Decomposition of Trichloroethylene by a Large Scale, High Flow Packed-Bed Gas Phase Corona Reactor

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Abstract

The use of a large scale packed bed corona reactor to decompose trichloroethylene in a gas stream at atmospheric pressure has been studied. We report efficient destruction in both air and nitrogen buffer gases. The results demonstrate the efficient TCE destruction, even in the absence of oxygen. We speculate that atomic nitrogen is the reactive species in this case. The production of noxious byproducts was minimal. The commercialization of this technology is underway.

Introduction

Gas phase corona reactors (GPCR) have been shown to convert hazardous materials like trichloroethylene[1], benzene, phosgene[2], cyanogen chloride, and other compounds[3] into more environmentally benign chemicals at near-atmospheric pressure and approximately 100^0 C. A typical corona reactor flows contaminate laden air through a void space that contains an ionized gas between two electrodes, at least one of which is closely shielded by a dielectric barrier. In a packed bed reactor, the inclusion of a suitable dielectric material in the void space generates a more active plasma due to the augmentation of the electric fields in the gaps. Small concentrations of gaseous waste are destroyed either by direct reaction with free electrons or, more likely, by reaction with the resultant radical and ionic species produced in the plasma. The most attractive feature of GPCR is that most of the input energy goes into heating the electrons rather than heating the entire gas stream, as is required in conventional incinerators or catalytic treatments. The inclusion of a dielectric packing material in the reactor results in easier operation due to the lower voltages required to initiate and maintain the corona. If it can be shown that surface mediated chemistry or photochemistry is important in the destruction process, the chemical properties of the packing material could have a significant impact as well.

The purpose of this study was to demonstrate the operation of a large flow rate packed bed GPCR designed for environmental applications, and to evaluate the effects of the background gas composition of the contaminant trichlorethylene (TCE). A small, laboratory scale packed bed GPCR was used in the background gas studies and preliminary studies designed to assess packing material effects on the overall destruction efficiency.

Experimental

The principal components of the packed bed GPCR and its power system are shown in Figure 1. The power supply consists essentially of a high voltage 60 hz transformer. The reactor is a quartz tube with an inner electrode formed by running a metal pipe or rod down the center of the reactor body and an outer electrode formed by wrapping aluminum foil or copper mesh on the quartz tube exterior. The resulting concentric tube arrangement provides the annulus for the generation of the plasma. The length of the outer electrode determines the length of the plasma zone. The effective volume for our reactors was approximately 0.1 liter and 24 liters for the small and large systems, respectively.

The large scale and small test reactors used similar power supply and measuring methods. As indicated in Figure 1, the deposited power was measured in several ways. For the large reactor power measurements were made both at the primary and secondary of the high voltage transformer. The small reactor measurements were all measured on the secondary. The current on the low voltage side of the reactor was measured using either a Resistor-Capacitor (RC) circuit according to the method of Rosenthal[4], or a current probe. In each case consistent agreement was obtained between the different measurements.

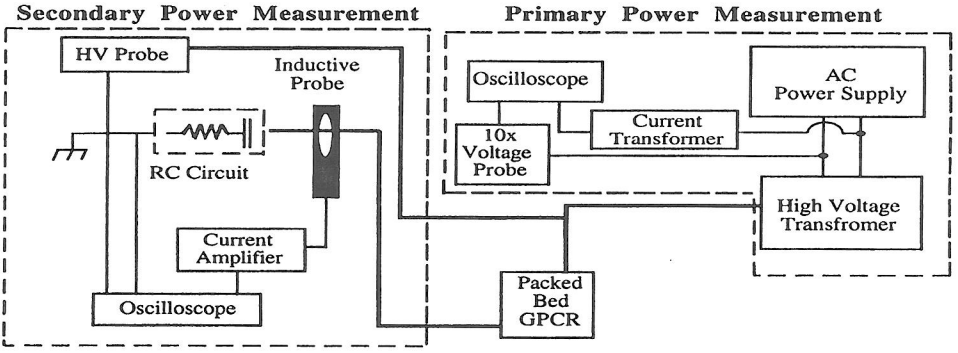

Figure 1 - Large Scale Reactor Schematic

The gas sent into the large scale GPCR was filtered, conditioned, and controlled with respect to temperature, humidity, and flow rate. Water vapor was added by a steam injection system, and contaminates were introduced using a syringe injection pump. The flow rate was measured by mass flow meters, and the temperature, humidity, and system pressure were recorded on a data logger. The bulk gas temperature inside the GPCR was measured using a Luxtron Fluoroptic Thermometer with a fiber optic probe.

The small scale test reactor used dry filtered compressed air or nitrogen as the feed gases. Humidity and TCE concentration were both controlled by passing a varying fraction of the carrier gas through an appropriately filled bubbler. The TCE concentration was observed to vary linearly with the flow through the bubbler, as expected. The reactor feed and exhaust gases were characterized using a differentially pumped mass spectrometer in a direct sampling mode. The absolute concentration was determined by

comparing the signal to that from calibrated gas mixtures.

The large scale GPCR feed gas and exhaust gas were characterized by several analytical instruments. analyzer was used for these experiments. Since NO_x was not observed, a commercial nitrogen oxide analyzer was reconfigured for ozone measurements. This was accomplished by bypassing the ozone generator and adding a calibrated flow of nitric oxide. The resulting chemiluminescent reaction served to measure the ozone content of the sample gas. A modified GC/MS was also used to monitor the sample gas. A valve placed at the end of the chromatographic column directed the gas sample to either a thermal conductivity detector or a mass spectrometer. Byproducts such as nitrogen dioxide, carbon monoxide, and others were separated on a Carbosieve column and quantified by the GC/MS. In addition, nitrogen and oxygen could be separated on the column and quantified. Finally, a Fourier transform infrared spectrometer was used to analyze the sample gas for nitrous oxide, ozone and other compounds.

Results and Discussion

Table 2 contains the results from the small reactor tabulated as exponential decay constants with respect to input power. The numbers are the exponents obtained by fitting the TCE concentration to a single exponential decay. A larger number represents a steeper slope, indicative of higher destruction efficiency. Figure 2 displays representative data which illustrates that the destruction of TCE follows primarily first order kinetics with respect to the input power. The power is reported in terms of Joules per liter of gas flow, which in principle corrects for difference in flow rates or residence times for the different packing materials and reactor volumes. This expectation was confirmed by observing the equivalence of changing the rate of power delivered by either changing the input voltage or the total flow rate.

Table 1 - Destruction efficiencies and off gas analysis

Packing Material	Buffer Gas	300 ppm TCE	550 ppm TCE	1100 ppm TCE
Soda Lime Beads	Dry Air	0.011	0.011	0.013
	Moist Air	0.0082	0.0073	0.0094
	Dry N_2	0.024	0.013	0.0077
	Moist N_2		0.005	
Chromium-Oxide Chips	Dry Air	0.008	0.0096	0.0093
	Dry N_2	0.024	0.017	0.01

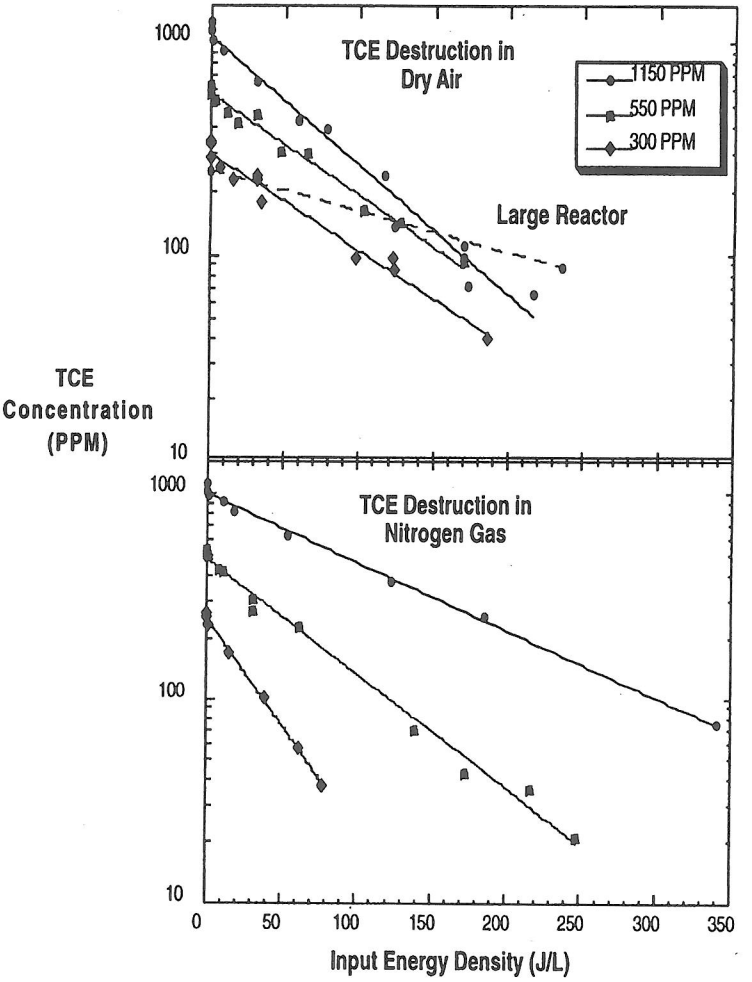

Figure 2- TCE Destruction in dry air and dry nitrogen

As can be seen from the data, both reactors were able to destroy TCE at varying

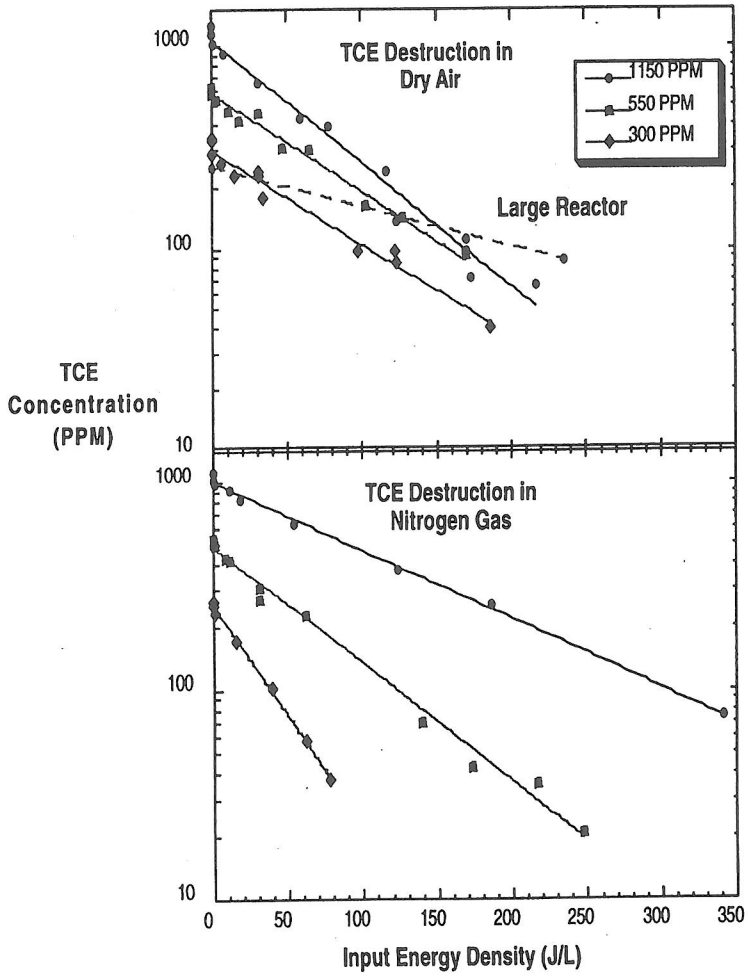

Figure 2- TCE Destruction in dry air and dry nitrogen

As can be seen from the data, both reactors were able to destroy TCE at varying

efficiencies. When the carrier gas is air, we observed both Cl_2 and phosgene in the offgas, although in smaller than expected amounts. Presumably this is due to wall reactions depleting chlorinated species. Under a nitrogen atmosphere, the only observed products were small amounts of atomic Cl, HCl and HCN. We were unable to detect higher mass chlorine containing products, again presumably due to wall reactions. More extensive efforts to study the reaction products will be made in the future.

Surprisingly, the destruction efficiency under an N_2 atmosphere is comparable to that found in air. This result indicates that oxygen radical and/or ionic species are not necessary for the operation of corona reactors, although they may still be major contributors when present. Although as noted, the reaction rate in N_2 is similar to that in air, there is one important difference. In each individual experiment the data show a logarithmic dependence on the power input, but the actual rate observed at a given concentration is inversely dependent on the *initial* concentration. This is consistent with the hypothesis that much of the destruction occurs via reactions with N radicals[5] most likely formed through dissociation of excited nitrogen molecules in the plasma. The nitrogen radical is very reactive, and in an N_2 atmosphere can only recombine, react with a surface, or react with TCE. Even at low contaminant concentrations, the TCE is in excess of the N radical, so destruction competes quite effectively with recombination reactions. However, the presence of large amounts of TCE suppresses the destruction process by quenching excited N_2, effectively reducing the ultimate concentration of N radicals in the plasma. Since any chlorine containing reaction products can be expected to be similarly effective at quenching N_2 excitations, the reaction rate is lower at a given concentration for higher initial concentrations. This hypothesis is further supported by our first experiment with moist gas, where the destruction rate declined precipitously at only 13% relative humidity. Further experiments are necessary to determine the destruction chemistry in nitrogen.

Cr_2O_3 was chosen as our first alternative packing material because of its good chemical and radiolytic stability. However, large differences were not seen in the performance of glass beads vs Cr_2O_3 chips, although preliminary experiments suggest that the Cr_2O_3 may work better under humid conditions. We note that the corona reactor turns on more easily and appears to operate more smoothly with Cr_2O_3 chips than with glass beads, probably due to higher fields present in the void space. We are continuing these studies with various packing materials to look for enhanced destruction due to specific chemical or photochemical reactions.

The amount of ozone produced in the large scale GPCR increases with the amount of power applied to the plasma reactor. The maximum concentration of ozone measured during the experiments was 165 ppm. The ozone concentration decreased with increasing humidity, but typically was many times greater than 0.1 ppm, the threshold limit value (TLV) for ozone. The GPCR effluent would therefore have to be treated to remove ozone. In practice, this can be accomplished by means of a room-temperature monolithic alumina catalyst, water scrubbing or other technology. However, other noxious gases of concern were either not detected or else not present in significant concentrations. For example, neither NO_2 nor NO were detected in the large scale packed bed GPCR off-gas. Since NO_x is considered a priority pollutant by the EPA, its absence is noteworthy. Low levels of NO_x were found in the off-gas of the small scale reactor. This is attributed to a higher power density attained in the small scale reactor. Additionally, carbon monoxide was not detected in the effluent of the large scale packed bed GPCR above its typical atmospheric levels. Other priority pollutants were below

their TLV values. For example, the nitrous oxide concentration never exceeded 20 ppm, which is below the 50 ppm N_2O TLV. Overall, a large scale packed bed GPCR should be able to decontaminate a gas stream without the need for significant off-gas pollution abatement.

The humidity of the carrier gas apparently plays an important role in the destruction efficiency of the reactor. A higher destruction efficiency can be achieved at low humidity in the feed gas. We speculate that a small amount of water vapor may be helpful in dispersing the applied power more evenly over the corona volume. For example the occurrence of large scale "lightning bolt" sparks is noticeably suppressed by even a small fraction of water in the gas. However, this benefit could have an upper limit due to competition between water and the contaminant for whatever reactive species (electrons, ions or radicals) are predominantly responsible for the beneficial destruction chemistry. Work on the smaller reactor suggests that in the case of glass beads, the addition of water vapor to a previously dry reactor instantly reduces the power dissipated in the reactor, resulting in a considerably lower destruction rate. Eventually much of the effect goes away once the reactor stabilizes at a new, hotter temperature. However, we do not as yet have enough data on this phenomenon to determine the efficiency of our GPCR at high humidity.

Future Work

The destruction of toxic compounds is not the only direction the GPCR program is taking; synthesis of commercially valuable compounds using plasma techniques is underway. Low temperature processing by GPCR is an interesting reaction media. The GPCR is being commercialized at two sites during FY96. Both government and industrial applications are being pursued.

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