt/ $\gamma\text{-Al}_2\text{O}_3$ , Cu/(ZSM5+ $\text{TiO}_2$ + $\text{Al}_2\text{O}_3$ )/ $\text{Al}_2\text{O}_3$ + $\text{SiO}_2$  (Table 5) [31]. The temperature dependencies of various product concentrations have been examined. The reaction intermediates were identified, and a possible mechanism of UDMH catalytic oxidation has been suggested. The catalysts and process conditions, allowing to achieve the complete oxidation of UDMH to  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and  $\text{N}_2$  with minimal concentrations of nitrogen oxides formed, were selected. Also the study of catalysts for UDMH oxidation in the aqueous solutions has been conducted, and selection of the most efficient catalysts was done [32].

Based on the studies conducted, the SRC has developed and fabricated a pilot plant for UDMH catalytic destruction with a capacity of 10 tons/year, where the adjustment and optimization of process parameters was accomplished. This technology can solve the following problems:

- 1) destruction of UDMH directly at the rocket bases using mobile plants;
- 2) destruction of the wastes containing UDMH, for example, rinsing fluids after cleaning UDMH tanks;
- 3) liquidation of the consequences of UDMH spills in emergency situations.

Laboratory kinetic setup for the study of UDMH catalytic oxidation consists of the following principal units: systems of compressed gas ( $\text{N}_2$  as UDMH carrier, air as oxidizer) and UDMH supply, mixer of  $\text{N}_2$ -UDMH vapour and air flows, gradientless quartz catalytic reactor with a vibro-fluidized catalyst bed, and the system of reaction mixture analysis based on a gas chromatograph Kristall 2000m with detectors FID and TCD. In addition, ECOM SG Plus gas analyzer was used to measure the  $\text{NO}$ ,  $\text{NO}_2$  and  $\text{CO}$  concentrations. In this communication we present some results of the experiments with catalysts IC-12-73 ( $\text{Cu}_x\text{Mg}_{1-x}\text{Cr}_2\text{O}_4/\gamma\text{-Al}_2\text{O}_3$ ), IC-12-74 ( $\text{Fe}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ ), AP-64 (0,64% Pt/ $\gamma\text{-Al}_2\text{O}_3$ ) and modified zeolite Cu/(ZSM5+ $\text{TiO}_2$ + $\text{Al}_2\text{O}_3$ )/ $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  (further abbreviated as «Cu/zeolite») (Table 5). These experiments were conducted under the following conditions: catalyst temperature 200-400°C, C(UDMH) in the initial reaction mixture  $0,55 \pm 0,05$  mmol/L ( $1,2 \pm 0,1$  vol.%), catalyst loading  $1 \text{ cm}^3$ , catalyst fraction 0,25-2 mm, reaction mixture gas hourly space velocity (GHSV)  $7200 \text{ h}^{-1}$ .

**Table 5**

Catalysts used for the laboratory kinetic study of UDMH oxidation by air.

Oxide catalysts	Noble metal catalysts	Catalysts of other types
IC-12-73 ( $\text{Cu}_x\text{Mg}_{1-x}\text{Cr}_2\text{O}_4/\gamma\text{-Al}_2\text{O}_3$ ) IC-12-74 ( $\text{Fe}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ ) IC-44 ( $\text{Fe}_2\text{O}_3+\text{Cr}_2\text{O}_3+\text{ZnO}$ ) perovskites $\text{Ca}_{0,7}\text{Sr}_{0,3}\text{FeO}_{2,5(3,0)}$ perovskites $\text{La}_{0,7}\text{Sr}_{0,3}\text{CoO}_{2,5(3,0)}$	AP-64 (0,64 % Pt/g- $\text{Al}_2\text{O}_3$ ) 0.5 % Pd/g- $\text{Al}_2\text{O}_3$ 32.9 % Ir/g- $\text{Al}_2\text{O}_3$	modified zeolite Cu/(ZSM5+ $\text{TiO}_2$ + $\text{Al}_2\text{O}_3$ )/ $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$ * CFC-1 and 2 (filamentous carbon with Ni, Al and Ni, Cu, Al) $\text{Si}_3\text{N}_4$ (with additions of 13.4 % $\text{Al}_2\text{O}_3$ and 2% $\text{SiO}_2$ )

\*further abbreviated as «Cu/zeolite»

As can be seen from Fig. 11a, the most active catalysts for UDMH deep oxidation to  $\text{CO}_2$  are IC-12-73 and AP-64, while catalysts IC-12-74 and «Cu/zeolite» can be used for UDMH deep oxidation only at the temperatures above 400°C. In the case of IC-12-73, noticeable increase of conversion to  $\text{CO}_2$  begins at 200°C, and at the temperatures above 300°C practically complete UDMH transformation into the

deep oxidation products  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and  $\text{N}_2$  is observed. For all the studied catalysts, at 200-300°C, along with the products of deep oxidation, 14 peaks corresponding to various intermediate products forming from UDMH, were revealed on the chromatograms and the mechanism of UDMH oxidation was suggested [31]. Figure 11b shows, that the highest  $\text{NO}$  concentrations are formed on AP-64 catalyst, while the lowest – on

IC-12-74 and IC-12-73 catalysts. «Cu/zeolite» catalyst demonstrates rather high C(NO), however it becomes lower at the temperatures above 360°C. In summary, IC-12-73 catalyst exhibited the best results

of UDMH oxidation to CO<sub>2</sub>, and low selectivity of nitrogen oxides formation. Consequently, this catalyst was selected for the usage in fluidized bed reactor of the pilot plant for catalytic destruction of UDMH.

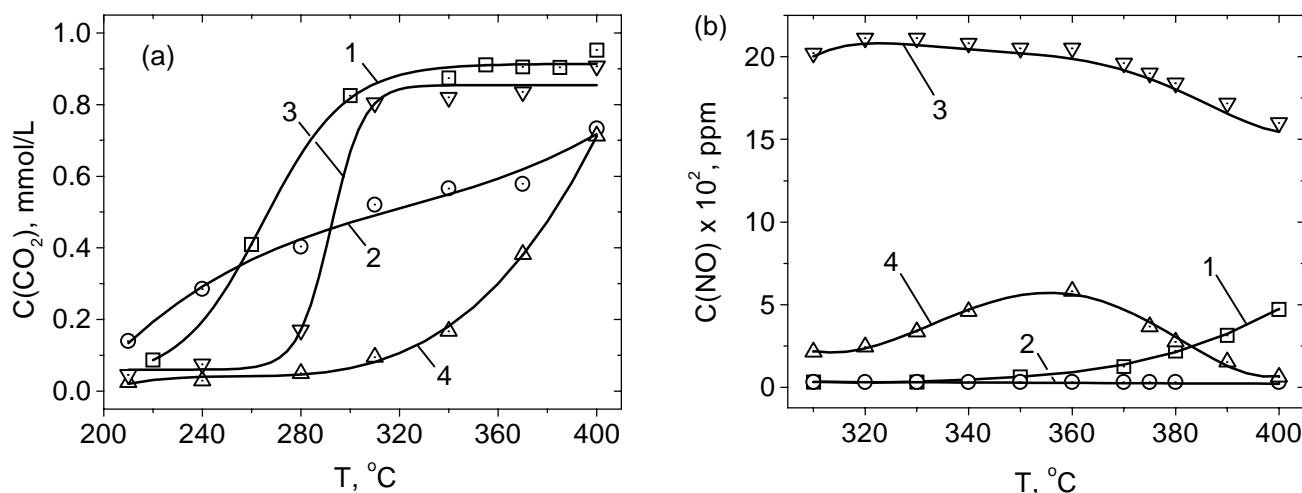


Fig. 11. Comparison of the temperature dependencies of CO<sub>2</sub> (a) and NO (b) concentrations upon UDMH oxidation on different catalysts. C(UDMH) = 0,55 ± 0,05 mmol/L, GHSV = 7200 h<sup>-1</sup>, 1 – IC-12-73 (Cu<sub>x</sub>Mg<sub>1-x</sub>Cr<sub>2</sub>O<sub>4</sub>/γ-Al<sub>2</sub>O<sub>3</sub>), 2 – IC-12-74 (Fe<sub>2</sub>O<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub>), 3 – AP-64 (0,64%Pt/γ-Al<sub>2</sub>O<sub>3</sub>), 4 – «Cu/zeolite».

Scheme of a pilot plant for UDMH destruction is shown in Fig. 12. It is similar to the plant early used for destruction of mixed wastes, but there are also important additions such as monolithic catalyst for the selective catalytic reduction (SCR) of nitrogen oxides and liquid phase slurry catalyst in the second scrubber. Pure UDMH or the mixture of water and UDMH is supplied from the tank (10) to the catalytic fluidized bed reactor (1). Compressed air is fed to the reactor in a quantity necessary for complete oxidation of UDMH at the temperatures of 500-700°C. The electric heater is used for preheating the catalyst bed in order to start the oxidation process. Gas leaving the reactor may contain nitrogen oxides, trace amounts of unoxidized UDMH, and dust of variable size resulting from the catalyst attrition and mineral part of treated wastes. Gas temperature at the reactor outlet is lowered to 350-450°C using water heat exchanger immersed in the catalyst bed. From the reactor, gas enters the cyclone (3), where dust particles of the size > 30 μ are separated from the gas stream.

At the second stage, gas passes through the reactor with monolithic catalysts (4) for the SCR of nitrogen oxides with ammonia, and then through oxidation catalyst for afterburning excess ammonia and residual UDMH. For further gas purification a jet scrubber

No 1 (5) is used, which acts both as a gas and dust trap and as a regenerative heat exchanger. Here, in the highly turbulent foam layer with a constantly refreshed surface, gas separation from medium-size particles (3-30 μ), UDMH traces and other toxic admixtures occurs, with concomitant gas cooling to 70-90°C. For further treatment gas is directed to the jet scrubber No 2 (6), where destruction of the UDMH traces is conducted over powder catalysts for the liquid-phase UDMH oxidation, added to the scrubber liquid [32,33].

After this scrubber, the gas saturated with water vapor enters the absorber-condenser (7), where its purification from the low-size particles (0,1-3 μ) takes place with final removal of the trace amounts of UDMH and gas cooling to 30-40°C. If any amount of UDMH is accumulated in the absorber-condenser it will be also oxidized in the scrubber liquid using the above mentioned catalysts for liquid-phase UDMH oxidation.

The series of pilot plant experiments were accomplished in two stages – testing of the main reactor with fluidized catalyst bed (Table 6) and testing during the simultaneous operation of the main reactor and off-gas treatment system: reactor for the SCR of nitrogen oxides and wet gas cleaning units (Table 7).

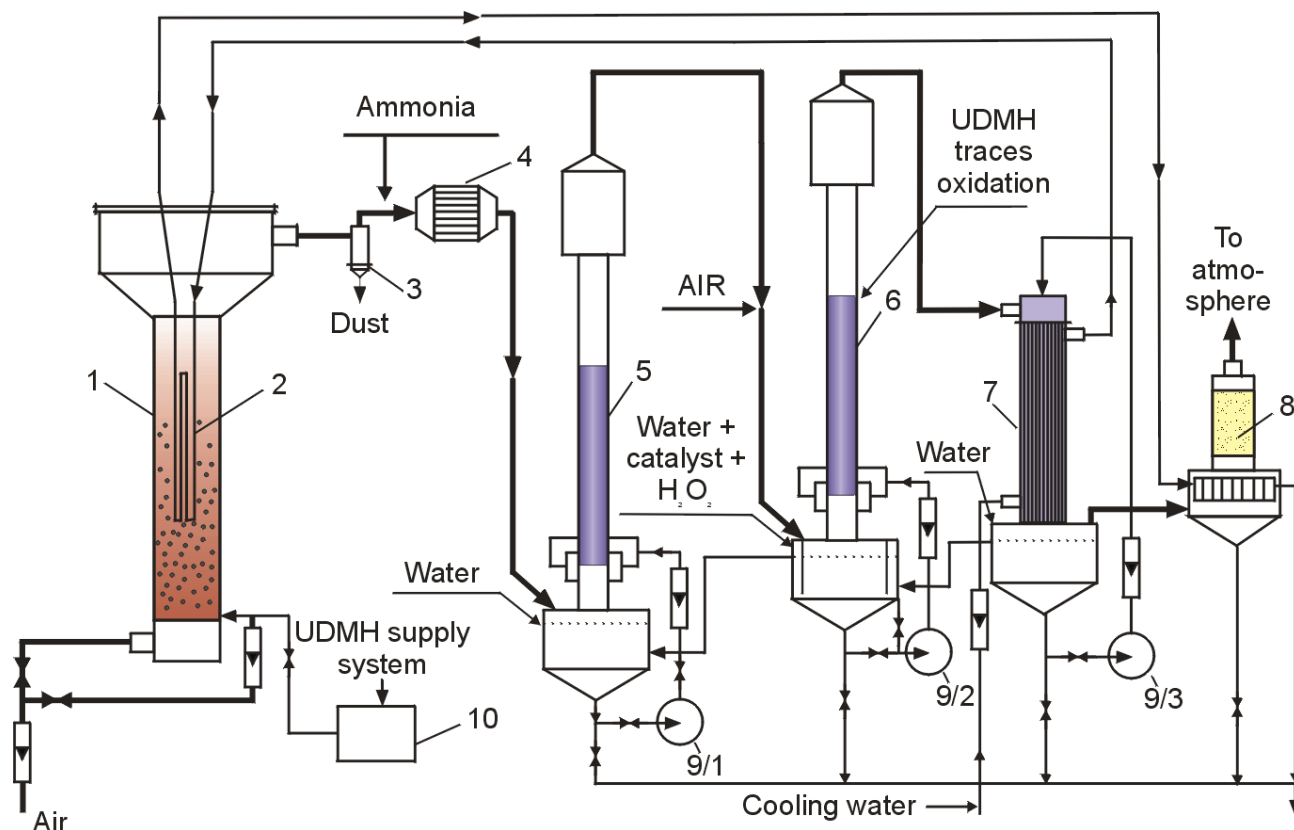


Fig. 12. Scheme of the pilot plant for the process of UDMH catalytic destruction: 1 - catalytic fluidized bed reactor; 2 - water heat exchanger; 3 - cyclone; 4 - SCR reactor; 5, 6 - jet scrubbers; 7 - absorber-condenser; 8 - aerosol filter; 9/1-9/3 - pumps, 10 - tank for UDMH.

In the first series of experiments, process parameters providing the most complete UDMH oxidation were determined. In further experiments parameters of the main reactor were specially chosen to provide the

presence of some residual UDMH in the exhaust gas. That was done in order to study the efficiency of UDMH removal from gas stream by the units of the off-gas treatment system.

**Table 6**

Results of testing the main reactor with fluidized catalyst bed.

Main air flow, m <sup>3</sup> /h	Air flowthrough injectors, m <sup>3</sup> /h	UDMH flow rate, L/h	Oxidizer excess coeff. $\alpha$	T in the main reactor, °C	Gas composition at the main reactor outlet, mg/m <sup>3</sup>		
					NO <sub>x</sub>	CO	UDMH
16.2	1.6	1.08	2.7	630	6000	< 5	< 0.05
16.2	1.6	2.24	1.31	675	6000	< 5	< 0.05
16.2	1.6	2.56	1.14	735	6000	< 5	0.075

**Table 7**

Results of the SCR reactor testing.

Conc. of UDMH (init.), mg/m <sup>3</sup>	Conc. of NO <sub>x</sub> (init.), mg/m <sup>3</sup>	Conc. of NH <sub>3</sub> (init.), g/m <sup>3</sup>	NH <sub>3</sub> flowrate, m <sup>3</sup> /h	T in the SCR reactor, °C	Gas composition at the SCR reactor outlet, mg/m <sup>3</sup>			
					UDMH	NO <sub>x</sub>	CO	NH <sub>3</sub>
2.14	2000	7.86	0.20	420	0.095	80	< 5	< 5

## Conclusion

In this paper we tried to demonstrate that the catalytic combustion is powerful instrument for both heat production and for processing of different types of wastes in environment protection.

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