Plasma methods for processing of toxic industrial waste

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Abstract: We present an experimental study of the thermal neutralization of toxic chlorine and bromine industrial wastes, as well as expired pesticides using a three-jet plasma reactor. Different physicochemical methods were used for analysis of the waste processing products. It is shown that plasma technology provides effective processing of toxic wastes.

Keywords: Methods, DC, RF, plasma, toxic, industrial

1. Introduction.

An alternative to conventional low-temperature methods of toxic wastes, such as incineration, is their destruction in thermal plasma, that takes place at a higher temperature. Using arc and other plasmas delivering temperatures of the order of 5000 K makes it possible to break down organic and inorganic compounds in plasma in a highly effective manner even without oxygen. The other merit is the possibility of good mixing in a plasma chemical reactor. This is an important factor in waste thermal processing. We are using a multi-jet plasma reactor that provides good mixing of plasma with treated wastes [1,2,3]. The plasma reactor includes a three-jet mixing chamber with three plasma torches attached . The installation includes a raw material feeding system into the plasma reactor. A system of a stub tube, a vacuum pump, and a set of evacuated flasks are used to extract the exhaust gas for analysis. The system include units for power and water supply for arc ignition. Control systems regulate work parameters of the installation. The system works on the following principle: interaction between the three intake plasma jets and waste produces hetero-phase flow in the mixing chamber that then forms a reaction zone along the length of the reactor dust. The physicochemical processes of waste thermal destruction take place just in this reactor and separation of the powder products take place in a hopper. Gases are conveyed into a special filter to remove ultra-dispersed fractions. The gases then pass through a wet scrubber and are exhausted into the atmosphere by a fan.

2. Processing and destruction of chloro-organic wastes [4].

Decomposition (destruction) products of the exhaust were analyzed. They were a mixture of trichloroethylene – 80%, nitrotoluene – 17%, nitro-benzo alcohol – 1,1%, nitro-benzo aldehyde – 1,1%, and carbon tetrachloride – 0,8%. No toxic components were observed in the final product. products. All experimental investigations were made with a constant waste feed of 3.6 kg/h. The variation in the plasma air supply was associated with a corresponding change in the plasma reactor carbon-oxygen-ratio. The waste conversion took place in chemically reducing atmosphere. Thermodynamic equilibrium calculations of the gas phase show a complete conversion of the organic substance into carbon monoxide, hydrogen, carbon dioxide and steam. Each sample contained hydrogen chloride and hydrogen sulfide in small concentrations. Free chlorine was not detected. The gaseous phase was analyzed by gas chromatography and a MAT 311 Varian mass-spectrometer. In some cases, the gas product contained an insignificant amount of soot indicating that local pyrolysis took place. The formation of soot could be eliminated using by a secondary air supply at the end of the reactor. All the experiments demonstrated a small concentration of nitrogen oxides in the gas phase. Thermodynamic calculations predicted that this should only occur in some oxygen atmosphere. This suggests that the formation of oxides in the plasma jet and the short reaction time prevented its decomposition.

3. Processing and destruction of bromine containing waste [5].

The study was performed with solid free-flowing wastes containing bromide phenols in different proportions. Elemental analysis of the wastes was made by different methods before the experiments. The average result obtained by these different methods are : C=30.03%; H_2=4.31%; Br=50.32%; N_2=0.51%; S=0.08%; O_2=14.75%. A previous thermal analysis for bromide-phenol wastes were analyzed for water and mineral impurities. A 2.5% bromine and water solution were prepared for the first run of bromine wastes. as a controlled dispersal solution feed into the plasma at high concentrations. The run of experiments with this solution was carried out at variable power settings and material feeding rates. The electric power consumed ranged from 95 to 120 kW. The plasma forming gas flow rate was 4.7 g/s. The material supply rate varied from 1.0 to 15.5 g/s. The degree of decomposition approached 100% for all the experiments of the run. A chemical analysis of exhaust gases for bromine and toxic components were made after every experiment. No toxic dioxins or oxides were detected. The possibility of increasing the efficiency of the process by using a doping solution was investigated at the second run of experiments. Three experiments using a 75% solution of wastes in a polar organic solvent were conducted for process optimization. During these runs, electric power varied from 80 to 110 kW, raw material rate ranged over 5.6-12.5 g/s/ and flow rate of the working gas was fixed at 6.0 g/s. The complete decomposition was observed at maximal raw material input. The incineration was incomplete and a lot of unoxidized carbon was precipitated in the water-alkaline scrubber. Exhaust gases produced during the plasma-chemical processing of the wastes was analyzed for the content of dioxides and their analogues, carbon oxides and dioxides, as well as for the concentration of hydrogen bromide. A mass spectrometer (Hewlett-Packard GC/MS 5890/5972) analysis of dioxides was performed applying the EPA 8270 method with gas filtration through methanol and it’s subsequent examination. No dioxide was found. The content of CO was analyzed by a separate high-resolution mass spectrometer (MX-1320). The observed m/z 29 peak had an intensity of 0.8% indicating the absence of CO in the gaseous phase. The content of oxygen was found to be low in the first experimental run and negligible in the second. The measurements demonstrated a high concentration of nitrogen. The proportion of HBR in the produced gaseous mixture was measured by the gravimetric chemical-analytical method by titration of HBr in a silver nitride solution and subsequent analysis of silver bromide by mass-spectrometry. The concentration of HBr in the gaseous phase at normal conditions on the first run upstream from scrubber was 0.337 g/l and downstream was 0.143 g/l. On the second run upstream from scrubber the HBr concentration was 0.03 g/l and downstream 0.015 g/l. HBr is a useful product for waste processing that involves pure bromine production. These experiments show that the yield of HBr during the first run applying water- waste emulsion feed is about an order of magnitude higher than the second run where an organic solvent was used. This plasma-chemical process had an excess of free carbon and a deficiency of air. Bromine vaporization and reduction with excess H_2O as in the first run is apparently the most efficient waste processing method.

4. Processing and destruction of pesticides with an expired term of validity.

Investigations were performed using different parameters in the plasma reactor for processing two pesticides - isophene ($C_{14}H_{18}O_7N_2$) and a concentrate of butyl ether of 2,4- dichlorphenoacetic acid ($C_4H_9CH_2COOC_6H_3Cl_2$), Both these pesticides consist of 50-60 % base material (butyl ether and isophene) and 40-50 % of filler substances consisting of kaolin, aerosil and silica gel. We performed a detailed gas analysis at the plasma reactor outlet. We analyzed the gas using gas chromatography mass-spectrometry and absorption spectroscopy in the ultraviolet (UVR), visible and infrared (IR) wavelength ranges. Absorption spectra in UVR, visible and near IR wavelength range ($0.2 < \lambda < 3.0$ μm) were recorded with a Varian UV- Vis -NIR- spectrophotometer Cary 500 Scan. Spectra in the distant IR area (2,5 to 25 μm) were detected by a Brucker Fourier spectrometer IFS28). The spectrographic analysis established that they weakly depend qualitatively on the type of the raw material used and are represented by three characteristic absorption bands: l= 0.2 to 0.25 μm, l=0.35 to 0.6 μm, and l = 2.5 to 25 μm. Because of the high optical density of the mixture in UVR we could not reliably interpret the recorded absorption maximums. The diffuse absorption bands of benzaldehyde C_6H_5CHO, propionaldehyde C_2H_5CHO, benzene C_6H_6, formaldehyde CH_2O, acetaldehyde C_2H_4O, etc. form a continuum. The visible region of the spectrum contains the electronic- vibrational-rotational absorption bands of molecules NO, NO_2, HNO_2, O_2, CO_2, C_2, AlO, AlH, HfO, CaO, FeO, CuO, CuH, CN, SiN, CH, and CHO. We could not identify a number of other absorptions peaks in the UVR range. The absorption spectra in the IR region detected the bands CH_3-, CH_2-, and CH- of hydrocarbons as well as CO_2, H_2O, N_2, NO_2, and traces of NO band, in the HNO_3 condensed phase. In the H_2CO_3 vapor phase, symmetric stretch oscillations of the carbonyl group C=O were demonstrated as were weak bands of OH and CO oscillation deformation. The data shows the complete thermal decomposition of pesticides in plasma airflow that is accompanied by oxidation and nitridation of decomposition products. The bands observed from CH_3-, CH_2-, CH-, and C=O groups are caused by the formation of secondary hydrocarbons at the outlet of the plasma reactor in the hardening zone. The simple oxides and nitrides that are produced are not highly toxic, nor cancerogenic, nor are they ecologically dangerous. Some of them can be separated, assembled, and used further. A Brucker mm wave GCMS) analysis of emanated gases was performed to determine the types of hydrocarbons produced and their quantitative content at the plasma reactor outlet . Chromato-mass-spectrometric analysis of exhaust gases was performed to determine which hydrocarbons were produced and what their quantitative content was in the plasma reactor outlet. Brucker mm wave Chromato-mass-spectrometer range of mass numbers was 28-400, with a resolving power R of ~ 10000, and a threshold of detectability of ~ 1 ppb (~10^{-3}). Samples were taken after quenching using the programmed pump SKS and were placed in Dreger two-layer absorb tubes. Activated charcoal was used as an absorbent. Sampling took 4 minutes. The pumping (circulation rate) velocity of the samples through the sorbents was 300 l/min. Preliminary separation of mixture components was carried out at the capillary column. A Quadrupole mass-analyzer was used as a mass-detector. Produced products were identified amass-spectrometer using data from the bank of standard substances. To increase the statistical significance of the identification we used two library search methods: a comparison of the analyzed spectrum with a standard library spectrum, and a reverse method, which compared library spectra with the analyzed one. A calculation was made of every component's concentration in the absorbed substance mass and compared to standardized chromatography data. Instrument error during the evaluation of different substance contents in analyzed gases mixture was less 30-40 %. After butyl ether processing without hardening, we found saturated, unsaturated, and aromatic hydrocarbons, ordinary and complicated ethers, alcohols, ketones, acids nitrogen containing and chloro-containing compounds in the products leaving the plasma reactor. Quenching methods significantly affected the composition of reactor off-gases. Chloro-containing and nitrogen containing compounds, as well as some substances which contain ether groups and aldehyde groups were not detected at the reactor outlet. Benzol derivatives appear instead. Absence of compounds with ether groups and aldehydes as well as increasing content of compounds of methylcellosolve and benzoic acid can be caused by processes of secondary quenching oxidation. Nitrogen containing substances can be changed in the presence of hydrogen into nitric acid or nitrozoacid, as seen in the spectroscopy analysis. Chloro - containing compounds can be changed into chlorine salt with bases of calcium, copper, and iron. Their presence was detected by spectroscopy

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