Decomposition of Chlorinated Organic Compounds in Gaseous Hazardous Waste using a Tunable Plasma Reactor

by

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Abstract

An experimental investigation was performed of the Cold Plasma Decomposition of the chlorinated methanes CC\textsubscript{4} (Tetrachloro Methane) and CH\textsubscript{3}Cl\textsubscript{3} (Trichloro Methane) and the chlorinated ethene C\textsubscript{2}HCl\textsubscript{3} (Trichloro Ethene) in gaseous hazardous waste using a Tunable Plasma Reactor.

The cold plasma in this reactor was generated by an electron beam. The electron and radical concentration of the cold plasma was controlled through the electron beam current, the average electron energy of the cold plasma was controlled through the sub-breakdown electric field voltage superimposed to the electron beam.

In addition to the “tunability” provided by the electron beam current and the electric field voltage, the mass flow rate of the gaseous hazardous waste through the cold plasma could be varied and chemical compounds that form reactive chemical species, such as radicals, upon electron irradiation could be added to the gaseous hazardous waste in order to enhance the “tunability”.

The chemical analysis of the reactor intake and exhaust was performed via Gas Chromatography with Electron Capture Detector, Thermal Conductivity Detector and Mass Selective Detector and via Stand-Alone, On-Line, Real-Time Mass Spectrometry developed in the present work on the basis of the Mass Selective Detector.

The electron beam dosimetry was performed via a combination of Facsimile Paper Radiography, Aluminum Plate Calorimetry, one-dimensional Monte-Carlo Simulation of the electron beam power deposition and N\textsubscript{2}O Chemical Dosimetry.

The cold plasma decomposition of CC\textsubscript{4} in air was found to be selective in the sense that a decreased intake concentration required a decreased electron beam dose to achieve a constant exhaust concentration.

The decomposition of CH\textsubscript{3}Cl\textsubscript{3} in dry air was found to require a higher electron beam dose than the decomposition of CC\textsubscript{4} in dry air. Also, the decomposition of CC\textsubscript{4} and CH\textsubscript{3}Cl\textsubscript{3} in dry air was found to require a ten to hundred times higher electron beam dose than the decomposition of C\textsubscript{2}HCl\textsubscript{3} in dry air.
Moreover, the decomposition of CCl₄ and CHCl₃ in wet air was found to require a higher electron beam dose than the decomposition in dry air. For a comparable intake and exhaust concentration, the electron beam dose was found to be up to five times higher in wet air than in dry air. No such effect of the relative humidity of air was observed for the decomposition of C₂HCl₃.

The superposition of an electric field to the electron beam was found to result in a lower exhaust concentration for CHCl₃ and C₂HCl₃ and a higher exhaust concentration for CCl₄ for a given electron beam dose and intake concentration in dry air. Also, the effect of the electric field on the exhaust concentration of CCl₄ and CHCl₃ was found to be larger in wet air than in dry air.

These experimental results were found to be consistent with bimolecular dissociative electron attachment as the chemical reaction primarily responsible for the decomposition. The selectivity of the decomposition of CCl₄ in dry air was modeled through a semi-quantitative heuristic equation on the basis of the G-Value for production of electrons.

In addition, a chlorine radical chain reaction with C₂HCl₃, initiated through bimolecular dissociative electron attachment to C₂HCl₃, was found to be very likely responsible for the low electron beam dose required for the decomposition of C₂HCl₃.

The decomposition of CCl₄ in dry air and wet air was found to result in the formation of CO, CO₂, HCl and Cl₂ as stable decomposition products and COCl₂ (Carbonyl Chloride) as an intermediate decomposition product. The decomposition of COCl₂ to sub ppm levels required a comparable electron beam dose as the decomposition of CCl₄ to sub ppm levels.

The decomposition of C₂HCl₃ in dry air and wet air was found to result in the formation of HCl and Cl₂ as stable decomposition products and COCl₂ and C₂HCl₃O (Dichloro Acetyl Chloride) as intermediate decomposition products. No chemical analysis was performed for the formation of CO and CO₂. The decomposition of C₂HCl₃O and COCl₂ to sub ppm levels required a ten to hundred times higher electron beam dose than the decomposition of C₂HCl₃ to sub ppm levels.

At a destruction and removal efficiency of higher than 99%, the energy expense for CCl₄ Cold Plasma Decomposition in dry air was found to be less than 150 eV per CCl₄ molecule decomposed or 25 kWh/kg of CCl₄ decomposed. These values were found to apply independently of the CCl₄ intake concentration.

Therefore, the Cold Plasma Decomposition of CCl₄ in a Tunable Plasma Reactor may be achieved at substantially lower operational cost than the customary Flame Decomposition, which, at a CCl₄ intake concentration of lower than 500 ppm, requires more than approximately 600 eV or 100 kWh/kg, respectively.

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