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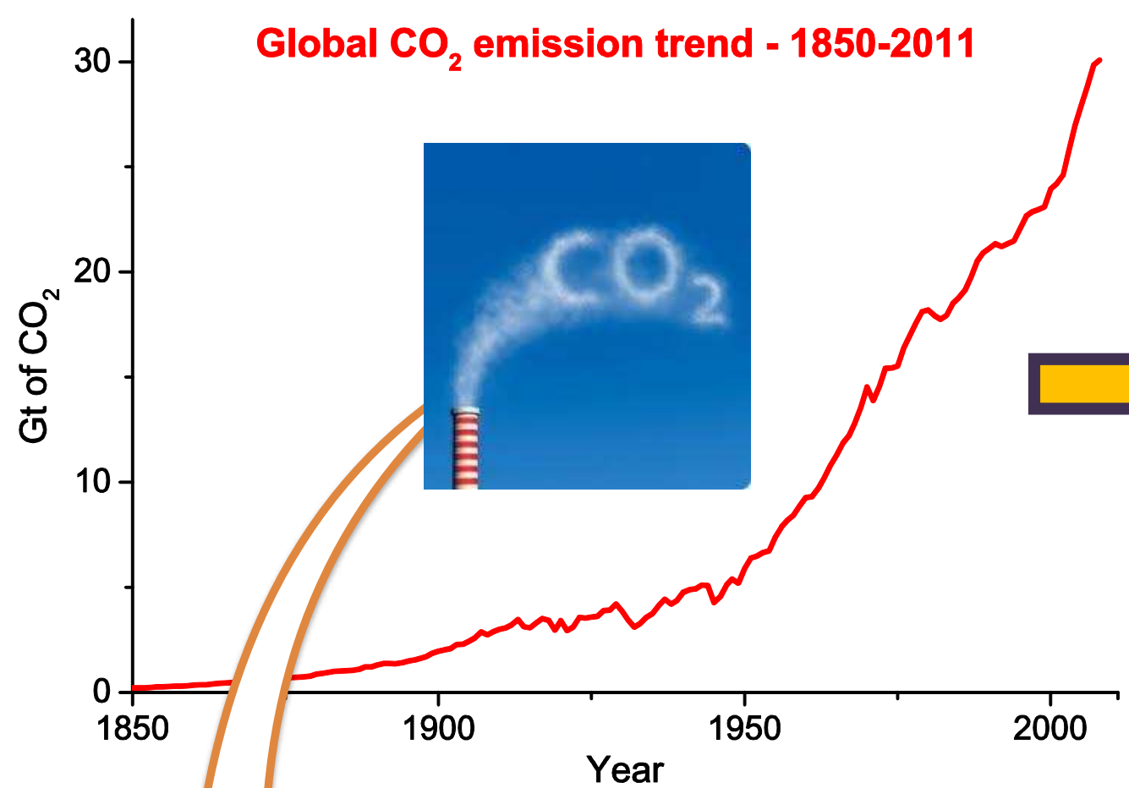
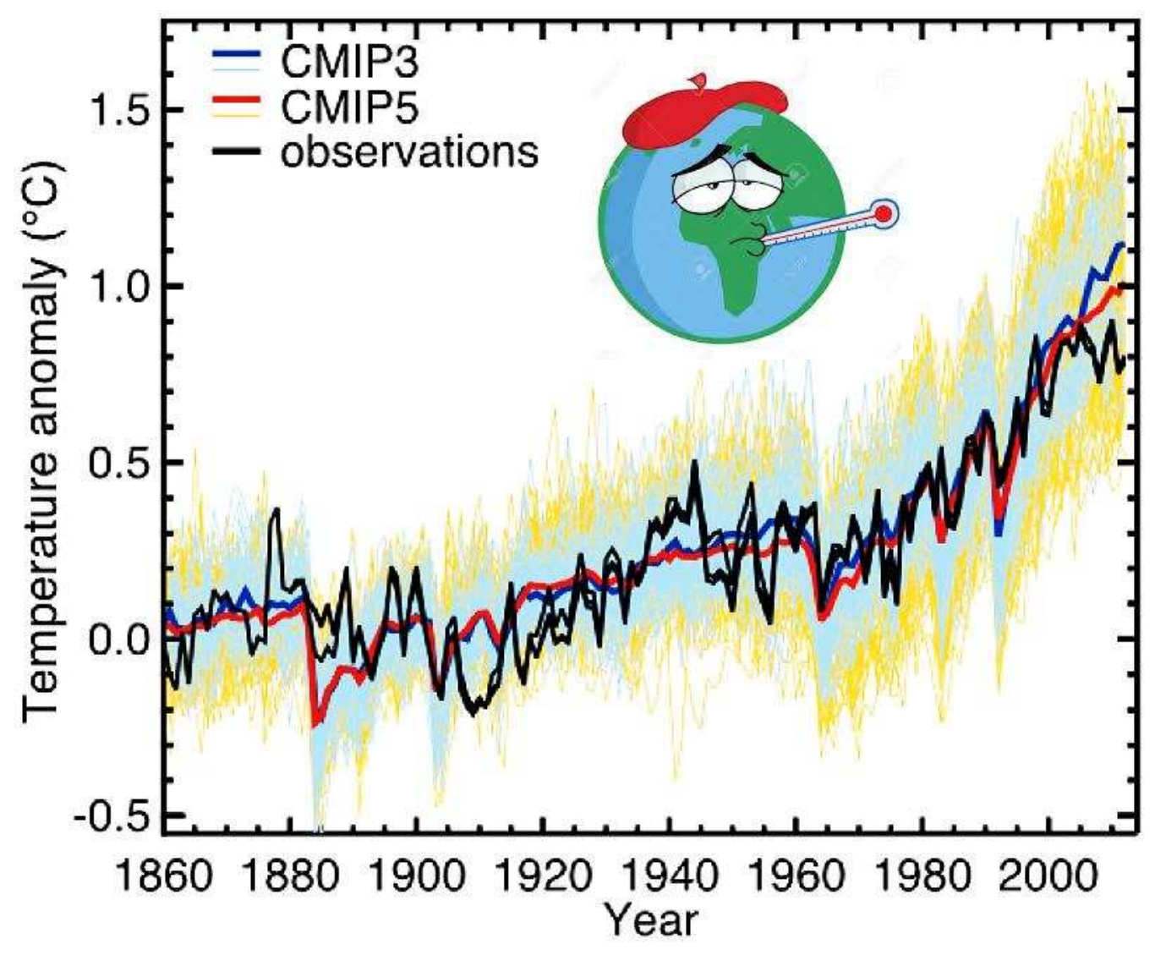
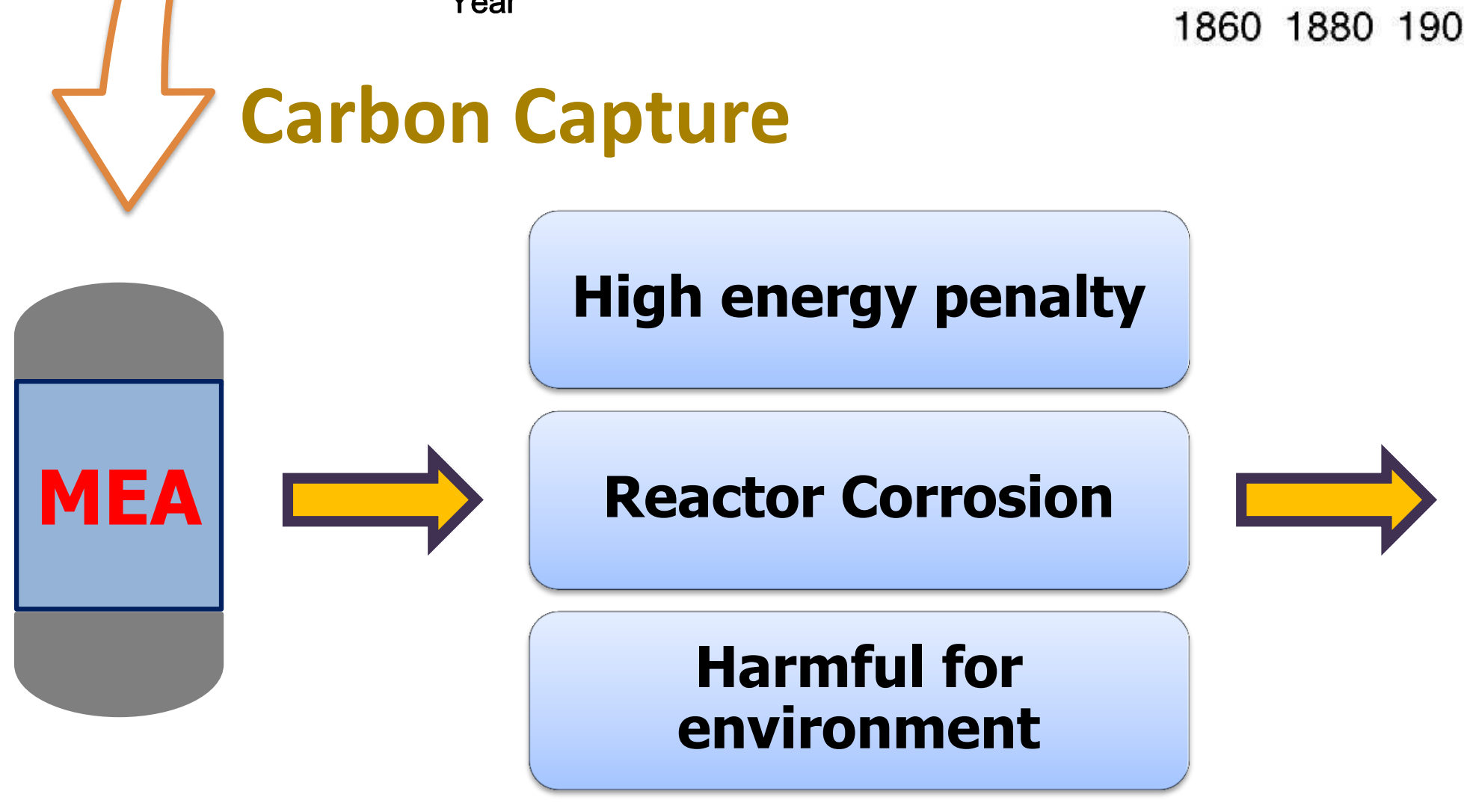
Eco-friendly synthesis of selective CO_2 sorbents for post-combustion capture: the key role of basicity

Abstract Selective CO_2 sorbents were successfully synthesized through carbonisation and physical (CO_2) activation of oak wood. ACs thus synthesized along with a commercial carbon (GAC) included for comparison purposes were tested for CO_2 capture. Under pure CO_2 and 35 °C, although having much lower surface areas (highest S_{BET} = 627 m^2/g), oak wood-derived carbons exhibited similar uptakes as those achieved by the commercial AC (S_{BET} = 1231 m^2/g). On the other hand, upon changing to post-combustion conditions (ca. 53 °C, 15 % CO_2/85 % N_2), oak wood-based sorbents exhibited as large as (OW250PA) or even greater (OW800PA) sorption capacity than the commercial AC. The higher selectivity shown by oak wood derivatives was associated with their substantial amount of Ca-based inorganic fraction (up to nearly 12 wt. % for OW800PA), evidently related to their outstanding basicity (up to 93 % for OW800PA). Conversely, commercial AC is characterized by a negligible inorganic content (less than 1 wt. %) and lower basicity (ca. 67 %). Accordingly, it was proved that under post-combustion conditions the contribution of a more favoured (basic) surface chemistry outweighs the texture effect. Basic functionalities ensured stronger interactions with the carbon dioxide molecule, therefore implying a more selective sorption at lower gas concentration. Moreover, sorbents selectivity toward CO_2 was obtained exploiting the advantageous properties (basicity) of the raw precursor rather than applying expensive and environmentally unsustainable chemical treatments.

What's the problem?







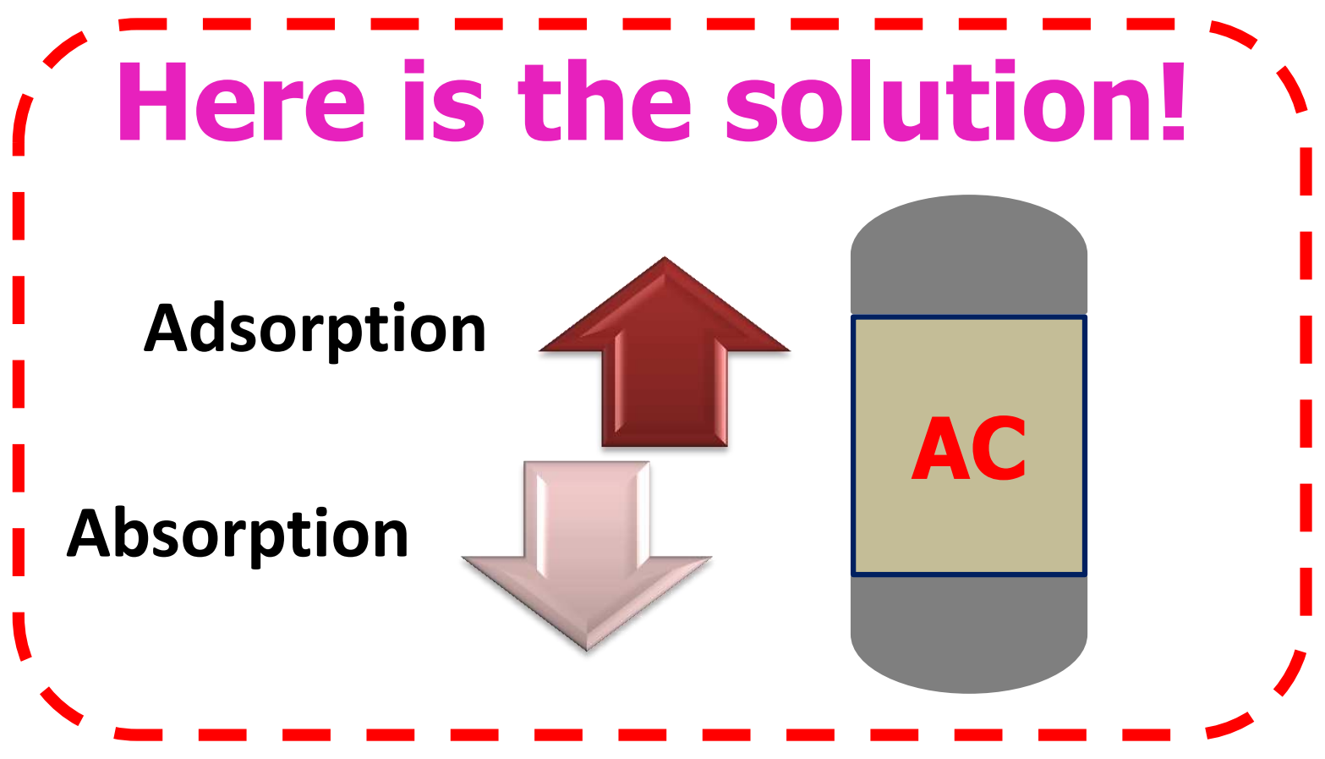
Carbon Capture

MEA

High energy penalty

Reactor Corrosion

Harmful for environment



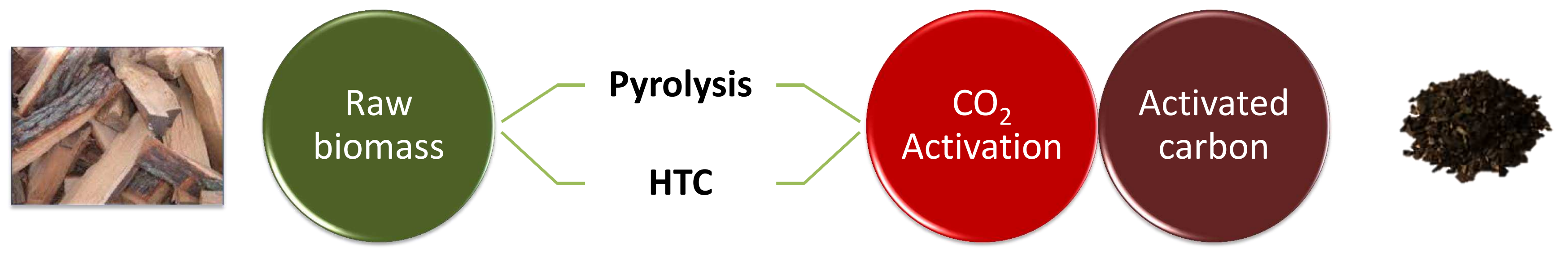
Here is the solution!

Adsorption

Absorption

AC

Eco-friendly methodology



Raw biomass

Pyrolysis

HTC

CO_2 Activation

Activated carbon

Oak wood (named as OW) was subjected either to traditional dry pyrolysis at 800 °C or to hydrothermal carbonization (HTC) at 250 °C. For both processes, desired temperature was hold for a dwell time of 1 h. Carbonization products, designated as OW800 and OW250 respectively, were then heat-treated (heating rate of 10 °C/min) in a horizontal tube furnace under CO_2 (0.6 l/min). Resulting activated carbons are referred to as OW800PA and OW250PA respectively.

Why is it interesting?

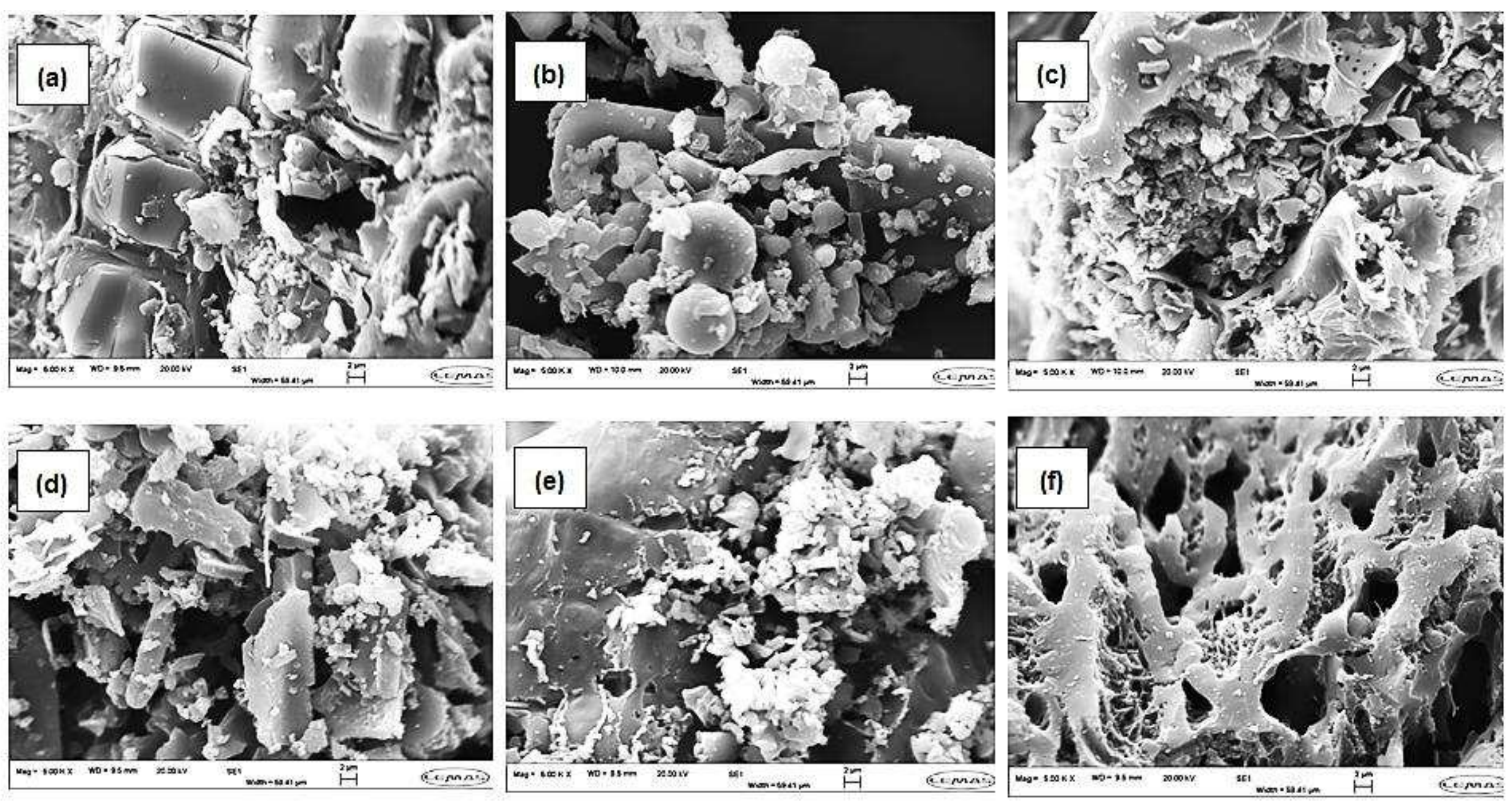


Figure 1. SEM micrographs at 5 Kx magnification for OW (a), OW250 (b), OW800 (c), OW250PA (d), OW800PA (e) and GAC (f)

Fig. 1 depicts the morphology of the materials. Unlike for the commercial carbon (GAC), raw oak wood and oak wood derivatives (chars/ACs) present inorganic particles dispersed onto their structure.

As proved by EDX chemical compositions (see Fig. 2) acquired onto the micrographs shown in Fig. 1, oak wood-based materials feature a significant inorganic content, mostly consisting of Ca-based compounds. These were identified by XRD as shown in Fig. 3. In particular, calcium hydroxide and calcium oxalate hydrate, initially present within the chars, were converted into calcium carbonate (carbonation) after activation process under CO_2.

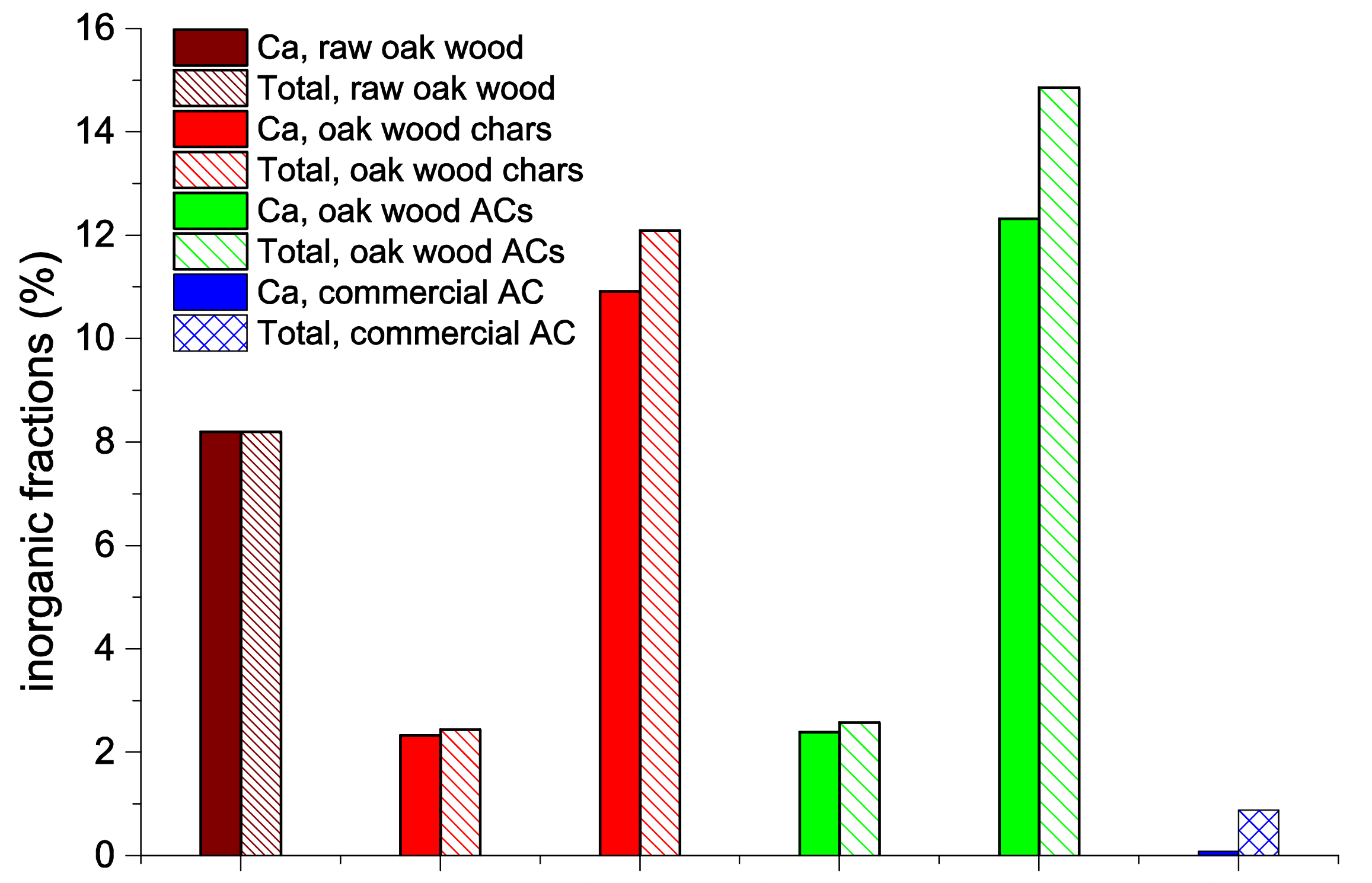


Figure 2. Ca and overall inorganic content obtained from EDX spectra acquired onto SEM images shown in Figure 1

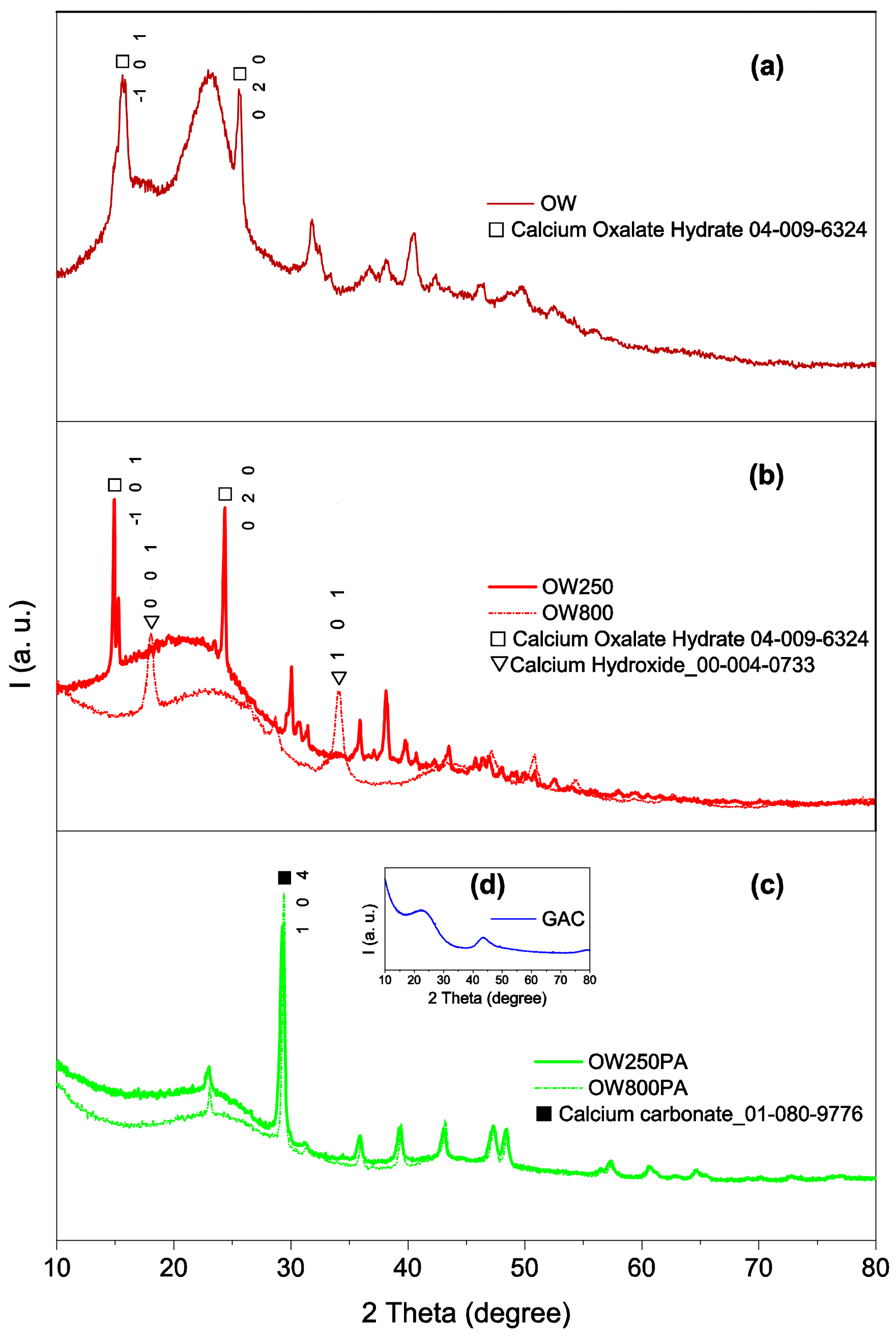


Figure 3. XRD patterns along with crystalline phase identified for raw oak wood (a), oak wood-based chars (b) and activated counterparts (c). Inset (d): XRD pattern for commercial carbon (GAC)

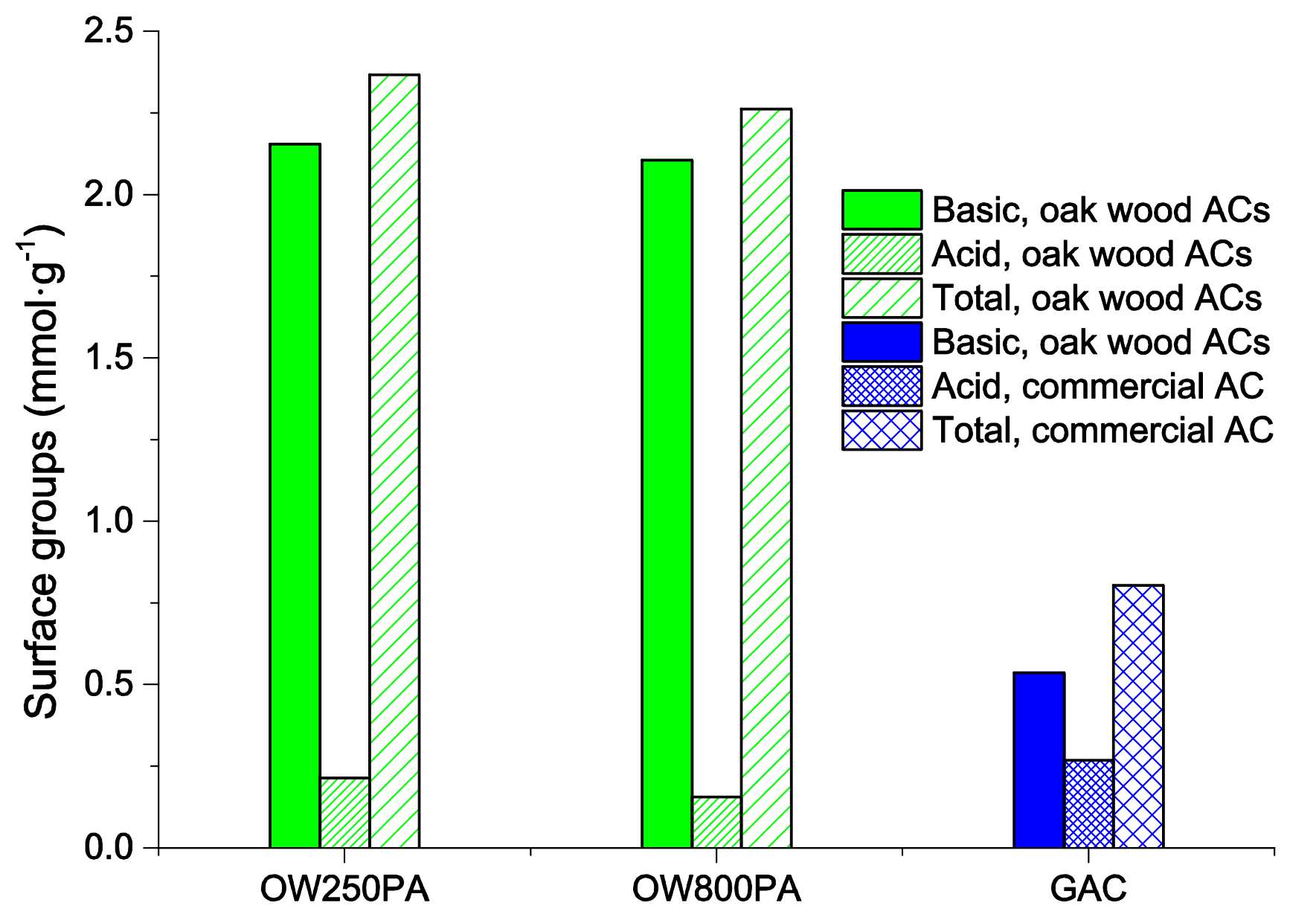


Figure 4. Surface groups number measured by Boehm's titrations for oak wood derived and commercial ACs

As illustrated by Figure 4, it is interesting to notice that oak wood-based ACs have a far more functionalized surface compared to that of GAC. Moreover, most of these functionalities are basic; as a result, basicity for oak wood ACs is much higher (up to 93 %) than that measured for the commercial carbon (ca. 67 %). In accordance with EDX and XRD results, it is reasonable to relate the more pronounced basic character of the oak wood derivatives to the presence of alkaline compounds within the carbon matrix.

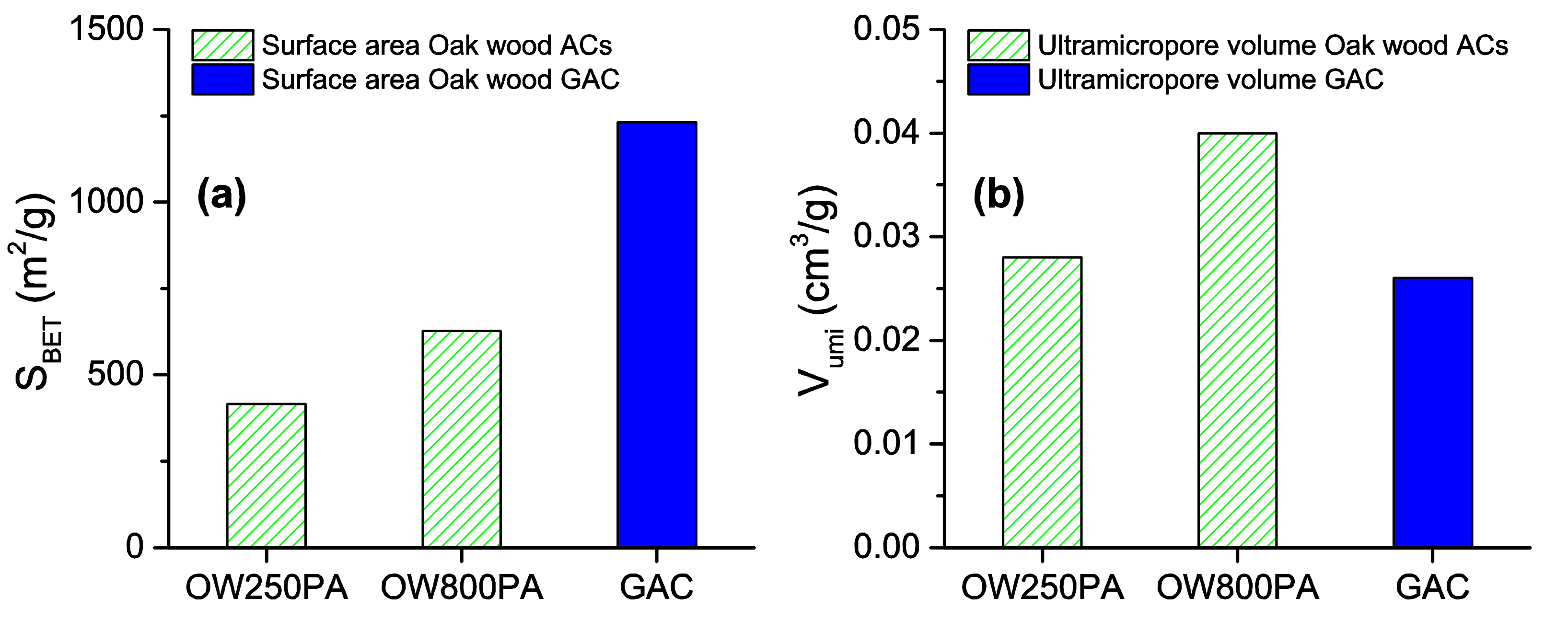


Figure 5. Textural parameters for oak wood-derived and commercial carbons: BET surface area (a) and ultramicropore volume (b)

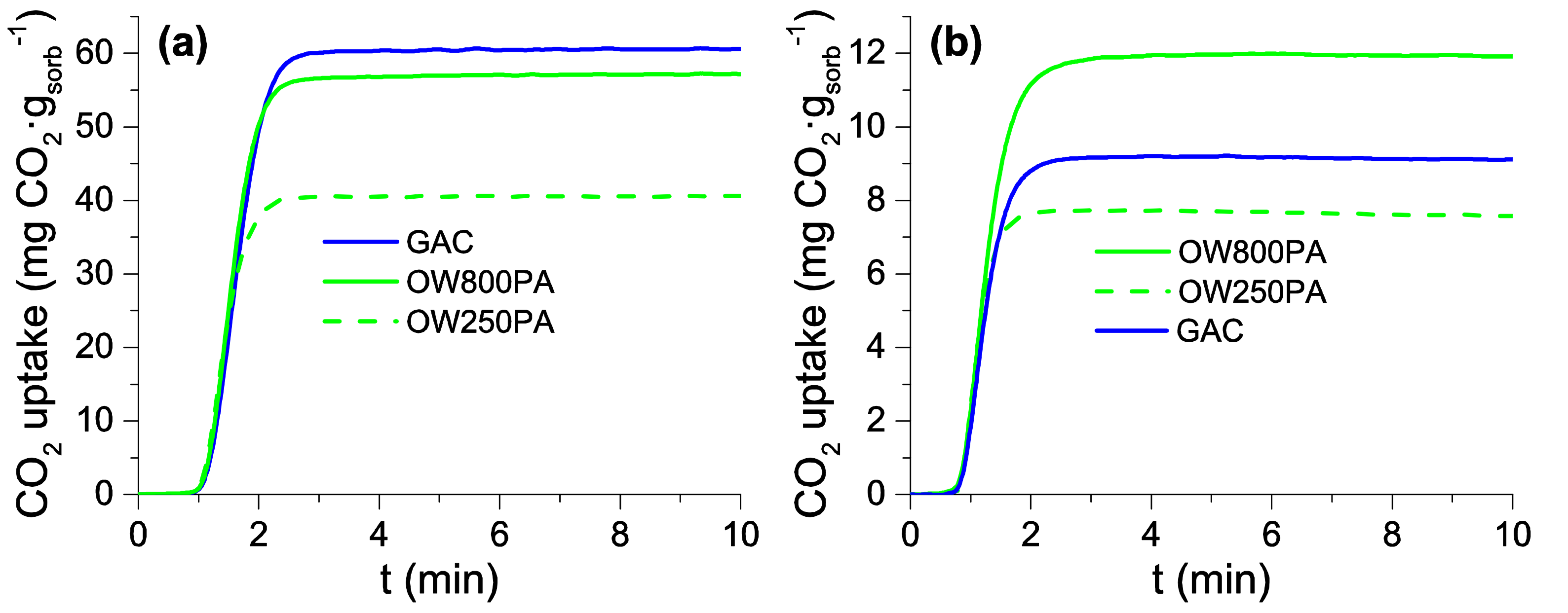


Figure 6. (a) Pure CO_2 uptakes at 35 °C and (b) 15 % CO_2 uptakes at 53 °C for oak wood derived and commercial carbon

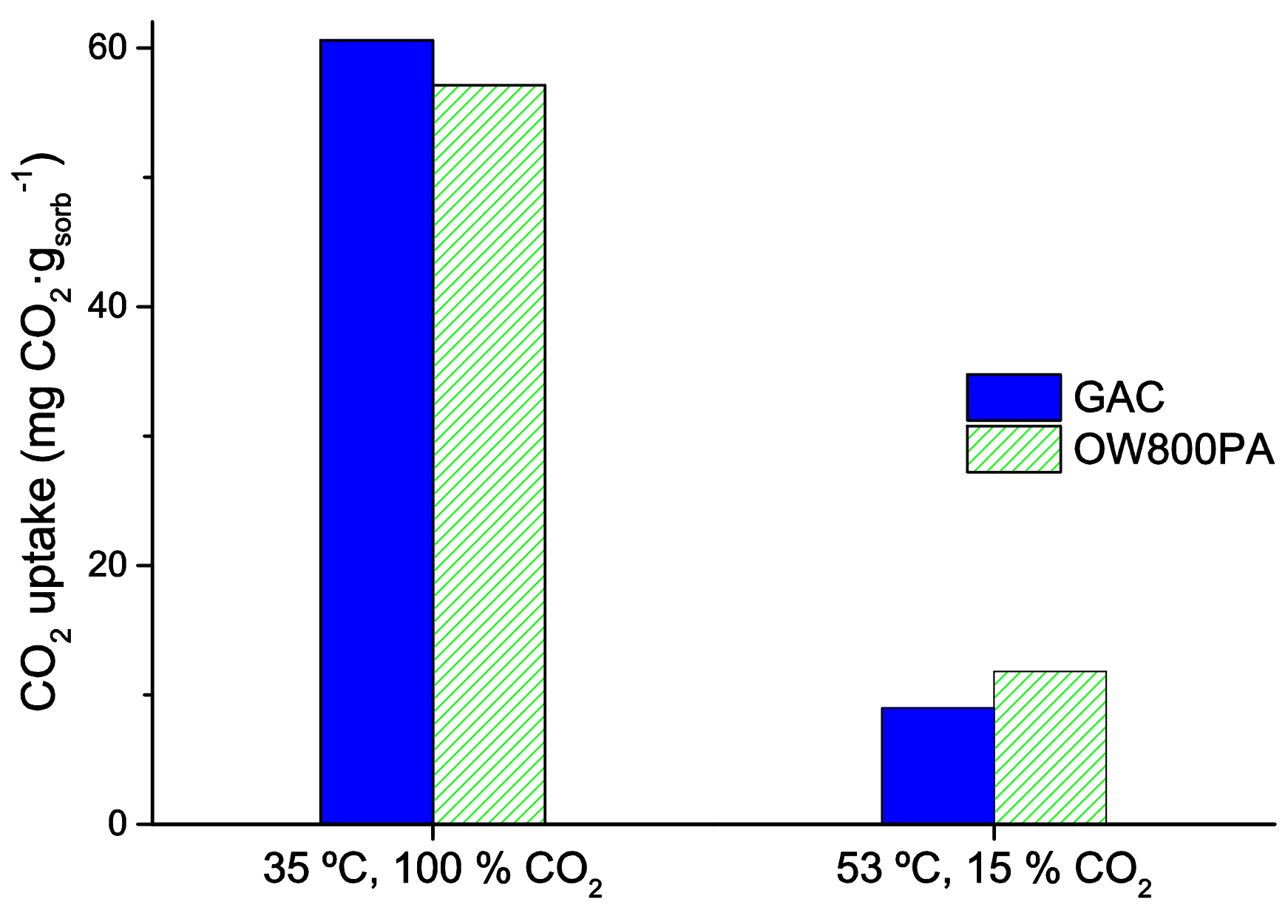


Figure 7. CO_2 uptakes measured at equilibrium under different conditions: comparison between OW800PA and GAC

As seen by Fig. 5a, commercial carbon's surface area is twice that of OW800PA. On the other hand, both samples show a low ultramicropore volume (Fig. 5b). This might explain the comparable pure CO_2 sorption measured at 35 °C (Fig. 6a), indicating that CO_2 is mainly adsorbed in narrowest pores (d<0.7 nm). Whereas, under post-combustion conditions, OW800PA exhibited larger uptakes than those achieved by GAC (Fig. 6b and 7). This behaviour was attributed to the higher basicity found for OW800PA (Fig. 4) which is responsible for a more selective CO_2 sorption.

Conclusions

Oak wood resulted to be an advantageous precursor for the synthesis of selective CO_2 sorbents. In particular, the alkaline compounds intrinsically incorporated within the raw material allowed producing highly basic sorbents without applying any chemical treatments. Under pure CO_2 and 35 °C, oak wood-derived ACs exhibited similar uptakes (ca. 60 mg CO_2·gsorb^{-1}) to those achieved by a commercial carbon having far larger surface area. On the other hand, under simulated post-combustion conditions (ca. 53 °C, 15% CO_2), OW800PA attained a higher sorption capacity (ca. 12 mg CO_2·gsorb^{-1}) than GAC (9 mg CO_2·gsorb^{-1}). This behaviour was attributed to the larger basicity measured for the oak wood-derived AC which is likely to be due to the larger inorganic fractions identified within the oak wood carbons' structure. The basic surface of the oak wood carbons ensured stronger interactions with the carbon dioxide molecule at higher temperatures and lower gas concentration. This proves that basicity can play a key role in the design of selective CO_2 sorbents under post-combustion conditions.

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