



Tailoring biomass-based activated carbon for CH₄ storage by combining chemical activation with H₃PO₄ or ZnCl₂ and physical activation with CO₂



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ABSTRACT

Coconut shell-based activated carbons intended for CH₄ storage were prepared by chemical activation with H₃PO₄ or ZnCl₂ and/or physical activation with CO₂. Efforts were focused to establish relationships among the activation procedure, the textural and physical-chemical properties of the resulting materials and their volumetric CH₄ uptake. The best results were achieved by using the combination of a relatively soft chemical activation with H₃PO₄ or ZnCl₂, just the sufficient to minimize the presence of macropores originated from the botanical structure of the precursor, followed by physical activation with CO₂ to develop a narrow pore size distribution mainly located around the optimum pore diameter/width for CH₄ storage. This combined methodology permitted to obtain excess volumetric CH₄ adsorption capacities as high as 94, 148 and 145 V/V for granular, powdered/compressed and monolithic carbons, respectively. The corresponding total CH₄ storing capacities were estimated to be 102, 165 and 163 V/V. It is worthy to highlight that the precursor was a low cost and abundant agricultural by-product, which is very important for large-scale applications such as gas transportation and gas storage in vehicular fuel tanks.

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1. Introduction

The employment of CH₄-based energy sources such as natural gas and biogas has grown considerably in the last three decades mainly because: (i) they are cheaper than petroleum derivatives; (ii) they are relatively clean-burning fuels if compared to coal and petroleum derivatives; (iii) there is a great interest of many nations in diversifying their fuel mix and reducing the reliance on imported oil. In the particular case of biogas, it is a renewable energy source and its use is important to reduce CH₄ emissions to the atmosphere (CH₄ is a very active greenhouse gas) and to stimulate a proper management of organic wastes. In turn, the interest in natural gas has intensified due to the recent discovery and exploration of huge shale gas reserves. Finally, it is valid to highlight that governments and scientists have addressed the attention towards natural CH₄

hydrates reservoirs, being that the amount of energy available in this form is estimated to be twice that of all other fossil fuels combined [1].

The main challenge in using CH₄-based fuels is to store relatively large gas amounts at room temperature and low pressure. In this context, adsorption in nanocavities of porous materials has shown to be an interesting alternative to substitute the compressed and liquefied forms. Special interest concerns vehicular application, because adsorbed CH₄ has permitted to store at 3.0 MPa amounts of energy similar to that stored in the compressed form at 20.0 MPa [2–4]. Outstandingly, while the compression of CH₄ at high pressures requires the use of heavy stainless steel vessels with constrained geometry for the sake of safety, low pressure adsorbed CH₄ systems make it possible to use conformable lighter tanks that can be easily integrated into the overall vehicle layout. Further, filling a tank at low pressures avoids the need of costly multi-stage compression, which drastically reduces the capital and operating costs. Alternatively, adsorption at 200 MPa permits to store around 50% more CH₄ if compared to the compressed gas at the same

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pressure [2].

Since for adsorbed gas applications the adsorbent is confined within a vessel of a given volume, an enhanced adsorption capacity on a volumetric basis is required. To match this goal, the adsorbent should present the highest possible porosity, with a pore size distribution that maximizes the density of the adsorbed phase [5,6]. In addition, spaces where adsorption does not considerably occur should be minimized; such spaces comprise material skeleton, macropores and interparticular space [7].

Among the adsorbents tested to store CH₄, activated carbons have rendered the best results [2,8] because they usually present elevated porosity and an adequate choice of both, precursors and activation parameters, permits to tailor the pore morphology in order to enhance the adsorption capacity of a given adsorbate. In addition, activated carbons: (i) have hydrophobic surface, which favors the adsorption of organics and mitigates the competitive adsorption of water; (ii) present higher mechanical strength, avoiding packing-related loss of efficiency; (iii) can be obtained from cheap and abundant precursors such as coals and biomass or petroleum residues.

At this point, it is valid to stress that remarkably high CH₄ uptakes have been reported in the literature for metal–organic frameworks (MOFs) [9–11]. However, most authors use the ideal single-crystal density to calculate the volumetric CH₄ adsorption capacity, which makes the determined values unrealistic. Further, the MOFs are originally in the form of light and fluffy powders, so that a conforming step is mandatory for practical applications. Nevertheless, MOFs present low mechanical stability under pressure, so that the application of a conforming pressure can easily lead to a drastic decrease of the textural properties, therefore compromising the adsorption performance of the resulting monolith [2,9]. In turn, activated carbons showed to withstand high pressures without any damage or loss of porosity [2].

Our research group has carried out intensive work related to the development of activated carbon intended for CH₄ storage. These works have been conducted following two main routes: (i) chemical activation of lignocellulosic precursors with H₃PO₄ or ZnCl₂ followed by physical activation with CO₂ [12–14]; (ii) chemical activation of petroleum-based pitch with KOH [2,7]. The first route has permitted to obtain granular carbons with good mechanical resistance and well developed porosities from abundant and cheap biomass residues such as olive stone and coconut shell. Further, the grains impregnated with the chemicals can be conformed into binderless monoliths, so that CH₄ excess volumetric adsorption capacities up to around 150 V/V were achieved [12,13]. In turn, the second route has rendered materials with even higher gravimetric CH₄ adsorption capacities. However, carbons are invariably obtained as a powder, so that a conforming step is required [2]. Finally, it is worthy to report that our group has identified for the first time the growth of synthetic methane hydrates in the nanospace of carbon materials, so that these systems arise as a promising alternative for CH₄ storage [15].

In a previous paper [16], we reported a study comparing the development of textural properties during activation of coconut shell by physical activation with CO₂ and chemical activation with H₃PO₄ or ZnCl₂. During physical activation, porosity is developed by carbon gasification due to the reaction “C + CO₂ → 2CO”. In turn, H₃PO₄ and ZnCl₂ act as templates for the pore formation during the chemical activation. In the present paper, the CH₄ adsorption capacity of the obtained carbons were evaluated, compared and related to the material properties and to the employed synthesis procedure. This study permitted to build an optimized activation methodology that involves the combination of the chemical and physical procedures. This way, granular, powdered/compressed and monolithic carbons with enhanced volumetric CH₄ storing

capacities were obtained.

It is important to highlight that, even though the present work was focused on CH₄ storage, the results and discussions presented herein can also be useful for preparing activated carbon intended for several other applications such as H₂ storage [8,17,18], carbon capture and storage [19–21] and gas separation (including biogas and natural gas purification) [22,23].

2. Experimental

2.1. Raw-material

A sample of dried endocarp of coconut shell (*Cocos nucifera*) originally from Mexico was used as the precursor for all preparations. It was crushed and sieved to separate different granulometries. The fraction in the range of 2.00–2.83 mm was used to prepare the granular carbons. Some characteristics of the shell were previously published [16].

2.2. Activation procedures

2.2.1. Chemical activation

For the preparation of granular carbons by chemical activation, the precursor was first impregnated with H₃PO₄ or ZnCl₂ by soaking the grains in a solution (2 mL per gram of precursor) whose concentration was adjusted to provide the desired mass ratio of phosphorous or zinc/precursor (these ratios will be expressed herein as X_P or X_{Zn}, respectively). The impregnated material was then carbonized up to 450 °C or 500 °C (for activation with H₃PO₄ and ZnCl₂, respectively) for 2 h under N₂ flow and subsequently washed to remove the chemical. More details about impregnation and washing steps are reported elsewhere [16]. According to the results reported in the supplementary materials (S1.1), these temperatures permit to attain a good balance between gravimetric methane uptake and bulk density, which favors the volumetric CH₄ adsorption capacity of the resulting samples.

2.2.2. Physical activation

For the physical activation, the starting material (the ground coconut shell or a previously chemically activated sample) was first carbonized under a flow of N₂ (100 mL/min) up to 850 °C (2 °C/min; 2 h). Then, the carbonized material was gasified with CO₂ (100 mL/min) at 750 °C. Even though physical activation of biomass-based carbons can be performed in a single step, as reported by Yang et al. [24], the two-step procedure was used in order to make it possible to separate the weight losses due to the CO₂ gasification (which is herein referred as burn-off) and the carbonization itself.

2.3. Monoliths preparation

The procedure to prepare monolithic chemically activated carbons was basically the same as above described for the synthesis of the granular samples (Subsection 2.2.1), except that grains with smaller granulometry were used (0.5–1.0 mm) and a conforming step was introduced between impregnation and carbonization. The conforming step was carried out by pressing under heating 5.0 g of impregnated grains for 30 min in a cylindrical mould with internal diameter of 2.0 cm. Different conforming pressures and temperatures were tested, as well as different chemical loadings.

2.4. Activated carbon labels

The prepared activated carbons were labeled according to the following rules:

- A first letter is used to indicate if the sample concerns a granular (G), a powdered/compressed (C) or a monolithic (M) carbon.
- For chemically activated carbons, the letter P or Z is used to indicate the chemical (H_3PO_4 or ZnCl_2 , respectively); this letter is followed by the X_P or X_{Zn} value multiplied by 100.
- For physical activation, the letter B is used followed by the respective burn-off (in percentage); a zero burn-off indicates that the sample (the precursor or a chemical activated carbon) was carbonized up to 850 °C, but it was not submitted to CO_2 gasification.
- For combined chemical/physical activations, the aforementioned codes are listed in sequence.

Typical examples for nomenclature: (i) GZ25 concerns the granular carbon chemically activated with ZnCl_2 with a X_{Zn} 0.25; (ii) Z25B00 refers to the same sample but after carbonization up to 850 °C; (iii) MP09B30 concerns the monolithic carbon chemically activated with H_3PO_4 with a X_P of 0.09, followed by carbonization up to 850 °C and subsequent gasification with CO_2 up to a burn-off of 30%.

Finally, PXX and ZXX refer to the whole series of samples chemically activated with H_3PO_4 or ZnCl_2 , respectively. In turn, BXX refers to all a series of carbons physically activated with CO_2 . Therefore, for example, the MP15BXX series includes all the monolithic carbons produced using a X_P of 0.15 followed by carbonization up to 850 °C and gasification with CO_2 up to different burn-offs values (including the MP15B00 sample).

2.5. Activated carbon characterization

The isotherms of N_2 (–196 °C) and CO_2 (0 °C) were recorded in a volumetric automatic system, Omnisorb 610. The specific surface area (S_{BET}) was determined from the N_2 adsorption isotherm by applying the Brunauer–Emmett–Teller equation. The micropore volume (V_{mic}) was determined by applying the Dubinin–Radushkevich (DR) equation to the N_2 adsorption isotherms. The volume of N_2 adsorbed at p/p_0 0.95 was termed $V_{0.95}$ and considered to be the sum of micro and mesopore volumes. The software Autosorb 1 was used to generate the non-linear density functional theory (NLDFT) pore size distribution (PSD) curves from the N_2 adsorption isotherms.

Helium densities (ρ_h) were determined in an automatic pycnometer Accupyc 1330 from Micromeritics. ρ_h was considered herein as equivalent to the carbon skeleton density (ρ_{sk}).

The bulk density (ρ_b) was determined by measuring the bulk volume (V_b) of a known mass sample. For granular carbons, V_b was measured by gently tapping the grains in a 50 mL graduate cylinder. For powdered/compressed carbons, V_b was determined as the volume occupied by the material compressed in a cylindrical mould at 450 kg/cm². Finally, for monolithic carbons V_b was determined by measuring the external piece dimensions with a caliper.

V_b can be considered as the sum of the V_{sk} , $V_{0.95}$ and V_w :

$$V_b = V_{\text{sk}} + V_{0.95} + V_w \quad (1)$$

V_{sk} is the skeleton volume. V_w , the waste volume, is considered herein to comprise the interparticle space plus large pores that do not considerably contribute for $V_{0.95}$ (called waste because these spaces are considered useless for adsorption).

V_b and V_{sk} correspond to $1/\rho_b$ and $1/\rho_{\text{sk}}$, respectively.

As stated above, ρ_{sk} will be taken as ρ_h . Therefore, V_w can be calculated as:

$$V_w = 1/\rho_b - V_{0.95} - 1/\rho_h \quad (2)$$

Once $V_{0.95}$ was assumed to correspond to the sum of the volumes of micro and mesopores, the volume of pores that do not contribute for $V_{0.95}$ would correspond to the volume of macropores (V_{mac}). Therefore, since it is plausible to consider that the interparticle space is similar for samples with similar granulometry, V_w is used herein to compare V_{mac} of granular carbons obtained by different procedures.

Excess isotherms of CH_4 adsorption were attained at 25 °C in a HPA 100 volumetric system from VTI (USA). The gas volume (STP conditions) adsorbed at 3.5 MPa was taken as the excess CH_4 adsorption capacity (V_{CH_4}). In turn, the total CH_4 storing capacity of a tank (V'_{CH_4}) was estimated by Eq. (3) [8].

$$V'_{\text{CH}_4} = V_{\text{CH}_4} + \rho_{\text{gas}} \left(1 - \rho_b / \rho_h \right) \quad (3)$$

Even though V'_{CH_4} represents more realistic values, excess CH_4 uptakes are more usually reported in the literature and, as such, V_{CH_4} will be primarily considered herein in order to facilitate comparisons.

The surface area, micropore volume, excess CH_4 adsorption capacity and total CH_4 storing capacity on a volumetric basis were calculated by multiplying the respective values on a mass basis by the material bulk density.

3. Results and discussion

For reasons of space, the N_2 and CH_4 isotherms and tables containing the characterization of the prepared samples are presented as supplementary materials.

3.1. Isolated activation methodologies

The present subsection concerns the preparation of granular carbons by physical activation with CO_2 or chemical activation with H_3PO_4 or ZnCl_2 . The N_2 adsorption-desorption isotherms and related data (supplementary materials S.1.2) show that the porosity on a mass basis continuously increases with increasing burn-off during physical activation with CO_2 and with increasing chemical loading during chemical activation with H_3PO_4 or ZnCl_2 .

Since adsorption is a surface phenomenon and micropores are the main responsible by the surface area in activated carbon, several authors have proposed relationships (chiefly linear) between CH_4 uptake and surface area or micropore volume [4,6,25–27]. Taking it into account and having in mind the need of storing high CH_4 amounts by volume unit, the volumetric V_{mic} and S_{BET} are presented as a function of burn-off or chemical loading in Fig. 1. The curves show that both volumetric V_{mic} and S_{BET} initially increase, reach a maximum and decrease thereafter. The occurrence of these maximums evidences that the porosity development occurs primarily by the enlargement of existent pores than by the creation of new ones, so that micropores grow and start to move into the mesopore range at higher activation degrees. Indeed, Fig. 2 shows that increases of burn-off or chemical loading are followed by pronounced pore enlargement.

Fig. 1 shows that the volumetric V_{CH_4} also reaches a maximum, being that this maximum occurs at lower activation degrees than those observed for S_{BET} and V_{mic} . Such behaviors can be related to that CH_4 is adsorbed with a maximum density within pores with dimensions (diameter or width in cylindrical or slit-shaped pores, respectively) around 0,76 nm [6] and, as depicted by Fig. 2, the higher the activation degree, the larger the fraction of pores with diameter/width falling considerably above 0,76 nm. Besides being able to accommodate two layers of adjacent adsorbed CH_4 molecules, as represented in Fig. 3, in such small pores the proximity of

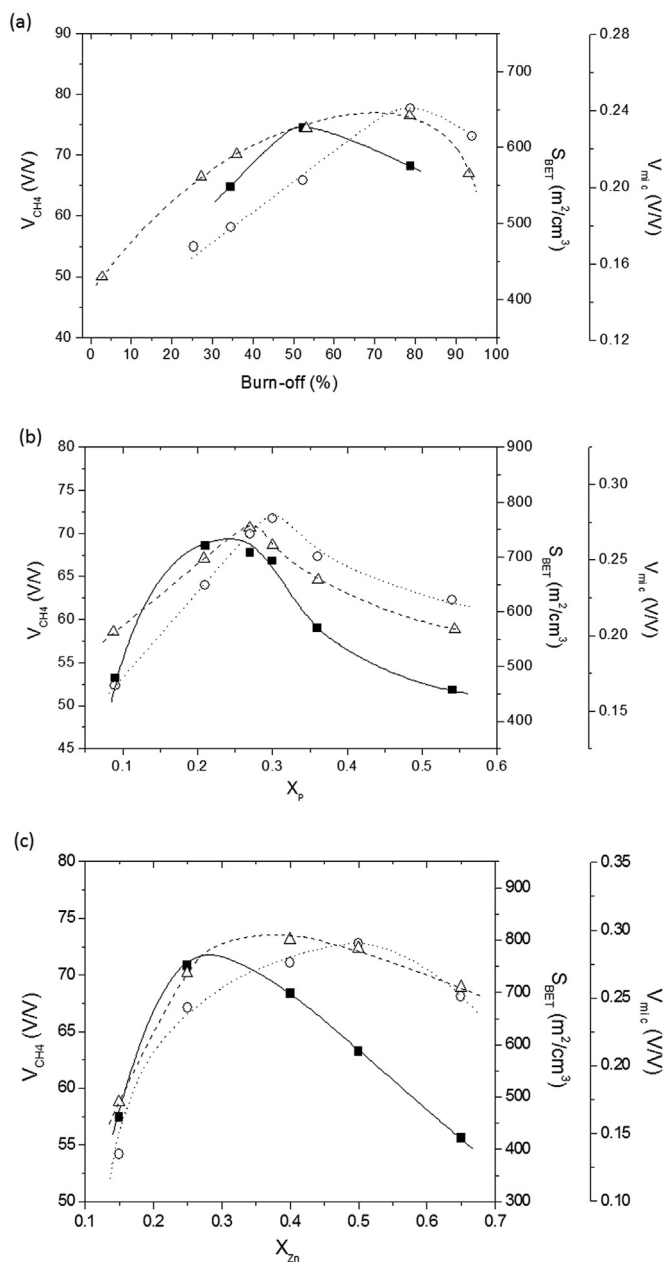


Fig. 1. Volumetric (■) V_{CH_4} , (○) S_{BET} and (Δ) V_{mic} of granular carbons prepared by: (a) physical activation with CO_2 ; chemical activation with (b) H_3PO_4 or (c) $ZnCl_2$.

the neighboring walls causes an overlapping of adsorption fields, so that the enthalpy of adsorption is enhanced and the pores are filled at relative low pressures with a high adsorbate density (close to that of the liquid phase) [28].

3.2. Physical activation versus chemical activation

We have previously reported [16] that physical activation with CO_2 renders materials with relatively low packing densities due to the presence of empty spaces that originate from conductor vessels present in the botanical structure of the precursor. Such empty spaces are considered herein as macropores. In turn, the attack of the dehydrating agents H_3PO_4 and $ZnCl_2$ during chemical activation leads the material to a plastic-like state in which the molecules have sufficient mobility to reorganize. During this stage, the

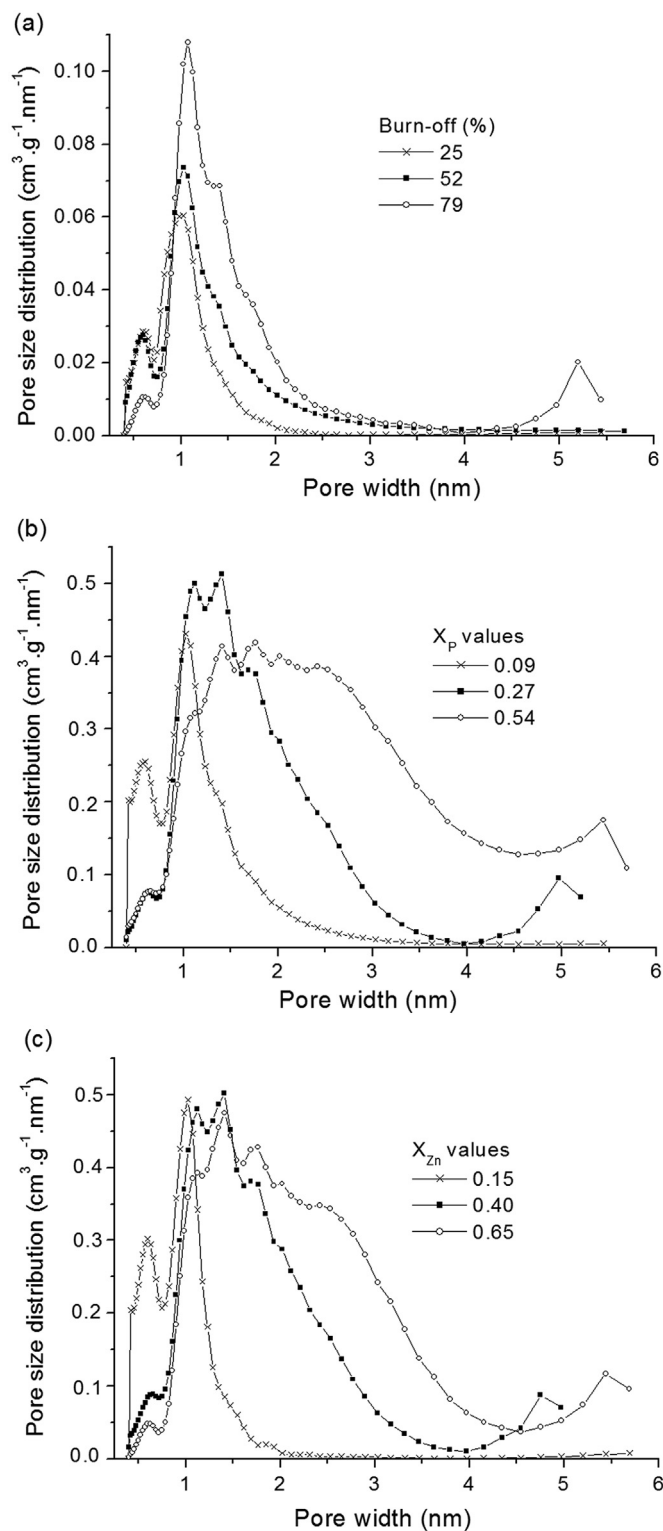


Fig. 2. PSD of granular carbons prepared by (a) physical activation with CO_2 or chemical activation with (b) H_3PO_4 or (c) $ZnCl_2$.

botanical structure of the precursor collapses, so that the occurrence of related macropores is prevented. Indeed, Fig. 4 portrays that chemically activated carbons present lower waste volume than physically activated carbons.

Concerning Fig. 4, an additional relevant aspect can be noted: V_w

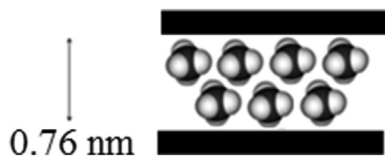


Fig. 3. Representation of the transversal section of a slit-shaped pore filled with CH_4 . (A colour version of this figure can be viewed online.)

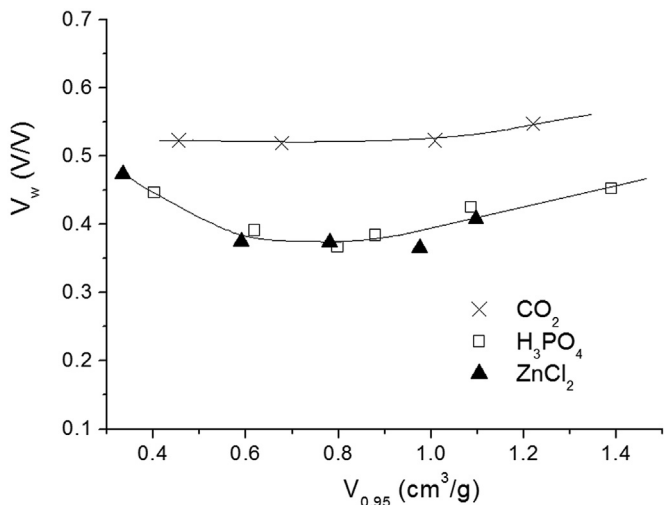


Fig. 4. Volumetric waste volume (V_w) for granular carbons obtained by chemical activation with H_3PO_4 or ZnCl_2 or physical activation with CO_2 . (A colour version of this figure can be viewed online.)

of chemically activated carbons initially decreases when the activation degree increases. This fact indicates that the chemical amounts used to generate the samples corresponding to the lowest activation degrees (X_p and X_{Zn} values of 0.09 and 0.15, respectively) were insufficient to completely prevent the occurrence of macropores.

If by one hand chemical activation suppresses the occurrence of macropores, which contributes to increase the bulk density of the resulting materials and, in this way, to enhance their volumetric adsorption capacities, by the other hand it renders carbons with: (i) lower skeleton density due to the lower employed activation temperatures (compare the data in Tables S3 and S4 with those of Table S5 – Supplementary materials); (ii) wider pore size distributions, as seen in the comparison of Fig. 2a with Fig. 2b and c and previously discussed in depth [16]. Lower skeleton density implies lower bulk density, which reduces the volumetric adsorption capacity; in turn, a wider pore size distribution is unfavorable for CH_4 uptake because it implies the presence of higher fractions of pores with diameter/width above the optimum value to adsorb CH_4 .

Summarizing, advantages are verified for each one of the activation methodologies. In the end, the maximum values verified for volumetric S_{BET} and V_{mic} were higher for chemically activated carbons (Fig. 5). Nevertheless, a higher volumetric V_{CH_4} was attained by physical activation, which highlights the importance of the pore size distribution for the CH_4 adsorption capacity.

3.3. The combined methodology: chemical activation followed by physical activation

The discussion reported in the previous section suggested a more efficient methodology to produce adsorbents with high

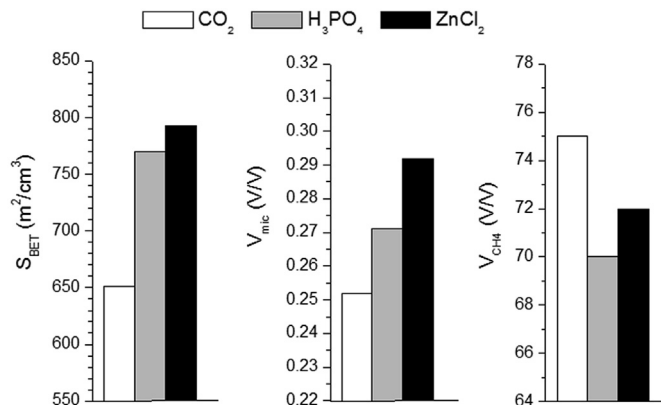


Fig. 5. Maximum values of volumetric S_{BET} , V_{mic} and V_{CH_4} verified for the granular carbons physically activated with CO_2 or chemically activated with H_3PO_4 or ZnCl_2 . (A colour version of this figure can be viewed online.)

volumetric adsorption capacity: the combination of a relatively soft chemical activation with H_3PO_4 or ZnCl_2 , just the sufficient to minimize the presence of macropores, followed by physical activation with CO_2 to increase the skeleton density and to develop a narrow pore size distribution centered around the optimum diameter/width for CH_4 adsorption.

At this point, it is valid to mention that this is not the first time that the combination of chemical activation with H_3PO_4 or ZnCl_2 and physical activation with CO_2 is employed. Our research group has already reported the gasification with CO_2 of peach stone-based granular carbons previously activated with ZnCl_2 [29] or H_3PO_4 [30]. It was pointed out that the referred activation procedure made it possible to conciliate high porosities with relatively high bulk densities. This way, the methodology was afterward used in order to produce carbons intended to methane storage [12–14]. In spite of it, a comprehensive study relating the properties of the resulting adsorbents to aspects involved in the combined activation pathway was still lacking to date. In the present work, the combined methodology was employed using different X_p and X_{Zn} in the chemical activation step.

3.3.1. Additional carbonization of chemically activated carbon

As stated in Subsection 2.2.2, the chemically activated carbons were additionally carbonized up to 850°C before gasification with CO_2 , which led to weight losses of about 8–10% due to the release of aliphatic side chains and heteroatoms. Since the carbon structure of biomass-based carbons undergoes pronounced aromatization in the range of $600\text{--}800^\circ\text{C}$ [31], this additional carbonization increased the skeleton density (compare ρ_h of samples GP09 with GP09B00, GP21 with GP21B00, GZ15 with GZ15B00 and GZ25 with GZ25B00 in Tables S3, S4, S6 and S7 – Supplementary materials). Furthermore, the grains shrank and a contraction of the pores took place, as evidenced by the reductions of S_{BET} and pore volumes and by the respective pore size distributions presented in Fig. 6. Therefore, the materials obtained after chemical activation using low chemical loadings and additional carbonization up to 850°C presented only a very incipient and narrow microporosity, besides a relatively high bulk density.

3.3.2. Gasification rates

Fig. 7 shows that the gasification rate is higher for the as-carbonized precursor (GB00 sample) than for the previously chemically activated carbons. In turn, the samples chemically activated with H_3PO_4 (GB09B00 and GB21B00) gasified at much higher rate than the samples chemically activated with ZnCl_2

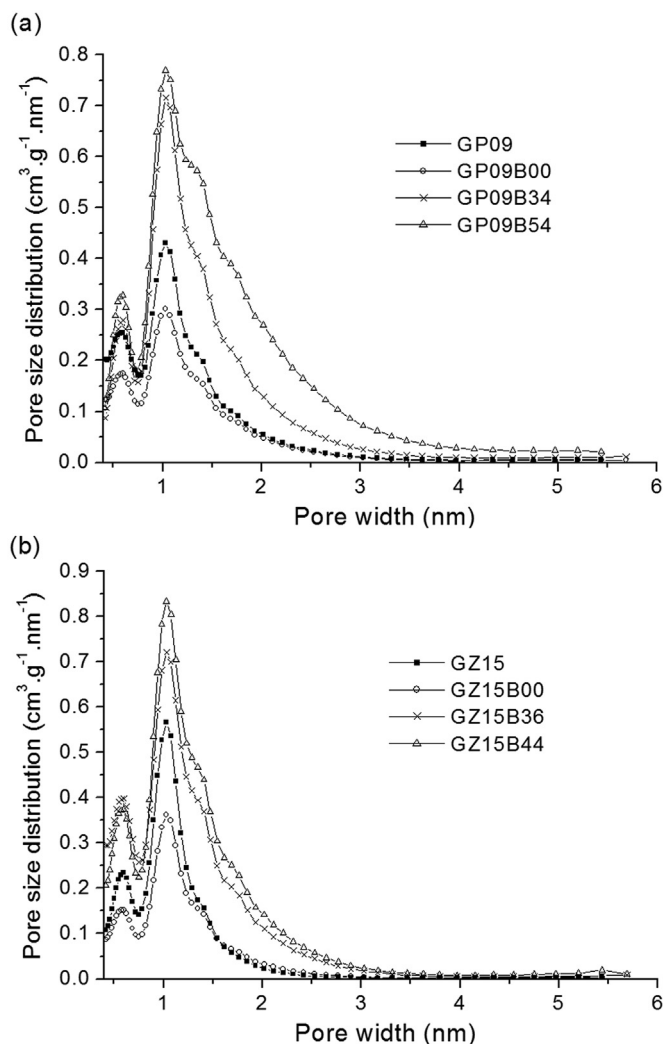


Fig. 6. PSD of granular carbons prepared by chemical activation with (a) H_3PO_4 or (b) ZnCl_2 , followed or not by additional carbonization up to 850°C and gasification with CO_2 . (A colour version of this figure can be viewed online.)

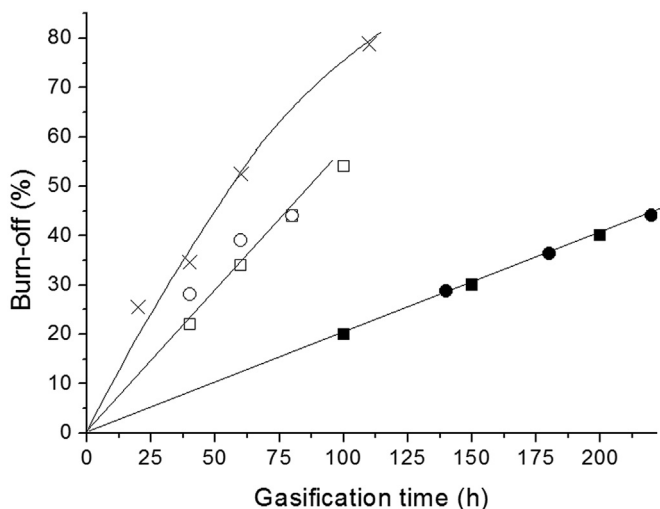


Fig. 7. Burn-off versus gasification time during physical activation with CO_2 of the samples GB00 (\times), GP09B00 (\square), GP21B00 (\circ), GZ15B00 (\bullet) and GZ25B00 (\blacksquare). (A colour version of this figure can be viewed online.)

(GZ15B00 and GZ25B00). These facts suggest that the gasification rate is related to the material hardness, which, as previously reported [16], is higher for chemically activated carbons, especially for those activated with ZnCl_2 . Supposedly, a higher hardness reflects a higher material ordering, which in turn increases the material resistance to gasification. Indeed, the fracture of the carbons activated with ZnCl_2 discloses a metallic shine in the interior of the grains, which suggests the existence of some ordering, while the fracture of the carbons activated with H_3PO_4 or CO_2 reveals a dull surface characteristic of disordered materials.

3.3.3. Waste volume

Fig. 8 confirms that, as expected, the waste volume of the carbons prepared by the combined methodology is lower than those verified for the adsorbents obtained by simple physical activation are. It is also valid to mention that the series corresponding to the lowest chemical loading, GP09BXX and GZ15BXX, present higher V_w in comparison with the GP15BXX and GZ25BXX series. This finding is in accordance with Fig. 4 and related discussions in Subsection 3.2, where it was portrayed that X_P and X_{Zn} values of 0.09 and 0.15, respectively, were not sufficiently high to prevent completely the occurrence of macropores.

3.3.4. Pore morphology

Fig. 9 highlights that, compared to the isotherms of physically activated carbons, the isotherms of carbons produced by the combined methodology present: (i) a less rounded knee, which is indicative of a narrower micropore size distribution; (ii) a lower inclination in the linear portion and a smaller hysteresis loop, if any, which are indicatives of lower mesopore content. These findings reveal that the combined methodology leads to the preparation of carbons with even narrower pore size distributions than those obtained by simple physical activation, which can be interpreted as follows. The sample carbonized in the absence of chemicals presents a highly disorganized structure constituted by aromatic sheets and strips, usually bent, with gaps between them [32]. During physical activation with CO_2 , the gas diffuses through the gaps and the pore structure is developed by gasification. Since the gaps present variable format and size, the generated pores are not homogeneous. On the other hand, the reorganization that takes place during chemical activation leads to a partial closing of the

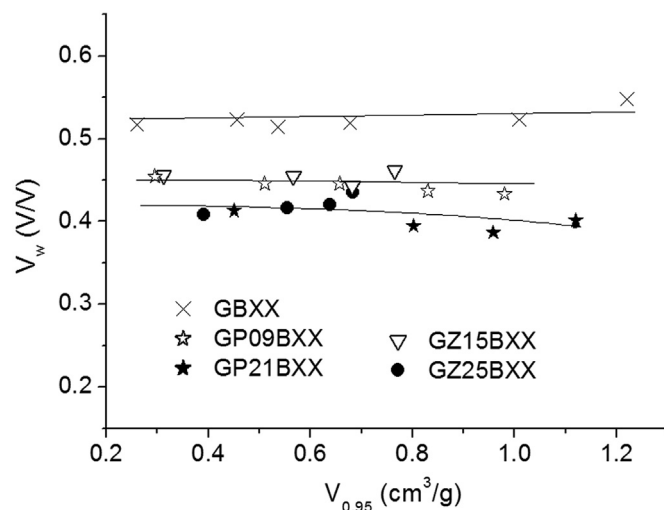


Fig. 8. Volumetric V_w for different series of granular carbons physically activated with CO_2 (after previous chemical activation or not). (A colour version of this figure can be viewed online.)

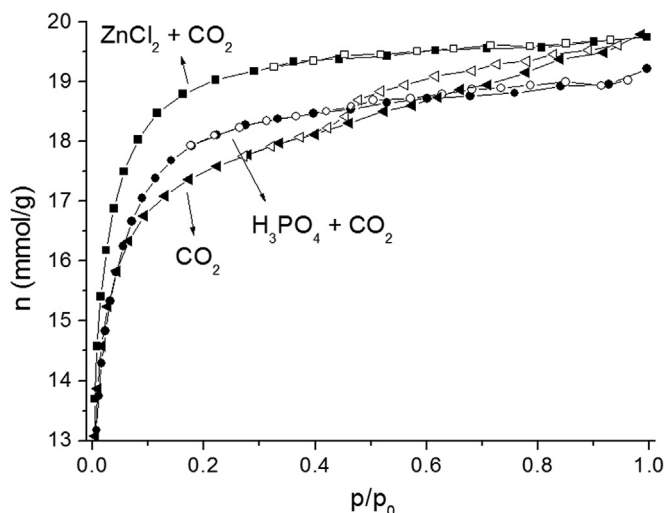


Fig. 9. N_2 adsorption-desorption isotherms of granular carbons obtained by physical activation with CO_2 (triangles) or the combination of chemical activation with H_3PO_4 (circles) or $ZnCl_2$ (squares) followed by gasification with CO_2 . Closed symbols: adsorption; open symbols: desorption. (A colour version of this figure can be viewed online.)

gaps. If a small amount of chemical is used, it is homogeneously distributed throughout the material and an incipient structure of homogeneous pores is created, which can uniformly be developed by gasification with CO_2 to generate a very narrow pore size distribution.

3.3.5. CH_4 storage capacity

Fig. 10 shows that, the same way as verified for the physical activation of the as-carbonized precursor (Subsection 3.1), the volumetric V_{CH_4} reaches a maximum and decreases thereafter. However, since the samples previously submitted to chemical activation present a more developed incipient porosity than the as-carbonized precursor, the maximums during their subsequent physical activation took place at lower burn-offs: in the range of 30–35% for the former compared to around 50% for the latter. At this point, it is worthy to highlight that the need of a weaker gasification is favorable because it contributes to better global yields and to the obtaining of carbons with higher mechanical resistance.

Since the samples that underwent the less severe chemical activations (corresponding to $X_p = 0.09$ and $X_{Zn} = 0.15$) presented a less developed pore structure at 0% of burn-off, they needed higher burn-offs to reach the maximum volumetric V_{CH_4} . Further, the corresponding series (GP09BXX and GZ15BXX) reached higher maximum volumetric V_{CH_4} values than the series GP15BXX and GZ25BXX, in spite of the higher waste volume of the former (see Subsection 3.3.3). These results evidence that it is better to use just a softer chemical activation, even though some macroporosity remains, followed by a more intense gasification with CO_2 to develop an appropriate porosity to store CH_4 .

As the granular carbons obtained by the combined methodology were able to conciliate the advantages of physical (higher skeleton density and narrower pore size distribution) and chemical (lower waste volumes) activations, the maximum volumetric V_{CH_4} enhanced with respect to those verified for the isolated methodologies.

The maximum value verified for the series corresponding to the use of $ZnCl_2$, 89 V/V, was higher than that verified for the series using H_3PO_4 , 85 V/V. This result can be related to the narrower pore size distribution that chemical activation with $ZnCl_2$ generates if

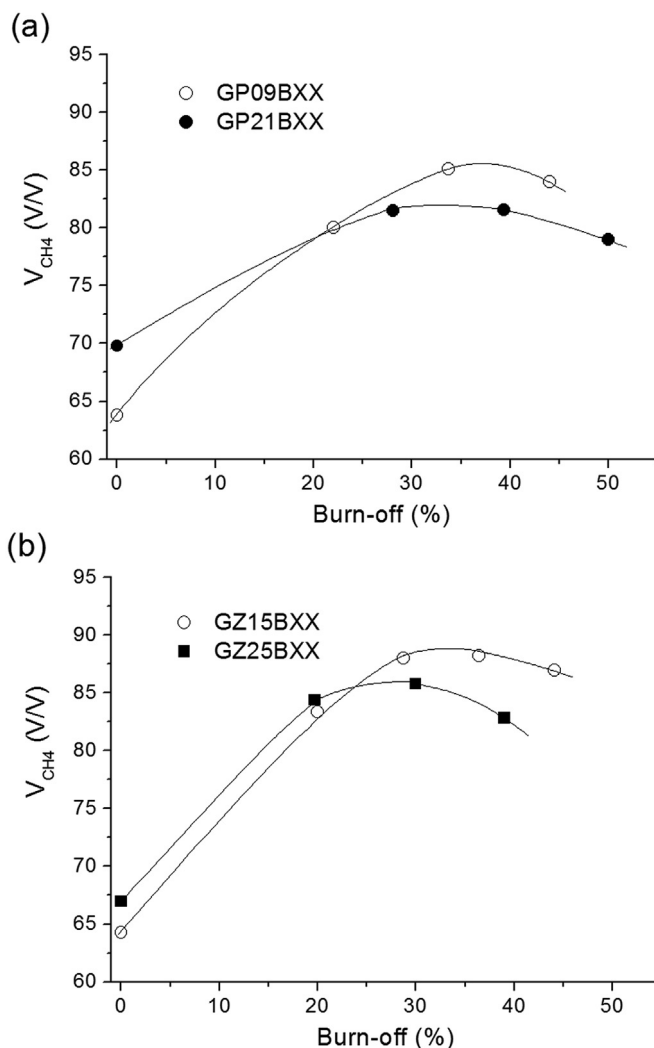


Fig. 10. Volumetric V_{CH_4} of granular carbons obtained by chemical activation with (a) H_3PO_4 or (b) $ZnCl_2$ followed by physical activation with CO_2 . (A colour version of this figure can be viewed online.)

compared to the activation with H_3PO_4 , a feature that has been previously pointed out [16].

3.3.6. Final considerations about the granular activated carbons

The V_{CH_4} presented above (Subsection 3.3.5) are relatively low due to the presence of higher interparticle space. However, this interparticle space can be reduced by the appropriate mix of particle with different sizes, as demonstrated in a previous work [14], so that V_{CH_4} can be further improved above 6%. In addition, it is worthy to highlight that the filling of the interparticle space with compressed gas considerably increases the total storing capacity. In the cases of the samples GP09B34 and GZ15B36, which presented volumetric V_{CH_4} values of 85 and 89 V/V, the total CH_4 storing capacities estimated by Eq. (3) reached 98 V/V and 102 V/V, respectively.

Although these values are still low for applications in which the drive range is a crucial factor, as it is the case of vehicular application, they can be considered reasonable for other applications, mainly if taken into account the easiness for obtaining the granular materials. For example, 100 V/V was the target established by Petrobras S.A. to make viable the gas transportation in mobile pipelines [33].

3.4. Carbon forms with increased bulk density

Enhanced volumetric adsorption capacities were achieved by producing activated carbons with reduced interparticle space, which was made by two different ways, as described in Subsections 3.4.1 and 3.4.2.

3.4.1. Powered/compressed carbons

Although powdered carbons are less appropriate from the point of view of application in gas storage systems, they can be conformed into monoliths by using a binder and applying heat and pressure [3,34]. In this context, some authors use to determine the volumetric adsorption capacity of powdered carbons by measuring their bulk volume when submitted to a given pressure in a mould. Then, they take the determined value as an estimative of the performance of monoliths that could be obtained, even though it is well known that binders usually obstructs part of the porosity or make it partially unavailable for adsorption [35]. At this point, it is worthy to stress that Casco et al. [2] and Celzard et al. [35] showed that activated carbons do not loss adsorption capacity after been submitted to compression at 753 kg/cm² and 222 kg/cm², respectively.

In the present work, the granular carbons that presented the best performance for CH₄ adsorption, GP09B34 and GZ15B36, were ground into a powder and submitted to a pressure of 450 kg/cm² in a mould. In this way, the bulk density of the resulting samples (termed CP09B34 and CZ15B36) increased from 0,49 cm³/g to 0,81 and 0,80 cm³/g, resulting in enhanced volumetric V_{CH_4} of 138 V/V and 148 V/V. Further, by applying Eq. (3), total CH₄ storing capacities of 155 V/V and 165 V/V were estimated.

3.4.2. Monolithic activated carbons

In the present work, cylindrical monolithic activated carbons were not prepared by the traditional method, in which a binder is used to bond together a previously prepared powdered activated carbon [3,34]. Instead of that, the monoliths were conformed by pressing precursor particles impregnated with H₃PO₄ or ZnCl₂ in a mould under heating, according to a previously described method [12,13]. In this method, the action of the dehydrating agent confers to the impregnated grains a self-sintering ability, making unnecessary the use of a binder.

The activation of the monoliths was carried out aiming to replicate as much as possible the combined methodology employed to prepare granular carbons, that is to say, a soft chemical activation with H₃PO₄ or ZnCl₂ followed by physical activation with CO₂.

By using H₃PO₄ as the chemical agent, X_p values and conforming temperature and pressure of 0.15, 190 °C and 160 MPa, respectively, we obtained the conditions that propitiated a better monolith conformation. The samples prepared under these conditions were subsequently submitted to physical activation with CO₂ to render the series MP15BXX. Outstandingly, in spite of its higher chemical loading, the monolithic sample MP15B00 presented a lower surface area and porosity than the granular sample GP09B00 (compare the data in Tables S6 and S8 – Supplementary materials). Such behavior evidences that, during the conformation step, considerable part of the chemical is removed from the impregnated sample due to the applied pressure.

A maximum volumetric V_{CH_4} of 145 V/V was verified for the MP15BXX series (Fig. 11) and a V_{CH_4} of 163 V/V was estimated for the sample MP15B33. These values are among the highest reported in the literature for monolithic activated carbons at similar adsorption temperature and pressure (298 K and 3.5 MPa). For example, Lozano-Castelló et al. reported a maximum V_{CH_4} of 140 V/V for monoliths produced from the activation of a Spanish anthracite with KOH and using different binders [3]. In turn,

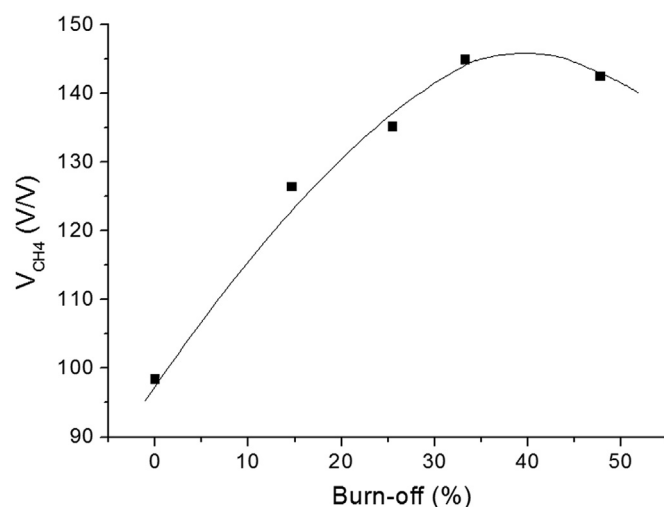


Fig. 11. Volumetric V_{CH_4} of the monoliths obtained by chemical activation with H₃PO₄ followed by gasification with CO₂ up to different burn-offs. ($X_p = 0.15$; conforming temperature and pressure of 190 °C and 160 MPa, respectively – MP15BXX series).

Policchio et al. [4] and Inomata et al. [36] reported maximum V_{CH_4} of 147 and 164 V/V, respectively, after physical activation with CO₂ of bindersless activated carbon pellets prepared by pressing cellulose microcrystalline samples.

Outstandingly, the maximum V_{CH_4} attained for the monoliths, 145 V/V, was higher than that verified for the sample CP09B34 (138 V/V), which derived from the powdering/compressing of the best sample of granular carbon obtained by chemical activation with H₃PO₄ followed by physical activation with CO₂. This behavior can be attributed to the occurrence of a lower waste space in the monoliths as a consequence of the preparation procedure, as discussed in the sequence.

Firstly, during the conforming step, the impregnated particles are in a plastic state due to the action of the dehydrating agent, which permits their deformation and, therefore, their accommodation in a way that minimizes the occurrence of interparticle space. In turn, independently of the pressure applied to the powdered carbon samples, considerable interparticle space always remains among their rigid particles. Secondly, it is needed to note that the monoliths were prepared using a X_p of 0.15 and, according to Fig. 4, this value is sufficient to reduce the waste volume to a minimum. Further, since part of the chemical is removed during the conformation step, as stressed above, a lower amount of H₃PO₄ remains in the interior of the particles during the subsequent carbonization, so that only a quite soft chemical activation takes place, as desirable for the attaining of a very narrow pore size distribution. Comparatively, during the production of granular carbons, such a narrow pore size distribution is achieved only by using much low chemical loadings which, in turn, are not sufficient to completely prevent the occurrence of macropores (see pertinent discussions in Subsection 3.2), so that the volumetric adsorption capacity is reduced.

Concerning the monoliths prepared using ZnCl₂, they presented failures that compromised their mechanical resistance. Therefore, the pieces were very susceptible to collapse during the subsequent carbonization/gasification. This behavior seems to be related to that ZnCl₂ is less efficient than H₃PO₄ to confer self-sintering ability to the impregnated grains (supposedly due to the weaker acidic character of the former). Therefore, the particles would not have been efficiently packed and adhered to one another, ending up in the occurrence of cracks in the pieces. Indeed, a comparison of Fig. 12a and b shows that, in the case of the monoliths produced

with H_3PO_4 , the particles are more packed and stuck together; on the other hand, in the case of the monoliths produced with ZnCl_2 , cracks can be clearly identified among the particles, as indicated by the arrows.

4. Conclusions

Granular, powdered and monolithic activated carbons intended for CH_4 storage were obtained from coconut shell. The adsorbents were prepared by chemical activation with H_3PO_4 or ZnCl_2 and/or physical activation with CO_2 . The maximum volumetric values of volumetric excess CH_4 adsorption capacity and total CH_4 storing capacity (V_{CH_4} and V'_{CH_4} , respectively) are summarized in Fig. 13. The best results were achieved by using the combination of a relatively soft chemical activation with H_3PO_4 or ZnCl_2 , just the sufficient to minimize the presence of macropores, followed by physical activation with CO_2 to increase the skeleton density and to develop a narrow pore size distribution mostly located around the diameter/width optimum for CH_4 adsorption. Thus, V_{CH_4} values of 90 and 94 V/V were verified for the granular carbons prepared using H_3PO_4 and ZnCl_2 as the chemical agent, respectively. The estimated V'_{CH_4} were 98 and 102 V/V. By powdering and

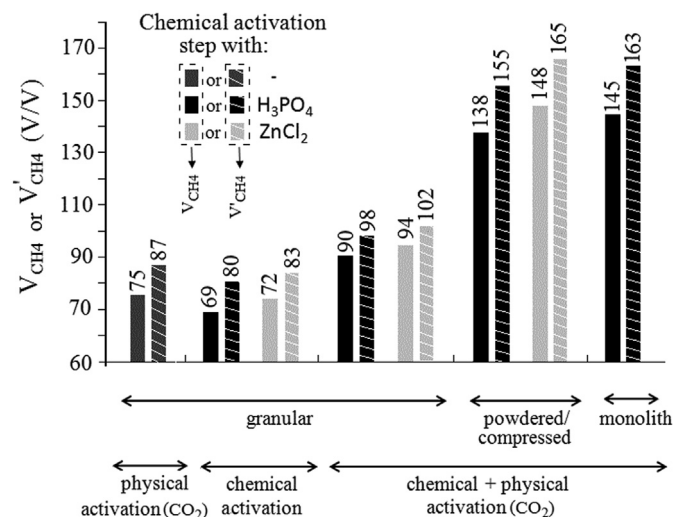


Fig. 13. Maximum V_{CH_4} and V'_{CH_4} verified for the different activated carbons produced in the present work. (A colour version of this figure can be viewed online.)

compressing these samples, the bulk density increased, so that V_{CH_4} enhanced to 138 and 148 V/V and V'_{CH_4} enhanced to 155 and 165 V/V. Finally, cylindrical monolithic carbons were prepared using a binderless methodology by compressing precursor grains impregnated with H_3PO_4 and ZnCl_2 . In the case of ZnCl_2 , the monoliths presented cracks that compromised their integrity. However, in the case of H_3PO_4 , monoliths with good mechanical resistance and V_{CH_4} and V'_{CH_4} values as high as 145 and 163 V/V were achieved, respectively.

The capacities of adsorbing and storing CH_4 verified for the samples produced in the present work are among the highest reported in the literature for activated carbons. It is valid to highlight that the materials were prepared from a low cost and abundant agricultural by-product, which is very important in large-scale application such as gas transportation and gas storage in vehicular fuel tanks. Besides, the adsorbents can directly be produced in the form of grains and monoliths with good mechanical resistance, as desirable for gas adsorption systems.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.carbon.2016.08.092>

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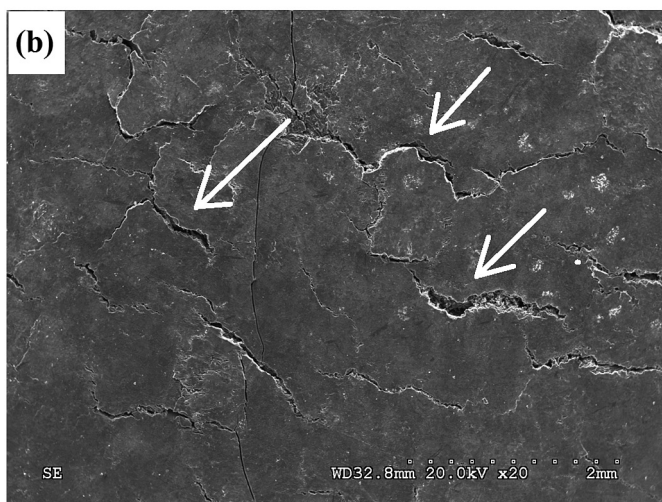
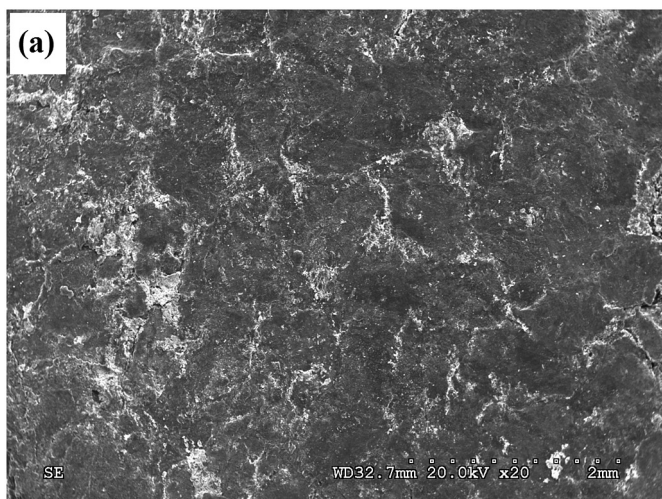


Fig. 12. Scanning Electron Micrographs ($\times 20$) of the superior surface of monoliths prepared using (a) H_3PO_4 or (b) ZnCl_2 as the chemical agent. (A colour version of this figure can be viewed online.)

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