



# Activated carbon monoliths for methane storage: influence of binder

D. Lozano-Castelló<sup>a</sup>, D. Cazorla-Amorós<sup>a</sup>, A. Linares-Solano<sup>a,\*</sup>, D.F. Quinn<sup>b</sup>

<sup>a</sup>*Departamento de Química Inorgánica, Universidad de Alicante, Apartado Correo 99, E-03080, Alicante, Spain*

<sup>b</sup>*Department of Chemistry and Chemical Engineering, Royal Military College of Canada, P.O. Box 17000 STN FORCES, Kingston, Ont., Canada K7K 7B4*

Received 8 November 2001; accepted 11 June 2002

## Abstract

In the present work, the agglomeration of a high adsorption capacity powdered activated carbon suitable for methane storage has been studied. Activated carbon monoliths have been prepared using the starting activated carbon and six different binders. Porous texture characterization of all the monoliths has been carried out by physical adsorption and helium density. Experimental methane adsorption capacity and delivery values have been obtained for all the samples. The results show that the adsorption capacities of the activated carbon monoliths are reduced with respect to the starting activated carbon. In addition to the adsorption capacity and delivery, the monolith density is also a crucial parameter for methane storage applications. This parameter has been obtained for all the samples. Moreover, the evaluation of the mechanical properties of the monoliths has been carried out with compression tests. According to our results, among all the binders studied, the one which produces monoliths with the best equilibrium between adsorption capacity and piece density has a methane delivery of 126 V/V. The important effect of the percentage of this binder in piece density and mechanical properties has been shown. Finally, a preliminary kinetic study of methane adsorption up to 4 MPa for the monoliths has shown that activated carbon monoliths do not present diffusional problems for adsorption of methane.

© 2002 Elsevier Science Ltd. All rights reserved.

**Keywords:** A. Activated carbon; C. Adsorption; D. Density; Mechanical properties

## 1. Introduction

Compressed natural gas vehicles (CNG) (which store natural gas at 210 bar) historically have been the most popular type of natural gas vehicle. Adsorbed natural gas (ANG) is a technology in which natural gas is adsorbed by a porous adsorbent material at relatively low pressures (35–40 bar). Natural gas storage using an adsorbent has been considered a promising technology for use in natural-gas fuelled vehicles [1–3]. Among adsorbents investigated, carbon materials are the most effective in the storage of natural gas at low pressures (e.g. 40 bar) [1–3]. Critical issues in the commercialization of adsorbed natural gas storage technology not only include the storage capability

of the adsorbent but also the facility of use and the cost of manufacturing.

The most important evaluation of an adsorbed natural gas (ANG) storage systems performance is the measurement of the volume of usable gas [4]. This is frequently called *delivery*, and it is defined as the volume of gas obtained from the storage vessel when the pressure is reduced from the storage pressure of 35 to 1 bar, at room temperature [4]. The delivery of gas from an activated carbon depends mainly on the micropore volume, the micropore size distribution and the packing density of the activated carbon [1–5]. In this application, where the storage volume available is a constraint, increasing the packing density of the adsorbent in order to increase the ANG energy density is very important. Due to the enormous importance of the packing density of the activated carbons for this application, one of the main objectives in this research area is to minimize the useless voids (meso, macro and interparticle space), where methane adsorption

\*Corresponding author. Tel.: +34-965-903545; fax: +34-965-903454.

E-mail address: [linares@ua.es](mailto:linares@ua.es) (A. Linares-Solano).

does not take place, while maintaining a high micropore volume. In the case of mainly microporous powder activated carbons, which do not present macroporosity, as is the case for the activated carbons presented in our previous studies [5,6], this void consists mostly of space between the particles. By producing the carbon as a monolith it is possible to reduce that interparticle void, maximising the bulk density [1,7]. These monoliths consist of cylindrically-shaped pieces, which pack uniformly, lessening wasted space in the storage vessel. Another advantage of producing carbons in an efficient space-filling form is that they are also strong and resist attrition.

The monoliths can be produced using a binder, which helps to keep the carbon particles in a compressed state. Conventional preparation methods [7,8] consist of mixing the activated carbon with a binder, compression and moulding using a hydraulic press and, finally, pyrolysis to improve the binder properties and decrease the weight of binder in the monolith. For this specific application, methane storage, the binder must possess certain properties: (i) it must produce monoliths with good mechanical properties using the lowest binder/activated carbon ratio to achieve the maximum amount of activated carbon, which is the adsorbent material; (ii) its pyrolysis must not produce pore blocking of the activated carbon. This last characteristic of the binder is very important, because the current focus is to increase the packing density, while retaining a high micropore volume, which is responsible for the methane adsorption.

At the moment, most of the binders used for this purpose reduce the adsorption performance of the activated carbon because they block the microporosity. Thus, due to the important role of the binder in this application, one of the objectives of this work is to try to find a good binder for preparing good activated carbon monoliths for methane storage applications. To do that, the behaviour of different binders in the preparation of activated carbon monoliths has been studied. The effect of the type and amount of binder on the micropore volume, methane adsorption capacity, piece density and delivery has been analyzed. The activated carbon used for the preparation of these activated carbon monoliths was the one which was the best for methane storage applications in a previous work [5]. Another objective of this work is to make a preliminary kinetic study of the adsorption process.

## 2. Experimental

### 2.1. Activated carbon monolith preparation

For the preparation of activated carbon monoliths, a powder activated carbon has been chosen from a series of chemically activated carbons prepared using KOH as the activating agent and a Spanish anthracite as the raw material [5]. This activated carbon was selected because, among all the activated carbons prepared under different

conditions, it possesses the highest methane delivery. After preparing a large quantity of this activated carbon, different binders have been used for the preparation of the activated carbon monoliths: a humic acid-derived sodium salt (HAS) from Acros organics, polyvinyl alcohol (PVA), a novolac phenolic resin (PR) (Georgia Pacific 5506), a proprietary binder from Waterlink Sutcliffe Carbons (WSC), Teflon (TF) from Du Pont and an adhesive cellulose-based binder (ADH) (Saint Honoré). The selection of these binders was carried out on the basis of several criteria. Humic acid was selected because a previous study showed that it is a good binder for making activated carbon pellets [9]. Phenolic resin and PVA have been used for preparing activated carbon monoliths for methane storage applications [8,10]. In one of these studies [8], it was found that the optimum amount of phenolic resin for the preparation of activated carbon monoliths for methane storage was 40 wt%. On the other hand, PVA gave good results with as little as 4 wt% binder content [10]. Teflon [11] has the advantages of not needing the pyrolysis step for improving the binder properties.

A series of mixtures of each binder, with the activated carbon and water were prepared. The sequence of steps used for each binder and the percentage of binder has been chosen according to the results obtained in preliminary experiments done in our laboratory, in order to obtain monoliths with the most suitable porous texture and mechanical properties [12]. The amount of binder added was calculated to be 15 wt% of the final monolith. These calculations are based on the weight lost by each binder during the pyrolysis process. This was known from previous experiments carried out separately, using only the binder. The binder/activated carbon mixtures were dried to a powder and then pressed into 1.6-cm diameter and 0.7–1.5 cm height cylindrical pellets in a heated mould. The temperature of the mould was 135 °C for the HAS, PR and WSC binders, 200 °C for the PVA and Teflon binders, while in the case of the binder ADH, the mould was not heated. The pressed monoliths prepared with HAS, PR, and WSC were then pyrolyzed at 750 °C for 2 h in order to completely carbonize the binder. In the case of the ADH monoliths, the pieces were dried in an oven at 200 °C overnight.

### 2.2. Characterization of the activated carbon monoliths

Porous texture characterization of all the monoliths was carried out by the physical adsorption of gases ( $N_2$  at 77 K and  $CO_2$  at 273 K) using an automatic adsorption system (Autosorb-6, Quantachrome). The micropore volume has been calculated from the application of the Dubinin–Radushkevich (DR) equation to the  $N_2$  adsorption at 77 K up to  $P/P_0 \leq 0.1$ . The volume of narrow micropores (size smaller than 0.7 nm) has been assessed from  $CO_2$  adsorption at 273 K. The density measurements have been carried out using a pycnometer (Micromeritics Accupyc

1330). The values of piece density have been obtained by weighing and measuring the dimensions of each monolith.

Methane adsorption isotherms at 298 K and up to 4 MPa have been carried out in a DMT high-pressure microbalance. The experimental results have been corrected for buoyancy effects related to the displacement of gas by the sample, sample holder, adsorbed phase and pan [13].

The amount of methane delivered has been measured experimentally for each activated carbon monolith. To determine the delivered V/V, two or three pieces of the same kind of monolith have been used to fill a vessel of 5 cm<sup>3</sup>, which was then pressurized to 3.5 MPa and allowed to cool under that pressure to 298 K. The gas is then released over a time period sufficient to allow the bed temperature to return to 298 K. The amount of methane delivered was measured by water displacement. To ensure that the delivered gas only came from the carbon volume, the carbon in the vessel was replaced by aluminium rods of the same volume. This was then pressurized to 3.5 MPa and the volume of the gas delivered on release to atmospheric pressure measured. This volume of gas, which results from the dead space in the valve and ancillary tubing, was subtracted from the volume of methane delivered from the carbon filled vessel so that the true V/V delivered from only the carbon monolith could be obtained.

Finally, a kinetic study at 298 K of the methane adsorption up to 4 MPa was carried out in a DMT high-pressure microbalance (Sartorius 4406) connected to a computer. During the experiment, the methane pressure is kept constant and the weight change is saved as a function of time. The amount of sample used in these experiments is around 300 mg. The experimental results have been corrected in the same way as the high-pressure methane adsorption isotherms.

The evaluation of the mechanical properties of the

monoliths (maximum compression strength and strain) was carried out by compression test using a universal test machine (Instron 4411). The typical monolith dimensions were 1.6 cm diameter and approximately 1 cm height. The compression rate was 0.5 mm/min.

Finally, some of the monoliths prepared were studied by SEM (JEOL JSM-35C).

### 3. Results and discussion

#### 3.1. Effect of the type of binder on the monolith properties

For the preparation of monoliths, several binders were used. Some of the binders have been used in previous studies and some are new binders.

Fig. 1 presents the nitrogen adsorption isotherms corresponding to the starting powdered activated carbon (KUA31752), this activated carbon after heat treatment up to 750 °C (sample KUA31752HT; this sample has been prepared for the reason given below) and the activated carbon monoliths prepared using different binders. All the isotherms are Type I isotherms, characteristic of microporous solids, and they show a plateau isotherm reflecting a minimum presence of mesopores. Thus, it can be said that the preparation process of the monoliths does not produce mesoporosity. The main differences in the methane isotherms of the monoliths compared to that of the powder is in the low relative pressure range, which corresponds to the microporosity. In that figure, it can be seen that all the monoliths have a lower nitrogen adsorption capacity than the starting activated carbon. This is expected because they contain 15 wt% of binder which does not contribute to the adsorption capacity of the monolith. However, it can be seen that these monoliths do not behave as an ideal

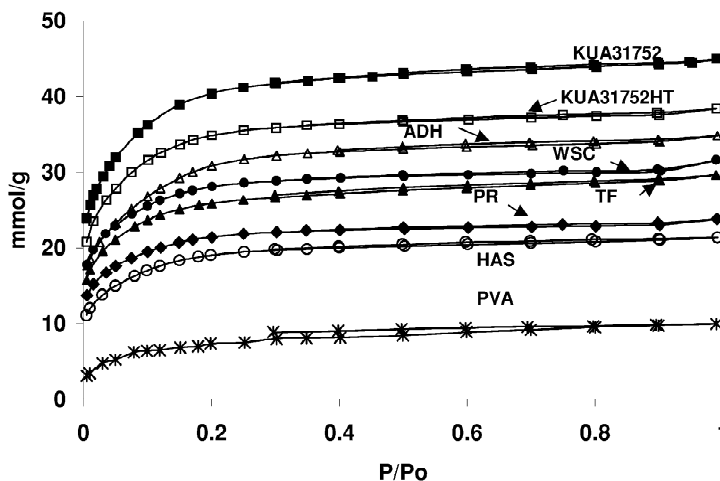


Fig. 1. Nitrogen adsorption isotherms at 77 K corresponding to the powdered activated carbons and the activated carbon monoliths prepared with different binders.

mixture, because the reduction in their adsorption capacity is higher than 15%. This fact can be due to the contribution of at least two factors. The first factor has to do with the binder, which may reduce the adsorption capacity of the monoliths due not only to the space that it occupies, but also because it can block the porosity. The second factor is related to the fact that the pyrolysis step, required for the preparation of some of the activated carbon monoliths, alters the micropore structure of the activated carbon used for the preparation of those monoliths.

To analyze the effect of the second factor, the starting activated carbon has been heat-treated up to the pyrolysis temperature of the monoliths (750 °C). As was previously mentioned, Fig. 1 also includes the nitrogen isotherm corresponding to this heat-treated activated carbon (KUA31752HT). It can be seen that the adsorption capacity decreases with respect to the starting activated carbon. However, this factor by itself does not explain completely the adsorption capacity reduction of the monoliths. Thus, the presence of binder must change the porous texture of the activated carbon, due to a blocking process. The N<sub>2</sub> adsorption isotherms suggest that the degree of micropore blocking is different for each binder as a consequence of their different behaviour in producing the monolith. The sequence in pore blocking seems to be PVA>HAS≥PR>TF≥WSC>ADH.

Table 1 presents the micropore volume calculated from N<sub>2</sub> and CO<sub>2</sub> data corresponding to the monoliths, the powdered activated carbon and the heat-treated powdered activated carbon. The micropore volume calculated from N<sub>2</sub> provides the total micropore volume, whereas the micropore volume calculated from CO<sub>2</sub> data corresponds to the narrow micropore volume (pore size<0.7 nm). The comparison of both gives us an idea of the micropore size distribution [14]. Thus, comparable volume values correspond to narrow micropore size distribution, while a higher difference ( $V_{N_2} > V_{CO_2}$ ) is related to a wider micropore size distribution. According to the  $V_{N_2}$  and  $V_{CO_2}$  values, it can be seen that, in general, the use of a binder produces

decreases in both total micropore volume and narrow micropore volume. It can also be observed that the reduction in the micropore volume calculated from CO<sub>2</sub> ( $V_{CO_2}$ ) presents the same sequence to that described above for the reduction in the nitrogen adsorption capacity (i.e. the highest reduction of  $V_{N_2}$  and  $V_{CO_2}$  corresponds to the PVA, and the lowest to the WSC and ADH). To analyze these trends more thoroughly, Table 1 also includes the percentage of  $V_{N_2}$  and  $V_{CO_2}$  with respect to the maximum micropore volume obtained if no pore blocking exists and considering that the binder does not contribute to the porosity. It can be observed that the monoliths which present the highest percentage are the WSC monoliths, indicating the lower pore blocking produced by this binder. It is shown that for the  $V_{CO_2}$  the percentage for these monoliths (WSC) exceeds 100%, which could be due to the fact that the binder does produce change in the micropore size distribution.

According to the micropore volumes and micropore size distribution, it seems that the best activated carbon monolith is the one prepared using the WSC and ADH binders. Before claiming the suitability of a particular binder, it should be said that the material density is very important for methane storage, as pointed out in an earlier study [5]. The piece density for all the activated carbon monoliths was calculated using the weight and the geometric volume. Table 2 includes the monolith density values and the packing density for the powder activated carbons. It can be observed that in all the cases, except for the monolith ADH, the monolith densities have considerably increased with respect to the packing density of the powdered activated carbon. It can be seen that, unfortunately, the monolith with the highest density (1 g/cm<sup>3</sup>) corresponds to the activated carbon monolith with the lowest nitrogen adsorption capacity (PVA). Then, it is expected that this monolith, even though it presents a high density, is not going to give good methane delivery results because of the low micropore volume. On the other hand, the phenolic resin, Teflon and WSC have a similar monolith density

Table 1

Porous texture characterization results for the powdered activated carbons and the activated carbon monoliths prepared with different binders

Sample	He density (g/cm <sup>3</sup> )	$V_{N_2}$ (cm <sup>3</sup> /g)	% of $V_{N_2}$ with respect to that expected <sup>a</sup>	$V_{CO_2}$ (cm <sup>3</sup> /g)	% of $V_{CO_2}$ with respect to that expected <sup>b</sup>
KUA31752	2.15	1.53	—	0.79	—
KUA31752HT	2.14	1.32	—	0.71	—
HAS	2.13	0.68	61	0.30	50
PVA	1.90	0.24	18	0.26	39
PR	2.10	0.80	71	0.48	80
WSC	2.14	1.07	95	0.63	105
TF	2.12	0.96	74	0.52	78
ADH	2.16	1.22	94	0.61	91

<sup>a</sup>  $V_{N_2}$  expected=(1.53×0.85) if the monoliths are not pyrolyzed;  $V_{N_2}$  expected=(1.32×0.85) if the monoliths are pyrolyzed.

<sup>b</sup>  $V_{CO_2}$  expected=(0.79×0.85) if the monoliths are not pyrolyzed;  $V_{CO_2}$  expected=(0.71×0.85) if the monoliths are pyrolyzed.

Table 2

Packing densities, monolith densities, experimental delivery values and compression test results corresponding to the activated carbons and activated carbon monoliths prepared with different binders

Sample	Monolith density (g/cm <sup>3</sup> )	Delivery (V/V)	Maximum compression strength (MPa)
KUA31752	0.51 <sup>a</sup>	145	—
KUA31752HT	0.51 <sup>a</sup>	—	—
HAS	0.64	85	0.15
PVA	1.00	29	>24
PR	0.56	107	9
WSC	0.58	126	22
TF	0.55	114	3
ADH	0.40	120	10

<sup>a</sup> Packing density of the powder samples.

(around 0.57 g/cm<sup>3</sup>) but different nitrogen adsorption capacity (Fig. 1).

Regarding methane adsorption capacities, it is known from previous studies [1,5,15] that a reasonably linear relationship exists between micropore volume and methane uptake. From an application point of view, the most important parameter for an ANG adsorbent is the delivery. Thus, in order to know which is the best binder for methane storage applications, experimental delivery measurements have been carried out for the monoliths prepared with each binder. Table 2 contains the experimental delivery values. As expected, the lowest delivery corresponds to the PVA monoliths due to their very low micropore volume per unit volume. The delivery result for the HAS monoliths is also poor. The delivery values for the rest of the monoliths is more related to the micropore volume and piece density. It should be remarked that the monolith ADH, even though it is the monolith with the highest micropore volume, it is not the one with the highest delivery due to its low piece density. The best delivery corresponds to the activated carbon monolith prepared using the WSC binder, which gave a delivery of 126 V/V. Teflon also produced a good monolith, which delivered 114 V/V.

In addition to the good adsorption/desorption properties of the activated carbon monoliths, another important characteristic is their mechanical properties. The storage vessel in a vehicle will be subjected to constant vibration, so a non-friable carbon is required for this application. Table 2 includes the results corresponding to the compression tests for each monolith. It can be observed that, except from the monoliths prepared with HAS and Teflon, the rest of the pieces prepared for this application have good mechanical properties. The best mechanical properties correspond to the monoliths prepared with PVA, which were not broken using the maximum load of the test machine (5 kN). It has to be remarked that the mechanical

properties of the monoliths prepared with WSC and ADH are also very good.

According to the methane adsorption capacity results (Table 2), the monoliths with the best properties for methane storage are those prepared using TF, WSC and ADH as binders, although the mechanical properties of the WSC and ADH are clearly much better than TF.

The activated carbon monoliths prepared with these three binders were observed using SEM and the pictures are shown in Fig. 2. As seen in these pictures, the more compact structure corresponds to the monolith prepared

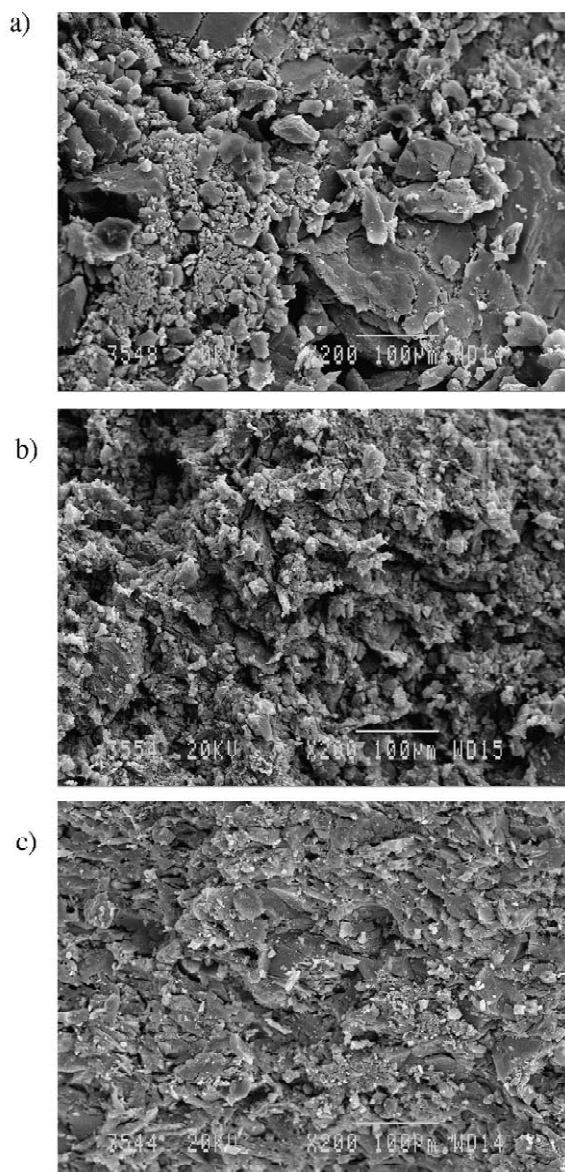


Fig. 2. SEM pictures of three activated carbon monoliths (a) TF, (b) ADH, (c) WSC.

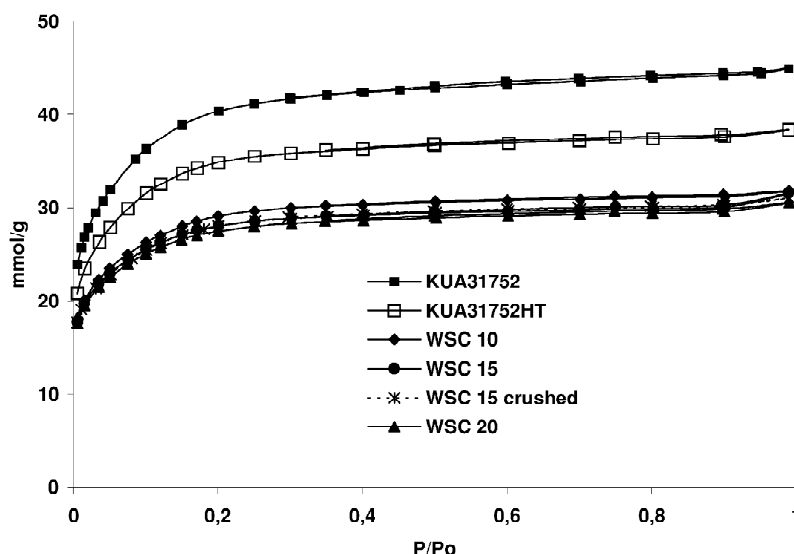


Fig. 3. Nitrogen adsorption isotherms at 77 K corresponding to the powdered activated carbons and the activated carbon monoliths prepared with different amounts of WSC binder.

with the binder WSC (Fig. 2c), in agreement with its best mechanical properties. On the other hand, the monolith prepared with TF has a more open structure (Fig. 2a), in which the voids between the particles can be observed. As in the mechanical properties, the binder ADH (Fig. 2b) is an intermediate case between the two other samples.

### 3.2. Effect of the percentage of binder

According to both the delivery and the mechanical properties, the best binder for the preparation of activated carbon monoliths from this activated carbon precursor seems to be the WSC. In order to know how both delivery and mechanical properties are affected by the amount of binder, activated carbon monoliths with a different percentage of this binder (WSC) (10, 15 and 20 wt% at the end of the preparation) were prepared.

Fig. 3 shows the nitrogen adsorption isotherms corresponding to the powdered activated carbon, the heat-treated activated carbon and the monoliths made with different amounts of WSC binder. It can be seen that the change in the adsorption capacity with the amount of binder is not very important.

Table 3 contains the helium density and micropore volume obtained from  $N_2$  ( $V_{N_2}$ ) and  $CO_2$  ( $V_{CO_2}$ ) adsorption data. Looking at the micropore volume values, it can be observed that an increase in the amount of binder produces a decrease in both  $V_{N_2}$  and  $V_{CO_2}$ .

In order to make sure that the monoliths presented in this study are homogeneous and the reduction of the adsorption capacity is not due to interparticle diffusional problems, the 15% WSC monolith has been crushed (WSC15 crushed) and porous texture characterization has been carried out. Fig. 3 presents the nitrogen isotherm corresponding to this sample. It can be observed that the nitrogen adsorption capacity is very similar in both cases, powder and monolith, indicating that the binder is homogeneously distributed throughout the monolith and it does not affect the gas transfer inside the pieces.

Fig. 4 shows the methane adsorption isotherms at 298 K and up to 4 MPa for these materials. It can be seen that a considerable reduction of the methane adsorption capacity of the monoliths exists with respect to the starting activated carbon and the heat-treated activated carbon. This behaviour is expected according to the results obtained from the  $N_2$  adsorption isotherms at 77 K.

Table 3

Porous texture characterization results, piece densities and delivery values corresponding to monoliths prepared with different percentages of binder WSC

Sample	He density (g/cm <sup>3</sup> )	$V_{N_2}$ (cm <sup>3</sup> /g)	$V_{CO_2}$ (cm <sup>3</sup> /g)	Monolith density (g/cm <sup>3</sup> )	Extrapolated delivery (V/V)	Experimental delivery (V/V)
WSC 10	2.16	1.11	0.67	0.53	124	123
WSC 15	2.14	1.07	0.63	0.58	129	126
WSC 20	2.11	1.04	0.61	0.58	127	118

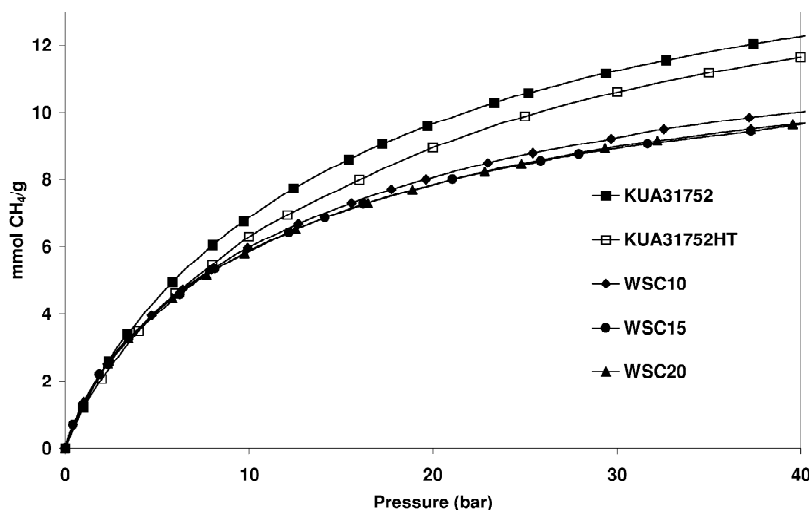


Fig. 4. Methane adsorption isotherms at 298 K corresponding to the powdered activated carbons and the activated carbon monoliths prepared with different amounts of WSC binder.

On the other hand, in Table 3 it can be observed that an increase in the amount of binder from 10 to 15 wt% produces an increase in the monolith density, which is very important for methane storage applications. The effect of the higher amount of binder is also apparent in the mechanical properties. In this sense, we could say that 10% of binder is close to the minimum amount of binder that can be used in the monoliths for them to remain as coherent pieces. However, in the case of the monoliths with 15% of binder, the mechanical properties are similar to those presented by the monoliths with 20%.

Those effects observed in piece densities and mechanical properties when the amount of binder is increased in a 5 wt% increment (from 10 to 15 wt%) are not the same as when we increase from 15 to 20 wt%. It can be seen (Table 3) that from 15 to 20 wt%, the monolith density remains almost constant. This suggests that a higher amount of binder seems not to be suitable for preparing activated carbon monoliths for methane storage.

As commented on before, the most important parameter for the adsorbents for this methane storage application is the delivery. From the methane adsorption isotherms and monolith densities, extrapolated delivery values can be obtained. These values are calculated as the difference between the amount of methane adsorbed per volume of sample at 3.5 MPa and atmospheric pressure. Moreover, this parameter has been measured experimentally using several pieces of the same sample to fill a 5 cm<sup>3</sup> vessel. Table 3 has the extrapolated and the experimental delivery values corresponding to those samples. It can be observed that both calculated and experimental values are very similar. According to the delivery results, the three activated carbon monoliths seem to have the same performance, because the lower piece density in the case of 10

wt% monolith is compensated by the higher methane adsorption capacity. However, if the mechanical properties are taken into account, the best amount of binder seems to be 15 wt%.

### 3.3. Kinetic study of the methane adsorption in activated carbon monoliths

From a practical point of view, e.g. when the tank is being filled up or when the vehicle's engine is demanding fuel, it is completely necessary that the adsorbent for ANG vehicles possesses a fast adsorption–desorption rate.

The use of activated carbons with extremely narrow micropores (samples where the micropore volume calculated from CO<sub>2</sub> data is higher than that calculated from N<sub>2</sub> data) points to a remarkable diffusion restriction [16,17]. Considering this fact and that very narrow pores also retain adsorbed methane at pressures down to 1 bar and cut down on the potential deliverable amount of methane, the adsorbents for ANG vehicles must have not only a high micropore volume but also a pore texture where extremely small pores are avoided. In general, highly-activated carbons with very high micropore volumes are used for this application. Due to the high porosity development, these types of material usually do not present kinetic problems, either on adsorption or desorption. However, when a binder is used to form a high density monolith, the pathway to access those micropores could be obstructed by the binder, leading to diffusional problems. In order to show that in the case of the activated carbon monoliths prepared in this study, the equilibrium is reached rapidly, Fig. 5 shows the curve corresponding to the methane adsorbed during the introduction of different methane pressures. The uptake in each step corresponds to one point

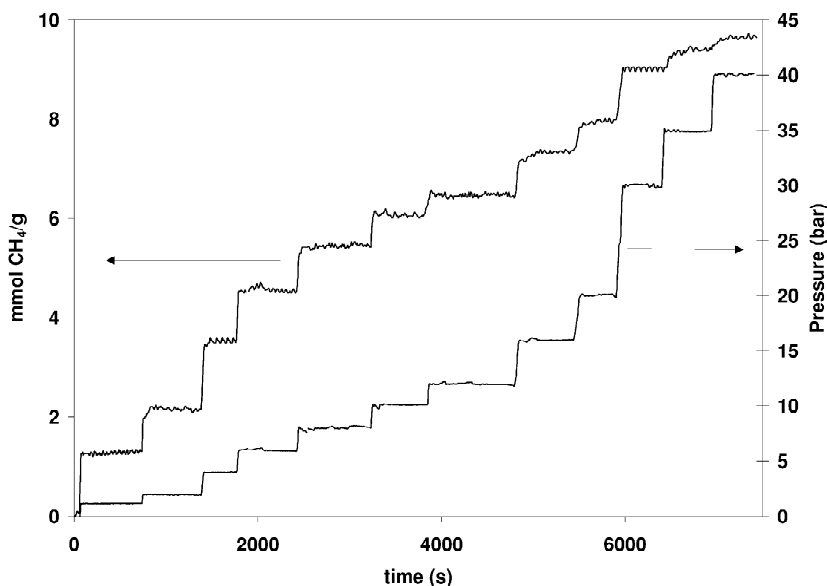


Fig. 5. Curves corresponding to the methane adsorbed and pressure during the introduction of different methane pressures in a methane adsorption isotherm.

in the methane adsorption isotherm for the monolith WSC15. It can be seen that an increase in pressure produces a rapid increase in uptake, up to the equilibrium value, indicating that no kinetic problems exist.

Another way to check that no diffusional problems exist in the monoliths is by obtaining the methane kinetic adsorption curves at 4 MPa and 298 K. Fig. 6 presents these curves for the powdered activated carbon (KUA31752) and the best monolith prepared for ANG

applications prepared in this study (WSC15). These curves have been referred to the amount of methane adsorbed in each case at equilibrium. It can be seen that both curves are very similar. This fact indicates that the monolith has no diffusional problems for methane adsorption when compared with the powder activated carbon. Fig. 6 also shows that after 120 s, which is approximately the time used for increasing the pressure from vacuum to 4 MPa, a constant value for methane uptake is reached. The fact that

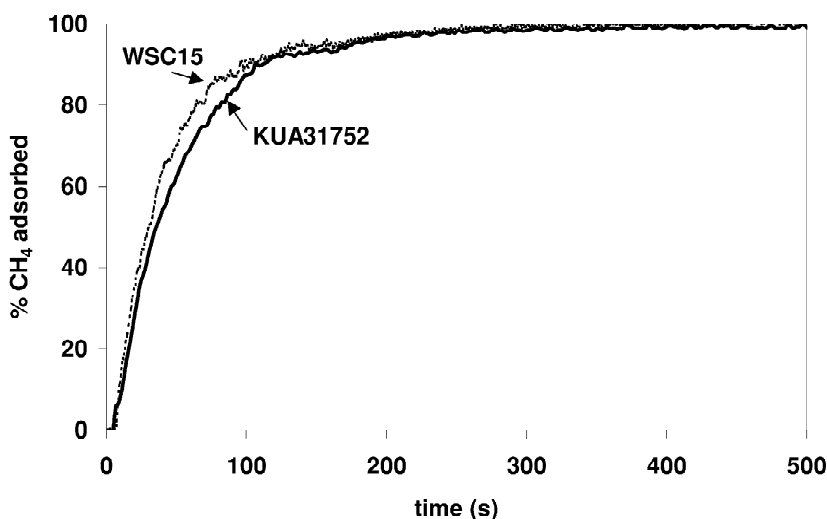


Fig. 6. Methane kinetic adsorption curves at 4 MPa and 298 K corresponding to the powdered activated carbon and the best monolith for ANG applications.



the samples adsorb methane at the same time as the pressure is increasing, again indicates that no kinetic problems exist.

From this preliminary kinetic study, it can be concluded that the monoliths do not present diffusional problems for the methane adsorption. However, it must be remarked that these experiments have been carried out in a high-pressure microbalance, where only around 300 mg of sample was used. Of course, the diffusional problems will depend on the monolith size, which is directly related to the distance that the gas must pass through in order to reach the activated carbon in the bulk of the monoliths. So, additional work using a different experimental set-up and larger monoliths should be carried out in order to corroborate these preliminary kinetic results.

#### 4. Conclusions

The study of the agglomeration with different types of binders of a high adsorption capacity powdered activated carbon suitable for methane storage has shown that most of the binders studied produce monoliths with good mechanical properties. However, the adsorption capacities of the activated carbon monoliths are reduced with respect to the starting activated carbon. This reduction is due to the reduction in the amount of activated carbon in the monolith and to a partial blocking of the porosity, which depends on the kind of binder used for the preparation of the monoliths. In terms of adsorption capacity, the best binder is the one which does not block the porosity or does it to the lowest degree. The pore texture characterization of the activated carbon monoliths prepared in this study has shown that, among all the binders studied, those which produce the least micropore blocking are PR, TF, ADH and WSC. Binding with PVA or the humic acid-derived sodium salt (HAS) result in monoliths with a considerably decreased adsorption capacity.

From an application point of view, it is known that not only the adsorption capacity is important, but also the monolith density is extremely important. According to our results, among all the binders studied, the one which produces monoliths with the best equilibrium between adsorption capacity and piece density, and consequently with the best delivery is the binder from WSC.

In this study, the important effect of the percentage of WSC binder in piece density and mechanical properties has been shown. It is concluded that in this case, the optimum amount of binder is 15%, which allows the preparation of monoliths with a remarkably high methane delivery value (considering that it is a monolith) of 126 V/V. Finally, a preliminary study has shown that activated carbon monoliths do not present diffusional problems for the adsorption of methane.

#### Acknowledgements

The authors wish to thank Dr A.T. Ryan of Waterlink Sutcliffe Carbons for providing their proprietary binder for use in this work. The authors also thank MCYT (Projects MAT 2000-0621 and AMB1999-1595-CE) for financial support. D. Lozano-Castelló thanks MEC for thesis grant.

#### References

- [1] Parkyn ND, Quinn DF. Natural gas adsorbed on carbon. In: Patrick JW, editor, Porosity in carbons, Edward Arnold, 1995, pp. 293–325.
- [2] Menon VC, Komarneni S. *J Porous Mater* 1998;5:43–58.
- [3] Cook TL, Komodromos C, Quinn DF, Ragan S. In: Burchell TD, editor, Carbon materials for advanced technologies, New York: Elsevier Science, 1999, pp. 269–302.
- [4] Wegrzyn J, Wiesmann H, Lee T. Low pressure storage of natural gas on activated carbon. In: Post Conference Proceedings of the Annual Automotive Technology Development, Dearborn, USA, 1992, pp. 1–11.
- [5] Lozano-Castelló D, Cazorla-Amorós D, Linares-Solano A, Quinn DF. Influence of pore size distribution on methane storage at relatively low pressure: Preparation of activated carbon with optimum pore size. *Carbon* 2002;40:989–1002.
- [6] Lozano-Castelló D, Lillo-Ródenas MA, Cazorla-Amorós D, Linares-Solano A. Preparation of activated carbons from Spanish anthracite I Activation by KOH. *Carbon* 2001;39(5):741–9.
- [7] Quinn DF, MacDonald JA. Natural gas storage. *Carbon* 1992;30(7):1097–103.
- [8] Chen XS, McEnaney B. Methane capacities of microporous carbons. In: European Carbon Conference Carbon, Newcastle, UK, 1996, pp. 576–7.
- [9] García-García Avelina. Ph.D. Thesis. Universidad de Alicante, 1997.
- [10] Bose TT. US Patent 004999330.
- [11] Teflon® PTFE 30, Du Pont. Product Information.
- [12] Lozano-Castelló D. Ph.D. Thesis. Universidad de Alicante, 2001.
- [13] Agarwal RK, Schwarz JA. Analysis of high pressure adsorption of gases on activated carbon by potential theory. *Carbon* 1988;26(6):873–87.
- [14] Rodríguez-Reinoso F, Linares-Solano A. Microporous structure of activated carbons as revealed by adsorption methods. In: Thrower PA, editor, Chemistry and physics of carbon, vol. 21, New York: Marcel Dekker, 1988, pp. 1–146.
- [15] Alcaniz-Monge J, De la Casa-Lillo MA, Cazorla-Amorós D, Linares-Solano A. Methane storage in activated carbon fibers. *Carbon* 1997;35(2):291–7.
- [16] Cazorla Amorós D, Alcañiz Monge J, Linares Solano A. Characterization of activated carbon fibers by CO<sub>2</sub> adsorption. *Langmuir* 1996;12(11):2820–4.
- [17] Cazorla Amorós D, Alcañiz Monge J, De la Casa Lillo MA, Linares Solano A. CO<sub>2</sub> as an adsorptive to characterize carbon molecular sieves and activated carbons. *Langmuir* 1998;14(16):4589–96.