Cyclic Regeneration of Activated Carbon in Fluidized Beds

Cyclic thermal regeneration of powdered activated carbon containing adsorbed sucrose was studied in fluidized beds at 1151°K and 101.3 kPa (1 atm). The regeneration process consists of three steps: 1) drying, 2), thermal decomposition, and 3), gasification of residual carbon with steam. The maximum restoration of adsorption capacity (98.5% recovery after each regeneration) was obtained when gasification removed an amount of carbon equal to the residual adsorbed carbon after thermal decomposition. It was verified that the time required to attain optimum regeneration could be determined from available kinetics data for the steam-carbon reaction. For our sucrose-activated carbon system this time was about 180 s at 1151°K.

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SCOPE

Activated carbon is widely used for removing organic pollutants from waste water. Economic considerations require regeneration of the spent carbon and the thermal process is most widely used. Also, powdered carbon is less expensive than the granular type so that fluidized-bed regeneration has some attraction. Thermal regeneration consists of three steps: 1), drying of the wet, spent carbon, 2), heating to temperatures of the order of 1100°K where thermal decomposition occurs rapidly, and 3) gasification of residual carbon. The second step is chemically complex, involving decomposition of original adsorbates, desorption of low-molecular weight products, and leaving residual adsorbed carbon. A major fraction of the original adsorbate is removed in this step. However, unless the residual carbon is removed, continued cycling operation results in buildup of residual carbon and reduction in adsorption capacity.

Effective design of regeneration processes for both powdered and granular carbon has been handicapped by lack of kinetics data for the regeneration reactions, and only recently have efforts been made to obtain such information. Suzuki et al. (1978) and Hashimoto et al. (1979) have studied the second step and given rate equations for the loss in weight due to decomposition reactions. Chihara et al. (1981a) investigated the thermal decomposition of adsorbed sucrose and proposed rate equations for a simple two-reaction sequence of decomposition processes. Also, Chihara et al. (1981b), using a thermal gravimetric apparatus, measured the kinetics of the third step employing steam for gasifying the residual carbon from sucrose adsorption.

There appears to be no information on the optimum conditions for regeneration when the activated carbon is to be used repeatedly in adsorption-regeneration cycles. The key factor is the extent of carbon gasification. The objective of our research was to determine the optimum extent of gasification in cyclic operation. Experimentally, powdered carbon with adsorbed sucrose was regenerated in a fluidized bed at 1151°K and 1 atm using steam.

If the optimum gasification and the kinetics of the reaction are known, the time of the third step can be calculated. The sucrose-steam-carbon system was chosen because kinetics had been studied (Chihara et al., 1981b). Then the predicted results using the known kinetics could be compared our observed data obtained by cyclic regeneration in the fluidized-bed reactors.

CONCLUSIONS AND SIGNIFICANCE

Preliminary experiments indicated that, with the proper amount of carbon and proper gas velocity, regeneration could be carried out under conditions of good mixing and little entrainment in fluidized beds. Small reactor tubes were used so that surface area, pore volume, adsorption capacity, and weight of carbon could all be measured without removing the carbon from the tube. Each reactor tube was subjected to five complete cycles of adsorption and regeneration and the above measurements were made for each cycle. Four reactor tubes were used so that four, different, steam-reaction times could be studied. Thermal decomposition and the reaction with steam were carried out at 1151°K.

The results showed that there is an optimum steam-reaction time for maximum restoration of adsorption capacity. For our sucrose-activated carbon system this time was about 180 s, and 98.5% of the initial capacity was recovered per cycle. For widely different steam-reaction times, cyclic operation results in greatly reduced adsorption capacity.

If only thermal regeneration were used (zero steam-reaction time) there was a sharp loss in adsorption capacity due to buildup of residual carbon from the sucrose. It is shown that such residual carbon has less capacity for adsorbing sucrose than the original activated carbon. The surface area also decreased with number of cycles when there was no steam gasification. For long, steam-reaction times (600 s), base activated carbon as well as residual carbon were gasified. Again a loss in adsorption capacity occurred, this time due to loss of base carbon. The gasification time for maximum retention of capacity corresponded closely to the state where the weight of carbon gasified was equal to the weight of residual carbon.

Rates of gasification evaluated from our fluidized-bed data agreed well with kinetics results obtained earlier (Chihara et al., 1981b) in a thermal gravimetric apparatus. This suggests that the kinetics data are suitable for designing regeneration equipment.

Surface areas agreed qualitatively with adsorption capacities and showed a maximum for 180 s gasification time. However, the quantitative changes in area with number of cycles and with gasification time were different than the changes in adsorption capacity. Hence, the direct evaluation of effectiveness of regeneration by adsorption is preferred.

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When activated carbon is to be used repeatedly in adsorption-regeneration cycles it is important economically that adsorption capacity be restored as far as possible after each regeneration. The extent of restoration is controlled primarily by the severity of carbon gasification. If too much gasification occurs, adsorption capacity is reduced because of loss of virgin carbon. If there is too little gasification, buildup of residual carbon also reduces capacity. The objective of our work was to determine optimum regeneration conditions for a particular system: regeneration of activated carbon used to adsorb sucrose from aqueous solutions. To accomplish this it was necessary to follow through several cycles (five were chosen) of adsorption and regeneration. Since laboratory-scale apparatus was used, transfer of the small amount of carbon from one vessel to another would cause serious losses and inaccurate results. Therefore, the experiments were designed so that all the processes and measurements during the cycles could be made without removing the carbon from the reaction tubes. Each cycle consisted of the following sequence:

1. Adsorption and measurement of amount of sucrose adsorbed
2. Drying
3. Regeneration, which consisted of the heating step for thermal decomposition of adsorbate followed by gasification with steam, and weighing.
4. Measurement of surface area and pore volume.

Since the results of this investigation are primarily experimental, and since numerous manipulations were involved, the experiments need to be fully described.

EXPERIMENTAL

Four reactor tubes were operated simultaneously in order to obtain results for different gasification times. Clear quartz tubes (see Figure 1a) with a conical lower (entrance) section were used. The inner diameters of the large and small sections were 0.021 and 0.004 m. The length of the reactor was 0.178 m while the total length of the quartz apparatus was 0.356 m.

Approximately 2×10^{-4} kg of virgin carbon particles were added to each tube at the beginning of the first cycle.

Adsorption and Drying

To each tube containing the carbon particles was added 20×10^{-6} m^3 of an aqueous solution containing 10,000 ppm of sucrose. The four tubes were shaken in a vibrator bath (constant temperature of 298°K) for three hours to reach equilibrium. Then the remaining solution was carefully removed with an injector and analyzed (with Beckman Total Organic Carbon Analyzer) for carbon content. The amount adsorbed $A_i(n)$ was determined from the difference between the amount of sucrose in the initial and final solutions. The reactor tubes containing the wet carbon were dried for 15 hours in an oven at 413°K. The time needed for equilibrium and the optimum drying temperature had been established in the prior study of Chihara et al. (1981a). This adsorption and drying procedure was followed after each regeneration and resulted in a weight of carbon = $A_i(n) + W_i(n)$.

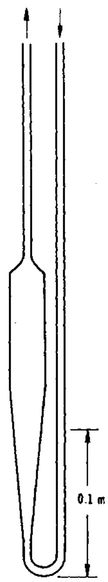

Figure 1a. Rector tube.

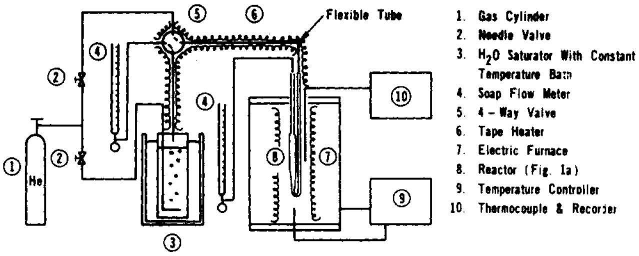

Figure 1b. Regeneration apparatus.

Regeneration

Apparatus. Figure 1b is a schematic drawing of the regeneration apparatus. Ultra high purity helium (99.999%) could be introduced to the bottom of the fluid bed (Figure 1a) either alone or saturated with water (at 336°K, corresponding to 22.4 mol % H_2O) by means of the four-way valve (5). The flow rate of helium in either stream was the same (2.5×10^{-6} m^3/s, at 25°C, 1 atm) for all runs. The possible effect of oxygen contamination in the helium was checked by weighing the reactor tube containing virgin carbon particles before and after pure helium flow at regeneration conditions. No discernible weight change was observed. The temperature of the electric furnace (7) was maintained at 1171°K.

Copper tubes (with small diameter, flexible portions), carrying the helium or helium-steam mixture, could be attached to the reactor tube at the cool ends extending outside the furnace. Thus, the tubes could be easily removed from the furnace for weighing, adsorption, drying, and measurement of surface area and pore volume.

Procedure. To start the regeneration step, helium was passed through the reactor tube for 600 s to remove air. Then the tube was slowly lowered into the furnace. Helium flow was continued for an additional 600 s. During this period the particles were completely fluidized in the conical section of the tube and were heated to 1151°K. The temperature rise was checked in a preliminary experiment by inserting a thermocouple into the bed. The final temperature of 1151°K (furnace temperature = 1171°K) was attained after about 180 s. It was found by Chihara et al. (1981a) that adsorbed sucrose, on the same activated carbon, decomposes leaving a non-volatile residue of adsorbed carbon during this kind of a heating process. This conclusion was tested in preliminary experiments. Tubes containing dried carbon particles, loaded with adsorbed sucrose, were introduced into the furnace and helium flow continued for a chosen time. The tubes were removed and weighed. No weight change was observed when the time was greater than about 200 s.

After the heating step, the gas flow was changed to the helium-steam mixture and continued for a different time in each of the four reactor tubes [0 s for tube #1, 180 s for #2, 360 s for #3, and 600 s for #4]. This gasification policy was continued after each regeneration; for example, the gasification time was always 180 s as tube #2 was subjected to the five adsorption-regeneration cycles.

Regeneration Conditions. An important factor in the gasification step is whether all the carbon particles are reacting at the same rate; that is, can bypassing or other types of imperfect mixing affect the results in the fluidized beds. To evaluate this situation, preliminary gasification runs were made with various gas velocities and sample weights. Visual observation indicated that a gas flow rate of 2.5×10^{-6} m^3/s was sufficient to fluidize the particles and not so large as to cause significant entrainment. Various weights of virgin carbon particles were added to the tubes and the reaction rate (g carbon/s) measured by weighing the tube after a reaction time of 2400 to 6000 s at 1088°K with a steam concentration of 4.9%. Chihara et al. (1981b) determined reaction rates in a TGA apparatus with the same virgin carbon (Type BPL, Pittsburgh Activated Carbon) and including the same temperature and steam concentration. In the TGA apparatus complete mixing was attained. The rate of the carbon-steam reaction depends upon the water and hydrogen concentrations. For the fluidized bed complete mixing was assumed in calculating these concentrations. The ratio of the rates in the fluidized bed to those obtained in the TGA apparatus were as follows:

Mass of carbon sample kg × 10^4	Ratio of reaction rates
30.0	0.05
10.	0.20
5.0	0.33
2.0	1.0
1.0	1.0

The decrease in ratio of rates for the larger samples is probably due to channeling. No "bubbles" were observed. These mixing results suggested that the sample weight be not greater than 2×10^{-4} kg. To reduce weighing errors this maximum was used.

A further set of preliminary runs were made with virgin activated carbon to determine approximately the time intervals needed to gasify an amount of carbon corresponding to the residual, deposited carbon after thermal decomposition. These results indicated that 120 to 180 s was adequate at a temperature of 1151°K.

Termination Procedure. After steam gasification, the gas flow was shifted to pure helium for 180 s. Then the reactor tube was removed from the furnace, allowed to cool, and weighed.

Surface Area and Pore Volume

The apparatus built to measure areas and pore volumes is shown in Figure 1c. The procedure, based upon nitrogen adsorption, was reasonably accurate and required only inexpensive, simple equipment.

For surface areas, a gas stream containing 7.5% nitrogen (remainder helium) flowed through the reactor tube at a rate of 6×10^{-6} m^3/s. The tube was immersed in a liquid nitrogen bath for 300 s, and then removed. The nitrogen desorbed while the tube warmed to room temperature was measured in a graduated cylinder. The surface was calculated by the single-point method using the BET equation. The multipoint procedure was also used in a preliminary test (nitrogen concentration range 2.5 to 7.5%) with virgin carbon. The difference between the areas calculated from the sample point and multipoint (straight line) methods was less than 3%.

Pore volumes were determined in the same apparatus by treatment with a gas stream containing 78% nitrogen. At this pressure pores of radii less than 5 nm are filled with liquid nitrogen, at equilibrium. From pore-size distribution information, the adsorption in pores greater than 5 nm radius was estimated to negligible.

For both area and volume measurements, correction was made for the nitrogen in the dead volumes of the apparatus from data for blank runs.

Cyclic Procedure

Virgin carbon whose properties are given in Table 1 was first screened to obtain a 100 to 150 mesh fraction. This fraction was boiled in water to remove fines and then dried in an oven at 393°K.

Each empty tube was dried in the furnace, at the same furnace temperatures (1171°K) as used for the steam-reaction steps, for 900 s and then weighed. Powdered, virgin carbon from the dried fraction was added. Then the tube was placed in the furnace and maintained at 1151 K with helium flow at a rate of 2.63×10^{-6} m^3/s. The purpose of this initial heat treatment was to remove any extremely fine particles and to remove volatile material. Afterwards the reactor tube with the carbon was again weighed.

After the initial heat treatment, the four steps listed at the beginning of the paper were carried out. This completed one cycle.

Figure 2 illustrates the weight changes during a cycle:

(1) An amount of carbon $W_i(n = 0)$ is in each tube after heat treatment and an amount $W_i(n)$ after the n-th regeneration for the ith tube. The corresponding surface areas and pore volumes are $S_i(n)$ and $P_i(n)$.
(2) Sucrose is adsorbed on the activated carbon giving a weight of adsorbed sucrose $A_i(n)$.
(3) During the drying step water is lost and some thermal decomposition occurs (Chihara et al., 1980a), reducing the adsorbed weight to $A_i'(n)$.
(4) The last step shown in Figure 2 consists of thermal decomposition (heating for 600 s) followed by gasification with steam at 1151°K. For tube #1 the gasification time is 0 s where the weight of sample is reduced to $W_1(n)$. Since deposited carbon builds up without steam reaction, $W_1(n + 1) - W_1(n)$ is positive for each cycle. This is indicated as step (4 − 1) in Figure 2. The weights for successively larger reaction times are illustrated as steps (4 − 2), (4 − 3) and (4 − 4).

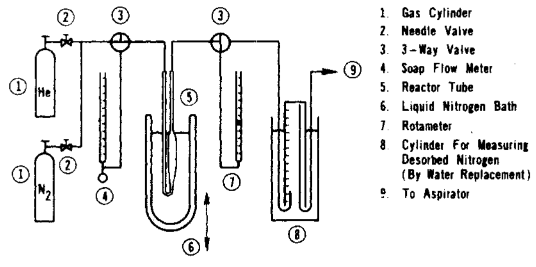

Figure 1c. Apparatus for surface-area and pore-volume measurement.

TABLE 1. PROPERTIES OF ACTIVATED CARBON

Origin:	bituminous coal (Pittsburgh Activated Carbon, type BPL)
Particle size:	100 to 150 mesh; $(R_p)_{Ave} = 6.25 \times 10^{-5}$ m
Particle density:	800 kg/m^3
Nitrogen surface area:	1.17×10^6 m^2/kg
Pore volume:	0.8×10^{-3} m^3/kg
Macropore volume:	0.25×10^{-3} m^3/kg (pore radius >5 nm)
Micropore volume:	0.55×10^{-3} m^3/kg (pore radius <5 nm)
Most probable micropore radius:	0.8 nm

TABLE 2. INITIAL VALUES, $W_i(0)$, $S_i(0)$, $P_i(0)$ AND $A_i(0)$ FOR CARBON SAMPLES IN TUBES 1, 2, 3, 4

Reactor tube, no., i	1	2	3	4
Steam Reaction Time, s	0	180	360	600
Dosed Carbon Weight × 10^4, kg	2.211	2.209	2.253	2.243
Carbon Weight* × 10^4, $W_i(0)$, kg	1.985	2.030	2.116	1.826
Total Surface Area,* $S_i(0)$, m^2	230	234	231	234
Total Micropore Volume,* $P_i(0) \times 10^6$, m^3	0.106	0.112	0.107	0.109
Total Sucrose Amount adsorbed,* $A_i(0)$, kg × 10^6	51	55	49	55

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*n = 0 designates the condition after the initial heat treatment.

The temperature and steam content of the regeneration gas were chosen from preliminary data so that the yield of carbon [(weight of carbon after regeneration)/(weight of virgin carbon after heat treatment)] would be about unity for a gasification time of 180 s. Hence, for tube #2, $W_2(n + 1) \simeq W_2(n)$. For tubes 3 and 4 the steam reaction time was sufficient to gasify some virgin carbon so that $W(n + 1) < W(n)$ for i = 3 or 4.

RESULTS AND DISCUSSION

Effects of Cyclic Operation

Table 2 summarizes the initial (n = 0) weights, surface areas, and pore volumes of the carbon samples in each reactor tube. The effect of cycling operation on the weight $W_i(n)$ of the carbon samples for each tube is shown in Figure 3, where $W_i(n)/W_i(0)$ is plotted versus the number of cycles.

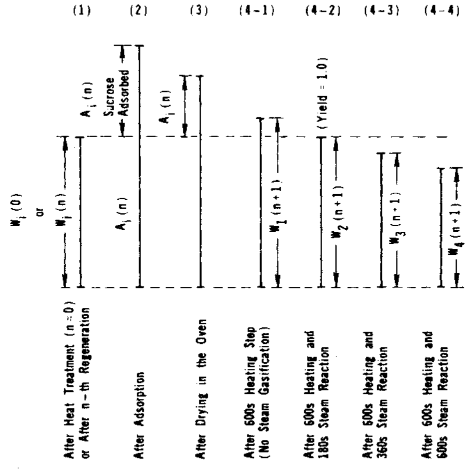

Figure 2. Weight changes in a single cycle.

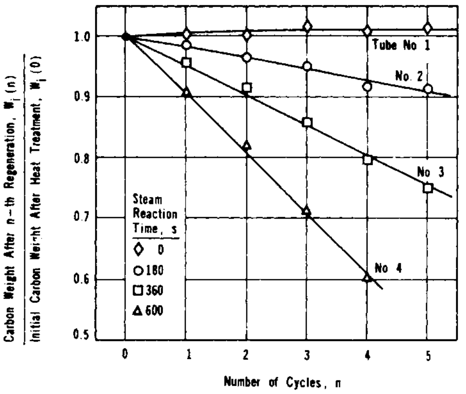

Figure 3. Carbon weight change with number of cycles.

From the TGA results of Chihara et al. (1981a) the weight of residual carbon (after thermal decomposition but with no steam gasification) should be 8.5% of the adsorbed sucrose, $A_i(n)$. If this result is adopted here, $W_1(5)/W_1(0)$ should reach a constant value of 1.094. Actually, the asymptotic result shown in Figure 3 for tube #1 is greater than unity (1.015), showing the effect of residual carbon, but less than 1.09. The difference is probably due to loss of carbon from the tubes. A likely cause is entrainment while removing the excess sucrose solution after the adsorption process. Using these figures the entrainment loss is calculated to be 3.16×10^{-6} kg for each cycle, or about 1.6% of the sample weight. If the same relative loss of carbon occurs in all the tubes, the line in Figure 3 for tube #2 would be essentially horizontal at $W_i(n)/W_i(0) = 1.0$. The lines for tubes 3 and 4 would still decrease significantly with number of cycles. This suggests gasification of some of the original activated carbon when the steam reaction time is greater than 180 s.

For a priori design of regneration process it is necessary to determine the steam-gasification time for maximum restoration of adsorption capacity. The kinetics results of Chihara et al. (1981b) should be applicable for predicting the extent-of-gasification vs. time relation. The measurements reported here of adsorption capacity in cyclic operation complete the data needed for design. These factors are considered next.

Experimental and Predicted Gasification Results

The data points in Figure 4 show the change in sample weight for each cycle, normalized with respect to the initial weight. These weight changes are the result of two factors: 1) an increase in weight due to residual carbon after thermal decomposition (the 600 s heating step in Figure 2), and 2), a decrease due to carbon gasification. The data points have been corrected for the entrainment loss of 3.16×10^{-6} kg per cycle. Comparison of data from one cycle to another shows some scatter. This is difficult to eliminate because of the necessary small weights of samples and the numerous operations involved. However, all that data show that with zero steam reaction time there is a buildup of residual carbon, and for long reaction times base carbon as well as residual carbon is gasified. The results for reactor tube #2 indicate a very small weight change, so that 180 s is sufficient to gasify residual carbon but not so much as to gasify a significant amount of original activated carbon.

The line in Figure 4 is a predicted result based upon the following rate equation for the rather slow stream-carbon reaction:

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

Parameters k_1, k_2, and k_3 were taken from the results of kinetics studies by Chihara et al. (1981b). These values are for gasification of either spent or virgin carbon and are for the same type of spent activated carbon, prepared by sucrose adsorption and thermal decomposition, as in this study. The values of the parameters and range conditions are:

$$k_1 = 1.65 \times 10^4 \exp(-2.27 \times 10^5)/R_g T); \text{ kg/(kg)(s)(Pa)} \quad (2)$$

$$k_2 = 2.84 \times 10^{-7} \exp\left(\frac{1.02 \times 10^5}{R_g T}\right); \text{ Pa}^{-1} \quad (3)$$

$$k_3 = 2.82 \times 10^{-3}; \text{ Pa}^{-1} \quad (4)$$

$$1002 \leq T \leq 1120°\text{K}$$

$$40 \leq p_{H_2O} \leq 6000 \text{ Pa}$$

$$0 \leq p_{H_2} \leq 500 \text{ Pa}$$

In using Eq. 1 to predict the line in Figure 4, complete mixing in the fluidized bed is assumed. The temperature and feed value of p_{H_2O} were constant at 1151°K and 2.30×10^4 Pa. For stirred-tank performance, the corresponding values of effluent concentrations were:

$$p_{H_2O} = 2.02 \times 10^4 \text{ and } p_{H_2} = 2.83 \times 10^3 \text{ Pa},$$

giving a rate $R = 1.80 \times 10^{-4}$ kg/(kg)(s). Hydrogen is a product of the steam-carbon reaction:

$$C + H_2O \rightarrow H_2 + CO \quad (5)$$

The agreement between the fluidized bed data points in Figure 4 and the predicted line is reasonably good, lending confidence to the validity of using Eq. 1 for predicting gasification rates. The agreement is interesting also since it was necessary to extrapolate to temperature and concentrations beyond those upon which Eq. 2 to 4 were based. The scatter in the data points is from cycle to cycle and not with reaction time. However, this scatter is random, showing that there is no significant change in reaction rate with the number of cycles.

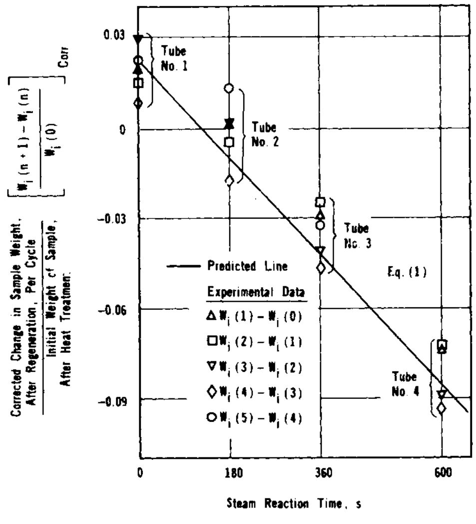

Figure 4. Predicted and experimental steam reaction results (T = 1151°K).

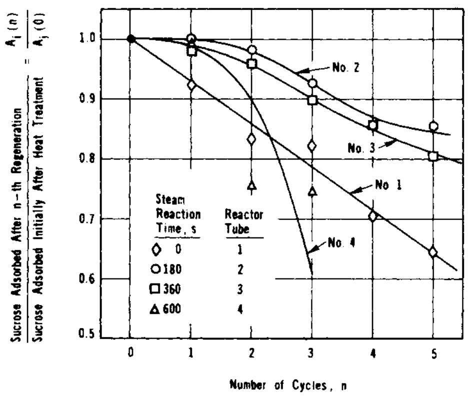

Figure 5. Effect of cycling on sucrose adsorption capacity.

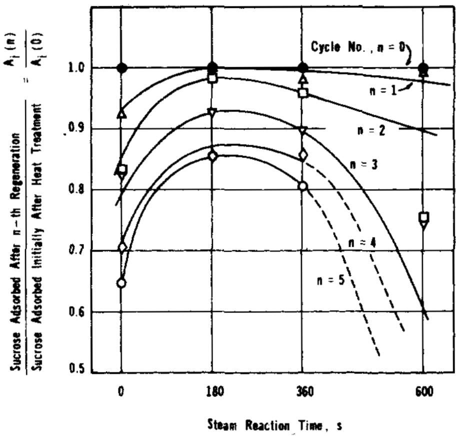

Figure 6. Effect of steam reaction time on sucrose adsorption capacity.

Adsorption Capacity after Regeneration

The direct measure of the effectiveness of regeneration is adsorption capacity. Our absorption results for sucrose, plotted as the weight of sucrose adsorbed $A_i(n)$ after regeneration vs. number of cycles, are shown in Figure 5, and vs. steam reaction time in Figure 6. The ordinates have been divided by the $A_i(0)$ values given in Table 2 in order to show the effect of repeated cycles. Figure 5 shows that there is a sharp loss in adsorption capacity for reactor tube 4. This is due to gasification of base carbon. The linear drop in capacity with number of cycles for tube 1 is due to buildup of residual carbon from sucrose decomposition. Restoration of adsorption capacity is best for tube 2. This optimum is more clearly shown in Figure 6 where the maximum capacity is attained at about 180 s gasification time (the reaction time for tube 2), although the curves are rather flat. As indicated in Figure 4, conditions in tube 2 correspond about to a yield of unity; that is, where the amount of carbon gasified is equal to the residual carbon remaining after thermal decomposition. These results suggest that adsorption capacity is being restored by removal of residual carbon at reaction times less than 180 s. Longer reaction times apparently reduce the available, activated carbon sites. The residual carbon does not have as high an intrinsic adsorption capacity as the base activated carbon. This is evident from Figure 7 which shows the relation between the relative adsorption capacity $A_i(n)/A_i(0)$ after each regeneration and the relative weight of carbon $W_i(n)/W_i(0)$ after the same regeneration. Both quantities have been corrected for entrainment. Each point on the left side of this figure corresponds to a different number of cycles for the case of no steam reaction (reactor tube 1). The drop in capacity is steep, showing the adverse effect of residual carbon covering the more active adsorption sites of original activated carbon. The drop in capacity in the right side of the figure is less steep because two opposing factors are applicable: residual carbon is removed by gasification, thus exposing active sites for adsorption, and the reduction in sites by gasification of activated carbon. For the long steam-reaction time used for reactor tube 4, the latter factor dominates. Optimum regeneration of adsorption capacity is attained when most of the residual carbon is removed, but little base carbon has been gasified. Figure 7 shows that regeneration to a yield of unity achieves this optimum capacity. However, it cannot be stated that all the residual carbon is consumed before gasification of virgin carbon is initiated.

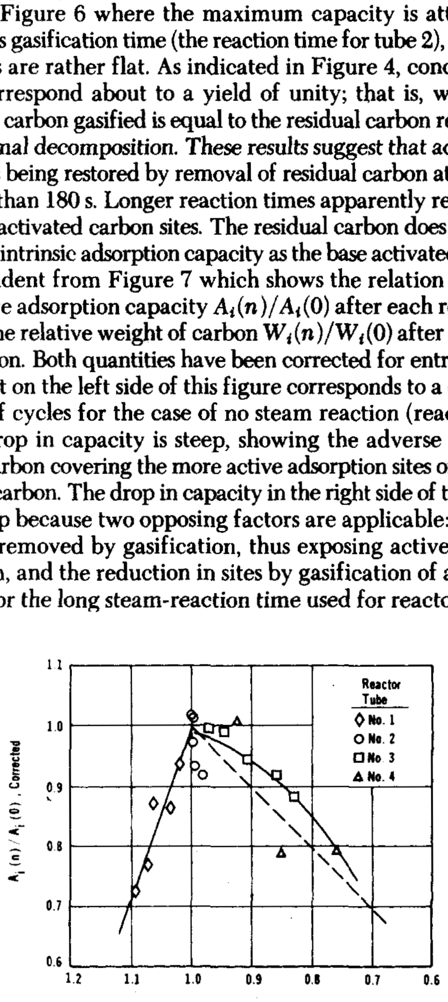

Figure 7. Relation between adsorption capacity and carbon weight.

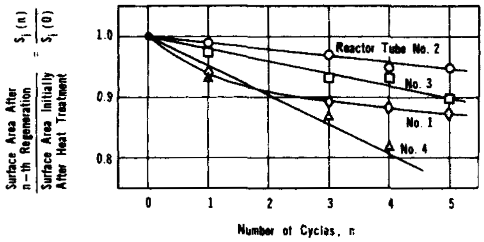

Figure 8. Effect of cycling on surface area.

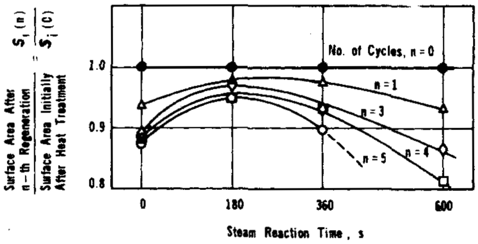

Figure 9. Effect of steam reaction time on surface area.

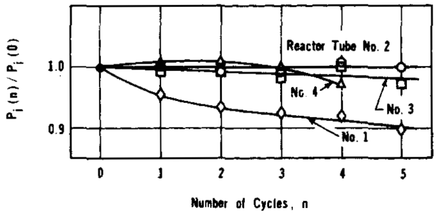

Figure 10. Effect of cycling on micro-pore volume.

In Figure 5 the total loss of adsorption capacity after the 5th regeneration is 14.5% for sample 2. If this loss is corrected for entrainment (1.58% per cycle) the total loss in capacity due to successive adsorption and regeneration is 7.3%. This gives a recovery per cycle of 98.5% for the optimum operating conditions corresponding to reactor tube 2.

Effect of Surface Area on Surface and Pore Volume

Figures 8 and 9 show surface area changes analogous to the adsorption capacity changes displayed in Figures 5 and 6. The maximum recovery of surface area is for a reaction time of 180 s (Figure 9), the same as for maximum adsorption capacity. However, comparing the two sets of figures indicates that restoration of surface area is not quantitatively a valid measure of adsorption capacity. Thus, Figure 6 shows a more pronounced drop in capacity at high reaction times than the fall in surface seen in Figure 9. Perhaps this is because the sucrose molecule, being larger than that of nitrogen, is less able to penetrate the smaller pores.

The effect of number of cycles on the change in micro-pore ($<$ 5 nm) volume, $P_i(n)/P_i(0)$, is small, as is evident from Figure 10. If the correction for sample loss by entrainment were made, P_i would show a slight increase after 5 cycles for reactor tubes 2 and 3. There probably is some change in pore-size distribution during regeneration.

ACKNOWLEDGMENT

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NOTATION

$A_i(n)$ = Sucrose adsorbed after nth regeneration, kg
$A_i'(n)$ = Sucrose adsorbed after nth regeneration and after drying in the oven for 15 hours, kg
i = Number of reactor tube
k_1 = Rate constant for steam-carbon reaction Eq. 1, kg/(kg)(s)(Pa)
k_2, k_3 = Parameters in rate equation, Pa^{-1}
n = Number of regenerations; $n = 0$ indicates conditions after initial heat treatment
p_{H_2}, p_{H_2O} = Partial pressures of hydrogen and steam, Pa
$P_i(n)$ = Pore volume after n-th regeneration, m^3
R = Rate of steam-carbon reaction, (kg of carbon reacted/(kg of virgin carbon unburned) (s)
R_g = Gas constant, kJ/(mol) (°K)
$S_i(n)$ = Surface of carbon in the ith tube after the nth regeneration, m^2
T = Temperature, °K
$W_i(n)$ = Weight of carbon in reactor tube i after the nth regeneration, kg

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A Study of the Volumetric and Phase Behavior of Binary Systems

Part I: Critical Properties of Propane-Perfluorocyclobutane Mixtures

The volumetric and phase behavior of propane-perfluorocyclobutane mixtures has been determined in the critical region. This system exhibits a minimum temperature point in its critical locus curve and forms a positive critical azeotrope. The measured critical points in this system and their correlation using an extended corresponding states principle are reported in this paper.

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SCOPE

The study of the volumetric and phase behavior of mixtures, in addition to yielding fundamental information on molecular interactions, is of great practical interest in chemical engineering operations. Of particular interest are non-ideal mixtures which exhibit azeotropic behavior over considerable ranges of pressure and temperature. In 1951, this laboratory began a study of azeotrope-forming systems which indicated that their phase diagrams may exhibit a great variety of forms depending on the differences in size, shape and chemical nature of the components. Further evidence of this variety of behavior is presented here in the study of the propane-perfluorocyclobutane system. This system was chosen principally because the critical pressures and temperatures of the components are relatively low, making it possible to span a considerable range of reduced pressures and temperatures with our apparatus. Our measurements therefore cover a major part of the phase diagram of this system—from second virial coefficients and vapor densities through vapor-liquid equilibria and critical states to compressed liquid densities. One objective of this work was to make available this range of self-consistent data for testing methods of prediction.

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