THE INFLUENCE OF CARBON GRANULE SIZES ON BUTANE BREAKTHROUGH CURVES

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ABSTRACT

Breakthrough curves of butane vapor passing through packed dry carbon beds have been measured to obtain information for the design of longer lasting carbon filters. Data for 1000 ppm butane challenge have been analyzed for adsorption capacities, rates, and pressure drop. Both unimpregnated BPL and metal ion/TEDA-impregnated carbons were used. The original carbons with granules in the 12-30 mesh size range were compared with each other and with sieved fractions in the 12-16, 16-20, and 20-30 mesh size ranges. The impregnants in a 12-30 mesh ASZM-T carbon reduced butane capacity by 55% and reduced adsorption rate by 36% compared with unimpregnated BPL carbon. The 16-20 mesh ASZM-T provided the best combination of capacity, adsorption rate, and pressure drop of the three granule size fractions.

INTRODUCTION

The chromium-free carbon (ASZM-T), now in production for military filtration systems, has resulted in a 25% increase in impregnant loading onto the carbon substrate (BPL carbon) compared with ASC carbon. Although the performance of ASZM-T has been maintained for standard agents, the additional impregnant loading reduces the capacity for modification to enhance reactivity with new vapors. This decrement appears to result from inefficient dispersion of the impregnant and increased blockage of adsorption and pore transition sites.

One possibility for recovering some of the adsorption capacity and rate lost due to added impregnants is to change the carbon granule size distribution within the packed carbon bed. Granule size selection and layering of different sizes within a filter bed can be performed. The studies presented in this paper focus on effects of granule size fractions on adsorption capacity, adsorption rate, breakthrough curve asymmetry, and pressure drop. Butane was used as the test vapor.

EXPERIMENTAL

A mixture of 1000 parts-per-million by volume of butane in dry (13-23 % relative humidity) air was prepared by bleeding 11.7 mL/min of butane into a flow of 11.7 L/min dry air. This mixture passed through a glass manifold and through a glass cylinder (6.9 cm inner diameter) packed to a depth of 2.0 cm with dry (as received) activated carbon. This flow rate corresponds to a residence time of 0.38 s, a linear velocity of 5.2 cm/s, and a flow of 32 L/min through a C-2 canister.

The butane in the air effluent from the center of the packed bed was sampled through a Teflon tube. The butane concentration was measured with either a portable flame ionization detector (Sensidyne, Clearwater, FL) or a photo acoustic infrared spectrometer (Bruel & Kjaer Type 1302). These measurements were made from the time of first introduction of butane to where the butane effluent concentration leveled off, indicating bed saturation and no further adsorption.

Beds were packed using a vacuum flow through the sample cylinder and slow, random, dropping of the carbon granules through a 1-m tube (the "snowflake" technique). Beds were packed by weight to 2.0 cm depth using bed depth vs. weight calibrations prepared for each granule size range and carbon type.

Pressure drop across the packed bed was measured several times during each test using a water manometer (Dwyer Model XX). Measurements were averaged.

Original carbon samples were taken from larger batches prepared by Calgon Carbon Corporation. The BPL activated carbon was Lot 1330, nominally 12-30 mesh size range. The ASZM-T carbon, Lot CO1142, also nominally 12-30 mesh, was a BPL carbon impregnated with 2% molybdenum, 5% copper, 5% zinc, 0.05% silver, and 3% triethylenediamine by weight.

Granule size fractions were prepared by sieving the original carbons through U.S.A. Standard Testing Sieves (W.S. Tyler, Inc.) Numbers 12, 16, 20, 30 and 40. Weight fractions obtained are shown in Table I.

TABLE I

Carbon Fractions by Weight

Carbon Type	< 12 Mesh	12-16 Mesh	16-20 Mesh	20-30 Mesh	> 30 Mesh
BPL	0 %	29.5 %	54.6 %	15.1 %	0.8 %
ASZM-T	0 %	19.2 %	58.0 %	22.0 %	0.7 %

RESULTS

Effluent butane concentrations plotted against time produced breakthrough curves such as those shown in Figure 1. These data were fit to a breakthrough curve equation to obtain parameters which can be related to adsorption capacity and adsorption rate at the stoichiometric time and curve asymmetry.[1] Curve asymmetry is expressed as a breakthrough curve fit parameter, G, which describes the increase in adsorption rate at lower penetration fractions, presumably due to more active adsorption sites being available at lower vapor loadings. Table II lists such derived parameters plus pressure drops for duplicate tests for four ASZM-T mesh size ranges, including the original 12-30 mesh. Table III lists these for the BPL activated carbon.

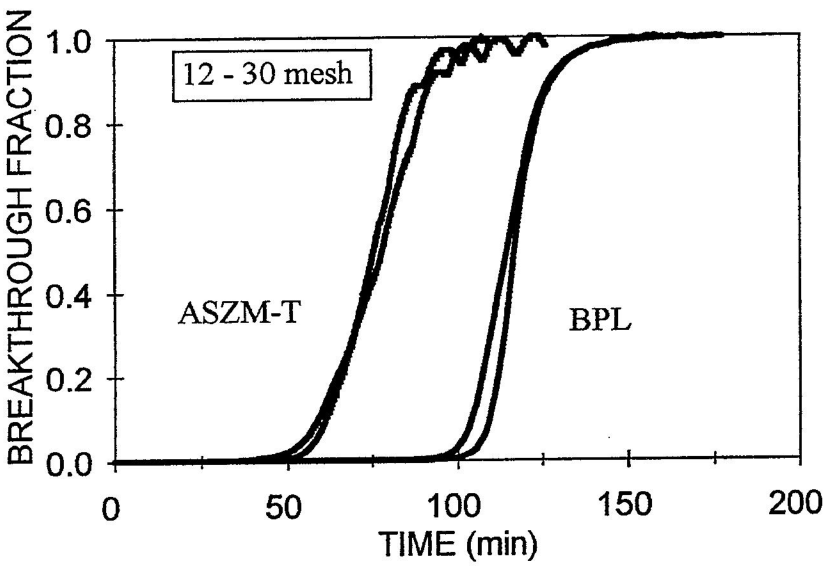

FIGURE 1. Breakthrough Curves for Original Carbons

Average granule sizes calculated for each mesh size range are listed in Tables II and III. Averages from duplicate tests were also taken for butane capacity, adsorption rate coefficient, asymmetry coefficient, and pressure drop. These average values are plotted against average granule sizes in Figures 2-5.

DISCUSSION

Figure 1 clearly shows the earlier and less steep breakthrough curves obtained with the ASZM-T carbon compared with the BPL carbon (both original 12-30 mesh size range). The earlier times are caused by lower capacities and the reduced slope by lower adsorption rate coefficients (Table II vs Table III). The impregnants in the 12-30 mesh ASZM-T carbon reduced average butane capacity by 55% and reduced adsorption rate by 36% compared with the BPL carbon. What is not easily seen from the breakthrough curves alone is the lower asymmetry for the ASZM-T carbon, reflected as smaller curve fit G parameters. A smaller G value means a relatively lower adsorption rate at earlier breakthrough times, i.e., shorter breakthrough times at low breakthrough fractions. This is undesirable, since low breakthrough fractions are of practical importance for protection against toxic gases and vapors.

TABLE II

ASZM-T Carbon Granule Size Effects

Carbon Granules		Stoichiometric Values				Asymmetry Coefficient		Stoichiometric Breakthrough Fraction	Pressure	Drop
Mesh Range	Average Size (mm)	Butane Capacity (mg/g)	Avg.	Adsorption Rate (min^{-1})	Avg.	G	Avg.		(inches water)	Avg.
12 - 30	1.15	35.4	35.1	1444	1620	-0.008	0.005	0.547	0.182	0.170
12 - 30		34.7		1796		0.017		0.522	0.158	
12 - 16	1.44	43.4	43.8	2330	2261	0.031	0.060	0.566	0.085	0.087
12 - 16		44.2		2192		0.088		0.521	0.088	
16 - 20	1.01	42.7	42.7	2959	2822	0.056	0.071	0.546	0.128	0.129
16 - 20		42.7		2684		0.086		0.549	0.130	
20 - 30	0.72	38.9	39.6	2822	2759	0.049	0.057	0.613	0.210	0.213
20 - 30		40.0		2866		0.113		0.529	0.220	
20 - 30		40.0		2588		0.008		0.529	0.210	

TABLE III

BPL Carbon Granule Size Effects

Carbon Granules		Stoichiometric Values				Asymmetry Coefficient		Stoichiometric Breakthrough Fraction	Pressure	Drop
Mesh Range	Average Size (mm)	Butane Capacity (mg/g)	Avg.	Adsorption Rate (min^{-1})	Avg.	G	Avg.		(inches water)	Avg.
12 - 30	1.15	79.0	78.1	2899	2543	0.088	0.071	0.547	0.115	0.118
12 - 30		77.2		2186		0.054		0.522	0.121	
12 - 16	1.44	71.4	71.0	1955	2324	0.100	0.081	0.566	0.079	0.079
12 - 16		70.7		2694		0.062		0.521	0.078	
16 - 20	1.01	82.1	81.7	3140	3184	0.088	0.090	0.546	0.115	0.115
16 - 20		81.2		3229		0.093		0.549	0.114	
20 - 30	0.72	76.4	77.6	3397	3469	0.151	0.114	0.613	0.185	0.188
20 - 30		78.8		3540		0.076		0.529	0.191	

Figure 2 shows that the ASZM-T butane capacities are significantly reduced (49%, 48%, and 35%) for all three average carbon granule sizes (0.72, 1.01, and 1.44 mm, respectively) compared with BPL capacities. Although the statistics are poor for only duplicate runs, it seems that the differences among the three granule sizes are real. For the ASZM-T carbon the capacity increases slightly with increasing granule size, indicating a non uniform distribution of impregnants over granule sizes. The smaller reduction in butane capacity for the largest average granule size may be due to relatively less impregnant by weight.

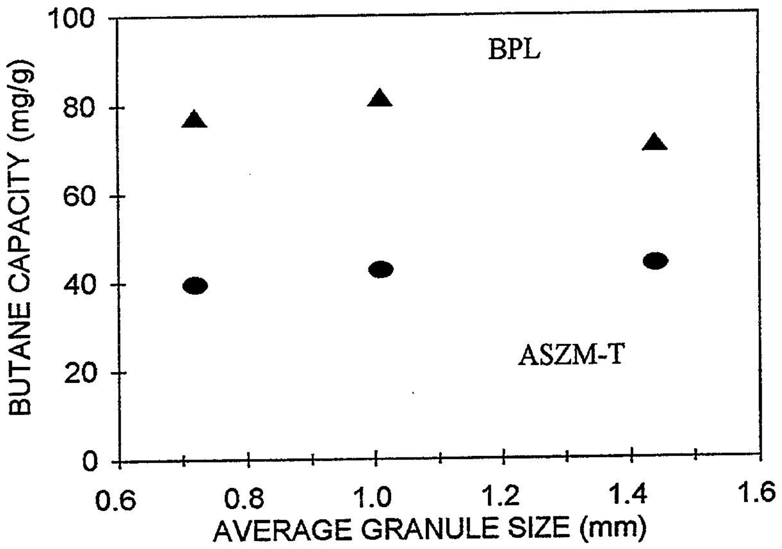

FIGURE 2.

Effect of Carbon Granule Size on Adsorption Capacities for 1000 ppm Butane.

Figure 3 shows similar comparisons of adsorption rate coefficients. The rate coefficients increase with decreasing average granule size for the BPL carbon, as expected.[2] With the ASZM-T carbon a rate plateau may have been reached below 1 mm granule size.[2] It also appears that the differences between the two carbons increase with decreasing granule size, indicating more effect of the impregnant on adsorption rate, perhaps by producing more transition pore blockage.

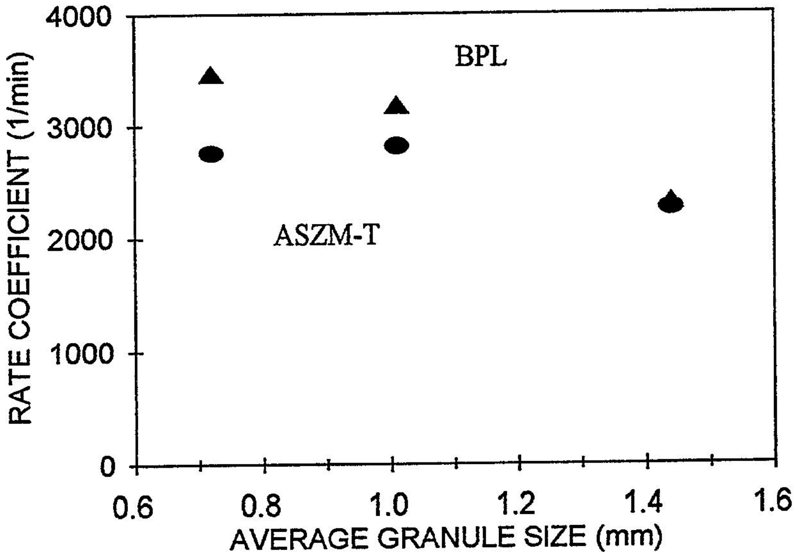

FIGURE 3.

Effect of Carbon Granule Size on Adsorption Rate Coefficients for 1000 ppm Butane.

Figure 4 shows that the desirable breakthrough curve asymmetry is reduced for all granule sizes of the ASZM-T compared with the corresponding BPL ones. This can be attributed to masking of the more active adsorption sites with impregnants. Average asymmetry was highest for the ASZM-T carbon at the intermediate average granule size, 1 mm.

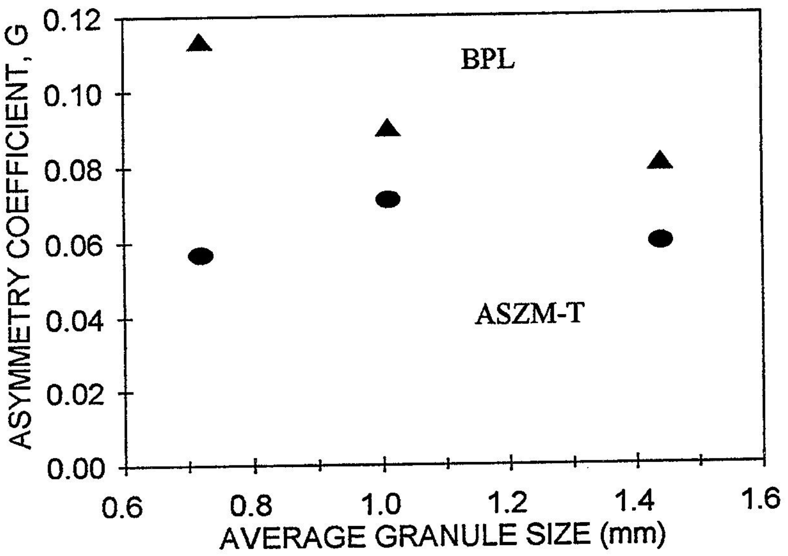

FIGURE 4.

Effect of Carbon Granule Size on Breakthrough Curve Asymmetry Parameters for 1000 ppm Butane.

Figure 5 shows effects of granule size on pressure drop across the test beds at the experimental conditions. Pressure drops decreased with increasing granule size, as expected. They were only slightly higher for the ASZM-T carbon than for the BPL, perhaps due to the impregnants.

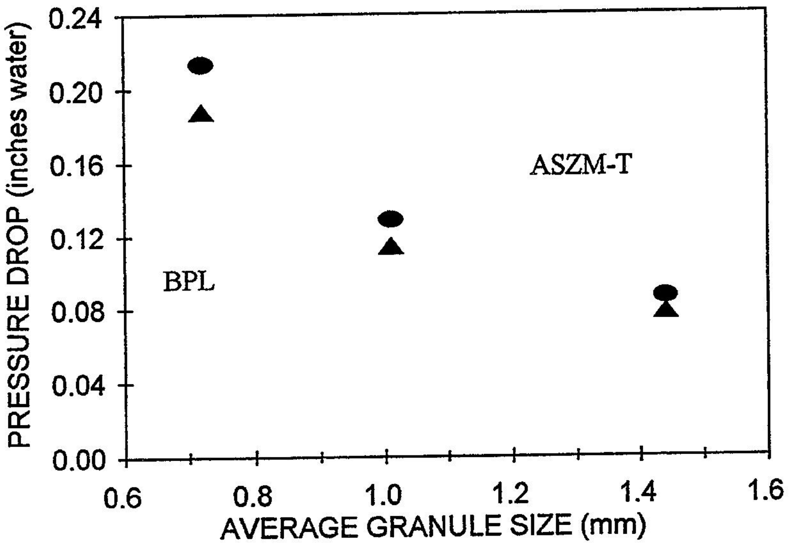

FIGURE 5.

Effect of Carbon Granule Size on Pressure Drops for 5.2 cm/s Airflow.

The duplicate butane breakthrough curves for the 16-20 mesh ASZM-T carbon fraction are compared with those of the original 12-30 mesh ASZM-T carbon in Figure 6. Breakthrough times for the 16-20 mesh fraction are considerably greater, particularly at the important smaller breakthrough fractions.

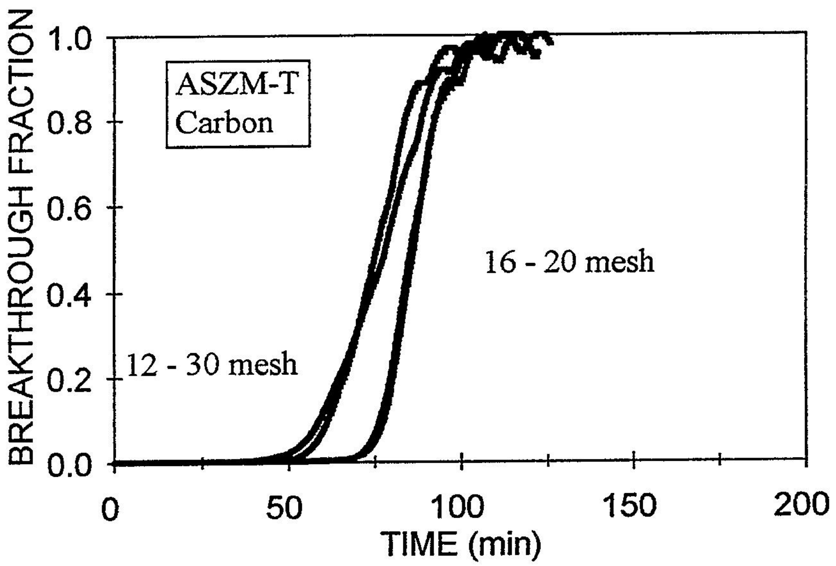

FIGURE 6. Breakthrough Curve Comparison for Two Size Ranges of ASZM-T Carbon.

CONCLUSIONS

Of the three granule size fractions of ASZM-T studied the intermediate 16-20 mesh had the best combination of butane capacity, adsorption rate, asymmetry, and pressure drop. The improvement in substituting the 16-20 mesh fraction for the 12-30 mesh carbon would recover about one-third the breakthrough time losses due to impregnants added to BPL carbon (cf., Figures 1 and 6). Since the 16-20 mesh fraction comprises a majority by weight of the original 12-30 carbon, separating it from the original and using it as a replacement, even discarding the other fractions, should no more than double the cost. There is an added benefit of a lower pressure drop for the 16-20 mesh carbon.

The greater capacity, adsorption rate, and asymmetry of the unimpregnated BPL carbon suggest that it might be helpful as a commixture or backup layer with ASZM-T carbon to increase breakthrough times, particularly at low breakthrough concentrations.

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