LA-UR- 93 - 3717

Conf-931164--1

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Submitted to: Annual meeting of the American Institute of Chemical Engineers, Student Poster Paper Presentation, St. Louis, Missouri.
November 7-12, 1993

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Form No. 836 R5
ST 2629 10/91

Optimization of a packed bed reactor for liquid waste treatment

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Abstract

We describe an optimization study of a packed bed reactor (PBR), developed for the treatment of hazardous liquid wastes. The focus is on the destruction of trichloroethylene (TCE). The PBR technology offers many distinct advantages over other processes: simple design, high destruction rates (99.99%), low costs, ambient pressure operation, easy maintenance and scalability. The cost effectiveness, optimal operating parameters and scalability were determined. As a second stage of treatment, a silent discharge plasma (SDP) reactor was installed to further treat offgasses from the PBR. A primary advantage of this system is closed loop operation, where exhaust gases are continuously recycled and not released into the atmosphere.

Introduction

The EPA regards incineration as the best technology for organic destruction. However, public acceptance of incinerators has declined to a point where alternatives must be evaluated and employed. Alternative technologies have been demonstrated for a wide range of compounds. This work focuses on the treatment of TCE,¹ using a two stage treatment system based on the packed bed reactor (PBR) and silent discharge plasma (SDP).

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Description of experimental apparatus

Figure 1 shows the experimental setup as currently employed. The first stage is the PBR, which consists of a main reactor enclosure (cylindrical metal pipe), bed packing material (alumina beads), and an electric furnace. Two reactors have been tested. The larger of the two is 16.4 cm OD, 120 cm long and the other is 6.35 cm OD, 106.7 cm long. The exhaust gasses pass through heat exchangers, a particulate filter, and the SDP. As a safety precaution, a redundant feature of activated carbon and soda lime traps is installed immediately preceding the stack.² The following equipment was used to analyze effluents:

- Gas flow meters and controllers
- Combustion gas analyzer (CGA)
- Gas chromatograph (GC)
- Fourier-Transform infrared (FT-IR) spectrophotometer
- Humidity probe

The GC is equipped with both a flame ionization detector (FID) and electron capture detector (ECD).

Figure 1: Packed Bed reactor/Silent Discharge Plasma Treatment System.

The prototype SDP has been used to demonstrate cold plasma destruction of compounds directly applicable to various off-gas waste streams (e.g., gas flows up to 112 slpm, with TCE/PCE/TCA concentrations as large as 2,000 ppm). This silent discharge plasma is produced by electrical discharges through gases, where one or both of the reactor electrodes are covered by a dielectric layer (we use glass). The geometry is usually planar (using metal and dielectric plates) or cylindrical (using metal and dielectric tubes). A typical planar cell has approximate dimensions of 71-cm length, 18-cm width, and 2.5-mm gap, equaling a mean discharge area of 1236 cm^2 and an active discharge volume of 310 cm^3 . Figure 2 illustrates the planar cell design. Both single and double dielectric barriers have been employed.³

The silent discharge plasma produces energetic electrons (typical energies of 1-10 eV), which in turn generate copious quantities of highly reactive free radicals. Within the transient, electrical microdischarge electrons are selectively heated. This results in an efficient transfer of electrical energy to desirable chemical reactions at near-ambient temperatures and pressures. Although the volume of the microdischarges is quite small, a statistically high number of discharges are spread out in space and time, resulting in a large effective processing volume ideally suited for high throughput chemical processing. Free radicals of atomic oxygen $O(^3P)$ and hydroxyl OH oxidize organic compounds to nonhazardous, easily managed compounds such as CO_2 , H_2O and HCl. The potential of nonthermal plasma processes (dielectric barrier, corona, pulsed corona, etc.) is being pursued through a variety of international research efforts directed at flue gasses and hazardous organics.³

Figure 2: Schematic diagram of planar dielectric-Barrier configuration for producing silent electrical discharges.

Representative double-barrier, planar SDP cell used in Los Alamos experiments.

Packed Bed Reactor

Both PBR's were used to test organic destruction. The small PBR was used to evaluate TCE destruction during the transition from liquid to gas phase while the large PBR was used to treat larger volumes of liquids (e.g., machining oils spiked with TCE). Understanding these reaction mechanisms allowed for effective treatment of waste streams. Therefore, the small PBR was used to model gas phase destruction of TCE, which is discussed later. Typical gas flow rates through the small PBR are on the order of 8 to 60 standard liters per minute (slpm) and the large PBR liquid rates are on the order of 2-30 ml/min with gas rates of 28 to 170 slpm. Test durations range from 1 to 8 hours.

Understanding the reactions in the gas phase are crucial for optimization of the packed bed system. One of the major concerns is the change of phase from liquid to gas in the large PBR. Waste streams are initially liquid, but the use of an atomizer and high temperatures changes the influx into a gaseous stream. To determine if phase change would help or inhibit the destruction of TCE, the small PBR was used to model gaseous TCE destruction. This determined the reactor's optimal operating parameters, scalability for the system.

The large PBR was primarily used for treatment of liquid feeds and slurries which include: TrimSol and DTE Lite spiked with 3 w/o TCE, kerosene spiked with 17 w/o o-dichlorobenzene (a surrogate for a polychlorinated biphenyl) and slurry solutions (containing shredded rubber gloves, vinyl, polyethylene, paper towels and Tyvek in polyactylate to suspend the solids). Flow rates for the machining oils and kerosene were between 2 to 7 ml/min and the slurry rates up to 100 ml/min , while air flows were 1 to 168 slpm. Temperatures were between 700-1100 °C for the slurries and oils and 1150 °C for the kerosene. When the silent discharge plasma (SDP) reactor is used as a second stage these temperatures can be reduced. The SDP destroys the remaining organics when the PBR operates at lower temperatures. This system has been tested and is discussed later. Typical combustion products include CO_2 , H_2O , CO and HCl. The condensate was water with a pH of about 1, in most cases, when chlorinated species were treated.

To complete reactor modeling, measured TCE destruction was used in conjunction with corresponding theoretical destruction at similar temperatures. Theoretical destruction was calculated by using PBR design equations⁴ given by:

$$V = F_{in} \int_{x_{in}}^{x_{out}} \frac{dx}{-r_a} \quad (1)$$

where V is reactor volume, F_{in} is the molar TCE flow rate, x_{in}, x_{out} is TCE destruction in and out of the reactor ($x_{in}=0$) and $-r_a$ is the reaction rate. The reaction rate is given by:

$$-r_a = kC_a^a \quad (2)$$

where k is the specific rate constant, C_a is TCE concentration and a is the reaction order. The theoretical specific rate constant was done by using the Arrhenious equation given by:

$$k = Ae^{\left(\frac{E_a}{RT}\right)} \quad (3)$$

where A is the frequency factor, E_a is the activation energy for TCE, R is a gas constant and T is a reactor temperature. The frequency factor, activation energies and reaction mechanisms are available.⁵ Figures 3 and 4 show the comparison between theoretical and experimental destruction of TCE at a flow rate of 8 slpm.

Figure 3: Linear comparison between theoretical and experimental TCE destructions for a flowrate of 8 slpm.

Figure 4: Logarithmic graph demonstrating divergence between theoretical and experimental TCE destruction at 8 slpm.

Figure 3 displays excellent correlation between theoretical and experimental TCE destruction while figure 4 shows the subtleties in the experimental data and how it changes from theoretical. Figure 4 demonstrates how the system diverges from theoretical at the higher temperatures. This divergence occurs because no system can demonstrate total destruction and therefore must "level-off" at some temperature. The divergence indicates the limitations of real-world processes and how reactions are inhibited. This determines the reactor's optimal operating parameters, cost effectiveness, either up or down sizing the reactor to satisfy various waste treatment needs and provide an accurate baseline for TCE destruction in the large PBR. Modeling information for the PBR is essential so that the complete system operating parameters can be determined. Similar agreement was obtained for all studied flowrates. Other flowrates studied were 16, 21, 28 and 60 slpm. Agreement between the various data sets has allowed for effective modeling of the small PBR.

Complete system operation

The large PBR/SDP system has been operated for processing DTE Lite oil spiked with 3 % TCE and kerosene spiked with 17 % o-DCB. Both treatments gave very encouraging results.

DTE Lite oil treatment in the large PBR was initially operated at 800 °C and increased to 1100 °C (due to energy content of the fuel) towards the end of the experiment, with an oil flow rate of 3 ml/min and an air flow rate of 84 slpm with an initial TCE concentration of 270 ppm. As stated earlier, reaction products are the same. Effluent TCE concentrations from the PBR were <25 ppb, with an effective TCE destruction of 99.9%. PBR modeling predicts similar destruction (<99.9%). This shows change of phase has little effect on TCE destruction.

Treatment of kerosene and 17 % o-DCB at a PBR operating temperature of 1150 °C, kerosene flow rate of 6 ml/min and an air flow rate of 6 scfm demonstrated 99.99991% o-DCB destruction before going through the SDP. This is sufficient for the Toxic Substances Control Act (TSCA) standards. The reactor temperature can be reduced to improve system lifetime and simplicity. This will lower the desired removal efficiency (DRE) of the PBR, but the second stage SDP can provide additional destruction. The trade-offs between PBR temperature and SDP power are now under examination.

Conclusions

The flexibility in this type of system has some distinct advantages over other technologies. The ease of operation, durability of the reactor and effective modeling will enable it to be an integral part of any waste treatment system, complex or simple. Its flexibility allows for the destruction of a wide range of wastes, from slurry solutions to PCB's.

A major concern was that the change of phase from liquid to gas in the large PBR could inhibit the destruction of TCE. Experimental results suggest that this transition has had no negative effect of TCE destruction. This has been verified by numerous tests and agreement with model predictions. The SDP has also been used independently. It is very effective in reducing VOC concentrations by greater than 99.99%. The implications of this allow this reactor to be modified for a wide variety of operations. Such things include, fugitive emission destruction, stack cleaning and various VOC destruction.

An additional advantage is that of closed loop operation. This is where no reaction products are released to the atmosphere. Exhaust from the SDP in figure 1 is recycled as the gas feed to the PBR atomizer. Chemical scrubbers remove carbon dioxide and acids.

The PBR is considered a thermal treatment unit, this is where no flame is produced and the reactions occur because of external heat supplied from the furnace heaters. This should simplify the process of acquiring a RCRA and or TSCA permits to destroy hazardous waste compared to incinerators.

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12/22/93