NOTATION

D_b = bulk diffusivity
D_e = effective diffusivity
$F(\lambda)$ = restrictive factor
T = temperature

Greek Letters

α = restrictive coefficient
ϵ = porosity
λ = ratio of molecular diameter of solute to pore diameter of alumina
τ = tortuosity
τ_o = tortuosity at $\lambda = 0$

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Thermal Regeneration of the Phenol-Carbon System

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Suzuki et al. (1978) divided the characteristics of thermal regeneration of spent activated carbon into three types according to the kind of adsorbate. Phenol, and other aromatic compounds with side chains, constituted type III adsorbates that were found to be desorbed slowly on heating and to leave a large residue at 1,073 K. We have confirmed this behavior with thermal gravimetric measurements (TGA experiments) for phenol adsorbed on a bituminous-base, activated carbon (Type BPL from Pittsburgh Activated Carbon Co.). However, the main purpose of this note is to describe the data of thermal regeneration as a function of temperature.

ADSORPTION ISOTHERMS

Figure 1 shows equilibrium isotherms for three different adsorbates, sucrose (Chihara et al., 1981), sodium dodecylbenzene sulfonate (DBS) (Umehara et al., 1982), and phenol, at 298 K on type BPL carbon. This carbon, whose complete properties are available (Chihara et al., 1981), has a broad pore size distribution (5 to >10,000 $\times 10^{-10}$m) and a high surface area (1×10^6 m^2/kg). The carbon (2.1×10^{-4} to 3.2×10^{-4} m particles) used for preparing the samples was first boiled with distilled water to remove fines and dried at 393 K in an oven until there was no further weight change. Then the particles were added to phenol-water solutions and placed in shakers in a bath at 298 K for three days. The upper isotherms for phenol were obtained from the phenol concentrations [determined by spectrophotometric (UV) analysis] of the solutions before and after adding the carbon particles. The lower isotherms were obtained by filtering the particles, drying in an oven at 393 K to constant weight (about three days), and weighing.

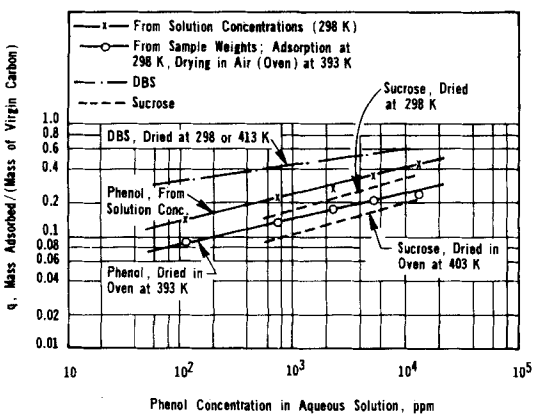

Figure 1. Adsorption isotherms: phenol on BPL carbon at 298 K.

Over the concentration ranges shown, all the isotherms are of the Freundlich type (straight lines in Figure 1). The adsorption capacity for phenol is somewhat higher than that for sucrose. The two isotherms for these two adsorbates indicate that about 38% of the adsorbed material is removed by drying in air at 393–403 K. In the case of sucrose, the desorbed material must be volatile decomposition products, while for phenol either volatile decomposition products or phenol itself could be evaporating from the carbon. Seewald (1974) found that phenol on carbon can react at room temperature in the presence of air to produce volatile products and dibenzofuran and oxydiphenyl ether.

In contrast, the isotherm for DBS is the same for samples dried at either 298 or 413 K, indicating that there is no low-temperature decomposition. The adsorption capacity of the carbon for the DBS is significantly higher than that for either phenol or sucrose.

TGA DATA

A Perkin-Elmer TGA apparatus, modified but slightly from that employed by Chihara et al. (1981), was used to measure both the

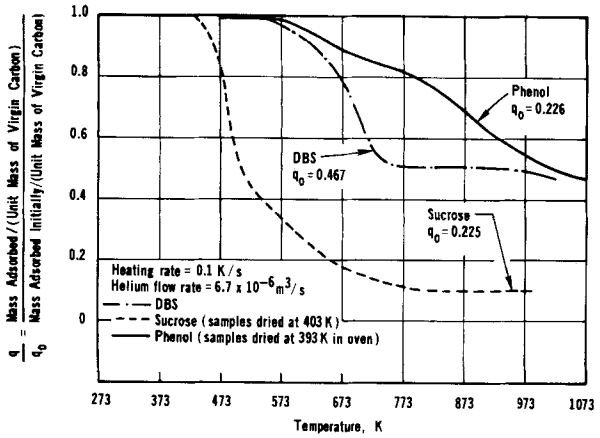

Figure 2. Typical TGA data for phenol.

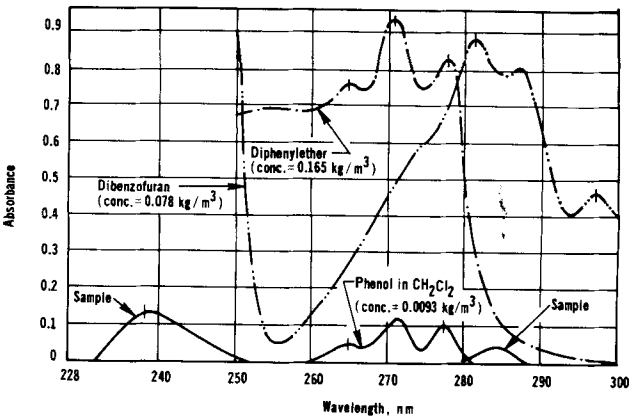

Figure 4. Absorbance vs. wavelength for sample collected from TGA effluent gas from 393 to 673 K.

weight vs. temperature and rate of weight change vs. temperature at constant heating rates. The samples used for these TGA runs had been dried in air at 393 K (as described earlier) and stored in bottles at 298 K. Preliminary experiments at different helium flow rates, different masses of carbon sample (different number of layers of particles in the basket) and at different heating rates were made to determine conditions for which transport effects were insignificant. Final data were taken with 5×10^{-6} kg of sample, helium flow rate of 6.7×10^{-7} m^3/s (298 K, 101.3 kPa), and at a heating rate of 0.1 K/s.

Figure 2 shows a typical weight vs. temperature curve for phenol for an intermediate initial loading, q_o = 0.226 kg/(kg of virgin carbon). A residue of about 47% of the initial weight of adsorbate remains on the carbon at 1,073 K, confirming that adsorbed phenol is difficult to desorb. In contrast, with sucrose there is a residue of but about 10% at 1,073 K. The residue for dodecylbenzene sulfonate also is large (about 45%). However, Chihara et al. (1981) found this to consist primarily of an inorganic residue, Na_2SO_4, not present with phenol. The results in Figure 2 show that after thermal regeneration a gasification process, for example, with steam, is necessary if most of the residue is to be removed. Phenol curves similar in shape to that shown in Figure 2 were measured for other q_o ranging from 0.091 to 0.307 kg/(kg virgin carbon). The weight of residue at 1,073 K was found to be directly proportional to the initial loading, q_o.

Figure 3 shows the rate of weight change, $m = dq/dt$, vs. temperature for four initial loadings. In all cases two maximum rates are observed, one at about 583 K and the second at 833–893 K, with a minimum rate at the intermediate temperature of 673 K. From the phenol curve in Figure 2 it is seen that only 11% of the absorbed weight, remaining at 393 K, is removed up to 673 K. Figure 3 shows that the rate of weight loss is relatively low in the range 393–673 K.

In an attempt to identify the material desorbing, the effluent gas from the TGA was passed through a trap containing liquid dichloromethane at dry-ice temperature. After a run, samples of the trap liquid were analyzed by UV spectroscopy and gas chromatography. Figure 4 shows the UV-absorbance spectra of the trap liquid collected from a TGA run up to 673 K, where the rate of desorption is a minimum. Also shown are curves for pure phenol, diphenyl ether, and dibenzofuran, in dichloromethane. There is some absorbance by the sample at the wave lengths where the three compounds absorb light, but the overlap is minimal. Gas chromatographic analysis indicated water, carbon dioxide, and very small amounts of phenol and the ether. These results are in agreement with those of Seewald (1974) who found that phenol on carbon can react, in the presence of air, to produce volatile products. Our samples were stored in bottles containing air. The greatest absorbance for the sample is at 239 nm, and is due to some unknown product of decomposition that is desorbed in the temperature range 393 to 673 K.

Forty-two percent of the adsorbed weight at 393 K is desorbed in the temperature range 673 to 1,073 K (Figure 2). The UV-absorbance curve for the sample collected in this higher temperature range is displayed in Figure 5 along with curves for pure phenol, diphenyl ether, and dibenzofuran, in dichloromethane. These data indicate that there was no dibenzofuran in the sample. This was confirmed by chromatographic analysis. The three absorbance peaks for the sample at 265, 271 and 277 nm are also at wavelengths where phenol and diphenyl ether have strong absorbances. Samples analyzed in the gas chromatograph gave peaks at the retention times for phenol and for the ether. Hence, both of these compounds were desorbed at temperatures between 673 and 1,073 K with a maximum rate near 863 K (Figure 3). The quantities of the desorbed species could not be determined quantitatively. This is because the small, 5×10^{-6} kg, TGA samples lead to very low

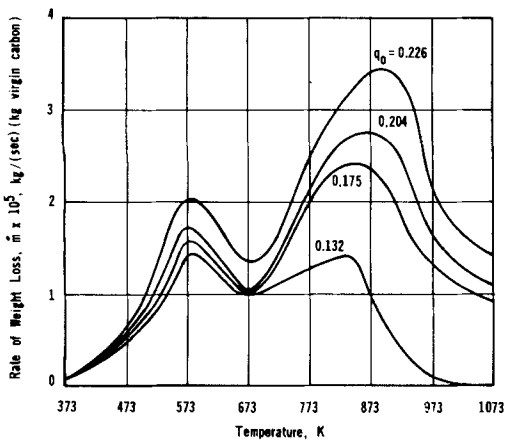

Figure 3. Rate of weight loss vs. temperature.

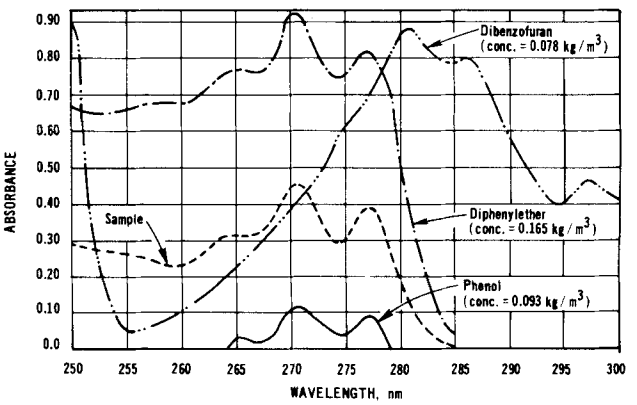

Figure 5. Absorbance vs. wavelength for sample collected from TGA effluent gas from 673 to 1,073 K.

concentrations in the effluent gas. Also the fractions absorbed in the dichloromethane trap were unknown. However, the analyses suggested that only a small amount of the total material was desorbed as phenol or diphenyl ether. Presumably, most of the desorbed substance were cracked products.

CONCLUSIONS

The results that we have found show that drying in air at 393 K results in desorption of 38% of the initial weight of phenol adsorbed on carbon from aqueous solutions. Subsequent heating to 673 K caused an 11% loss in weight of the material remaining at 393 K. Water, carbon dioxide, and very small amounts of phenol and diphenyl ether were identified as some of the desorption products in this temperature range, but UV analysis indicated that other species were also being desorbed. Additional heating to 1,073 K resulted in a further 42% loss in the weight of material remaining at 393 K. Phenol, and particularly cracked products, were desorbed in this high-temperature range. Of the material remaining after drying at 393 K, there was a residue of 47% after heating to 1,073 K.

ACKNOWLEDGMENT

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NOTATION

$\dot{m}$ = rate of weight loss, kg/(s) (kg of virgin carbon)
q = mass adsorbed/(mass of virgin carbon); q_o = mass adsorbed initially
T = temperature, K

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Statistically Rigorous Parameter Estimation in Dynamic Modeling Using Approximate Empirical Models

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INTRODUCTION

In the last few centuries the tools of physics have been developed to the stage that sets of predictive equations, called models, for many natural phenomena can be constructed. These models usually take the form of differential and integral equations that must be solved numerically. Although numerical simulation and algorithm efficiency are presently common topics, the most important questions of modeling, namely adequacy and statistical reliability of the proposed dynamic models, have not received appropriate attention. It is precisely these aspects that must finalize the model building process.

The goal of modeling is to deduce the mathematical description of a physical process. Typically, this mathematical description takes the form of a mechanistic model. In such models we believe the governing equations are tentatively known but the values of physical constants, called parameters, must be determined. The basic philosophy of modeling has been developed by Box and coworkers (Box and Hunter, 1965; Box and Draper, 1965; Box et al., 1973; Box et al., 1978) who proposed general criteria for parameter estimation defined in terms of model responses. Particular attention in their works was given to model adequacy which they assessed through an analysis of the confidence regions for the parameters. Their ideas were discussed using a number of simple models which allow analytical solutions.

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