

Natural Gas Storage in Microporous Carbon Obtained from Waste of the Olive Oil Production

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A series of activated carbons (AC) were prepared from waste of the olive oil production in the Cuyo Region, Argentina by two standard methods: a) physical activation by steam and b) chemical activation with ZnCl_2 . The AC samples were characterized by nitrogen adsorption at 77 K and evaluated for natural gas storage purposes through the adsorption of methane at high pressures. The activated carbons showed micropore volumes up to $0.50 \text{ cm}^3 \cdot \text{g}^{-1}$ and total pore volumes as high as $0.9 \text{ cm}^3 \cdot \text{g}^{-1}$. The BET surface areas reached, in some cases, more than $1000 \text{ m}^2 \cdot \text{g}^{-1}$. The methane adsorption -measured in the range of 1-35 bar- attained values up to $59 V_{\text{CH}_4}/V_{\text{AC}}$ and total uptakes of more than $120 \text{ cm}^3 \cdot \text{g}^{-1}$ (STP). These preliminary results suggest that Cuyo's olive oil waste is appropriate for obtaining activated carbons for the storage of natural gas.

Keywords: *activated carbon, natural gas storage, agricultural wastes*

1. Introduction

Activated carbon (AC) is a porous material prepared from the carbonization and activation of organic compounds, especially of vegetal origin; the substrates so obtained show high micropore volumes as well as important surface areas. AC is a versatile adsorbent, whose textural and surface characteristics depend on the raw material of departure and on the particular method employed for its preparation¹⁻³.

There exist two recognized methods to prepare activated carbons: physical and chemical activation^{4,5,6,7}. Physical activation involves, as a first step, the carbonization of the precursor by thermal processes and, in a second step, the activation in the presence of agents such as CO_2 and steam, among others. On the other hand, chemical activation is a one-step method that involves the carbonization of the precursor in the presence of chemical agents such as KOH, NaOH, ZnCl_2 , MgCl_2 , and H_3PO_4 ^{6,8,9}, which are added to reach the desired porosity. The simplest and most commonly used methods in scientific research are physical activation with steam and chemical activation with zinc chloride^{4,7,10,11,12}. The activation with ZnCl_2 implies the degradation of cellulose following dehydration and carbonization in order to obtain a porous structure, in which the final carbon properties are conditioned not only by the nature of the precursor but also by the impregnation conditions, the carbonization temperature, etc^{4,13}. In the physical activation process, a lignocellulose precursor is carbonized under an inert atmosphere with the aim of obtaining a char (i.e. a substrate of a low adsorption capacity) which is then subjected to a partial and controlled gasification at high temperatures in the presence of steam. This gasification eliminates selectively, in first place, the most reactive carbon atoms, afterward the most disordered ones, and finally some of the structural carbons for generating (according

to the synthesis conditions) different textural characteristics of the obtained materials^{4,5}.

A series of substances has been used as the raw material, among them some agricultural wastes^{14,15} that are abundant in the Cuyo region such as kernels proceeding from several fruits. A waste that has considerably increased in quantity during the last years, is that derived from the olive oil industry by reason of the great profit increase that has experimented the olive oil industry in Argentina; this, involves concern for the excess of this waste without a specific application up till now. Therefore, the production of activated carbons from this kind of waste is an interesting proposal for this sector; moreover by taking into account that most of the AC consumed in Argentina is imported from other countries due to the insufficient local production.

Among the available energy resources in South America, natural gas (NG) has notably increased its production and consumption during the last years¹⁶⁻¹⁸; consequently, some deficiencies should be eliminated such as its NG storage both in fixed or mobile deposits, considering that Compressed Natural Gas (CNG) involves its storage at pressures over 180 bars. Our focus is in the security improvement for the gas handling, the efficiency in the storage capacity, and the diminution of costs. One alternative method for NG storage is by means of proper adsorbents, utilizing the Adsorbed Natural Gas technique (ANG)^{18,19,20}, which has not been commercialized at the moment. From a practical point of view, the quantity of natural gas stored in an adsorbent can be expressed in terms of stored gas, in normal (STP) conditions vs. volume of adsorbent^{21,22}. The use of proper adsorbents can lead to the storage of natural gas at 20-40 bars of pressure. In fact, the methane density at these pressures can be increased more than four times by using activated carbons, which

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can store more than $150 V_{\text{CH}_4}/V_{\text{AC}}$ (i.e. 150 volumes of CH_4 per unit volume of AC), equivalent to compress this gas at more than 160 bar. The AC micropore volume determines the capacity of this adsorbent to store methane at room temperature and pressures up to 40 bars^{23,24}. The ideal pore size for storing methane is approximately 0.8 nm thus corresponding to a separation between adjacent pore walls of two times the diameter of the CH_4 molecule; the experimental aim is to prepare materials with a high micropore volume²⁵. AC obtained from olive oil fulfils this last requirement, while also showing some other interesting characteristics; in spite of these advantages, only a few works have been devoted to this subject, none of them involving olive oil waste from the Argentinian Cuyo region. The waste product that remains after the almost total extraction of oil from olive, after being compressed and exposed to solvent extraction, has been denominated as olive lex and its use as a precursor for AC preparation has been scarcely cited in bibliography.

In this work, it is described the development of AC from olive lex through either chemical activation by zinc chloride or physical activation by steam and its performance at pressures up to 40 bars during the adsorption of methane, the main component of natural gas.

2. Experimental

2.1. Preparation of AC samples

2.1.1. Chemical activation by zinc chloride

Olive lex, the material of departure, was kindly provided by Olivi Hnos. Mendoza (Argentina); this raw product contained pieces of olive pulp, peel, and seed. The precursor was sieved into three fractions of different particle size according to the mesh opening that was employed: (-20) for particle sizes smaller than 0.84 mm; (-10+20) for particle sizes between 0.84 and 2 mm; and (+10) for particle sizes larger than 2 mm. Afterward, these samples were dried at 383K; a mass of 5 g of the dry product was impregnated with a ZnCl_2 solution following the procedure described in the bibliography²⁴. For the preparation of the samples utilized in this work, it was used a 1:1 weight/weight ratio of ZnCl_2 /precursor mass for each AC adsorbent set. For the (+10) sieved sample, two more samples were prepared by employing 0.5:1 and 2:1 ZnCl_2 /precursor ratios. 60 mL of distilled water were added to each particular mixture of ZnCl_2 and the dry precursor. Then, they were subjected to continuous stirring at 353 K, until the complete evaporation of the remnant liquid. Next, the previous impregnated precursor was carbonized in a horizontal oven at 773 K for one hour under a N_2 atmosphere, at a rate of 10 K/min and a flux of 180 mL/min, followed by a cooling process performed at the same pace under the inert atmosphere. Finally, the resultant material was put in contact with 60 mL of an 1:1 aqueous solution of HCl (38 vol. (%)) by one hour and washed several times with distilled water for removing the ZnCl_2 excess as well as the residual organic matter up to neutral pH. To finish, the AC samples were dried at 333 K for 12 hours and labeled as Zn1/1 (-20), Zn1/1 (-10+20), Zn1/1 (+10), Zn0.5/1 (+10), and Zn2/1 (+10), according to the quantity of Zn salt used in the preparation and the mesh size.

2.1.2. Physical activation with steam (water vapor)

This experimental procedure involves two steps: first the carbonization of the precursory material at 773K for one hour in a retort oven. Initially, the oven is packed with the required amount of precursor and is sealed in order that the vapors given off during the early steps of the heating process can expel all remaining oxygen from the system. Next, the material is left cooling to room temperature ready for activation with steam at high temperatures. The activation step

was made inside an AISI 316 tubular stainless steel reactor (30 mm diameter, 300 mm length) located inside an electrical oven of hexagonal section equipped with an electronic temperature controller. During the initial heating up to the selected activation temperature, the reactor is kept under an inert N_2 atmosphere. The water vapor required for the reaction was flowed to the reactor by means of a Cole Parmer Masterflex peristaltic bomb working in conjunction with an electronically controlled temperature atomizer. Table 1 lists the experimental operation conditions chosen to prepare each of the AC samples, where F represents the steam flow (in mL per minute) that was employed during the activation process.

2.1.3. Methods and techniques

N_2 Adsorption-desorption isotherms at 77 K were performed in an Autosorb-1MP (Quantachrome-USA) instrument in order to determine some textural properties of the AC samples. Each adsorbent was previously degassed at 523 K for 12 hours. Specific surface area were calculated by the BET equation and the pore size distribution by a Non-Local Density Functional Theory approach, NLDFT.

Methane adsorption analyses were performed at room temperature by means of an HPVA 100 volumetric instrument (VTI Corporation-USA) in a range of pressures extending from 1 to 40 bars. This instrument can measure adsorption isotherms up to 100 bars of pressure in a wide range of temperatures.

3. Results and Discussion

Figure 1 shows the N_2 adsorption-desorption isotherms at 77 K corresponding to the AC samples prepared by chemical activation. The isotherms are Type IV, according to the Brunauer-Deming-Deming-Teller (BDDT)²⁶ classification, and in the low pressure region a steep adsorption is observed thus proving the presence of micropores. The hysteresis loop confirms the presence of mesopores; the Type H4 loop

Table 1. Physical activation conditions.

Sample	Activation conditions				
	Raw material	Precursor mass (g)	Temperature (K)	Time (min)	F (mL/min)
LAAF1	Olive Lex	80	1173	120	1.33
LAAF2	Olive Lex	80	1173	120	2.27
LAAF3	Olive Lex	39	1173	150	0.65

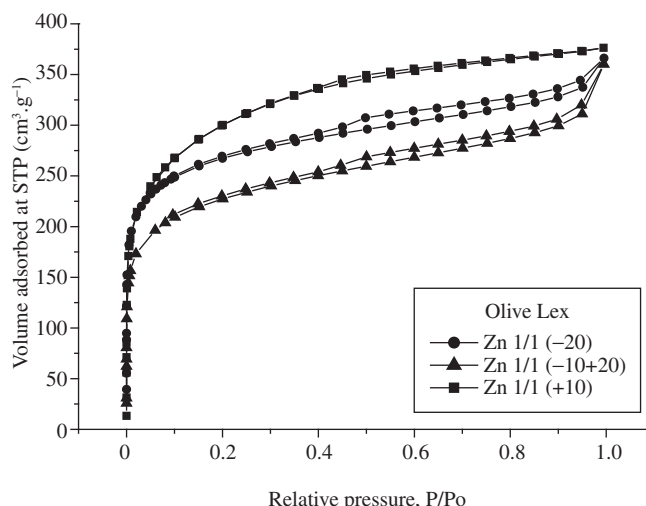


Figure 1. N_2 adsorption-desorption isotherms for the samples sieved with different mesh sizes.

show adsorption and desorption branches parallel to each other and almost horizontal^{27,28,29}. These characteristics correspond to materials having pores of slit-like shapes (commonly found for carbons). The sample (+10) mesh, i.e. the one with the largest particle size, shows the higher adsorption along all of the pressure range, thus possessing the highest specific surface area as well as the highest total pore volume.

The raw material contains pieces of olive pulp, peel and seed with a preponderant proportion of the last one. The contribution of the seed in the properties of the final substrate seems to guarantee a high specific surface area. In turn, the peel, i.e. the component with the smaller mesh granulometry, provides a contribution of an intermediate surface area to the final substrate. Following this line of thought, the pulp, with the intermediate granulometry, appears to provide the smaller contribution to the final surface area of the AC.

Figure 2 shows the pore size distribution (PSD) of the AC samples; this distribution was calculated by the NLDFT formalism. The PSD evidence the presence of mesopores (voids of more than 20 Å) in all AC samples, which quantity slightly grows with the increase of the precursory particle size. The Zn1/1 (-20) sample, mainly originated from peel, shows a large proportion of ultramicropores, i.e. voids of widths lesser than 0.7 nm, while the sample obtained from the precursory constituted of the bigger particle sizes presents a larger proportion of supermicropores, i.e. micropores larger than 0.7 nm and mesopores.

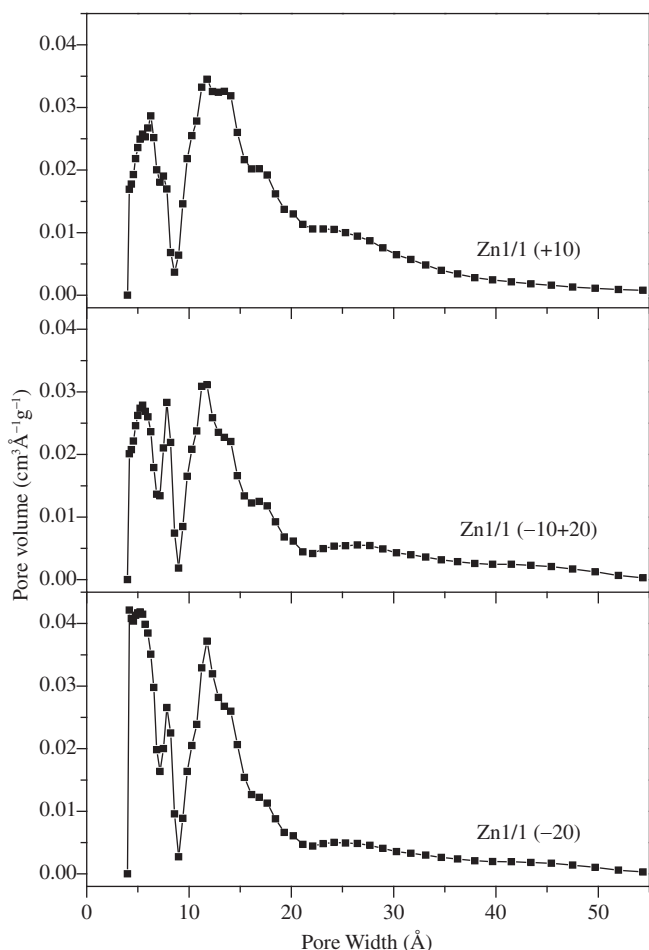


Figure 2. Pore Size Distribution by DFT method for the samples sieved at different mesh sizes.

Since the activated carbon endowed with the largest specific surface is that synthesized from a precursory (+10) mesh, this carbon was selected for chemical activation from $ZnCl_2$ /raw material mixtures corresponding to 0.5:1 and 2:1 ratios. Figure 3 shows the N_2 isotherms of these samples. It is noticed that the Zn0.5/1 (+10) sample, shows a Type I-isotherm, according to BDDT classification²⁶, having no hysteresis cycle which is a characteristic of many microporous solids; a small external surface area is also evident where the adsorption capacity is related to a high internal surface area². The Zn2/1 (+10) sample depicts a Type IV isotherm and present a type H4 hysteresis loop, according to the IUPAC classification, thus corresponding to pores with slit shape, characteristic of several activated carbons.

Figure 4 shows the pore size distribution (NLDFT) of the samples sieved at +10 meshes. It is observed that the AC sample, prepared with the smallest quantity of activating agent, scarcely display pores larger than 20 Å, thus the material is mostly formed by micropores as suggested by the isotherm shape. The porosity increases with the increase in the amount of the activating agent, and the Zn2/1 (+10) sample has the largest micro and mesopore volumes. It is noticeable in each PSD a bimodality effect in pores smaller and bigger than 0.8 nm (8 Å) of diameter, which can be associated to the raw material characteristics for this kind of activating agent.

Table 2 shows the textural parameters of the AC substrates prepared from chemical activation. The specific surface area (S_{BET}) was calculated through the BET equation; the total pore volume (V_T) was estimated by N_2 adsorption at 0.98 relative pressure by the Gurvich rule; the micropore volume was obtained from application of the Dubinin-Radushkevich method.

In the Table 2 it is corroborated what is seen in the Figure 4 where, for the same ratio of activating agent to precursory material, it appears a dependence of the specific surface on the granular size composition of the sample. With an increase in the quantity of the activating agent (AA/M), the pore total volume increases practically in a lineal way. However, this does not happen with the PSD values, where the tendency is to observe the presence of micropores up to a limit where mesopores start to grow up.

For the same relationship AA/M, V_T values remain constant, but the PSD suggests a dependence on the sample composition (granule size).

In order to compare with a second activation method, which is cheaper and widely spread at industrial scale, the precursory samples were subjected to a physical activation. Figure 5 shows the N_2 iso-

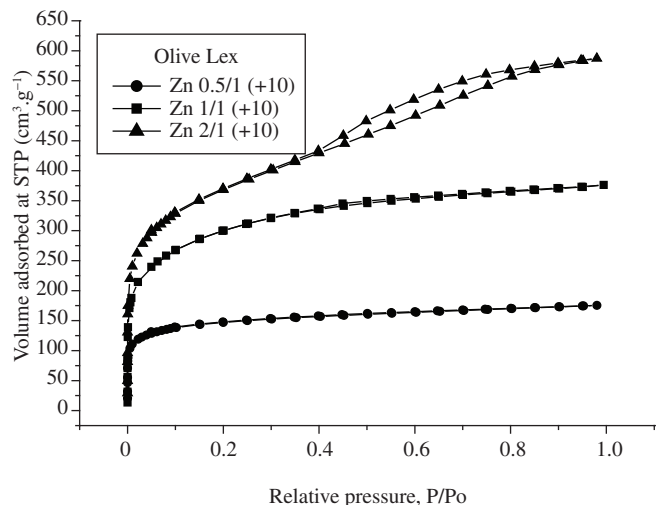


Figure 3. N_2 adsorption-desorption isotherms for the samples sieved at (+10) mesh size.

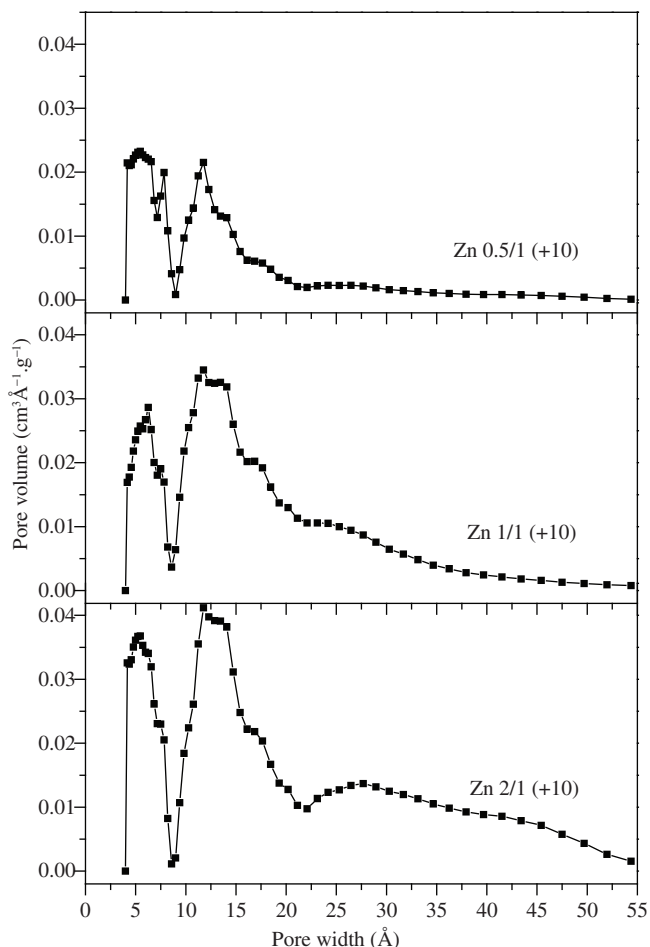


Figure 4. Pore Size Distribution by DFT method for the samples sieved at (+10) mesh size.

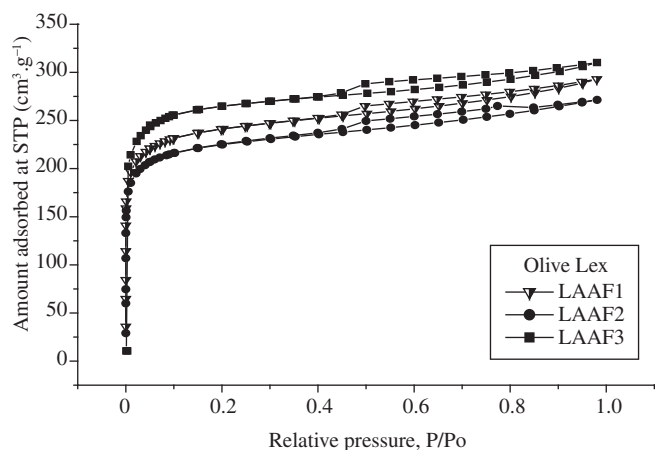


Figure 5. N₂ adsorption-desorption isotherms for the physically activated samples.

terms of the physically activated samples proceeding from carbonized olive lex as the raw material; the samples are labeled as LAAF_n (Table 1). The increase in the agent/material per minute (F/mass) ratio employed for the preparation of the LAAF1 and LAAF2 samples resulted in not improvement of the specific surface area. However, the increase of the activation time for the LAAF3 sample provided an enlarged surface area. The sorption curves of Figure 5 are Type IV isotherms, according to the BDDT²⁶ classification, with an associated hysteresis cycle of the H4 Type²⁹.

The specific surface areas of the physically activated carbon samples are high, and then interesting and their shape reveals that they mostly consist of micropores. In Figure 6, it is shown the pore size distribution, NLDFT, for these samples. It can be noticed that the samples exposed to the same activating time (LAAF1 and LAAF2) keep showing a bimodal distribution, which almost disappears when the activation time increases. The increase in the activating agent quantity

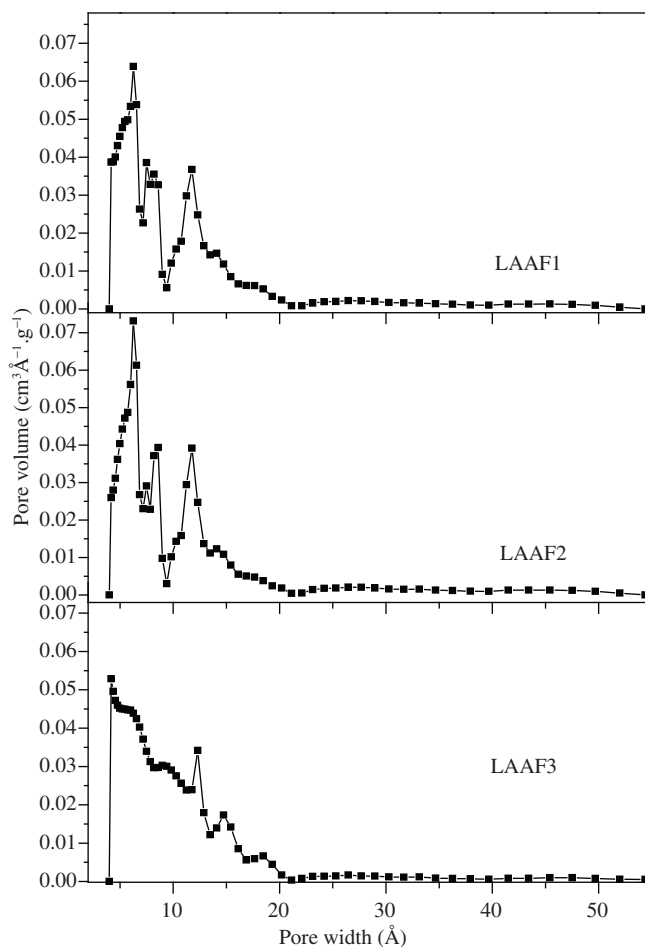


Figure 6. Pore Size Distribution by DFT method for the physically activated samples.

Table 2. Comparative data of the activated carbons using ZnCl₂.

Sample	Activating agent	ZnCl ₂ /precursor ratio (w/w)	Precursor amount (g)	S _{BET} (m ² ·g ⁻¹)	V _T (cm ³ ·g ⁻¹)	V _μ (cm ³ ·g ⁻¹)
Zn1/1 (+10)	ZnCl ₂	1/1	5	1052	0.58	0.51
Zn1/1 (-10+20)	ZnCl ₂	1/1	5	816	0.56	0.40
Zn1/1 (-20)	ZnCl ₂	1/1	5	977	0.56	0.44
Zn0.5/1 (+10)	ZnCl ₂	0.5/1	5	542	0.27	0.22
Zn2/1 (+10)	ZnCl ₂	2/1	5	1291	0.91	0.52

makes no difference in the PSD shape and goes against the S_{BET} , which is shown both in the table and in the isotherms. When the activating time increases new pores of about 8-10 Å are created in the microporous zone, without a significant variation in the total pore volume.

Table 3 shows the textural data for the physically activated samples, there it can be noticed that the increase in the agent/material proportion per minute (R) only achieves a minor diminution of the S_{BET} . However, by increasing the activation time in 30 minutes, an increase in the specific surface area is produced. The pore volumes show no important variations for the three samples in question.

In order to study the potential use of the variety of synthesized AC substrates for natural gas storage, methane adsorption was performed. CH_4 adsorption isotherms were determined up to a pressure of 40 bar at 298 K. Figure 7 shows the resultant CH_4 isotherms for the (+10) size samples (activated with ZnCl_2) at different proportions of the Zn salt and the precursor. It can be observed that the samples with the larger pore volumes for micro, meso and macropores and bigger superficial area depict a higher adsorption capacity for methane (See Table 2). Then, for these samples there exist a correlation in their adsorption capacity for both methane and nitrogen, reported also for other authors^{20,22,30}.

Methane isotherms associated to the physically activated samples are shown in Figure 8. At pressures up to 16 bars, the samples show minor differences and it again appears a correlation with that observed for the nitrogen adsorption, which evidences an analogy in the methane and nitrogen adsorption behavior. At pressures higher than 16 bar, this behavior changes therefore confirming that the apparition of micropores smaller than 1.2 nm (12 Å) affects the methane adsorption.

Table 4 shows the ratio of the volume of adsorbed methane versus the adsorbent volume (Q') calculated at 35 bar of pressure according to the following equation²²:

$$Q' = V_{\text{CH}_4} / V_{\text{AC}} = Q \cdot M \cdot \mu \cdot \delta_{\text{app}} \quad (1)$$

Table 3. Compared data for physically activated carbons.

Sample	Activating agent	R (mL.g ⁻¹ /min)	S_{BET} (m ² .g ⁻¹)	V_T (cm ³ .g ⁻¹)	$V\mu$ (cm ³ .g ⁻¹)
LAAF1	H ₂ O	0.0167	913	0.45	0.40
LAAF2	H ₂ O	0.0284	852	0.42	0.38
LAAF3	H ₂ O	0.0167	1015	0.48	0.40

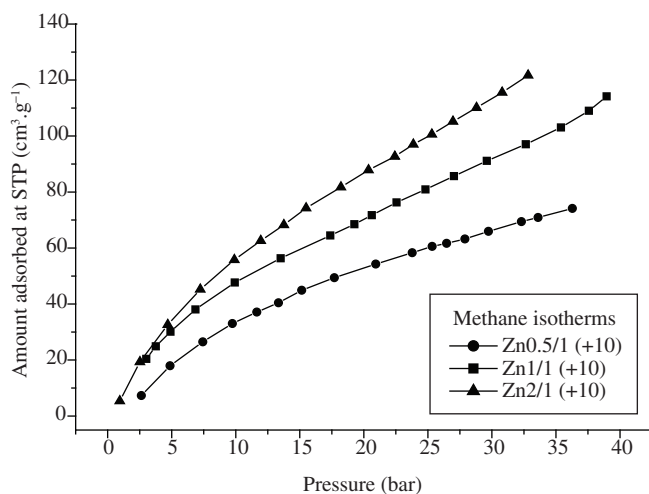


Figure 7. Methane isotherms for the samples activated with ZnCl_2 .

where Q is the molar storage capacity (mol of methane/kg of activated carbon), M is methane molecular weight (g/mol), μ is the volume occupied by 1 gram of methane in STP (1.5 dm³.g⁻¹) conditions, and δ_{app} apparent density of the CA (g/cm³).

Table 4 indicates that the physically activated samples correspond to the best CH_4 storage values; also that these samples have a scarce amount of mesopores and depict large apparent densities. Moreover, these results suggest that samples including an important proportion of large micropores (supermicropores) produce the best results for the storage of methane at pressures around the reference value (35 bar).

4. Conclusions

Activated carbons of a very low cost were successfully prepared from olive pomace (a mixture of olive pulp, peel and seeds) following the almost total extraction of the oil. These materials showed surface areas up to 1000-1200 m².g⁻¹ with a micropore volume of about 0.50 cm³.g⁻¹.

Three different precursors, according to the particle size of their constituting grains, were chemically activated by the annealing of a sample containing a 1:1 weight ratio of ZnCl_2 /olive pomace precursor. The dry pomace sample containing the largest particle size (+10), which we assume is principally composed of olive seed, was the one that adsorbed more nitrogen than any other along all the pressure range, thus evidencing a high specific surface area and a large pore volume. The pore size distribution showed that all these carbon samples are principally microporous with a slight presence of mesopores that increases with the particle size of the precursory waste. For the same particle size (+10) of the precursory material, an increase in the amount of the activating agent enlarged the porosity of the final carbon. For methane adsorption, the carbon samples having

Table 4. Methane storage.

Sample	δ_{ap} (g/cm ³)	$Q' = V/V$
Zn0.5/1 (+10)	0.46	36
Zn1/1 (+10)	0.39	43
Zn2/1 (+10)	0.38	52
LAAF1	0.49	59
LAAF2	0.53	57
LAAF3	0.50	55

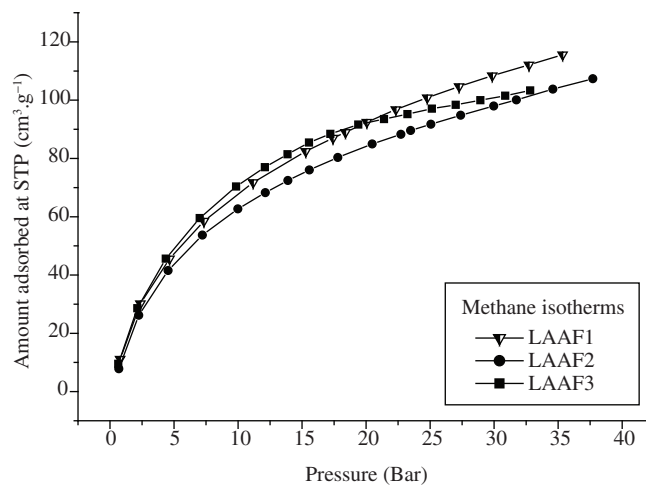


Figure 8. Methane Adsorption isotherms for the physically activated samples.

the largest porosities and the highest surface areas represented the best alternatives for CH₄ storage.

The physically activated samples showed high specific surfaces and porosities in the microporous range. The increase of the activation time resulted in an increase in the quantity of the smaller micropores, something that was detrimental with respect to methane adsorption in the pressure value of reference (35 bar). The carbon samples containing pores of widths between 1 and 2 nm showed the best methane adsorption characteristics.

All carbon samples showed a significant capacity for the adsorption of methane, reaching saturation values near to 120 cm³.g⁻¹ (STP), equivalent to a V_{CH₄}/V_{AC} ratio of about 59, which corresponded to a 35 bar pressure. This characteristic proved the potential that have these activated carbons to store natural gas in an efficient way with the incentive of their low production cost.

Further studies are necessary not only to optimize the synthesis process but also to achieve a more successful correlation between the textural characteristics and the storage capacity.

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