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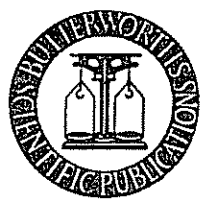

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Molecular Sieve Properties of Activated Anthracite

J. E. METCALFE III, M. KAWAHATA and P. L. WALKER Jr

A raw anthracite which exhibited molecular sieve properties for the adsorption of n-*butane,* iso*butane and* neo*pentane at 30°C was activated with carbon dioxide to 34·8% burn-off. It is of interest that along with a large increase in adsorption capacity and rate of adsorption, the activated anthracite also retained its molecular-sieve behaviour.*

IT IS well known that coals exhibit molecular-sieve properties. Such properties are characterized by a much higher adsorption capacity for *n*-butane than for *iso*butane at room temperature[1] and particularly by activated physical adsorption of nitrogen and argon at 77°K[1–5]. However, this molecular-sieve behaviour in raw coal is of little practical value, since the diffusion rate of the adsorbate into the pore system is usually very slow and the total adsorption capacity is usually very low.

There is an increasing interest and use, today, of molecular-sieve materials by the petroleum industry for the separation of straight- from branched-chain hydrocarbons. Synthetic crystalline zeolites are being used almost exclusively for this purpose[6]. Charcoals made from the pyrolysis of certain polymers show promise[7]. In this paper, the possibilities of producing a suitable molecular-sieve material by the activation of anthracite is considered.

EXPERIMENTAL

Anthracite used

A Pennsylvania anthracite from the Western Middle field, which was ground in a fluid energy mill to an average particle size of 6 μ on a weight basis, was used in this study. The proximate analysis (air-dry basis) of the anthracite was: moisture, 1·2; volatile matter, 8·2; fixed carbon, 79·4; and ash, 11·2 per cent.

Devolatilization of the anthracite

Prior to activation, the anthracite was devolatilized in a nitrogen atmosphere at 950°C for six hours. No attempt was made to analyse the product gases during devolatilization; but from previous studies on kinetics of volatile matter release from anthracite, most of the gas released was hydrogen[8].

Activation of anthracite

Because of the fine particle size of anthracite used, a down-flow fixed bed reactor was employed. The reactor, which was 5·7 cm i.d., 8·3 cm o.d. and 61 cm long, was made of 10–18 steel tubing. The anthracite sample holder, which could be inserted into the reactor, was 304 stainless steel. Its dimensions were 4·8 cm i.d., 0·165 cm wall thickness and 43 cm long. The bottom was perforated to allow passage of the gases. Gas mixing and preheater sections were present, before the reactor. The entire apparatus is described in detail elsewhere[9].

For a run, an oven-dried sample of devolatilized anthracite of known weight was placed in the sample holder. The sample was heated to activation temperature in nitrogen and then reacted with a 90 per cent carbon dioxide–10 per cent carbon monoxide gas mixture, at a total pressure of 1 atm. Following reaction, the sample was cooled in nitrogen and the percentage burn-off measured from the loss in sample weight. Carbon monoxide was added to the inlet reacting gas stream so that more uniform activation through the bed would occur. That is, it minimized the effect of small amounts of product carbon monoxide strongly retarding the gasification reaction[10].

Apparatus to measure properties of anthracite

Mercury density—The mercury density of the samples was determined by mercury displacement, using a mercury porosimeter[11]. Prior to the measurement, the samples were outgassed in the porosimeter at room temperature for one hour. The total pressure was then raised to 2000 lb/in^2. At this pressure, mercury is forced into openings greater than *ca.* 1000 Å. Therefore, it is expected that the voids between anthracite particles were completely filled. At the same time, the volume of mercury forced into pores above 1000 Å within the anthracite particles is thought to be negligible[12].

Helium density—Prior to the measurement, the samples were outgassed at 125°C for eight hours. The helium densities were determined by the conventional method in which a measured quantity of helium was expanded into a sample holder (held at 30°C) of known volume containing a sample of known weight. A 30 minute period was found adequate to reach equilibrium.

Adsorption apparatus—A static adsorption apparatus of the typical design[13], containing mercury float valves, was used. All adsorption studies were conducted at 30° ± 0·1°C. Prior to measuring the free space with helium, the samples were outgassed at 250°C for seven hours. Because of the very slow diffusion of the hydrocarbon adsorbates into the raw and devolatilized anthracites, 24 hours was allowed to reach equilibrium for each adsorption point. For the activated samples, a one-hour equilibration time was found sufficient. The adsorbates used, *n*-butane, *iso*butane, and *neo*pentane, were obtained from the Matheson Co. and were of greater than 99·9 per cent purity.

RESULTS AND DISCUSSION

It was decided to activate anthracite of micron size in this study in order to attain the optimum in uniform particle activation and to decrease adsorption equilibration time to a mimimum. P. L. WALKER, Jr and co-workers[14] discuss the effect of particle size on non-uniformity of gasification. M. KAWAHATA and P. L. WALKER, Jr[12], who studied the effect of particle size of an anthracite on extent of activation under otherwise similar conditions, showed that the specific pore volume developed increased sharply with decreasing particle size in the range 16 to 150 mesh.

Unfortunately, however, the handling of 6 μ anthracite during activation proved to be a problem. Initially, activation in a fluid bed apparatus, which

was previously used successfully to treat 100 × 150 mesh anthracite[15], was attempted; but excessive carry-over of the 6 μ material from the reactor made fluidization impractical. In the down-flow fixed bed reactor which was used for activation, it became evident that channelling of the gas was a problem. This apparently resulted in non-uniform reaction through the bed. That is, from the total percentage of burn-off and the change in mercury density of anthracite during a run, the fraction of activation which took place within the anthracite particle (arbitrarily defined as internal activation as contrasted to removing external volume and thereby decreasing particle size) could be estimated. For the seven activation runs made, the percentage of internal activation varied widely, up to 100 per cent, with no trend being found with changing activation temperature between 750° and 840°C. Results for the sample with 100 per cent internal activation only are given here, to show under the best conditions what type of molecular-sieve properties activated anthracite can have.

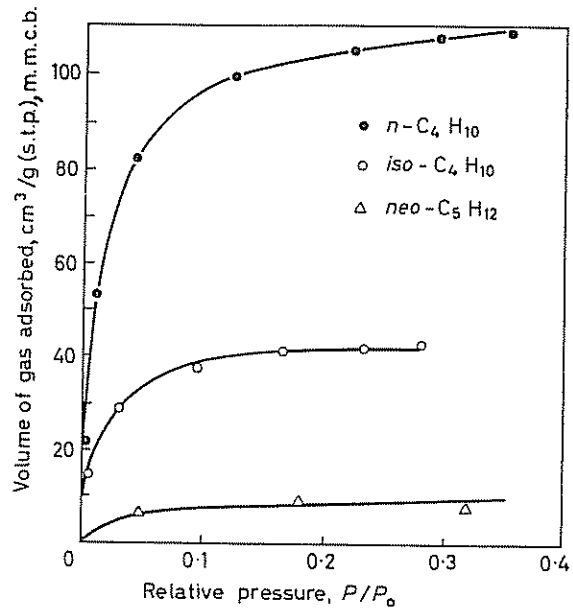

Figure 1. Hydrocarbon adsorption at 30°C on anthracite activated to 34·8 per cent burn-off at 840°C

The activated sample to be considered here, was reacted at 840°C for 23·5 h to 34·8 per cent burn-off. *Figure 1* shows the isotherms for the adsorption of hydrocarbons on this sample. The isotherms can be closely approximated by the Langmuir equation, from which monolayer adsorption volumes can be estimated. These volumes for the activated and raw anthracite are given in *Table 1*. Monolayer volumes for the devolatilized anthracite are not given, since they were very small and could not be accurately measured. For *n*-butane adsorption at a relative pressure of 0·3, the volume adsorbed on the devolatilized anthracite was roughly ten per cent of that adsorbed

on the raw anthracite. This indicates significant closure and contraction of pores, which were previously open to *n*-butane, upon heating of the raw anthracite to 950°C. Such a result has been previously reported upon the heat treatment of bituminous chars to higher temperatures[16]. Contraction is also seen to produce a significant increase in the activation energy for diffusion of gases from anthracite[17].

From *Table 1*, it is seen that the volume available to the hydrocarbons is sharply increased upon activation, as expected. Of more importance is the

Table 1. Monolayer volumes for different hydrocarbons on raw and activated anthracite (m.m.f.b.)

Material	V_m, cm^3/g (*s.t.p.*)		
	n-C_4H_{10}	*iso*-C_4H_{10}	*neo*-C_5H_{12}
Raw	12·6	8·6	2·3
Activated	134	54·5	15·5

Table 2. Densities and total open pore volume in raw, devolatilized, and activated anthracite (m.m.f.b.)

Material	*Mercury density* g/cm^3	*Helium density* g/cm^3	*Total open pore Volume,* cm^3/g
Raw	$1{\cdot}24_5$	$1{\cdot}43_8$	$0{\cdot}10_8$
Devolatilized	$1{\cdot}51_0$	$2{\cdot}01_0$	$0{\cdot}16_5$
Activated	$0{\cdot}95_7$	$2{\cdot}15_6$	$0{\cdot}58_1$

fact that the adsorption rate is markedly increased and that wide differences in the pore volume available to the hydrocarbons still exist.

Table 2 summarizes the results for the mercury and helium densities and total open pore volume on a mineral matter free basis (m.m.f.b.). To place the density results on a m.m.f.b., the mercury and helium density of the mineral matter in all samples was taken as 2·7 g/cm^3 [18]. The total open pore volume is considered to be the volume in pores < 1000 Å and $> 2{\cdot}5$ Å in diameter. The lower limit is set by the size of pore into which helium can diffuse at a significant rate at 30°C[19].

On the basis of these results, the nature of the molecular pore system in the anthracites can be clarified further. From mercury porosimeter data on anthracite activated to 38 per cent burn-off, it has been shown that about 94 per cent of the total open pore volume is located in pores < 28 Å in diameter[12]. According to the Kelvin equation, pores of up to about this diameter will be filled by the hydrocarbons studied at a relative pressure of 0·3. Therefore, the assumption is made that the volume of hydrocarbons adsorbed at a relative pressure of 0·3* is located in pores between a lower

* The volumes adsorbed at a relative pressure of 0·3 agree closely with the V_m values calculated from the Langmuir equation.

limit (below which the hydrocarbon will not enter at 30°C) and 1000 Å. Then, by subtracting these pore volumes from the total open pore volume, distribution data in the molecular pore size range can be determined. In agreement with D. W. BRECK and co-workers[20] and others, the minimum effective pore size into which a hydrocarbon can penetrate is taken as the diameter of the circumscribed circle of minimum cross-sectional area of the hydrocarbon molecule. These minimum dimensions are 4·9, 5·6 and 6·5 Å for *n*-butane, *iso*butane, and *neo*pentane, respectively.

These results are summarized graphically in *Figure 2*. It is seen that even though the total pore volume is increased on devolatilization (presumably

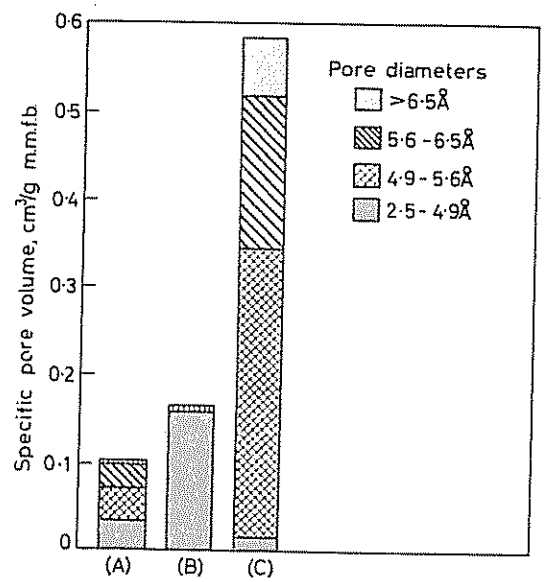

Figure 2. Pore volume distributions in raw (A), devolatilized (B) and activated (C) anthracites

by volatile matter release unblocking and enlarging pores by activation[21]), the amount of pore volume available to *n*-butane and larger hydrocarbons sharply decreases. Comparing the volume distributions for the raw with the activated anthracite, it is seen that in spite of a large increase in total pore volume upon activation, the pore volume between 2·5 and 4·9 Å has decreased. This would suggest that there is little pore volume below 4·9 Å to be opened up by additional burn-off of this anthracite. It is to be emphasized that the volume reported below a minimum effective pore size is a function of adsorption temperature. The volume would be expected to increase with increasing adsorption temperature, because of activated diffusion, expansion of the pores and an increasing magnitude of vibration of the atoms around a pore opening.

It is of interest to compare the activated anthracite with Type A synthetic zeolite pellets for adsorption of *n*-butane and *iso*butane[20]. At room temperature, the 5A zeolite has a capacity of *ca.* 50 cm³ (s.t.p.) *n*-butane/g and 2 cm³ *iso*butane/g. It is thought that the adsorption of *iso*butane primarily occurs

on the binder holding the small zeolite particles together in the pellet. The ratio of gases adsorbed is *ca.* 25. In contrast, the activated anthracite has a capacity of *ca.* 110 cm^3 *n*-butane/g (m.m.c.b.) and 40 cm^3 *iso*butane/g. The ratio of gases adsorbed is *ca.* 2·8. Pelletizing the anthracite for use in fixed bed operations would be expected to lower the separation ratio. It is obvious, then, that this activated anthracite sample does not show the sharp molecular-sieve effect demonstrated by the zeolite. This is to be expected, since a range of molecular pore size is present in the raw and activated anthracite. Nevertheless, because of the relatively low cost of activated anthracite, it may have possible applications for rough separations in conjunction with zeolites.

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Fuel Technology Department,
Pennsylvania State University,
University Park, Pa

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