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SITE DEMONSTRATION OF THE ZENOGEM™ TECHNOLOGY TO TREAT HIGH STRENGTH WASTEWATERS

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INTRODUCTION

High strength organic wastewaters are encountered at hazardous waste sites in the form of leachate and in some cases groundwater. The ZenoGem™ Process is designed to remove biodegradable materials, including most organic contaminants, from wastewater to produce a high quality effluent. This technology was accepted into EPA's Superfund Innovative Technology Evaluation (SITE) program in summer 1992; this paper summarizes the technology demonstration performed at a Superfund site in 1994.

DESCRIPTION OF THE TECHNOLOGY

The ZenoGem™ Process consists of an integrated bioreactor and ultrafiltration membrane system, or ultrafilter. After equalization, wastewater enters the bioreactor, where contaminants are biologically degraded. In this tank, a biomass develops which contains bacterial cultures that break down organic contaminants. Ideal conditions for biomass growth are maintained, including introduction of air to assure sufficient aerobic conditions and optimal process temperatures. The contents are constantly mixed by the introduction of air bubbles through a series of manifolds from the tank bottom. The tank is totally enclosed; air is recycled and a purge is emitted through a carbon adsorption unit before being discharged into the atmosphere. A mixture of sludge solids and un- filtered wastewater from the ultrafilter is recycled back to the bioreactor and remains in the treatment system for periods of several weeks. The bioreactor's size is significantly reduced because of this long sludge retention time. Conversely, the hydraulic residence time in the bioreactor is relatively short.

The ultrafilter receives feed flow from the bioreactor. It separates treated wastewater from biological solids and soluble materials with higher molecular weights. Ultrafiltration (UF) is a pressure-driven (typically at 60 to 70 pounds per square inch) cross flow filtration process in which the water to

be processed flows tangentially over the surface of a membrane filter capable of separating both insoluble materials (bacteria, colloids, suspended solids) and higher molecular weight soluble materials from the treated water. The membrane system consists of a series of tubes, in ten-foot modules and approximately three inches in diameter, into which the cylindrical membrane filters are inserted. Feed flow to the UF system is continuously pulled off the bioreactor and fed into the UF system: the treated filtrate (or permeate) flows through the membrane while the remaining feed is concentrated and returned to the bioreactor.

SITE DEMONSTRATION OF THE TECHNOLOGY

The SITE demonstration of the technology was conducted at the Nascolite Superfund site in New Jersey during the period from September through November 1994. The groundwater at this 17.5 acre site is contaminated with volatile organic compounds (VOCs) which result from past operations at the facility, which included manufacturing of polymethyl methacrylate plastic sheets, commonly known as acrylic or plexiglass.

The results of the remedial investigation/feasibility study for this site confirmed extensive contamination of the groundwater with VOCs. In March 1988, a record of decision (ROD) was signed requiring remedial actions of ground water extraction with on-site treatment and re-injection of the treated effluent. Methyl methacrylate (MMA) is the major contaminant, with groundwater levels approximating 12,000 mg/l. Other contaminants at the site include a number of VOCs, including toluene, ethylbenzene, carbon disulfide, styrene, 2,4-dimethylphenol, benzene, trichloroethylene, vinyl chloride.

For demonstrations, the ZenoGem™ process equipment has been mounted inside a trailer. Prior to the EPA SITE demonstration, it has performed major demonstrations on two types of residues: (a) a combination of firefighting training residues and contaminated groundwater containing burned and unburned fuel, and (b) wastewater containing aircraft fire fighting foam compounds, oil, greases, benzene, toluene, ethylbenzene, xylenes and suspended solids.

RESULTS

The results of the 89-day test run conclusively demonstrated the efficient removal of MMA and COD from the highly contaminated groundwater. Due to the timing of the end of the demonstration and the deadline for this extended abstract, the data presented is preliminary and has not yet been validated. The results of the analytical data are shown in Table 1. The concentration of MMA and COD in the groundwater feedstock, permeate, and product are shown in Table 1 as 10-day averages up to the shock loading on November 8. During start-up, process feed rate was approximately 300 gallons per day (gpd) and was gradually increased to 563 gpd by October 11, 1994. After the initial shock loading, the process feed rate started at 50 gpd and lined out at 150 gpd. The resulting reductions in MMA and COD are also shown. The MMA removal was essentially 100% for the entire operation. The COD removal for the permeate averaged 84% up to the shock loading and 95% after the shock loading. The product COD removal averaged 97% for the periods in which data are available.

The shock loading test demonstrated the flexibility of the process in handling a sudden increase of concentration of contaminants. The process was able to withstand the increased concentration and with the reduction of feedrate after the 4-hour shock was able to achieve the 95% reductions in MMA and COD very quickly. This indicated the dynamic nature of this integrated process.

TABLE 1. DEMONSTRATION TEST RESULTS

	Feedstock		Permeate				Product			
	MMA	COD	MMA		COD		MMA		COD	
Date	Conc. (mg/l)	Conc. (mg/l)	Conc. (mg/l)	% Red.	Conc. (mg/l)	% Red.	Conc. (mg/l)	% Red.	Conc. (mg/l)	% Red.
9/2-9/11*	1618	3467	2.968	99.80	467	84.28	N/A†	N/A	N/A	N/A
9-13-9/25	2307	5564	0.743	99.95	452	81.22	N/A	N/A	N/A	N/A
9/26-10/6	2209	5847	0.027	100.0	577	90.54	N/A	N/A	N/A	N/A
10/7-10/19	1720	4694	0.018	100.0	485	89.09	N/A	N/A	N/A	N/A
10/20-10/31	2142	4973	0.020	100.0	1007	78.21	0.020	100.0	54	99.01
11/1-11/7	2134	9317	0.020	100.0	3214	80.83	0.020	100.0	198	96.73
11/8	2020	5910	0.020	100.0	1170	80.20	0.020	100.0	100	98.31
11/8	7140	19600	0.020	100.0	1180	93.98	0.020	100.0	121	99.38
11/9-11/18	6984	17585	0.017	100.0	927	94.67	0.020	100.0	165	99.16
11/20-11/23	8342	19921	0.025	100.0	936	95.27	0.020	100.0	868	95.99

*Average values for days noted.
†Data not available

Overall, the process ran very smoothly. The system was computer controlled with an alarm system that activated a beeper retained by the operator. The run demonstrated that the process operation was so smooth and flexible that unattended operation is extremely viable for extended periods.

The groundwater used for the demonstration was very odoriferous and contained free product. The resulting product from the process was odorless, absent of suspended solids, and was accepted by the local sewage treatment plant for disposal at $22.50 per 6,000-gallon tanker. The sampling and analyses of all of the tankers showed a clear and odorless product.

CONCLUSIONS

The process was very effective in reducing highly concentrated organic contamination to POTW disposable levels. The process effectively demonstrated the complete removal of MMA and over 95% removal of COD.

The process demonstrated unattended operation, flexibility during sustained operations, and an ability to easily handled a four-fold increase in contaminant concentration during shock loading. The process could operate smoothly over a wide range of conditions and would recover quickly from upsets encountered in Superfund operations such as loss of electricity, quadrupling of feed concentration, free product in feedstock, and adverse weather conditions.

RECOVERY OF MONOMERS FROM RECYCLED PLASTICS

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INTRODUCTION

Plastics make up approximately 20% by volume of the material disposed of in landfills in the United States. The increased interest in recycling has focused attention on ways to expand our current recycling efforts. Such efforts to recycle more of our plastic waste must include versatile processes that can address the heterogeneous nature of postconsumer plastics streams in the most cost-effective manner. Types of commodity plastics typically found in a postconsumer stream include high-density polyethylene (HDPE), low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), polypropylene (PP), polyethylene terephthalate (PET), polyvinyl chloride (PVC), and polystyrene (PS). In addition to plastics such as these, a number of organic and inorganic constituents will be present, including paper, paint, food, and various metals. These constituents are present as a result of introduction into the plastics during manufacturing (to give a plastic product selective properties) or as residual matter from use by the consumer. The Energy & Environmental Research Center (EERC) is one of several groups in the United States and Europe that, over the last several years, has worked toward developing a process to thermally break down postconsumer plastics to hydrocarbon liquids and gases. Such a process, sometimes referred to as thermal depolymerization, thermal recycling, or feedstock recycling, produces hydrocarbon liquids and gases that could be used for the manufacture of new plastics or other petroleum products. The specific slate of products depends on processing conditions. The EERC has completed studies on various aspects of thermal depolymerization using fluidized-bed technology, including a fundamental examination of the products as a function of temperature, bed material, and feed mix (1). This and subsequent studies have identified several relatively high-value products possible from the process, including ethylene (C_2^-), propylene (C_3^-), and butylenes. An U.S. Environmental Protection Agency (EPA)-sponsored program at the EERC, just beginning, proposes to better define optimal process conditions for making these olefins (propylene, ethylene, and butylenes). Past work at the EERC has also indicated that optimal processing conditions exist for these olefin yields. The proposed the EPA work is based on information, presented here, that was obtained in studies completed at the EERC under the sponsorship of the American Plastics Council (APC) and the U.S. Department of Energy (DOE).

METHODOLOGY

Two sets of screening tests were completed on the EERC's 1–4-lb/hr continuous fluid-bed reactor (CFBR) bench-scale test unit (Figure 1). The intention of these tests was to determine the effect of temperature and gas residence time on the olefin yield from a postconsumer plastics thermal decomposition process. Two different bed materials, sand and CaO, were used. From earlier work, it was apparent that product yields in general are dependent on feed material, decomposition temperature, gas residence time, and bed material. Twenty-five tests were run in the CFBR, the parameters and yield results of which are given in Table 1. The base blend material, used for the first set of tests, consisted of 60% HDPE, 20% PS, and 20% PP virgin resin (percentages are on a weight basis). The postconsumer

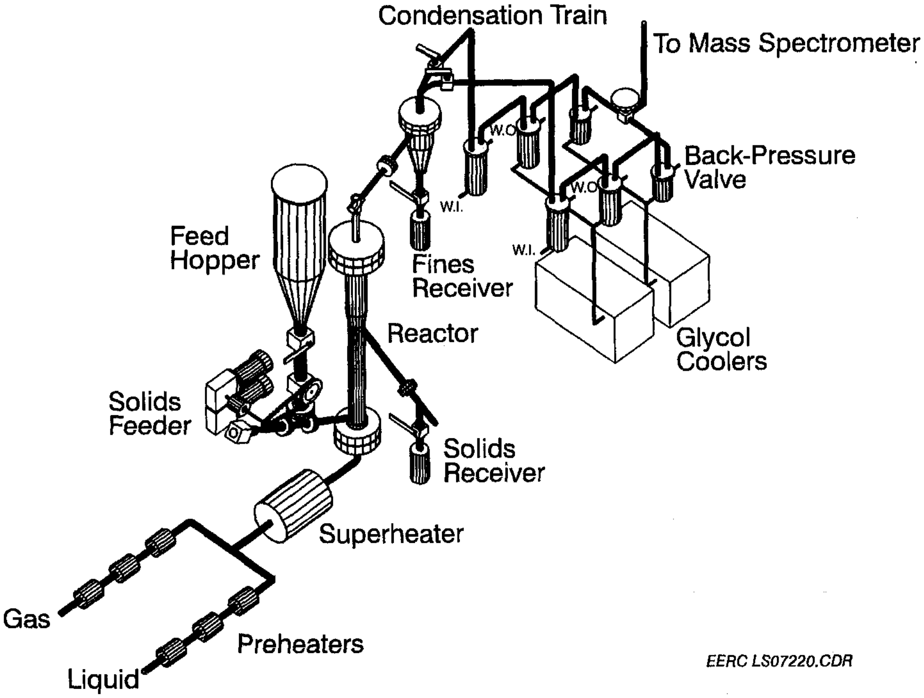

Figure 1. 1-4-lb/hr CFBR unit.

blend, used for the second set of tests, consisted of the following approximate composition 59.2% HDPE, 20.1% PET, 0.6% PVC, 10.7% PS, 10.7% PP, and 4.7% LDPE. The base blend was chosen for the first set of tests in order to separate the coking effects from PET (if any) from the coking that may result from severe temperatures. While coke formation was not quantified, it is desirable to know if it is a result of the particular composition of feed material or of the temperature chosen.

RESULTS

Figure 2 shows the $C_2^=$ + $C_3^=$ yields for the three test series performed with the base blend at residence times of 6, 16, and 30 seconds. Yields are calculated as weight of a particular product divided by the moisture-ash free feed material. The $C_2^=$ + $C_3^=$ yield will be referred to as "the olefin yield." Yield percent is defined as mass of a particular product divided by mass of moisture-, ash-free plastic fed. Even though other olefins (i.e., butylenes) are present in the gas stream, these two components are the most prevalent and will be used as an indication of conversion to olefins. Other components in the product gas stream include H_2, CH_4, CO, CO_2, C_2H_6, C_3H_8 and other hydrocarbon gases up to C_5's. The majority of the product gas stream is N_2 since it is used as the reactor fluidization gas. A small amount of uncondensed liquid are also present. The three test series using base blend were all completed in a sand bed. All three residence time series show an initial increase in olefin yield with temperature, a peak at about 700°C, then decreased olefin yield. This is consistent with earlier work with HDPE, which showed that at the higher temperatures (750°-850°C), liquids became more aromatic, liquid yield increased, and gas yield decreased (1). For the 6-second residence time tests, the $C_2^=$ maximum is at about 750°C, and for $C_3^=$ it is at about 700°C. CH_4 yield increases continually with temperature; H_2 increases until 825°C, where yield drops slightly. For the 16-second residence time test, $C_3^=$ yield peaks at about 650°C, and $C_2^=$ yield at about 700°C. CH_4 and H_2 yields increase with temperature over the entire temperature range. For the 30-second residence time series, $C_3^=$ yield is highest for the

TABLE 1. CFBR TEST RESULTS

Run Number	Temp. °C	Liquid Yield, wt%	Gas Yield, wt%	$C_2^=$ Yield, wt%	$C_3^=$ Yield, wt%	H_2 Yield, wt%	CH_4 Yield, wt%	Material Balance
6-second Residence Time, Base Blend, 10 psig, Sand Bed								
M422	600	72	28	2.1	2.6	0.0	0.7	107
M423	650	45	55	8.0	9.7	0.1	2.4	108
M424	700	30	70	17.9	15.8	0.3	6.0	98
M425	750	35	65	21.0	0.2	0.4	9.6	95
M426	800	32	68	17.4	0.9	1.2	14.0	95
M427	825	50	49	14.7	0.0	1.0	13.4	86
16-second Residence Time, Base Blend, 10 psig, Sand Bed								
M431	600	47	53	11.0	14.0	0.2	4.6	104
M430	650	32	68	15.3	17.2	0.3	6.9	103
M429	700	32	68	22.6	15.2	0.7	14.0	104
M428	750	35	65	21.0	5.6	0.9	16.7	103
30-second Residence Time, Base Blend, 30 psig, Sand Bed								
M432	600	48	50	11.9	15.2	0.2	7.8	101
M433	650	51	49	14.6	13.8	0.4	10.2	96
M434	700	30	70	24.6	7.4	1.1	27.2	105
M435	750	62	36	10.3	0.6	1.2	20.0	88
6-second Residence Time, Postconsumer Plastics Blend, 10 psig, Sand Bed								
M437	600	30	69	3.6	5.1	0.0	1.2	104
M438	650	13	82	9.3	9.9	0.3	3.9	108
M439	700	8	83	16.5	14.2	0.3	6.0	107
M440	750	13	82	18.2	6.9	0.5	8.7	110
M441	800	8	90	17.0	1.4	1.1	10.4	104
6-second Residence Time, Postconsumer Plastics Blend, 10 psig, CaO Bed								
M442	600	51	47	7.9	10.3	0.4	2.7	108
M443	650	30	60	16.8	19.3	0.7	6.0	96
M444	700	29	69	19.4	13.9	0.9	8.4	122
M445	750	28	69	32.1	0.0	1.5	17.7	117
15-second Residence Time, Postconsumer Plastics, 10 psig, CaO								
M447	700	28	59	21.7	6.9	1.3	18.4	106
M446	750	30	53	22.0	0.0	1.2	18.3	117

600°C test. $C_2^=$ and CH_4 yields peak at around 700°C, and H_2 yield increases over the entire temperature range. It should be noted that no tests were completed above 750°C for the 16- and 30-second residence time series because of prohibitive amounts of coking.

Figure 3 shows the $C_2^=$ + $C_3^=$ yields for the three test series performed with postconsumer plastics at residence times of 6 and 15 seconds. Test series were completed using a sand bed at 6 seconds and a CaO bed at 6 and at 15 seconds. For the series in a sand bed, maximum olefin yield occurred at 700°C, similar to the series using the base blend. Ethylene yield peaked at 750°C, and $C_3^=$ yield at 750°C. The series in a CaO bed, however, had its maximum olefin yield at 650°C. Here, $C_2^=$ yield again peaked at 750°C, while $C_3^=$ reached a maximum at 650°C. CaO has been observed to act as a cracking agent, lowering the temperature required to produce a specified liquid yield, relative to sand (1). Only two tests were completed at the 15-second residence time because of a lack of time. These two points, though, are seen to follow the same general trend of lower olefin yield with increased temperature after the maximum.

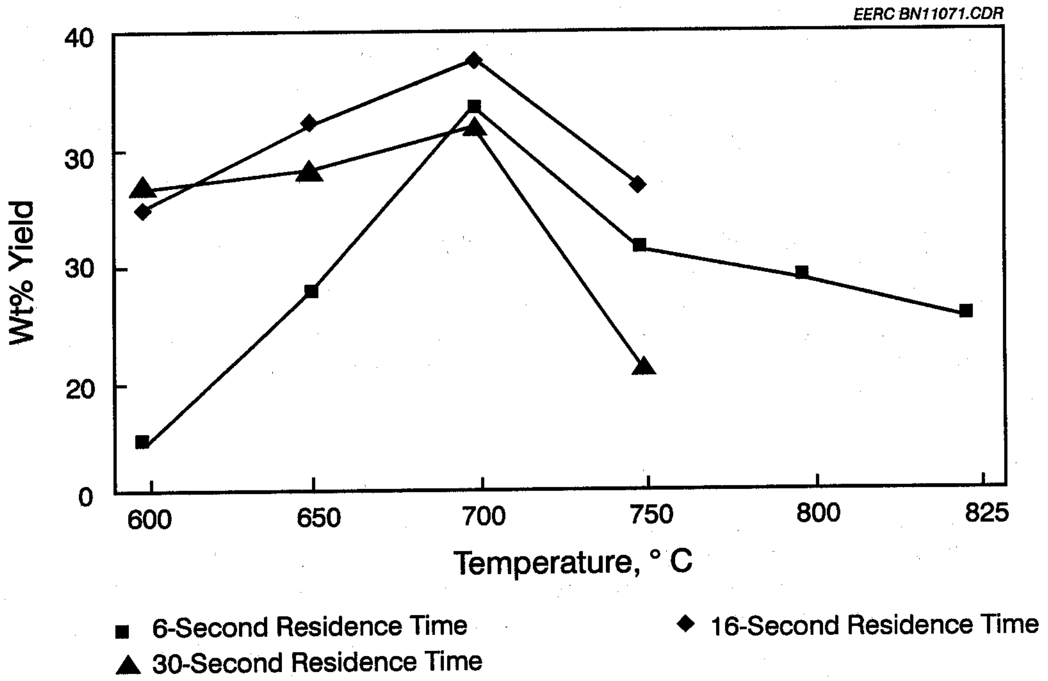

Figure 2. C_2^- + C_3^- Yield from base blend in a sand bed.

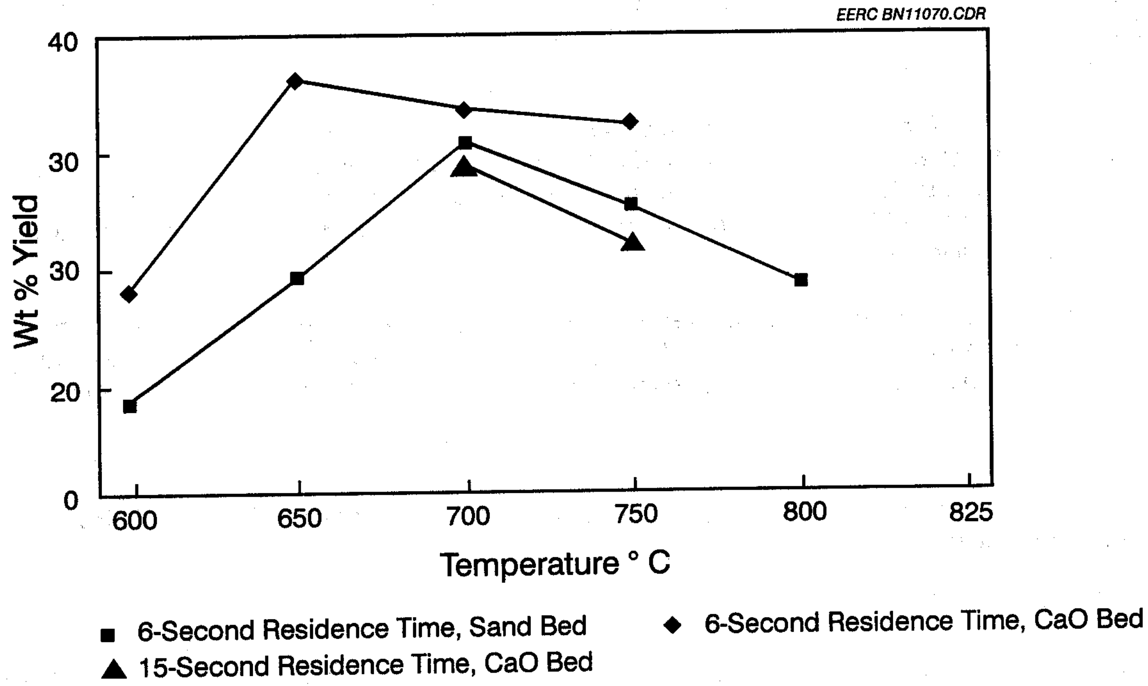

Figure 3. C_2^- + C_3^- yield from postconsumer plactics.

Referring to Table 1, the base blend tests had maximum combined $C_3^=$ and $C_2^=$ yields at 700°C for all three residence times examined. The highest combined $C_3^=$ and $C_2^=$ yield occurred at a residence time of 16 seconds (38%), followed by the 6-second residence time (34%). For the postconsumer tests, the highest combined yield was at a temperature of 700°C for the 6-second sand bed test (31%), and at a temperature of 650°C for the 6-second CaO bed test (36%). The highest overall $C_3^=$ and $C_2^=$ yield, 38%, occurred at a 16-second residence time and a temperature of 700°C, using the base blend.

Conditions for producing olefins will also produce significant quantities of liquids. The character of the liquids from the tests presented here was determined using a gas chromatography flame ionization detector (GC-FID) to obtain simulated boiling point distributions and also by comparing this information with gas chromatography mass spectroscopy (GC-MS) data from known plastics decomposition products to identify specific components. These liquids are fairly aromatic and may be useful as a chemical feedstock.

CONCLUSIONS

The two most important conclusions from the olefin work performed to date at the EERC are 1) olefin yield from a thermal depolymerization process depends on decomposition temperature, gas residence time, feed material mix, and bed material and 2) a temperature can be identified for maximum olefin yields (at a fixed gas residence time and with a specific bed material). For an inert (sand) bed, the temperature for maximum olefin yield is about 700°C, and for a CaO (catalytic) the temperature is about 650°C. The existence of a maxima for olefin yield is of particular importance; if plastics are decomposed at a temperature higher than the optimal temperature for olefin yield, overall gas yield decreases, and the relative percentages of $C_2^=$, $C_3^=$, and $C_4^=$ in the gas stream decrease, while those of H_2 and CH_4 increase. CaO bed material acts as a catalyst, enabling processing at lower temperature with equivalent yields, relative to a sand bed. This effect was also observed in an earlier depolymerization studies at the EERC (1). In the upcoming work for EPA, temperature and residence time will be focused to a smaller range of conditions to more narrowly define the optimal process conditions. The effect of pressure is also being contemplated, as the olefins produced will be introduced into an (pressurized) olefin plant.

The effect of PET in thermal depolymerization processes has been examined in the APC/DOE-sponsored projects, as well as in a project for 3M. PET will be present in postconsumer streams in concentrations of 10% to 30% and has been seen to have a significant impact on fluid-bed operation and on liquid products. PET will continue to be considered in all of the research efforts concerning thermal depolymerization at the EERC.

A decision, based on an economic evaluation of the process will have to be made as to the fate of the liquids coproduced from a plastics-to-olefins process. These liquids will either be considered a coproduct or recycled to the process. Future efforts will include characterization of these liquids.

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TWO-PHASE OZONATION OF CHLORINATED ORGANICS

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INTRODUCTION

In the last few years the amount of research being conducted in the field of single-phase ozonation has grown extensively. However, traditional aqueous-phase ozonation systems are limited by a lack of selective oxidation potential, low ozone solubility in water, and slow intermediate decomposition rates. Furthermore, ozone may decompose before it can be utilized for pollutant destruction since ozone can be highly unstable in aqueous solutions. Naturally occurring compounds such as $NaHCO_3$ also affect ozone reactions by inhibiting the formation of OH· free radicals. To compensate for these factors, excess ozone is typically supplied to a reactor. Since ozone generation requires considerable electric power consumption (16 - 24 kWh/kg of O_3), attempts to enhance the ozone utilization rate and stability should lead to more efficient application of this process to hazardous waste treatment.

To improve the process, ozonation may be more efficiently carried out in a two-phase system consisting of an inert solvent (saturated with O_3) contacted with an aqueous phase containing pollutants. From practical considerations, the non-aqueous phase must meet the following criteria: 1) non-toxic, 2) very low vapor pressure, 3) high density (for ease of separation), 4) complete insolubility in water, 5) reusability, 6) selective pollutant extractability, 7) high oxidant solubility, and 8) extended O_3 stability. Previously published studies (1) have indicated that a number of fluorinated hydrocarbon compounds fit these criteria. For this project, FC40 (a product of 3M Co.) was chosen due to its low vapor pressure (3 mm Hg) and high specific gravity (1.9). The primary advantages of the FC40 solvent are that it is non-toxic, reusable, has an ozone solubility 10 times that of water, and that 85 % of the ozone remains in the solvent even after 2 hours. This novel two-phase process has been utilized to study the rapid destruction of pentachlorophenol (PCP), 1,3 dichlorobenzene (DCB), trichloroethylene (TCE), and organic mixtures.

METHODS

Ozonation studies were conducted using pentachlorophenol (PCP), trichloroethylene (TCE), and 1,3-dichlorobenzene (DCB) (Aldrich Chemical) as parent compounds. For all experiments, the non-aqueous solvent was FC40, obtained from 3M Co. The initial concentration ranges were varied for each compound: PCP at 10 - 100 mg/L for pH 3.5 - 11.7, TCE at 1442 mg/L for pH 4.4 - 10.0, and DCB at 26 mg/L and 78 mg/L for pH 2.1 - 11.2. The first stage of the study was to determine the partitioning coefficient for each compound studied. The next stage consisted of determining the effect of various variables on parent compound degradation (such as the ratio of O_3 to pollutant, reaction time, and initial pH).

Analysis of the parent compounds in the aqueous phase were conducted following the guidelines outlined EPA Methods 624 and 625 using a Hewlett-Packard 5890 Series II Gas Chromatograph with an attached 5971A Quadrupole Mass Selective Detector (GC/MS) equipped with NIST/EPA/MSDC 49K Mass Spectral Database. For analysis of the solvent phase, the parent compounds were extracted with methanol and analyzed by GCMS. Besides quantifying the parent compounds, selected intermediates and reaction products were also analyzed. Organics acids from PCP ozonation were monitored on HPLC