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REDUCTIVE PHOTO-DECHLORINATION (RPD) PROCESS FOR SAFE CONVERSION OF HAZARDOUS CHLOROCARBON WASTE STREAMS

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INTRODUCTION

A novel technology designated "Reductive Photo-Dechlorination" (RPD) has been developed and successfully tested for environmentally safe treatment of waste streams containing hazardous chlorinated hydrocarbons. This RPD process employs ultraviolet (UV) light in a reducing atmosphere and at moderate temperatures to efficiently convert chlorocarbon contaminants into valuable hydrocarbons such as methane, ethane, ethylene, acetylene and hydrogen chloride. The UV light promotes carbon-chlorine bond cleavage and long-chain radical reactions with the hydrogenous bath gas leading to the thermodynamically and kinetically favored hydrocarbon products at a conversion of +99%.

The RPD process is schematically shown in Figure 1. The pilot-scale prototype consists of five main units: (1) Input/Mixer; (2) Photo-thermal Reactor; (3) Scrubber; (4) Separator/Storage; and (5) Recycling. Chlorinated waste streams can be introduced in one of three ways: liquid, vapor or adsorbates (to activated carbon). Chlorocarbon solvents are fed into a vaporizer, mixed with a reducing gas and passed into the Photo-thermal Reactor. Air laden with chlorocarbon vapors is first passed through a separator (condenser) which removes chlorinated materials as liquid. Chlorinated contaminants adsorbed onto activated carbon are removed as vapors by purging with a mildly heated reducing gas. Then, the vapors are passed into the Photo-thermal Reactor.

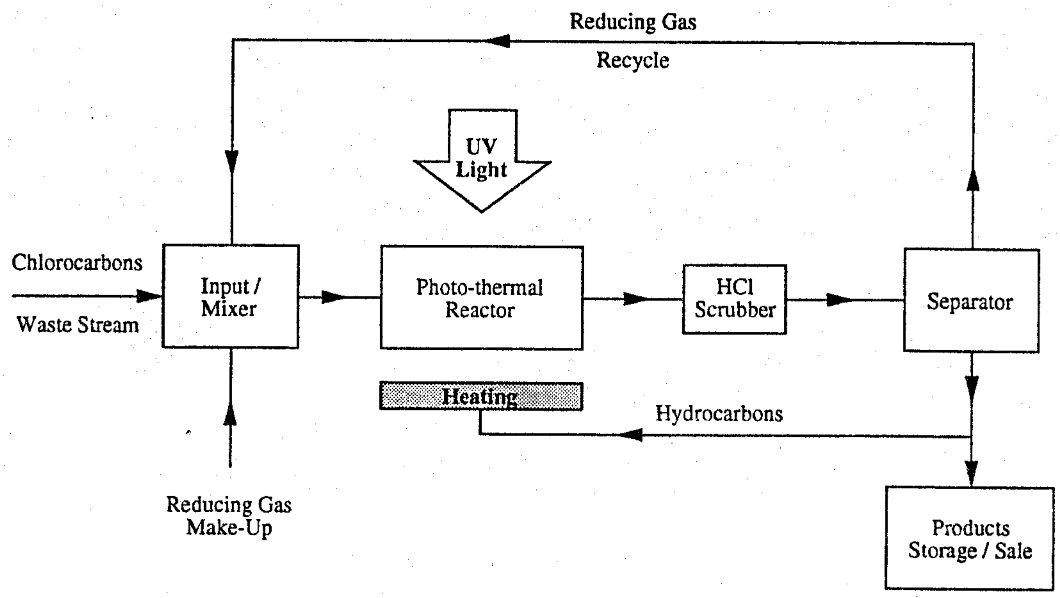


Figure 1. ENERGIA's Reductive Photo-Dechlorination (RPD) Process.

The Photo-thermal Reactor is the heart of the RPD technology. Here the mixture is irradiated and heated. The UV light breaks the C-Cl bond and the temperature sustains long-chain radical reactions. After a suitable residence time, conversion and dechlorination are fully completed. Hydrogen chloride is scrubbed from the mixture which proceeds to the separator. After separation, excess reducing gas is recycled back to the Input/Mixer. Valuable hydrocarbon products are collected and sold. There is also an option for recycling a portion of the hydrocarbon products as an auxiliary fuel to heat up the Photo-thermal Reactor.

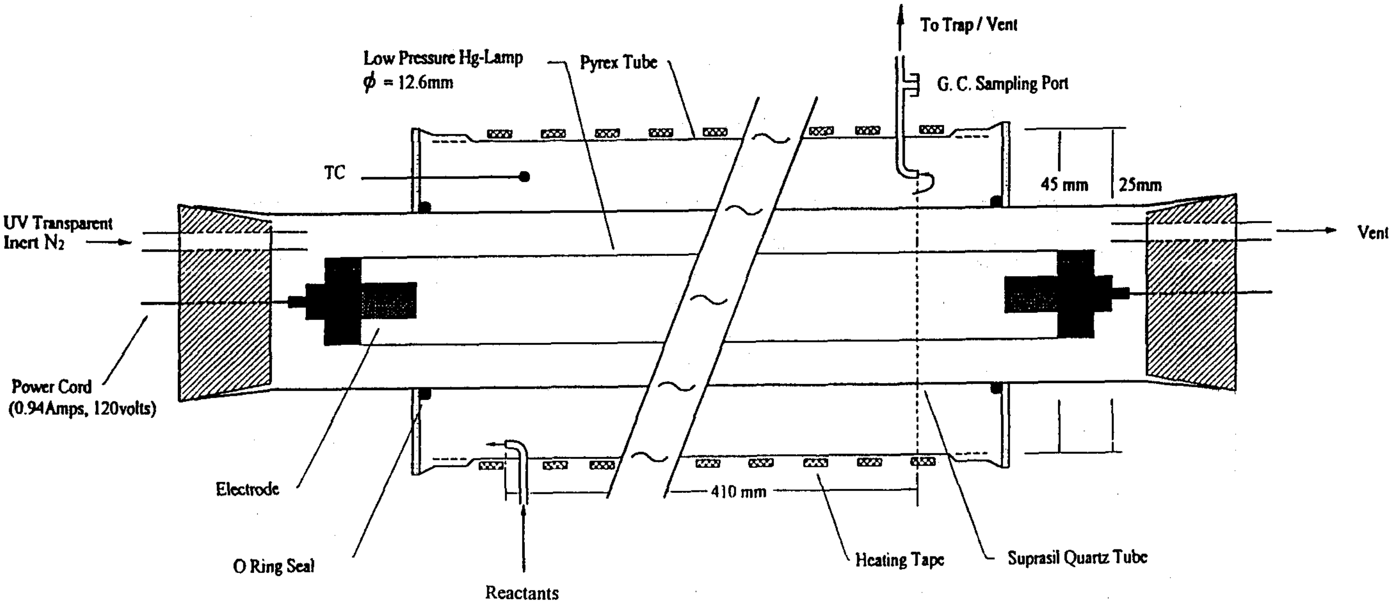
METHODOLOGY

The RPD treatment was successfully tested with a representative chlorocarbon 1,1,1-trichloroethane (TCA). The tests were conducted in a Photothermal Annular Flow Reactor, schematically illustrated in Figure 2. The photothermal Annular Flow chamber is the volume bounded by two concentric tubes: an outer pyrex tube (l = 51 cm, ϕ = 4.5 cm) wrapped with a heating tape, and an inner <u>suprasil</u> quartz tube (l = 71 cm, ϕ = 2.5 cm) containing a low-pressure Hg lamp. The heated section of the reactor is insulated with a ceramic blanket. The reactor can be heated up to 750 °C.

The low-pressure Hg lamp is specially designed to ENERGIA's specifications. Inert gas (N_2 or Ar), transparent to UV irradiation, is continuously flown over the lamp, to displace air surrounding the lamp so that UV light is not attenuated by oxygen (present in air). This also reduces the thermal load due to external heating. To avoid lamp damage, the lamp electrodes are located in the cool end-zones of the reactor. And, if necessary, they can be cooled by auxiliary fans.

Mixtures of Chlorocarbon/H_2/Ar flow through the electrically heated reactor and are exposed to UV irradiation along the constant temperature thermal zone. Samples for GC and GC/MS analyses are drawn at the entrance and exit of the photothermal chamber.

Key Features of the annular flow reactor are: i. Operating Conditions: T = ambient - 650 °C, P = 1 atmosphere, ii. Long residence time, τ = 10 - 260 sec, iii. Large reactor volume = 451 cc, iv. Uniform exposure to UV irradiation, v. Optical path length = 1 cm, vi. Accessible wavelengths: 185, 254, 313 nm (Hg), 222 nm (Cd), 215 nm (Zn).



<u>Figure 2</u>. Schematic of the Annular Flow Reactor.

Experiments were performed without and with UV light, under otherwise identical conditions. Experiments with the UV light off are designated Reductive Thermal-only (RT), and experiments with the light on are designated Reductive Photo-Dechlorination (RPD).

The conditions selected for both sets of experiments (RT and RPD) are:

Flow Mixtures:	1.0% TCA/45.0% H_2/Balance Ar
Pressure:	1 atmosphere
Temperature:	430 °C, 520 °C, 590 °C
τ Range:	15 - 260 sec
Light Source:	Low-Pressure Hg Lamp

These conditions were chosen to optimize the process for achieving +99% (conversion and dechlorination).

RESULTS

Experimental results are presented in terms of Percent Conversion, Percent Dechlorination and Selectivity. Percent Conversion is the percent consumption (disappearance) of the parent molecule (i.e. TCA), without regard to the identification of the products. Percent Dechlorination is the percent conversion of TCA to chlorine free products. Selectivity is the normalized molar fraction of each product relative to <u>all</u> products.

Percent Conversion and Percent Dechlorination were measured as a function of residence time (τ) at three temperatures, 430, 520 and 590 °C.

At the lower temperature (430 °C), percent conversion was very low for RT (less than 30%) and significantly higher (80%) for RPD. At higher temperatures (520 °C and 590 °C), complete conversion (100%) was obtained for both RT and RPD processes. Consequently, the difference between the two processes was only in their respective selectivities. As will be pointed out below, RPD demonstrated almost complete dechlorination, whereas RT did not.

Percent dechlorination obtained during RT treatment at 430 °C and at 15 - 60 sec was quite low ~5% and at 260 sec it was still low, about 9.0%. However, during RPD treatment, it increased from 9 to 47% with the same increase in τ. At slightly higher temperature, i.e., at 520 °C, during RT treatment, it increased very slowly from 30 to 40%, with the increase in residence time from 15 to 260 sec. In contrast, during RPD treatment, it increased rapidly from 41 to 92% with modest increase in residence time (to 130 sec). At 590 °C (see Figure 3), percent dechlorination obtained during RPD treatment was remarkable. Even at the shortest studied τ (15 sec), reasonable amount of dechlorination (~65%) was obtained. It increased dramatically to +98% (at τ = 100 sec) and at τ > 100 sec, +99% dechlorination was obtained. There was also improvement during RT treatment. Percent dechlorination increased monotonically from 37 to 77%, with increasing in residence time up to 260 sec. But it fell short of complete dechlorination obtained by RPD.

These experimental results have demonstrated greater than 99% conversion and complete dechlorination at 590 °C and $\tau \geq 60$ sec. Figure 4 depicts products selectivity. It clearly shows the advantage of RPD (black bars) over Reductive Thermal-only (RT) (open bars) treatment under otherwise identical conditions. In both cases conversion is +99%. However, while the RT is limited to 51% dechlorination, the RPD exhibits +99%. It is apparent that the RPD process is capable of safe and efficient conversion of all chlorinated hydrocarbon contaminants to valuable hydrocarbon products (mainly ethane and methane).

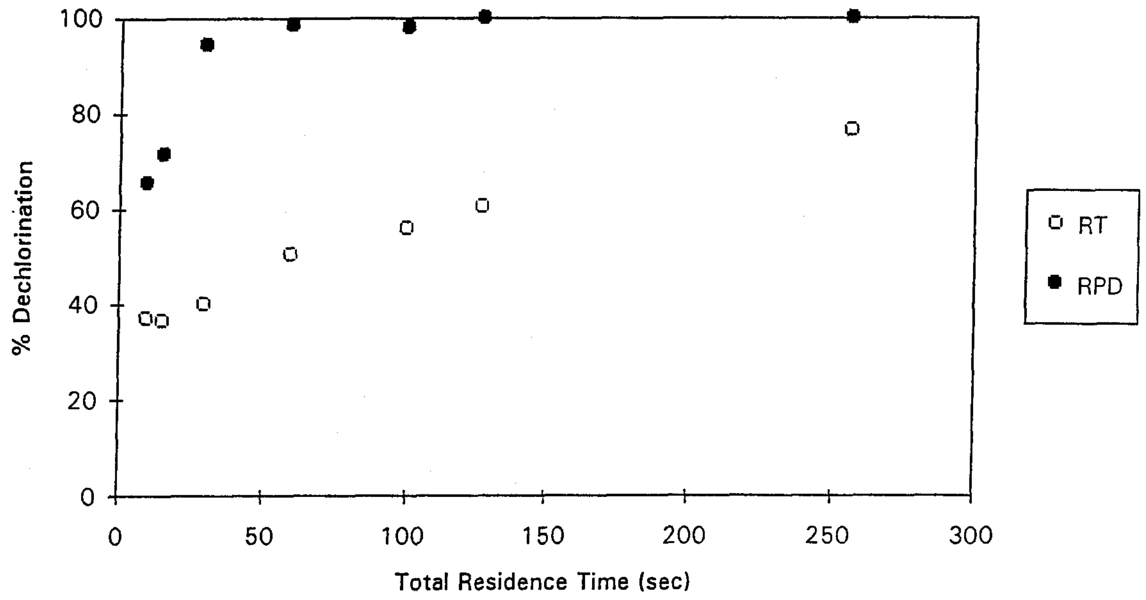


Figure 3. Percent Dechlorination as a Function of Residence Time (τ) during RT/RPD Treatment at 590 °C.

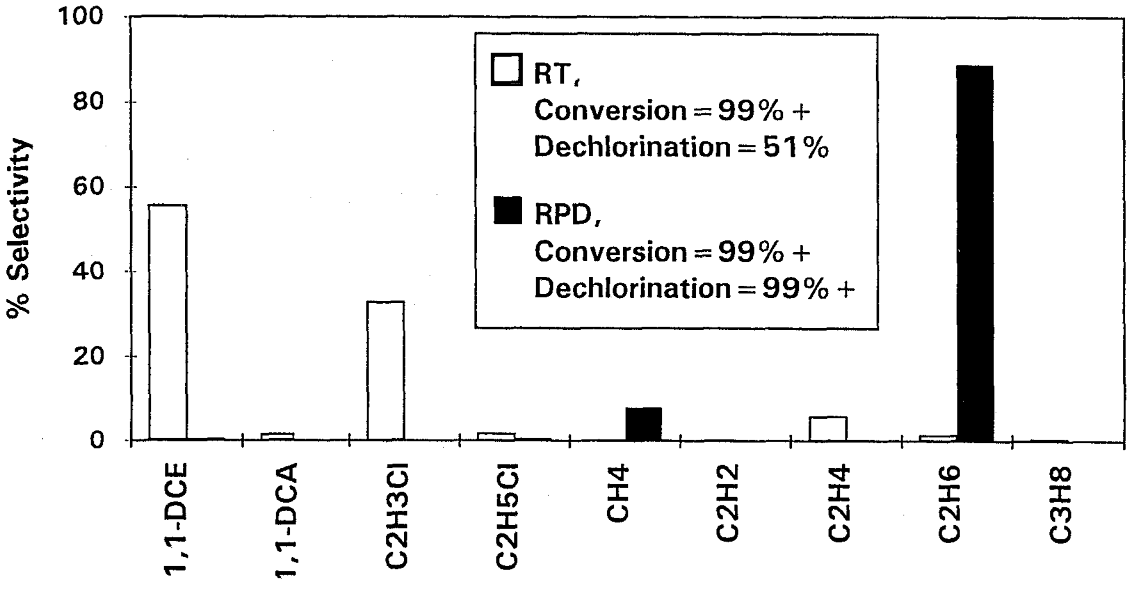


Figure 4. Product Selectivity during RT/RPD Treatment of TCA at 590 °C and 60 sec.

In order to compliment the experimental effort, a detailed kinetic modeling study was also performed. It provided insight into the reaction mechanism and identified the key elementary steps determining the reaction pathways for rapid conversion of chlorocarbons to environmentally acceptable products. Using this kinetic model, a comparison was made between experimental data and computer modeling results for RT and RPD treatments of TCA. A good agreement was evident.

WASTE APPLICABILITY

The RPD process can be effectively applied to liquid or gaseous waste streams containing saturated and unsaturated chlorocarbons. It was tested for TCA, TCE, DCE, DCA, vinyl chloride, ethyl chloride, DCM, and chloroform. It may also be applicable to PCE, carbon tetrachloride, and chlorinated aromatics to be tested.

The RPD process is specifically cost-effective for the following on-site remedial operations:

(1) In-situ treatment of chlorinated wastes discharged from Soil Vapor Extraction (SVE).

(2) Direct treatment of Off-Gas streams containing chlorocarbons.

(3) On-site regeneration of Activated Carbon saturated with chlorocarbons removed by adsorption from waste streams.

(4) Pretreatment of waste streams entering Catalytic Oxidation systems, reducing the chlorine content and thereby promoting oxidation and longevity.

(5) Small-scale, on-site remediations in R&D and testing laboratories, chemical hoods, clean rooms, etc.

CONCLUSIONS

Bench-top experimental results have successfully demonstrated the feasibility of the RPD process. They have established that the optimal operating conditions for achieving +99% dechlorination of TCA are ~ 590 °C and $\tau \geq 60$ sec. Preliminary cost analysis showed that the RPD is extremely competitive with other remedial processes. Its estimated cost is less than $1/lb. of treated chlorocarbons. The RPD process has successfully completed the bench-top developmental stage and is the basis on which a pilot-scale prototype unit is being constructed. A demonstration SITE program will follow after which the RPD technology will be available for commercialization.

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