

Regeneration of Spent Carbon by a Novel Oxidative Thermal Process

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An oxidative thermal regeneration process was developed and evaluated for its potential applicability in several environmental areas. The feasibility of the process is affected strongly by the gradual carbon loss, energy consumption, physical changes of carbon, and effective destruction efficiency of adsorbed materials during the regeneration. The aim of the study is to determine the optimum conditions to maintain acceptable destruction efficiency for adsorbed organics, controlling oxidant flow rate. Prior to its applications, various preliminary tests were carried out to determine the effects of experimental parameters on the process. The tests performed were reaction temperature, carbon loss, surface area, surface structure, and adsorptive property. The results of these tests show that the parameters are dependent on oxidant flow rate, and suggest that the process is comparable and, in some ways, possibly superior to conventional regeneration techniques because the oxidative process is a single step and less energy intensive.

Introduction

The discharge of hazardous waste into the environment has emerged as a topic of mounting concern in recent years. Much of it is in the form of wastewater.¹ Clearly, the treatment of this wastewater is thus of vital importance to reduce the human health risks and environmental contamination related to the hazardous waste. A wide array of technologies have been introduced for elimination or minimization of hazardous waste. One of the most prevalent methods for wastewater treatment is adsorption by activated carbon.^{2,3} Activated carbon is excellent adsorbent in wastewater treatment for removing refractory organic compounds that persist in environment and resist biodegradation.^{4,5} However, carbon treatment is economically practical only if the spent carbon is regenerated and therefore can be recycled in the process. The most frequently used regeneration method, wet air oxidation, is, however, highly energy intensive and is not useful in cases when very strongly adsorbing or highly toxic compounds are present.⁶⁻⁸

The present study was directed toward the development and evaluation of a low-cost, effective method for the regeneration of spent carbon as well as testing the effectiveness of this technique for decontamination of hazardous waste. The newly developed oxidative regeneration technique is based on the limited surface oxidation of carbon through the passage of a flame front in a direction counter to the flow of oxidant. For this reason, this technique was termed the counterflow oxidative system (COS). The process is carried out in a single step, and can be used for the thermal treatment of hazardous organic wastes which are not efficiently treated by conventional carbon regeneration techniques. These include hazardous species such as polychlorinated biphenyls (PCBs) and other chlorinated chemicals, which produce dangerous, toxic, or carcinogenic species such as phosgene or dioxin under certain thermal processes. The entire process is carried out with minimum external energy. The reaction is exothermic, and the energy

is derived from oxidation of carbon surface and adsorbed organics in a localized zone, utilizing most of the available oxidant. Once fully developed, this technique will reduce the regeneration and decontamination costs substantially.

Experimental

A reactor was constructed with a 1 cm wide $\times$ 30 cm long quartz tube. A schematic diagram of the reactor is shown in Figure 1. The tube was connected to gas supply and exhaust lines with stainless steel cajon fittings. The fittings were obtained from St. Louis Valve and Fittings Corp., St. Louis, MO. The flow of oxygen was controlled with a calibrated rotameter. Commercially available activated car-

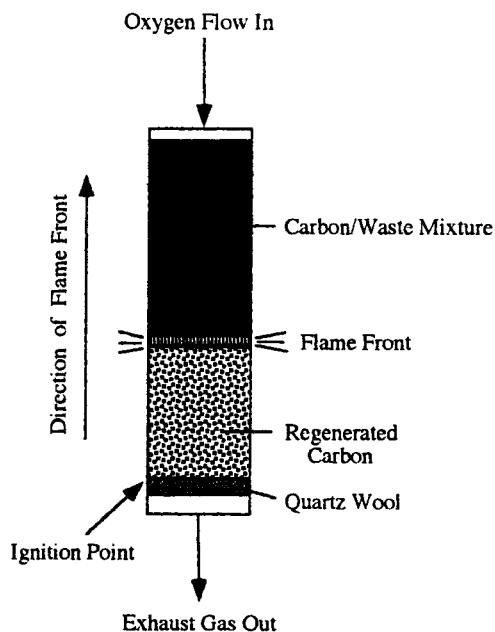


Figure 1. A Schematic Diagram of the COS Reactor.

bon (Darco, Granular, 20-40 mesh) was purchased from Aldrich. A weighed aliquot of the carbon was poured into the reactor from the top and packed by tapping the reactor tube. The packing density was determined by measuring the height of packed carbon bed. The end fitting was then connected to the tube and oxidant flow was started. After flow equilibration for 5 minutes, the charge in the reactor was ignited by applying heat at the bottom of the column with a propane torch or applying current to a resistive heater until ignition was achieved. Heating was discontinued at the point when the flame front propagated itself and moved counter to oxygen flow. The oxygen flow was stopped when the flame front reached the top of the carbon. The flame front velocity (V_{ff}) was determined by dividing the height of carbon bed in tube by total burn time. The values were 1.83 cm/min at 60 mL/min oxygen flow rate, 2.55 cm/min at 120 mL/min, 5.70 cm/min at 350 mL/min, and 7.86 cm/min at 600 mL/min, respectively. After cooling, the regenerated carbon was removed from the reactor.

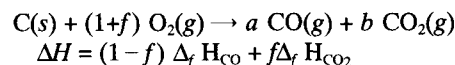
The loss of activated carbon during regeneration materially affects the economic viability of the process. The amount of carbon loss was determined gravimetrically. The off-gas compositions produced from carbon gasification during regeneration were analyzed with an on-line GC. The gases were separated with a carbosieve (60-80 mesh) packed column at 80 °C oven temperature. Helium was used as the carrier gas and its flow rate was 20 cc/min. The concentration of the separated gases was determined with a thermal conductivity detector (TCD), by measuring the response relative to standard gas mixtures obtained from Scott Specialty Gases, Inc., Durham, NC. The gases monitored were CO, CO₂, H₂, CH₄, and O₂. The temperature of the regeneration process is an important parameter which affects surface characteristics and the destruction of adsorbed species. A number of attempts were made at direct temperature measurement with temperature transducers such as platinum sensors connected to a pyrometer and an infrared sensor. However, due to the transient nature of the reaction zone, these measurements proved difficult to reproduce. For this reason, an indirect measure was obtained from the ratio of CO/CO₂ in the off-gases. The changes in the surface area resulting from the regeneration process were determined by the N₂ BET method. The determinations were carried out with a Quantasorb Surface Area Analyzer (Model QS-10, Quantachrome Corp., Syosset, NY). Surface characterization of the virgin and regenerated carbons was carried out with a scanning electron microscope (Model JSM-35CF, Joel Datum LTD, Tokyo, Japan).

The most revealing test of the impact of regeneration on carbon adsorbent is a direct comparison of their adsorptive properties for the solutes of interest before and after regeneration. Regenerated carbons were contacted with mineral oil containing a mixture of PCBs in a 250 mL flask agitated in a constant temperature bath at 21 °C. The initial concentration of PCBs in the mineral oil was 100 ppm. The equilibration period was 1 day order. After equilibration, aliquots of the oil were withdrawn from the flask and diluted with 5 mL hexane. The PCB concentrations before and after adsorption on virgin and regenerated carbons were determined with a GC interfaced to an electron capture detector (ECD).

Results and Discussion

Carbon Loss. Carbon loss is a crucial factor in determining the economics of the regeneration process. The carbon loss for the COS was found to be dependent on the oxygen flow rate. The amounts of loss were in the range of 5% to 15% with changes in oxygen flow conducted at experimental scope.

Off-Gas Compositions. The reaction of carbon with oxygen in the COS produces CO, CO₂, and surface oxygen complexes. The first step in the reaction is chemisorption of oxygen on the carbon surface to form the surface oxides. The gaseous products are then formed by thermal decomposition of the surface oxygen compounds. The ratio of CO and CO₂ concentration with increase in the oxygen flow rate varied from 1:0.7 to 1:1. Heat output (ΔH) of COS was calculated from the CO/CO₂ concentration and was found to range from 55-60 kcal/mol of carbon. The standard heat output (ΔH) per mole of carbon for COS was calculated from the following expression.



Where, $a+b=1$, $a+2b=2(1+f)$, and f =mole fraction of CO₂ in the off gas. This reaction is difficult to control in conventional regeneration reactors where violent reactions result from excess oxygen, and excessive carbon loss can easily occur, resulting in a decrease in average particle size. Conversely, in the COS, the oxygen is limited in supply and permits a better control of the reaction and carbon loss.

Determination of Reaction Temperature. Direct measurement of the transient flame front by conventional means *e.g.*, thermocouple, Pt resistance thermometer, and IR measurement proved futile. An estimation was based on relative concentration of the CO and CO₂. Since this ratio varied with the oxygen flow, it was obvious that temperature would be strongly dependent on this parameter as well. The COS temperature determination was calculated according to the following procedures.

A known amount of carbon was placed in a quartz tube of cross-section A and length L . The number of moles of carbon per cm³ is $C_c=w/(12AL)$. In a section of this tube of length (L), the carbon and oxygen initially at T will be converted to carbon (C), CO(g), and CO₂(g) at temperature T' , with loss of some of the carbon (Δn_c). All of the oxygen delivered at a volumetric flow rate (F , cm³/sec) and pressure P (atm) is assumed to be consumed. The amount of oxygen consumed depends on the total burn time. This calculation neglects oxygen which is present in the interparticle pore and intraparticle pore space at the beginning of the burn. The flame advances through this section at a linear burning rate (B , cm/sec). The time required is $t=L/B$. The volume of O₂ burned is: $V_{O_2}=Ft=FL/B$. Moles of O₂ burned are: $\Delta n_{O_2}=kFPL/BT$, where $k=0.001/0.08205=0.01219$ molK/cm³atm. The ratio of carbon to oxygen burned is: $\Delta n_c/\Delta n_{O_2}=2/(1+f)$, and $\Delta n_c=2kFPL/BT(1+f)$. f =mole fraction of CO₂ in product stream. The total moles of carbon involved is $n_c=AC_cL$, so $\Delta n_c/n_c=2kFP/AC_cBT(1+f)$. The process is: $(n_c/\Delta n_c)C(s, T)+(1+f)O_2(g, T) \rightarrow fCO_2(g, T')+(1-f)CO(g, T')+[(n_c/\Delta n_c)-1]C(s, T')$ and is assumed to occur adiabatically, so that

$$O = f[\Delta_f H_{CO_2} + \int_T^T C_{PCO_2} dT] + (1-f)[\Delta_f H_{CO} + \int_T^T C_{PCO} dT] \\ + [(n_c/\Delta n_c) - 1] \int_T^T C_{PC} dT$$

with enthalpies of formation at T , which is taken as 298.15 K. The final temperature, T' , was estimated from enthalpies of formation and heat capacities of CO and CO₂ gas. The iterative calculation started to calculate the average heat capacity terms over the range 298.15 K $\rightarrow$ T' ;

$$H_x = f \int_T^T C_{PCO_2} dT + (1-f) \int_T^T C_{PCO} dT + [(n_c/\Delta n_c) - 1] \int_T^T C_{PC} dT \\ C_p(\text{avg}) = H_x / (T' - 298.15)$$

Then, a better approximation (T'') was calculated. $T'' = 298.15 + [393509f + 110525(1-f)] / C_p(\text{avg})$. The calculated temperature is shown in Figure 2. The results showed that the flame temperature varied from 1,100 K to 1,900 K with the change in oxygen flow rate. It effects desorption and degradation of adsorbed species, and surface characteristics of the carbon. Favorably, the high temperature is desirable for destruction of adsorbates, thus allowing more thorough regeneration and activation of the surface. It, however, extracts a price in terms of increased burn-off and deterioration of physical properties of the carbon particles.

Surface Structure. The scanning electron micrographs, given in Figure 3, showed readily observable physical changes in the carbon surface. Virgin carbon exhibited a relatively smooth surface. The regenerated carbons gradually developed a sponge-like appearance with large macropores, due to the fracture of the particles caused by thermal stress. These physical changes in carbon particles can make faster transport of solutes from the solution into the interior micropores and would be expected to affect the adsorption kinetics of the carbon in dynamic (non-equilibrium) situations such as flow-through column.

Adsorptive Capacity. A better measure of changes of adsorptive properties of regenerated carbons was obtained by examining the adsorptive behaviour of PCBs in mineral oil/carbon systems. The analysis showed that, in all

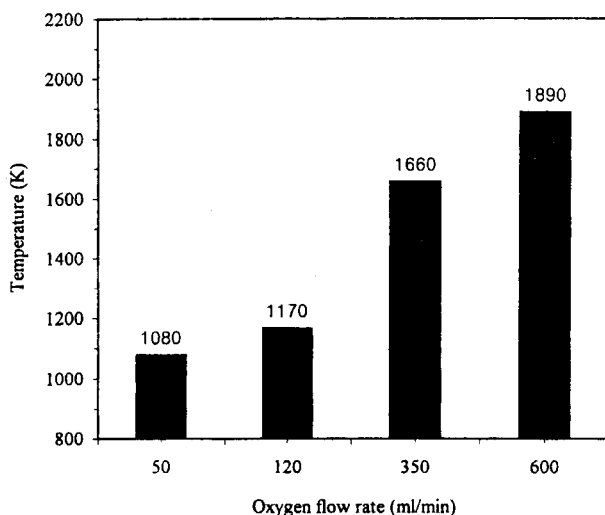


Figure 2. Effect of Oxygen Flow on Temperature of COS. (Determined by Thermodynamic Data Based on CO/CO₂ Ratio)

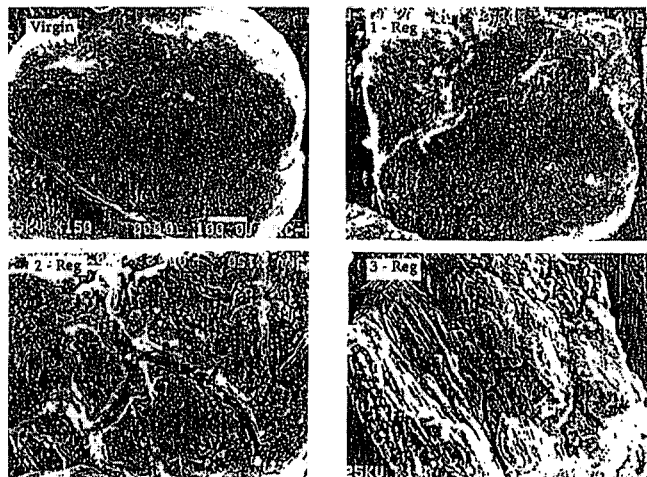


Figure 3. Scanning Electron Micrographs of Virgin and 1,2,3-Regenerated Darco Carbons (Magnification 150x).

cases, the concentration of residual PCBs in mineral oil was nearly the same. The results support that COS does lead to the conclusion that the adsorptive capacity of the carbon after COS regeneration remains largely intact.

BET Surface Area. The large surface area of activated carbon plays a key role in its exceptional adsorptive capacity. Therefore, it is essential that the high surface be preserved during the regeneration process. The results were somewhat surprising and showed that the process resulted in a small but measurable increase in the surface area. The increase was most noticeable (15%) after the first regeneration cycle, and the surface area then remained relatively constant after the second regeneration cycle. A plot of percent changes in aggregate surface area related with carbon loss in successive batch regeneration experiments was given in Figure 4. In contrast to other regeneration techniques, the result was a steady decline in the aggregate surface area.

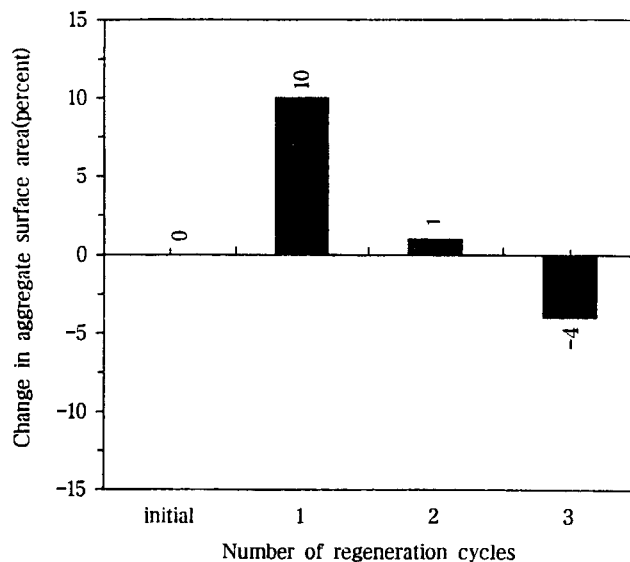


Figure 4. Effect of COS on Aggregate Surface Area.

Conclusion

Various pre-tests were carried out to obtain the optimum conditions for maximum destruction efficiency of adsorbed organics. The temperature of flame front, carbon loss, and the changes in physical properties of carbon during COS were found to be strongly dependent on oxygen flow rate. The temperature reached was high enough to insure complete destruction of the organic chemicals. The carbon loss was controllable. The analysis of specific surface area after 3 successive COS cycles indicated that the adsorptive capacity of the carbon remains largely intact. The result was supported by batch adsorption experiments of regenerated carbons with PCB contaminated oil. The overall results obtained during the studies demonstrate that COS is a single step regeneration/destruction process, and could prove to be highly effective for the regeneration of spent carbon.

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Application of a Novel Carbon Regeneration Process for Disposal of APEG Treatment Waste

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The chemical waste treatment, APEG (alkali/polyethylene glycol) process has been shown to be effective for the dechlorination of PCBs in transformer oil. Considerable amount of PCBs, however, still remains in the waste exceeding the 25-50 ppm limit set by regulatory agency. A new thermal regeneration technology has been developed in our laboratory for disposal of hazardous organic wastes. Due to the limited oxidation of carbon surface through the reverse movement of flame front to oxidant flow, this technology was termed counterflow oxidative system (COS). Specially, the oxidant flow in the COS process is a principal parameter which determines the optimum conditions regarding acceptable removal and destruction efficiency of adsorbed organic wastes at minimal carbon loss. The COS process, under optimum conditions, was found to be very effective and the removal and destruction efficiency of 99.99% or better was obtained for residual PCBs in the waste while bulk ($\geq 90\%$) of carbon was recovered. Any toxic formation of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzo furans (PCDFs) were not detected in the regenerated carbon and impinger traps. The results of surface area measurement showed that the adsorptive property of regenerated carbon is mostly reclaimed during the COS process.

Introduction

Modern society operates on electric power and a world without electric power is unthinkable. Transformers are integral components of electric power distribution system. The operation of these components is dependent on dielectric materials in the components. In the case of power transformers, the dielectric materials should possess a high dielectric constant and also be chemically and thermally stable. PCBs were found to possess these properties.^{1,2} However, due to the potential environmental threat and toxicity associated with PCBs,³⁻⁵ these chemicals in transform-

ers have been retrofilled with mineral oil or other dielectric fluids.⁶ Although the resulting transformers generally have small amounts of PCBs, falling between 100-2,000 ppm, these levels still exceed the USEPA (United States Environmental Protection Agency) mandated level of 25-50 ppm.⁷ Since the number of transformers is so numerous worldwide, the PCB contaminated dielectric fluids represent a significant environmental problem.

The disposal of PCBs has been a major area of concern. The approaches for this purpose have been addressed through incineration and chemical dechlorination. The high temperature incineration^{8,9} is straightforward. However, this