Adsorption of Benzene from Nitrogen by Fixed Beds of Activated Carbon

E. K. LANDIS[1], JOHN J. GESER[2], and LAWRENCE N. CANJAR
Department of Chemical Engineering, Carnegie Institute of Technology, Pittsburgh, Pa

THIS WORK is the initial effort in a long program designed to study the mechanism of adsorption in gas solid systems. The data obtained here are not sufficiently precise to determine parameters in an adsorption rate equation which has been developed and presented elsewhere (*1, 2, 4*). The lack of precision is a relative one and is due to the inability to manually record the concentration of an effluent stream of an adsorber for which the concentration-time curve is very steep. The extensive data obtained on this system are presented in a compact form. While not precise enough for theoretical studies of adsorption mechanism, the data are reliable and accurate and can be used with confidence for design purposes and adsorption breakthrough studies. The original data can be obtained from L.N. Canjar at Carnegie Institute of Technology.

The experimental apparatus and procedure is described in detail by Landis (*5*) and briefly in the article that follows by Campbell, Landis, and Canjar (*2*). Mixtures of nitrogen and benzene were passed over beds of activated carbons immersed in an oil bath maintained at 100° F. The significant difference between the experiments in this work and the companion work was an appreciable temperature rise in the adsorbent beds from the relatively rapid adsorption process. Campbell and others did not measure a significant temperature rise in the work they describe, although their experimental apparatus and procedure were the same.

Table I gives a summary of the experimental conditions under which runs were made. a ll runs were made using fresh adsorbent except 17, 18, 19, 20, and 51. These were made after four successive regenerations to determine the extent of loss of activity. No such effect was found. The carbon designated P.C.C. (Pittsburgh Coke and Chemical Co.) is manufactured from coal, and carbon designated as BC (Barneby-Cheney) is from coconut.

Table I. Operating Conditions for Each of the Experiments on Activated Carbon

Run[a]	L_b, Bed Depth/G. Carbon, Inch/G.	Particle Size, U. S. Sieve Range	N_2 Flow Read SCFM	N_2 Flow Cor. SCFM	x_0
2	0.1513	6 × 8	0.08118	0.08451	0.07898
3	0.1513	6 × 8	0.09045	0.09488	0.07890
4	0.1513	6 × 8	0.05700	0.05814	0.08129
5	0.1513	6 × 8	0.12675	0.13380	0.04447
6	0.1513	6 × 8	0.1271	0.13447	0.05465
7	0.1496	12 × 30	0.09881	0.10365	0.07905
8	0.1496	12 × 30	0.09443	0.09896	0.08082
9	0.1496	12 × 30	0.08570	0.08947	0.08106
10	0.1496	12 × 30	0.05195	0.05314	0.08514
11	0.1496	12 × 30	0.05132	0.05255	0.08369
12	0.1496	12 × 30	0.12445	0.13098	0.05569
13	0.1484	8 × 12	0.04494	0.04584	0.08334
14	0.1484	8 × 12	0.04526	0.04607	0.07920
16	0.1470	12 × 16	0.09880	0.10386	0.08397
17	0.1470	12 × 16	0.04890	0.04994	0.06324
18	0.1470	12 × 16	0.0500	0.05081	0.04177
19	0.1470	12 × 16	0.1477	0.15817	0.02250
20	0.1470	12 × 16	0.04974	0.05057	0.05271
49	0.1420	8 × 12	0.1273	0.13367	0.04090
50	0.1409	8 × 12	0.1299	0.13351	0.04267
51	0.1420	8 × 12	0.03980	0.04105	0.07134

[a] Manufacturer and designation of carbon for Runs 49 and 51 is BC-KH2; Run 50 is BC-KE1; all the rest are P.C.C.-BPL.

DATA ANALYSIS

Engell and Coull (*3*) have suggested that a linear relationship exists between the argument of the probability integral and the gas concentration at any point in an adsorption divided by the inlet gas concentration if the argument of the probability integral is proportional to time. Figure 1 is a typical plot of data obtained in this work using probability graph paper and demonstrates that the system benzene-nitrogen over activated carbon does give the suggested linear relationship.

The probability integral is given by

$$F(Z) = \int_{-\infty}^{Z} \frac{-1}{(2\Pi)^{1/2}} \exp. (-Z^2/2)\, dZ \qquad (1)$$

To find the relationship between the argument, Z, and time, t, it is necessary to take note of some experimental limitations. Since the analytical procedure for determining gas compositions is not perfect, the lowest concentration that can be determined in the bed is one that is greater than the uncertainty in the zero point reading. For this reason, some arbitrary value of x_b is designated as the break-point composition and the corresponding time, t_b, as the break-point time. For the same reason, it is impossible to determine an exact time when the bed is saturated and therefore an arbitrary saturation composition, x_s, and

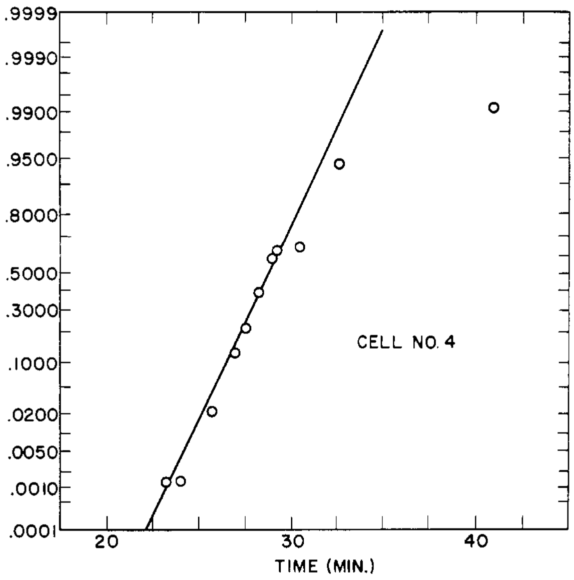

Figure 1. Relative adsorption of benzene from nitrogen on activated charcoal

(PCC-BPL 12 × 30 charcoal; 100° F. initial temperature; 0.05255 SCFM nitrogen flow; 1 atm. pressure; x_s = 0.08369)

---

[1] Present address, University of Alabama, University, Ala.

[2] Present address, California Research Corporation, Richmond, Calif.

corresponding time, t_s, are designated. Defining a time parameter,

$$t' = t - \frac{t_b + t_s}{2} \tag{2}$$

and letting

$$Z = (2)^{1/2} h t' \tag{3}$$

the relationship between a gas composition in the bed and time at a certain height of the bed is given by

$$\frac{x}{x_s} = \int_{-\infty}^{Z} \frac{1}{(2\Pi)^{1/2}} \exp. (-Z^2/2)\, dZ \tag{4}$$

From Equations 2 and 3, it is apparent that the $Z - t$ relationship is of the form

$$Z = At + B \tag{5}$$

The experimental data were fitted to Equation 5 by the method of least squares. Since it is more reasonable to assign

Table II. Break-Through Times for the System Benzene on Carbon at 100° F. Least Squares Fit of Data to the Equation

$$Z = A\ (t - KL)$$

Run No.	Cell	L, Foot	A	$-B(AKL)$	K, Equation 16	t_b, Min.	t_s, Min.
2	5	0.1708	0.5330	4.8438	53.20	1.913	16.262
	6	0.2242		6.2022	51.51	4.462	18.811
3	3	0.08083	0.8332	3.2636	48.46	−0.6726	8.506
	4	0.1200		4.6082	46.09	0.9412	10.120
	5	0.1633		5.7010	41.89	2.253	11.432
	6	0.2067		8.0643	46.84	5.089	14.268
4	6	0.2042	0.5274	6.5321	60.66	5.135	19.636
5	5	0.4008	0.3731	9.0657	60.62	14.049	34.548
	6	0.5025		11.4169	60.90	20.351	40.849
6	4	0.3008	0.3866	5.4710	35.16	4.260	24.043
	5	0.4025		7.2807	62.60	8.941	28.724
	6	0.5050		8.9932	46.07	13.371	33.154
7	4	0.1992	0.6806	5.1126	37.72	1.893	13.130
	5	0.2983		7.9936	39.37	6.126	17.304
	6	0.3975		10.8199	40.00	10.279	21.516
8	4	0.1992	0.6487	5.5822	43.21	2.710	14.500
	5	0.2983		7.9826	41.24	6.411	18.200
	6	0.3975		10.3142	40.00	10.005	21.795
9	2	0.0992	0.6750	2.9714	44.39	−1.263	10.067
	3	0.1975		5.7914	43.44	2.915	14.245
	4	0.2975		8.7517	43.58	7.300	18.631
	5	0.3967		11.8386	44.22	11.873	23.204
10	5	0.3967	0.4493	11.9444	67.02	18.073	35.095
	6	0.4967		15.0169	67.30	24.912	41.934
11	4	0.2967	0.3860	8.4161	73.50	11.897	31.710
	5	0.3958		11.0599	72.38	18.746	38.559
	6	0.4942		13.6015	71.30	25.330	45.144
12	5	0.3958	0.5449	11.5081	53.35	14.102	28.137
	6	0.4942		14.2885	53.06	19.204	33.240
13	4	0.1967	0.3791	6.4168	86.06	6.839	27.013
	5	0.2958		9.6924	86.42	15.480	35.654
	6	0.3942		12.8264	85.84	23.747	43.921
14	6	0.3942	0.3238	12.0853	94.69	25.514	49.133
16	4	0.1950	0.5055	3.5199	35.71	0.602	14.528
	5	0.2925		5.5098	37.26	3.335	18.464
	6	0.3900		7.2713	36.89	6.820	21.949
17	3	0.09750	0.3957	3.8121	98.81	−0.0301	19.298
	4	0.1950		7.6814	99.55	9.748	29.076
	5	0.2925		11.6085	100.70	19.673	39.001
	6	0.3900		15.5410	100.70	29.611	48.939
18	3	0.09750	0.2868	4.1348	147.86	1.084	27.750
	4	0.1950		8.1031	144.89	14.920	41.587
	5	0.2925		12.1312	144.61	28.965	55.632
	6	0.3900		15.9382	142.49	42.239	68.906
19	3	0.09750	0.5335	4.5585	87.64	1.377	15.712
	4	0.1950		8.7618	84.22	9.255	23.591
	5	0.2925		13.0078	83.35	17.214	31.550
	6	0.3900		17.2926	83.11	25.246	39.581
20	4	0.1950	0.4165	4.5119	55.55	1.652	20.014
	5	0.2925		7.0525	57.89	7.752	26.114
	6	0.3900		9.4744	58.33	13.566	31.929
49	2	0.03583	0.4268	0.6864	44.88	−7.351	10.568
	3	0.1067		3.0853	67.78	−1.731	16.189
	4	0.2242		6.9041	72.17	7.217	25.136
50	5	0.04667	0.7484	0.3118	8.927	−4.693	5.526
51	4	0.2242	0.3148	5.3369	75.62	4.806	29.101

equal weights to the primary variables, x and t, it is necessary to assign weights when the variables are Z and t. A least squares analysis shows that

$$A = \frac{\Sigma\omega(t - \bar{t})\,(Z - \bar{Z})}{\Sigma\omega(t - \bar{t})^2} \tag{6}$$

and

$$B = \bar{Z} - A\bar{t} \tag{7}$$

where

$$\bar{t} = \frac{\Sigma\omega t}{\Sigma\omega} \tag{8}$$

$$\bar{Z} = \frac{\Sigma\omega Z}{\Sigma\omega} \tag{9}$$

and

$$\omega = \text{exp.}\, -Z^2 \tag{10}$$

Experimental time-concentration data were obtained at five different points in the adsorption bed. Equation 5 was fitted to the data obtained at each of these points. Preliminary examination indicated that there was no significant difference in the least squares value for A from point to point in the bed. This meant that the adsorption wave did not change shape as it traveled through the bed. The A values for all points in the bed obtained for the same operating conditions were lumped into one value, and these lumped values are presented in Table II for each experimental run. The value of B in Equation 5 varied from point to point in the bed. These are also reported in Table II.

The parameter B is proportional to the length of the bed, and the constant of proportionality is obtained directly from static equilibrium data and operating conditions. The amount of benzene adsorbed per pound of adsorbent bed, from the beginning of its exposure to benzene until it is saturated, is given by

$$We = \frac{4MG\int_0^{t_s}(x_0 - x)\,\mathrm{d}t}{\rho\pi D^2 L} \tag{11}$$

Data which fit Equation 5 exactly produce symmetrical S-shaped curves when plotted as x *vs.* t on rectilinear coordinates. This means that the integral in Equation 11 is given by

$$\int_0^{t_s}(x_0 - x)\,\mathrm{d}t = x_0\left(\frac{t_s + t_b}{2}\right) \tag{12}$$

From Equations 11 and 12, it follows that

$$\frac{t_s + t_b}{2} = \frac{We\,\pi\, D^2 L\rho}{4\,MG\,x_0} \tag{13}$$

Further, by comparing Equations 2 and 3 with Equation 5

$$B = -A\left(\frac{t_b + t_s}{2}\right) \tag{14}$$

and combining this with Equation 13

$$B = -AKL \tag{15}$$

where

$$K = \frac{We\,\pi\, D^2\rho}{4\,MG\,x_0} \tag{16}$$

Therefore, K can be obtained directly by knowing the bed density, mass flow rate, diameter of the tube and static equilibrium data in the form of We *vs.* x_s curves.

A comparison of equilibrium data obtained from B values in this work and data obtained using static methods by the Pittsburgh Coke and Chemical Co. on their activated carbon product is presented in Figure 2. The scatter reflects the uncertainty in the parameter A since this was used to convert values of B into K via Equation 15. Table II also presents values of K calculated from the experimental data along with calculated break times and saturation times corresponding to $x_b/x_0 = 0.0001$ and $x_s/x_0 = 0.9999$.

Some data on the temperature variation in the adsorption bed were also obtained. These are presented in Table III along with gas concentrations which were measured for Runs 9 and 49. As pointed out earlier, these measurements were made manually and it was difficult to record both temperature and composition. In the two runs for which compositions were measured, the precision of these measurements are understandably poor. A thermocouple was placed in the center of the absorbent bed of the third cell in such a manner that it was in contact with and completely surrounded by the particles at the effluent end of each cell. This resulted in a time lag between the temperature wave

Table III. Variation of Bed Temperature with Time for Carbon Runs

Run No.	Time, Min.	Temp., ° C.	x/x_s
9	6.91	. . .	0.00686
	7.83	35.05	. . .
	9.49	. . .	0.7417
	10.42	90.00	. . .
	10.91	. . .	0.9205
	11.83	83.50	. . .
	20.33	35.60	. . .
	23.16	. . .	0.9978
	40.42	35.00	. . .
10	12.45	37.50	. . .
	15.40	74.10	. . .
	17.15	82.50	. . .
	18.44	77.60	. . .
	27.98	38.60	. . .
	41.70	37.30	. . .
49	3.76	37.14	. . .
	4.07	. . .	0.00137
	4.09	. . .	0.00719
	5.28	40.81	. . .
	5.58	. . .	0.1705
	5.94	44.75	. . .
	6.46	. . .	0.2819
	7.24	. . .	0.5308
	7.71	59.12	. . .
	8.24	. . .	0.7217
	8.89	. . .	0.8274
	9.60	62.16	. . .
	10.44	63.16	0.9422
	10.84	58.36	. . .
	12.47	49.15	. . .
	13.55	. . .	0.9934
	15.52	39.50	. . .
	17.77	. . .	0.9990
	19.64	37.60	. . .
	23.36	37.36	. . .
	30.50	37.35	. . .
51	2.10	36.52	
	3.70	36.52	
	4.18	36.73	
	5.54	37.98	
	6.25	41.05	
	6.93	46.60	
	8.07	59.06	
	9.37	70.70	
	10.53	71.71	
	11.03	66.49	
	14.43	48.30	
	17.84	39.35	
	19.92	37.74	
	21.95	37.20	
	24.98	36.87	
	31.20	36.70	
	39.15	36.63	

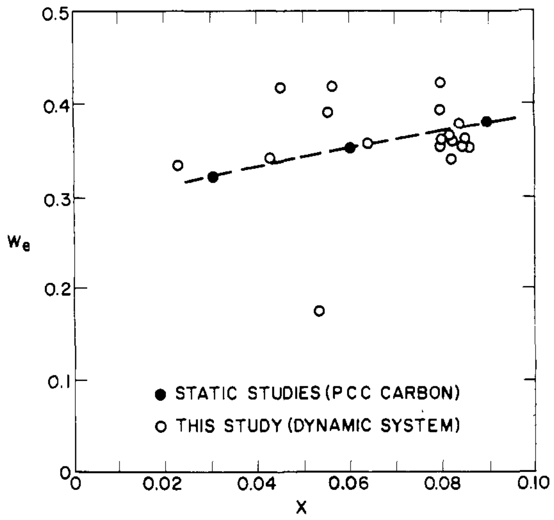

Figure 2. Equilibrium benzene adsorption on activated charcoal at 100° F.
(Dynamic system points calculated from Equation 11)

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
ρ = bulk density of adsorbent carbon, lb./cube ft.
ω = 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.