

MICROWAVE DESTRUCTION OF TRICHLOROETHYLENE IN A H₂O - O₂ - AR PLASMA

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INTRODUCTION

As of 1997, total U. S. emissions of volatile organic compounds (VOC) had fallen to an estimated 19×10^6 tpy (tons per year) while total NO_x emissions continued to rise to about 24×10^6 tpy¹. Among VOC categories, solvent usage increased to roughly to 6.5×10^6 tpy². Of especial concern are those compounds that are toxic air contaminants (TAC), or that may produce toxic by-products while undergoing capture and treatment. Chlorinated solvents, chlorofluorocarbons and sulfur hexafluoride fall into such a category because of their higher activation energies and low biodegradability under oxidative conditions. In terms of millions of U.S. tons of carbon equivalents, i.e., a measure of greenhouse gas potential, an increase of about 67% (16×10^9 tpy) has occurred in the emissions of HCFCs, PFCs, and SF₆ during the decade of the 1990's². Although increases in emissions have occurred, concentrations of emitted streams may actually be decreasing because of improved production methods or capture of these pollutants. Control costs generally increase as concentrations decrease, e.g., the cost of catalytic incineration of VOCs increases from about \$5,000/ton to \$50,000/ton for a compound such as benzene as its concentration drops from 100 ppm, to 10 ppm, resulting in even the least costly of combustion control measures impractical for low concentration streams. Control costs for NO_x range from roughly less than about \$1000/ton for advanced burner technologies to over \$5,000/ton for exhaust gas treatments³. Development of efficient control strategies for low concentrations of these compounds while avoiding NO_x formation is highly desirable.

Conventional methods for removing volatile organic compounds (VOC's) from gas streams include absorption, adsorption, condensation, and incineration (including thermal and catalytic). Among these technologies, adsorption is an efficient and economical method for moderate to low concentration streams. Nevertheless, adsorbates (such as VOCs) must be removed periodically after they saturate the adsorbents (e.g., activated carbon or zeolites) and require further treatment.

There are two conventional regeneration methods: steam and hot gas regeneration. The former requires a steam generation facility while leaving the adsorbent bed wet with condensate, thus requiring that time and equipment be available to dry out the bed before its reuse. Moisture in the condensate can also lead to undesirable chemical reactions between the VOCs and bed materials. Regeneration with a hot gas is accomplished by heating the adsorbent (and adsorbate) to a temperature sufficient to desorb the adsorbate. The flow of hot gas not only heats the adsorbent, but also purges the adsorbate as it is desorbed resulting in a lower final concentration factor. Effective adsorbents also create a problem in regeneration, since generally, the more effective the adsorbent the more difficult it is to remove the adsorbate. Thus, a long regeneration time and large purge gas volumes are required. Moreover, the heating requirements are large since not only the adsorbent, but also the adsorbent support, the adsorbent column, associated conduits and the purge gas itself often must be heated. If a higher temperature purge gas was used, the desorption could be more rapid, but thermal degradation could yield undesirable intermediate by-products and shorten the life of the adsorbent reducing its capacity. In the case of activated carbon the potential for a fire exists.

Microwave regeneration utilizes "dielectric heating" which eliminates many of the above drawbacks and provides benefits unobtainable with conventional regeneration. In the microwave regeneration process, heat is generated internally, i.e., within the adsorbent bed either by heating the adsorbate directly and/or the adsorbent. It does not need to be conveyed through a fluid; therefore a minimal amount of purge gas is used and large concentration factors can be obtained. Minimal heating of ancillary mass occurs, reducing over all energy requirements and cooling time. As a result, a microwave regeneration process makes it possible to desorb VOCs from adsorbents rapidly and efficiently. In addition, the microwave system can be used for the destruction of the desorbed waste stream.

Microwave technology for waste treatment

Plasma processing for environmental remediation applications is a developing technology. The primary interest in plasma processes has been in the area of combustion, due to the ability to generate extremely high temperatures, approaching 10,000 K, in the gas phase. By comparison,

most chemical thermal processes, such as incineration, operate at temperatures ranging from 2000 to 2500 K. The higher temperatures attainable in a plasma process minimize the potential for the *in situ* formation of polynuclear aromatic hydrocarbons (PAH), dioxins and furans, that are major concerns of incineration processes. The cooling of a plasma is rapid and not conducive to molecular growth processes that yield complex molecules. However, thermal systems that are operated with air suffer from a common problem - the production of oxides of nitrogen (NO_x).

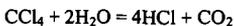
Recently there has been a growing interest in potential applications of high-frequency plasmas. For example, Wang et al.⁴ reported the use of a RF plasma system to convert dichlorodifluoromethane to methane and acetylene in a hydrogen environment. Microwave plasmas may also be applied to the remediation of off-gas streams. Microwave plasmas possess a number of advantages over plasmas generated by other types of electrical excitation which make them attractive for this application: (1) production of high ionization levels and molecular dissociation without excess heating of the contained gas; (2) construction of reaction vessels which are simple, free from contamination and less subject to damage because of the absence of internal electrodes; (3) production of little electrical interference; (4) absence of high voltages which can be easily contacted by operating personnel, i. e., absence of shock hazardous; (5) potentially lower power consumption; (6) and the ability to tolerate high concentrations of water. The latter feature is particularly important because it means that energy can be fed directly into a flow with high water concentration and a stable plasma can be established.

Although the microwave plasma process has been successfully applied in the metals⁵ and microelectronics industries⁶, the application of microwave plasma technology to hazardous waste treatment is very limited. Bailin et al.⁷ first investigated the decomposition of organic compounds by passage through a microwave-induced oxygen plasma. The basic idea in their study was to apply microwave discharge energy to break chemical bonds of organic compounds under reduced pressure conditions. Hertzler et al.⁸ oxidized halocarbons with molecular oxygen directly in a low-pressure tubular flow microwave plasma discharge reactor. Although conversion of parent compounds exceeded 99.99%, a complete product analysis was not provided, and, therefore effluent toxicity could not be determined. Moreover, in the above studies, the organic compounds were introduced in liquid form into the plasma reactor. In other words, a microwave plasma was used to treat liquid organic wastes.

Researchers in Japan have been particularly active in promoting plasma technology for waste remediation. They have included microwave plasma systems in their studies. Suzuki et al.⁹ investigated the use of a microwave heated oxygen plasma for the conversion of metal chlorides into oxides. The method was shown to be successful in the conversion of a wide range of metals, from transition metals to lanthanides, with results that were consistent with an equilibrium analysis. Shimizu et al.^{10, 11} studied the decomposition of trichlorotrifluoroethane with a microwave induced argon plasma. They used SiC fibers to assist in the generation of the plasma. The plasma was operated at one atmosphere pressure with small amounts of O₂ added to ensure complete conversion of C to CO₂. Somewhat surprisingly, they found that pulsed microwave operation achieved better destruction of the waste feed than DC operation. However, the reason for this behavior was not discovered.

Chlorine that is present in waste materials is most conveniently sequestered as HCl. When Cl is bonded to H it is effectively removed from participation in all further reactions, except at very high temperatures. Ultimately, HCl needs to be handled with devices such as wet scrubbers where it can be neutralized. Dechlorination of wastes is an important first step in reducing the toxicity of remediation by-products through the prevention of formation of compounds such as tetra-chloro-dibenzo-dioxin (TCDD).

The dechlorination of these compounds is thermodynamically favored by reaction in a reducing environment. Barat and Bozzelli¹² showed that an overall reaction of the form



exhibited large equilibrium constants

T, K	K _p
300	3.8 x 10 ⁴³
800	7.6 x 10 ²⁵

When oxygen is present in the system, O competes with Cl for bonding with H atoms. Hence, the ideal conditions for dechlorination are reducing, not oxidative. Barat and Bozzelli used a quartz flow reactor, driven by a microwave plasma, to examine the reaction of H₂ and H₂O with chlorocarbons. Reactions with H₂ yielded non-parent chlorocarbons, low molecular weight hydrocarbons, and soot. Reactions with water yielded only carbon monoxide and carbon dioxide.

The production of carbon monoxide was a necessary side effect of the stoichiometry that was used; insufficient oxygen was available to ensure complete oxidation of the available carbon. Ravindran et al.¹³ have shown from thermodynamic arguments that a similar dechlorination in hydrocarbon rich environments is also possible.

EXPERIMENTAL

A continuous microwave generator (low ripple magnetron, 1.5 KW, 2450 MHz; Gerling Laboratory) and a plasma tuner (ASTEX) were used to generate a steam plasma. A schematic diagram illustrating the gas flow paths is shown in figure 1. The main components of the system consisted of a plasma reactor (AX 7200), a plasma tuner, microwave generator and microwave wave-guide. Continuous microwave power from the magnetron was conducted through a waveguide to the plasma torch. The forward and reflected powers from the plasma torch could be maximized and minimized by adjusting the tuning stubs on the plasma tuner. The forward power was maintained at 600W and the reflected power was maintained below about 100 W. The plasma reactor consisted of a 1/4" O.D. ceramic tube through which the mixture to be reacted was passed, and an outer quartz tube housing.

Argon, oxygen and steam were used as gases from which a plasma was generated. The Ar was utilized as a basic carrier and reference gas, the O₂ provided stoichiometric oxidation requirements for the chlorinated hydrocarbon tested and steam provided a reactive atmosphere containing additional hydrogen. Steam was generated by a coiled-tubing heater and was carried by Ar gas. All plasma gas flow rates were controlled by rotameters meters and were introduced to the plasma torch as shown in Figure 1. The total flow rate of gases was held constant at 10 lpm. The proportion of steam was established by trial-and-error to obtain an intense plasma. All the lines from the flow meter to the torch were heated to prevent steam condensation.

A solvent, trichloroethylene (TCE) was selected as the target compound and introduced through the ceramic tube in the plasma reactor. Destruction and removal efficiency (DRE) for TCE was calculated from measured concentrations remaining and the known flow rates to determine the efficiency of the steam plasma. The effluent gas from the plasma reactor was passed through two traps. The first trap consisted of a coiled water concentrator and an Erlenmeyer flask, in which the most of the steam was condensed. A second back-up trap was used to condense the remaining water vapor. Gas samples were collected on an adsorbent bed of Carbotrap C. A gas sampling loop and switching valve were used to inject gas samples to the GC from a by-pass line exiting the second trap. Liquid samples were also collected from the first and the second traps. The reactor effluents were analyzed with an on-line GC equipped with a TCD detector (TCE) and by GC/MS (adsorbent tubes - TCE and other by-products), and a specific ion meter for chloride. The Carbotrap samples were soxhlet extracted for 20 hours with methylene chloride with deuterated phenanthrene and terphenyl added as internal standards. The samples were evaporated down to 0.5 mL prior to injection into a HP GC/MS system.

RESULTS AND DISCUSSION

The DRE for TCE was evaluated in the microwave system for a series of microwave powers at a condition of 30% steam with an O₂ flow rate of 0.5 lpm and an argon flow rate of 6 lpm. The concentration of TCE in the input flow to the plasma was 1700 ppm. The small amount of O₂ was added to ensure that sufficient O₂ was available in the system to complete the oxidation of TCE. The post plasma gases were analyzed on a GC. The results are shown in Table 1.

Table 1. DRE and Cl⁻ ion concentration in post plasma gases at different operating powers

Power (W)	DRE (%)	Cl ⁻ (ppm)
200	58	10800
300	99.8	38700
400	100	52000
500	100	56200
600	100	56900

It is apparent that the plasma system is quite capable of achieving significant destruction at operating powers as low as 400 W. The chloride ion concentration is a measure of the HCl that is formed and is second measure of the accuracy of the sampling system and analysis. The constant Cl⁻ concentration at powers above 400 W confirms the conclusion that all the input chlorine was sequestered as HCl under these conditions.

Experiments were also conducted with a power of 600 W and a TCE input concentration of 1700 ppm but with varying concentrations of steam in the plasma. The results of those tests are shown in Table 2.

The presence of steam is seen to have an important impact on the effectiveness of the microwave destruction process. The effect of steam that is shown in Table 2 is consistent with the observation of Barat and Bozzelli that at the temperatures of the microwave plasma, thermodynamics favors the dechlorination of chlorinated hydrocarbons.

Finally, the Carbotrap samples were analyzed on a GC/MS system for products of incomplete combustion. The microwave power was 600 W with 30% steam and 1700 ppm of TCE. This analysis did not find any evidence of dioxins or furans, showing that a high DRE can be achieved without the production of other products of incomplete reaction.

Table 2. DRE at 600 W of input microwave power with varying steam concentrations

Steam fraction of flow (%)	DRE
0	99.78
5	99.9
10	100
20	100
30	100

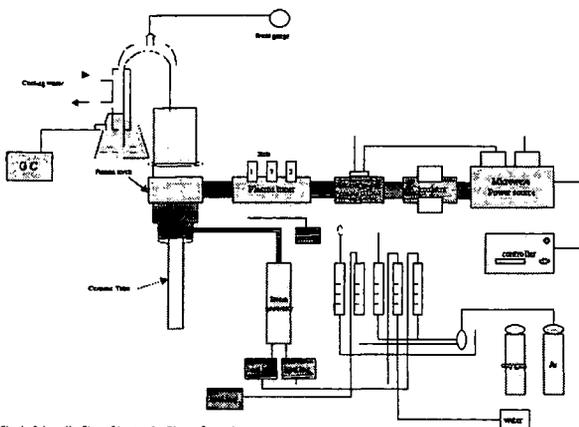


Fig. 1 Schematic Flow Diagram for Plasma Generator

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