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**Research Paper** 

# Effect of Pore Size Distribution on Methane Storage at Low Pressure: Preparation of Activated Carbon for ANG Storage

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Abstract- Natural gas is used as fuel for automobiles due to its high calorific value and relatively clean burning fuel compared to gasoline. It can be stored by liquefaction and compression. For transportation fuel, liquefaction is impractical and requires high pressures (20MPa) and an expensive multistage compression facility. Adsorbed Natural Gas (ANG) method can be used to store natural gas at relatively low pressure (3-4 MPa) that can be achievable by single stage compression. Activated carbons prepared from cocummut shell and activated by KOH were studied for methane storage application. The effect of different variables of the activation process (KOH/carbon ratio, pyrolysis temperature and time) on methane storage and delivery was analysed. In addition to the well known effect of the micropore volume and packing densityuy, spetial attention was paid to the effect of the micropore size distributyion has in methane storage performance. It wa shown that this parameter is also a key parameter in the application of activated carbon for methane storage application. Activated carbon prepared from a cheap raw material and using a single stage activation process has reached very high methane storage (150v/v). The experimental data were analysed usinh Toth model and data were fitted well with the model.

Key words: Adsorbed Natural Gas (ANG), Activated Carbon, Adsorption, Micro porosity, Pore size distribution etc.

### Introduction

Natural gas is the major clean fuel before hydrogen fuel becomes commercially available<sup>[1]</sup>. The use of natural gas as an automotive fuel presents recognized advantages. Those advantages include reduced vehicle emission, lower maintenance and savings in fuel cost over gasoline. However, its low volumetric energy density at ambient temperature (1L of natural gas will yield 0.04MJ on combustion, while 1L of natural gasoline will yield 34.8MJ0makes its unattractive as a transportation fuel due to limited driving range .one way to make it suitable for vehicular application is to store an adequate amount of it in the on board fuel tank<sup>[2]</sup>.

Due to the lower critical Temperature of  $CH_4$  (191K), this gas can not be liquefied by pressure alone at room temperature. Compressed Natural Gas (CNG) is an alternative solution that is used worldwide (there are more than a million CNG vehicles in use). However, CNG requires a high pressure resistance cylindrical vessel that is generally difficult to integrate within a limited space and CNG cylinders are high cost.

Adsorbed Natural Gas (ANG) system can be an alternative that overcome the above mentioned problems. To make ANG storage system competitive with CNG storage

system, the natural gas was stored in relatively low pressure (35 to 40 bar). In this application the ultimate requirement is to maximize the gas storage density in order to store maximum volume of gas per volume of storage vessel (v/v) Thus after various studies<sup>[3,4,5,6,and7]</sup> it has concluded

Thus after various studies<sup>[3,4,5,6,and7]</sup> it has concluded that the requirement for an ANG adsorbent are (i) High adsorption capacity ,(ii) A predominantly micro porous adsorbent in order to maximize the deliverability at ambient pressure, (iii) High adsorption and desertion rates,(iv) It should be in expensive to the end user, (v) It has to be extremely hydrophobic. In general, micro porosity in carbons is created by removal of the carbon atom by activation process. However after the evolution of micro porosity to a certain optimum degree, further activation to increase the micro porosity is accompanied with mesopore and macropore evolution. For methane storage application, the ideal carbon would be a carbon with optimum combination of micropore volume, pore size distribution and surface area. To attain the above condition, the activated carbon must be carefully prepared.

Thus in this study, the effect of different variables of the activation process (KOH/carbon ratio, pyrolysis

temperature and time) was studied on activated carbon and storage capacity was calculated. The effect of micropore size distribution and surface area on storage capacity was analyzed and the experimental results were analyzed with Toth model.

## Material and Methods

#### Preparation of Activated Carbon and Characterization

A series of activated carbon were prepared from a locally available coconut shell using KOH as an activating agent. The precursor was grounded and sieved to a particle size range of 300 micron and mixed with the minimum amount of saturated KOH solution required to prepare a paste. After that, required volume of KOH solution was added according to the KOH/carbon ratio studied (2/1, 3/1, 4/1 and 5/1). The resulting mixture was pyrolysed with different temperature range (600-900°C) and time (1-3h) combinations. After initial water washing, the pyrolysed samples were washed repeatedly with water, then with a 5M solution of HCl to remove the activating agent and later with distilled water again to remove chloride ions.

The nomenclature of each sample includes the carbon name (CS), activating agent (K), the KOH/carbon ratio (ie, 3/1 would be 31), the pyrolysis temperature (for example, 600°C would corresponds to 60) and the pyrolysis time in hours. Thus for an activated carbon prepared with a KOH/carbon ration of 3/1 and which was pyrolysed at 800°C for 3h, the nomenclature would be CSK31803.]

Porous texture characteristics of all samples were carried out by physical adsorption of gases (N<sub>2</sub> at 77K and CO<sub>2</sub> at 273 K) using an automatic adsorption system. The micropore volume and surface are were calculated from the application of BET method to the N<sub>2</sub> adsorption at 77K. The relative pressure range of P/P<sub>0</sub>  $\leq$ 0.33 was used for the calculation of pore size distribution from the N<sub>2</sub> adsorption data by applying Horvoth-Kowazoe method. The adsorbate investigated was methane with purity of 99.9%.

#### **Experimental setup and Procedure**

The experimental apparatus used a static volumetric method. A schematic diagram of it is shown in Figure 1 The apparatus was constructed with stainless steel tubes and valves. A loading cell volume of 1100cm<sup>3</sup> and an adsorption cell volume of 210cm<sup>3</sup> were used. Pressure measurements were made using two pressure transducers and which is connected with computer through data logger. Vacuum pump was used to remove any gases present in the pipeline.

The adsorbate was introduced in to the loading cell till the pressure was stabilized. Then the adsorption step was carried out. The adsorption equilibrium state was considered to have been achieving when the pressure of the system was constant. This usually occurred with in 30 to 40 min and we have measured the equilibrium pressure after the initial adsorption. Equilibrium experiments were carried out for all activated carbons at room temperature and pressure up to 35 bar.

#### **Results and Discussion**

In order to produce the activated carbon with best volumetric methane storage capacity, a study of three more important variables was carried out. According to their importance, the study of these three variables was developed following a Sequential order. First of all, the effect of KOH/carbon ratio was studied to find the best activated carbon prepared using different KOH/carbon ratio with best equilibrium between micropore volume and surface area, i.e the carbon with the highest volumetric adsorption capacity. Later keeping constant the KOH/carbon ratio chosen in the previous step, the effect of the pyrolysis temperature is presented. The lost variable studied will be the pyrolysis time.

#### Effect of KOH/carbon ratio

Fig 2 presents the  $N_2$  adsorption isotherms corresponding to the activated carbon prepared using different KOH/carbon ratios. All the samples shows type-I isotherm according to the IUPAC classification <sup>[8]</sup> characteristics of microporous solids. The minimal slope of the isotherms indicates that the activated carbons are essentially micoroporous solids. It can be seen that from 2/1 to 5/1 ratio the high ratio the higher the nitrogen adsorption capacity. However, for the 5/1 ratio the nitrogen adsorption capacity decreases due to the more aggressive activated condition. Table 1 contains the BET surface area and the micropore volume calculated from  $N_2$  adsorption.

Another way to observe the isotherm adsorption data is to calculate the pore size distribution from the adsorption isotherm applying a model. Fig 3 presents the pore size distribution obtained for these samples applying Horvath-Kawazoe equation to the  $N_2$  adsorption data. It is shown that sample with the narrowest pore size distribution is the sample prepared with a KOH/carbon ratio 2/1 and 3/1. In addition, it can be observed that the higher the KOH/carbon ratio widens the pore size distribution and corresponds to the higher mean pore size.

It has been noted that the volumetric methane adsorption capacities reached with most of these samples are very high, being one of the highest published values up to now <sup>[2]</sup>. It can seen that, even though the sample with the highest methane adsorption capacity on volumetric basis was the sample with a 4/1 ratio (Fig 4), the highest volumetric methane delivery was obtained with a 3/1 ratio, due to the sample having a higher packing density and narrow pore size distribution. Table 1 contains the delivery values corresponding to the activated carbon prepared using different KOH/carbon ratios.

Fig 4 presents the methane adsorption isotherm on a volumetric basis for each activated carbon. It is shown that the highest methane adsorption capacity corresponds to the sample with the highest micropore volume (CSK41701) (see table1). However the main point that we would like to remark on this graph is the effect of the micropore size distribution on the methane adsorption capacity.Table1 shows that the micropore volume for the 5/1 sample is higher than the micropore volume corresponding to the 3/1.

However in Fig 4, it can be observed that methane adsorption for the 5/1 lower. This is due to the widen micropore size distribution for this sample as it was previously shown in Fig 3. These results show the importance of both micropore volume and micropore size distribution on methane uptake.

#### **Effect of Pyrolysis Temperature**

For methane storage using this raw material, the best KOH/carbon ratio for the preparation of activated carbon at 700°C seems to be 3/1. The effect of pyrolysis temperature

was studied (from 600 to 900°C) using this constant KOH/carbon ratio (3/1) and the same soaking time (1h).

Fig. 5 presents the methane adsorption isotherms (on a volumetric basis) corresponding to those samples prepared at different pyrolysis temperature. As expected considering the micropore volumes, the samples prepared from 600 to 800°C show an increase in the methane uptake with the pyrolysis temperature.

This increase is progressive for the three lower temperatures (methane uptakes are 130,150,155v/v at 35 bar, for the samples prepared at 600,700 and 800 °C respectively). The samples prepared at 900 °C have lowest methane adsorption capacity (120v/v). Which may be due to the lower micropore volume and low surface area as shown in Table 2 due to the presence of mesopores and a much lower micropore volume this sample does not present the suitable pore structure required for good methane adsorption capacity. The results show that the optimum pyrolysis temperature was 700 °C.

#### **Effect of Soaking Time**

Once the KOH/carbon ratio (3/1) and pyrolysis temperature (700°C) were selected. The effect of the pyrolysis time must be studied. Fig.6 shows that the methane adsorption capacity for the three samples is very similar. From these results it can be said that the effect of the soaking time at this pyrolysis temperature (700°C) is not so important and that 1h of pyrolysis would be enough for the preparation of good activated carbon.

#### **Kinetic Model**

To correlate the experimental equilibrium data Toth model have been used. The Toth model is commonly used for heterogeneous adsorbents such as activated carbon<sup>[7]</sup> because of its correct behavior at both low and high pressure range. The Toth equation can be represented by equation 1.

$$N = \frac{mP}{(b + P^{-t})^{\frac{1}{t}}} -1$$

Where N is the amount adsorbed, m is the saturated amount adsorbed, P is the equilibrium pressure, b is the equilibrium constant and t is the parameter that indicates the heterogeneity of the adsorbent. The methane adsorption equilibrium data at various temperatures were fitted with the Toth model and shown in Fig. 7 and the relevant parameters of the Toth equation are listed in table 3.

The solid line in Fig.7 denotes the adsorption isotherms plotted according to the Toth equation. The Toth equation provided the best fit to the experimental adsorption isotherms of methane. The parameters obtained from the Toth equation were well matched with the data reported in literature [7].

#### Conclusion

KOH activation of a carbon produced from coconut shell produces highly microporous structures that are especially good for methane storage application. In fact, controlling certain preparation variables, it was possible to obtain an activated carbon (ie.CSK31701) that has one of the highest methane uptakes and delivery reported in the literature using powdered samples. This work has shown the importance of micropore size distribution on the methane adsorption capacity. It was seen that a sample with a higher micropore volume but a much wider micropore size distribution presents a lower methane uptake than a sample with a lower micropore volume, where a large proportion of pores have the optimum size for the methane adsorption. Thus with these results it was concluded that the methane adsorption capacity not only depends on micropore volume but also strongly depends on the micropore size distribution.

Thus it was seen that the best activated carbon for ANG storage system is one with a medium degree of activation, which possess the best equilibrium between micropore volume and size distribution. The best condition for preparing an activated carbon for this application from the chief raw material used in this study seem to be KOH/carbon ratio(3/1), a medium pyrolysis temperature(700°) with a 1h soaking time and also the results are well fitted with Toth model.

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#### Particle BET surface Packing Pore volume Pore size range CH<sub>4</sub> uptake CH<sub>4</sub> delivery Sample size range area density $(cm^3/g)$ (nm) (v/v)(v/v) $(m^2/g)$ $(g/cm^3)$ (µm) 541 0.3254 1.2-2.3 CSK21701 25-100 0.286 138 126 CSK31701 25-100 750 1.6-2.6 0.5355 0.295 150 135 CSK41701 25-100 1050 0.7722 0.276 1.2-4.8 154 130 991 0.8-4.9 CSK51701 25-100 0.6781 0.281 135 124

# Table 1: Porous texture characterization results, densities and calculated methane uptake and deliveries for the activated carbons prepared with different KOH/carbon ratio (pyrolysis at 700°C for 1h)

# Table 2: Porous texture characterization results, densities and calculated methane uptake and deliveries for the activated carbons prepared with different temperature (KOH/carbon=3/1 at 1h)

Sample	Particle size range (µm)	BET surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	CH <sub>4</sub> uptake (v/v)	CH <sub>4</sub> delivery (v/v)
CSK31601	25-100	742	0.321	130	115
CSK31701	25-100	750	0.295	150	135
CSK31801	25-100	890	0.271	152	132
CSK31901	25-100	650	0.331	120	102

### Table 3: Parameters of the Toth equation for Activated carbon at different temperature

Sample	Temperature (K)	m(mol/Kg)	b(bar)	t
CSK31601	600	12.47	14.9	2.668
CSK31701	700	45.69	80.49	1.461
CSK31801	800	23.48	33.64	0.5172
CSK31901	900	11.66	11.28	1.776



# Figure 1: Experimental set up for Methane adsorption

- 1. Loading cell
- 2. Adsorption cell
- 5. Vacuum pump

V1, V2, V3, and V4- Valves.3& 4. Pressure transducers6. Methane cylinder



Figure 2: Nitrogen adsorption isotherms (77K) corresponding to the activated carbons prepared using different KOH/carbon ratio (pyrolysis at 700°C for 1h)



Figure 3: Pore size distribution obtained applying the Horvath-Kawazoe equation to the  $N_2$  adsorption data.



Figure 4: Methane adsorption isotherms (298K) for the activated carbons prepared using different KOH/carbon ratio (pyrolysis at 700°C for 1h)



Figure 5: Methane adsorption isotherms (298K) for the activated carbons prepared at different temperatures (KOH/carbon 3/1 for 1h)



Figure 6: Methane adsorption isotherms (298K) for the activated carbons prepared at different time interval (KOH/carbon 3/1 at 700°C)



Figure 7: Methane adsorption isotherms of activated carbon prepared at different temperatures fitted to Toth model (●CSK3180, +CSK31701,■ CSK31601, ○ CSK31901)