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Chemical Detoxification of Trichloroethylene and 1,1,1-Trichloroethane in a Microwave Discharge Plasma Reactor at Atmospheric Pressure

by

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INTRODUCTION

Chlorinated hydrocarbons, in particular 1,1,1-trichloroethane (TCA) and trichloroethylene (TCE), are found in more than 10% of all hazardous waste streams at Department of Energy-Defense Production (DOE-DP) facilities (Fore, 1986). These waste streams include mixed waste, contaminated soils and groundwater, off-gases, and bulk liquids. This widespread problem is the result of the extensive use of chlorinated hydrocarbons as cleaning and degreasing solvents. Due to the human and environmental hazards associated with chlorinated hydrocarbons, the safe and efficient remediation of these waste streams has become an important aspect of DOE's environmental restoration program.

Thermal combustion, i.e., incineration, is the primary technology recommended by the Environmental Protection Agency (EPA) for the destruction of chlorinated hydrocarbons. Incinerator systems (e.g., rotary kilns, liquid injection combustors, fixed hearths, and fluidized bed combustors) can meet current EPA regulations (Keitz et al., 1984). However, due to the flame-inhibiting properties of halogenated hydrocarbons, these incinerator systems require the addition of auxiliary fuels, higher operating temperatures, and longer residence times than

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comparable systems designed for hydrocarbon waste streams (Oppelt, 1987). In addition, it is difficult to avoid products of incomplete combustion (PIC's) due to a wide variation in the actual residence time and nonuniform temperature profiles and flow distributions in these systems (Hung and Pfefferle, 1989). The net result is incinerator systems designed for chlorinated hydrocarbon waste streams have a higher capital equipment and operating costs than comparable systems designed for hydrocarbon waste streams (Santoleri, 1988).

The nature of the waste stream (e.g., low level contamination in soils or groundwater, bulk liquid storage) is an important criteria for selecting the most efficient and economical remediation technology. While incineration is a viable treatment technology for highly concentrated hazardous chemicals, it is less so for dilute concentrations found in waste streams such as groundwater, soil, and off-gases. Often the hazardous chemical must be separated from the primary waste stream and concentrated prior to incineration which increases both the overall capital and operating costs.

Consequently, there is a considerable research effort seeking alternative technologies for destroying chlorinated hydrocarbon wastes. Examples of alternative technologies include thermal processes, such as catalytically stabilized thermal combustion (Hung and Pfefferle, 1989) and supercritical water oxidation (Rofer and Streit, 1989), chemical and physical processes, such as photocatalyzed oxidation (Lawrence Livermore National Laboratory, 1990; Pacheco et al., 1989) and plasma technology, and bioremediation (Chem. Eng. News, 1989).

Although plasma processing has been successfully applied in the metals (Zanetti, 1983) and microelectronics industries (Fraser, 1990), the application of plasma technology to hazardous waste treatment has only recently begun (Lee, 1989). The application of plasma technology to hazardous waste treatment has focussed on two methods of plasma generation, arc discharge and high frequency discharge.

In an arc discharge, the thermonic emission of electrons from metallic electrodes is used to sustain the plasma (Bell, 1974). Much of the initial development work has focussed on arc discharge technology (Zanetti, 1983; Herlitz, 1986; Lee, 1989; Copsey, 1991). Some examples of commercial applications of arc discharge technology for hazardous waste treatment are a portable system developed by Pyrolysis Systems of Wellington, Ontario, for treating chemical waste removed from Love Canal, New York (Zanetti, 1983; Lee, 1989) and a pilot plant for treating unsorted municipal waste by SKF Steel Engineering in Hofors, Sweden (Herlitz, 1986).

In a high frequency discharge, microwave or radiofrequency radiation is used to break down and sustain the plasma discharge. Typically, a frequency greater than 1 MHz is required to sustain the plasma (Shohet, 1987). A high frequency discharge differs from an arc discharge in that there are no electrodes, which are a source of possible contamination, present inside the reactor. Microwave or radiofrequency plasma discharge degradation of halogenated hydrocarbons has been investigated by a limited number of research groups (Hertzler, 1979; Bozzelli and Barat, 1988; Barat and Bozelli, 1989; Wakabayashi et al., 1989).

Hertzler (1979) investigated the oxidation of halogenated hydrocarbons with molecular oxygen in a low-pressure tubular flow microwave-induced discharge plasma reactor. Although conversion of parent hydrocarbon exceeded 99.99%, a complete product analysis was not provided, and, therefore, effluent toxicity could not be determined.

Barat and Bozzelli (Bozelli and Barat, 1988; Barat and Bozelli, 1989) have investigated the microwave-induced plasma degradation of chloroform, trichloroethylene, and chlorobenzene with water vapor or hydrogen at low pressures (~5-10 torr) in a tubular flow reactor. Conversion of the parent chlorinated hydrocarbons ranged from 50 to almost 100%. At conversions of >80%, at least 85% of the chlorine was converted to HCl, with the remaining chlorine in the form of nonparent chlorinated hydrocarbons.

Wakabayshi et al., (1989) have investigated the radiofrequency-induced, 4 MHz, plasma degradation of trichloroethylene, trichlorofluoromethane, trichlorotrifluoroethylene, carbon tetrachloride, and chloroform with water vapor at atmospheric pressures in a tubular flow reactor. Conversions of the parent halogenated hydrocarbon ranged from 89 to 100% with the primary products being the halogenated acid and nonparent halogenated hydrocarbons.

At Argonne National Laboratory, we are investigating the viability of a microwave discharge plasma reactor operating at atmospheric pressure as a remediation technology for chemically detoxifying dilute concentrations of volatile organic compounds, such as chlorinated hydrocarbons, in particular TCA and TCE, and potentially nonchlorinated hydrocarbons found in off-gas waste streams and in air stripping operations. By chemical detoxification, we mean the chemical conversion of chlorinated hydrocarbons to less toxic compounds such as carbon dioxide, water, and hydrogen chloride.

EXPERIMENTAL

The microwave discharge plasma reactor is shown schematically in Figure 1.

Microwave radiation, at a frequency of 2450 MHz and a variable forward power range of 0-7 kW, is generated by a Cober Electronics, Inc. S6F Industrial Microwave Generator. The microwave radiation is directed to the reactor by a waveguide, operating in the TE_{10} mode, manufactured by Associated Science Research Foundation, Inc. A tuneable "short" is used to couple the microwave radiation with the plasma. Reflected power is measured with a Hewlett Packard Model 435B Power Meter.

The reactor, a 1-in. OD quartz tube, intersects the waveguide at a 90° angle to the direction of microwave radiation propagation. A second quartz tube, approximately 18-mm in OD and 5-in. in length, is inserted in the quartz reactor tube. The position of this quartz liner is adjusted so that the plasma is confined within it. The plasma is approximately 2 inches in length under normal operating conditions. The purpose of this inner quartz liner is to protect the surface of the quartz reactor tube from electron bombardment. Electron bombardment of the quartz surface results in a phase transformation from quartz to christobalite, as determined by x-ray diffraction. The reactor is cooled during operation by force convection of air at ambient temperature which limits the upper forward power range to approximately 1-kW for continuous operation (~8 hrs). Forward power inputs as high as 3-kW have been applied for shorter operating periods (generally 1 hr or less).

The plasma is initiated by evacuating the system to approximately 50 torr at a forward input power of 600 watts and contacting the reactor wall with a vacuum leak detector (Electro-Technic Products). The reactor is slowly brought to operating pressure, 1.0 to 1.1 atm, with either argon (Matheson or AGA UHP Grade - 99.999%) or an oxygen-argon mixture (20% Oxygen Matheson or AGA Certified Standard). These carrier gases are used without further purification. The inlet gas stream composition and flowrate is controlled using Matheson Model 601, 602, 603, and 610 series flow controllers equipped with metering valves. The forward input power is then adjusted to the desired level (Table No. 1).

The liquid reactants, either 1,1,1 trichloroethane or trichloroethylene (Aldrich, Research Grade, or Mallinckrodt Chemicals, Analytical Grade) and water (Aldrich, HPLC Grade, or Mallinckrodt Chemicals, ChromAR HPLC grade) are used without further purification. The desired reactants are introduced to the reactor as a vapor by bubbling the carrier gas through a liquid reservoir contained in a gas washing bottle.

Chemical analysis of the reactor feed and effluent streams is accomplished primarily by gas chromatography by periodically removing a small volume of the stream (0.5-5.0 ml) with a gas-tight syringe manufactured by Unimetrics Corporation. Chlorinated hydrocarbons are analyzed using a 6' x 1/8" 10% SP-2100 supported on Chromosrob WAW (Supleco) with an helium carrier, operated isothermally at either 40°C or 70°C, in a Varian Model 3700 Gas

Chromatograph equipped with a thermal conductivity detector. A Varian Model CDS111 Integrator is used to quantify the GC peaks. Carbon dioxide, carbon monoxide, and methane are analyzed using a 10' x 1/4" CTR-II column (Alltech) with a helium carrier and hydrogen is analyzed using a 6' x 1/8" 5A Molecular Sieve column with an argon carrier, both columns operated isothermally at 40°C, in a Hewlett-Packard Model 5890 Series II Gas Chromatograph equipped with two thermal conductivity detectors. A Hewlett Packard Model HP3396A Integrator is used to quantify the GC peaks. Nonchlorinated hydrocarbons are analyzed using a 6' x 1/8" Poropak Q column, operated from 100°C to 200°C at a rate of 10°C/min, in a Varian Model 3700 Gas Chromatograph equipped with a flame ionization detector and a Hewlett Packard Model HP3396A Integrator. Identification of all GC peaks is accomplished by comparison of the retention time of a pure sample with that of an unknown peak in the chromatograph.

Due to experimental difficulties, only an estimation of the chlorine and hydrogen chloride yields can be made. This estimation is accomplished by the following procedure. The amount of hydrogen chloride removed from the effluent stream by a sodium hydroxide solution during a given time interval is determined by measuring both the changes in pH, by acid-base titration, and the Cl^- concentration by AgCl precipitation. By comparing the amount of the HCl removed from the effluent stream to the amount of TCA or TCE introduced to the reactor during a given time period, a qualitative estimation of the HCl yield can be obtained. At high flowrates or TCA/TCE feed concentrations; however, the caustic scrubbers are not completely effective at removing HCl from the effluent stream. The Cl_2 yield is estimated from an overall mass balance. A number of samples of the effluent stream were analyzed by mass spectroscopy in an attempt to determine the HCl and Cl_2 concentrations.

RESULTS AND DISCUSSION

The chemical detoxification of chlorinated hydrocarbons in an thermal incineration can be represented stoichiometrically by the following equation (Tsang, 1990):

$$C_nH_{m+p}Cl_p + (n + m/4)O_2 \dashrightarrow nCO_2 + (m/2)H_2O + pHCl \quad \text{(Eq. 1)}$$

This equation describes the predominant product formation as long as there is sufficient oxygen to convert all the carbon and hydrogen to CO_2 and H_2O, respectively, and the hydrogen to chlorine ratio is greater than or equal to 1. For chlorinated hydrocarbons such as trichloroethylene, which has a hydrogen to chlorine ratio of 1/3, Cl_2 is produced in addition to HCl (Bose and Senkan, 1983).

Since HCl is the desired product for chlorine, it is necessary to increase the hydrogen concentration for incineration systems for hydrogen-deficient chlorinated hydrocarbons. One approach for increasing the hydrogen content in an incinerator is to add a hydrocarbon, such as propane, to the feed stream.

An alternative approach to oxidative degradation is to react the chlorinated hydrocarbon with hydrogen in an reducing atmosphere. As Bozzelli and Barat (1988) have discussed, the reaction of chlorinated hydrocarbons with hydrogen to yield hydrocarbons and hydrogen chloride is thermodynamically favorable. However, such a process is not viable for many remediation waste streams.

Water, H_2O, is an alternative to hydrogen for chemically detoxifying chlorinated hydrocarbons. Water can serve as both a hydrogen source for the elimination of chlorine as HCl and an oxygen source for the elimination of carbon as CO_x. As in the case of the reaction of chlorinated hydrocarbons with hydrogen, the reaction with water is thermodynamically favorable (Bozzelli and Barat, 1988).

Water as a reactant is very attractive from an overall process viewpoint. It is abundant and cheap, and in the case of contaminated groundwaters, for example, it might eliminate the need to separate the chlorinated hydrocarbon from the groundwater. While earlier investigations have focussed on the reaction of chlorinated hydrocarbons with water in the absence of oxygen (Bozzelli and Barat, 1988; Barat and Bozzelli, 1989; Wakabayshi et al., 1989), we are investigating the reaction of chlorinated hydrocarbons in an oxygen-water atmosphere.

I. REACTION OF 1,1,1-TRICHLOROETHANE WITH OXYGEN

The reaction of 1,1,1-trichloroethane (TCA) with oxygen (O_2) in a microwave discharge plasma was investigated under various conditions, including varying the O_2/TCA molar feed ratio and the forward power input to the reactor, to investigate the effect of these operating parameters on the overall TCA conversion and the resulting product distribution. The results of these experiments are summarized in Table No. 2.

The primary reaction of TCA and O_2 in a microwave discharge plasma can be described by a global stoichiometry which is identical to that found in thermal combustion (Eq. 2):

$$C_2H_3Cl_3 + 2O_2 \text{ ---> } 2CO_2 + 3HCl \qquad \text{(Eq. 2)}$$

This equation is applicable in the presence of excess oxygen, O_2/TCA ratio greater than 2, and a forward power input of 600 watts which is above the minimum required to sustain the plasma (Table No. 1). When these operating conditions are met, in excess of 98.3% of the initial TCA loading is observed to react yielding CO_2 and HCl as the major products. No H_2 or nonparent chlorinated hydrocarbons are observed within our detection limits by GC analysis. Recovery of chlorine as HCl is nearly 100%, although these results are qualitative as previously discussed. At a O_2/TCA ratio of 1.5, which is less than that required for complete oxidation of the carbon, both CO and CO_2 are formed and soot formation is observed.

As the forward power input to the reactor is decreased to 450 watts, which is the minimum power input required to maintain a 20% oxygen/argon plasma (Table No. 1), the primary carbon oxide product is CO and formation of soot particles is observed indicating incomplete oxidation of the carbon even in the presence of excess oxygen (O_2/TCA molar feed ratio of 165). The formation of nonparent chlorinated hydrocarbons, such as methylene chloride and trichloroethylene, are also observed. Similar results are observed under oxygen-deficient conditions as the forward power input approaches the minimum required to sustain the plasma.

The soot particles are deposited on the inner wall of the quartz liner in a nonuniform distribution during the course of the reaction. These soot particles absorb microwave radiation at 2450 MHz, which was confirmed by observing both a decrease in the reflected power as soot formation occurred and that the soot particles "glowed red" when microwave radiation was admitted to the reactor in the absence of a plasma.

The ability of soot particles to absorb microwave radiation decreases the amount of energy available to the plasma at a given forward power input. As soot formation increases, a point is reached where there is an insufficient amount of energy available to sustain the plasma and the plasma will be quenched. If the introduction of TCA to the reactor is halted before the plasma is quenched, the formation of some CO and CO_2 is observed. This suggests that under certain conditions, the reaction of TCA and O_2 may involve both homogeneous and heterogeneous reaction mechanisms.

The carbon in the soot particles is amorphous as determined by x-ray diffraction. Chlorine is present, as determined by x-ray phosphorescence, although a carbon/chlorine ratio could not be determined. There is no evidence for the presence of any molecular compounds in the soot particles.

II. REACTION OF TRICHLOROETHYLENE WITH OXYGEN

The results of the reaction of trichloroethylene (TCE) and oxygen (O_2) in a microwave discharge plasma are summarized in Table No. 3. The global stoichiometry for the reaction of TCE with O_2 in a microwave discharge plasma (Eq. 3) is identical to that observed in thermal combustion.

$$C_2HCl_3 + 2O_2 \text{--->} 2CO_2 + HCl + Cl_2 \qquad \text{(Eq. 3)}$$

Conversion of TCE in excess of 99% is observed for O_2/TCE ratios ranging from 20.4-190 and a forward power input of 800 watts. Qualitatively, approximately 40% of the chlorine is recovered as HCl which is in agreement with the theoretical yield of 33% based on Eq. 3. The primary carbon product is CO_2, although CO formation is observed at the lower O_2/TCE ratio.

It is known from the investigation of the combustion of TCE that the reaction proceeds in two steps (Bose and Senkan, 1983). The first step involves the rapid oxidative decomposition of TCE as described in Eq. 4.

$$C_2HCl_3 + O_2 \text{--->} 2CO + HCl + Cl_2 \qquad \text{(Eq. 4)}$$

The second step involves the subsequent oxidation of CO to CO_2 as shown in Eq. 5.

$$2CO + O_2 \text{--->} 2CO_2 \qquad \text{(Eq. 5)}$$

Although this oxidation may possibly be quite fast, it is inhibited by HCl and Cl_2 and is subsequently very slow in thermal combustion processes involving chlorinated hydrocarbons.

Although we have not performed a mechanistic investigation of the reaction of TCE and O_2 in a plasma, the formation of CO at lower O_2/TCE ratios, i.e., increasing $(HCl + Cl_2)/O_2$ ratios, would suggest that a similar two step process is occurring. This result would not be surprising since the destructive oxidation of TCE with O_2 in a thermal incinerator or a plasma reactor both involve free radical chemistry.

III. REACTION OF 1,1,1-TRICHLOROETHANE WITH WATER

The reaction of TCA with H_2O in a microwave discharge plasma was investigated under various conditions, including varying H_2O/TCA molar feed ratio and forward power input to the reactor. The objective was to investigate the effect of these operating parameters on the overall TCA conversion and resulting product distribution. The results of these experiments are summarized in Table 4.

Ideally, one would prefer for the degradation of TCA to occur according to the stoichiometry described by Eq. 6a.

$$C_2H_3Cl_3 + 4H_2O \text{ ---> } 2CO_2 + 3HCl + 4H_2 \qquad \text{(Eq. 6a)}$$

The stoichiometric amount of H_2O is defined as the amount required to convert all the carbon to CO_2 and the chlorine to HCl. However, under no conditions is the complete conversion of carbon to CO_2 observed; CO is always observed.

For H_2O/TCA molar feed ratios ranging from 10.4 to 62.3 and a forward power input of 600 watts, conversions of TCA in excess of 98.3% were observed with the primary products being CO, CO_2, H_2, and HCl. CO_2 selectivity, defined as $CO_2/(CO + CO_2)$, is observed to decrease, from 0.694 to 0.274, as the H_2O/TCA molar feed ratio decreases from 62.3 to 10.4. A more appropriate stoichiometry equation would be Eq. 6b,

$$C_2H_3Cl_3 + 3H_2O \text{ ---> } CO + CO_2 + 3HCl + 3H_2 \qquad \text{(Eq. 6b)}$$

Note as the CO yield increases, the H_2/CO_x ratio decreases from 2 (no CO) to 1 (no CO_2). The observed H_2/CO_x ratios range from 3.73 to 1.96 under the above conditions, which indicates excess H_2 is being produced.

One possible explanation for the incomplete conversion of carbon to CO_2 is the water-gas shift reaction (Eq. 7).

$$CO_2 + H_2 \text{ ---> } CO + H_2O \qquad \text{(Eq. 7)}$$

Note that the sum of Eqs. 6a and 7 is Eq. 6b. As observed, the CO_2 selectivity decreases with a decrease in the H_2O/TCA molar feed ratio as expected according to Le Chatelier's principle.

As the forward power is decreased at a near constant H_2O/TCA ratio, 19.0-22.1, the conversion of TCA decreases from 99.9% at 600 watts to 84.8% at 300 watts, which is slightly above the minimum power required to sustain the plasma (Table No. 1). The CO_2/CO_x ratio is relatively constant ranging from 0.452 at 600 watts to 0.487 at 300 watts. At 300 watts, considerable soot formation is observed with the formation of simple alkanes, CH_4, C_2H_4, and C_2H_6. As discussed previously, soot formation adversely affects the overall reactant conversion and the product distribution by reducing the effective power available to the plasma at a given forward power input.

IV. REACTION OF TRICHLOROETHYLENE WITH WATER

The reaction of TCE and H_2O in microwave discharge plasma was investigated under various conditions,including varying the H_2O/TCE molar feed ratio, forward power input to the reactor, and residence time, to investigate the effect of these operating parameters on the overall TCE conversion and the resulting product distribution. The results of these experiments are summarized in Table No. 5.

Ideally, one would like for the reaction of TCE by H_2O to occur according to a stoichiometry similar to that discussed for TCA (Eq. 6a). However, since TCE is hydrogen-deficient for the complete conversion of the chlorine to HCl, H_2O would provide both the oxygen for CO_2 and hydrogen for HCl formation (Eq. 8a).

$$C_2HCl_3 + 4H_2O \text{ ---> } 2CO_2 + 3HCl + 3H_2 \qquad \text{(Eq. 8a)}$$

Consequently, one less mole of H_2 would be produced for each mole of TCE consumed compared to TCA if the reaction of H_2O with TCA or TCE was to proceed as described by Eq. 6a or Eq. 8a, respectively.

As discussed for the reaction of TCA with H_2O, the complete conversion of carbon to CO_2 is not observed. For H_2O/TCE molar feed ratios ranging from 173 to 10.3 and a forward input power of 600 watts, the CO_2/CO_x ratio decreases from 0.905 to 0.528. As with TCA, a more appropriate equation is Eq. 8b.

$$C_2HCl_3 + 3H_2O \dashrightarrow CO + CO_2 + 3HCl + 2H_2 \qquad \text{(Eq. 8b)}$$

The H_2/CO_x ratio should range from 1.5 (no CO) to 0.5 (no CO_2). The observed H_2/COx ratios range from 3.33 to 1.11 for the above described conditions. As expected, the H_2/COx ratio for the reaction of TCE with H_2O is less than that for the reaction of TCA with H_2O under similar conditions.

Increasing the residence time by a factor of 9 did not result in any significant improvement in the CO_2 selectivity. For example, at a residence time of 290 ms, the CO_2/CO_x ratio observed is 0.528 at a H_2O/TCE molar feed ratio of 10.3 and a forward power input of 600 watts. At a residence time of 2500 ms, the CO_2/COx ratio is 0.698 at a H_2O/TCE ratio of 16.3 and 600 watts forward power input. A small amount of soot formation was observed in both cases. No increase in the overall TCE conversion was observed due to the limitations of the GC analysis.

V. THE REACTION OF TRICHLOROETHYLENE WITH A MIXTURE OF OXYGEN AND WATER

As has been demonstrated, chlorinated hydrocarbons react with O_2 in a microwave discharge plasma yielding primarily CO_2 and HCl if the H/Cl ratio of the reactant molecule is greater than or equal to 1 or CO_2, HCl, and Cl_2 if the H/Cl ratio is less than 1. Water will react with chlorinated hydrocarbons, serving as both an oxygen source for the formation of CO_x and hydrogen source for the formation of HCl; however, CO is formed in preference to CO_2.

Alternatively, if the chlorinated hydrocarbon is reacted with a mixture of H_2O and O_2, it might be possible to eliminate all the chlorine as HCl and the carbon as CO_2 as long as there is a stoichiometric excess of H_2O and O_2.

The results of the reaction of TCE with a mixture of O_2 and H_2O in a microwave discharge plasma are summarized in Table No. 6. Conversions of TCE of >99% are observed with the primary products being CO_2 and HCl. Qualitatively, all the chlorine is recovered as HCl. A maximum Cl_2 concentration of 4 ppm is observed by mass spectroscopy in the effluent stream for a H_2O/TCE ratio of 2.40 and a O_2/TCE ratio of 18.8. No CO is detected by gas chromatography.

CONCLUSIONS

We have demonstrated a microwave discharge plasma reactor can effectively detoxify dilute vapor concentrations of TCA or TCE using either O_2, H_2O vapor, or a O_2-H_2O vapor mixture as the coreactant in an argon gas stream at atmospheric pressures. Both the conversion of either TCA or TCE and the resulting product distribution are a function of the forward power input to the reactor. The primary products are CO, CO_2, HCl, Cl_2, and H_2, with the actual selectivity and yield depending on the reactant feed mixture and forward power input to the plasma reactor. As the forward power input approaches the minimum required to sustain the plasma, the overall TCA or TCE conversion decreases, incomplete oxidation of carbon to CO_2 occurs, soot formation occurs, and the products include nonparent chlorinated hydrocarbons and/or simple hydrocarbons.

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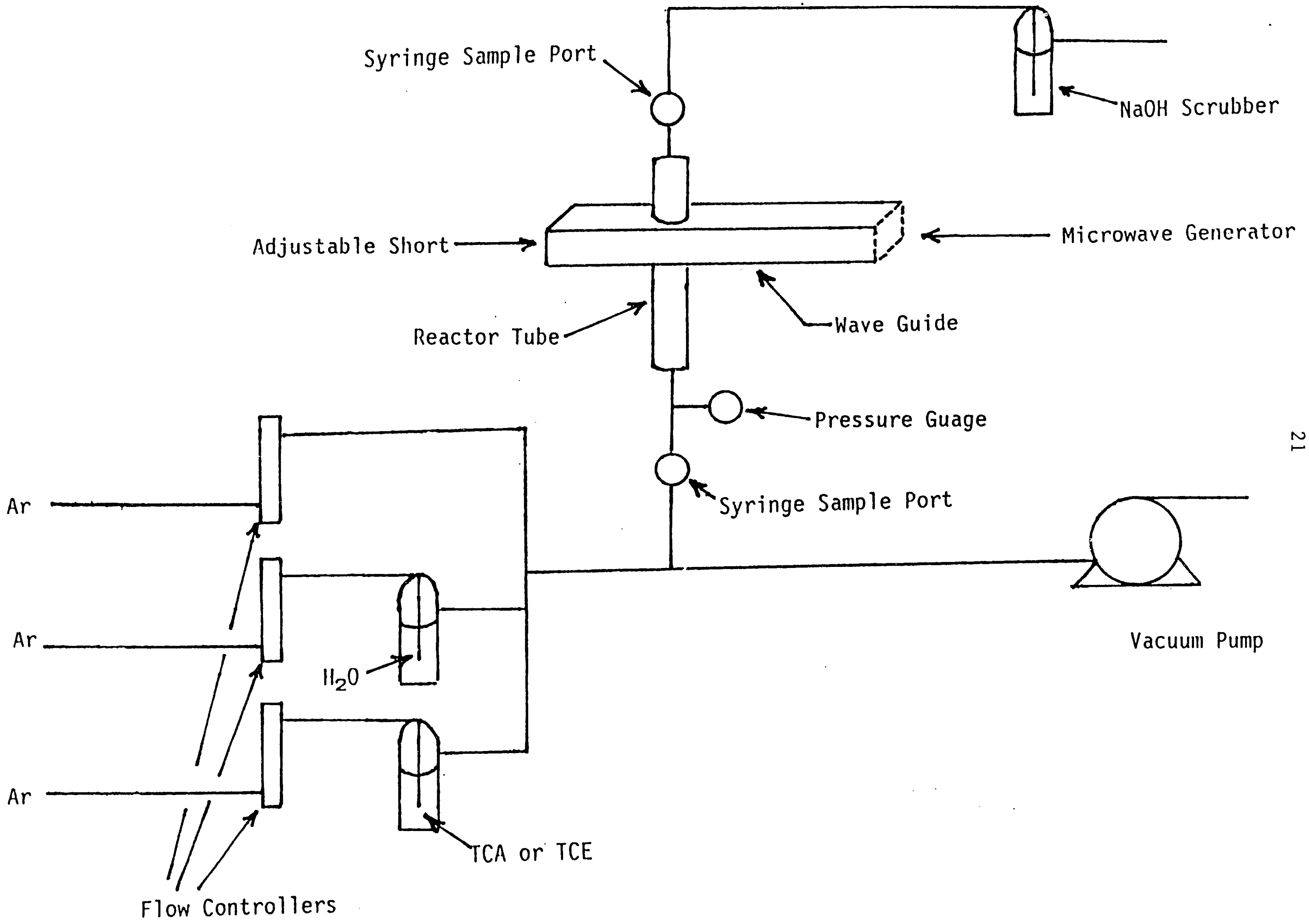
Figure 1



Schematic of Reactor System

TABLE NO. 1

MINIMUM FORWARD POWER INPUT REQUIRED TO SUSTAIN PLASMA IN SOME GASEOUS ATMOSPHERES AT 1.0-1.1 ATM USING MICROWAVE RADIATION AT 2450 MHz

GAS	FORWARD POWER (watts)
Argon	150
2.45% H_2O/Argon	220
20.13% Oxygen/Argon	450
Nitrogen	450

TABLE NO. 2

REACTANT FEED CONCENTRATION AND PRODUCT DISTRIBUTION FOR THE REACTION OF 1,1,1-TRICHLOROETHANE AND OXYGEN

FORWARD POWER (watts)	O_2/TCA RATIO	MOLE FRACTION ($x10^3$) TCA(1)	TCA CONV(2)	MOLAR RATIO		PERCENT HCl	RESIDENCE TIME (ms)
				CO_x/TCA(3)	CO_2/CO_x(4)		
600	150	1.31	0.995	2.0	1.00	~100	290
600	4.4(5)	43.0	0.983	2.0	0.965	92	2000
600	1.5	1.35	0.990	---(6,7)	0.534(8)	---	290
450	165	1.12	0.994(6)	1.3	0.099	---	290
400	1.5	1.45	0.962	---(6,7)	0.589(8)	---	290
300	1.5	1.36	0.753(9)	---(6,7)	0.372(8)	---	290

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(1) Mole fraction of TCA in feed stream.

(2) If no TCA is observed in the effluent stream, then the minimum amount of TCA detectable by GC is substituted.

(3) Ratio of the concentration of CO and CO_2 in effluent stream to that of TCA in feed stream.

(4) Defined as $CO_2/(CO + CO_2)$ in effluent stream.

(5) This sample analyzed by mass spectroscopy.

(6) Carbonaceous deposits formed.

(7) Due to fluctuations in CO_x yields, a mass balance was not obtainable.

(8) Average value observed during ~1 hr period.

(9) Effluent stream contained CH_2Cl_2, C_2HCl_3 and other unidentified chlorinated in small yields (total yield <1% initial TCA feed).

TABLE NO. 3

REACTANT FEED CONCENTRATIONS AND PRODUCT DISTRIBUTION FOR THE REACTION OF TRICHLOROETHYLENE AND OXYGEN

FORWARD POWER (watts)	O_2/TCE RATIO	MOLE FRACTION (x 10^3) TCE(1)	TCE CONV(2)	MOLAR RATIO		PERCENT HCl	HCl/Cl_2 RATIO	RESIDENCE TIME (ms)
				CO_x/TCE(3)	CO_2/CO_x(4)			
800	190	0.990	0.995	2.0	1.0	~40	0.7	290
800	20.4	8.25	0.999(5)	2.0	0.997	~40	0.7	260
600	12.9(6)	15.0	0.967	2.0	0.97	27	0.4	2300

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(1) Mole fraction of TCE in feed stream.

(2) If no TCA is observed in the effluent stream, then the minimum amount of TCE detectable by GC is substituted.

(3) Ratio of the concentration of CO and CO_2 in effluent stream to that of TCE in feed stream.

(4) Defined as $CO_2/(CO + CO_2)$ in effluent stream.

(5) A small quantity (<<1% based on initial feed concentration of TCE) of an unidentified chlorinated hydrocarbon was observed by GC analysis. The retention time did not correlate with $CH_{3-x}Cl_{1+x}$ (where x = 0 to 3). Possibly phosogene.

(6) This sample analyzed by mass spectroscopy.

TABLE NO. 4

REACTANT FEED CONCENTRATIONS AND PRODUCT DISTRIBUTION FOR THE REACTION OF 1,1,1-TRICHLOROETHANE + H_2O

FORWARD POWER (watts)	H_2O/TCE RATIO	MOLE FRACTION ($x10^3$) TCA(1)	TCE CONV(2)	MOLAR RATIO		H_2/CO_x	PERCENT HCl	RESIDENCE TIME (ms)
				CO_x/TCA(3)	CO_2/COx(4)			
600	62.3	0.388	0.997	2.0	0.694	3.73	>90	200
600	36.4	0.332	0.983	2.0	0.633	2.58	>90	150
600	24.2	0.990	0.999	2.0	0.559	2.97	>90	200
600	19.9	0.604	0.999	1.9(5)	0.452	2.03	>90	150
600	17.0	0.708	0.992	1.9(5)	0.432	1.96	>90	150
600	10.4	2.27	0.997	1.9(5)	0.274	1.96	---	190
400	19.0	0.633	0.999	1.9(5)	0.391	2.06	---	150
300	22.1	0.542	0.848	1.4(6)	0.487	2.74	---	150

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(1) Mole fraction of TCA in feed stream.

(2) If no TCA is observed in effluent stream, then the minimum amount of TCA detectable by GC is substituted.

(3) Ratio of the concentration of CO and CO_2 in effluent stream to that of TCA in feed stream.

(4) Defined as $CO_2/(CO + CO_2)$ in effluent stream.

(5) Carbonaceous deposits formed.

(6) Considerable carbon deposits, with the observance of CH_4, C_2H_4, and C_2H_6 in the effluent stream. Plasma extinguished after approximately 40 minutes at these conditions.

TABLE NO. 5

REACTANT FEED CONCENTRATIONS AND PRODUCT DISTRIBUTION FOR THE REACTION OF TRICHLOROETHYLENE + H_2O

FORWARD POWER (watts)	H_2O/TCE RATIO	MOLE FRACTION ($x10^3$) TCE(1)	TCE CONV(2)	MOLAR RATIO			PERCENT HCl	RESIDENCE TIME (ms)
				CO_x/TCE(3)	CO_2/CO_x(4)	H_2/CO_x		
600	173.	0.14	99.	2.0	0.905	3.33	>90	290
600	42.8	0.56	100.	2.0	0.836	1.98	>90	290
600	27.8	0.846	99.8	2.0	0.570	1.11	>90	290
600	22.9	1.02	99.8	2.0	0.630	1.52	>90	290
600	10.3	2.28	99.2	~2(5)	0.528	1.27	>90	270
600	16.3	1.43	99.7	~2(5)	0.698	1.58	---	2500
500	14.8	1.58	99.7	~2(5)	0.695	1.49	---	2500
400	10.8	2.17	99.8	~2(5)	0.652	1.54	---	2500
800	25.2	0.938	99.5	2.0	0.783	1.31	---	290
600	33.7	0.701	99.4	2.0	0.769	1.54	---	290
500	32.6	0.723	99.4	2.0	0.805	1.50	---	290
400	31.8	0.743	99.4	2.0	0.674	1.12	---	290

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(1) Mole fraction of TCE in feed stream.

(2) If no TCE is observed in the effluent stream, then the minimum amount of TCE detectable by GC is substituted.

(3) Ratio of the concentration of CO and CO_2 in effluent stream to that of TCE in feed stream.

(4) Defined as $CO_2/(CO + CO_2)$ in effluent stream.

(5) Carbonaceous deposits formed.

TABLE NO. 6

REACTANT FEED CONCENTRATIONS AND PRODUCT DISTRIBUTION FOR THE REACTION OF TRICHLOROETHYLENE + H_2O + O_2

FORWARD POWER (watts)	H_2O/TCE RATIO	O_2/TCE RATIO	(x 10^3) TCE(1)	TCE CONV(2)	MOLAR RATIO CO_x/TCE(2)	CO_2/CO_x(4)	Cl_2 (5)	PERCENT HCl	RESIDENCE TIME (ms)
800	25.7	202	0.890	0.990	2.0	1.0	$<2\times10^{-6}$	~100	290
800	6.37	49.9	3.44	0.997	2.0	1.0	---	~100	270
800	2.40	18.8	8.56	0.999	2.0	1.0	$<4\times10^{-6}$	~100	260

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(1) Mole fraction of TCE in feed stream.

(2) If no TCE is observed in the effluent stream, then the minimum amount of TCE detectable by GC is substituted.

(3) Ratio of the concentration of CO and CO_2 in effluent stream to that of TCE in feed stream.

(4) Defined as $CO_2/(CO + CO_2)$ in effluent stream.

(5) Determined by mass spectroscopy.

END

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01/23/92