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PLASMA METHODS FOR TECHNOLOGY PROCESSING OF TOXICAL INDUSTRIAL WASTES.

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Abstract. Experimental study of thermal neutralization of some toxic chlorine and bromine industrial wastes, as well as of pesticides with a expired term of validity was carried out in the three-jet plasma reactor. Different physical-chemical methods were used for analysis of products of waste processing. It was shown that plasma technology provides effective processing of toxic wastes.

1. INTRODUCTION.

Alternative to conventional low-temperature methods of toxic wastes incineration is their destruction in thermal plasma, which takes place at high temperature. Using arc and other plasmas delivering temperature of the order of 5000 K makes possible to break down organic and nonorganic compounds in plasma is highly effective even without oxygen. The other merit is possibility of good mixing in plasmochemical reactor, this is the important factor of wastes thermal processing. This process can be realized in the multi-jet plasma reactor which provides good mixing of plasma with treated wastes [1,2]. The plasma reactor including three-jet mixing chamber with attached three plasma torches. The installation contains a system of raw material supply into the plasma reactor. A system of stub tube, vacuum pump and a set of evacuated flasks was used to extract exhaust gas for analysis. There were also units for power and water supply, for arc ignition and for control system of work parameters of the installation. The system works on the following principle: interaction between three intakes plasma jets and wastes produces in the mixing chamber a certain heterophase flow which then forms the reaction zone over the whole length of the reactor dust. The physical-chemical processes of wastes thermal destruction take course just in this reactor and separation of the power products takes place then in a hopper whereas gases are conveyed into special filter to remove ultradispersed fractions. Gases pass then through a lye scrubber and are exhausted into atmosphere by a fan.

2. PROCESSING AND DESTRUCTION OF CHLOROORGANIC WASTES [3].

Decomposition (destruction) products of the real withdrawals were analyzed. The withdrawals were the mixture of the following products; trichloroethylene – 80%, nitrotoluene – 17%, nitrobenzoalcohol – 1,1%, nitrobenzoaldehyde – 1,1%, carbon tetrachloride – 0,8%. Toxic connections were not established in the composition of exiting products.

All experimental investigations were made with a constant waste feed of 3,6 kg/h. The variation of the plasma air supply was connected with a corresponding change of the

carbon-oxigen-ratio in the plasma reactor. On the other side the increase of the plasma generator. Due to the realized air supply the waste conversion was happen in all cases in a reduction atmosphere. In agreement with the calculation of the thermodynamic equilibrium the analysis of the gas phase shows a complete conversion of the organic substance into carbon monoxide and hydrogen respectively carbondioxide and stream. Each sample contained hydrogen chloride and hydrogen sulfide in small concentrations. Free chlorine was not be detected. The gaseous phase was analysed by means of gas chromatography and the mass-spectrometer MAT 311 Varian.

In some cases the product gas contained a insignificant amount of soot which points out that locally a pyrolysis regime took place. The formation of soot could be stopped by supply secondary air at the end of the reactor. In all experiments in gas phase a small concentration of nitrogen oxides was found, although in the thermodynamic calculations it occured only in oxygenous atmosphere. This fact may be connected with the formation of the oxides in the plasma jet and the short reaction time prevented the decomposition.

3. PROCESSING AND DESTRUCTION OF BROMINE CONTAINING WASTE [4].

Study was done with the solid free-flowing wastes containing bromide phenols with different proportions. Elemental analysis of the wastes was made by different methods before experiments. The average results obtained by different methods are: C=30,03%; H_2=4,31%; Br=50,32%; N_2=0,51%; S=0,08%; O_2=14,75%. The previous thermal analysis was also used for bromide-phenol wastes which seeked for content of water and mineral impurities.

Water solution of 2,5% bromine mass was prepared for the first run of bromine wastes. It was expedient for the sake of monitoring dispersc solution feed into the plasma heat medium at the high concentration of material. The run of experiments with this solution was carried out at variation of power and material feeding rate. Consumed electric power ranged over 95-120 kW, plasmaforming gas flow rate accounted for 4,7 g/s, and material supply varied from 1.0 to 15,5 g/s. The degree of decomposition amended to 100% for all experiments of the run. Chemical analysis of exhausting gases for content of bromine and toxic components was made after every experiment. No toxic dioxin and oxide was detected.

Possibility to increase the efficiency of the process at the expense of the solution doping was investigated at the second run of experiments. Three experiment, with the 75% solution of wastes in a polar organic solvent were made for processing optimization. At this run, electric power varied from 80 to 110 kW, material rate ranged over 5,6-12,5 g/s and flow rate of the working gas was taken at the constant level 6,0 g/s. The complete decomposition was observeth maximal material rate, but the incineration was incomplete and a lot of unoxidizedcarbon was settled out in the water-alkaline scrubber. Exhausting gases produced during the plasmochemical processing of the wastes were analyzed for the content of dioxides and their analogues, carbon oxides and dioxides, as well as for concentration of bromine hydrogen. Mass-spectrometer Hewlet-Packard GC/MS 5890/5972 was used for analysis of dioxides applying EPA 8270 method with gas filtration through methanol and the subsequent examination of methanol solution. All experiment exhibit no dioxide. Content of CO was analyzed by mass-spectrometer MX-1320 with high resolution. The observed m/z 29 peak had intensity 0,8% that indicates the absent of CO in the gaseous

phase. As to content of oxygen, it was found to be low in the first experimental run and negligible in the second one. On the other hand, the measurements demonstrated high concentration of nitrogen. Proportion of HBR in the produced gaseous mixture was measured by gravimetric chemical-analytical method with titration of HBr by silver nitride solution and subsequent analysis of silver bromide by mass-spectrometry. The concentration of HBr in the gaseous phase at normal conditions was determined both runs: for optimal experiment of the first run upstream from scrubber – 0,337 g/l and downstream of it – o,143 g/l; for optimal experiment of the second run upstream from scrubber – 0,03 g/l and downstream of it – 0,015 g/l.

The component HBr can be considered as a useful desired product of such a wastes processing that can be used for pure bromine production. The experiments have shown that the yield of HBr in the first run applying water-emulsion feed of the wastes is about an order higher then in the second run when organic solvent was used and the plasma-chemical process proceeded at the excess of free carbon and deficient air. Bromine vaporization and reduction at the excess of H_2O according to the first variant is apparently the most efficient method of the wastes processing.

4. PROCESSING AND DESTRUCTION OF PESTICIDES WITH A EXPIRED TERM OF VALIDITY.

Investigations are carried out in different regimes of the work of plasma reactor for processing of two pesticides - isophene ($C_{14}H_{18}O_7N_2$) and concentrate of butyl ether of 2,4-dichlorphenoacetic acid ($C_4H_9CH_2COOC_6H_3Cl_2$), with expired term of validity.

Both these pesticides contsist of 50-60 % of base material (butyl ether and isophene) and 50-40 % of the filler substances, which contains of kaolin, aerosil and silica gel.

The detailed analysis of gases at the outlet of plasma reactor is executed. The methods of chromato- mass-spectrometry and absorption spectroscopy in ultraviolet (UVR), visible and infrared (IR) wavelength range are used.

Absorption spectra in the UVR, visible and near IR wavelength range ($0,2 \leq \lambda \leq 3,0$ μm) were recorded with spectrophotometer "Cary 500 Scan" of the firm "Varian" (USA), in such spectra in the distant IR area ($2,5 \leq \lambda \leq 25$ μm) – were detected by Furie spectrometer "IFS28" of the firm "Brucker" (Germany).

The analysis of the obtained spectrograms made it possible to establish that they weakly depend qualitatively on the type of the raw material used and are presented by three characteristic absorption bands: $\Delta\lambda = 0,2 \div 0,25$ μm, $\Delta\lambda = 0,35 \div 0,6$ μm and $\Delta\lambda = 2,5 \div 25$ μm.

Because of the high optical density of mixture in the UVR region of the spectrum we could not interpret reliably the recorded maximums of absorption. They can be the diffuse absorbtion bands of hydrocarbons of the type of the benzaldehyde C_6H_5CHO of the propionaldegida C_2H_5CHO, benzene C_6H_6, formaldehyde CH_2O, acetaldehyde C_2H_4O, etc. with transsitive into the intensive continuum.

The visible region of the spectrum is presented by the electron- vibrational-rotational absorption bands of molecules NO, NO_2, HNO_2, C_2, AlO, CaO, FeO, CuO, CN, SiN, CH. However we could not identified a number of the maximums of absorption as well as in the spectrograms of UVR range.

In the absorption spectra in the IR region we discovered the bands CH_3-, CH_2-, CH- of the groups of hydrocarbons and NO_3 - group, bands CO_2, H_2O, N_2, NO_2, the traces of bands

NO, bands of the condensed phase HNO_3, of the vapor phase H_2CO_3, the bands of the valency oscillation of the carbonyl group C=O, and also the weakly intensive bands of the deformation oscillations OH and CO. Obtained data testify about the intensive thermal decomposition of pesticides in the plasma airflow, which is accompanied by oxidation and nitriding of the products of decomposition. Bands CH_3-, CH_2-, CH-, and C=O groups are caused by the formation of the secondary hydrocarbons at the outlet of the plasma reactor in hardening zone. Formed simple oxides and nitrides are not highly toxic or cancerogenic substances and are not ecologically dangerous. Some of them can be separated, assembled and used further.

Chromato-mass-spectrometric analysis of emanated gases was performed for a determination of a type of produced hydrocarbons and their quantitative content in the outlet of plasma reactor. Chromato-mass-spectrometer "MM" of "Brucker" firm (Germany) was used, range of mass numbers was 28-400, resolving power R was ~ 10000, threshold of detectability was ~ 1 ppb. Samples were taken after hardening zone with help of programme pump SKS and were placed at two-layer absorb tubes of the firm "Dreger". Activated coal and tenaks were used as absorb substances. Duration of sample taking was 4 min, velocity of pumping (circulation rate) of samples trough sorbents was 300 l/min.

Prelimenary separation of mixture components was curried out at the capillary column. Quadrupole mass-analyser was used as a mass-detector.

Produced products were identified by the comparison of complete mass-spectrum of analyzed substance or of its separate peaks with mass-spectra from the bank of standard substances. In order to increase statistic significance of the identification we used two methods of library search: a straight one, which provides computer comparison of analyzed spectrum with each library spectrum consequently, and a reverse method, which provides comparison of library spectra consequently with analyzed one.

For a calculation of every component concentration an evaluation of absorb substance mass and data of normalization of chromatometry results were used. Instrumental error of an evaluation of different substance contents in analyzed gases mixture was less 30-40 %.

5. RESULTS OF THE CHROMATO-MASS-PECTROMETRIC ANALYSIS OF THE COMPOSITION OF WASTE GAS DURING THE PLASMA-CHEMICAL PROCESSING OF PESTICIDES

Results of tests in the experiments with isophene and butyl ether processing are presented in the tables A and B. Plasma-forming gas - technical air. Average value of the specific enthalpy of plasma along the length of reactor H~6000 kJ/kg.

After butyl ether processing without hardening we found saturated, unsaturated and aromatic hydrocarbons, ordinary and complicated ethers, alcoholes, ketones, acids nitrogencontaining and chlorcontaining compounds in the products leaving plasma reactor.

As the table shows, a hardening changes significantly the composition of reactor off-gases. Clorcontaining and nitrogencontaining compounds, as well as some substances which contain ether groups and aldehyde groups were not detected at the outlet of reactor. Benzol derivations appear instead of them. Absence of compounds with ether groups and aldehyde ones and content increasing of compounds of types of methylcellosolve and benzoic acid can be caused by processes of secondary oxidation in the zone of hardening.

TABLES A.

PESTICIDE ON THE BASIS OF ISOPHENE $C_{14}H_{18}O_7N_2$

Designation of the substance	The chemical formula	Concentration in the waste gas flow, mg/l
		With the charge of raw material, with the hardening
Methyl nitrate, 1,3 propandioldinitrat, 1,3 propenediol	CH_3NO_3 $C_3H_6N_2O_6$ $C_4H_6N_4O_{11}$	Σ=2,3
3-heptanone	$C_7H_{14}O$	0,17
Isoamyl nitrite	$C_5H_{11}NO_2$	0,06
2-propyl-1- pentanol	$C_8H_{18}O$	0,59
3,5,5-trimethylhexanol	$C_9H_{20}O$	0,04
3,5-dimethyloctane	$C_{10}H_{22}$	0,04
Undecane	$C_{11}H_{24}$	0,09
2,2-dimethyl-3-hexanol	$C_8H_{18}O$	0,71

TABLES B.
PESTICIDE ON THE BASIS OF R-BUTYL ETHER $C_4H_9CH_2COOC_6H_3CL_2$.

Designation of the substance	The chemical formula	Concentration in the waste gas flow, mg/l		
		With the charge of raw material, without the hardening	With the charge of raw material, with the hardening	Without the raw material, without the hardening
Methyl cellosolve	$C_3H_8O_2$	0,63	3,01	1.18
Diisopropyl ether	$C_6H_{10}O$	3,08	-	6,86
Heptanone, 3	$C_7H_{14}O$	0,44	-	-
Hexanol, 2-ethyl	$C_8H_{16}O$	1,64	-	-
Heptene 1/3	C_7H_{14}	2,24	5,1	-
Butylisocyanate	C_5H_9NO	2,61	-	-
2-nitrophenol	$C_6H_5NO_3$	0,78	-	-
Acetophenone	C_8H_8O	2,68	-	1,88
Benzoic acid	$C_7H_6O_2$	5,12	6,76	7,30
Benzophenone	$C_{13}H_{10}O$	0,91	3,29	4,03
Acetophenone, 8-chloro	C_8H_7ClO	4,35	-	6,13
Heptachlorepoxide	$C_{10}H_5Cl_7O$	3,28	-	-
Xylene	C_8H_{10}	-	0,15	-
Benzene trimethyl	C_9H_{12}	-	0,09	-
Undecane, dodecane, tridecane	$C_{11}H_{24}$, $C_{12}H_{26}$, $C_{13}H_{28}$	-	Σ=0,13	
Butanol, ethyl	$C_6H_{14}O$	-	-	2,92
Isobutylacetate	$C_6H_{12}O_2$	-	-	0,15

Nitrogencontaining substances can be performed in the presence of hydrogen into nitroacid or nitrozoacid, that was proved by the spectroscopy analysis. Chlorcontaining compounds can be performed into chlorine salt at the base of calcium, copper and iron, presence of with was detected also by spectroscopy method.

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