SPECTROSCOPIC DIAGNOSTICS OF PLASMA-CHEMICAL REACTOR
WORKING MEDIUM AT PESTICIDE UTILIZATION


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ABSTRACT

Spectroscopic diagnostics of working medium of three-jet electric arc plasma-chemical reactor used for pesticides processing and destruction was carried out. Dispersed pesticides of aromatic hydrocarbon and chlorohydrocarbon types were studied: isoprene (N\textsubscript{14} I\textsubscript{18} I\textsubscript{2} N\textsubscript{2}), concentrate of butyl ether of 2,4-dichlorophenoxyacetic acid (N\textsubscript{4} I\textsubscript{6} N\textsubscript{2} I\textsubscript{1} N\textsubscript{6} I\textsubscript{3} N\textsubscript{1}), methaldehyde (N\textsubscript{2} I\textsubscript{4} I\textsubscript{0}), and pentothiuram, consisting of thiram (CN\textsubscript{2})_{2}NCSSCN(CN\textsubscript{2})_{2} and of nitropentachlorobenzene C\textsubscript{6} Cl\textsubscript{6} NO\textsubscript{2}.

Introduction

Processing or neutralization of industrial toxic wastes is actual problem for many industrial countries of the world. The traditional technologies of waste treatment in various furnaces and combustion chambers are characterized in rather low temperature of the process (1500-1700 °E). Therefore, the processed product may contain a considerable amount of primary and secondary (formed during the processing) toxins. Additional injection of oxygen or liquid fuel in the combustion devices results in small raise of the process temperature, consequently the contents of toxins in the residual product does not change essentially.

The most essential results on the toxic waste processing have been obtained with application of arc reactors. Use of low-temperature plasma for toxic waste neutralization allowed to increase the minimal temperature in the reactionary zone up to 1900-2500 K and exclude thereby the gas-phase reactions of formation of ultrotoxic chlorine compounds: phosgene, dioxines, polyhalogenated biphenils and furans. The achievable degree of toxin decomposition amounts 99.99999%. This work is to develop the techniques of determination of gas composition after plasma-chemical reactor and to study the dependence of gas composition and contents of N\textsubscript{2} and CO at pesticides neutralization.

Experimental

The set-up contains three arc jet DC plasmatrons, mixing chamber, plasma-chemical reactor and supply system.
Each plasmatron consists of rod thermocathode, annular anode and gas distributive ring for injection of plasma forming gas (air). The generated in plasmatrons plasma jets form a uniform plasma flow in the mixing chamber of plasma-chemical reactor, where intermixing, heating and chemical transformations of processed waste take place.

The mixing chamber is a hollow truncated water-cooled metal cone with disclosing corner of 60°. The plasmatrons are located symmetrically on a surface of the chamber. The corner between a direction of plasma jets and axis of mixing chamber equals 60°. Diameter of outlet of the mixing chamber is 100 mm. There is a unit for injection of processed materials in the top part of mixing chamber. Scraper feeder is used as the waste injection devices.

The plasma-chemical reactor includes the main body, unit of exhaust gas quenching, intermediate bunker for allocation of solid fractions from the flow of exhaust gases, gas mixer and sampler for the exhaust gas analysis.

The reactor main body consists of a set of water-cooled cylindrical metal sections of 100 or 50 mm in height and 100 mm in diameter. Such design allows to create the reactor of length up to 700 mm. Besides, there are special water-cooled 20 mm section with quartz windows for observation of plasma radiation. This section may be mounted anywhere along the reactor length or between the reactor and mixing chamber. The quenching unit is intended for injection of cold air to fix the component composition of waste processing products due to prevention of further chemical reactions in the processed material.

The plasma-chemical reactor operating mode at power input N = 165 kW and plasma forming gas rate (air) ~10 g/s ensured average over the reactor volume specific enthalpy of plasma 1 ~ 6000 J/g, sufficient for pyrolysis of herbicides and pesticides. The consumption of processed pesticides at the tests was 0.47, 0.97, 0.92 and 0.43 g/s for isophene, butyl ether, methaldehyde and pentathuram, respectively. The tests were carried out at reactor operation with quenching and without quenching, with dilution and without dilution of exhaust gas with cold air. The airflow rates for quenching and dilution were ~10 g/s (20 g/s at double quenching) and 17 g/s (34 g/s at double dilution), respectively. Quenching unit was placed after last section of the reactor and dilution unit was set at a distance of 560 mm from the quenching unit. The water-cooled gas sampler was placed before ventilation duct in a spatial zone of the gas flow remote from the quenching unit by 1750 mm, where the gas temperature is about 800 K and chemical transformations of the exhaust gas is interrupted.

For determination of the controllable component concentrations in the exhaust gas flow the absorption spectroscopy methods will be used. The concentrations of nitrogen oxides and carbon monoxide were measured with the help of developed techniques and automated spectrometer complex ASC.

The NO concentration will be determined from an absorption of probing light beam in UV spectral range in bands of NO β system (λ = 226 nm), the CO concentration – from absorption in vibration bands of the basic electronic state X^1Σ^+ in IR spectral range (λ ~ 4800 nm), the concentration of nitrogen dioxide NO2 – from absorption in bands at λ = 448.0 nm. The automated spectrometer complex developed for the control of plasma processing of pesticides consists of a set of functionally complete blocks (Fig. 1) allowing the complex configuration to be changed in accordance with specificity of its operating mode. Recording part of the complex consists of a spectral block 3, blocks of radiation detectors 4, 5 and control computer 6.

At determination of contents of NOx and CO the value of an analytical signal S will be found by extinction I(λ)/I(λ), measured in a spectral band Δλ, of probing radiation intensity of source 1 after passage of an exhaust gas-filled vessel.
Fig. 1. Block diagram of the automated spectrometer complex "ASC":
1 - block of sources of probing light; 2 - high-temperature gas vessel;
3 - spectral block; 4, 5 - blocks of radiation detectors; 6 - control computer;
7, 7', 8 - projecting optics; 9 - rotary mirror.

Gas for the analysis will be sampled into a vessel 2 from gas outlet located apart more
of 1.5 meters from the reactor exit where the gas temperature is \( T \approx 350 \) K and chemical
transformations of the gas is interrupted. The vessel will be filled with a gas by pumping
through it the part of exhaust gas flow. Working pressure in the vessel is \( P = 1 \) atm. For
tenfold changing the detection limit of controllable components the vessel will have two
optical lengths: 10 cm (variant of single passage of probing radiation) and 100 cm (variant of
multiple passage of probing radiation). To assure a prolonged lifetime of the vessel all optical
elements of the vessel will be manufactured of nonhygroscopic materials (quartz and BaF\(_2\))
and a SiO\(_2\) coating will protect mirror optics.

The block of sources of probing light 1 is completed with deuterium, xenon and tape
tungsten lamps. Their working spectral ranges are \( 190\cdot300, 300\cdot700 \) and \( 500\cdot5000 \) nm
at radiation instability of no more than 0.06 %/min, 2 and 1 %/hour, respectively. Application of
these lamps as well as optical windows 2' and 2'' of quartz and BaF\(_2\) in the vessel 2 gives a
possibility to control the exhaust gas composition by electronic and vibration absorption
spectra in a wavelength range from 200 nm up to 5000 nm.

Monochromator-spectrograph MS 3504, manufactured by Belarus-Japan JV "SOLAR-
TII", will be used as a spectral block 3. A distinctive feature of the monochromator-
spectrograph is widening of a spectral working range up to \( \Delta\lambda = 200\cdot5000 \) nm as a result of
possibility of automatic replacement of diffraction gratings. The block will be completed with
radiation detectors – CCD-bar 4 for ultraviolet, visible and near infrared spectral ranges and
pyroelectric detector 5 for spectral range 2000+5000 nm.

The calibration of a recording tract of "ASC" for CO and NO\(_x\) (ascertaining of
quantitative dependence of an analytical signal \( S \) from concentration of molecules \( N \)) will be
fulfilled by measurements of magnitudes \( S_{m=1,2,3,...} \) for reference concentrations \( N_{m=1,2,3,...} \) of
nitrogen oxides and carbon monoxide at filling the vessel by reference gas mixtures \( N_2\cdotCO\)
and N₂+NO₂. The concentrations N̂_{CO} or N̂_{NOx} in the exhaust gas flow will be determined by the measured values S* with use of obtained quantitative dependence S=F(N).

For determination of NO and CO concentrations in the plasma-chemical reactor exhaust gases the calibrating dependence was linearized and set into the data processing program of ASC complex. For determination of NO₂ concentration the registration tract was gauged according to design-experiment technique with use of absorption cross-section (σ_v) of the selected absorption lines. Literary data and experimental data obtained with the help of an absorbive laser spectrometer for small concentrations of nitrogen dioxide were used for determination of σ_v. For experimental measurement of σ_v the optical gas-analysers based on a laser intracavity spectrometer with a tuneable multimode dye laser was used as a probing light source. The algorithm of processing of registered NO₂ absorption spectra consists in measuring relative radiation intensity, in determining spectral dependence of absorption constant, in determining concentration of absorbing sites from absorption cross-section and in determining bulk concentration of nitrogen dioxide in the gaseous medium.

Results and Discussion

The experiments under the above-stated scheme were fulfilled for isoprene, butyl ether, methaldehyde and pentathium.

Each reactor operating mode is represented by twenty values of bulk concentration of NO, recorded at intervals 1 s. For all reactor operating modes with pesticides the NO content in the exhaust gas is lower, than for modes without feeding of pesticides into the reactor. This is, apparently, resulted from fixation of nitrogen and oxygen, present in hot air, with products of pesticide decomposition. The quenching of exhaust gas reduces the bulk content of NO at neutralization of isoprene, butyl ether and pentathium. At methaldehyde processing the influence of quenching is less clear. The dilution of exhaust gas with air also results in lowering the bulk content of NO. The simultaneous use of double quenching and dilution leads to diminution of the NO content by a factor of 1.4-1.5 in comparison with the operating mode without quenching and without dilution.

Decomposition products, remaining in the reactor after processing, can influence on subsequent operation of the plasma-chemical reactor. In some cases replacement of processed pesticide results in rising the NO concentration in an exhaust gas flow by factor 2-3. Deposition of solid fractions of pesticide decomposition products on the reactor walls resulting in change of conditions of exhaust gas cooling in quenching unit and dilution unit seems to be a reason of this. Estimations on the base of calculation data of equilibrium air composition shows that at temperatures of 1000 < T < 2500 K, existing in gas-outlet channel, lowering of its value by 200-300 K can change of NO concentration in more than 2 times.

The concentration of nitrogen dioxide weakly depends on a kind of processed pesticide. The results of measuring of NO and NO₂ contents in the exhaust gas flow at neutralization of pentathium depending on the reactor mode are given in Fig. 3.

It is seen from Fig. 3, that increasing of air flow rate for quenching and/or dilution results in monotonous decreasing of NO and NO₂ contents in the exhaust gas flow. The ratio of NO and NO₂ concentrations is ~ 5, that specifies that oxidizing of nitrogen monoxide is practically single possible channel of NO₂ formation under considered conditions.
Fig. 2. The NO content in the exhaust gas flow (1- isophene, 2- butyl ether, 3- methaldehyde, 4- pentathuran) for various operating modes (a- without quenching and without dilution; b- with quenching and without dilution; c- with double quenching and without dilution; d- with quenching and with dilution; e- with double quenching and with dilution). □- with feeding of pesticides. O- without feeding of pesticides.

Measurement of carbon monoxide concentration in the exhaust gas flow was found to be impossible, since at pesticide neutralization an analytical signal of CO absorption recorded by ASC was on the level of inaccuracy of the measurements for all reactor modes.

**Conclusion**

It was found on the base of data obtained, that used three-jet plasma reactor is the suitable technological device for neutralization of wide list of herbicides and pesticides, including chlorine containing ones.

The study of exhaust gas composition shows such substances as nitrogen oxides NO and NO₂, carbon monoxide CO need monitoring at pesticide neutralization.

Absorption spectroscopy is a simple and operative method of ecological safety checking of process of plasma neutralization of pesticides. The method ensures to estimate the content of controlled substances in an exhaust gas mixture during pesticide processing. The content of nitrogen monoxide may be monitored by molecular band of NO γ-system (λ = 226.3 nm), nitrogen dioxide – by NO₂ molecular band at λ = 448.0 nm, carbon monoxide – by fundamental band of CO (λ = 4.6 μm).
Fig. 3. The NO (□, O) and NO₂ (X, V) bulk concentration in an exhaust gas flow depending on operating mode of the reactor (dashed line – without pesticide, solid line – with pentathiuram).

For elimination of influence of additional absorption due to chemical compounds formed in the reactor at processing different pesticides, it is necessary to use a spectral apparatus with spectral resolution no lower than 1 nm as well as to have a possibility of detailed verification of the absorption spectrum in a vicinity of controlled components.

The application of quenching of exhaust plasma flow with cold air with flow rate equal to that of plasma forming gas results in lowering plasma temperature from ~3500 K to ~2300 K and thus to reduce nitrogen oxides content in the exhaust gas mixture down to the level of 0.1%. In a mode with quenching the content of derived hydrocarbons is also reduced. The further lowering of NOₓ concentration down to the level of ambient air standard (0.4×10⁻³ %) can be obtained by gradual cooling of exhaust gas mixture down to temperature of ~850 K. To eliminate the appearance of dioxines formed at temperatures of 520-720 K, it is necessary to realize the subsequent quenching of the flow from 0 ~ 850 K down to 0 ~ 500 K.