

CHARACTERISTICS OF ACTIVATED CARBONS CONTROLLING CH₄ AND CO₂ SEPARATIONS

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Introduction

Separation of gases is a very interesting process in several industries (chemical, petrochemical, and related industries). Although cryogenics and absorption remain the most widely used processes for this purpose, the last two decades have seen a tremendous growth in research activities and commercial applications of adsorption-based gas separation processes.

Separation by an adsorptive process is based on the selective accumulation of one or more components of a gas mixture on the surface of a microporous solid. The adsorptive separation is achieved by one of the three mechanisms: steric, kinetic or equilibrium. Most processes operate through the equilibrium (or competitive) adsorption of the gases mixture.

Carbonaceous adsorbents are useful in separation processes due to their good kinetic properties and high adsorption capacities.

This work presents the experimental study of the separation of a methane / carbon dioxide mixture by activated carbons. Methane / carbon dioxide separation is required in two important applications: (1) landfill gas which contains approximately 50% each of CH₄/CO₂; and (2) tertiary oil recovery where the effluent gas contains approximately 80% CO₂ and 20% of CH₄ plus other light hydrocarbons [1].

Experimental

Two series of activated carbon have been used for this study. One of them consists on physically activated carbons prepared from almond shell, using steam at 800 °C as activating agent. The pyrolysis time has been modified in order to obtain activated carbon with different characteristics. The other series consists of chemically activated carbons from a Spanish anthracite which has been activated using potassium hydroxide following the process described elsewhere [2]. In that study additional variables has been analyzed (activating agent/carbon ratio, N₂ flow, heating rate, pyrolysis temperature and pyrolysis time). Surface area characterization of all samples has been carried out by physical adsorption (N₂ at 77 K and CO₂ at

273 K) using an automatic adsorption system (Autosorb-6, Quantachrome). The CH₄/CO₂ separation studies have been accomplished in a modified BTRS-Jr reactor connected to a mass spectrometer (MSC200, Balzers) for gas analysis. The process has been studied at atmospheric pressure and 298 K in a flow reactor using a total flow rate of 60 ml/min (33 ml/min CH₄, 27 ml/min CO₂) and 0.25 g of sample[3]. For comparative purpose, two commercial molecular sieves, Takeda 3A and 5A have been studied under the same conditions.

Results and discussions

Table 1 contains the porous texture characterization results obtained by applying the BET equation to N₂ adsorption at 77 K and the DR equation to N₂ adsorption at 77 K and CO₂ adsorption at 273 K. Three different activated carbon materials can be observed; the chemically activated carbons (KUA1 series), the physically activated almond shell (B series) and the two molecular sieves. It can be seen that the use of different raw precursors, activation methods and activation degrees allow to have activated carbons with very different pore characteristics.

Table 1. Pore characterization results.

Sample	S BET (m ² /g)	V(CO ₂) (cm ³ /g)	V(N ₂) (cm ³ /g)	Delayed time (s)
KUA1L0	930	0.40	0.46	5.4
KUA1L3	2021	0.67	0.89	6.6
KUA1L11	726	0.37	0.33	4.2
KUA1L15	2085	0.59	0.95	5.4
KUA1L26	2949	0.59	1.15	5.6
KUA1GC	1788	0.80	0.83	8.0
B13	542	0.29	0.31	2.6
B31	715	0.37	0.39	2.7
B74	1038	0.40	0.59	2.6
Takeda 3A	0	0.22	0	1.5
Takeda 5A	570	0.30	0.27	1.2

Figure 1 shows, as an example, the CH₄ and CO₂ breakthrough curves for a selected sample (KUAL3). These curves show the gases composition after the adsorption bed. Thus, the curves are inversely related to the amount adsorbed by the carbon. In this figure, notice that observed the previous step where He passes through the sample. Afterwards, the CH₄/CO₂ mixture is passed

through the adsorption bed. Firstly, the experiment has been carried out without the sample, using glass marbles in order to obtain a similar height bed that in the rest of the cases. This experiment (blank), as is expected, does not show delay between both gases, CH₄ and CO₂. Subsequently, the same experiment has been carried out with the sample. Comparing the signal corresponding to CH₄ in each experiment, with and without activated carbon, it can be deduced that CH₄ adsorption does not exist, because there is no difference between the time where the two signals appear. The latter experiment shows that the CO₂ signal (mass 44) suffers an important delay from the CH₄ signal (mass 15) indicating that, activated carbons have a higher affinity for CO₂ adsorption than CH₄. Thus, from these plots, the CO₂ delay time has been calculated for each sample. The values corresponding to the delay time are presented in Table 1.

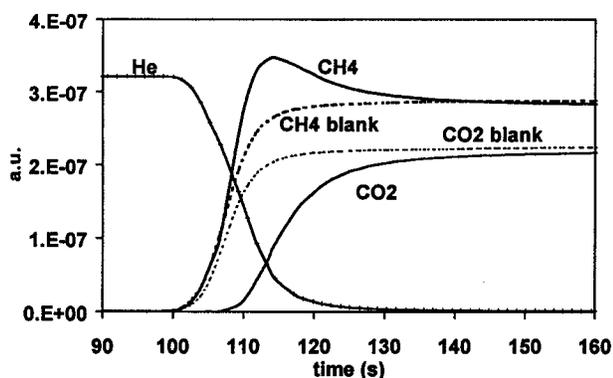


Figure 1. Breakthrough curves for sample KUA1L13.

Table 1 shows that chemically activated carbons present a high delay time which varies from 4 to 8 seconds, indicating that these materials have a CO₂ adsorption capacity higher than the CH₄. It can be observed that those delay times depend on the pore characterization results presented by the sample. A relationship between the narrow micropore volumes (V_{CO_2}) and the delay time has been obtained for these chemically activated carbons. Figure 2 shows a good correlation between these two experimental parameter values, indicating that in these type of materials a higher narrow micropore volume produces a higher CO₂ adsorption capacity which produces a higher delay time. Additionally, the results indicate that the delay time does not depend on the micropore volume obtained from N₂ adsorption at 77 K (V_{N_2}).

The relationship obtained for the chemically activated sample has not been observed for neither, Takeda samples nor for the physically activated carbons. The latter materials present the same delay time, even though they have different micropore volumes, presumably due to a different affinity for CO₂. This different behaviour

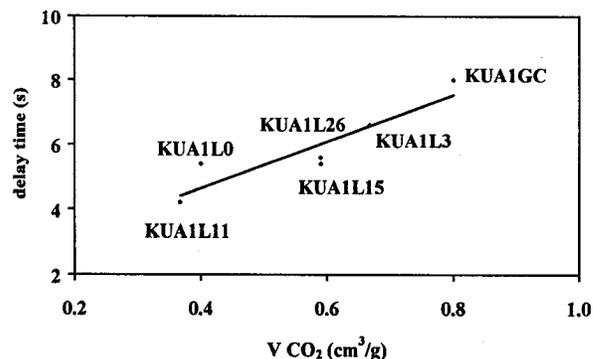


Figure 2. Relationship between delay time and V_{CO_2} obtained for the chemically activated carbons.

between all type of materials, indicates that the CO₂ adsorption capacity, in a CO₂/CH₄ mixture, not only depends on the micropore volume presented by the samples, but also on the type of material and presumably, mainly on the activation process.

Conclusions

A chemically activated anthracite can be used for CH₄/CO₂ separation. Higher narrow micropore volume produces higher delay time between the signals corresponding to both gases and hence a better CH₄/CO₂ separation. Micropore volume obtained by N₂ adsorption at 77 K is not directly related to the delay time. The CH₄/CO₂ separation process seems not only to depend on the narrow micropore volume, but also on the raw material and activation process, which can affect the affinity of the activated carbon materials for the CO₂ adsorption.

Acknowledgments

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