Multifunctional porosity in biochar

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Multifunctional Porosity in Biochar

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Abstract: Biochar is the black fine-grained residue obtained by pyrolitic decomposition processes of biomass, achieved at moderate temperatures under oxygen-limiting conditions. This pyrolysis residue has a hierarchical pore structure resulting in a large specific surface area accompanied by a strong adsorption capacity. Due to the relevant presence of mesopores, biochar can have different roles in storage applications, ranging from for the adsorption of pollutant gases, such as carbon dioxide, to the shape-stabilization of phase-change materials (PCMs), used for thermal energy storage. Biochar is overcoming the leakage problem of PCMs by their encapsulation in the mesopores, whereas the same mesopores are the passageway to the micropores which constitute the packing space for gas adsorption.

Keywords: Biochar, Composite Materials, Biomass Based Porous Carbon, Mesoporous Materials, Mesoporous Biochar, Phase Chance Materials, Shape Stabilized Phase Change Materials, Latent Heat Storage Biocomposites, Carbon Dioxide Adsorption

1. Introduction

Biochar is the black fine-grained product of pyrolysis, the conversion technology of biomass based on thermochemical decomposition processes achieved at moderate temperatures (350–700°C) under oxygen-limiting conditions (Brassard et al., 2019, Bartoli & Giorcelli, 2022). Besides biochar proper, which is the major products of biomass pyrolysis (Kan et al., 2016), liquid (bio-oil) and gas (syngas) products are obtained from the thermal decomposition too (Han & Kim, 2008, Undri et al., 2015, Ok et al., 2018, Bartoli et al., 2020).

The principal use of biochar is as amendment in agricultural soils (Brassard et al., 2019, Ok et al., 2015), but due to its high compatibility with cement, asphalt and polymer, biochar is also proposed as a filler for these materials (Tan et al., 2021, Zhao et al., 2014, Zhang et al., 2018, Das et al., 2021). The state-of-the-art of biochar-enhanced construction materials is given in (Zhang et al., 2022), where their merits have been highlighted, such as the ability of acting in humidity regulation, thermal insulation, and noise reduction. The incorporation of biochar in cementitious materials has been largely investigated also by Danish et al., 2021, Maljaee et al., 2021, Tan et al., 2021, Suarez-Riera et al., 2022. For other non-soil applications of biochar, as a filler in polymeric composites, reviews have been given by Bartoli et al., 2020, 2022, Ziegler et al., 2017, and Lepak-Kuc et al., 2021.
Biochar has a hierarchical pore structure, which is resulting in a large specific surface area accompanied by a strong adsorption capacity (Liang et al., 2022). Moreover, physical and chemical activation of this structure can be used to promote the biochar to cost-effective and environmentally friendly active carbon material for multiple applications (Tan et al., 2017). Besides its use as a filler, and due to the relevant presence of mesopores in it, biochar can have multifunctional roles in storage applications, ranging from for the adsorption of pollutant gases, such as carbon dioxide (Chen et al., 2017), to the shape-stabilization of phase-change materials (PCMs) used for thermal energy management (Liang et al., 2022). Biochar is overcoming the leakage problem of PCMs in the fluid phase by their encapsulation in its mesopores, whereas the same mesopores are the passageway to the micropores which become the packing space for gas adsorption. Biochar can act also as a filter, for instance in water pollution treatment (He et al., 2022), or for electric energy storage in supercapacitors (Cheng et al., 2017).
A phase-change material, PCM, is a substance which is able of absorbing and releasing energy at its phase transition, having therefore a natural use in heating and cooling applications (Du et al., 2018). The most used phase transition is that between solid and liquid phases. By melting and solidifying at a given temperature, a phase change material can store or release energy. In this case, the PCM is a latent heat storage (LHS) material. An easy example of LHS material is ice (heat of fusion, 333.55 J/g). Water/ice is therefore a well-known phase change material, which can be used to store winter cold to cool buildings in summer (Sparavigna et al., 2011). In the last few decades, several organic substances,

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such as hydrocarbons (Daniarta et al., 2022) and paraffins (Akgün et al., 2007), have been adapted to have applications of PCMs to a wide temperature range. Today, research is aiming to enhance PCM performance, to improve encapsulation by using the eco-friendly biochar too (Sparavigna, 2022).

For buildings, besides its use in the PCM encapsulation, biochar is proposed for CO_2 adsorption (Schmidt, 2014, Legan et al., 2022, Pandey et al., 2022, Jiang et al., 2023), and for improving construction materials (Zhang et al., 2022). Biochar therefore can be potentially interesting for the huge market of building materials (Sivanathan et al., 2020).

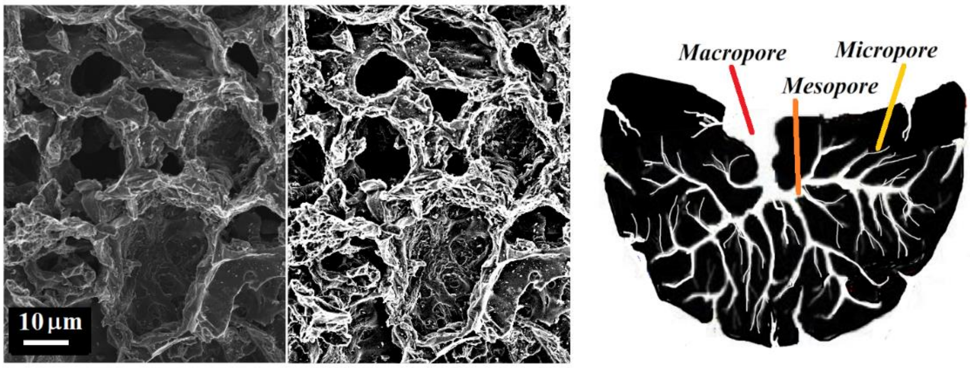

Figure 1 – On the left and middle, a detail of a scanning electron microscope image of biochar from ground coffee (image courtesy Mauro Giorcelli, Department of Applied Science and Technology, Polytechnic University of Turin, Italy; discussion about coffee biochar is given in Giorcelli and Bartoli, 2019). On the right, the hierarchy of the pores in biochar. We can see the pores from macro- to micro size. Let us note that the cavities which we can see in the SEM imagery, as in the left image, are much larger than the macropores sketched on the right. According to IUPAC classification, micropores have size less than 2 nm, mesopores from 2 nm to 50 nm, and macropores have size greater than 50 nm. Then, we must imagine the walls of the cavities shown by the SEM imagery pierced by the apertures of macropores. From macropores the mesopores are departing to reach the micropores. Some very large macropore apertures on the biochar cavity walls seem being visible in the same SEM image, courtesy M. Giorcelli.

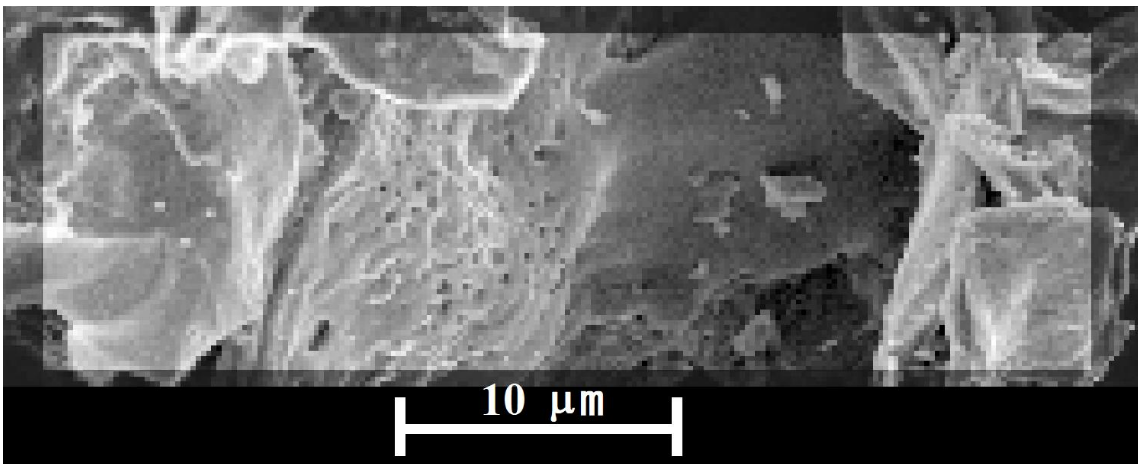

Figure 2 – A detail (processed to enhance luminosity and contrast) of the SEM image of biochar, Fig.1, from ground coffee (image courtesy Mauro Giorcelli, Polytechnic University of Turin, Ref. Giorcelli & Bartoli, 2019). As previously told, we must imagine the walls of biochar cavities pierced by the relatively large apertures of macropores.

2. Pores in biochar

Pores in biochar are present in the form of micro-, meso- and macropores, according to the classification given by IUPAC. A micropore is a pore having a size less than 2 nm, a mesopore a size from 2 nm to 50 nm, and a macropore a size greater than 50 nm (Fang et al., 2010). Pore size is generally the distance between two opposite walls of the pore and therefore it is the diameter in the case of cylindrical pores (Salamon, 2014). Regarding the macropores, Lu and Zong, 2018, considered biochar derived from different feedstocks and pyrolysis conditions, to establish quantitatively the environmental serves of these materials. Biochar pores are suitable habitats for microbe and fungi communities (Lu & Zong, 2018). The biochar macroporous characteristics were measured by means of nitrogen adsorption and the mercury intrusion porosimetry. The pore size distribution has been observed as possessing bimodal peaks, in the range 5-15 μm and 1.5-5 μm, for the biochar obtained from herbaceous plants and broad-leaf forests. The biochar from coniferous forests had two pore size peaks in the range 6-25 μm and 1.5-3 μm, respectively. The measurements made by Lu and Zong show that biochar had substantial storage pores, from 0.5 μm to 50 μm, which are constituting about the 85% of total pore volume. The remaining pore volume, according to Lu and Zong, is due to small transmission and residual pores. Let us stress that the pores measured by Lu and Zong are like the large cavities that we can see in the SEM images (Figs. 1). In literature, the vessel cavities in wood are generally mentioned as pores (about wood and delignified wood see Sparavigna, 2023). Then, the "macropores" that we can see in SEM imagery of biochar from wood are given by the vessel structure of it.

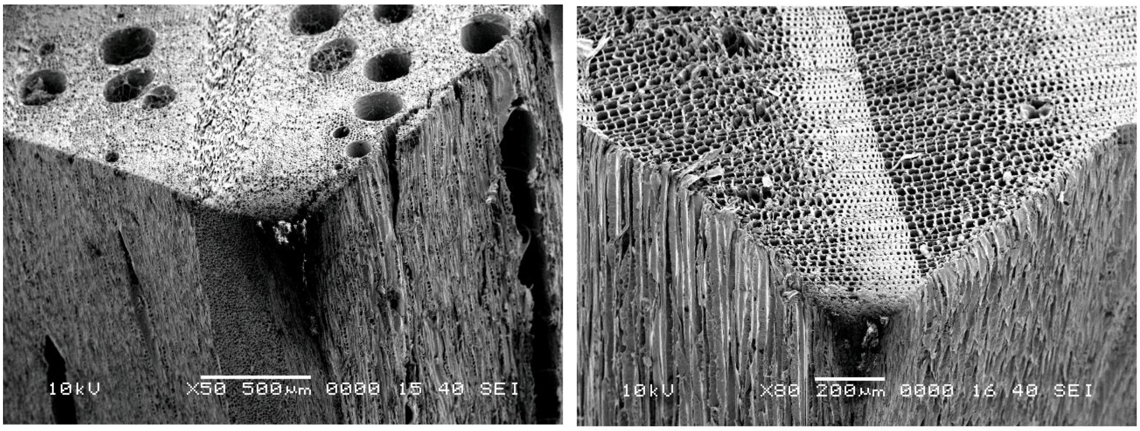

Figure 3 - Scanning electron microscope images showing the structure of hardwoods (Oak, left) and softwoods (Pine, right). Courtesy McKDandy (the author) at English Wikipedia. The file is licensed under CC Attribution-Share Alike 3.0, https://commons.wikimedia.org/wiki/File:Hard_Soft_Wood.jpg, (archived).

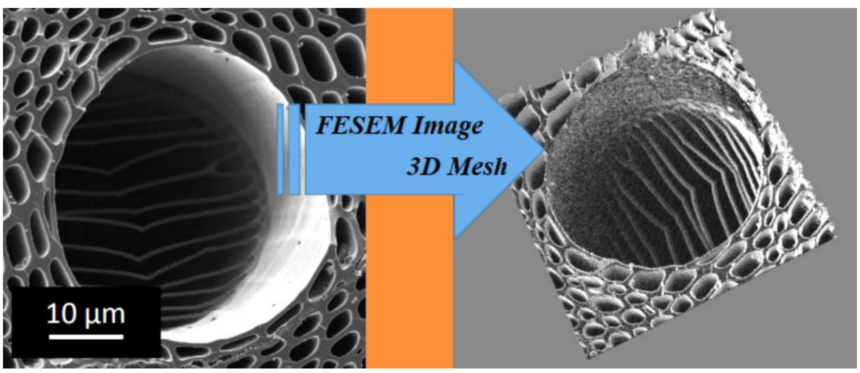

Figure 4 - Scanning electron microscope image and its 3D rendering, showing a pore in biochar from wood, Acer Saccharinum, commonly known as silver maple (Sparavigna et al., 2017).

A recent review, proposed by Leng et al., 2021, is accounting for the effects of biomass and pyrolysis parameters on biochar surface area and porosity. The nature of biomass feedstock and the temperature of pyrolysis are the main factors influencing the pore structure. According to their studies, Leng and coworkers suggest that the best candidate for biochar is the ligno-cellulosic biomass as wood and woody biomass. The moderate pyrolysis temperatures used for biochar are also those suitable for the best development of the pore structure. Further improvement can be achieved by means of additional activation treatments or by using other methods, such as carbonaceous coating and templating. Regarding the size of the pores in biochar, the macropores are generally good for the diffusion of substances, the mesopores are acting as channels for mass transfer and the micropores are constituting a "trapping space" (Leng et al., 2021, Chen et al., 2017). Macropores in biochar are suitable for the microflora settlement (Quilliam et al., 2013). Mesopores and micropores are suitable to store water and dissolved substances in it, that is, these pores retain the supply substances for microbial metabolism (Leng et al., 2021, Brewer & Brown, 2012). As given by Leng and coworkers, because of its micro-, meso- and macropores, biochar is a natural structure with hierarchical porosity. Some chemical activation is favorable to establish a true hierarchically porous structure, where each class of pores has its specific function.

To see how pyrolysis conditions are influencing porosity and pore size distribution of biochar, the recent research by Muzyka et al., 2022, is available. The nitrogen adsorption and desorption isotherms of the investigated biochar samples are giving curves that may be categorized as type II isotherms with hysteresis loops. These isotherms are typical of adsorbents categorized as microporous according to IUPAC classifications. (Muzyka et al., 2022). Using the Brunauer–Emmett–Teller (BET) model, the biochar microporous characteristics were validated by deducing a larger proportion for the microporous fraction. As it is possible to observe from results proposed in the Figure 5 of Muzyka et al., 2022, the percentage of micropores is strongly increased respect that of mesopores when the pyrolysis process passes from 500°C to 700°C. The specific surface area is strongly influenced by the temperature process.

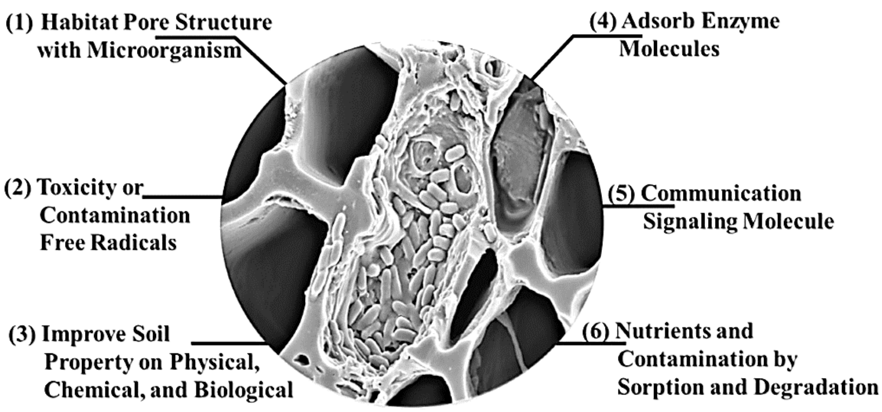

Figure 5 – Image courtesy by Lee et al., 2022, provided under Creative Commons Attribution (CC BY) License 4.0, in Sustainability. In the figure, Lee and coworkers are proposing the role of biochar on microbial activity. It is argued that "the interaction between biochar and soil microbes can alter microbial communities and their metabolic pathways, thereby altering soil processes … [consequently] biological fertilizers and formulations using *biochar carriers* will be more concentrated and beneficial to the effective change of the related microbial communities" (Lee at al., 2022, mentioning Zhu et al., 2017).

3. The importance of being mesoporous

Conditions for a relevant presence in biochar of mesopores exist, and we can find recent literature about the specific production of "mesoporous biochar". This biochar was obtained by pyrolysis of brewing industry wastes (Machado et al., 2020). From the malt bagasse, the mesoporous biochar, and a bio-oil rich in palmitic acid have been obtained. The best production of biochar was at 500 °C for 10 min. The resulting mesoporous character of biochar is relevant for being used as adsorbent. Again, by means of the physisorption analysis based on BET model, the pores of the material are observed being contained in the region with a pore size between 40 and 200 Å (4 and 20 nm). Therefore, the solid material obtained by Machado and coworkers was a mesoporous material.

As told in the Introduction, biochar is considered for the encapsulation of phase change materials to obtain building materials for the latent energy storage. Let us note that shape stabilization and encapsulation are two different approaches to the leakage problem (Khadiran, et al., 2015, Abdeali et al., 2020). The encapsulation - let's say, the "true" encapsulation - is based on the specific creation of a capsule shell for the PCM. The shape-stabilization is based on the use of a porous material which is infiltrated by the fluid. However, it is common to find the shape-stabilization simply defined as "encapsulation" (in the review by Trisnadewi and Putra, 2020, the shape stabilization for thermal energy storage has been considered in general).

To shape-stabilize or, let us say, to "encapsulate" organic PCMs, the solid scaffolds of the biomass-derived porous carbons have been recently proposed in (Bordoloi et al., 2022). In the article by Bordoloi and coworkers, the investigated PCM "green composites" involve biochar from the biomass of sugarcane bagasse, water hyacinth and yellow oleander, in single, binary, and ternary mixtures. The experiments confirm biochar being good for PCM encapsulation. For what concerns the porosity of the biochar, Bordoloi and coworkers observe that the *mesoporous structure* of biochar "is highly appreciated as scaffold material", whereas the microporous structure is "affecting in a negative manner" the PCM thermal storage. For what concerns the macroporous structure, it is providing "the less capillary force". The researchers also noted that the presence in biochar of active hydroxyl groups is enhancing the sorption capability of the organic phase-change material (Bordoloi et al., 2022).

To explain why micropores are negatively affecting the storage, we can use the words by Bordoloi and coworkers: the mesoporous structure is the most preferred option as encapsulating medium “because the presence of too small pores (microporous) results in molecular motion hindrance, thus hampering desired thermal performance, and too large (macropores) pores cannot offer liquid stability of molten PCM". Bordoloi and coworkers are mentioning Khadiran et al., 2015, who consider the previous work by Chapotard and Tondeur (1983) demonstrating the critical role of the average diameter of activated carbon pores in influencing the system performance in thermal energy storage (TES) based on PCM. In the case that the pores are too small, - Khadiran et al. are telling - the molecular motion of the phase-change material is hindered, and consequently the performance of PCM for TES reduced. On the other hand, "if the pores are too large, the capillary force is not sufficient for the PCM to remain in liquid form", according to theoretical and experimental results (Chapotard and Tondeur, 1983, Py et al., 2001, Ferrari and Robertson, 2000). In the case of the activated carbon, the waxes used for PCM are well retained in the micropores but in them the waxes lose their phase-change properties. The waxes in the macropores have a "significant leakage tendency" (Khadiran et al., 2015, Chapotard & Tondeur, 1983, Py et al., 2001). According to Khadiran and coworkers, the "optimum texture" of the active carbon, suitable for supporting PCMs, is the mesoporous one (Py et al., 2001). The activated carbon produced by Khadiran and coworkers is in the range of the mesoporous size (2 - 50 nm), and therefore has a high potential to be considered for supporting material to shape stabilize the PCMs.

4. Dominant mechanisms

Lv et al. 2022, consider the "structural characteristics and surface functional groups of biochar" and their effects on the thermal properties of organic PCMs. The support is waste phoenix leaf biochar and the organic PCMs are paraffin, stearic acid, and polyethylene glycol. In their abstract, the authors tell that the "dominant mechanisms" in the organic PCM encapsulation by biochar are the pore-filling, the presence of hydrogen-bonding and hydrophobic interaction between biochar and PCM, "and other potential mechanisms." Lv and coworkers have evaluated the specific surface area and pore volume of biochar using BET and BJH (Barrett–Joyner–Halenda) methods, finding that the pore diameter of biochar without "physical activation" was distributed between 1.8 and 4.8 nm. Larger mesopores are observed after physical activation. As explained by Colomba et al., 2022, biochar can be "physically activated" by means of a mild oxidant such as steam or carbon dioxide. Lv and coworkers note that after the physical activation, "a clear and orderly pore structure could be followed, and the porosity increased significantly", moreover the wall of the pores of the steam activated biochar "was thinner and smaller than that of biochar activated with CO_2". Experiments tell that the biochar which is physically activated had "richer structural characteristics" than pristine biochar, with a consequent enhanced encapsulation capacity for PCM (Lv et al. 2022). Lv et al. summarize their experimental investigation, saying that the structural features and surface functional groups interaction, with other potential mechanisms, are impacting the encapsulation capacity and efficiency of "biochar encapsulated PCMs".

Among the primary findings by Lv et al. we can find that the specific surface area, total pore volume, and pore diameter of the considered biochar are depending on pyrolysis temperature. The surface functional groups of biochar can enhance intermolecular interaction and hydrogen-bonding between the support and the organic PCM. The physically activated biochar, in particular activated by steam, has structural characteristics that can enhance the encapsulation capacity for PCM. Moreover, a higher pyrolysis temperature produces a higher graphitization of biochar and consequently an increase of thermal conductivity, positively affecting the biochar composite PCM efficiency. Atinafu et al., 2020, proposed a discussion and experimental results about the "tuning surface functionality" of biochar to increase the capacity of energy storage for organic PCMs (esters, paraffin waxes, glycols and fatty alcohols and acids). The reason to use organic PCMs is because they are non-corrosive, nontoxic, and a low supercooling is observed (Atinafu et al., Jeon et al., 2019). A reason to use biochar is that it is "up to six times cheaper" than activated carbons and it has active surface functional groups, for instance C=O, OH, COOH, which are suitable for applications such as heavy metal removal, biodegradation and so on (Atinafu et al. and references therein; regarding the biochar used in the treatment of wastewater, see Sparavigna, 2023).

Although relevant research on biochar-based composite PCMs exists, Atinafu and coworkers stress that "the design conditions for biochar production and the corresponding properties of derived products are still in their infant stage" (referring to Mašek et al., 2018, Sedlak, 2018).
To improve replication of experiments and for benchmark investigations, in 2015 the United Kingdom Biochar Research Centre (UKBRC), University of Edinburgh, produced *standard biochar products* to be used by the scientific community. This biochar was used as reference material by various research centers (Mašek et al., 2018). In the work by Atinafu et al., 2020, we can find investigated biocomposites based on UKBRC biochar and lauryl alcohol (1-dodecanol) as organic PCM. The reason of using biochar and 1-dodecanol is the following: "the abundant surface functional groups of biochar vs. hydroxyl functional groups of 1-dodecanol" can be useful for investigating the role of "intermolecular interaction on the thermal properties of biocomposites and loading performance of biochars" (Atinafu et al., 2020). "The specific surface areas of biochars are *relatively small compared with porous carbons*, making them inconvenient for impregnating large-molecular-size PCMs, such as polyethylene glycol (PEG). Thus, liquid small molecular size organic PCMs were selected", to have a better impregnation in biochar (Atinafu et al., 2020).

Atinafu and coworkers concluded that the organic PCMs are "encapsulated" in biochar by capillary force and surface tension; moreover, the interaction between the functional biochar and organic PCMs is relevant to determine the thermal behavior of composite PCMs. The researchers are also stressing that thermal stability is improved. The thermal stability is a very important parameter for composite PCMs because they may be subjected to degradation under the repetition of storage cycles. A material which is reliable for applications needs to be chemically, physically, and thermally stable, after many thermal cycles have been performed (Rathod, 2018).

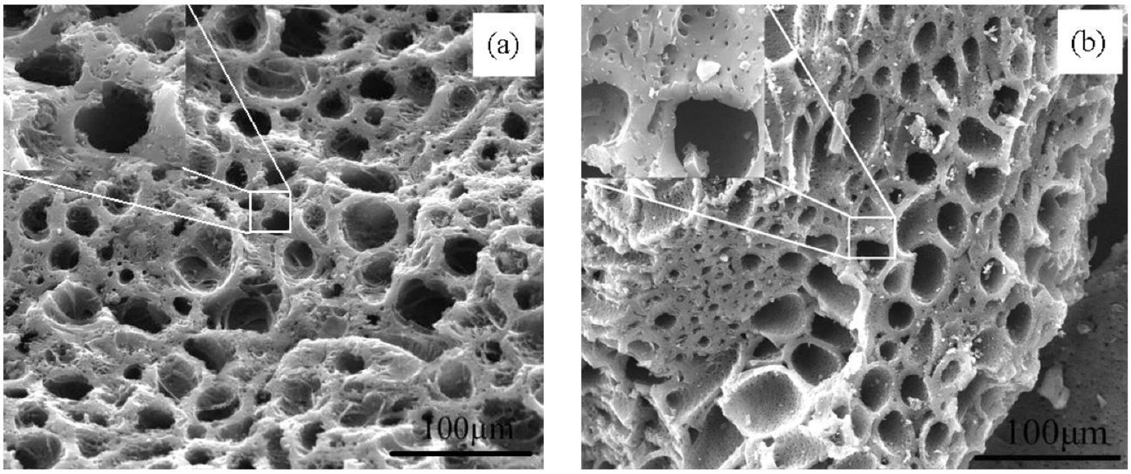

Figure 6 - Two SEM micrographs of carbonized coconut shells, courtesy by Song et al. 2013, provided under Creative Commons Attribution (CC BY) License 3.0, in Sustainability. Song et al. tell that SEM imagery shows "many large pores with honeycomb shape [that] are formed on the surface of coconut shell carbons". The coconut shells, cleaned and dried, were crushed and sieved to grains of about 1–2 mm. Then coconut shells were carbonized in N_2 gas up to the temperature of 500 °C. After carbonization, these grains were mixed with water and KOH, which "is effective in creating well-developed pores in coconut shell carbons" (Song et al., 2013).

5. Pinecone, coconut, and others for bio-composites

In the introduction of their article of 2020, Das and coworkers explain that to have an improved stability and performance of a PCM, it is better to use a supporting material in the form of a network with pores from the micro- to the macroscale, where the PCM can be inserted and trapped. Otherwise, it is necessary to encapsulate the PCM. The encapsulation, however, is producing an additional cost, besides adding thermal resistance due to the presence of the capsule shell (a low thermal conductivity is disturbing the process of the thermal conversion). An interesting solution to avoid encapsulation is the use of polymeric networks, such as in the high-density polyethylene composite and paraffin.

About the use of biochar, Das and coworkers report the work by Wan et al., 2019, that used pinecone biochar (PB) as a supporting matrix for palmitic acid (PA). The research about PB/PA composites by Wan and coworkers displayed that the palmitic acid is linked to biochar by the capillary force and the surface tension. The palmitic acid is physically absorbed by the pinecone biochar. The pore size distribution of the pinecone biochar shows three peaks at 2.3 nm, 3.2 nm and 4.0 nm, with an average pore diameter of 3.078 nm, "which suggested that the PB [pinecone biochar] was mesoporous biochar" (Wan et al., 2019).

Considering that biochar can be an adaptable material for the thermal energy storage due to its surface properties, porosity and abundance, Das and coworkers prepared an eco-friendly composite WH-PCM based on biochar made of water hyacinth, defined WH 550, and paraffin wax. The average pore size of WH 550 is about 12 nm and therefore the biochar has a mesoporous structure. The presence of this mesoporosity, according to Das et al., "is suitable for the *absorption of melting organic compounds* like paraffin wax during the phase change cycle". After the solidification of the composite, *the shape is maintained*, without any seepage of melted paraffin. The new composite material possesses superior thermal conductivity over pure PCM, "as well as *better stability* due to the high carbon content and porosity of the developed biochar".

In Jeon et al., 2019, we can find biocomposites made by using coconut oil impregnated biochar given from pinecone, pine sawdust, and paper mill sludge raw materials. The aim of the research proposed by Jeon et al. was the characterization of a latent heat storage of biocomposites (LHSBCs). The article considers the following features: "chemical stability, latent heat storage performance, thermal conductivity, and thermal stability" of the LHSBCs. The proposed LHSBC is based on a biochar with average pore diameter ranging from to 2 to 45 nm. According to IUPAC classification, all biochar used in LHSBCs are mesoporous materials. The researchers are also noting that, as the pyrolysis temperature increased, the surface area and pore volume tended to increase, because more volatile elements are released. According to the research by Jeon et al., the LHSBC is suitable as a latent heat storage insulation material. The pore characteristics of the biochar are suitable for supporting PCM.

In a study proposed by Atinafu et al. (2020), a "mesoporous biochar" was introduced as a support for PCMs made of different n-alkanes (dodecane, tetradecane, and octadecane). The n-alkanes were infiltrated in the spruce biochar by means of a vacuum impregnation method. According to the Barrett–Joyner–Halenda (BJH) model, the pore-size distribution exhibited a large proportion of mesopores, with size from 3.1 to 6.4 nm. The functional groups of biochar (such as −COOH and −OH) are anchoring and stabilizing the organic PCM via the hydrogen bonding. The behavior shown by these biochar/PCM composites is consistent with that of other stable composite PCMs, obtained through paraffin and graphene nanoplates as support, stearic acid and ultrathin-wall mesoporous carbon foam and PCMs/rice husk biochar (Zhou et al., 2020, Zhang et al., 2020, Jeon et al., 2019).

The review by Jiang and coworkers, 2022, contains many references about biomass-derived porous carbons for PCM to be used specifically for building energy efficiency. Let us mention just two biochar, produced from walnuts and almonds. Biochar can be obtained from walnut shell (WS) (Hekimoğlu et al., 2021). Walnut shell carbon (WSC) and activated WSC (AWSC) were used as shape stabilizer and enhancer of the thermal conductivity for the methyl palmitate (MP) PCM. In the article by Chen et al., 2018, we can find a new form-stable composite phase change material (PEG/ASB) composed of almond shell biochar (ASB) and polyethylene glycol (PEG). ASB was produced from agricultural residues by a pyrolysis method. Also in this case, the experimental investigation indicated that PEG/ASB was possessing favorable phase change properties, suitable for thermal energy storage.

Yang et al., 2022, are proposing an *anisotropic* biochar supported PCM composite for solar-thermal energy conversion and storage. Hemp stems were converted into biochar possessing three-dimensional multi-level *anisotropic* pores. The material is supporting PEG. Tian et al., 2022, are proposing *anisotropic* reed-stem-derived biochar for paraffin wax, again for the solar-thermal energy conversion and storage. Li et al., 2023, designed corn straw/paraffin wax shape-stabilized phase change materials. According to the researchers, the loading efficiency is up to 99.7% and the phase change enthalpy above 185 J/g. This is not a biochar-based composite, but it interesting because Li and coworkers have prepared a "green heat insulating mat" based on the composite. "And the size can be tailored as demand".

Phase change materials can be used for an efficient battery thermal management system (BTMS) for electric vehicles (Goud & Raval, 2022). Goud and Raval mention some drawbacks of PCMs, that is poor thermal conductivity, volume expansion and leakage. A shape stable PCM solve these drawbacks, and a biochar based SSPCM can be a cheap and sustainable solution too. The PCM is the myristyl alcohol. The shape stability, according to the study by Goud and Raval, is observed for PCM with minimum of 24% biochar from neem tree.

Yazdani et al., 2022, consider the use of biochar additive for low-grade thermal energy storage. It is reported the experimental investigation of a latent heat storage (LHS) system, temperature range 20–50 °C. Applications are heat sink and storage for high-power electronics devices and low-temperature district heating (LTDH). Biochar additive is investigated to enhance the thermal properties of the PCM.

Another use of biochar as an additive is given by Xiong et al., 2022. Low-cost and eco-friendly biochar was prepared from garlic stems, a "common food waste in Singapore" and used to dope paraffin wax (PW). The thermal properties of PW doped with garlic stem biochar (GSB) was investigated. The researchers observed that the GSB microparticles, prepared at 700 °C, have a flake-like structure. This form of GSB allows the formation of additional pathways for the heat transfer in PW. "The improved heat transfer performance was mainly ascribed to the high degree of graphitization and the interconnected porous carbon structure of the GSB microparticles" (Xiong et al., 2022).

Comparative analysis of biochar and other forms of carbon, with respect to PCM loading in the thermal energy-storage capacities, has been proposed by Atinafu et al., 2021. The considered materials for the comparison are four: biochar, activated carbon, carbon nanotubes, and expanded graphite. These materials have been introduced to support heptadecane. The researchers observed that the intermolecular interaction between PCM and the shape supporting material, and the surface functionality of it are fundamental parameters for the performance of composites. Furthermore, pore structures and pore size distributions have "a c*ombined effect* on the crystallinity of heptadecane in the composite PCMs" (Atinafu et al.). In another work by Atinafu et al., 2021, a composite material is studied, obtained by means of biochar derived from bamboo, multiwalled carbon nanotubes and liquid n-dodecane for a new energy storage material. This is a hybrid material, which is providing a favorable morphological framework for the PCM stabilization and thermal energy storage capacity. The synthesis strategy proposed by Atinafu and coworkers is that of creating a platform to produce "biochar-based multifunctional PCMs" suitable for specific applications.

Further studies about the biomass-derived porous carbons composite PCMs for building energy efficiency have been proposed by Jiang et al., 2022, and by Kim et al., 2022. In these studies, biochar is recognized as an environmentally friendly product able of enhancing the energy efficiency of buildings. The base is in the integration of common construction materials with latent heat storage biocomposites (Jeon et al., 2019). Besides its role in construction materials, the eco-friendly biochar is a material suitable to adsorb several organic and inorganic specific substances.

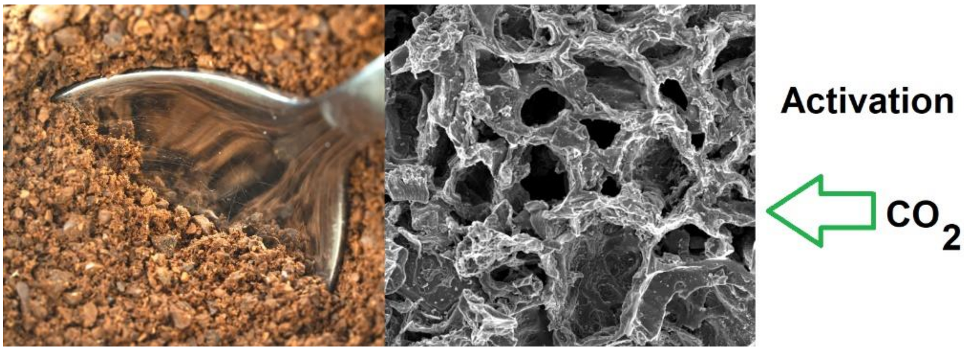

Figure 7 – Ground coffee (image courtesy Martin Hetto, here used according to Pixabay Content License, image link https://pixabay.com/photos/coffee-ground-grains-roasted-brown-5187386/). Once activated, the ground coffee biochar (image courtesy Mauro Giorcelli) turns into a CO_2 adsorbent.

6. Coffee and CO_2

It could seem odd to consider a specific material for biochar, but coffee has multiform applications, and one of them is quite relevant to our discussion about the porous framework. From spent coffee grounds we can have biochar and bio-oil by means of the "complete utilization" of them, devised by Vardon et al., 2013. The coffee biochar is used as a filler of polymers and epoxy resins (Arrigo et al., 2019, Giorcelli & Bartoli, 2019, Alhelal et al., 2021), for adsorptions of micropollutants and Ibuprofen (Shin et al., 2020, 2022), and in other applications, such as for supercapacitor electrodes (Andrade et al., 2020). This biochar has been also proposed for composite PEG PCMs, with the introduction of reduced graphene oxide (Hu, et al., 2021). Hu and coworkers say that the composite has "excellent leakage-proof performance". Regarding the bio-oil, there is an interesting study by Chen et al., 2016, on the coffee industrial residue (CIR) pyrolysis. The pyrolysis temperature is, according to Chen and coworkers, the most influential factor on the components yields of bio-oil, in this case palmitic acid, linoleic acid, oleic acid and octadecanoic acid, besides the caffeine of course. Chen and coworkers are proposing a solution for the component separation of bio-oil.

From coffee, the spent coffee grounds, we can have biochar as a scaffold for PCMs. However, this biochar has a remarkable specific application, and this has been disclosed by Mukherjee et al., 2021. In this case, it is the set of its micropores, used to store the carbon dioxide captured from flue gas. The researchers investigated the role of pyrolysis temperatures (400–600 °C) and heating rates on the produced biochar. In the research by Mukherjee and coworkers, evaluating "the surface composition and textural properties, the CO_2 adsorption capacity" of biochar was considered "under varying adsorption temperatures at ambient pressure". According to the research results, "the binding process is physical in nature". One of the samples, that named SCG-600, "could be proposed as promising biochar that possesses a combination of higher surface area, well-developed microporous structure, heterogeneous and basic surface functional moieties to meet the specific requirements in dynamic CO_2 adsorption" (Mukherjee et al., 2021).

The physical phenomenon is the stacking in biochar micropores. Chen et al., 2017, considered the structure evolution of biochar, according to the used biomass and pyrolysis conditions, correlated to the gas pollutant adsorption performance. "As greenhouse gas CO_2 adsorption, biochar attracted increasing concerns. Biochar as a porous adsorbent, displayed great potential and negative carbon emission advantages" (Chen et al. are mentioning Shen & Fan, 2013). The biochar CO_2 capture performance is influenced by its texture property, and by its surface chemistry. Physics and chemistry are synergically acting in CO_2 capture. "During the process of absorbing CO_2, the macropore structure can enhance the diffusion of carbon dioxide to reduce the pressure drop", the mesopore structure is providing "one passageway for the mass transfer of gas-solid interface reaction", and finally, the micropore structure is forming "the packing space for the CO_2 adsorption" (Chen et al., mentioning Shen & Fan, 2013). "The abundant basic sites, delocalized π electrons of aromatic rings and unsaturated valences, interacting with CO_2 molecules at gas-solid interfaces, can act as the CO_2 adsorption of active sites" (Chen et al., 2017).

In Guo et al., 2022, the recent advances in biochar for CO_2 capture have been proposed. Actually, the CO_2 capture is a strategy considered to reduce the amount of this greenhouse gas into atmosphere. “The development of adsorption materials that are both economically feasible and effective is the most critical issue. Biochar is a promising candidate for CO_2 capture among the capture materials. It offers a diverse range of raw materials and a lower environmental impact than other adsorbent materials. … [However,] biochar needs to be modified in practical applications to improve physico-chemical properties such as specific surface area, pore structure, and surface functional groups” (Guo et al., 2022).

Guo et al. are discussing the mechanisms of CO_2 capture by biochar, providing many specific references (see please them as given in Guo et al., 2022). In the Section entitled “CO_2 physisorption on biochar”, the researchers write that several biochar samples “with varying surface areas and pore structures have been investigated and used for CO_2 adsorption by effectively utilizing their physical properties”. At the beginning, we have the pyrolyzed biomass. During pyrolysis, dehydration and release of volatile constituents “form biochar pores and rudimentary pores”. However, the biochar’s CO_2 capture is depending “on micropores less than 1 nm in diameters”. The reason is that “narrow micropores are close to the dynamic diameter of CO_2 molecule and have a stronger attraction to CO_2 due to overlapping adsorption forces and potential fields from neighboring pore walls” (Guo et al., 2022). For what is regarding macro- and mesopores, the “macropores enhance CO_2 diffusion to reduce pressure drop, mesopores provide a passageway for mass transfer at the gas-solid interface, and micropores form the packing space for CO_2 adsorption (Guo et al., mentioning Shen and Fan, 2013)”. The physical adsorption produced by the pores, can be improved by adjusting the pore distribution: we need “lots of micropores, appropriate mesopores, and small macropores with high specific surface area to produce biochar with multi-stage porous structures” (Guo et al., mentioning Chen et al., 2017).

Angin et al., 2013, determined a less contribution of micropores to adsorption capacity at high temperatures. This fact is attributed to the phenomenon of pore widening and coalescence of adjacent pores.

As stressed by Guo et al., “specific surface area and microporosity are interrelated, where the generation of many small micropores will result in a large specific surface area. The larger surface area provides more active sites for CO_2 adsorption through physical adsorption”. Then, the specific surface area seems being “the most important characteristic of biochar in CO_2 adsorption”. Mentioning Mukherjee et al., 2021, Guo and coworkers pinpoint that “the adsorption kinetics of coffee grounds biochar followed a pseudo-first-order kinetic model and had a low activation energy, and it reflects the adsorption’s physical nature” (Guo et al., mentioning Zhang et al., 2014). However, several other phenomena are relevant, such as those related to the CO_2 chemisorption on biochar. Of them, we find detailed discussion in Guo et al., 2022.

Conclusion

As told by Kim et al., 2020, the utilization of biomass wastes as carbon precursors is attracting “much attention because they are easily obtainable, cheap, and environmentally beneficial”. The spent coffee ground, that we considered in the last Section, can be contemplated as a paradigmatic example of this interest for the biomass waste. Coffee waste “is highly promising because coffee is one of the world’s favorite beverages and the coffee market has been continuously growing, which means the spent coffee grounds are superabundant” (Kim et al., 2020).

We have seen that the spent ground coffee has several uses, and the last mentioned is as CO_2 adsorbent. Many other biomass wastes could be considered. Since in the several applications, such as for gas adsorption, liquid encapsulation, treatment of wastewater pollution (see Sparavigna, 2023), porosity is the main ingredient, the conversion of biomass waste in a multifunctional porous carbonaceous material must be appreciated as a highly promising research field.

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