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Adsorption of methane in activated carbons obtained from coconut shells using H_3PO_4 chemical activation

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Abstract Activated carbon samples from coconut shells (Brazilian coconut species "Coco da Baía") were prepared by chemical activation with phosphoric acid as the activating agent. Samples were characterized by nitrogen adsorption isotherms at 77 K. Some samples were randomly chosen in order to perform methane adsorption experiments under pressures between 1 and 60 bar at 303 K. A close relationship between surface area, micropore volume and methane adsorption capacity for carbons prepared from the same starting material was observed. The highest methane storage capacity in the tested samples was found to be 95 v/v at 303 K and 35 bar, which is comparable to results obtained for commercial samples indicated for this application. A moderate concentration of phosphoric acid (around 35%) seems to favor high surface areas, micropore volumes and, hence, gas storage capacity. The inclusion of an acid wash step before carbonization and the use of inert gas flow during carbonization also seem to enhance the development of porosity. This result suggests that activated carbons prepared from "Coco da Baía" by chemical activation with phosphoric acid have potential to be used as a storage media for natural gas.

Keywords Chemical activation · N_2 isotherms · Carbon · Adsorption · Gravimetric measurements · Methane

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1 Introduction

Natural gas (NG) is a non-renewable natural resource still available in great amounts and sub-utilized in its energetic potential. NG has about 90% of methane, it is cheap and has a relatively clean combustion when compared to other fossil fuels such as gasoline and diesel. However, it has a major drawback as fuel: the high transportation costs due to the difficulty of achieving high energy densities in appropriate containers.

The adsorption of natural gas in porous materials, in which case the gas may be stored (ANG) under moderate pressures (between 3.5 and 4.0 MPa), has been studied as an alternative for its storage and transport (Parkyns et al. 1995; Sun et al. 1996; Lozano-Castelló et al. 2002a, 2002b; Azevedo et al. 2007; Bastos-Neto et al. 2005; Walton et al. 2005; Zhang et al. 2008; Prauchner and Rodriguez-Reinoso 2008). According to Cook et al. (1999), activated carbon (AC) is the most adequate material for NG storage systems due to its textural properties—such as surface area and micropore volume—which may be tailored according to a given adsorbate, besides being hydrophobic and having high affinity for organic substances.

There are essentially two activation methods to prepare activated carbons: physical and chemical. They can be used separately or in combination with one another. The physical method comprises carbonization and activation of the precursor (usually a lignocellulosic material) under a given fluid flow at high temperatures. The most commonly used fluids in physical activation are water vapor (steam) and carbon dioxide. In the chemical activation, the raw material is impregnated with a chemical agent such as $ZnCl_2$, H_3PO_4, KOH and NaOH. After that, the precursor is heated to 450–800 °C, very often under an inert atmosphere. The activation agents induce important changes in the pyrolytic decomposition of the lignocellulosic materials, since they promote dehydration and depolymerization of constituent biopolymers, favoring the conversion of aliphatic to aromatic compounds at lower temperatures (Gómez-Serrano et al. 2005).

This study presents results of synthesis, characterization and methane adsorption isotherms for activated carbons with textural properties potentially adequate for NG storage purposes. The activated carbon samples have been prepared by chemical activation of coconut shells using H_3PO_4 under different experimental procedures. The effects of textural characteristics (surface area and micropore volume) and synthesis procedure on the methane adsorption capacity have been analyzed.

2 Experimental

2.1 Sample preparation

The samples were prepared by chemical activation with phosphoric acid as activating agent. Initially, the precursor (coconut shells) was crushed into powder form and sieved to get a uniform particle size (average size of 2.38 mm). Part of this material was washed with a 10% (weight) sulfuric acid solution for 2 h and then the material was washed with distilled water so as to ensure total removal of acid (by pH check). The other part was washed only with distilled water. The samples were dried at 100 °C for 2 hours. Impregnation was carried out at 85 °C for 2 h with phosphoric acid solutions at increasing concentrations (29, 36, 44 and 53% w/w). The ratio between raw material (g) and phosphoric acid (mL) was 1:2 (Molina-Sabio et al. 2003). After impregnation, the samples were carbonized (under air atmosphere) at 450 °C (heating rate of 1 °C/min) for 2 h. For one of the samples, the carbonization process was carried out under nitrogen flow (500 mL/min). After carbonization, the samples were washed with distilled water up to pH 6 in order to thoroughly remove the remaining phosphoric acid. Finally, the samples were dried at 100 °C (heating rate of 1 °C/min) for 2 h.

2.2 Characterization

Nitrogen adsorption isotherms at 77 K were measured for the prepared AC samples using an Autosorb-1 MP apparatus (Quantachrome, U.S.A.). Specific surface areas were determined according to the BET method and micropore volumes were estimated using the Dubinin-Radushkevich (DR) equation (Rouquerol et al. 1999). The total pore volume was calculated as the adsorbed volume at $P/P_0 \approx 1$, assuming that the pores are totally filled with liquid adsorbate. The average pore width was determined from Eq. 1. This method considers that the activated carbon contained only slit-shaped graphitic pores.

$$w_P = 2 \cdot \frac{V_P}{a_{BET}} \cdot 10^4 \tag{1}$$

where: w_P = Average pore width (Å); V_P = Total pore volume (cm^3/g); a_{BET} = Specific surface area (m^2/g).

The pore size distribution was evaluated by the Density Functional Theory (DFT) together with Monte Carlo simulation method as available at the Quantachrome's software (Vishnyakov and Ravikovitch 2000; Ravikovitch et al. 1998; Lastoskie et al. 1997).

2.3 Methane adsorption isotherms

Six of the synthesized materials and two commercial AC samples (C1: Ultraporus, from FBC, Brazil; C2: MV07, from Multivacuo, Brazil) were chosen in order to perform methane adsorption experiments in a gravimetric equipment using a magnetic suspension coupling (Rubotherm, Germany), see Fig. 1.

The activated carbon sample is degassed *in situ* at 100 °C until no mass variation in the system is observed. After that, the experiment temperature (303 K) is set and methane pressure is increased stepwise (0.01 until approximately 6 MPa) inside the measuring chamber. Mass variations at equilibrium (Δm) are recorded for each pressure step. For each sample, an experiment with helium (non-adsorbed) is carried out in order to determine the specific volume of the solid phase and hence account for the buoyancy effects on measurements with adsorbing gases, such as methane. Likewise, an experiment with no sample and helium (or any gas of known equation of state) must be performed—blank experiment—in order to account for the buoyancy effects on the equipment parts inside the measuring chamber. Further experimental details may be found elsewhere (Bastos-Neto 2005).

The adsorbed excess mass of methane may be calculated from Eq. 2.

$$m_{ex}(P,T) = \Delta m(P,T) + (\bar{V}_b + \bar{V}_s) \cdot \rho(P,T) \tag{2}$$

where: Δm = Mass variation at equilibrium detected by the equipment per unit mass of the sample (g/g sample); $\bar{V}_b$ = Specific volume of balance components inside the measuring chamber (cm^3/g sample), as calculated from blank experiment; $\bar{V}_s$ = Specific volume of the solid phase (adsorbent) of the sample (cm^3/g sample), as calculated from helium experiment; ρ = Methane density (g/cm^3); P = Pressure (bar); T = Temperature (K).

The specific stored mass (m_{arm}) may be calculated from Eq. 3 and takes into account both the excess adsorbed gas

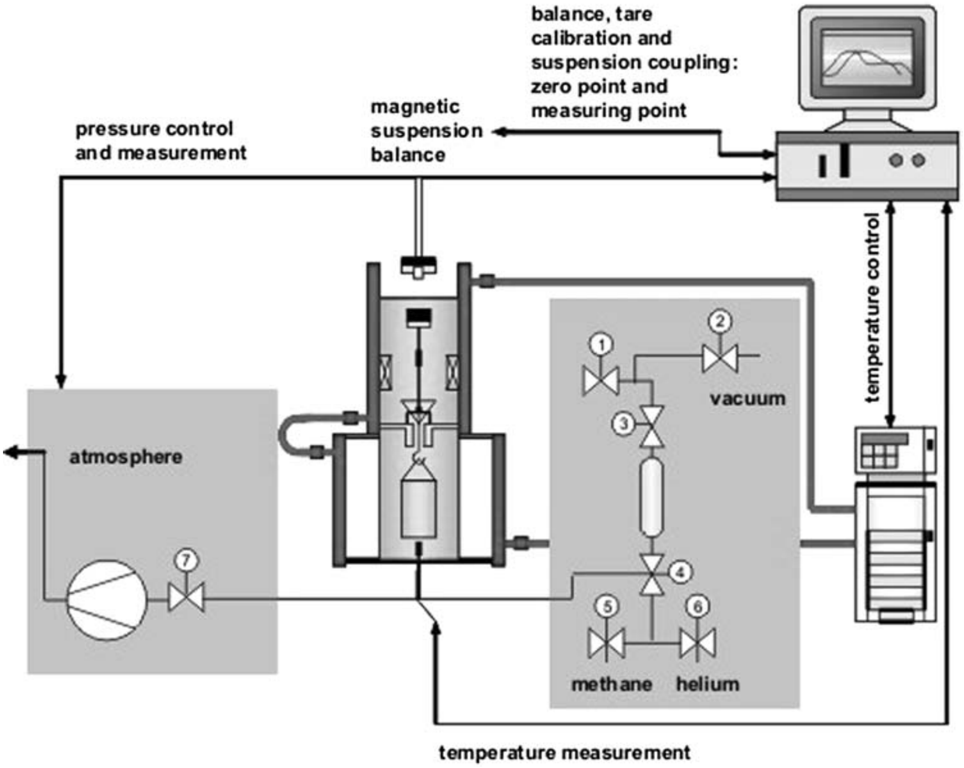


Fig. 1 Experimental setup of the gravimetric equipment for adsorption isotherm measurements at high pressures

and the gas that is compressed in the voids of the GN storage vessel (including AC pores and interparticular voids).

$$m_{arm}(p,T) = m_{ex}(p,T) + \left(\frac{1}{\rho_b} - \overline{V}_s\right) \cdot \rho(p,T) \tag{3}$$

where: ρ_b = Packing density (g sample/cm^3 bed).

The packing density (ρ_b) of the materials was calculated from the mass of regenerated AC sample necessary to fill a calibrated cylinder (100 mL), using loose packing.

Another way to quantify the stored gas capacity in a reservoir is to express it in terms of volume of stored gas in standard conditions, per vessel volume (v/v), as expressed in Eq. 4:

$$V_{arm}(p,T) = \frac{R \cdot T_0}{M \cdot p_0} \cdot m_{arm}(p,T) \cdot \rho_b \tag{4}$$

where: M = Molar mass of methane (16.04 g/mol); ρ_b = Packing density (g sample/cm^3 bed); T_o = 293.15 K; p_o = 1 bar (standard conditions); R = Ideal gas constant (83.14 bar·cm^3·mol^{-1}·K^{-1}).

3 Results and discussion

The activated carbon samples were prepared (average size 0.9 mm) and labeled as PAC-W1/W2-N, where: PAC = Phosphoric Acid Concentration (% w/w); W1 = Wash of the precursor only with distilled water; W2 = Wash of the precursor with sulfuric acid and distilled water; N = Carbonization under nitrogen flow.

The textural parameters measured for the synthesized samples and for two commercial reference samples (C1 and C2) are summarized in Table 1. These values evidence the effect of the previous treatment of the precursor with sulfuric acid on the characteristics of the resulting materials. It was observed that the total pore volume increases in all samples whose precursor material was washed with sulfuric acid. This can be explained by the meso and macroporosity from lignocellulosic materials that originally reflect the botanic texture of the precursor (Molina-Sabio and Rodríguez-Reinoso 2004). The sulfuric acid degrades and redistributes the raw material biopolymers, triggering even more the development of meso and macropores. In this new structure, the phosphoric acid may act more efficiently to form micropores during the chemical activation. The only exception to this finding was the sample activated with 53% w/w phosphoric acid, for which specific surface area and micropore volume decreased 10% after treatment with H_2SO_4. Total pore volume was about the same regardless the procedure. This leads us to think that the pre-treatment of lignocellulosic material with acid may be advantageous only for low to moderate concentrations of the chemical activation agent. Among the samples of the W2 series—those prewashed with sulfuric acid—best textural properties were obtained for the sample activated with 36% phosphoric acid.

Table 1 Textural parameters of AC samples prepared in this work and two reference samples (C1 and C2). Packing density was only determined for those samples to be tested for methane adsorption

Sample	BET surface area (m^2/g)	Total pore volume (cm^3/g)	Micropore volume (cm^3/g)	Average pore width (Å)	Micro porosity (%)	Packing density (g/cm^3)
29-W1	520	0.34	0.30	13.0	88.5	0.32
29-W2	727	0.42	0.38	11.6	91.4	–
36-W1	783	0.49	0.43	12.4	87.7	–
36-W2	844	0.55	0.50	13.1	90.8	0.45
44-W1	536	0.37	0.32	13.7	88.0	–
44-W2	767	0.51	0.44	13.2	87.1	0.33
53-W1	779	0.50	0.44	12.9	87.7	0.35
53-W2	693	0.51	0.40	14.7	79.4	0.28
53-W2-N	1441	0.86	0.73	12.0	84.6	0.26
C1	828	0.55	0.44	13.3	80.5	0.32
C2	1906	1.24	0.98	13.0	79.7	0.25

A less explicit but similar behavior is found for the samples of the W1 series, which confirms that carbons with better textural properties are likely to be obtained with moderate concentrations (around 35%) of activation agent.

One of the samples (53-W2-N) was carbonized under nitrogen flow. Experimental conditions were the same as those for the previous samples, except during this carbonization stage, in which the pyrolysis was performed under an inert gas flow. Both surface area and micropore volume were substantially increased for this sample (nearly two-fold), although packing density slightly decrease. A typical chemical composition of lignocellulosic materials could be taken as 48% C, 6% H and 45% O (González et al. 1995). In the chemical activation process, the reagents act as a dehydrating agent in which H and O are removed. If carbonization takes place in the absence of an inert atmosphere, a very large amount of hydrogen and oxygen is removed and reacts with carbon atoms forming hydrocarbons and/or carbon monoxide and/or carbon dioxide (Molina-Sabio and Rodríguez-Reinoso 2004). Probably, this phenomenon decreased the gasification efficiency, leading to a less developed porous structure.

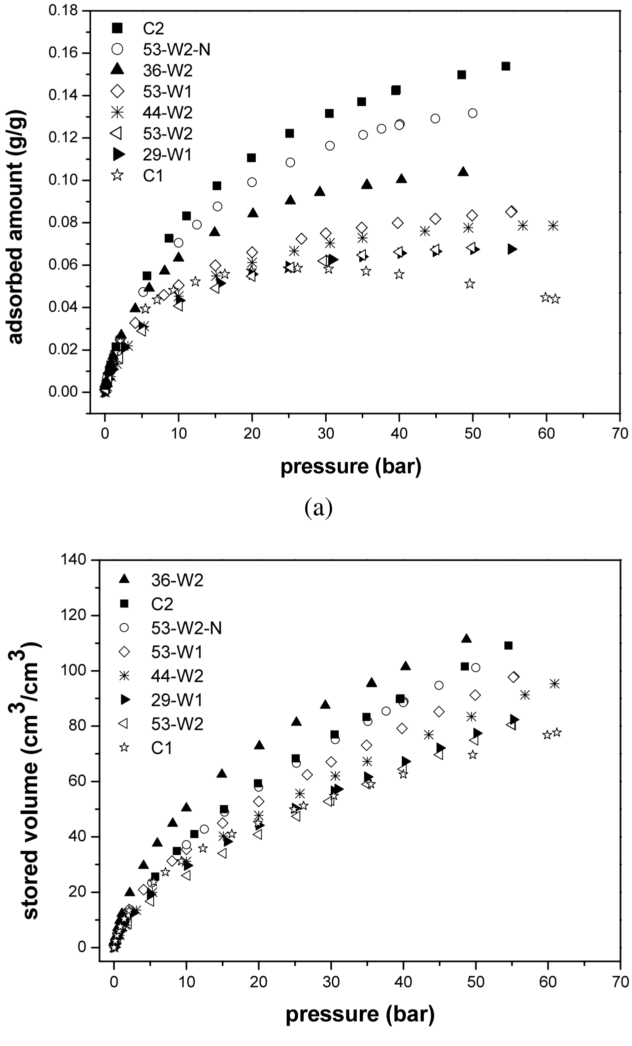
Regarding the average pore size, it has been reported that an adsorbent for methane storage should have an optimal pore size ranging from 8 to 15 Å (Sun et al. 2001). For the AC samples synthesized in this work, an average pore width between 11 and 15 Å was achieved, which lies within this ideal range. Nevertheless, the different activation procedures (previous acid wash and H_3PO_4 concentration) did not seem to have had much influence on this parameter, since all synthesized samples showed average pore sizes very close to one another.

Six samples were randomly selected in order to measure methane adsorption equilibrium data. For the sake of comparison, two other commercial samples (C1 and C2) were also submitted to methane adsorption experiments.

Packing density is an important parameter because it has a direct impact on the storage capacity per unit volume (see Eq. 3). A good packing density should minimize the useless voids (interparticle space), increasing the methane adsorption efficiency and delivery by the ANG systems (Lozano-Castelló et al. 2002b; Pupier et al. 2005). The packing densities were determined for each sample and the results are also shown in Table 1.

The methane adsorption isotherms and calculated stored volumes are shown in Figs. 2(a) and (b), respectively. Figure 2(a) shows that the best adsorption capacity on a mass basis was achieved for commercial sample C2, which is also the sample with higher specific surface area and micropore volume. Yet, sample C2 stores less methane (on a volumetric basis) than sample 36-W2 for pressures up to 50 bar. This should be due to the fact that the latter shows the highest packing density of all studied samples. Among the synthesized ACs, sample 53-W2-N shows the greatest adsorbed excess (g/g) and its volumetric storage capacity is comparable to that of commercial sample C2, despite its poorer textural parameters.

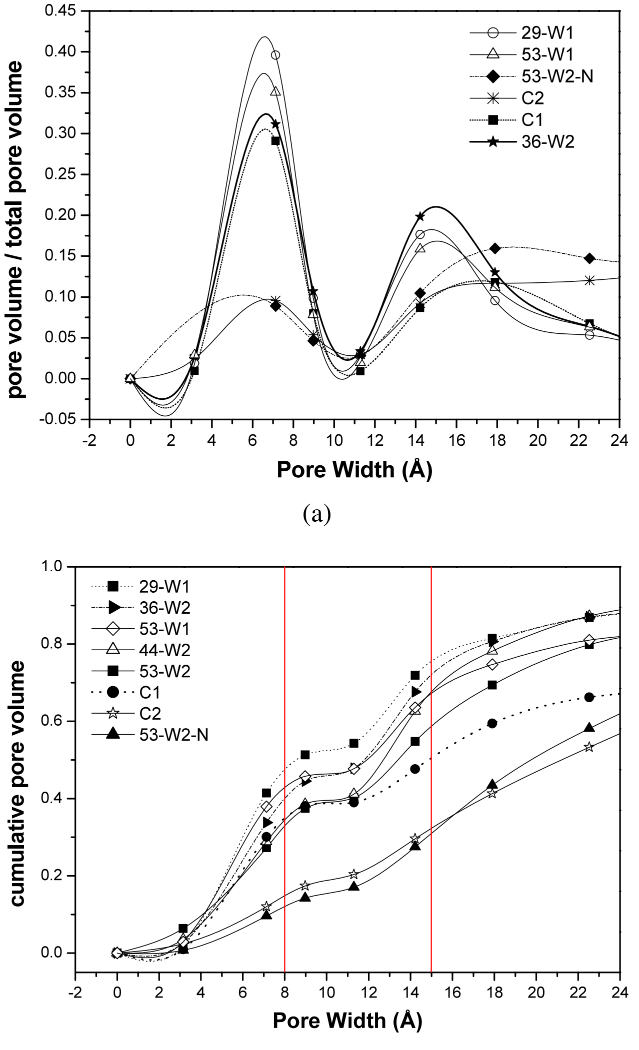
Sample C1 presented the lowest adsorption capacity of all. Nevertheless, its specific surface area and micropore volume lie in an intermediate range, when compared to the other samples. For a specific surface area of 828 m^2/g and micropore volume 0.443 cm^3/g, the absorbed excess at 35 bar for sample C1 was only 57.2 mg/g, whereas sample 29-W1 presented an absorbed excess of 64.1 g/g, even though its specific surface area and micropore volume were lower than those for C1. Evaluating pore size distribution by the DFT/Monte Carlo methods (Fig. 3), it was found that sample C1 has one of the lowest pore volume fraction within



(a)

(b)

Fig. 2 Adsorption excess isotherms (**a**) and stored volume (**b**) of methane on selected AC samples prepared from coconut shells and commercial AC samples at 303 K



(a)

(b)

Fig. 3 Pore size distribution (**a**) and cumulative pore volume (**b**) by DFT/Monte Carlo methods for some samples, as obtained from adsorption isotherms of N_2 at 77 K

the ideal range (8 to 15 Å), when compared to sample 29-W1 and other synthesized carbons. Additionally, sample C1 showed low microporosity as compared to most samples. A microporosity of 80.5% was calculated for C1 and an average microporosity of 86.5% for the other samples. On the other hand, sample 29-W1 presented the highest accumulated pore volume fraction within the suggested range, even though it has the lowest values of surface area and micropore volume (520 m^2/g and 0.3 cm^3/g, respectively). This allowed achieving higher methane adsorbed excess as compared to sample C1.

The adsorbed excess and respective stored volumes at 35 bar and 303 K for the samples under study are summarized in Table 2. For comparison, some previously reported values for stored volumes (V/V) for powdered activated carbons from distinct precursors are presented in Table 3. By examining samples C2 and 36-W2, the specific surface area and micropore volume of C2 are 2.26 and 1.96 higher than those of sample 36-W2, respectively. This translates into a larger adsorbed excess for C2, 1.41 as much as that measured for 36-W2 at 3.5 MPa and 303 K. However, packing density for 36-W2 is 1.81 times greater than C2, which is enough to ensure a stored volume of methane 1.14 times (v/v) larger than for C2. A high packing density is essential to achieve a high storage capacity on a volumetric basis, and consequently, high energy density. These results show that 36-W2 has great potential for natural gas storage, especially on a volumetric basis, offering good competitiveness in comparison to commercial sample C2. Carbonization of this sample in an inert environment should also be considered, although it may lead to an undesirable decrease in packing density.

For the pair 44-W2/53-W1, textural properties values are quite similar. Surface areas and micropore volumes had less than 2% and 1% difference against one another, respectively. This explains the similar methane adsorbed excesses obtained experimentally, although sample 53-W1 shows slightly better results possibly due to a narrower average pore width (Table 1) and a larger pore volume fraction concentrated on the range of 8 to 15 Å (Fig. 3).

The methane adsorbed excess for some selected samples (at 35 bar and 303 K) as a function of the specific surface area and micropore volume are shown in Figs. 4(a) and (b), respectively. The histograms illustrate that, in general, the higher the surface area and the micropore volume are, the greater adsorbed excesses are achieved. The only sample that distinctively falls apart from this general trend (illustrated by the red line) is commercial sample C1, which has probably been prepared from a different starting material and/or activation procedure.

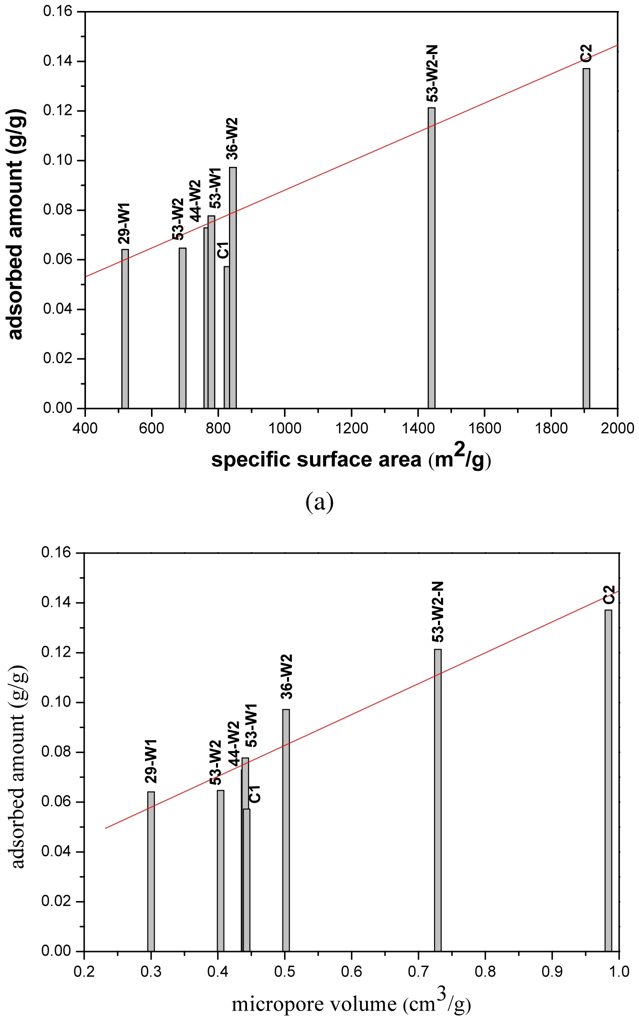
4 Conclusions

Activated carbon samples have been prepared from coconut shells by chemical activation with phosphoric acid aiming for natural gas storage. Some variations in the activation scheme were introduced, such as pre-treatment with sulfuric acid and carbonization under inert atmosphere (N_2). Methane adsorption isotherms were measured for selected samples and storage capacities (on mass and volume basis) were analyzed in the light of the textural characteristics and the preparation procedure.

Concerning sample preparation, the results have shown that moderate concentrations of phosphoric acid (around 35%) favor enhanced textural parameters in the resulting samples. Washing the precursor with sulfuric acid has improved the textural properties for most samples, except those prepared with the highest phosphoric acid concentration

Table 2 Adsorbed excess and stored volume at 35 bar and 303 K

Sample	Adsorbed amount (mg/g)	Stored volume (cm^3/cm^3)
C1	57.2	59
C2	**137.1**	**83**
29-W1	64.1	62
36-W2	**97.2**	**95**
44-W2	72.9	67
53-W1	77.7	73
53-W2	64.7	59
53-W2-N	**121.3**	**82**



(a)

(b)

Fig. 4 Adsorbed excess of methane at 35 bar and 303 K as a function of the specific surface area (**a**) and micropore volume (**b**)

Table 3 Previously reported values for stored volume for distinct precursors

Precursor	Reference	Conditions	Stored volume (V/V)
Waste tires	Brady et al. (1996)	3.5 MPa, 298 K	45–50
Bituminous coal	Sun et al. (1996)	3.5 MPa, 298 K	68–76
Anthracite	Lozano-Castelló et al. (2002b)	4 MPa, 298 K	82–166
Coconut shell	Prauchner and Rodriguez-Reinoso (2008)	3.5 MPa, 298 K	64–94
Petroleum Coke	Zhang et al. (2008)	3.5 MPa, 298 K	105–134

(53%). The acid pre-wash showed to have a positive influence in the development of porosity. The nitrogen flow in the pyrolysis stage was proven to be important, since it provides a considerable improvement in the sample properties, with a 108% increase in surface area and an 80% increase in micropore volume. However, it also led to a sharp drop in packing density. Further studies should be carried out, since there must be a trade-off between packing density and developed porosity.

Additionally, the importance of the textural properties as a screening criterion of adsorbents for gas storage was verified. Textural characteristics, such as surface area and micropore volume, have strong influence in the methane excess adsorption capacity (on a mass basis), as previously reported in other studies (Sun et al. 2001; Lozano-Castelló et al. 2002b; Bastos-Neto et al. 2007; Zhang et al. 2008; Prauchner and Rodriguez-Reinoso 2008). Additionally, packing density was essential to ensure a high storage capacity in terms of volume, as shown for sample 36-W2.

By comparison with commercial AC samples and with previously reported values found in the literature, we concluded that the AC materials prepared from coconut shells by chemical activation with moderate concentrations of phosphoric acid have promising potential as natural gas storage media. Carbonization under inert atmosphere shows promise of interesting results yet to be further investigated.

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