

TUNABLE HYBRID PLASMA DECOMPOSITION
OF DILUTE CONCENTRATIONS OF CC14 IN AIR

M. J. Truex
L. Bromberg
D. R. Cohn
M. Koch
R. M. Patrick
P. Thomas

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Pacific Northwest Laboratory
Richland, WA 99352

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TUNABLE HYBRID PLASMA DECOMPOSITION
OF DILUTE CONCENTRATIONS OF CCl_4 IN AIR

L. Bromberg
D. R. Cohn
M. Koch*
R. M. Patrick
P. Thomas

Plasma Technology and Systems Division
Plasma Fusion Center
Massachusetts Institute of Technology
167 Albany Street
Cambridge, Massachusetts 02139
(617) 253-5524

Introduction

At the Department of Energy Hanford site, a large quantity of the industrial solvent carbon tetrachloride (CCl_4) was used and subsequently disposed of in leaching fields. Efforts under the Volatile Organic Compound - Arid Integrated Demonstration Program (VOC-Arid ID) are directed at vapor extraction of carbon tetrachloride from the ground and its subsequent decomposition in the contaminated humid air stream [1].

We are developing a mobile electron-beam driven plasma reactor for versatile efficient on-site decomposition of CCl_4 and other VOCs in carrier gases at atmospheric pressure. The decomposition of the VOCs could result in the generation of CO_2 , light hydrocarbons, and reactive chlorine compounds. The latter dissolve and/or dissociate in aqueous solutions.

Technology Objectives

The reactor uses an electron-beam generated plasma whose electron density and thus chemical reaction rates can be controlled by the electron-beam current and whose electron temperature and thus chemical reaction rate constants can be controlled by a superimposed sub-breakdown electric field. The combination of an electron beam and a sub-breakdown electric field gave rise to the name Tunable Hybrid Plasma (THP) reactor. Such a reactor could be suitable for the decomposition of a wide range of concentrations of a variety of hazardous chemical compounds in carrier gases [2,3].

The reactor will use electron-beam energies below 300 keV. For these energies there exists well-established commercial technology with high reliability and low maintenance time requirements. Moreover, shielding requirements are modest, and the electron-beam technology can be self-shielded. Over a hundred electron-beam units of this type are in commercial use. 100 kW level units have a cost in the range of \$5/Watt.

The goal for the power requirement for a practical THP device is on the order of 10 kWhr/lb of CCl_4 destroyed. The attainment of this processing efficiency in a system with high availability should make it possible to meet the overall goal of a relatively low cost system for environmentally attractive on-site destruction of CCl_4 .

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Initial Results with Laboratory Device

In this paper we describe results of initial experiments on decomposition of CCl_4 in a laboratory-scale THP reactor operated at atmospheric pressure with zero imposed electric field. The mechanism for the plasma-induced decomposition of CCl_4 that we have been considering is dissociative electron attachment. The electrons produced by the electron beam selectively interact with the CCl_4 . Low electron energies obtained without the presence of an imposed electric field should be sufficient for this particular process, because as shown in Figure 1, the dissociative attachment reaction rate constant is very large at these temperatures [4]. The use of an imposed electric field could be advantageous for co-contaminants and other VOCs and may also be of value in control of byproduct effects.

A schematic diagram of the laboratory-scale THP reactor is shown in Figure 2. An electron beam of 100 keV energy is introduced into a reaction chamber through a 25 mm thick aluminum foil. The foil is mechanically supported by a water-cooled copper support grid. The electron beam current can be adjusted from 0 to 4 mA. The electron-beam cross section upon entering the reaction chamber is a square 2.5 x 2.5 cm². The depth of the reaction chamber in the electron beam direction is 1.6 cm.

The CCl_4 intake mole concentration and the relative air humidity were controlled by means of volume flow meters and bubblers of 250 cm³ and 100 cm³ capacity for H₂O and CCl_4 , respectively. The CCl_4 exhaust mole concentration was determined by a 1992 Hewlett-Packard Model 5890 Series II gas chromatograph. The chromatographic separation of CCl_4 was achieved by a Series 530 mm capillary column obtained from Hewlett-Packard.

CCl_4 intake mole concentrations ranged from nominally 20 ppm to 700 ppm, with relative air humidities at either 0% or 20%.

Figure 3 shows the CCl_4 exhaust mole concentration for different intake concentrations as a function of the electron-beam specific power deposition in the air stream. The results in this figure were obtained with dry air at atmospheric pressure. Flow rates between .08 ft³/min and .35 ft³/min were used. The specific power deposition is given in kW per kg/sec of gas flow; 1 kW/kg/sec corresponds approximately to a 1 K adiabatic temperature rise in air. A high degree of CCl_4 destruction can be obtained with adiabatic temperature rises (15-150 K) that are substantially below those needed for standard thermal destruction. Moreover, the CCl_4 exhaust mole concentrations can be reduced to very low values (<1 ppm).

The selectivity of the process is indicated by the dependence of the power deposition density requirements upon the CCl_4 intake mole concentration. This is particularly illustrated in Figure 4 where the data from Figure 3 is plotted in terms of fractional removal. For 90%

fractional removal, the specific power deposition was about 15 kW/kg/sec for 26 ppm intake concentration, 60 kW/kg/sec for 166 ppm intake, and 160 kW/kg/sec for 663 ppm. Thus the specific power deposition could be reduced by a factor of about 3 as the intake concentration was reduced by a factor of about 4 (from 663 ppm to 166 ppm). The specific power deposition was reduced by a factor of about 10 as the intake concentration was reduced by a factor of about 25 (from 663 ppm to 26 ppm). For a non-selective thermal process (where all the molecules in the gas stream must be heated), there would have been no decrease in the power deposition density as the intake concentration was reduced.

Approximately twice as much electron beam specific power density was generally required for the same fractional removal with humid air. Conclusions and Future Directions. The initial data show a high degree of destruction over a wide range of CCl₄ concentrations at low gas temperatures. The experimental results in dry air correspond to a relatively modest energy requirement of 10-20 kWhr per pound of CCl₄ decomposed. Moreover, the low temperature process may provide more control over byproducts than would be the case in a high temperature thermal treatment process. Although energy requirements are increased in the presence of humid air, the temperature rise could still be moderate. Moreover, it may be possible to use a dryer to selectively remove the water vapor.

Future work will include investigations of possible ways to further improve efficiency and studies of decomposition products. A field test using a commercial electron-beam source is planned for 1994. In addition, application to a variety of VOCs will be studied in the laboratory.

In summary, these results indicate promising prospects for practical development of a THP reactor for on-site decomposition of CCl₄ and other VOCs. Since electron beam energies can be below 300 keV, the THP reactor can use well-established commercial electron-beam technology with modest shielding requirements and high reliability. Potential applications of the THP include both environmental restoration and containment of underground waste plumes. In addition, the THP may also find use in treatment of industrial waste streams.

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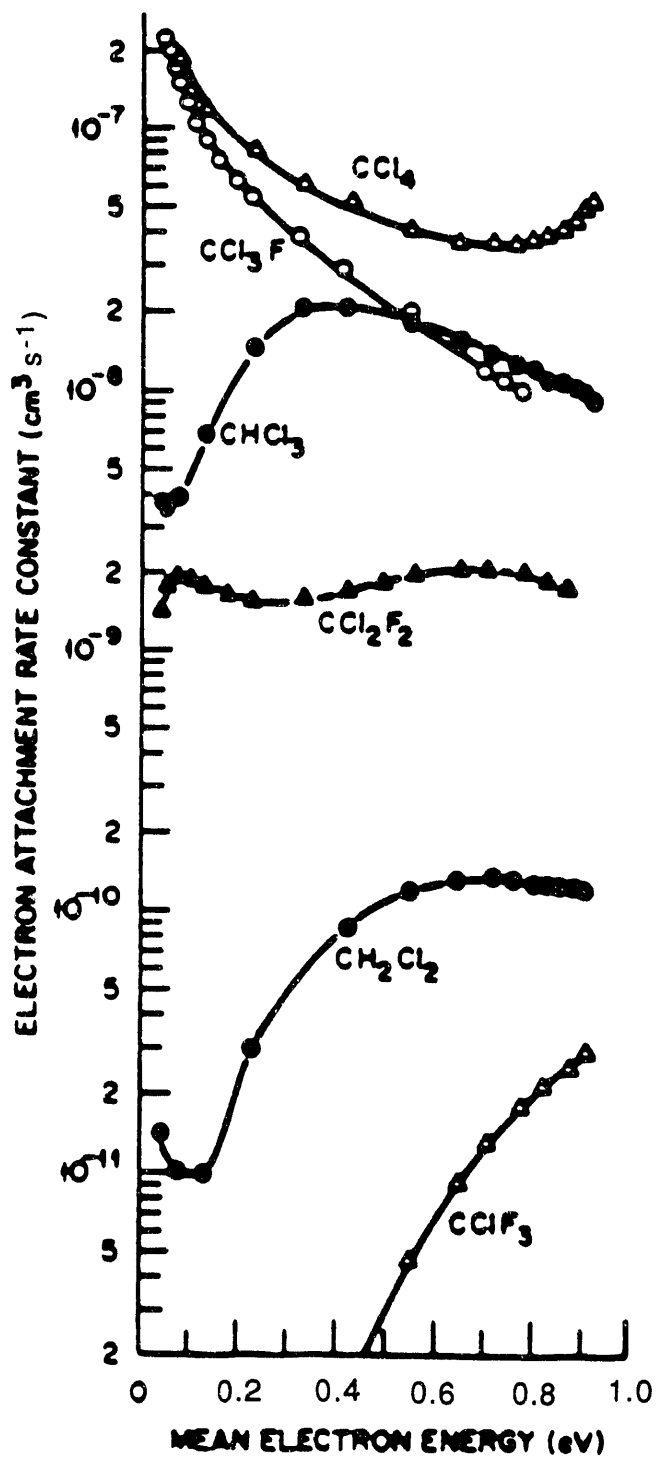


Figure 1 Electron Attachment Rate Constant Versus Mean Electron Energy for CCl₄, CHCl₃, CH₂Cl₂, CCl₃F, CCl₂F₂, CClF₃ [from Reference 4]

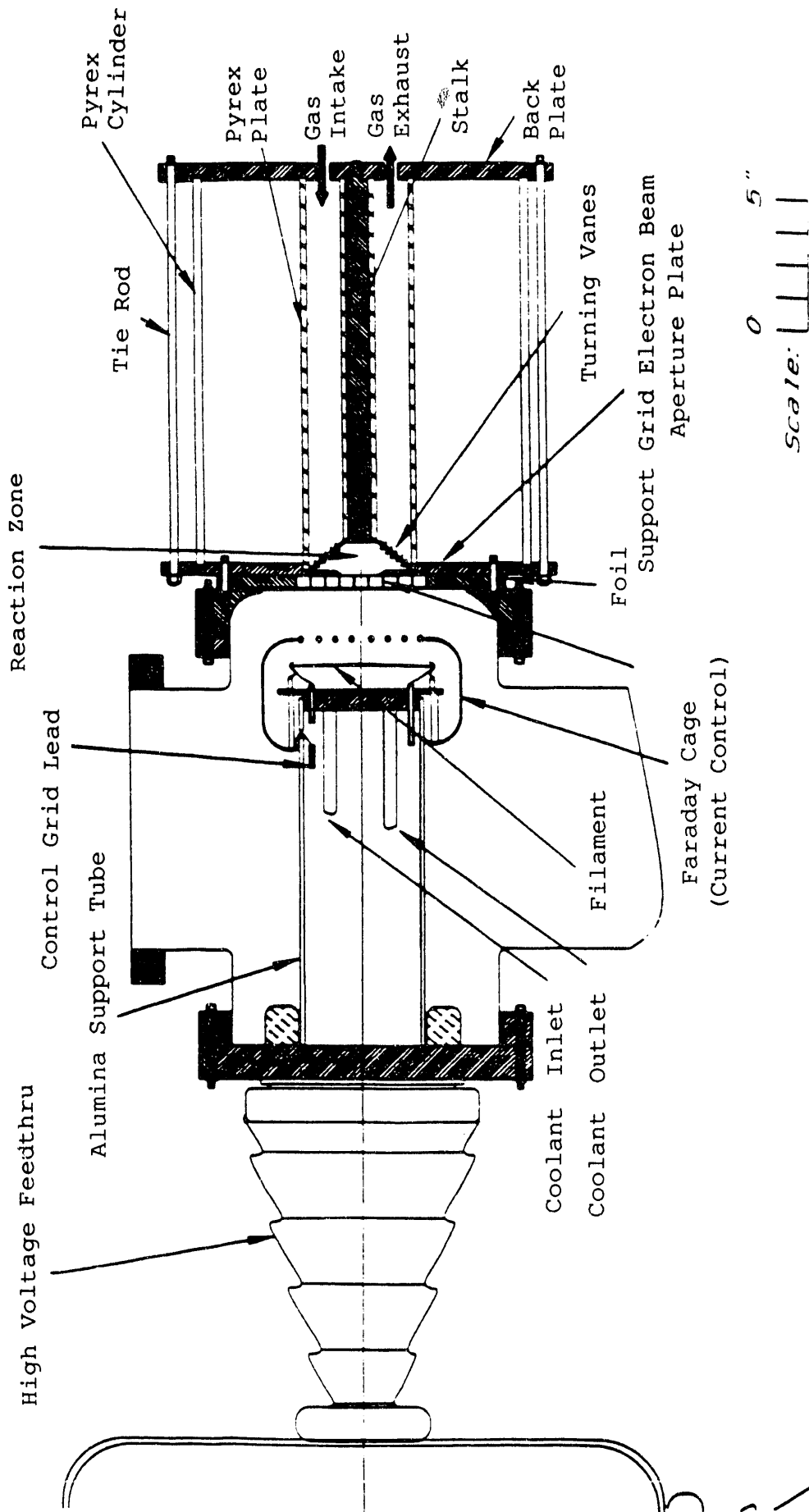


Figure 2 Laboratory-Scale Tunable Hybrid Plasma Reactor

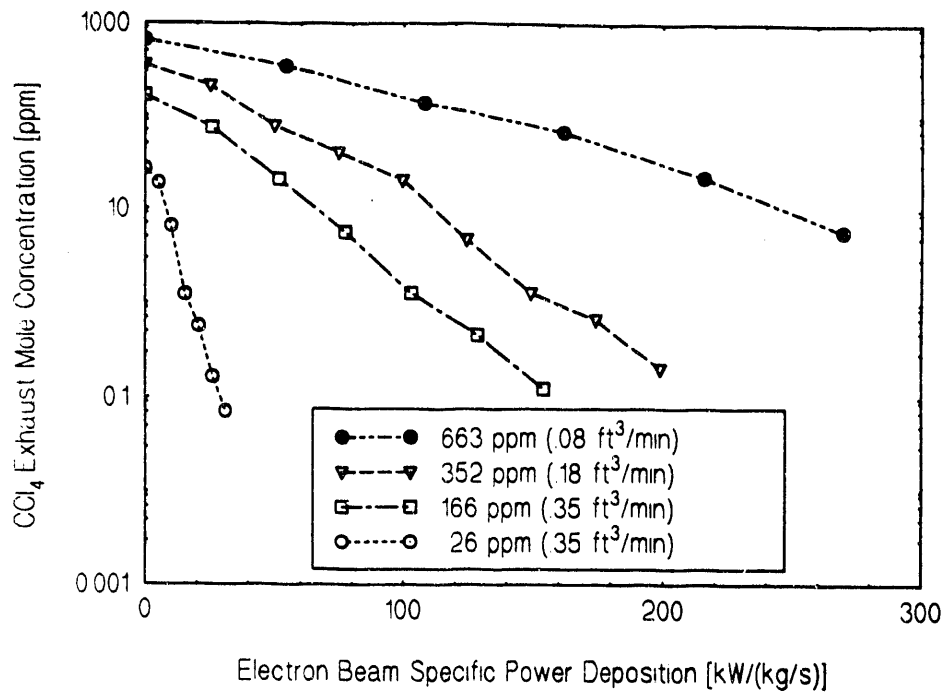


Figure 3 Dependence of CCl_4 Exhaust Mole Concentration on Electron-Beam Specific Power Deposition

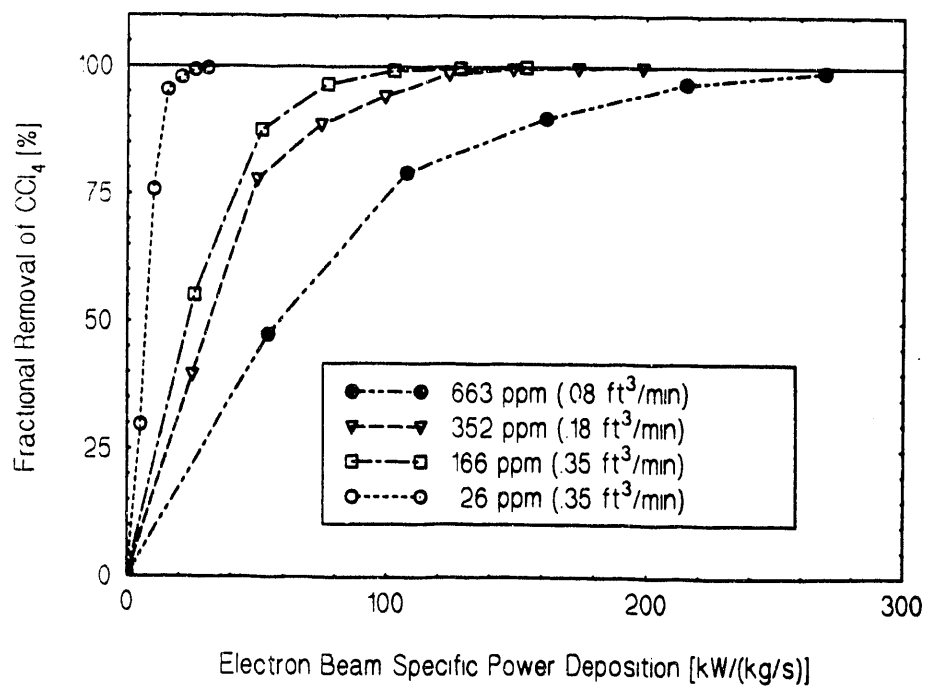


Figure 4 Dependence of Fractional Removal of CCl_4 on Electron-Beam Specific Power Deposition

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