TABLE 1. KINETIC PARAMETERS FOR HIGH-TEMPERATURE (SECOND PROCESS) DECOMPOSITION

m, K/s	$q_{\infty h}/q_{oh}$	$E_3 \times 10^{-4}$ J/mol	$(k_3)_o$, s^{-1}
0.1	0.92	5.78	1.9
0.2	0.91	5.95	4.6
0.3	0.93	6.12	8.7

ACKNOWLEDGMENT

The final assistance of NSF Grant CPE-8026101 is gratefully acknowledged.

NOTATION

a = fraction of total DBS absorbed as $\bar{D}_1$
b = fraction of total DBS adsorbed as $\bar{D}_2$
$\bar{C}$ = residual adsorbed material
$\bar{D},\bar{D}_1,\bar{D}_2$ = adsorbed forms of sodium dodecylbenzene sulfonate
E_1 = activation energy of decomposition of DBS to intermediate, J/mol
E_2 = activation energy of desorption for Eq. 2, J/mol
E_3 = activation energy of decomposition of intermediate to adsorbed residual material, J/mol
G_1,G_2,G',G'_1,G'_2 = gaseous products
$\bar{I},\bar{I}_1,\bar{I}_2$ = intermediate products retained on the carbon
k_1 = first-order rate constant for decomposition of DBS to intermediate, 1/s
k'_1 = first-order rate constant for Eq. 14
$(k_1)_o$ = preexponential factor for k_1, s^{-1}
k_2 = first-order rate constant for desorption step of adsorbed reactive solid, s^{-1}
k'_2 = first-order rate constant for Eq. 15, s^{-1}
$(k_2)_o$ = preexponential factor of Arrhenius equation for k_2, s^{-1}
k_3 = first-order rate constant for decomposition of intermediate to adsorbed residual material, s^{-1}
$(k_3)_o$ = preexponential factor of Arrhenius equation for k_3, s^{-1}
m = constant heating rate, K/s
q = mass adsorbed per unit mass of initial virgin carbon
q_o = mass adsorbed initially (time = 0) per unit mass of initial virgin carbon; q_{oh} = mass adsorbed at beginning of second process
q_∞ = mass adsorbed at infinite time (per unit mass of initial virgin carbon) for first process; $q_{\infty h}$ = mass adsorbed at 1,023 K for second process
R_g = gas constant, J/(mol)(K)
$\bar{S}$ = adsorbed product of decomposition
T = temperature, K
t = time, s

Greek Letters

α_1,α_2 = coefficients defined by Eq. 13
β_1, β_2 = coefficients defined by Eq. 17

LITERATURE CITED

Chihara, K., M. Suzuki, and J. M. Smith, "Regeneration of Powdered Activated Carbon, Part I Thermal Decomposition Kinetics," *AIChE J.*, **27**, 213 (1981); "Part II Steam-Carbon Reaction Kinetics," *ibid*, **27**, 220 (1981)

Hernandez, L. A., and P. Harrriott, "Regeneration of Powdered Active Carbon in Fluidized Beds," *Environ. Sci. & Tech.*, **10**, 454 (1976)

Suzuki, M., D. M. Misic, O. Koyama, and K. Kawazoe, "Study of Thermal Regeneration of Spent Activated Carbons: Thermogravimetric Measurement of Various Single-Component Organics Loaded on Activated Carbons," *Chem. Eng. Sci.*, **33**, 271 (1978)

Walker, Jr., P. L., F. Rusinko, Jr., and L. G. Austin, "Gas Reactions of Carbon," *Adv. in Cat.*, 11, Academic Press, New York (1959)

Manuscript received July 30, and accepted December 14, 1982.

Part II: Gasification Kinetics with Steam

TADASHI UMEHARA, PETER HARRIOTT and J. M. SMITH

University of California
Davis, CA 95616

The kinetics of the reaction between steam and thermally-regenerated activated carbon containing DBS residue was studied at 973 to 1,062 K and atmospheric pressure. The results fit a Langmuir-Hinshelwood rate equation originally developed for the oxidation of other types of carbon with steam. The rates of reaction were relatively high. Auxiliary experiments with added Na_2SO_4 indicated that the non-volatile inorganic residue from DBS has a catalytic effect.

Readsorption measurements on regenerated samples demonstrated that thermal regeneration alone resulted in considerable loss (35%) in adsorption capacity but that thermal regeneration followed by steam gasification could completely restore the adsorption capacity for DBS on the remaining virgin carbon.

SCOPE

The results of Part I showed that about half of the original adsorbate remained on the activated carbon after thermal regeneration to 748 K. Furthermore, little of this residue from DBS (sodium dodecylbenzene sulfonate) was removed by heating to 1,023 K. Accordingly, oxidation is necessary in order to gasify the carbonaceous residue and restore the adsorption capacity of the carbon. Because of the nonvolatile inorganic content of DBS, there may be a buildup of material on the carbon even after gasification. This buildup will depend on the amount of

---

P. Harriott is on leave from Cornell University, Ithaca, N.Y.

inorganics dissolved when the regenerated carbon is exposed to waste solution. The purpose of Part II is to study the kinetics of the steam-residue. oxidation reactions, including the effect of the inorganic residue (presumably sodium sulfate). Also some data were obtained for the adsorption capacity, for DBS, of the regenerated material.

The samples for gasification were prepared by drying, as described in Part I, and thermally regenerated with helium at atmospheric pressure in the TGA equipment at a rate of temperature rise of 0.3 K/s. The temperature was held constant when it attained the desired level for kinetics measurements (between 973 and 1,062 K), and a mixture of helium and steam, and hydrogen (for some runs), was then passed over the sample. The rate of oxidation was measured by following the change of sample weight with time. Data were obtained for steam concentrations from 0.02 to 5.0 mol % and hydrogen concentrations from 0.0 to 0.6 mol %. Since there was little thermal regeneration over the temperature range 973 to 1,062 K, the oxidation rates at different temperatures refer to samples of essentially the same composition. The oxidation rates were evaluated by subtracting from the observed weight change that due to thermal regeneration (in the absence of steam).

Additional oxidation rate data were obtained for samples of virgin carbon, virgin carbon impregnated with Na_2SO_4, and samples with adsorbed DBS that had been thermally regenerated and washed with water (to remove inorganic salts).

CONCLUSIONS AND SIGNIFICANCE

The steam gasification rates could be correlated by a Langmuir-Hinshelwood type equation similar to that used for sucrose residues (Chihara et al., 1981) and originally developed for explaining the kinetics of the steam-carbon reaction (Walker et al., 1959). The reaction rates were much higher than observed for sucrose residue, but showed the same change from first-order to near-zero order as the concentration of steam was increased. However, the activation energy E_1 for the DBS residue, 1.64×10^5 J/mol, was less than that ($E_1 = 2.27 \times 10^5$ J/mol) for the sucrose samples. For both types of adsorbates, hydrogen reduced the rate of oxidation with steam.

The higher rates of oxidation of the DBS residues is believed to be due to the catalytic activity of the nonvolatile inorganic residue. Evidence for this was obtained by measuring rates for virgin carbon on which various amounts of Na_2SO_4 had been adsorbed prior to regeneration, and by measuring rates for DBS samples containing different amounts of inorganic residue. The rate was found to increase with the amount of inorganic material in both kinds of experiments. Also, the rate of gasification was approximately the same when the samples contained the same fraction inorganic material, either as added Na_2SO_4 (to virgin carbon) or as inorganic residue in the DBS samples. Further, washing thermally regenerated samples with water (which should dissolve some of the inorganic material), and then gasifying with steam, significantly reduced the reaction rate.

Readsorption measurements for DBS on the regenerated samples showed that regeneration by thermal means only (to 1,023 K), resulted in a loss of 35% of the adsorption capacity per unit mass of virgin carbon. However, regeneration with steam, until the mass of sample was equivalent to that of the virgin carbon plus inorganic residue, completely restored the adsorption capacity of the virgin carbon.

Because of the non-volatile inorganic residue, regeneration kinetics of spent carbon containing DBS are different than observed for purely organic contaminants. For thermal regeneration the rates for DBS were slower and obeyed different rate equations than for sucrose as explained in Part I. The purpose in Part II is to establish the kinetics for oxidation with steam of the residual organic residue after thermal regeneration, with particular emphasis on the influence of the inorganic residue.

EXPERIMENTAL

The apparatus and procedure for the steam oxidation follow closely those described in detail in Part II of Chihara et al. (1981). Samples of activated carbon with adsorbed DBS were prepared as described in Part I. These samples were then thermally regenerated in a helium stream in the TGA apparatus, up to the temperature of 973 to 1,062 K at a heating rate of 0.3 K/s. After a chosen reaction temperature was attained, the helium stream was replaced with two separate streams, one of helium and a second containing helium, steam, and hydrogen (for some runs). Then the temperature was held constant during the oxidation run. Since two streams of different composition were fed to the heater containing the sample, it was necessary to ensure complete mixing. The method developed by Chihara et al. (1981) of adding a doughnut-shaped flange to the top of the furnace achieved this purpose. This is shown in Figure 2 by the agreement of the rates of oxidation at 1,032 K for different flow rates (1.33 and 2.67×10^{-6} m^3/s).

In the TGA apparatus the gas flows on top of and around the sample holder rather than through the bed of particles. Hence, in a reaction system there can be a significant concentration gradient of reactant gas (steam in our experiments) down through the layers of particles in the sample holder. Hence, rate measurements when several layers of particles are in the holder do not represent intrinsic rates. Preliminary data were obtained with different numbers of layers of particles at 1,032 K. The results for one, four, and five layers are shown in Figure 2. The rate was reduced by 66% when five layers were used. This layer effect, to a lesser degree, was also observed in the prior work with sucrose (Chihara et al., 1981). The greater effect of mass transfer resistance with DBS samples is due to the intrinsic steam oxidation rate being much greater than it was with sucrose samples. (Compare slopes of DBS and sucrose curves in Figure 1.) The final kinetics data were obtained with one layer of particles.

Small amounts of oxygen in the gas streams can distort the results for the steam reaction, because the carbon-oxygen reaction is relatively fast. Hence, we tried to reduce oxygen contamination. An ultra high-purity helium (99.999% purity, stated oxygen content less than 1 ppm) was used for most of the runs. Hydrogen purity was 99.99%, but since its maximum concentration was but 0.6%, oxygen from this source was low. The steam mixture was prepared by passing a part of the total helium flow through a saturator containing degassed liquid water held at a constant temperature.

There was some small weight loss when pure helium was passed over the sample of virgin carbon. (The data for 1,002 K are shown by the virgin carbon–helium curve at the bottom of Figure 1.) If this loss is due to the oxygen-carbon reaction, it is believed that most of the oxygen comes from very small leaks in the apparatus. In any event the sample weight changes were corrected for this small weight loss.

A larger correction was necessary for the thermal decomposition that occurred when a flow of pure helium was passed over the DBS sample maintained at the reaction temperature. The weight vs. time curve for this thermal decomposition is shown for 1,002 K by the DBS-helium curve in Figure 1.

OXIDATION KINETICS WITH STEAM

Figure 1 for 1,002 K shows the type of weight vs. time data obtained. Curves A to E are for $q_o = 0.522$. Similar results were obtained for two other q_o values. The small weight loss during heating of the DBS samples from 822 to 1,002 K is due to the thermal decomposition and gasification described as the "second process" in

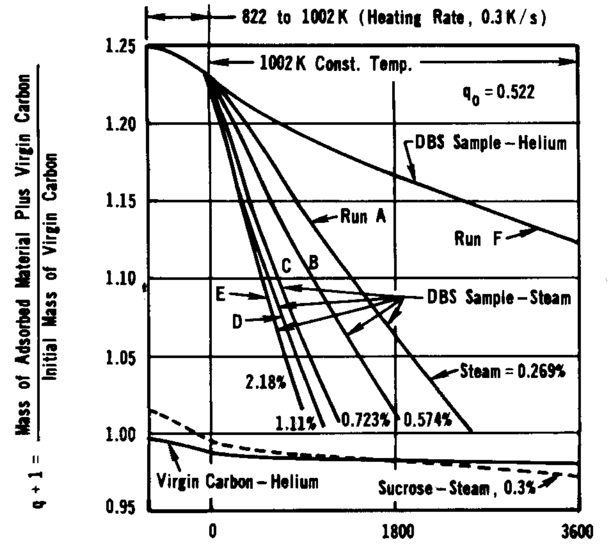

Figure 1. Mass vs. time for steam gasification (no hydrogen).

Part I. At $t = 0$ for runs labelled A to E the gas feed stream was changed from pure helium to the steam mixture and the temperature maintained at 1,002 K. The earlier result (Chihara et al., 1981, for sucrose sample—steam 0.3%) is shown for comparison. The rates of reaction are much greater for the DBS samples, although some of the increase could be due to the larger adsorption capacities (q_o values) for DBS. It is interesting to note that the opposite trend was found for thermal regeneration. As indicated in Figure 2 of Part I, the thermal regeneration rate for sucrose samples up to 748 K is larger than that for DBS samples. The rate of the steam reaction was evaluated from the slopes of the lines obtained by subtracting the weight decrease at a given time for the DBS sample—helium curve, from the weight decrease for the DBS sample—steam curve, for example by subtracting the weight decrease from run F from that of run A. This subtraction was necessary in order to separate the weight change due to thermal decomposition from that due to the steam reaction. The procedure requires the assumption that the presence of steam in low concentrations has no effect on the thermal decomposition that occurs at these temperature levels. The data in Figure 1 indicate nearly straight lines at times up to several hundred seconds. Thus, the rate was zero order with respect to mass of carbon in this time interval.

Effects of Steam and Hydrogen Concentrations

The rates of the steam reaction, determined as described and over the fraction-gasified range indicated in Figure 1, are shown in Figure 2 for various temperatures and steam concentrations. No hydrogen was present. The fraction gasified, as indicated by the decrease in $(q + 1)$ to about unity in Figure 1 is sufficient to regenerate all the adsorption capacity of the original virgin carbon. This is evident from the capacity data discussed later. The first-order behavior at low steam concentrations and trend toward zero order at higher concentrations follows the well-established rate equations for the steam-carbon reaction (Ergun, 1962; Ergun and Mentser, 1965; Walker et al., 1969). According to this formulation, the effects of hydrogen and steam concentrations on the initial rate for a fixed q_o can be expressed by the equation

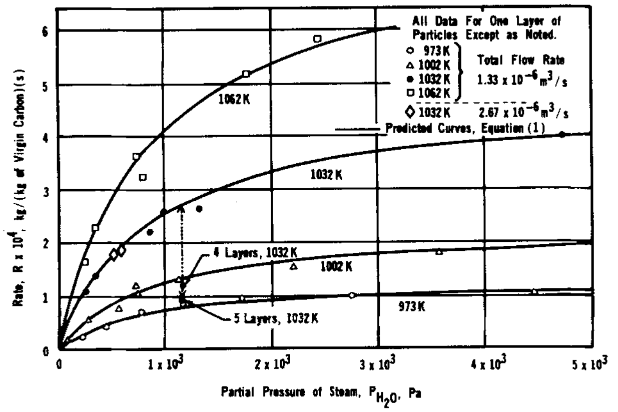

Figure 2. Effect of steam concentration on reaction rate (no hydrogen).

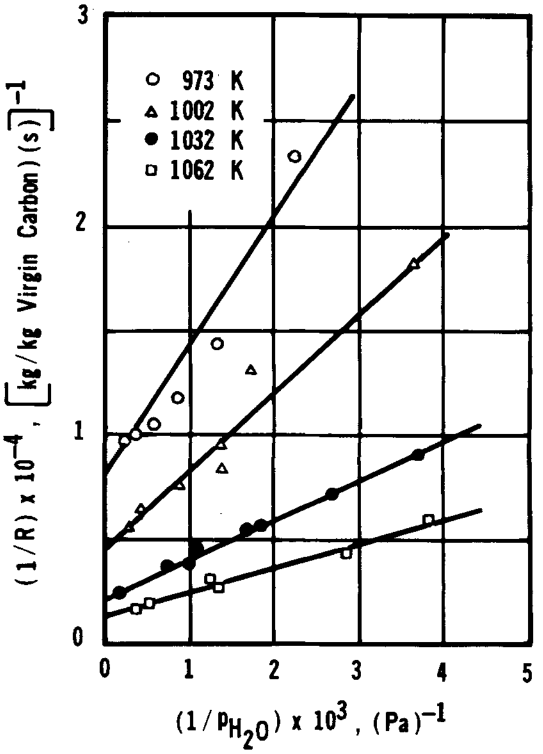

Figure 3. Linearized plot of rate data (no hydrogen).

$$R = \frac{k_1 p_{H_2O}}{1 + k_2 p_{H_2} + k_3 p_{H_2O}} \qquad (1)$$

Here we define R as kg burned per second per kg of virgin carbon existing when the sample reaches reaction temperature. This basis is chosen rather than the original virgin carbon because a slight weight change of virgin carbon occurs during thermal regeneration to reaction temperature. At 1,002 K, Figure 1 shows that q at $t = 0$ for the virgin carbon-helium sample is -0.012, so that 1.2% of the virgin carbon has already been gasified at the beginning of the steam reaction.

The curves in Figure 1 have a linear region starting at zero time and it is for this region that Eq. 1 is applied.

Figure 3 shows the agreement of the experimental data with Eq. 1. The plot of the data is according to the linear-form equation,

$$\frac{1}{R} = \frac{k_3}{k_1} + \frac{k_2}{k_1 p_{H_2O}} p_{H_2} + \frac{1}{k_1 p_{H_2O}} \qquad (2)$$

The values of the constants k_1 and k_3 determined from the slope and intercept of the lines in Figure 3 for each temperature are given in Table 1. For this evaluation of k_1 and k_3, P_{H_2} in Eq. 2 was zero. The fit is good except at 973 K. At this lowest temperature,

TABLE 1. KINETIC CONSTANTS FOR STEAM-GASIFICATION REACTION FOR q_o - 0.522

Temp., K	973	1,002	1,032	1,062
k_1, kg/(kg)(s)(Pa)	1.59×10^{-7}	2.66×10^{-7}	5.36×10^{-7}	8.70×10^{-7}
k_2, $(Pa)^{-1}$	6.66×10^{-3}	4.70×10^{-3}	2.60×10^{-3}	1.48×10^{-3}
k_3, $(Pa)^{-1}$	1.27×10^{-3}	1.17×10^{-3}	1.13×10^{-3}	1.13×10^{-3}

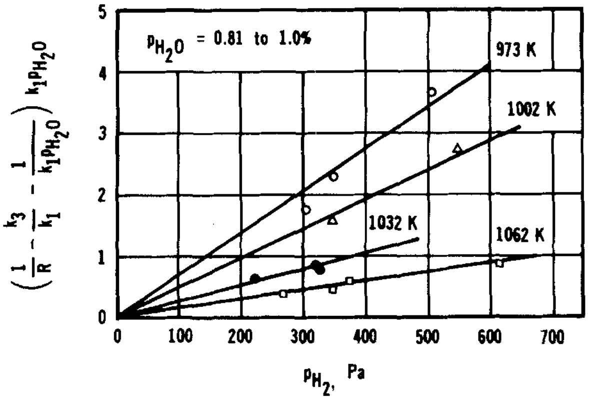

Figure 4. Linearized plot of rate data: effect of hydrogen.

the low gasification rates reduced the accuracy of the results. The curves, labeled predicted in Figure 2, were drawn with the k values given in Table 1 and agree well with the experimental points.

When the hydrogen concentration in the gas feed to the TGA apparatus was increased from zero, the rate decreased rapidly at low p_{H_2O} and more slowly at higher p_{H_2O}, as suggested by the inverse relationship of Eq. 1. The experimental data plotted as

$$\left[\frac{1}{R} - \left(\frac{k_3}{k_1} + \frac{1}{k_1 p_{H_2O}}\right) k_1 p_{H_2O}\right] \text{ vs. } p_{H_2}$$

are shown in Figure 4. The linear relationship suggested by Eq. 2 is followed except that the deviations are again larger at the lowest temperature, 973 K. Values of k_2 obtained from the slopes of the lines in Figure 4 are also given in Table 1. Comparison of these k values for DBS samples with the corresponding values, in Table 2 of Chihara et al. (1981), for sucrose samples should correspond to the much greater rate of the steam reaction for the DBS samples (Figure 1). While k_1 for DBS is about 2×10^{-7} kg/(kg)(s)(Pa) at 1,002 K, that for sucrose samples is about one order of magnitude less, 2×10^{-8}. Similarly, k_3 for DBS is about 1×10^{-3} $(\text{Pa})^{-3}$ while for sucrose samples it was about 2×10^{-3} $(\text{Pa})^{-1}$. Thus, both k_1 and k_3 are different in the direction of giving a higher rate of reaction for the DBS samples.

Effect of Temperature

Figure 5 is an Arrhenius plot for k_1. The activation energy E_1 is 1.64×10^5 J/mol. The corresponding activation energy was higher, 2.27×10^5 J/mol for the sucrose samples. The values of k_2 (associated with hydrogen) are also shown in Figure 5. They decrease with increasing temperature as expected if k_2 were a measure of a heat of adsorption. If the effect of hydrogen is so treated, using the van't Hoff equation, the heat of adsorption is $\Delta H_{H_2} = -1.7 \times 10^5$ J/mol, somewhat higher than the value of -1.0×10^5 J/mol found by Chihara et al. (1981) for the sucrose samples. The results for k_3 do not vary significantly with temperature, as indicated by the upper line in Figure 5. The same independence of temperature was found for the sucrose samples. The activation energies in the literature for the combined effect of temperature on the steam-carbon reaction for many types of carbon usually fall within a range from 2 to 3×10^5 J/mol.

We conclude that Eq. 1 is adequate for expressing the rate of reaction for the steam oxidation of thermally regenerated samples of carbon containing DBS.

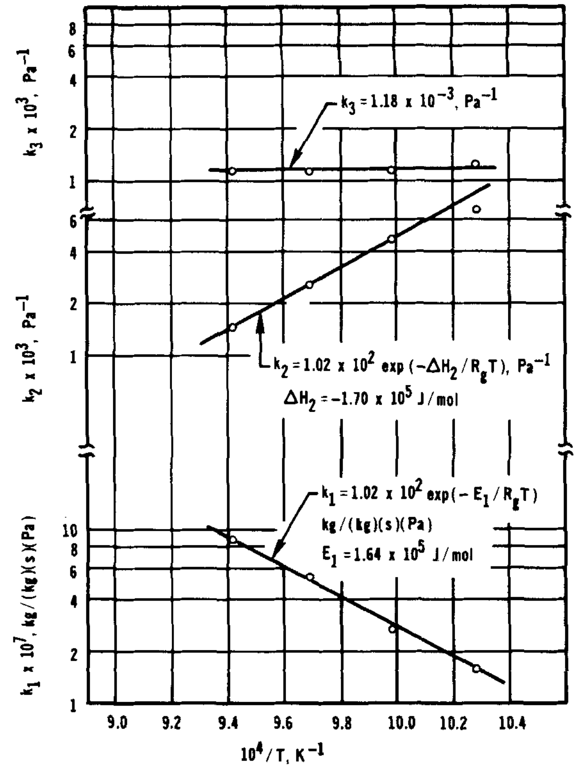

Figure 5. Effect of temperature on rate constants.

EFFECT OF INORGANIC RESIDUE ON OXIDATION KINETICS WITH STEAM

The very fast gasification rate for DBS samples (in comparison with the rate for sucrose samples) illustrated in Figure 1 suggests that the inorganic residue may have a catalytic effect. Although not shown in Figure 1, the fast rate continues until about 80% of the virgin carbon has been gasified. Since Na_2SO_4 is the probable inorganic residue, weight versus time data were obtained with samples of virgin carbon which had been soaked in aqueous Na_2SO_4 solutions. Results at a steam reaction temperature of 1,062 K are illustrated in Figure 6 for two levels of adsorbed sodium sulfate (q_o = 0.062 and 0.117 kg adsorbed per kg of virgin carbon). The dashed lines representing these results show that increasing the amount of adsorbed Na_2SO_4 by about 80% increases the rate of gasification (slope of the lines) about 500%. The increase in rate in going from zero Na_2SO_4 (the solid line labeled virgin carbon) to q_o = 0.062 kg/kg is noticeable but not very large. The other two solid lines in Figure 6 are for DBS samples with Na_2SO_4 quantities calculated to be similar to those for the dashed lines. These q_o values (0.059 and 0.107 kg/kg) were determined by assuming that all the organic residue from DBS is sodium sulfate, and that it is formed during thermal decomposition by the reaction, given in Part I, which produces one mole of Na_2SO_4 from two moles of DBS. The corresponding total q_o values are 0.287 and 0.522 kg/kg. The slopes

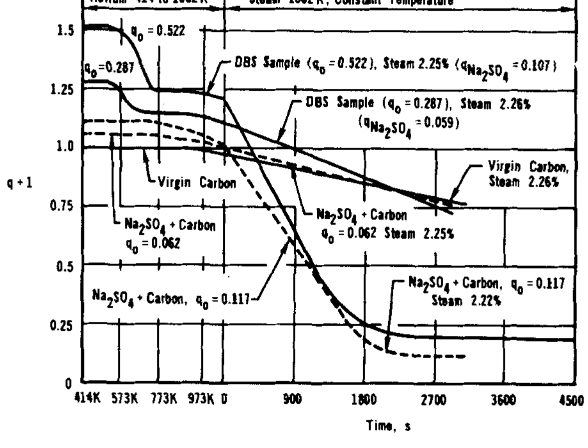

Figure 6. Effect of sodium sulfate on steam gasification.

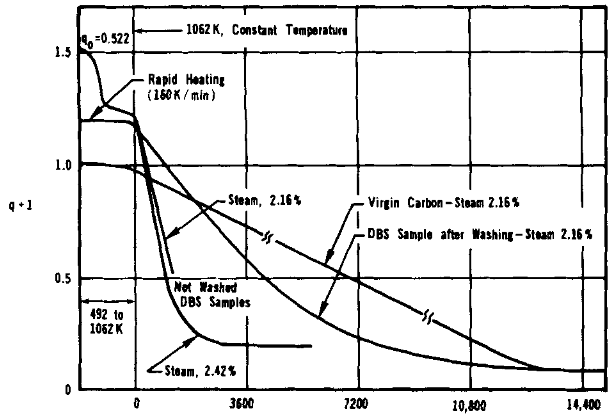

Figure 7. Effect of washing in water on steam gasification.

of the dashed and solid lines for about the same amount of Na_2SO_4 are similar. These results provide evidence that the inorganic residue from DBS, which is likely to be Na_2SO_4, acts as a catalyst for the gasification reaction with steam. This agrees with previous work (McKee, 1981) showing the catalytic effect of sodium on the gasification rate of carbon.

As a further test, a run was made with a DBS sample first thermally regenerated to 1,023 K in the TGA apparatus. The sample then was washed with deionized water and dried in an oven at 393 K. About 13% of the adsorbed material was dissolved during the washing process. The washed sample was replaced in the TGA unit, rapidly heated to 1,062 K, and then gasified with steam at constant temperature. Figure 7 compares the weight vs. time curves for this washed DBS sample with a not-washed sample (the q_o = 0.522 kg/kg curve from Figure 6). Washing is seen to reduce the rate significantly, presumably by removing the catalytic Na_2SO_4. The slope of line for the washed sample during the early stage of gasification with steam is greater than that for virgin carbon, indicating that some catalytic activity remained.

ADSORPTION CAPACITY AFTER REGENERATION

To relate the weight change during regeneration to the restoration of adsorption capacity, some data were obtained for the amount of DBS adsorbed on regenerated samples. The same adsorption procedure as employed to prepare the original DBS samples (Part I) was used. Samples of carbon plus adsorbate at three stages of regeneration were studied. The first sample had been subjected only to thermal regeneration up to 1,023 K. At this stage q - 0.243 kg adsorbed/(kg of virgin carbon). The adsorption capacity for DBS of this sample was 65% of that of virgin carbon, that is fresh carbon that had not been subjected to regeneration. This reduced adsorption capacity is shown in Figure 8 where the line represents the adsorption capacity for the fresh virgin carbon, as determined in Part I (Figure 1). The data for the regenerated samples are referred to the mass of virgin carbon, not to the mass of regenerated sample.

The second sample had been thermally regenerated to 1,023 K and then gasified with steam until q was reduced to 0.107 kg/kg. This q value corresponds to about 20% of the original DBS adsorbed (q_o = 0.522 kg/kg) which is, in terms of mass, the amount of residual inorganic residue (taken as Na_2SO_4). The reaction time with steam was 960 s. For this sample readsorption capacity was essentially the same as that of the fresh virgin carbon, as shown in Figure 8. This result is explainable if it is assumed that during the readsorption step the residual Na_2SO_4 was dissolved in the aqueous DBS solution, and that any carbonaceous residue remaining after the steam reaction had the same adsorption capacity as the virgin carbon. An independent measurement was made for the adsorption capacity of activated carbon for Na_2SO_4 from aqueous solutions, using the procedure described in Part I. The amount adsorbed was about 10% of that of DBS, indicating that Na_2SO_4 could dissolve in an aqueous solution of DBS.

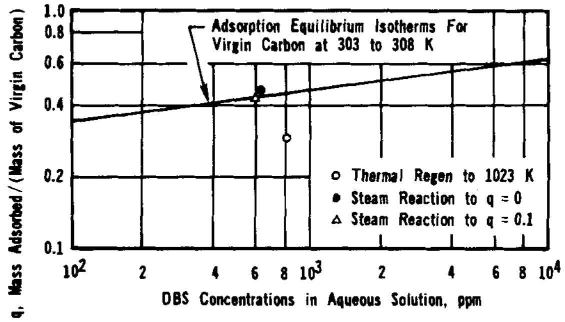

Figure 8. Adsorption equilibrium data for regenerated samples and for virgin carbon.

The third sample was regenerated like the second sample except that the steam reaction was continued until q = 0. The capacity of this material for DBS adsorption, as shown in Figure 8, is essentially the same as that of fresh carbon. Some of the virgin carbon has been gasified at this longer steam-reaction time (1,500 s) so that the adsorption capacity of the sample itself (carbon plus inorganic residue) is less than that of the fresh sample. In Figure 8 the line is based upon virgin carbon, while data points are based upon the amount of remaining carbon calculated by assuming that the inorganic residue is Na_2SO_4. The significant result from the third sample is that prolonged steam-reaction time did not affect the adsorption capacity of the carbon.

ACKNOWLEDGMENT

The financial assistance of National Science Foundation Grant CPE- 8026101 is gratefully acknowledged.

NOTATION

E_1 = activation energy for rate constant k_1, J/mol
ΔH_{H_2} = enthalpy of adsorption for hydrogen, J/mol
k_1 = rate constant for the steam-gasification reaction, Eq. 1; kg/(kg of virgin carbon when the sample attains reaction temperature)(s)(Pa)
k_2, k_3 = parameters in rate Eq. 1, Pa^{-1}
p_{H_2O}, p_{H_2} = partial pressures of steam and hydrogen, Pa
q = mass adsorbed per unit mass of virgin carbon
R = rate of steam-gasification reaction, (kg of carbon reacted)/(kg of unburned virgin carbon after thermal regeneration)(s)
R_g = gas constant, J/(mol)(K)
T = temperature, K

LITERATURE CITED

Chihara, K., M. Suzuki, and J. M. Smith, "Regeneration of Powdered Activated Carbon, Part I Thermal Decomposition Kinetics," *AIChE J.*, **27**, 213 (1981); "Part II Steam-Carbon Reaction Kinetics," *ibid*, **27**, 220 (1981).

Erun, S., "Kinetics of the Reactions of Carbon Dioxide and Steam with Coke," *U.S. Bur. Mines Bull.*, 598 (1962).

Ergun, S., and M. Mentser, "Reaction of Carbon with Carbon Dioxide and Steam," *Chemistry and Physics of Carbon*, **I**, Marcel Dekker Inc., New York, 203 (1965).

Walker, Jr., P. L., F. Rusinko, Jr., and L. G. Austin, "Gas Reactions of Carbon," *Adv. in Cat.*, **11**, Academic Press Inc., New York and London, 133 (1959).

McKee, D. W., "The Catalyzed Gasification Reactions of Carbon," *Chemistry and Physics of Carbon*, Marcel Dekker Inc., **16**, 1 (1981).

Manuscript received July 30, and accepted December 14, 1982.