

Effect of pyrolysis temperature on CH₄ adsorption properties of microporous carbon material

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Abstract— this paper investigates the production of a series of activated carbon pellets without a binder (ACP) using olive stones by chemical process and activated with phosphoric acid were studied for CH₄ storage applications. The total surface area, pore volume, and average pore volume were evaluated from the analysis of N₂ adsorption isotherm data. The characterization of carbon materials is performed by scanning electron microscopy (SEM). The effect of pyrolysis temperature on textural and gas adsorption capacities of the ACP were investigated by adsorbing CH₄ at room temperature in the pressure range between 1 and 23 bars. The results reveal that all the ACP had high CH₄ adsorption capacity and the highest CH₄ adsorption value is 4.73 mmol/g obtained at 23 bars.

Keywords— Porous materials, Olives stones, Pyrolysis temperature, CH₄ storage.

I. INTRODUCTION

Activated carbon is defined as a carbonaceous material with a large internal surface area and highly developed porous structure resulting from the processing of raw materials under high temperature reactions. It's composed of 87% to 97% carbon but also contains other elements depending on the processing method used and raw material it is derived from [1]. Although activated carbon can be produced from almost any raw material, it is most cost effective and environmentally conscious to produce activated carbon from waste materials. The pore structure of activated carbons depends on many factors. Among them, the composition of the starting material,

heat treatment, activating agents and post treatment methods. Activated carbon can be manufactured from several carbon raw materials, such as Corn Cob [2], apricot stone [3, 4], grape seeds [5], almond shells [6, 7], olive stones [6, 8], coconut shells [9], cherry stones [5, 10], oil-palm shells [11], sugar cam wastes [12], and nutshells [13]. The production of an economical carbon adsorbent for natural gas storage has been actively pursued in recent years. Natural gas, whose main component is methane, is an advantageous fuel as compared with other more conventional energy sources because of its abundance and cheapness and as a fuel for vehicles. Upon combustion, natural gas burns more cleanly than gasoline, with respect to atmospheric ozone formation and carbon monoxide emissions [14].

Capture, separation and storage of this gas is present social issues essential both in environmentally and economically. Most research works have been focused on the texture of microporous carbon, and the ideal carbonaceous adsorbents designed for methane storage should combine the highest possible micropore volume and the highest possible apparent density [15,16–19]. Most research suggested that the amount of methane uptake increases when micropore predominates in the carbon, whereas the volume of larger pores does not contribute significantly to the adsorption of methane [16,20].

The methane can also be valued as a source of clean energy as a fuel for vehicles. The aim of the present work is to prepare a series of chemically activated carbon pellets using olive stone as carbon precursors. The adsorption capacities CH₄ on the prepared activated carbons are also presented. The paper pays special attention to the influence of temperature treatment of activated carbon pellets on the pore volume and pore size

distribution studying the way that these properties affect the volumetric gas adsorption capacity.

II. EXPERIMENT

Olives stones were chosen as raw material, since they are extensively generated in Tunisia, olives stones were obtained from local olive manufactures, her particle size in the range of 1.25 mm- 4 mm is used [21]. A series of activated carbon pellet were prepared in our laboratory using olives stones in two steps process: chemical activation and carbonization. In the chemical process, some amount of granular olives stones was mixed with aqueous solution containing 50% H_3PO_4 (w/w) at the weight ratio of 1/3. The suspension of the olives stones in chemical impregnation solution was mixed at 110 °C for 9 hours. Impregnate olives stones powder was used as raw material; with a size of about 80 μm . A mass of 0.6 g of the raw material was placed between the pistons in the dice and the mechanical pressure, P, was loaded on them for 1 min by an oil hydraulic machine. After the compression, the impregnate olives stones ejected from the dice were columnar pellets. The pellets were thermally activated in a fixed bed vertical reactor tubular furnace under nitrogen continuous flow for 3 hours at different carbonization temperatures in the range from 350 °C to 1000 °C. After cooling, activated carbon pellet was washed for several times with hot water until the pH of washing solution became neutral. The samples were dried at 110 °C to get the final product. The nomenclature of each sample includes the pyrolysis temperature and the abbreviation of activated carbon pellets (ACP): for example the activated carbon pellet carbonized at 410 °C will be denoted ACP410. The surface area and the porous texture of the carbons were characterized using nitrogen sorptiometry at 77 k on the automatic Quantchrome Autosorb1 C apparatus. Scanning electron microscope (SEM) was used to investigate the morphology of the samples. In this paper homemade adsorption instrument made by the research team MADIREL chemistry lab Provence was used to test adsorption capacities of CH_4 over the activated carbon pellets at 303 k in the pressure range between 1 and 23 bars after degassing with a vacuum pump overnight and at temperature 423 k (figure 1).

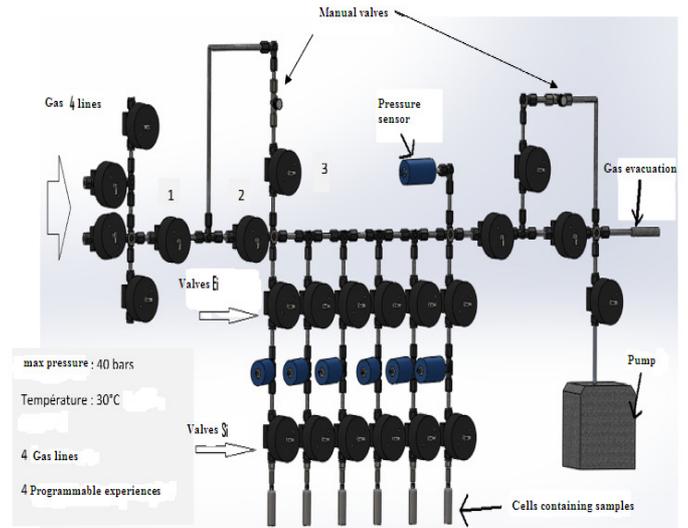


Fig. 1. High-throughput adsorption apparatus

III. RESULTS

Figure 2 shows the N_2 sorption isotherms of the activated carbon pellets samples at -196 °C. Shapes of the activated carbon pellets samples isotherms prepared at high pyrolysis temperature, designed by ACP800 and ACP1000, show that these isotherms are between types I and II according to the IUPAC classification [22]. This shape suggests a strong development of microporosity. It is characteristic of the presence of microporous structure with rather narrow pore size distribution. However the shapes of the other isotherms of activated carbon pellets are of type II. This indicates that these carbonaceous solids are also essentially micro-porous. One can observe that after a relative pressure of 0.7, there is an increase of adsorbed amount, and this is most probably due to the presence of mesopores, where there is deposition of multi-layer as the pressure goes up and condensation of N_2 occurs near saturation. The minimal slope of the isotherms indicates that the activated carbons are essentially microporous solids. Activation and pyrolysis of the raw olives stones by inert gas (N_2) allow increase in the porosity. This rise is probably due to the elimination of volatile matters produced during pyrolysis and release of the surface to create new pores in the carbon structure.

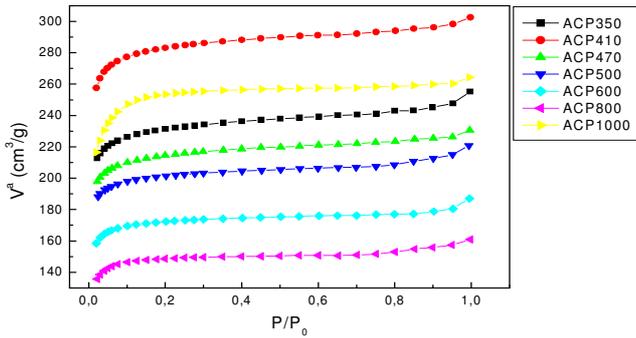


Fig. 2. N₂ adsorption isotherms of pellets activated carbon. Vⁿ is the volume of liquid nitrogen adsorbed per gram of the sample.

Scanning electron micrographs observation of activated carbon pellets (ACP1000) is shown in Figure 3. The examination of the structure of samples shows the presence of macropores of various sizes and geometries at the surface. Micrographs show some regular structured shape: plane and thin stacked forms of a few mm and with large interparticle voids.

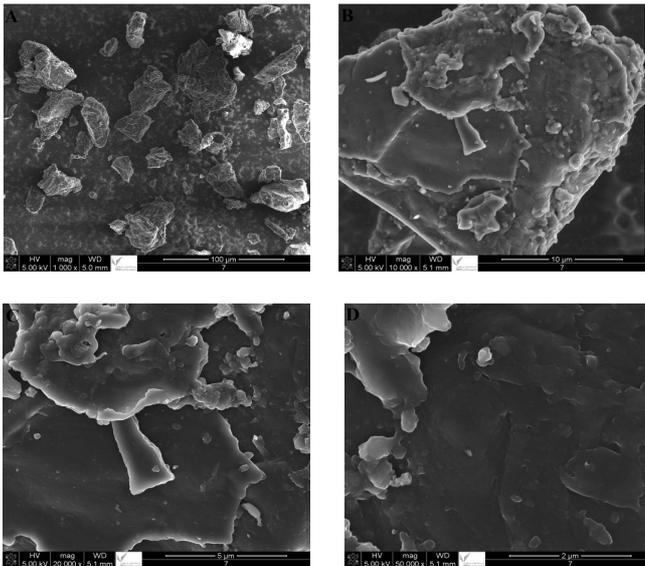


Fig. 3. Scanning electron micrographs of ACP1000 sample.

Figure 4 shows the methane adsorption corresponding to those samples prepared at different pyrolysis temperatures. It can be seen that in general, CH₄ adsorption capacity increases with the micropore volume with the existence of some exception. Comparing the shape of CH₄ adsorption isotherms with that of N₂ adsorption isotherms, it can be said that they follow similar trends, which indicates that methane adsorption mainly occurs in the microporosity. That the highest methane adsorption

capacity corresponds to the sample with the highest micropore volume (ACP410). However, the main point that we would like to remark on this graph (figure 4) is the effect of the micropore size distribution on the methane adsorption capacity.

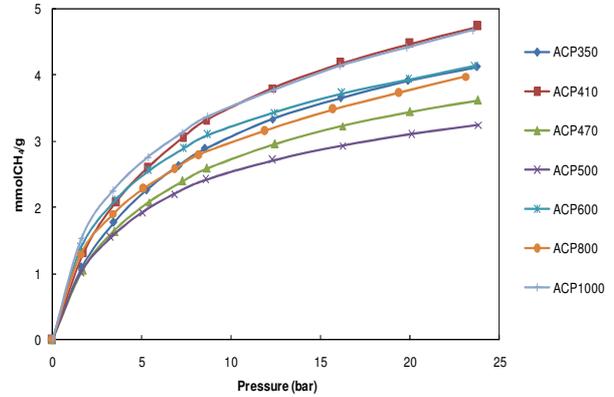


Fig. 4. Methane adsorption isotherms at room temperature

Fig. 5. represents BET surface area determined from N₂ adsorption data versus the CH₄ adsorption capacity at 23 bar. A linear relation is found between CH₄ storage capacity and BET surface area. We see that there are samples with micropore volume higher than the above values with deviate upward with respect to this line. This deviation happens for all those samples which have a considerable contribution of narrow porosity (pore size lower than 0.8 nm) which is not accessible to N₂ at 77 k but which can be reached by CH₄ at room temperature. These results show the importance of both micropore volume and micropore size distribution on CH₄ uptake.

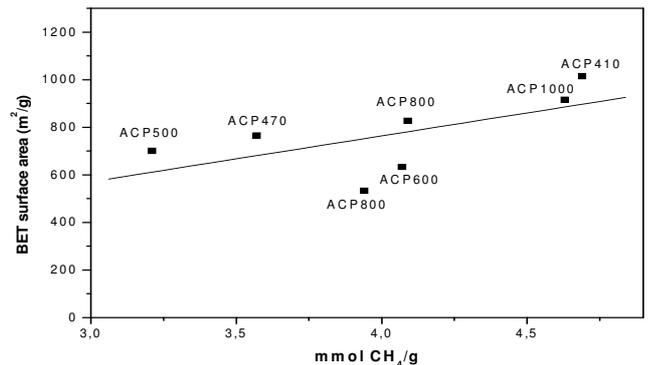


Fig. 5. Relationship between the CH₄ adsorption capacity at 23 bar and room temperature with the BET surface area calculated from N₂ adsorption isotherms.

IV. CONCLUSIONS

This work presents the study of the influence of pyrolysis temperature on the pores texture and the gas storage capacity of activated carbon and has shown the importance of micropore size distribution on the CH₄ adsorption capacity. It was seen that a sample with a higher micropore volume but a much wider micropore size distribution presents a lower gas storage uptake than a sample with a lower micropore volume where a large proportion of pores have the optimum size for methane adsorption, thus with these results it was demonstrated that CH₄ adsorption capacity not only depends on the micropore volume but also strongly depends on the micropore size distribution. The results of this study show that N₂ adsorption at 77 K does not adequately describe CH₄ adsorption capacity because the accessibility of this gas is kinetically restricted due to narrow microporosity.

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