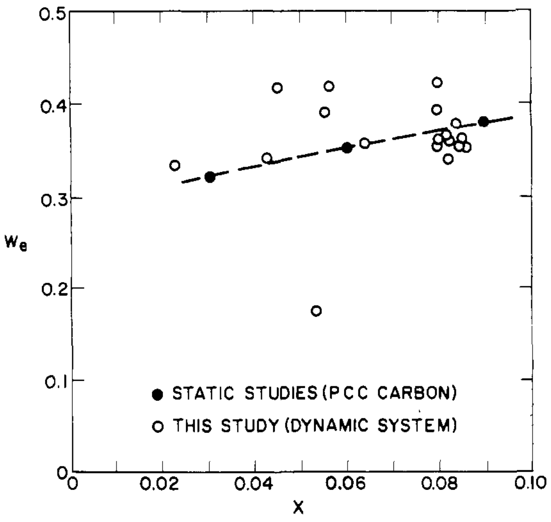

Figure 2. Equilibrium benzene adsorption on activated charcoal at 100° F.
(Dynamic system points calculated from Equation 11)

and the concentration wave for which a correction had to be made.

## ACKNOWLEDGMENT

Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

## NOMENCLATURE

$A$ = parameter in least squares analysis
$B$ = parameter in least squares analysis
$D$ = diameter of adsorption bed, ft.
$G$ = flow rate, lb.-moles/min.
$h$ = constant, the modulus of precision in statistical considerations
$K$ = parameter, equal to $B/AL$
$L$ = distance from inlet to same point in adsorption bed, ft.
$M$ = molecular weight of benzene
$t$ = time in minutes
$t_b$ = break time corresponding to a gas concentration $x_b$
$t_s$ = saturation time corresponding to a gas concentration $x_s$
$t'$ = time parameter defined by $t - (t_b + t_s/2)$
$We$ = equilibrium weight of benzene adsorbed per pound of carbon
$x$ = lb.-moles benzene/lb. mole nitrogen in gas stream
$x_0$ = inlet concentration of benzene
$x_b$ = break point concentration
$x_s$ = saturation point concentration
$Z$ = argument of probability integral
$\rho$ = bulk density of adsorbent carbon, lb./cube ft.
$\omega$ = weighing factor, exp. $-Z^2/2$

## LITERATURE CITED

(1) Campbell, Larry, M., Geser, John J., Canjar, L.N., *A.I.Ch.E. J.* **8**, No. 4 (1962).
(2) Campbell, Larry M., Landis, E.K., Canjar, L.N., J. CHEM. ENG. DATA **7**, No. 3 (1962).
(3) Engel, H.C., Coull, James, *Trans. A.I.Ch.E.* **38**, 947 (1942).
(4) Geser, John J., Campbell, Larry M., Canjar, L.N., *A.I.Ch.E. J.* **8**, No. 4 (1962).
(5) Landis, E.K., PhD. dissertation, Carnegie Institute of Technology, 1959.

RECEIVED for review October 23, 1961. Accepted March 2, 1962.

# Adsorption of Benzene from Nitrogen by Fixed Beds of Alumina

M. LARRY CAMPBELL,[1] E. K. LANDIS,[2] and LAWRENCE N. CANJAR
Department of Chemical Engineering, Carnegie Institute of Technology, Pittsburgh, Pa.

A MODEL for predicting the rate of adsorption which was developed earlier (*2, 3*) has been applied to data taken on the adsorption of benzene from a nitrogen gas stream by spheres of alumina in fixed beds at 100° F.

## APPARATUS

The experimental apparatus was the same as that used by Landis (*5*). It consisted of five tubes, each 6 inches long, in a series with thermal conductivity cells before and after each tube to measure the gas concentration. The tubes contained the adsorbent sample and were fed by a nitrogen stream which passed through a benzene saturation system. The adsorption beds were immersed in a constant temperature mineral oil bath which was automatically controlled at 100° F. A flow sheet for the adsorption system is shown in Figure 1.

Part of the nitrogen leaving the cylinders of pure nitrogen was bypassed to the reference side of the thermal conductivity cells. The main stream entered the saturation system where it was split again. Part of it entered a tank 6 inches in diameter and 5 feet in length where liquid benzene was vaporized by external heating coils. The nitrogen was supersaturated with benzene in this tank and then flowed to a condenser coil immersed in a bath of melting acetophenone where benzene was condensed and collected. After leaving the condenser the gas was mixed with the part which had been previously bypassed. By a series of valves, flow rates in the bypass and through the saturation system could be regulated, and this in turn allowed concentrations to be varied from run to run.

The benzene-nitrogen mixture entered the adsorption tubes which were 1 inch in diameter. They were packed in the following layers from bottom to top: perforated gas distribution plate; glass wool to promote further gas distribution; glass beads of approximately the size of the adsorbent sample; adsorbent sample; glass beads; glass wool.

This elaborate method of packing was used to ensure good gas distribution and a developed velocity profile entering the adsorbent bed.

---

[1] Present address, Esso Research and Engineering Co., Linden, N. J.
[2] Present address, University of Alabama, University, Ala.

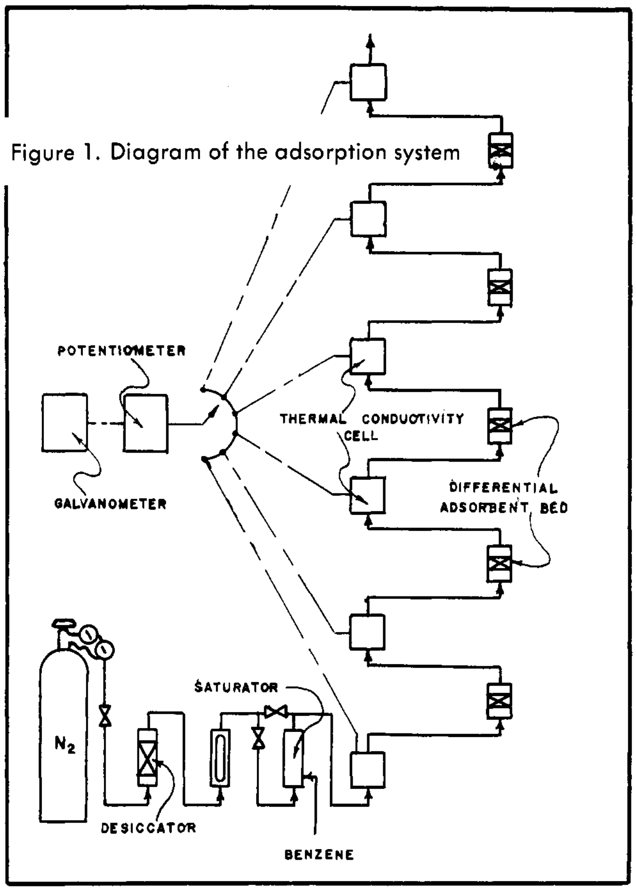

Figure 1. Diagram of the adsorption system

The gas leaving each adsorption tube entered a thermal conductivity cell. After each cell, there was a pressure tap leading to a mercury manometer so that pressure corrections could be made for cell readings. A constant predetermined flow of gas was always put through both the reference and sample side of the cell.

A calibrated rotameter was used to measure the flow of nitrogen. Calibration curves for the cell electromotive force (e.m.f.) as a function of concentration were obtained by a gravimetric procedure.

## PROCEDURE

The cells were allowed to come to thermal equilibrium for 3 hours. Pure nitrogen passed through the sample side of each cell after the adsorption tubes. The first cell, the one before any of the adsorption tubes, was used to measure the concentration of the gas leaving the saturation system.

After the cells had reached 100° F. and the gas concentration held steady, a run was initiated by switching from the pure nitrogen to the gas sample. E.m.f. readings from the cells were then observed manually with a potentiometer and galvanometer and recorded at the time the reading was taken. A run was terminated when the readings from all cells remained constant for a period of time.

In addition to these data, the room temperature, barometric pressure, and flow rate were recorded for each run. The gas concentration never fluctuated more than 0.5% about the mean for a run, and the rotameter had an accuracy of the scale reading of 2%.

Gas concentrations were measured, and the time required for the gas to pass from one cell to another was substracted from the time readings to give the true time.

The fresh adsorbent was activated in an oven at 350° F. and then weighed. The sample was regenerated after each run by passing pure nitrogen through the beds for 3 hours at a bed temperature of 275° F. There was no noticeable decrease in the capacity of the adsorbent with use.

The data were taken on Alcoa H151 alumina spheres of ⅛- and ¼-inch diameters. (Detailed data are available in a master's thesis by M.L. Campbell, Carnegie Institute of Technology.) Bed lengths varied from 2 to 10 inches. Gas concentrations between 3 and 8 mole % benzene in nitrogen were used. Flow rates varied from 0.05 to 0.15 SCFM.

## DATA ANALYSIS

The equations used here were presented in an article by the author (*2*). Briefly, the development involves the assumption that the resistance to mass transfer can be split into two parts, external and internal. The external part is described using the usual driving force and mass transfer coefficient and is given by

$$\frac{dy}{dt} = \frac{k_C a_y P T_S x_0}{R T^2 \rho_B q_\infty}(y - y^*) \tag{1}$$

The rate of transfer of material in the partial is described by the following equation:

$$dq/dt = K_p[(1 - X_{N_2})\, q_\infty - q^*] \tag{2}$$

Equation 1 was derived assuming a constant pattern for the adsorption wave through the bed. However, this system does not exhibit constant wave pattern as illustrated in Figure 3. This is to be expected because of the linearity of the equilibrium adsorption isotherm (Figure 2). The break-through curves do approach constant pattern as bed length is increased. Therefore the assumption is not invalid. This fact is demonstrated in Figure 3 where the break-through curves for Run 4A are plotted.

The following steps were used in applying these equations:

The amount of benzene adsorbed at saturation was calculated by graphically integrating the area above the effluent curve. The data were plotted and a least squares line was drawn through it.

Values of $dy/dt$ were found at various times and Equation 1 was used to find $y^*$. The mass transfer correlation presented by Hougen and Watson (*4*) was used to find $k_C$. The following equation was used to calculate the external transfer area

$$a_v = \frac{6(1 - \epsilon)}{D_P} \tag{3}$$

Values of $\epsilon$ were obtained from Brown and others (*1*, Figure 221).

Assuming constant plug flow, isothermal conditions, negligible radial concentration gradients, and negligible axial dispersion, the following material balance for a differential element of adsorption bed can be written

$$F(\partial C/\partial z)_t + \epsilon A_x(\partial C/\partial t)_z + A_x \rho_B(\partial q/\partial t)_z = 0 \tag{4}$$

This equation was used to find $dq/dt$ graphically at the points where $dy/dt$ were found. The middle cell was used for the calculations for greater accuracy in slope taking.

The interfacial partial concentration, $q^*$, was calculated from $y^*$.

With the values obtained in the previous steps, a particle transfer coefficient, $K_P$, was assumed, and $X_{N_2}$ values for the data points were calculated. $K_P$ was adjusted until $X_{N_2}$ was never negative. The results of applying these equations follow.

## RESULTS

The values of $k_C a_v$ and $K_P$ are tabulated in Table I. The maximum $\Delta y$ for all runs of the ⅛-inch spheres was 0.037, and the maximum for the ¼-inch was 0.046. The average value of $K_P$ is $13.30 \times 10^{-2}$, 1/min. for the ⅛-inch diameter spheres. The $K_P$ values do not seem to be a function of flow rate nor bed length. For example, in Run 7A, $K_P$ equals

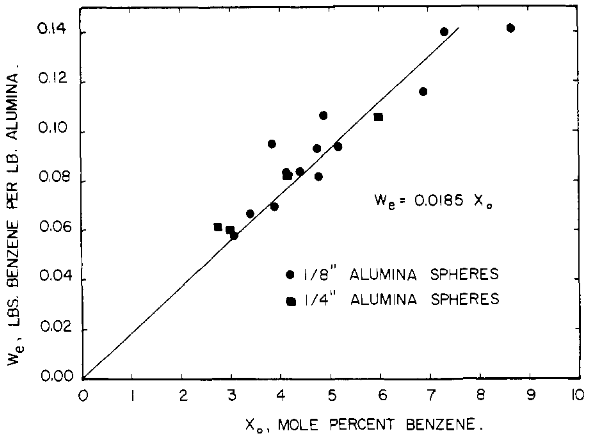

Figure 2. Equilibrium adsorption of benzene on alumina at 100° F. calculated from flow experiments

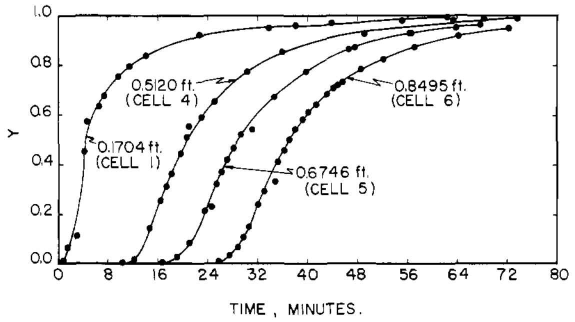

Figure 3. Relative adsorption of benzene on ⅛-inch spheres of alumina at 100° F. Inlet composition, 6.802 mole % benzene in nitrogen. Flow rate of nitrogen, 0.0537 SCFM

Table I. Transfer Coefficients for the Benzene-Nitrogen-Alumina Adsorption System

| Run No. | $x_0$, Mole % | $F_{N_2}$[a] | $k_C a_v$, Ft./Min. | $K_P$, 1/Min. |
|---|---|---|---|---|
| | | ⅛-Inch Spheres | | |
| 1A | 6.439 | 0.0507 | 1370 | $10.00 \times 10^{-2}$ |
| 3A | 3.275 | 0.1665 | 2420 | $13.57 \times 10^{-2}$ |
| 4A | 6.802 | 0.0537 | 1460 | $10.70 \times 10^{-2}$ |
| 7A | 3.731 | 0.0502 | 1340 | $12.90 \times 10^{-2}$ |
| 8A | 4.525 | 0.1246 | 2090 | $13.70 \times 10^{-2}$ |
| 9A | 4.648 | 0.0795 | 1690 | $14.70 \times 10^{-2}$ |
| 10A | 2.972 | 0.1372 | 2175 | $17.55 \times 10^{-2}$ |
| | | ¼-Inch Spheres | | |
| 12A | 5.614 | 0.0503 | 459 | $5.20 \times 10^{-2}$ |
| 13A | 3.968 | 0.0764 | 550 | $11.70 \times 10^{-2}$ |
| 14A | 2.886 | 0.1066 | 651 | $10.65 \times 10^{-2}$ |

[a] Cube foot nitrogen at STP/min.

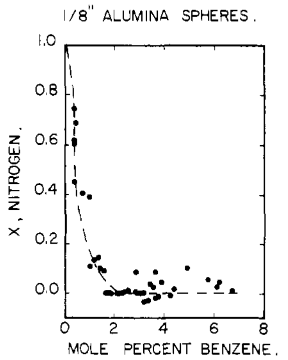

Figure 4. Empirical factor $X_{N_2}$ as a function of gas composition at 100° F. and 1 atm. for benzene adsorption on ⅛-inch alumina spheres with nitrogen as the carrier gas

$12.9 \times 10^{-2}$, 1/min. at 0.348 feet (Cell 3) and at 0.5120 foot (cell 4) and in Run 8A $K_P$ equals $13.7 \times 10^{-2}$ 1/min. at 0.5120 foot (Cell 4) and $11.4 \times 10^{-2}$ 1/min. at 0.6746 foot.

The qunatity $X_{N_2}$ is plotted *vs.* gas concentration in Figure 4 for the ⅛-inch diameter particles. As found previously for another system (*2*), there seems to be a definite relationship between the two quantities. It can be seen that $X_{N_2}$ becomes zero around a gas concentration of 3 mole % benzene. This also occurred at roughly the same concentration for the ¼-inch diameter particle. There was some fluctuation of $X_{N_2}$ about zero above 3 mole %. This was due to errors in plotting the data and taking slopes.

A mathematical model for the rate of adsorption has been used to represent data taken on the adsorption of benzene from nitrogen by spheres of alumina in a packed bed. The particle transfer coefficient has been found to be independent of flow rate, and bed length. The factor, $X_{N_2}$, shows a definite relationship to the gas concentration.

This is the third system to which this model has been applied successfully (*2*, *3*). The other two involve the adsorption of methane from hydrogen on activated carbon and silica gel at −115° F. The very variety of conditions which the systems represent tends to confirm the usefulness of this model.

## ACKNOWLEDGMENT

Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

## NOMENCLATURE

$a_v$ = external transfer area of particle, square foot surface/cube foot bed
$A_x$ = cross-sectional area of bed
$C$ = concentration of absorbate in fluid phase, moles/cube foot
$D_P$ = particle diameter
$F$ = volumetric flow rate, cube foot/min.
$F_{N_2}$ = volumetric flow rate of nitrogen, SCFM
$k_C$ = external mass transfer coefficient, moles transferred/min. square foot surface (moles/cube foot)
$K_P$ = particle transfer coefficient, 1/min.
$P$ = bed pressure, atm.
$q$ = average adsorbate concentration in particle, lbs. adsorbate-lb. absorbent
$q^*$ = adsorbate concentration on particle at interface
$q_\infty$ = adsorbate concentration in equilibrium with inlet gas
$R$ = gas constant
$t$ = time, min.
$T$ = temperature of bed, ° F.
$T_S$ = standard temperature, 72° F.
$x$ = mole per cent adsorbate in gas
$x_0$ = mole per cent adsorbate in inlet gas
$x^*$ = mole per cent adsorbate in gas at interface
$X_{N_2}$ = empirical parameter
$y$ = $x/x_0$
$z$ = bed length
$\epsilon$ = bed perosity, cubic foot void/cube foot bed
$\rho_B$ = bulk density, lbs. adsorbent/cube foot bed

## LITERATURE CITED

(1) Brown, G.G., others, "Unit Operations," p. 213, John Wiley, New York, 1950.
(2) Campbell, M.L., Geser, J.J., Canjar, L.N., *A.I.Ch.E. J.* 8, No. 4 (1962).
(3) Geser, J.J., Ph.D. dissertation, Carnegie Institute of Technology, 1961.
(4) Hougen, O.A., Watson, K.W., "Chemical Process Principles," Pt. III, p. 987, New York, John Wiley, 1947.
5) Landis, E.K., Ph.D. dissertation, Carnegie Institute of Technology, 1959.

RECEIVED for review October 23, 1961. Accepted March 2, 1962.