SCALE-UP OF A DIELECTRIC-BARRIER-DISCHARGE

PLASMA REACTOR AND TOLUENE REMOVAL

EFFICIENCY

By

NEHA SINGH

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Madhav Institute of Technology and Science,

M.P., India

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Thesis Approved:

Dr. Arland H. Johannes

Thesis Adviser

Dr. Gary L. Foutch

Dr. John N. Veenstra

Dr. A. Gordon Emslie

Dean of the Graduate College

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CHAPTER I

INTRODUCTION

PROBLEM

The Oklahoma City Air Logistics Center performs surface coating operations for aircraft in paint booths at Tinker Air Force Base (TAFB). The solvent used to dissolve the aircraft paint contains Volatile Organic Compounds (VOC) and because of the no discharge emission standards regulated by Environmental Protection Agency (EPA) the use of these paints is prohibited. For the present project, toluene was chosen as a representative VOC because it is safe and easy to handle.

The process of surface coating is not continuous and is of short duration; thus, TAFB needs a technology with an instant-on / instant-off capability. Previous research conducted at Oklahoma State University indicated the potential of Dielectric-Barrier-Discharge (DBD) plasma reactors to remove VOCs from the air streams. Experiments were carried out to determine the removal efficiency of a plasma reactor and the scale-up of the reactor to a pilot scale.

PLASMA TECHNOLOGY

The removal of gaseous pollutants using electric discharge is a new technique. The first report on the chemical effect of an electrical discharge was published in the 18th century (1796); a German research group discovered that hydrocarbons were converted into an oil-like product when exposed to electric discharge. Several studies were conducted on air pollution control using a DC or AC corona discharge, but the removal efficiencies (percent of pollutant removed) calculated for those studies were low.

Most of the research conducted previously at Oklahoma State University proved that the DBD plasma reactor was effective in removing the gaseous pollutants from the air stream. Piatt (1988) achieved 45 % methane removal efficiency. Desai (1992) and Magunta (1995) achieved 90 % removal efficiency for H_2S . Carbon tetrachloride was removed from air at efficiency greater than 90 % by Hurst (1993).

OBJECTIVES

In this project, the TRE of a tubular dielectric barrier discharge plasma reactor was investigated under the fourth phase of a project for Tinker Air Force Base (TAFB). The destruction or removal efficiency of the reactor is defined as the percent removal of toluene from the air stream and is calculated by:

Toluene Removal Efficiency = $\left[\frac{\text{Inlet - Outlet}}{\text{Inlet}}\right]$ concentration * 100 Equation 1-1

The objectives of this study were to determine:

- the joint effect of number of reactor tubes, secondary voltage, and retention time of toluene gas on the toluene removal efficiency (TRE) of the DBD plasma reactor;
- the effect of 30-50% relative humidity on the TRE of the DBD plasma reactor;
- the effect of the toluene gas influent concentration on the TRE of the DBD reactor;
- the amount of ozone generated while carrying out toluene removal experiments;
- the possibility for the scale-up of the reactor to pilot-scale.

RESEARCH OUTLINE

Experimental System

The experimental system consisted of variable numbers of plasma reactor tubes inside a plexiglass housing, an AC power supply, a step-up transformer, and toluene gas feed tank (100 and 240 ppm).

Variables

- number of reactor tubes;
- secondary voltage (Refer to Figure 3-1);

- retention time of toluene;
- humidity of air entering the reactor and;
- toluene influent concentration.

Table 1-1 presents a range of operating parameters.

Operating Parameter	Range
Number of tubes	2-8
Secondary Voltage	9600-14625 V
Retention time	1.6-4.6 s
Humidity	30-50 %
Toluene Concentration	100 and 240 ppmv

Table 1-1: Range of operating parameters

CHAPTER II

REVIEW OF LITERATURE

INTRODUCTION

Volatile Organic Compounds (VOCs) are chemicals that can vaporize at normal temperature and pressure. VOCs can have short-term or long-term health effects on human beings [Urashima and Chang, 2000]. Much research has been carried out to remove or destroy VOCs since their health effects have been observed in people living near industries and workers via emission of gases and ground water contamination [Urashima and Chang, 2000]. VOCs are emitted from a wide range of products such as pesticides, cleaning supplies, paint strippers, permanent markers, photographic solutions, and office equipment including copiers and printers. Exposure to VOCs may cause eye-throat irritation, headaches, loss of coordination, and kidney damage. VOCs are currently removed from air streams along with other pollutants such as acid gases (SO_x, NO_x, and HCl etc.), toxic gases (Hg, dioxins etc.), radioactive gases (I, Kr etc) by using one of the technologies described in later pages of this section (Table 2-4) [Urashima and Chang, 2000].

STATE OF ART: PLASMA

A "Plasma is a collection of positively and negatively charged particles in an otherwise neutral gas" [Eliasson and Kogelschatz, 1991]. Application of sufficient electric field (> breakdown field) to a gas can lead to gas molecule ionization and electrical conduction with the appearance of free energized electrons. The energized electrons (1-20 eV, Kim 2004) have more kinetic energy as compared to the rest of the gas molecules and drift toward the positive terminal. On their way to the positive electrode they encounter other gas molecules and undergo collisions thereby transferring some of their energy to the molecules and losing some energy as photons. The collision leads to the formation of chemically reactive species such as ions and electrons, and carries out other chemical and physical processes inside the plasma. The emitted electrons are called secondary electrons, which have more kinetic energy than the primary energized electrons.

Plasma processes mainly involve electron-electron, radical initiation and termination, excitation, ionization reactions that lead to the removal of gaseous pollutants from the air. Along with the pollutant removal, this process also generates other gases such as ozone. Chang and Urashima (2000) (refer to Figure 2-1) described the various processes taking inside in a plasma process as:



Figure 2-1: Possible phenomenon occurring inside plasma initiated reaction by Chang and Urashima (2000)

Classification

A plasma can be classified by temperature. If all the ions, molecules and electrons are in thermal equilibrium, the plasma is known as isothermal or thermal plasma; whereas, if the energized electrons are at higher temperature than the rest of the gas molecules, the plasma is known as a non-thermal (NTP) or cold plasma. The most attractive feature of a NTP is that it is generated at ambient conditions. This project is about the NTP reactors.

There are a variety of non-thermal plasma reactors classified on the basis of power source used, reactor configuration, presence of dielectric, mode of discharge etc. Some of them are described as follows [Eliasson and Kogelschatz, 1991]:

1. Corona discharge

Corona discharge occurs at very low pressure (1.0 bar) and if the operating pressure is increased, the discharge becomes unstable and turns into a highcurrent arc discharge. Non-homogeneous electrode geometries such as point or plate electrode are used to stabilize the discharge. There are two types of corona discharges, one is positive corona (occurs due to positive charges) and other one is negative corona (occurs due to negative charges). Care should be taken while applying the electric voltage to generate a corona, because if it exceeds a certain value the corona can produce a spark. Because of the operating conditions and smaller volume exposed to corona action than the total discharge volume, this discharge is not used for industrial applications. Corona is used where less excited species are required such as an electrostatic precipitator or a copying machine. Table 2-1 summarizes the characteristics of corona discharge [Eliasson and Kogelschatz, 1991].

Characteristics	
Pressure	1 bar
Electric field	0.5-50 kV/cm
Reduced field	2-200 Td, variable
Electron energy	<i>5</i> eV, variable
Electron density	10 ⁻¹³ cm ⁻³ , variable
Degree of ionization	Small, variable

Table 2-1: Characteristics of a corona discharge [Eliasson and Kogelschatz, 1991]

2. Glow discharge

Glow discharge is generated when a high potential difference (10 V/cm) is developed between the two flat electrodes immersed in a low pressure environment (< 10 mbar) causes electrical breakdown of the gas. Due to the high electron density and high electron energy, the process of excitation of the neutral atoms or molecules is easy. Low current and voltage are required to generate glow discharge, but because of low pressure and low mass flow, it can not be used for industrial applications. Table 2-2 presents the characteristics of a glow discharge plasma and the numbers are a rough indication of the conditions required.

characteristics	
Pressure	< 10 mbar
Electric field	10 V/cm
Reduced field	50 Td
Electron energy	0.5-2 eV or 5000-20000 k
Electron density	10 ⁸ - 10 ¹¹ cm ⁻³
Degree of ionization	$10^{-6} - 10^{-3}$

Table 2-2: Characteristics of a glow discharge [Eliasson and Kogelschatz, 1991]

3. Dielectric barrier discharge (DBD) [Eliasson and Kogelschatz, 1991] DBD is a class of high-voltage gaseous discharge (0.1-100 V/cm) which occurs at atmospheric pressure (1.0 bar). This type of discharge is also called silent discharge. During breakdown, the reduced field corresponds to very high electron energy (1-10 eV) which is sufficient to break bonds between chemical molecules (Table 2-3). The most important feature of DBD or silent electric discharge is the presence of a dielectric layer, which covers one or both the electrodes. The dielectric is responsible for the proper functioning of the discharge by performing two important tasks:

a. controls the charge transported by a micro discharge; and,

b. distributes the micro discharges over whole electrode area.

Characteristics	
Pressure	1 bar
Electric field	0.1-100 V/cm
Reduced field	1-500 Td
Electron energy	1-10 eV
Electron density	10 ¹⁴ cm ⁻³
Degree of ionization	10 ⁻⁴

Table 2-3: Characteristics of a DBD [Eliasson and Kogelschatz, 1991]

4. Microwave discharge [Eliasson and Kogelschatz, 1991]

Microwaves (0.3 to 10 GHz) induce plasma in this type of discharge. Microwave discharge is generally produced in a resonant cavity or waveguide structure. Usually a frequency of 2.45 GHz is used to generate plasma. Because of this high frequency the generated plasma is far from the thermodynamic equilibrium.

Though this kind of plasma is easy to operate, but it's not very useful industrially because its applications are limited to elemental analysis and lasing media.

5. Radio frequency discharge [Eliasson and Kogelschatz, 1991] Radio waves (2-60 MHz) can generate plasma. Due to the larger wavelength of the electric field than the dimensions of the vessel, a homogeneous plasma is produced. This type of plasma works at pressure less than or equal to 1 bar.

Plasma chemistry in a DBD reactor

DBD Plasma chemistry

In a DBD plasma generation, at least one of the electrodes is covered with a dielectric material. A DBD plasma process requires alternating (AC) voltage for the application because of the presence of the dielectric barrier, which is an insulator for direct current (DC) voltages. Preferred materials for a dielectric barrier are glass, silica glass, thin polymer layers or ceramic materials. The electric field has to be very high to transport current through the gap. The preferred working frequency for a DBD is about 10 MHz [Kogelschatz, 2002], because at high frequency the dielectric is not an effective charge absorber. At atmospheric pressure and a very high electric field (greater than the breakdown voltage), a number of micro discharges are observed which are responsible for the chemical reactions occurring in the gap.

Micro discharge formation

When the electric field, applied to the gas, approaches the breakdown field of the gas, a local ionization occurs in the discharge volume. The electrons quickly ionize other atoms and molecules. These electrons produce a high space charge and self-propagating streamers (current) are generated. A space charge is the localized region of excess negative charge that occurs near a metal.

These streamers travel much faster than the electrons and upon reaching the anode they are reflected back to the cathode and form a very thin "cathode fall layer" [Kogelschatz, 2002]. In this situation, the current can flow only through the conducting channels. Hence, the charge accumulates at the dielectric surface leading to the reduction of electric field and therefore after some time ionization and micro discharge flow stops.

In a DBD plasma, the energized electrons transfer their total energy to the neighboring atoms and molecules of the gas in the discharge volume. The dielectric limits the current flow through collisions. Thus, there is a greater risk of spark or arc formation in the system. The characteristics of the micro discharges depend on the gas properties, operating pressure and temperature, properties of the dielectric and electrode geometry.

Micro discharge plasma chemistry

The chemical reactions in a plasma reactor are initiated by the ionic and the excited species formed as a result of the electron collisions with the gas

molecules and atoms. Each micro discharge acts like an individual plasma reactor, where the chemical reactions take place. Energy dissipation and discharge activity occur in the micro discharge volume. By increasing the applied voltage, the density of micro discharges will increase, thus there is no change in the characteristics of the micro discharges by scaling-up the reactor, which requires higher voltage to be applied. The initial active species formation process with respect to the energy consumed influences the efficiency of the DBD plasma process. The active species formation depends on the available area between the two electrodes and the reduced field [Kogelschatz, 2002].

Other Technologies

There are few technologies available currently that can remove VOC from the air stream; namely, thermal incineration, adsorption, and biofilteration. A comparison was made between various technologies to show that the NTP technology is better than other technologies (Table 2-4).

Many technologies have been investigated for the removal of VOCs. Several have proved to be less than successful due to high capital investment costs and low efficiency. The choice of pollution control technology depends on many factors such as [Urashima and Chang, 2000]:

- removal efficiency;
- energy efficiency of removal, (i.e.) effective energy input to fluid flow;
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- pressure drop of the devices;
- reusable material production rate;
- unwanted byproducts concentration;
- annual cost.

There are many methods available for large scale VOC removal including;

1. Thermal oxidation technology [Urashima and Chang, 2000] This technology operates at very high temperatures (760-980^oC) and requires huge amounts of energy. The major disadvantage of this technology, apart from the high energy requirement, is the generation of dioxins and furan at high temperature. Thermal oxidation technology is not a very efficient in treating low VOC concentration (< 1000 ppmv).

2. Thermal recuperative oxidation [Urashima and Chang, 2000]

This technology also works at very high temperature, therefore operation cost is very high and a heat exchanger is required before the exhaust gas is released into the atmosphere. Thermal recuperative oxidation can remove 95 % of toluene at $730-930^{\circ}$ C operating temperature.

3. Catalytic oxidation [Urashima and Chang, 2000]

This process requires catalyst, which works for a certain range of temperature (250-400^oC), and has disposal problems. Due to the short lifetime of catalyst, catalyst replacement is required. Catalyst is selective to a certain type of VOC, therefore many catalysts are required to treat mixed gas.

4. Adsorption [Urashima and Chang, 2000]

The adsorbents such as activated carbon, zeolite are used to retain VOCs on their surface. Adsorbents require regeneration and disposal regularly. The VOC removal efficiency is 90% at low concentration but cost of operation is relatively high.

5. Biofiltration [Urashima and Chang, 2000]

This technique requires a bed of active microorganism operating at a specific temperature and humidity. Contaminated gas is allowed to pass through the bed with long residence time, leading to a clean and odorless gas. The main advantage of this technology is the low operating cost since bed replacement is required every five to seven years. The disadvantage of biofiltration is the requirement of large gas volume and longer residence time.

6. Membrane separation [Urashima and Chang, 2000]

A semi permeable membrane is used to separate VOC from a waste gas stream. This process requires high pressure and high flowrates for its operation.

7. UV oxidation [Urashima and Chang, 2000]

Short wavelength ultraviolet with oxygen-based oxidants are used to oxidize the VOC into carbon dioxide and water vapor in presence of UV light. Low pressure glow discharges or high pressure non-thermal plasma are used to generate UV. The major disadvantages are low efficiency and long residence time requirements. Table 2-4 lists the advantages and disadvantages of the technologies described above.

TECHNIQUES	ADVANTAGE	DISADVANTAGE	COST (OPERATING & CAPITAL COSTS/GAS FLOW RATE)
Thermal incineration Recuperative	≈ 70 % of energy can be recovered	NO _x , dioxins and Furan production, high installation cost	\$15 to 124(m³/h)
Thermal Incineration Regenerative	≈ 95-98 % energy recovery is possible	NO _x , dioxins and Furan production, high installation cost	\$30 to 370 (m ³ /h)
Catalytic Oxidation	≈ 70% energy recovery is possible, no dioxides and Furan forms, much less energy than thermal oxidizers	Deactivation with time, sensible to poisoning (by Pb, As, halogens, S), disposal of used catalyst	\$30-200 (m³/h) (fixed), \$20-60(m³/h) (fluidized)
Adsorption	Product recovery can offset annual- operating cost, can be used as a concentrator	Pressure drop, sensitive to plugging & poisoning, disposal of used adsorption material	\$25-117(m³/h) (carbon based)
Biofiltration	Simple process, low energy requirements, completion VOC breakdown	Pressure drop, sensitive to temperature changes, voluminous, unsuitable for highly halogenated compounds	\$20-60(m³/h)
Membrane Separation	Selective VOC removal	Pressure drop, high gas pressure operation, strong membrane dependence, cleaning requirement	Not available (N/A)
UV Oxidation	Simple process, complete VOC breakdown	Window cleaning, efficiency of UV lamps, residence time limitations	N/A

Table 2-4: Convention	technologies to remov	e VOCs [IIrashima	and Chang 20001
	technologies to remov	e vocs [orasiiiiia	

The advantages of NTP technology over conventional technologies include:

- high energy density,
- high efficiency,
- controllable reactor atmosphere,
- small reactor size,
- small volume of off-gases,

- lower capital investment in process equipment, •
- efficiency, and •
- No combustion products affecting the quality of products.

Plasma technology operates over a large range of gas flow conditions and concentrations. Specifically, the NTP reactor works at ambient conditions, it has high energy density, high energy efficiency, better heat transfer, and small reactor size. All of these points make NTP an attractive technology for the removal of VOCs from air.

INTERPRETATION OF THE CURRENT KNOWLEDGE

Hazardous effects of Toluene

Toluene (C_7H_8) is a clear aromatic hydrocarbon, which is hardly soluble in water. It is also known as methylbenzene or phenyl methane. Toluene is mainly used as a solvent. The physical properties of toluene are listed in Table 2-5.

Table 2-5: Physical properties of toluene [USHA]				
Density and phase	0.8669 g/cm ³ , liquid			
Solubility in water	0.053 g/100 mL (20-25°C)			
Solubility in ethanol, acetone, hexane,	Fully miscible			
uicilioi ometriane				
Melting point	93°C (180 K)/(-135.4°F)			
Boiling point	110.6°C (383.8 K)/ 231.08°F			
Critical temperature	320°C (593 K)/ 608°F			
Viscosity	0.590 cp at 20°C/ 68°F			
Dipole moment	0.36D			

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Toluene is a common VOC and is hazardous to human beings, because it is less soluble in water. Upon inhalation toluene can not exit the body, and has to be

metabolized before excretion. In large doses, it can cause nausea. Long term frequent inhalation can lead to irreversible brain damage. Toluene can also enter the human body through contact with contaminated soil or drinking water. According to OSHA standards, the Permissible Exposure Limit (PEL) of toluene for eight hours is 100 ppm, (i.e.) 375 mg of toluene/ m³ of air. The Short-Term Exposure Limit (STEL) is 150 ppm for a period of 15 minutes. The maximum, or ceiling limit is 500 ppm, which means the toluene concentration should never be greater in a location where humans can be exposed.

Destruction of toluene [Urashima and Chang, 2000]

The radicals formed due to the collision of energetic electrons with the gas molecules, carry out the destruction of toluene in the reactor. Figure 2-2 shows the probable dissection sites after the electron impact. The first possible reaction can be the removal of hydrogen, thereby rupturing the C-H bond (357 KJ/mol bond energy). The second reaction can be the electron impact removal of hydrogen from the aromatic ring which has higher bond energy (469 J/ mol). A third possibility could be breakage of C-C bond (high bond energy, 420 J/mol), with the formation of methane and benzene radicals. There can be one more probability of dissociation of benzene ring into ethylene or butylene.



Figure 2-2: Toluene destruction sites by corona torch [Urashima and Chang, 2000]

The reactions for the toluene destruction are as follow;

$$C_6H_5.CH_3 + X^+ \rightarrow C_6H_5.CH_2O + X$$

where X^+ can be O^+ , O_3^+ , N^+ , N_2^+ and the rate of the reaction of the order of $10^ ^{10}$ cm³/s. Table 2-6 lists other conventionally known reactions of toluene destruction.

16	2-0. Flashochennical reactions [or ashima and chang, 2000]			
	Reactions	Rate, cm ³ /s		
	$C_6H_5.CH_3$ + e \rightarrow C_6H_5 + CH_3	10⁻ ⁶ f T _e		
	$C_6H_5.CH_3 + O \rightarrow C_6H_5.CH_2 + H$	8.4*10 ⁻¹⁴		
	$C_6H_5.CH_3 + O_3 \to C_6H_5.CHO_2 + H_2O$	1.5*10 ⁻²²		
	$C_6H_5.CH_3 + OH \rightarrow C_6H_5.CH_2 + H_2O$	7.0*10 ⁻¹³		
	$C_6H_5.CH_3 + OH \rightarrow C_6H_5.CH_3.OH$	5.2*10 ⁻¹²		

Table 2-6: Plasmochemical reactions [Urashima and Chang, 2000]

Where f is the frequency factor and T_e is electron temperature.

BYPRODUCTS FORMATION

Side reactions are possible during the destruction of volatile organic compounds by the NTP process. These side reactions lead to the generation of byproducts which can be organic or inorganic. Some of the inorganic products formed in a non-thermal plasma process are O_3 , NO, NO₂, N₂O, and CO.

The generation of these products varies with the applied voltage [Yamamoto, 1997]. There are two methods suggested in the literature [Yamamoto, 1997] to control the production of these byproducts. The first one is, by reducing the operating voltage which will lower the volatile decomposition and the second method is by controlling the contents of the background gas, for example by controlling the oxygen concentration to minimize the NO_x emission. Figure 2-3 shows that the concentration of generated ozone is a function of the applied voltage. It first increases with an increase in voltage and then decreases with further increase in voltage. A similar trend was observed by Oda 2003 using different reactor geometry.



Figure 2-3: The typical VOC decomposition and concentration of inorganic byproducts [Yamamoto, 1997].

PERFORMANCE EVALUATION

Kim et al. 2002 provides various models to calculate the energy efficiency of a NTP reactor. They showed that the removal of NO is a function of specific energy input (SIE) and with the increase in SIE the NO concentration decreased. Based on this observation, they established a generic equation for NO removal,

Efficiency =
$$\eta = \frac{[NO]_0 - [NO]}{[NO]_0} = 1 - \exp(-k_E * P_{SIE})$$
 Equation 2-1

Where η is the removal efficiency of the reactor, [NO] and [NO]₀ are outlet and inlet concentrations of NO in ppm, P_{SIE} is the SIE in KJ/Nm³, and the energy constant (k_E) in Nm³/KJ, which is a function of parameters such as gas temperature, and gas composition.

SCALABILITY

Scale-up of a plasma reactor is a function of specific energy consumption, which is calculated from input power divided by weight of treated gas. According to Agnihotri (2003), there exists a scale-up parameter β (Joule/ liter) for pollutant X, given by the equation;

$$\frac{[X]}{[X_0]} = \exp \frac{-P}{Q * \beta}$$
 Equation 2-2

Where P (Watt) is the power supplied to change the pollutant concentration from $[X_0]$ to [X]. Q (liters/second) is the flow rate of the air stream and β is the slope of the plot between -P/Q and ln ($[X_0]/[X]$). The value of β for toluene as calculated by Agnihotri is 99.0 J/L for a planer DBD reactor configuration.

To study the factors affecting the scale-up of the plasma reactor, the number of reactor tubes was increased one by one until a decent glow of non-thermal plasma was observed at the highest workable voltage. It was found that no more than eight tubes could be used in the scale-up study. Independent parameters were assumed to be affecting the scale-up of the plasma reactor, and were determined using the Buckingham-pi method to develop dimensionless numbers.

EFFECT OF HUMIDITY

Humidity is assumed to increase the removal efficiency of a plasma reactor because of the presence of OH⁻ radicals. To confirm this Yamashita et al. 1996

tried to determine the effect of humidity on the TRE of the surface discharge induced in a NTP reactor for CFC-113. But due to experimental errors, their result is not reliable.

A similar study was done by Yu-fang et al. 2006 which showed that the removal efficiency of toluene in a wire-plate DBD plasma reactor increased due to the presence of 0.2 % H₂O. Figure 2-4 shows the variation in the removal efficiency of the plasma reactor with respect to the humidity at different energy density. Figure 2-4 shows that the TRE first increases, and then decreases with an increase in humidity. A similar trend was observed at different energy density (J/L). Figure 2-4 also suggests that there is an optimum % humidity which gives maximum removal efficiency. The decrease in the removal efficiency after the optimum humidity may be a result of the presence of more OH⁻ ion, which may be responsible for other side reactions.



Figure 2-4: Dependence of TRE on humidity [Yu-fang et al. 2006]

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CHAPTER III

METHODOLOGY

EXPERIMENTAL SYSTEM

Electrical system

As shown in Figure 3-1 an AC power supply was plugged into a wall outlet (120 V, 60 Hz) using a split extension cord. The primary side of a step-up transformer derived its power from the AC power supply. One of the secondary sides of the transformer was connected to the end of the inner solid-steel electrode of a tubular plasma reactor and the other was connected approximately at the center of the outer electrode of the plasma reactor; i.e. at the copper winding. All the tubular reactors were connected in parallel to each other inside the casing using stretched hose-clamps. Figure 3-2 gives a clear picture of the electrical system. Power was measured at three locations in the circuit; (a) at the wall outlet, (b) between AC power source and transformer, and (c) between transformer and the quartz casing. A multimeter was used to record the voltage and current at all three locations except for the voltage at the secondary location; which was recorded using a Fluke multi-meter 23.



Figure 3-1: Electric circuit, Power measurement locations



Figure 3-2: Experimental set-up, from left to right; AC power supply, Transformer, Plasma reactor

System geometry

Toluene gas of known concentration was fed to the tubular plasma reactor through ³/₄ inch stainless steel tubing. A flowmeter, a digital thermometer, and a pressure gauge were connected before and after the reactor to record the flowrate, temperature and pressure of influent and effluent streams (shown in Figure 3-3). T-intersections fitted on ³/₄ inch metallic tubing were used to make these connections. Sampling ports were located before and after the reactor to draw the samples of influent and effluent streams. The inlet and outlet samples of the gas were analyzed in a gas chromatograph (GC).



Digital Thermometer, (4) Sampling port, (5) Plasma reactor

Humidity system

The zero-grade (dry) air was allowed to bubble through a series of three (1 liter) Erlenmeyer flasks, partially filled with tap water, placed in a constanttemperature water-bath at 20 ^oC (Figure 3-4 and 3-5). Before starting the experiment, the influent gas was made approximately 30-50 % humid. A humidity probe recorded the relative humidity in the system, which was placed inside a glass container sealed at the top with an inlet and outlet openings for the effluent stream of the reactor whose humidity was to be measured.



Figure 3-4: Humidity system



Figure 3-5: A picture of humidity system
EQUIPMENT SPECIFICATIONS

Plasma reactor

Depending on the operating conditions being evaluated, plasma was created in one or more tube reactors. Each reactor was made of guartz glass which has a low dielectric constant and low coefficient of thermal expansion. The reactor tube consisted of a hollow glass tube with a steel rod placed coaxially inside the tube (Figure 3-6, 3-7 and 3-8). Teflon spacers were used to prevent contact of the glass tube with the metal electrode. Copper tape was wrapped around the glass tube as an outer electrode and a coaxial steel rod was the inner electrode. A toluene-air mixture was allowed to flow through the annulus between the inner metallic-electrode and inner surface of the glass tube. G. D Holland, 2002 at Oklahoma State University developed the specified tubular design (Table 3-1) for the plasma reactor.

Table 3-1: Tubular reactor di	mensions
Length of a copper rod	3.292 ft
Length of a quartz tube	4 ft
Diameter of a quartz tube	0.033 ft
Annular volume of a reactor	1.67 E-3 ft ³

Table 3-1: Tubular reactor di	mensions
ength of a conner rod	3 292 ft



Fig 3-6: A tubular DBD plasma reactor



Fig 3-7: Crossection of a tubular reactor R = distance from the center of the steel rod to the inner surface of the glass tube. d = difference in the radius of hollow glass tube and coaxial steel rod.



Figure 3-8: A picture of a tubular reactor

Multiple-tube reactor

The multiple-tube reactor consisted of a hollow Plexiglass cylinder casing and two-end pieces to close the cylinder. The casing has holes at both ends. One or more tubular plasma reactors were placed inside the hollow casing. A total of 26 reactors could be placed inside the casing. To assemble the system, the reactor tubes were inserted through the holes on both ends of the casing (Figure 3-9). These holes were slightly bigger than the outer diameter of the reactor tube, and were kept airtight using rubber O-rings. The tubes were electrically connected in two locations; at one of the ends and at the center of the tubes using hose clamps. With all the reactor tubes seated inside the casing, both the ends of the casing were closed with the two end cap pieces. Contaminated gas entered through one of the end cap pieces. The number of these tubular reactors inside the casing was changed according to the experimental design. The ends of the casing were closed using two Plexiglass lids, and cork gaskets and vacuum seal grease was used to air-tighten both ends.



Figure 3-9: Quartz casing with two reactor tubes inside it

AC Power source

A power source was used to regulate the power supplied to the step-up transformer. A California instruments model 1001TC, series 850 T AC Power Source (Figure 3-10) was used to control the primary voltage. This power supply was plugged into a standard 120 V AC, 60 Hz standard wall plug.



Figure 3-10: AC Power source

Transformer

A step-up transformer (Franceformer Model 15060P category 15060 and series 1205), was used to get the desired AC voltage. The transformer was capable of producing 15000 V, 60 mA with 120 V, 60 Hz, 7.5 A on the primary side (Figure 3-11)



Figure 3-11: A transformer

Gas Chromatograph

An SRI 8160 C Gas Chromatograph (GC) was used to measure toluene concentration in gaseous samples (Figure 3-12). The GC was connected to a computer through software called Peak Simple. This software reported the analysis of the gas samples. A Hamilton 1002 syringe (Figure 3-13) with a Luer lock fitting and capacity of 2.5 ml was used to inject the sample into the GC's inlet port. The operating specifications for the GC are provided in Table 3-2.

	operating opeenteations
Combustion gas	Air (7 psig, 250 ml/min)
Combustion gas	Hydrogen (25 ml/min)
Carrier gas	Helium (4 psig, 10 ml/min)
Column temperature	70 ° C
Injector	70 ° C
FID temperature	375 ° C

Table	3-2:	GC d	operating	specifications



Figure 3-12: SRI Gas chromatographer



Figure 3-13: A Swagelok syringe

Temperature, flow rate and pressure drop measurement

Two Sunbeam digital probes, two Riteflow^R flow meters and kits, and two pressure gauges were used to measure the temperature, flow rates and pressure of influent and effluent streams of the reactor. The flow meter was made of

borosilicate glass tube with a stainless steel float inside the tube. Refer to Figure 3-3 (system geometry) to understand the order of these measuring devices into the system.

Humidity probe

A Cooper SRH77A digital instrument humidity-temperature probe was used to measure the percent relative humidity in the experimental system. It was connected after the flow meter measuring the effluent flow from the plasma reactor. Figure 3-14 shows the humidity probe that was used in the present experiment.



Figure 3-14: A humidity probe

<u>Multi-meter</u>

An Extech 380942 digital multi-meter (Figure 3-15) was used to measure the voltage and root-mean-square current in the circuit. To measure the current from the wall, the range selection on the meter was set on 4000 mA and to read

primary current, the knob was set on 400 mA. The current readings were taken by simply holding the clutch of the multimeter around the wire through which current is flowing. The voltage was read on 400 V AC setting using the probes.



Figure 3-15: A multimeter

Fluke multi-meter 23

A Fluke multi-meter 23 (Figure 3-16) was used to read the voltage across a 100 ohm resistance connected on the secondary side of the transformer. By measuring voltage across a known resistance, the current flowing through the circuit can be determined by using Ohm's law (I_{sec} = Voltage / Resistance).



Figure 3-16: A fluke meter

EXPERIMENTAL PLAN

GC Calibration Curve

Before each experiment was started, a calibration curve was prepared to allow for calculation of the mass of toluene in a sample. Samples of known volume (0.1, 0.2 up to 1.5 ml) were drawn from the exit end of the reactor and injected into the GC. The mass of toluene in a sample was calculated and sample calculations are shown in the Appendix. Peak Simple software was used to report amounts of toluene injected in terms of peak area. The areas of the peaks were plotted against the known mass of toluene. The calibration curve determined the mass-detection limit of the GC, i.e. the minimum mass of toluene that could be recognized by the GC. The detectable range was found to be 30-600 nanograms.

2^k design

The experiments were planned keeping three variables in mind, and they were:

- Number of reactor tubes,
- Secondary voltage, and
- Retention time.

A 2^k factorial design was followed to study the joint effects of the chosen variables on the TRE of the reactor [Montgomery, 2001]. Because of limited resources, a single replicate of the 2^k design was used to design the experiments. According to the method, 2^k experiments are needed to account for the joint effect of k variables on the response curve. Thus, for three variables (2³) a minimum of eight experiments were required to be performed. Two different values (high and low) for each variable were selected to show their effects on the response. These values were selected based on the operating limitations of the equipment and optimum range of values. In addition to the chosen numbers for each variable, one more number was selected for the experiments. This number was the mean of the chosen high and low numbers. The selected values for all the variables are shown in Table 3-3.

	Table 3-3: List of selected variables							
Number of tubes	Secondary voltage, V	Retention time, seconds						
2	9000	1.4						
5	12000	2.7						
8	14625	4.3						

Table 3-3: List of selected variables



Figure 3-17: 2³ design represented by a cube [Montgomery, 2001]

2³ factorial design can be understood by drawing a cube whose corners are represented by 3 main variables and their combinations. Figure 3-17 shows that Based on the 2^k design, different combinations of the above values were assigned as experimental conditions, and they are listed in Table 3-4.

Experiment	Reactor	Actual	Secondary	Toluene	Humidity,
	Configuration,	Retention	Voltage, V	concentration,	% RH
	tubes	Time, sec		ppm	
1	8	4.3	9000	100	0
2	8	4.3	14625	100	0
3	8	1.8	9000	100	0
4	8	1.8	14625	100	0
5	2	4.9*	9000	100	0
6	2	4.9*	14625	100	0
7	2	1.4*	9000	100	0
8	2	1.4*	14625	100	0
9	5	2.7	12000	100	0
10	5	2.7	12000	100	0
11	5	2.7	12000	100	0

Table 3-4: Experimental conditions

* These values were changed according to the readable range of flow meter.

Variation of concentration

After the completion of first eleven experiments (as described above) the concentration of toluene was changed to 240 ppm. The other variables were chosen from the results of the first eleven experiments. The experiments, which gave the best TRE, were repeated with different toluene concentration (240 ppm). Three experiments were performed to determine the effect of change in toluene concentration. Refer to Table 3-5 for the experimental conditions.

Experiments	Reactor configuration, # tubes	Retention time, sec	Secondary voltage, V	Toluene concentration, ppm	Humidity, % RH	
12	2	4.9	14625	240	0	
13	5	2.7	12000	240	0	
14	8	4.3	14625	240	0	

Table 3-5: Ex	perimental	conditions	for con	centration	experiments

Variation of humidity

The humidity of the system was varied up to 30-50 % by using the humidity setup. The choice of the humidity range was based on the average humidity of Oklahoma throughout a year. The experiment was executed in the same fashion as the rest of the runs. Humidity was added to the system after the inlet flow meter. Table 3-6 presents the experimental conditions for the humidity runs.

	Table 5-0. Experimental conditions for numury experiments							
Experiments	Reactor configuration,	Retention	Secondary	Toluene	Humidity,			
	# tubes	time, sec	voltage, V	concentration,	% RH			
15	2	1.4	9000	100	40			
16	2	1.4	14625	100	39			
17	5	2.7	12000	100	46			

Table 3-6: Experimental conditions for humidity experiments

Summa canisters

TRE of the reactor was calculated for all the experimental runs. Inlet and outlet samples from the reactor were collected only once for the conditions described below using summa canisters (Figure 3-18) and were sent to the Pace laboratory in Minnesota for analysis.

Reactor tubes= 2

Toluene influent concentration = 240 ppmv

Primary voltage = 117 V

Retention time = 1.6 seconds

Relative humidity = 30 %

The obtained analyses confirmed the results obtained in the laboratory at OSU and also suggested that other chemicals were present in the reactor's effluent samples which were not detected by the OSU GC. The sample collection procedures for the summa canisters are described in the next chapter.



Figure 3-18: A 1 L summa canister

CHAPTER IV

FINDINGS

The results of all the experiments are presented in this chapter. Among all the variables (including primary voltage, number of tubes, and retention time) the most significant variable was determined using statistical techniques (Tukey's test) [Montgomery, 2001]. Regression models were developed to predict the removal efficiency of DBD reactors and to evaluate the amount of ozone generated during the toluene removal process. The dependence of removal efficiency on various parameters such as retention time, number of tubes and primary voltage is shown by plots. The results of the scale-up study of the plasma reactor are also presented. Table 4-1 summarizes the results of all the 17 experiments within experimental error.

Experiment	Reactor configuration, tubes	Actual retention time, sec	Secondary voltage, V	Toluene concentration , ppm	Humidity, % RH	% TRE Averaged over 24 minutes
1	8	4.3	9000	100	0	32
2	8	4.3	14625	100	0	78
3	8	1.8	9000	100	0	19
4	8	1.8	14625	100	0	43
5	2	4.9	9000	100	0	98
6	2	4.9	14625	100	0	100
7	2	1.4	9000	100	0	85

Table 4-1: Experimental result

8	2	1.4	14625	100	0	98
9	5	2.7	12000	100	0	59
10	5	2.7	12000	100	0	61
11	5	2.7	12000	100	0	62
12	2	4.9	14625	240	0	100
13	5	2.7	12000	240	0	100
14	8	4.3	14625	240	0	100
15	2	1.4	9000	100	30-50	92
16	2	1.4	14625	100	30-50	44
17	5	2.7	12000	100	30-50	36

REMOVAL EFFICIENCY VERSUS ENERGY DENSITY

For an influent toluene concentration of 100 ppmv, an exponential decay in the effluent concentration and corresponding rise in the TRE was observed (Figure 4-1) at different values of retention time and number of tubes. Similar results were observed by Koutsospyros et al. 2005 for ammonia in a parallel plate capillary plasma discharge reactor. Moreover, Koutsospyros pointed out that the observed exponential trend in the effluent concentration was independent of the retention time, initial concentration, reactor volume, chemical nature of the target species, and presence of other interfering parameters, which can also be observed in the Figure 4-1. It can be seen (Figure 4-1) that irrespective of the experimental conditions the effluent concentration of the reactor follows an exponential curve with the energy density.

Energy density $(J/ml) = \frac{Wall \text{ power } (W) * \text{Retention time } (Sec)}{\text{Air flowrate } (ml)}$ Equation 4-1



Figure 4-1: Effluent concentration vs. Energy density

CONTAMINANT RETENTION TIME

At 100 ppmv of influent toluene concentration, mass of toluene (nanograms/ KWhr) removed per tube was examined for different primary voltages. Mass of toluene (ng) in a sample was calculated using calibration curve using following formula.

$$ng = \frac{\text{Sample volume(ml)}}{1000} * [\text{Mol. wt. (g/mol)*Conc. (ppmv)}]_{\text{of toluene}} * \left[\frac{\text{Density (kg/m^3)}}{10^6 \text{ kg*Mol. wt. (kg mol)*1000}}\right]_{\text{of toluene}}$$

Equation 4-2

ng/KW/br/tube-	Mass of toluene in a sample (ng)	austion 4-3
ing/ K win/ tube –	Secondary power (KW) * Retention time (hr) * number of tubes	quation 4-5

Figure 4-2 shows that more toluene was removed at 0.03-0.04 KV of primary voltage, rather than at maximum primary voltage (0.058 KV), which suggests that there exist an optimum value of primary voltage which can give maximum efficiency. It can also be seen in the plot that more toluene was removed at lower retention time. This may be due to the occurrence of some reversible reactions or side reactions occurring inside the reactor at higher retention time. Other possibilities include channeling and boundary layer effects (Dr. A.H Johannes, 2007).



Figure 4-2: Mass of toluene removed vs. Primary voltage

REACTOR VOLUME

Effect of reactor volume on the removal efficiency of toluene was assessed by increasing the number of number of tubes, from 2 to 8, and thereby increasing the reactor volume 4 times the original volume. For both the configurations i.e. 2 and 8 tubes, the removal efficiency increases with the increase in the energy density. Energy density was calculated by using following equation 4-1 and data are shown in the figure 4-3. The smaller volume reactor (2 tubes) was found to be more effective in terms of achieving overall higher removal efficiency. Because of different ranges of energy density, it is difficult to conclude which reactor configuration (2 or 8 tubes) is better.



Figure 4-3: Effect of reactor volume on the TRE at different energy density

HUMIDITY

The effect of water vapor (% RH) on the TRE of the reactor at an influent concentration of 100 ppm is depicted in figure 4-4. It can be concluded that the addition of water vapor increased the removal efficiency of the plasma reactor at low and high primary voltages (72 and 117 V). This may be due to an increase in OH⁻ ion concentration in the plasma zone when water vapor is present which are responsible for the increased reactivity of the reactor. A similar study performed by Fang-Yu et al. 2006 on a wire-plate DBD plasma reactor showed that the TRE of the plasma reactor with 50 ppmv of influent toluene increases with the increase in 0.2 % of humidity (Figure 4-5). Figure 4-5 also suggests that at all the humidity levels there is an increase in applied voltage with increasing energy density, but in the present case there is no change in the TRE at higher humidity with respect of primary voltage, which may be due to experimental errors.







Figure 4-5: Dependence of applied voltage on energy density for selected humidity in the DBD system with the gap of 8mm. 50ppmv toluene, 100 ml/min, 5% O2 [Fang-Yu et al. 2006]

TOLUENE INFLUENT CONCENTRATION

The effect of toluene influent concentration on the removal efficiency is shown in the plot shown below (Figure 4-5). It can be seen that for an influent concentration of 240 ppm, the removal efficiency of the reactor was found to be lower than that at 100 ppm at same number of reactor tubes. It may be due to increased side reactions of other generated ions at higher concentration. This appears to be an advantage of plasma reactions since most of other technologies decrease in efficiency with decrease in contaminant's concentration.



Figure 4-6: Effect of influent toluene concentration on removal efficiency

According to the experiments performed by Kim et al. (2002), the NO removal efficiency of a tubular NTP reactor, maintained at a constant temperature inside an oven, decreased with increasing NO influent concentration at both 50°C and 100°C; which is just opposite to what was observed in present study (data shown below). But this difference may be because of using different type of pollutant or the increased temperature.

Conditions		NO concentration				
		100 (ppm)	200 (ppm)	300 (ppm)	400 (ppm)	
At 50°C	Removal efficiency	92%	55%	36%	29%	
At 100°C	Removal efficiency	80%	41%	29%	22%	

SCALE-UP OF PLASMA REACTOR

The Buckingham pi theorem was used to perform similitude and modeling analysis for the scale-up study. According to the Buckingham pi theorem, "if an equation involving k variables is dimensionally homogeneous, it can be reduced to a relationship among (k-r) independent dimensionless products, where r is the minimum number of reference dimensions required to describe the variables" [Okiishi 2005].

Because of the complexity of the variables, the system was assumed to be divided into two sub-systems: a) the electrical system, and b) the flow system. The dimensionless numbers (details are given in appendix 3 & 4) for both the systems respectively are; 1) the ratio of power supplied to the reactor, after the transformer, to the total power supplied from the wall power socket ($P_{secondary}/P_{wall}$), and 2) Reynolds number ($D_{annular}*V_{air}*\rho_{air}/\mu_{air}$). The power ratio varied from 0.57 to 0.67 while the Reynolds number varied from 204 to 1257 for all the experiments. Hence the flow was laminar throughout the experiments. Figure 4-6 shows the relationship between both the dimensionless numbers at different reactor geometry (2 and 8 reactor tubes). It can be seen in the plot (4-6) that power ratio does not change with respect to Reynolds number at higher primary voltage whereas at lower primary voltage the power ratio decreased with increasing Reynolds number. Moreover, plot shows the same trend between the data points which suggests that relation between the dimensionless

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groups is independent of reactor geometry. More number of experiments is required to be performed considering 5 variables in 2^{K} factorial design with at least 3 replications to find the relation between the dimensionless groups. A knowledge of the relation between the electrical and flow system would help in the scale-up of a pilot scale reactor.



Figure 4-7: Dimensionless numbers at different primary voltage

In addition to dimensionless numbers, a scale-factor was calculated using the equation suggested by Agnihotri 2003. The ratio of power supplied to the reactor, to the air flow rate was plotted against the ratio of effluent to the influent toluene concentration and is shown in figure 4-7. The slope of the

straight line fitting the data gives the value of the energy constant (Ke, reciprocal of scale-up factor) Ke = $1/\beta = 0.0012$.



Figure 4-8: Scale-up factor for 100 ppmv toluene inlet concentration at 0% RH

The value of β can be used to determine the power requirements of the reactor for a given flow rate of the gas.

REGRESSION MODEL

A regression model was used to determine how removal efficiency of the DBD reactor was affected by system variables (primary voltage, number of tubes, and retention time). A 2^k factorial design for unreplicated experiments was employed

to determine the minimum number of experiments that needed to be performed. To determine the joint effects of the 3 variables, namely secondary voltage, volumetric flow rate and number of tubes, on the removal efficiency of the plasma reactor, experiments were carried out at all possible combinations of high and low values for each of the three variables. Due to the scarcity of resources and time, the experiments were not replicated.

Tukey's test for Non-additivity [Kirk, 1995]

Tukey's test for non-additivity was employed to analyze the experimental data and to develop the regression model. A non-additive regression model is where the response of an experiment is affected not only by its variables but also by the interaction among the variables. An additive regression model is one which disregards the effect of the interaction among the variables on the experimental response. This means that the additive model contains only the main effects of all the variables. The additive model is simpler than the non-additive model. Tukey's test for non-additivity confirms whether the assumed normally distributed data follows additive or non-additive models. To perform Tukey's test, a null and an alternative hypothesis were assumed:

Ho = The model is non-additive.

Ha = The model is additive.

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The probability of non-additivity was then calculated from the F-distribution using the following equations [Kirk, 1995]. The general equations (written for three variables) for both the models are as follows:

1. Non-additive model

$$Y = \alpha + \beta + \gamma + \alpha\beta + \beta\gamma + \alpha\gamma + \alpha\beta\gamma + e$$
 Equation 4-5

Where

Y = removal efficiency of the plasma reactora, β , and $\gamma = main effects of three system variables$ $a<math>\beta$, a γ , $\beta\gamma$, a $\beta\gamma = effect$ of interaction of the system variables e = residual

2. Additive model

$$\mathbf{Y} = \boldsymbol{\alpha} + \boldsymbol{\beta} + \boldsymbol{\gamma} + \boldsymbol{e}$$

Where

Y = removal efficiency of the plasma reactor

 α , β , and γ = main effects of three system variables

$$[Y] = \left[\sum_{i=1}^{n} \sum_{k=1}^{p} \sum_{l=1}^{p} Y_{ijkl} \right]^{2}$$

n p²

Equation 4-7

Equation 4-6

[ABC] =	$\sum_{k=1}^{p} \sum_{l=1}^{p} \frac{\left(\sum_{i=1}^{n} \mathbf{Y}_{ijkl}\right)^{2}}{n}$	Equation 4-8
[A] =	$\sum_{j=1}^{n} \frac{\left[\sum_{i=1}^{n} \sum_{k=1}^{p} \sum_{l=1}^{p} \mathbf{Y}_{ijkl}\right]^{2}}{\mathbf{np}}$	Equation 4-9
[B] =	$\sum_{k=1}^{p} \frac{\left[\sum_{i=1}^{n} \sum_{l=1}^{p} \mathbf{Y}_{ijkl}\right]^{2}}{\mathbf{np}}$	Equation 4-10
[C] =	$\sum_{l=1}^{p} \frac{\left[\sum_{i=1}^{n} \sum_{k=1}^{p} \mathbf{Y}_{ijkl}\right]^{2}}{\mathbf{np}}$	Equation 4-11
SSNONADD =	$\frac{\left(\sum_{j=1}^{p}\sum_{i=1}^{n}d_{ij}Y_{ij}\right)^{2}}{\left(\sum_{i=1}^{n}d_{i.}^{2}\right)\left(\sum_{j=1}^{p}d_{.j}^{2}\right)}$	Equation 4-12
SSREM =	SSRES - SSNONADD	Equation 4-13
SSTO =	[ABC]-[Y]	Equation 4-14
SSA =	[A] – [Y]	Equation 4-15
SSB =	[B] – [Y]	Equation 4-16
SSC =	[C] – [Y]	Equation 4-17
SSRES =	[ABC] – [A] – [B] – [C] + 2 [Y]	Equation 4-18
dfREM =	dfRES - 1	Equation 4-19
FNONADD =	SSNONADD/dfNONADD SSREM/dfREM	Equation 4-20

Where

i, j, k, l, p = System variables

n = Number of replications

[Y] = Fractional removal efficiency

- [ABC] = Main effect of all 3 variables on removal efficiency
 - [A] = Main effect of retention time on removal efficiency
 - [B] = Main effect of number of reactor tubes on removal efficiency
 - [C] = Main effect of primary voltage on removal efficiency
- SSNONADD = Sum of square of non-additivity
 - SSREM = Sum of square of error
 - SSTO = Total sum of square
 - SSA = Sum of square of retention time
 - SSB = Sum of square of number of reactor tubes
 - SSC = Sum of square of primary voltage
 - SSRES = Sum of square of residual
 - dfREM = Degrees of freedom of error
- FNONADD = F-distribution value for non-additivity
 - dNONADD= Degrees of freedom of non-additivity

If the calculated probability (FNONADD) is greater than the "significance level", which was set as 5% [Montgomery, 2001], then the null hypothesis is wrong. That is, the data follows the additive model or there is no interaction among the

Source of variation	SS	df	MS	Fo
Retention time	0.087	1	0.087	-0.027
Number of tubes	1.092	1	1.092	-0.335
Primary voltage	0.1806	1	0.1806	-0.055
Residual	-4.403	1	-4.403	1.3501
Non-additivity	2.1194	1	2.1194	-0.65
Error	-6.522	2	-3.261	
Total	-3.043	7		

Table 4-2: Tukey's test of non-additivity

variables. If the probability of non-additivity is greater than the "significance level" then it can be concluded that data follows the non-additive model. Table 4-2 shows the value of F-distribution for non-additivity.

Where

$$SS = Sum of squares$$

 $df = Degrees of freedom$
 $MS = Mean square$
 $F_0 = F - distribution$

The calculated probability of the non-additivity was less than the significant F_{\circ} value, this proved that the experimental data followed the additive model. The regressed model was as follows:

$$Y = 0.67875 + 0.09* X_1 + 0.38* X_2 + 0.14* X_3$$
 Equation 4-21

Where,

0.67875 =	mean of all the fractional conversions
0.09, 0.38, 0.14 =	effect estimates of retention time, number of tubes
	and primary voltage
X_1 , X_2 , and $X_3 =$	either 1 or -1, and it depends on its high or low levels

Table 4-3 shows the experimental and model response. The experiments were named according to the level of the parameters, for instance the run number [1] is the experiment which had all the parameters at minimum level; [a] is the experiment which had parameter A at higher, and B and C at lower level; [ab] is the one which had A and B at higher and C at lower level.

The residual was plotted against the experiment of removal efficiency (Figure 4-8). The adequacy of the model can be explained by the scattering of the data. If there is no relation among the data points, the model is adequate. Figure 4-8 shows that the points were scattered in a uniform manner and they seemed to have same order of ordinate. This suggests that model is not effective in predicting the TRE. Replication of first eleven experiments is required to get a better model.

Run	Experimental removal efficiency (ERE)	Removal efficiency modeled (REM)	Residual = ERE-REM
1	0.85	0.069	0.781
а	0.98	0.249	0.731
b	0.2	0.836	-0.636
С	0.98	0.341	0.639
ab	0.3	1.016	-0.716
bc	0.43	1.108	-0.678
ac	0.99	0.521	0.469
abc	0.7	1.289	-0.589

Table 4-3: Removal efficiency regression model accuracy check



Figure 4-9: Residual vs. Experimental response for TRE

OZONE GENERATION

Experiments were performed to calculate the amount of ozone generated at 100 ppmv influent toluene concentration and at 0 % humidity. Figure 4-9 shows the amount of ozone generated in milligrams per liter of air flow rate verses the energy density in KWhr/L. The amount of ozone generated increased exponentially with an increase in applied energy density. This is probably the result of the greater availability of more reactive species at high energy density.



Figure 4-10: Ozone produced vs. Energy density

A regression model was developed using Tukey's non-additivity test, similar to what was done for the TRE, to calculate the amount of ozone produced in the experiment. Table 4-4 summarizes the Tukey's test result.

Table 4-4: Tukey's test					
Source of variation	SS	df	MS	Fo	
Retention time	1.406267	1	1.406267	-0.17018	
Number of tubes	0.200048	1	0.200048	-0.02421	
Primary voltage	1.031349	1	1.031349	-0.12481	
Residual	-11.6134	1	-11.6134	1.40542	
Non-additivity	4.913215	1	4.913215	-0.59458	
Error	-16.5266	2	-8.2633		
Total	-8.97572	7			

Where,

SS =	Sum of squares		
df =	Degrees of freedom		
MS =	Mean square		
$F_0 =$	F - distribution		

The model to predict ozone production is shown below.

 $Y = 1.289 + 0.42 * X_1 + 0.16 * X_2 + 0.36 * X_3 \label{eq:Y} \mbox{Equation 4-22}$

Table 4-5 shows the experimental and model response.

Table 4-5: Ozone generation regression model accuracy check					
Run	Experimentally measured ozone (EMO)	Ozone generation model (OGM)	Residual, e = EMO-OGM		
1	1.865934	0.3490	1.5169		
а	0.246206	1.1911	-0.9449		
b	1.161239	0.6688	0.4924		
С	2.601357	1.0707	1.5307		
ab	0.869824	1.5073	-0.6375		
bc	0.708572	1.3869	-0.6783		
ас	0.878321	1.9092	-1.0309		
abc	1.982159	2.2255	-0.2433		

The absence of trend among the data points in figure 4-10 suggests that the model is effective in evaluating the amount of ozone generated from the experiments, though more experiments are required to get a model with less residual.



Figure 4-11: Residual vs. experimental response for ozone generation

SUMMARY

These results suggest that plasma reactor has efficiently removed (TRE > 90%) toluene from the air stream. More than 90% conversion of toluene can be achieved with this technology. The experiments were carefully planned using 2^k factorial method and successfully executed to show the effects of system variables on the removal efficiency of the reactor. The regression models provided the insight into how the system variables are affecting removal efficiency. The equation given by Agnihotri (2003) was helpful in calculating the scale-up factor. Simple fluid-mechanics concepts were incorporated to carry out the scale-up study on the plasma reactor. On the whole this project was

successful in achieving its objectives, but more care has to be taken while performing experiments to avoid human errors. The limited availability of resources may have affected the accuracy of this project by affecting the number of experiments to be performed. Hence, there is still a scope of improvements in this project.

CHAPTER V

CONCLUSION AND RECOMMENDATION

A DBD plasma reactor was scaled-up and examined for its ability to destroy gaseous toluene in an air stream. A total of seventeen experiments were performed to study the effect of some of the chosen parameters including toluene inlet concentration, retention time of toluene inside the reactor, number of reactor tubes, applied voltage to the reactor, and relative humidity of the influent air.

The results from this project are summarized below.

- TRE increases with energy density.
- More toluene was removed at lower retention time.
- There exists an optimum value of applied voltage at a particular retention time that gives maximum toluene removal.
- The Reynolds number is inversely proportional to the power ratio at lower primary voltage while at higher primary voltage power ratio stays constant with respect to Reynolds number.
- The energy coefficient for toluene was found to be 0.0012 L/J.
The following are the recommendations for the future research:

- Graduate students working on this project in future should have a knowledge of statistical tools and methods. Graduate level courses such as advanced statistics and Research Methods would be of great help.
- Due to lack of resources, the experiments were not repeated. Replication of the experiments would provide more accurate data and better estimates of experimental error.
- A simpler reactor design with less joints, can help in controlling leaks from the system.
- Attention must be paid to the GC; especially the operating conditions such as flow rates of carrier gas, conditions of column material, and injection port.
 Plugging of the inlet port or column can lead to misleading results. For better results, GC should be baked time to time (once a week).

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APPENDIX-I

PROCEDURES

GC calibration

- 1. Switch-on the computer.
- 2. Select peak simple software.
- 3. Turn on the hydrogen (25 ml/min), air (250 ml/min) and helium (10 ml/min, carrier gas) to start GC.
- 4. Switch on the GC.
- 5. Switch-on the flame-ionization detector at a temperature of 150 °C.
- 6. Set the oven temperature at 70 $^{\circ}$ C.
- 7. Set the desired number of tubes in the reactor.
- 8. Turn on the toluene (100 ppm) tank and fix the flow rate to a required value.
- After waiting for two minutes start taking sample at the exit end of the reactor after every 5 minutes with varied sample volume ranging from 0.1 to 2.5 ml, with an increment of 0.1 ml, using a swage lock syringe.
- 10. Inject the sample in to the GC.
- 11. Hit the space bar key on the keyboard to initiate the run.
- 12. Peak simple integrates the peak area for every injected sample.

- 13. Plot mass injected (ordinate) and peak area (abscissa).
- 14. A sample of constant volume was injected atleast thrice to check the consistency of peak area.

Sample drawing procedure

- Insert the needle of a syringe with a swage lock in the sample drawing port.
- 2. Flush the needle five times to ensure that there is no residual air in the syringe.
- 3. Take the sample of maximum possible volume and pull syringe back from the port before turning off the swage lock.
- 4. Hand the syringe in the air with needle facing up and push the plunger to desired volume.
- 5. Lock the syringe.
- 6. Inject the sample into the GC inlet port.
 - a. Insert the needle in the injection port of GC.
 - b. Turn on the swage lock.
 - c. Inject the sample.
 - d. Pull the needle back.
- 7. Place the syringe in the needle cleaner until next sample is taken.

Destruction Experiment

- 1. Review material safety data sheets.
- Ensure all the electrical connections are secure before starting the experiment.
- 3. Turn on the hydrogen and helium (carrier) gas for starting GC.
- 4. Set the power supply at the desired primary voltage but do not leave it on.
- 5. Before starting the experiment, calibrate the GC (follow the procedure as described above).
- 6. Switch on the computer and have peak simple open on the computer screen.
- 7. Turn on the toluene tank, fix the flow rate to a required value and switch on the stop-watch.
- 8. Wait for 2 minutes to ensure that there is no oxygen inside the reactor
- 9. Draw the first sample of 1.1 ml using a swage lock syringe at the reactor exit
- 10. Inject the sample into the GC (follow the sample drawing procedure as described above).
- 11. Push the space bar key to initiate the run.
- 12. As soon as peak simple integrates the area, save the information and end the run.
- 13. At the 10th minute in the stop watch, draw the second sample of same volume (1.1 ml) at the reactor exit
- 14. Switch on the power supply after drawing sample and reset the stop-watch. Record the electrical data at this point namely Current and voltage on the

wall plug, current at the primary side of the transformer, and fluke meter reading. This sample is taken to analyze the TRE as soon as the reactor is turned on.

- 15. Again at the 8th minute in the stop-watch draw a sample from the reactor's inlet and inject it into the GC.
- 16. At 24th minute at the reactor exit and as soon as sample is taken turn off the power supply after reducing the amplitude to zero and inject the sample in the GC.
- 17. At 32nd minute take last exit sample and inject in the GC.
- 18. Mass of toluene injected in the GC from the sampling port can be calculated using the calibration data of the GC (described above).
- 19. TRE is calculated by knowing the mass of toluene present in the inlet and outlet sampling ports.
- 20. These steps are followed for all the experiments with different values assigned to the variables.

Amount of ozone generated

- 1. Collection of the sample:
 - a. Collect 400 ml of KI solution in 2 gas washing bottles, each with 400 ml.
- 2. Absorption of ozone:

- a. Pass the effluent stream from the reactor exit through the two gas washing bottles in series, until the second bottle just begin to turn yellow.
- 3. Titration
 - a. To reduce pH of the collected KI sample, add 20 ml of 1N H_2SO_4 , transfer the solution to 4 containers (100 ml each, except for the last container, which will have a few ml more than the rest of the 3 containers, because of added H_2SO_4).
 - b. Titrate the solution in all 4 containers with $0.005N Na_2S_2O_3$ titrant until the yellow color of discharged iodine is almost discharged.
 - c. Add 4 ml of starch indicator solution and keep titrating to the end point, where blue color disappears.
- 4. Blank test
 - a. Take 400 ml KI solution, and add 20 ml 1N $\rm H_2SO_4$ and 4 ml of starch indicator solution to it.
 - i. If blue color appears, titrate with 0.005N $Na_2S_2O_3$ until blue color disappears
 - ii. If no blue color appears, titrate with 0.005 N iodine solution until a blue color appears. Titrate the resulting solution with 0.005N Na₂S₂O₃ until blue disappears. Record the difference.
- 5. Calculation of amount of ozone generation

a. mg O₃ / L =
$$\frac{(A \pm B) * N * 24000}{\text{ml sample}}$$

Equation A-1

Where,

A = ml titrant for sample

B = ml titrant for blank test (positive or negative)

 $N = normality of Na_2S_2O_3$

The precision of this test is $\pm 1\%$ for concentrations of 3 mg O₃/l or greater.

6. Standardization of 0.1 N Na₂S₂O₃

Dichromate method:

- a. 0.1N K₂Cr₂O₇ solution:
 - Add 4.904 g anhydrous potassium dichromate K₂Cr₂O₇, of primary standard quality to deionized water then dilute it to 1000 ml to make 0.1N K₂Cr₂O₇.
- b. Add 10 ml 0f 0.1N K₂Cr₂O₇, 1 g of KI, and 1 ml of concentrated H_2SO_4 to 80 ml of deionized water with continuous stirring.
- c. Let the mixture sit for 6 minutes in dark.
- d. Titrate with $0.1N Na_2S_2O_3$ titrant.
- e. Normality of Na₂S₂O₃ = $\frac{1}{ml Na_2S_2O_3 \text{ consumed}}$ Equation A-2

Summa canister sample collection

- 1. Turn-off the electrical devices and gas flows.
- 2. Take both the pressure gauges off the plumbing system.
- 3. Fix two summa canisters in place of pressure gauges.
- 4. Start the experiment
- 5. When it's the time to take the sample, turn the side-flip-knob up.
- 6. As soon as the hissing sound of the gas goes-off, turn the flip-knob down.
- 7. Simililarly take the sample in the other summa canister too.
- 8. When the experiment is over, take the summa canisters out of the system.

CALIBRATION CURVE

A known mass of toluene was injected into the GC and it was plotted against the peak area of toluene. The same relationship was used to calculate the mass of toluene in the unknown sample. The calibration curve was very useful to calculate the mass of toluene in the destructed effluent sample from the reactor and therefore the removal efficiency of the plasma reactor.



Injection Vol (mL)	Mass (ng)	Time (min)	Area	Average Time	Average area	
0.1	38	3.18	136	3 17	137	
0.1	50	3.15	139	5.17	157	
0.5	188	-	1,188	3 1 2	1 107	
0.5	100	3.12	1,207	5.12	1,107	
1.0	377	3.13	2,804	3 1 2	2 805	
1.0	577	3.11	2,806	5.12	2,005	
15	565	3.10	4,102	3 17	4 080	
1.5	202	3.23	4,076	5.17	7,009	

Mass of toluene (ng)

 $= \frac{\text{Sample volume (ml)*10}^{-3} * \text{Mol. wt.(g/mol) *Conc.(ppm)* Density of air (kg/m^3)}}{10^6 \text{ kg of air* Molecular weight of air (kg/mol)*1000}}$

For a sample of 0.1 ml from the 100 ppm toluene tank,

Mass of toluene = $\frac{0.1 \text{ ml}^*.001^*92.14 \text{ g/mol}^*100 \text{ ppm}^*1.185 \text{ kg/m}^3}{106 \text{ kg} * 0.029 \text{ kg/mol}^*1000} = 38 \text{ ng}$

REYNOLDS NUMBER CALCULATION

Reynolds number = $\frac{\text{Annular diameter (m)}}{\text{Kinematic viscosity of air (m²/s)}} * \frac{\text{Flow rate of air (m³/s)}}{\text{Annular area (m²)}}$ Annular diameter = Outer diameter (m) - Inner diameter (m) Annular crossectional area = $\Pi/4$ * (Annular diameter)² Annular diameter = (10-6.32)*.001 m = 0.00368 m Annular crossectional area = $\Pi/4$ * (0.00368 m)² = $1.06*10^{-5}$ m² Flow rate = $0.97 * 10^{-5}$ m³/s Kinematic viscosity of air at room temperature = $1.56 * 10^{-5}$ m²/s Reynolds number = $0.00368 * \frac{0.97 * 10^{-5}}{1.06*10^{-5}} * \frac{1}{1.56 * 10^{-5}} = 215$

POWER RATIO CALCULATION

Power = Voltage * Current * cosine (phase angle)

Power ratio = $\frac{\text{Secondary power (calculated after transformer)}}{\text{Wall power (calculated before AC power supply)}}$

OZONE CALCULATION

mg O₃ / L =
$$\frac{(A \pm B)* N* 24000}{\text{ml sample}}$$

Where,

A = ml titrant for sample

B = ml titrant for blank test (positive or negative)

 $N = normality of Na_2S_2O_3$

for A = 84.7 ml, B = 5.35 ml, N = 0.005 N, and sample volume = 400 ml

mg O₃/L = $\frac{(84.7-5.35)*0.005}{400}$ = 23.8 mg/L

100 ppmv @ dry air data

<u>1.</u>		,
Concentration into		
reactor =	100	ppm
Number of Tubes =	8	tubes
Volume per tube =	47.30	mL per tube
Flow Through Reactor =	5,321	mL/min
retention time =	4.3	sec
Wall Voltage =	123.1	Volts
Primary Voltage =	72	Volts
Secondary Voltage =	9,000	Volts
Wall Current =	5.06	Amps
Primary Current =	1.20	Amps
Resistor =	100	Ohms
Measured Δ Volts =	0.987	Volts
Secondary Current =	10	Mamps
Wall Power =	622.886	volt-amps
Primary Power =	86.4	volt-amps
Secondary Power =	88.83	volt-amps
Temperature =	25	°C
MW Toluene =	92.14	gm



Concentration into reactor =	100	Ppm
Number of Tubes =	8	Tubes
Volume per tube =	47.30	mL per tube
Flow Through Reactor =	5,321	mL/min
retention time =	4.3	Sec
Wall Voltage =	122.1	Volts
Primary Voltage =	117	Volts
Secondary Voltage =	14,625	Volts
Wall Current =	6.59	Amps
Primary Current =	1.77	Amps
Resistor =	100	Ohms
Measured Δ Volts =	1.472	Volts
Secondary Current =	15	Mamps
Wall Power =	804.639	volt-amps
Primary Power =	207.09	volt-amps
Secondary Power =	215.28	volt-amps
Temperature =	25	°C
MW Toluene =	92.14	



Concentration into reactor =	100	Ppm
Number of Tubes =	8	Tubes
Volume per tube =	47.30	mL per tube
Flow Through Reactor =	12,283	mL/min
retention time =	1.8	Sec
Wall Voltage =	121.5	Volts
Primary Voltage =	72	Volts
Secondary Voltage =	9,000	Volts
Wall Current =	4.91	Amps
Primary Current =	1.19	Amps
Resistor =	100	Ohms
Measured Δ Volts =	0.996	Volts
Secondary Current =	10	Mamps
Wall Power =	596.565	volt-amps
Primary Power =	85.68	volt-amps
Secondary Power =	89.64	volt-amps
Temperature =	25	°C
MW Toluene =	92.14	



<u>4.</u>

Concentration into reactor =	100	Ppm
Number of Tubes =	8	Tubes
		mL per
Volume per tube =	47.30	tube
Flow Through Reactor =	12,283	mL/min
Retention time =	1.8	Sec
Wall Voltage =	121.5	Volts
Primary Voltage =	117	Volts
Secondary Voltage =	14,625	Volts
Wall Current =	6.60	Amps
Primary Current =	1.75	Amps
Resistor =	100	Ohms
Measured Δ Volts =	1.478	Volts
Secondary Current =	15	Mamps
Wall Power =	801.9	volt-amps
Primary Power =	204.75	volt-amps
Secondary Power =	216.1575	volt-amps
Temperature =	25	°C
MW Toluene =	92.14	



Concentration into reactor =	100	ppm
Number of Tubes =	2	Tubes
		mL per
Volume per tube =	47.30	tube
Flow Through Reactor =	1,164	mL/min
Retention time =	4.9	Sec
Wall Voltage =	122	Volts
Primary Voltage =	72	Volts
Secondary Voltage =	9,000	Volts
Wall Current =	5.51	Amps
Primary Current =	1.34	Amps
Resistor =	100	Ohms
Measured Δ Volts =	1	Volts
Secondary Current =	10	Mamps
		volt-
Wall Power =	672.22	amps
		Volt-
Primary Power =	96.48	amps
		Volt-
Secondary Power =	93.96	amps
Temperature =	25	°C
MW Toluene =	92.14	



<u>6.</u>

Concentration into reactor =	100	Ppm
Number of Tubes =	2	Tubes
Volume per tube =	47.30	mL per tube
Flow Through Reactor =	1,164	mL/min
retention time =	4.9	Sec
Wall Voltage =	121	Volts
Primary Voltage =	117	Volts
Secondary Voltage =	14,625	Volts
Wall Current =	7.10	Amps
Primary Current =	1.95	Amps
Resistor =	100	Ohms
Measured Δ Volts =	1.600	Volts
Secondary Current =	16	Mamps
Wall Power =	856.97	volt-amps
Primary Power =	228.15	volt-amps
Secondary Power =	234	volt-amps
Temperature =	25	°C
MW Toluene =	92.14	



<u>7.</u>

Concentration into reactor =	100	Ppm
Number of Tubes =	2	Tubes
Volume per tube =	47.30	mL per tube
Flow Through Reactor =	3,936	mL/min
retention time =	1.4	Sec
Wall Voltage =	122	Volts
Primary Voltage =	72	Volts
Secondary Voltage =	9,000	Volts
Wall Current =	5.240	Amps
Primary Current =	1.310	Amps
Resistor =	100	Ohms
Measured Δ Volts =	1.065	Volts
Secondary Current =	11	Mamps
Wall Power =	641.38	volt-amps
Primary Power =	94.32	volt-amps
Secondary Power =	95.85	volt-amps
Temperature =	25	°C
MW Toluene =	92.14	



Concentration into reactor =	100	Ppm
Number of Tubes =	2	Tubes
		mL per
Volume per tube =	47.30	tube
Flow Through Reactor =	3,936	mL/min
retention time =	1.4	Sec
Wall Voltage =	122.4	Volts
Primary Voltage =	117.0	Volts
Secondary Voltage =	14,625	Volts
Wall Current =	7.05	Amps
Primary Current =	1.91	Amps
Resistor =	100	Ohms
Measured Δ Volts =	1.569	Volts
Secondary Current =	16	Mamps
Wall Power =	862.92	volt-amps
Primary Power =	223.47	volt-amps
Secondary Power =	229.46625	volt-amps
Temperature =	25	°C
MW Toluene =	92.14	



Concentration into reactor =	100	Ppm
Number of Tubes =	5	Tubes
Volume per tube =	47.30	mL per tube
Flow Through Reactor =	5,321	mL/min
retention time =	2.7	Sec
Wall Voltage =	122.4	Volts
Primary Voltage =	96	Volts
Secondary Voltage =	12,000	Volts
Wall Current =	5.94	Amps
Primary Current =	1.55	Amps
Resistor =	100	Ohms
Measured Δ Volts =	1.270	Volts
Secondary Current =	13	Mamps
Wall Power =	727.056	volt-amps
Primary Power =	148.8	volt-amps
Secondary Power =	152.4	volt-amps
Temperature =	25	°C
MW Toluene =	92.14	



Concentration into reactor		
=	100	Ppm
Number of Tubes =	5	Tubes
Volume per tube =	47.30	mL per tube
Flow Through Reactor =	5,321	mL/min
retention time =	2.7	Sec
Wall Voltage =	121.8	Volts
Primary Voltage =	96	Volts
Secondary Voltage =	12,000	Volts
Wall Current =	5.88	Amps
Primary Current =	1.57	Amps
Resistor =	100	Ohms
Measured Δ Volts =	1.274	Volts
Secondary Current =	13	Mamps
Wall Power =	716.184	volt-amps
Primary Power =	150.72	volt-amps
Secondary Power =	152.88	volt-amps
Temperature =	25	°C
MW Toluene =	92.14	



Concentration into reactor =	100	Ppm
Number of Tubes =	5	Tubes
Volume per tube =	47.30	mL per tube
Flow Through Reactor =	5,321	mL/min
retention time =	2.7	Sec
Wall Voltage =	122.1	Volts
Primary Voltage =	96	Volts
Secondary Voltage =	12,000	Volts
Wall Current =	5.98	Amps
Primary Current =	1.53	Amps
Resistor =	100	Ohms
Measured Δ Volts =	1.278	Volts
Secondary Current =	13	Mamps
Wall Power =	730.158	volt-amps
Primary Power =	146.88	volt-amps
Secondary Power =	153.36	volt-amps
Temperature =	25	°C
MW Toluene =	92.14	



Summary:

		primary		secondary			wall					
Expt no.	tubes	voltage, V	current, Amps	Instantaneous power, W	voltage, V	current, Amps	phase radian	power, W	voltage, V	current, Amps	phase radian	power, w
1	8	72	1.20	86.40	9000	0.010	-0.72	277.28	123.10	5.06	-0.71	472.37
2	8	117	1.77	207.09	14625	0.015	-0.73	399.02	122.10	6.59	-0.70	615.42
3	8	72	1.19	85.68	9000	0.010	-0.72	256.64	121.50	4.91	-0.71	452.41
4	8	117	1.75	204.75	14625	0.015	-0.73	396.93	121.50	6.60	-0.70	613.33
5	2	72	1.34	96.48	9000	0.010	-0.72	314.02	122.00	5.51	-0.71	509.79
6	2	117	1.95	228.15	14625	0.016	-0.73	446.18	121.00	7.10	-0.69	662.58
7	2	72	1.31	94.32	9000	0.011	-0.72	289.04	122.00	5.24	-0.71	484.81
8	2	117	1.91	223.47	14625	0.016	-0.73	449.12	122.40	7.05	-0.69	665.52
9	5	96	1.55	148.80	12000	0.013	-0.72	349.49	122.40	5.94	-0.70	556.08
10	5	96	1.57	150.72	12000	0.013	-0.72	341.17	121.80	5.88	-0.70	547.77
11	5	96	1.53	146.88	12000	0.013	-0.72	351.86	122.10	5.98	-0.70	558.46

Power ratio	flow rate, ml/min	velocity, m/s	Reynolds	N0 ppmv	N ppmv	LN(N0/N)	P/Q
0.59	5321	0.24	117	91.740	62.630	-0.382	974.253
0.65	5321	0.24	117	95.200	21.290	-1.498	2335.163
0.57	12283	0.54	270	88.780	71.780	-0.213	418.530
0.65	12283	0.54	270	99.280	56.420	-0.565	1000.163
0.62	1164	0.21	102	96.410	1.770	-3.998	4973.196
0.67	1164	0.21	102	75.800	0.000	-13.538	11760.309
0.60	3936	0.70	346	120.000	17.557	-1.922	1437.805
0.67	3936	0.70	346	92.890	1.470	-4.146	3406.555
0.63	5321	0.38	187	84.330	34.190	-0.903	1677.880
0.62	5321	0.38	187	95.020	37.490	-0.930	1699.530
0.63	5321	0.38	187	97.660	37.060	-0.969	1656.230

% Efficiency	retention time	Energy density, J/ml	Mass Removed (ng)	ng/KWh/tube	applied volts, KV	ppm removed
31.731	4.300	0.666	120.6	1.127E-08	0.009	29.110
77.637	4.300	0.867	306.2	1.194E-08	0.015	73.910
19.148	1.800	0.276	72.9	1.641E-08	0.009	17.000
43.171	1.800	0.374	177.6	1.673E-08	0.015	42.860
98.164	4.900	13.139	394.7	1.160E-07	0.036	94.640
100.000	4.900	17.077	364.6	4.530E-08	0.059	75.800
85.369	1.400	3.695	424.9	4.469E-07	0.036	102.443
98.417	1.400	5.073	378.8	1.682E-07	0.059	91.420
59.457	2.700	1.254	207.3	2.867E-08	0.019	50.140
60.545	2.700	1.235	238.3	3.253E-08	0.019	57.530
62.052	2.700	1.259	251.9	3.529E-08	0.019	60.600

100 ppmv @ humid air (30-50% RH) data

12.		- · · · ·
Concentration into		
reactor =	100	ppm
Number of Tubes =	2	tubes
Volume per tube =	47.30	mL per tube
Flow Through Reactor $=$	3,936	mL/min
retention time =	1.4	sec
Wall Voltage =	122	Volts
Primary Voltage =	72	Volts
Secondary Voltage =	9,000	Volts
Wall Current =	5.470	Amps
Primary Current =	1.360	Amps
Resistor =	100	Ohms
Measured Δ Volts =	1.083	Volts
Secondary Current =	11	Mamps
Wall Power =	666.79	volt-amps
Primary Power =	97.92	volt-amps
Secondary Power =	97.47	volt-amps
Temperature =	25	°C
Humidity =	30-50	%
MW Toluene =	92.14	



Concentration into reactor =	100	ppm
Number of Tubes =	2	tubes
Volume per tube =	47.30	mL per tube
Flow Through Reactor =	3,936	mL/min
retention time =	1.4	sec
Wall Voltage =	121	Volts
Primary Voltage =	117	Volts
Secondary Voltage =	14,625	Volts
Wall Current =	7.200	amps
Primary Current =	1.950	amps
Resistor =	100	ohms
Measured Δ Volts =	1.591	Volts
Secondary Current =	16	mamps
Wall Power =	874.08	volt-amps
Primary Power =	228.15	volt-amps
Secondary Power =	232.68	volt-amps
Temperature =	25	°C
Humidity =	30-50	%
MW Toluene =	92.14	



Concentration into reactor =	100	ppm
Number of Tubes =	5	tubes
Volume per tube =	47.30	mL per tube
Flow Through Reactor =	5,321	mL/min
retention time =	2.7	sec
Wall Voltage =	123	Volts
Primary Voltage =	96	Volts
Secondary Voltage =	12,000	Volts
Wall Current =	6.220	amps
Primary Current =	1.590	amps
Resistor =	100	ohms
Measured Δ Volts =	1.296	Volts
Secondary Current =	13	mamps
Wall Power =	761.95	volt-amps
Primary Power =	152.64	volt-amps
Secondary Power =	155.52	volt-amps
Temperature =	25	°C
Humidity =	30-50	%
MW Toluene =	92.14	



Summary:

exp	retention time,s	number of tubes	primary voltage	% Relative humidity	average TRE
11	1.4	2	72	30-50%	100
12	1.4	2	117	30-50%	100
13	2.7	5	96	30-50%	100

240 ppmv @ dry air data

15.	• •	
Concentration into reactor		
=	240	ppm
Number of Tubes =	2	tubes
Volume per tube =	47.30	mL per tube
Flow Through Reactor =	3,936	mL/min
retention time =	1.4	sec
Wall Voltage =	121.6	Volts
Primary Voltage =	117	Volts
Secondary Voltage =	14,625	Volts
Wall Current =	7.09	amps
Primary Current =	1.94	amps
Resistor =	100	ohms
Measured Δ Volts =	1.580	Volts
Secondary Current =	16	mamps
Wall Power =	862.144	volt-amps
Primary Power =	226.98	volt-amps
Secondary Power =	231.075	volt-amps
Temperature =	25	°C
MW Toluene =	92.14	



Concentration into reactor =	240	ppm
Number of Tubes =	5	tubes
Volume per tube =	47.30	mL per tube
Flow Through Reactor =	5,321	mL/min
retention time =	2.7	sec
Wall Voltage =	121.6	Volts
Primary Voltage =	96	Volts
Secondary Voltage =	12,000	Volts
Wall Current =	6.76	amps
Primary Current =	1.83	amps
Resistor =	100	ohms
Measured Δ Volts =	1.497	Volts
Secondary Current =	15	mamps
Wall Power =	822.016	volt-amps
Primary Power =	175.68	volt-amps
Secondary Power =	179.64	volt-amps
Temperature =	25	°C
MW Toluene =	92.14	


<u>17.</u>

Concentration into reactor		
=	240	ppm
Number of Tubes =	8	tubes
Volume per tube =	47.30	mL per tube
Flow Through Reactor =	5,321	mL/min
retention time =	4.3	sec
Wall Voltage =	121.9	Volts
Primary Voltage =	117	Volts
Secondary Voltage =	14,625	Volts
Wall Current =	6.65	amps
Primary Current =	1.76	amps
Resistor =	100	ohms
Measured Δ Volts =	1.476	Volts
Secondary Current =	15	mamps
Wall Power =	810.635	volt-amps
Primary Power =	205.92	volt-amps
Secondary Power =	215.865	volt-amps
Temperature =	25	°C
MW Toluene =	92.14	



Summary:

exp	retention time,s	number of tubes	primary voltage	% Relative humidity	average TRE	concentration
15	1.4	2	117	0%	92	240
16	2.7	5	96	0%	44	240
17	4.3	8	117	0%	36	240

APPENDIX-9

GAS CERTIFICATES

	3- 244		CERTIFIEI	WORKING CLA
Scott Specialty (Gases	·	Single-Certified	Calibration Standard
9810 BAY AREA BLVD, PASADENA, T	X 77507		Phone: 281-474-5800	Fax: 281-474-5857
	Cortified	Working	n Class Calibrativ	on Standard
CERTIFICATE OF ACCONACT.	Certified	WORKIN		
Project No.: 04-50145-001			Customer	No.
Item No.: 04023912 TAL P.O. No.: TFANCHER 120406			OKLAHOMA STATE TAMYRA FANCHER/	UNIVERSITY ENV ENG.
Cylinder Number: ALM052781			207 ENGINEERING S	OUTH 74078
Certification Date: 19Dec2006 Expiration Date: 01Jan2009		~		
CERTIFIED CONCENTRATION		and the second		
Component Name	(Moles)		<u>(+/-%)</u>	
TOLUENE	240.	PPM BALANCE	5	the first state
TRACEABILITY				
Traceable To				
Scott Reference Standard				
				1
				· · · · · · · · · · · · · · · · · · ·
	2			
APPROVED BY:	Bane	<u> </u>	DATE: _12	-19-06
APPROVED BY:	Band	<u>Un</u>	DATE: _12	-19-06
APPROVED BY:	Bane	<u>La</u>	DATE: _12	-19-06

APPENDIX-10

REMOVAL EFFICIENCY MODEL

								A*B ([IJ.)		
	B, number of tubes,j					В	, j				
	2 8			A, i	2	8	av	y.j.	d.j.		
		С, р	rimary v	oltage	e,k	1.6	0.915	0.31	5 0.0	515	-0.064
A, re	t. time,i	72	117	72	117	4.6	0.985	0.5	0.7	425	0.0638
	1.6	0.85	0.98	0.2	0.43	yi	0.95	0.40	8 0.6	788	
	4.6	0.98	0.99	0.3	0.7	di	0.2713	-0.2	7		
		A*C (I.K	(.)					B*C (J.k	()		
	С,	k					С,	k			
A, i	72	117	yk	d	.k	В, ј	72	117	yk	d	k
1.6	0.525	0.705	0.615	0.06	375	2	0.915	0.985	0.95	0.2	71
4.6	0.64	0.845	0.7425	0.06	375	8	0.25	0.565	0.4075	-0.2	27
yi	0.5825	0.775	0.67875			у.j.	0.5825	0.775	0.6788		
di	0.09625	0.09625				d.j.	0.0962	0.096			

100 ppm @ dry air

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TUKEY'S TEST

					Fo from F-	SSN	8.65E-03
Source of					Table @(significanc	ΣΣΣ Υ	5.43
variation	SS	df	MS	Fo	level = 0.25)		/.3/1225
Α	-7.3712	1	-7.3712	-0.3845037	5.83		4.4283
В	-7.3712	1	-7.3712	-0.3845037	5.83	[A] [B]	0
С	-7.3712	1	-7.3712	-0.3845037	5.83	[0]	0
Non-addi	8.65E-03	1	0.00865	0.00045116	5.83	SST	-2 942925
Error	19.1708	1	19.1708			SSA	-7 371225
Total	-2.9429	7				SSB	-7 371225
						SSC	-7.371225
						SSRES	19.17075
						SSREM	19.16
						dfNONAD	1
						dfRES	1

OZONE GENERATION MODEL

expt no.	tubes	wall voltage, V	current, Amps	power, W	Mass Removed (ng)	flow rate,ml/ min	Retenti on Time (s)	Mas removed per tube, g/KWhr	mg O3/L air
1	8	123.10	5.06	622.89	120.6	5321	4.3	2.03E-05	1.70
2	8	122.10	6.59	804.64	306.2	5321	4.3	3.98E-05	5.00
3	8	121.50	4.91	596.57	72.9	12283	1.8	3.05E-05	0.94
4	8	121.50	6.60	801.90	177.6	12283	1.8	5.54E-05	0.77
5	2	122.00	5.51	672.22	394.7	1164	4.9	0.000216	2.37
6	2	121.00	7.10	859.10	364.6	1164	4.9	0.000156	10.80
7	2	122.00	5.24	639.28	424.9	3936	1.4	0.000855	5.05
8	2	122.40	7.05	862.92	378.8	3936	1.4	0.000564	9.51
9	5	122.40	5.94	727.06	207.3	5321	2.7	7.6E-05	4.47
10	5	121.80	5.88	716.18	238.3	5321	2.7	8.87E-05	5.20
11	5	122.10	5.98	730.16	251.9	5321	2.7	9.2E-05	4.78

100 ppm @ dry air

		B number o	of tubes,j		
		b1		b2	
		C, primary	voltage,k		
	A, ret. time,i	c1	c2	c1	c2
	a1	1.87	2.6	1.161	0.7085
	a2	0.246	0.878	0.87	1.982
ABC SUMM	IARY TABLE			average	
		c1	c2	y.k.	d.k.
		a1	a2		
	b1	1.87	0.878	1.374	-1.204403146
		a2	al		
	b2	0.87	0.7085	0.789	-1.789153146
		a2	a1		
	b1	0.246	2.6	1.423	-1.155403146
		a1	a2		
	b2	1.161	1.982	1.572	-1.006903146
average	yl	1.03675	1.542125	2.578	
	dl	-1.54165315	-1.036278146		

djkl	SUMMARY	TABLE:	SSNONA	DD 4.91321467
	c1	c2	yjkl	10.3136126
b1	a1	a2	[y]	26.5926511
	-1.80723	-1.93726	[ABC]	17.6169323
b2	a2	a1	[A]	27.9989181
	-3.41482	-1.43937	[B]	26.7926991
b1	a2	a1	[C]	27.6240006
	-2.88203	-1.21479	SSTO	-8.97571887
b2	a1	a2	SSA	1.40626699
	2.929704	-2.2954	SSB	0.20004799
			SSC	1.03134949
			SSRES	-11.6133833
			SS ERR	-16.526598

TUKEY'S TEST

Source of variation	SS	df	MS	Fo
Dotontion time	1 406267		1 406267	0.17010
Recencion ume	1.406267	1	1.406267	-0.17018
Number of tubes	0.200048	1	0.200048	-0.02421
Primay voltage	1.031349	1	1.031349	-0.12481
Residual	-11.6134	1	-11.6134	1.40542
Non-addi	4.913215	1	4.913215	-0.59458
Error	-16.5266	2	-8.2633	
Total	-8.97572	7		

APPENDIX-11

SUMMA CANISTERS' REPORT

Pace Analytical *

Pace Analytical Services, Inc. 1700 Elm Street, Suite 200 Minneapolis, MN 55414 Phone: (612)607-1700 Fax: (612)607-6444

January 30, 2007

John Veenstra Oklahoma State University 207 Engineering South Stillwater, OK 74078

RE: Project: PLASMA Pace Project No.: 1044833

Dear John Veenstra:

Enclosed are the analytical results for sample(s) received by the laboratory on January 15, 2007. Results reported herein conform to the most current NELAC standards, where applicable, unless otherwise narrated in the body of the report.

If you have any questions concerning this report, please feel free to contact me.

Sincerely, Frand Pater

Daryl Peterson

daryl.peterson@pacelabs.com Project Manager

Illinois Certification #: 200011 Iowa Certification #: 368 Minnesota Certification #: 027-053-137 Wisconsin Certification #: 999407970

Enclosures

cc: Artie Southern, Oklahoma State University School of Civil and Env. Engin.

REPORT OF LABORATORY ANALYSIS

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Pace Analytical Services, Inc. 1700 Eim Street, Suite 200 Minneapolis, MN 55414 Phone: (\$12)607-1700 Fac: (\$12)607-8444

ANALYTICAL RESULTS

Project: PLASMA				
Pace Project No.: 1044833				
Sample: 6973	Lab ID: 1044833001	Collected: 01/09/07 06:52	Received: 01/15/07 09:00 Matrix: Air	
Parameters	Results Units	Report Limit DF	Prepared Analyzed CAS No.	Qual
TO16 MSV AIR	Analytical Method: TO-15	;		
Acetone	28.2 ppbv	4.6 8.35	01/25/07 23:23 67-64-1	IC
Benzene	ND ppby	4.3 8.35	01/25/07 23:23 71-43-2	
Bromodichioromethane	ND ppby	4.3 8.35	01/25/07 23:23 75-27-4	
Bromoform	ND ppby	4.3 8.36	01/25/07 23:23 75-25-2	
Bromomethane	ND ppbv	4.3 8.36	01/25/07 23:23 74-83-9	
1,3-Butadiene	ND ppbv	4.3 8.36	01/25/07 23:23 106-99-0	
2-Butanone (MEK)	ND ppbv	4.6 8.35	01/25/07 23:23 78-93-3	
Carbon disulfide	ND ppbv	4.2 8.35	01/25/07 23:23 75-15-0	
Carbon tetrachloride	ND ppbv	4.3 8.35	01/25/07 23:23 56-23-5	88
Chlorobenzene	ND ppbv	4.3 8.35	01/25/07 23:23 108-90-7	
Chloroethane	ND ppbv	4.3 8.35	01/25/07 23:23 75-00-3	
Childroform	ND ppbv	4.3 8.36	01/25/07 23:23 67-66-3	
Chloromethane	15.9 ppbv	4.2 8.35	01/25/07 23:23 74-87-3	
Cyclohexane	ND ppbv	4.3 8.35	01/25/07 23:23 110-82-7	
Dibromochloromethane	ND ppbv	4.4 8.36	01/25/07 23:23 124-48-1	
1,2-Dibromoethane (EDB)	ND ppbv	4.3 8.36	01/25/07 23:23 105-93-4	
1,2-Dichlorobenzene	ND ppbv	4.3 8.36	01/25/07 23:23 95-50-1	
1,3-Dichlorobenzene	ND ppbv	4.3 8.35	01/25/07 23:23 541-73-1	
1,4-Dichlorobenzene	ND ppbv	4.3 8.36	01/25/07 23:23 105-46-7	
Dichlorodifuoromethane	ND ppby	4.3 8.35	01/25/07 23:23 75-71-8	
1,1-Dichlorbethane	ND ppbv	4.3 8.35	01/25/07 23:23 75-34-3	
1,2-Dichloroethane	ND ppby	4.3 8.35	01/25/07 23:23 107-06-2	
1,1-Dichloroethene	ND ppby	4.3 8.36	01/25/07 23:23 /5-35-4	
cis-1,2-Dichloroethene	ND ppov	4.3 8.36	01/25/07 23:23 156:59-2	
1 2-Dishlerosses	ND ppov	8.4 8.35	01/25/07 23:23 155-50-5	
sis-1 2-Dichlerenseese	ND ppby	4.3 0.30	01/25/07 23:25 76/67/5	
frank 1,3-Dichlerossnane	ND ppby	4.3 0.30	01/25/07 23:23 10051-01-5	
Dichlorofetrafluoroefhane	ND ppby	4.5 0.50	01/25/07 23:25 10061-02-6	
Ethyl acetate	ND poby	43 835	01/25/07 23-23 141-78-6	
Ethylacetate	ND poby	4.3 8.35	01/25/07 23:23 100-41-4	
4-Ethyltoluene	ND poby	4.4 8.35	01/25/07 23:23 622-96-8	
n-Heptane	ND peby	4.3 8.36	01/25/07 23:23 142-82-5	
Hexachloro-1,3-butadiene	ND ppby	4.2 8.35	01/25/07 23:23 87-68-3	IC
n-Hexane	5.8 poby	4.4 8.35	01/25/07 23:23 110-54-3	
2-Hexanone	ND poby	4.6 8.36	01/25/07 23:23 591-78-6	
Methylene Chloride	222 ppbv	86.5 166.4	01/25/07 22:48 75-09-2	88
4-Methyl-2-pentanone (MIBK)	ND ppby	4.6 8.35	01/25/07 23:23 108-10-1	
Methyl-tert-butyl ether	ND ppby	8.4 8.35	01/25/07 23:23 1634-04-4	
Propylene	ND ppbv	16.7 8.36	01/25/07 23:23 115-07-1	
Styrene	ND ppby	4.6 8.36	01/25/07 23:23 100-42-5	
1,1,2,2-Tetrachloroethane	ND ppbv	4.3 8.35	01/25/07 23:23 79-34-5	
Tetrachloroethene	ND ppbv	4.3 8.35	01/25/07 23:23 127-18-4	
Tetrahydrofuran	ND ppbv	4.3 8.35	01/25/07 23:23 109-99-9	
Toluene	7.3 ppbv	4.3 8.35	01/25/07 23:23 108-88-3	
1,2,4-Trichlorobenzene	ND ppbv	4.3 8.35	01/25/07 23:23 120-82-1	
1,1,1-Trichloroethane	ND ppbv	4.3 8.36	01/25/07 23:23 71-55-6	

Date: 01/30/2007 02:13 PM

REPORT OF LABORATORY ANALYSIS

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PLASMA

Pace Analytical Services, Inc. 1700 Elm Street, Suite 200 Minnespolis, NN 55414 Phone (612)607-1700 Fax: (612)607-6444

ANALYTICAL RESULTS

Project: PLASMA Pace Project No.: 1044833				
Sample: 6973	Lab ID: 1044833001	Collected: 01/09/07 05:5	52 Received: 01/15/07 09:00	Matrix: Air
Parameters	Results Units	Report Limit DF	Prepared Analyzed	CAS No. Qual
TO16 MSV AIR	Analytical Method: TO-15			
1,1,2-Trichiproethane	ND ppby	4.3 8.36	01/25/07 23:2	/3 79-00-5
Trichloroethene	ND ppby	4.3 8.35	01/25/07 23:2	3 79-01-6 88
Trichlorofluoromethane	ND ppby	4.2 8.35	01/25/07 23:2	3 75-69-4 CC
1,1,2-Trichlorotrifluoroethane	ND ppby	4.3 8.36	01/25/07 23:2	3 76-13-1
1,2,4-Trimethylpenzene	ND ppby	4,3 8.36	01/25/07 23:2	3 95-63-6
1,3,5-Trimethylbenzene	ND ppby	4.3 8.35	01/25/07 23:2	108-67-8
Vinyl acetate	ND ppby	4.6 8.36	01/25/07 23:2	13 108-05-4
Vinyl chloride	ND ppby	4.3 8.35	01/25/07 23:2	3 75-01-4
måp-Xylene	ND ppby	8.4 8.35	01/25/07 23:2	13 1330-20-7
o-Xylene	ND ppby	4,3 8.36	01/25/07 23:2	3 95-47-6

Date: 01/30/2007 02:13 PM

REPORT OF LABORATORY ANALYSIS

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Pace Analytical Services, Inc. 1700 Elm Street, Suite 200 Minneapolis, MN 55414 Phone: (612)607-1700 Fax: (612)607-6444

ANALYTICAL RESULTS

Project: PLASMA Pace Project No.: 1044833

Sample: 6853	Lab ID: 10448330	02 Collected: 01/09/0	07 06:57	Received: 01	/15/07 09:00 N	latrix: Air	
Parameters	Results U	nits Report Limit	DF	Prepared	Analyzed	CAS No.	Qual
TO16 MSV AIR	Analytical Method: T	0-15					
Acetone	129 ppbv	34.3	62.4		01/25/07 23:54	67-64-1	IC
Benzene	ND ppbv	32.4	62.4		01/25/07 23:54	71-43-2	
Bromodichioromethane	ND ppbv	31.8	62.4		01/25/07 23:54	75-27-4	
Bromoform	ND ppbv	32.4	62.4		01/25/07 23:54	75-25-2	
Bromomethane	ND ppbv	31.8	62.4		01/25/07 23:54	74-83-9	
1,3-Butadiene	ND ppbv	32.4	62.4		01/25/07 23:54	106-99-0	
2-Butanone (MEK)	ND ppbv	34.3	62.4		01/25/07 23:54	78-93-3	
Carbon disulfide	ND ppbv	31.2	62.4		01/25/07 23:54	75-15-0	
Carbon tetrachioride	ND ppbv	31.8	62.4		01/25/07 23:54	56-23-5	88
Chlorobenzene	ND ppbv	32.4	62.4		01/25/07 23:54	108-90-7	
Chloroethane	ND ppby	31.8	62.4		01/25/07 23:54	75-00-3	
Chioroform	ND ppbv	31.8	62.4		01/25/07 23:54	67-66-3	
Chloromethane	ND ppby	31.2	62.4		01/25/07 23:54	74-87-3	
Cyclohexane	ND poby	32,4	62.4		01/25/07 23:54	110-82-7	
Dibromochloromethane	ND ppby	33.1	62.4		01/25/07 23:54	124-48-1	
1.2-Dibromoethane (EDB)	ND poby	32.4	62.4		01/25/07 23:54	106-93-4	
1.2-Dichlorobenzene	ND poby	31.8	62.4		01/25/07 23:54	95-50-1	
1.3-Dichlorobenzene	ND poby	31.8	62.4		01/25/07 23:54	541-73-1	
1.4-Dichlorobenzene	ND poby	31.8	62.4		01/25/07 23:54	105-46-7	
Dichlorodifluoromethane	ND ppby	31.8	62.4		01/25/07 23:54	75-71-8	
1.1-Dichlorpethane	ND poby	32,4	62.4		01/25/07 23:54	75-34-3	
1.2-Dichlorpethane	ND poby	32.4	62.4		01/25/07 23:54	107-06-2	
1.1-Dichlorpethene	ND poby	32,4	62.4		01/25/07 23:54	75-35-4	
cis-1.2-Dichlorgethene	ND poby	32.4	62.4		01/25/07 23:54	156-59-2	
trans-1.2-Dichlomethene	ND poby	62.4	62.4		01/25/07 23:54	156-60-5	
1.2-Dichloropropane	ND poby	32,4	62.4		01/25/07 23:54	78-87-5	
cis-1.3-Dichloropropene	ND poby	31.8	62.4		01/25/07 23:54	10061-01-9	
trans-1 3-Dichlomoronene	ND ppby	32.4	62.4		01/25/07 23:54	10061-02-6	
Dichlorotetrafluorpethane	ND poby	35.6	62.4		01/25/07 23:54	76-14-2	
Ethvi acetate	ND poby	31.8	62.4		01/25/07 23:54	141-78-6	
Ethylbenzene	ND ppby	37.4	67.4		01/25/07 23:54	100-41-4	
4-Ethyltoluene	ND poby	33.1	62.4		01/25/07 23:54	622-96-8	
n-Heptane	ND poby	32.4	62.4		01/25/07 23:54	142-82-5	
Hexachloro-1.3-butadiene	ND poby	31.2	62.4		01/25/07 23:54	87-68-3	IC
n-Hexane	39.1 poby	33.1	62.4		01/25/07 23:54	110-54-3	
2-Hexanone	ND poby	34.3	62.4		01/25/07 23:54	591-78-6	
Methylene Chloride	197 poby	32.4	62.4		01/25/07 23:54	75-09-2	33
4-Methyl-2-pentanone (MIBK)	ND poby	34.3	62.4		01/25/07 23:54	108-10-1	
Methyl-tert-butyl ether	ND poby	57.4	67.4		01/25/07 23-54	1634-04-4	
Propylene	ND poby	125	62.4		01/25/07 23:54	115-07-1	
Styrene	ND poby	34.3	62.4		01/25/07 23:54	100-42-5	
1.1.2.2-Tetrachiomethane	ND poly	32.4	62.4		01/25/07 23-54	79-34-5	
Tetrachloroethene	ND poly	32.4	62.4		01/25/07 23-54	127-18-4	
Tetrahydrofuran	ND only	37.4	62.4		01/25/07 23-54	109-99-9	
Thuene	113000 ppby	44ED	7999		01/26/07 14-10	108-89-3	A3
1.2.4-Trichinmhenzene	ND notw	32.4	62.4		01/25/07 23-54	120-82-1	~
1.1.1-Trichiomethane	ND mshu	32.4	67.4		01/25/07 23-54	71-55-5	
Date: 01/30/2007 02:13 PM	REPOR	T OF LABORATORY		YSIS			Page 6 of 12

REPORT OF LABORATORY ANALYSIS

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ANALYTICAL RESULTS

Project: PLASMA Pace Project No.: 1044833

Sample: 6953	Lab ID: 1044833602	Collected: 01/09/07	06:57	Received: 01/15/07	09:00	Matrix: Air	
Parameters	Results Units	Report Limit	DF	Prepared An	slyzed	CAS No.	Qua
TO16 MSV AIR	Analytical Method: TO-15						
1,1,2-Trichloroethane	ND ppby	32,4 6	2.4	01/25	07 23:54	79-00-5	
Trichloroethene	ND ppby	32,4 6	2.4	01/25	07 23:54	79-01-6	88
Trichiorofluoromethane	ND ppby	31.2 6	2.4	01/25	07 23:54	75-69-4	00
1,1,2-Trichlorotrifluoroethane	ND ppby	32.4 6	2.4	01/25	07 23:54	76-13-1	
1,2,4-Trimethyloenzene	ND ppby	31.8 6	2.4	01/25	07 23:54	95-63-6	
1,3,5-Trimethylbenzene	ND ppby	32,4 6	2,4	01/25	07 23:54	108-67-8	
Vinyl acetate	ND ppby	34.3 6	2.4	01/25	07 23:54	108-05-4	
Vinyl chloride	ND ppby	31.8 6	2.4	01/25	07 23:54	75-01-4	
måp-Xylene	ND ppby	62,4 6	2.4	01/25	07 23:54	1330-20-7	
o-Xylene	ND ppby	32.4 6	2.4	01/25	07 23 54	95-47-6	

Date: 01/30/2007 02:13 PM

REPORT OF LABORATORY ANALYSIS

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QUALITY CONTROL DATA

Project:	PLASMA
Pace Project No.:	1044833

 QC Batch:
 AJR/5105

 QC Batch Method:
 TO-15

 Associated Lab Bamples:
 1044833001, 1044833002

Analysis Method: TO-15 Analysis Description: TO15 MBV AIR

METHOD BLANK: 305269

Associated Lab Samples: 1044833001, 1044833002

		Blank	Reporting	
Parameter	Units	Result	Limit	Qualifiers
1,1,1-Trichloroethane	ppbv	ND	0.52	
1,1,2,2-Tetrachiproethane	ppbv	ND	0.52	
1,1,2-Trichloroethane	ppbv	ND	0.52	
1,1,2-Trichlorofrifuoroethane	ppbv	ND	0.52	
1,1-Dichloroethane	ppbv	ND	0.52	
1,1-Dichloroethene	ppbv	ND	0.52	
1,2,4-Trichlorobenzene	ppbv	ND	0.52	
1,2,4-Trimethylbenzene	ppbv	ND	0.51	
1,2-Dibromoethane (EDB)	ppbv	ND	0.52	
1,2-Dichlorobenzene	ppbv	ND	0.51	
1,2-Dichloroethane	ppbv	ND	0.52	
1,2-Dichloropropane	ppbv	ND	0.52	
1,3,5-Trimethylbenzene	ppbv	ND	0.52	
1,3-Butadiene	ppbv	ND	0.52	
1,3-Dichlorobenzene	ppbv	ND	0.51	
1,4-Dichlorobenzene	ppbv	ND	0.51	
2-Butanone (MEK)	ppbv	ND	0.55	
2-Hexanone	ppbv	ND	0.55	
4-Ethyltoluene	ppbv	ND	0.53	
4-Methyl-2-pentanone (MIBK)	ppbv	ND	0.55	
Acetone	ppbv	ND	0.55	IC .
Benzene	ppbv	ND	0.52	
Bromodichioromethane	ppbv	ND	0.51	
Bromoform	ppbv	ND	0.52	
Bromomethane	ppbv	ND	0.51	
Carbon disulfide	ppbv	ND	0.50	
Carbon tetrachioride	ppbv	ND	0.51	88
Chlorobenzene	ppbv	ND	0.52	
Chloroethane	ppbv	ND	0.51	
Chloroform	ppbv	ND	0.51	
Chloromethane	ppbv	ND	0.50	
cls-1,2-Dichloroethene	ppov	ND	0.52	
cis-1,3-Dichipropropene	ppov	ND	0.51	
Cyclohexane	ppbv	ND	0.52	
Dipromochioromethane	ppov	ND	0.53	
Dichlorodhubromethane	ppov	ND	0.51	
Dichlorotetranuoroetnane Situd esetete	ppov	ND	0.57	
Euryi adelale	ppov	NU	0.51	
Eurypenzene Nevachlorn-1 3-butadiene	ppov	ND	0.52	ic.
mexacinoron, providurene milio-Volana	ppov	ND	0.50	
map Affent	ppov	ND	1.0	
Methylene Chloride	ppov	ND	1.0	
	PD04			
Date: 01/30/2007 02:13 PM	REF	ORT OF LAB	URATORY A	NALYSIS

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QUALITY CONTROL DATA

Project:	PLASMA
Pace Project No.:	1044833

METHOD BLANK: 305269

Associated Lab Samples: 1044833001, 1044833002

		Blank	Reporting	
Parameter	Units	Result	Limit	Qualifiers
n-Heptane	ppbv	ND	0.52	
n-Hexane	ppbv	ND	0.53	
o-Xylene	ppbv	ND	0.52	
Propylene	ppbv	ND	2.0	
Styrene	ppbv	ND	0.55	
Tetrachioroethene	ppbv	ND	0.52	
Tetrahydrofuran	ppbv	ND	0.52	
Toluene	ppbv	ND	0.52	
trans-1,2-Dichloroethene	ppbv	ND	1.0	
trans-1,3-Dichloropropene	ppbv	ND	0.52	
Trichloroethene	ppbv	ND	0.52	88
Trichlorofluoromethane	ppbv	ND	0.50	cc
Vinyl acetate	ppbv	ND	0.55	
Vinyl chloride	ppbv	ND	0.51	

LABORATORY CONTROL SAMPLE: 305270

		Spike	LCS	LCS	% Rec	
Parameter	Units	Conc.	Result	% Rec	Limits	Qualifiers
1,1,1-Trichloroethane	ppbv	10.6	8.6	81	60-134	
1,1,2,2-Tetrachiproethane	ppbv	10.6	10.1	95	55-141	
1,1,2-Trichloroethane	ppbv	10.7	8.8	83	64-129	
1,1,2-Trichlorotrifluoroethane	ppbv	10.9	9.6	88	55-137	
1,1-Dichloroethane	ppbv	10.7	10.5	98	59-136	
1,1-Dichloroethene	ppbv	10.8	12.0	112	60-137	
1,2,4-Trichlorobenzene	ppbv	10.4	13.8	133	50-150	
1,2,4-Trimethylbenzene	ppbv	10.4	10.3	99	63-137	
1,2-Dibromoethane (EDB)	ppbv	10.5	9.5	91	61-136	
1,2-Dichlorobenzene	ppbv	10.4	10.6	102	60-139	
1,2-Dichloroethane	ppbv	10.6	9.3	88	56-141	
1,2-Dichloropropane	ppbv	10.5	9.3	88	57-131	
1,3,5-Trimethylbenzene	ppbv	10.4	9.9	95	61-134	
1,3-Butadiene	ppbv	10.7	8.6	80	53-140	
1,3-Dichlorobenzene	ppbv	10.5	10.6	101	59-136	
1,4-Dichlorobenzene	ppbv	10.5	10.4	99	59-130	
2-Butanone (MEK)	ppbv	10.4	10.9	105	54-133	
2-Hexanone	ppbv	10.4	9.0	86	54-139	
4-Ethyltoluene	ppbv	10.3	10.4	101	61-138	
4-Methyl-2-pentanone (MIBK)	ppbv	10.4	9.1	87	53-139	
Acetone	ppbv	10.3	9.4	92	50-139 K	C
Benzene	ppbv	10.6	8.3	78	64-125	
Bromodichloromethane	ppbv	10.4	8.7	84	61-131	
Bromoform	ppbv	10.4	9.4	90	66-138	
Bromomethane	ppbv	10.1	9.6	95	55-135	
Carbon disulfide	ppbv	10.4	10.2	98	50-150	
Carbon tetrachioride	ppbv	10.7	8.4	78	58-135 8	8

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QUALITY CONTROL DATA

Project: PLASMA Pace Project No.: 1044833

LABORATORY CONTROL SAMPLE:	305270					
		Bpike	LCB	LCS	% Rec	
Parameter	Units	Conc.	Result	% Rec	Limits	Qualifiers
Chlorobenzene	ppbv	10.6	8.2	78	62-139	î
Chloroethane	ppbv	10	9.6	96	56-140	
Chieroform	ppbv	9.8	12.2	125	50-150	CC
Chloromethane	ppbv	9.9	11.6	117	56-144	
is-1,2-Dichloroethene	ppbv	10.7	10	93	62-135	
is-1,3-Dichloropropene	ppbv	10.5	10.1	96	64-133	
yclohexane	ppbv	10.2	8.3	82	54-139	
bromochloromethane	ppbv	10.4	9.9	95	50-150	
ichiorodifluoromethane	ppbv	10.1	10	99	60-130	
chiorotetrafluoroethane	ppbv	9.9	9.0	91	59-130	
hyl-acetate	ppbv	9.8	10.3	105	60-132	
hylbenzene	ppbv	10.5	10.3	98	65-140	
xachloro-1,3-butadiene	ppbv	10.4	13.6	131	50-150	10
Sp-Xylene	ppbv	20.8	20.1	97	60-132	
sthyl-tert-butyl ether	ppbv	10.2	9.9	97	50-150	
sthylene Chloride	ppbv.	10.8	12.6	\$17	56-138	
Heptone	ppbv	10.2	9.5	93	62-135	
Hexane	ppbv	10.1	11.2	111	62-134	
Cylene	ppbv	10.6	10.0	94	64-132	
opylene.	ppbv	10.6	10.3	97	56-125	
yrene	ppbv	10.5	10.1	96	69-134	
trachloroethene	ppbv	10.5	8.5	81	60-137	
drahydrofuran	ppbv	10.2	11.2	109	52-139	
luene	ppbv	10.6	9.3	88	69-130	
ns-1,2-Dichloroethene	ppbv	10	9.7	97	50-150	
ns-1,3-Dichloropropene	ppbv	15	9.8	85	70-142	
chiorcethene	ppbv	10.4	8.3	80	60-134	33
chlorofluoromethane	ppbv	10.2	6.7	66	56-141	CC
nyl acetate	ppbv	10.6	9.8	92	61-142	
Inyl chloride	ppbv	10	8.8	88	66-132	

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REPORT OF LABORATORY ANALYSIS

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Pace Analytical Services, Inc. 1700 Ein Street, Suite 200 Minnepole, MN 55414 Phone: (\$12)607-1700 Fax: (\$12)607-5444

QUALIFIERS

Project:	PLASMA
Pace Project No.:	1044833

DEFINITIONS

DF - Dilution Factor, if reported, represents the factor applied to the reported data due to changes in sample preparation, dilution of the sample aliquot, or moisture content.

ND - Not Detected at or above adjusted reporting limit.

J - Estimated concentration above the adjusted method detection limit and below the adjusted reporting limit.

MDL - Adjusted Method Detection Limit.

3 - Surrogate

1,2-Diphenylhydrazine (8270 listed analyte) decomposes to Azobenzene.

Consistent with EPA guidelines, unrounded data are displayed and have been used to calculate % recovery and RPD values.

LCS(D) - Laboratory Control Sample (Duplicate)

MB(D) - Matrix Spike (Duplicate)

DUP - Sample Duplicate

RPD - Relative Percent Difference

NC - Not Calculable.

ANALYTE QUALIFIERS

- A3 The sample was analyzed by serial diution.
- CC The continuing calibration for this compound is outside of method control limits. The result is estimated.
- IC The Initial calibration for this compound was outside of method control limits. The result is estimated.
- BB This analyte did not meet the secondary source verification criteria for the initial calibration. The reported result should be considered an estimated value.

REPORT OF LABORATORY ANALYSIS

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QUALITY CONTROL DATA CROSS REFERENCE TABLE

Project: Pace Project No.:	PLASMA 1044833				
Lab ID	Sample ID	GC Batoh Method	QC Batch	Analytical Method	Analytical Batch
1044833001	6973	TO-15	AIR/S105	×.	-3
1044833002	6963	TO-15	AIR/\$105		

Date: 01/30/2007 02:13 PM

REPORT OF LABORATORY ANALYSIS

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Sar	mple (Cond	lition	Upon Receipt		
Pace Analytical Client Name	:_Qv	chah	io ma	St. Ubriv	Project #	1044833
Courier: □ Fed Ex 🖞 UPS □ USPS □ Clier Tracking #: 127374E \239\$756991	nt 🗆 C	Comme	ercial	Pace Other	Op Pro Pro	ional j. Due Date: j. Name:
Custody Seal on Cooler/Box Present: Uyes	εų r	10	Seals	intact: jyes	CV NO RESS	WHEN PERSON IN THE LOCAL PROPERTY OF THE PERSON OF
Packing Material: Bubble Wrap Bubble	Bags	[] N	one	Other		
Thermometer Used 230194010	Type	of Ice:	Wet	Blue None	Date and I	e, cooling process has begun nitials of person examining
Cooler Temperature APV D	BIOIO	gical	issue	Comments:	contents	R
Chain of Custody Present:	Ves	□No	ÓМА	1.		
Chain of Custody Filled Out:	(ZiYes	ΠNo	⊡n/A	2.		
Chain of Custody Relinquished:	Yes	□No	DN/A	3.		
Sampler Name & Signature on COC:	Yes	⊡No		4.		
Samples Arrived within Hold Time:	Øyes		□n/A	5.		-
Short Hold Time Analysis (<72hr):	Yes	¢ No		6.		
Rush Turn Around Time Requested:	□Yes	PNo	□n/A	7.		
Sufficient Volume:	Ø/Yes	□N0	⊡n/A	8.		
Correct Containers Used:	4 Yes	[]No	□n/A	9.		
-Pace Containers Used:	APres	[]No	⊡n/a		-	
Containers Intact:	A Yes			10.		and the second
Filtered volume received for Dissolved tests	Yes	DNo	AN/A	11.		
Sample Labels match COC:	∯ Yes	ΠNσ	□n/A	12.		
-Includes date/time/ID/Analysis Matrix:	AU	r (A	H			
All containers needing preservation have been checked.	[]Yes	No	THNA	13.		
All containers needing preservation are found to be in compliance with EPA recommendation.	□Yes	□No	B N A	·		
exceptions: VDA, coliform, TOC, O&G, WI-DEO (water)	Yes	Ø.No		Initial when completed	Lot # of added preservative	
Samples checked for dechlorination:	Yes		ØŃ/A	14.	I	
Headenace in VOA Vials (Semm):	Yes	2 No		15.		
Trin Blank Present	□ Yes	0No		16.		and the second
Trip Blank Custody Seals Present	Ves	ANO	□n/A			127
Pace Trip Blank Lot # (if purchased):		Q.				
					Fairbar F	H i V Dharin
Client Notification/ Resolution:			Date/	Time	Field Data Red	uneor Y/N
Person Contacted:			- Date/			
Commentar negotation.						
				7		
Project Manager Review:	00	-			Date:	01/15/07

Note: Whenever there is a discrepancy affecting North Carolina compliance samples, a copy of this form will be sent to the North Carolina DEHNR Certification Office (i.e out of hold, incorrect preservative, out of temp, incorrect containers)

F-ALLC003rev.3, 11September2006

VITA

Neha Singh

Candidate for the Degree of

Master of Science

Thesis: SCALE-UP OF A DIELECTRIC-BARRIER-DISCHARGE PLASMA REACTOR AND TOLUENE REMOVAL EFFICIENCY

Major Field: Chemical Engineering

Biographical

Personal Data: Born on December 30th 1982 in a small town of M.P, India

Education: Graduated from M.I.T.S with bachelor degree in Chemical Engineering in June 2005; Completed requirements of master degree in Chemical Engineering from Oklahoma State University in December 2007. Name: Neha Singh

Date of Degree: December, 2007

Institution: Oklahoma State University

Location: Stillwater, Oklahoma

Title of Study: SCALE-UP OF A DIELECTRIC-BARRIER-DISCHARGE PLASMA

REACTOR AND TOLUENE REMOVAL EFFICIENCY

Pages in Study: 118

Candidate for the Degree of Master of Science

Major Field: Chemical Engineering

- Scope and Method of Study: This study was aimed at determining the removal efficiency of a scaled-up plasma reactor. Toluene was chosen as representative VOC. Effects of system variables including toluene retention time, reactor volume, toluene concentration, primary voltage and humidity on removal efficiency were determined. The regression models were generated to calculate removal efficiency and the amount of ozone generated from the experiment. Moreover, a scale-up factor was calculated using an equation suggested by Agnihotri 2003.
- Findings and Conclusions: TRE increases with energy density. More toluene was removed at lower retention time. There exists an optimum value of applied voltage at a particular retention time that gives maximum toluene removal. The Reynolds number is inversely proportional to the power ratio at lower primary voltage while at higher primary voltage power ratio stays constant with respect to Reynolds number. The energy coefficient for toluene was found to be 0.0012 L/J.