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Biochar Shape-Stabilized Phase-Change Materials for Thermal Energy Storage

A. C. Sparavigna

Department of Applied Science and Technology, Polytechnic University of Turin, Italy

Email: amelia.sparavigna@polito.it

Abstract

Biochar is the black fine-grained residue of the pyrolysis of biomass. It is the product of a thermochemical decomposition at moderate temperatures under oxygen-limiting conditions. This residue has a pore structure with large specific surface area, accompanied by a strong adsorption capacity. Due to the presence of a mesoporous framework, biochar can be used to shape-stabilize phase-change materials (PCMs), which are substances absorbing and releasing thermal energy at phase transitions. Biochar is overcoming the leakage problem of PCMs, by encapsulating their liquid phases in the pores. Consequently, biochar and PCMs, in particular the organic PCMs, can be used to produce eco-friendly stable composites, which can be useful for heating and cooling applications. Here we propose a discussion of recent literature about development and applications of biochar-based composite PCMs. In particular, the literature about the role of biochar mesopores in the encapsulation of PCM is highlighted.

Keywords: Phase Change Materials, Shape Stabilized Phase Change Materials, Biochar, Composite Materials, Biomass Based Porous Carbon, Mesoporous Materials, Mesoporous Biochar, Phase Change Composites, Thermal Management, Thermal Conductivity, Latent Heat Storage Biocomposites

Subject Areas: Materials Science.

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Introduction

A phase change material, PCM, is a substance which is able of absorbing and releasing energy at its phase transition. Therefore, a PCM finds its natural use in the heating and cooling applications (Du et al.,2018). The most used phase transition is the fusion between solid and liquid phases. By melting and solidifying at a given temperature, a phase change material is able to store or release energy. In this case, being the transition of the first order (Binder, 1987), the PCM is a latent heat storage (LHS) material. An example of LHS material is the 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). However, phase

transitions may also be considered between solid-solid structures. Actually, solid-solid phase change materials are subjected to an increasing interest due to their high energy-storage density, besides possessing inherent advantages over solid-liquid PCMs (Fallahi et al., 2017). For instance, the problem of leakage in the liquid phase is avoided.

In the past, water/ice was considered the main, or let us tell the only available PCM. In the last few decades, several substances, such as hydrocarbons (Daniarta et al., 2022) and paraffins (Akgün et al., 2007), have been adapted to have further applications of PCMs to a wide temperature range. For instance, PCMs are used for Ultra Low Temperature (ULT) freezers, so that the World Health Organization, WHO, mentioned them in its logistic guidance for the vaccinations regarding the Covid-19 pandemic. In fact, PCMs are used in ULT logistics, where thermal energy storage is fundamental (Sparavigna, 2021). This logistics takes advantage of the fast progress in materials science, which is providing new substances for PCMs, and also of the technologies which are receiving support from these materials.

Today, several researches are aimed at enhancing PCM performance. The drive of these researches is mainly the huge potential market for building heating and cooling (Sivanathan et al., 2020). For buildings, other materials are under investigation, such as biochar, for CO₂ absorption for instance (Schmidt, 2014, Legan et al., 2022, Pandey et al., 2022, Jiang et al., 2023). In fact, sustainable biochar-enhanced construction materials are attracting an extensively increasing interest (Zhang et al., 2022).

Biochar is the fine-grained residue of the pyrolysis of biomass. It is the product of the thermochemical decomposition at moderate temperatures (350–700°C) under oxygen-limiting conditions (Brassard et al., 2019). Besides biochar proper, liquid (bio-oil) and gas (syngas) products are obtained from the thermal decomposition (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, because of its high carbon content, stability, porosity and surface area (Brassard et al., 2019, Ok et al., 2015). However, due to its highly functionalised surface, biochar is exhibiting high compatibility with cement, asphalt, and polymer (Tan et al., 2021, Zhao et al., 2014, Zhang et al., 2018, Das et al., 2021). In (Zhang et al., 2022), we can find a study regarding the state-of-the-art biochar-enhanced construction materials. In the review some merits of these construction materials have been highlighted, for instance the humidity regulation, thermal insulation and noise reduction. Actually, the incorporation of biochar in cementitious materials is largely investigated (Danish et al., 2021, Maljaee et al., 2021, Tan et al., 2021, Suarez-Riera et al., 2022). For other non-soil applications of biochar, such as energy storage, polymeric composites, recycling materials, sensors and catalyst production, reviews have been given by Bartoli et al., 2020, 2022, Ziegler et al., 2017, and Lepak-Kuc et al., 2021.

Here, we are interested to the use of biochar in PCMs. As stressed by Liang et al, 2022, biochar has a pore structure with large specific surface area, accompanied by a strong adsorption capacity; therefore the biochar-based composite PCMs can take advantage of the abundant presence of pores to efficiently encapsulate PCMs. The consequent applications are in the fields of the use of solar energy, in energy-saving devices and, as mentioned at the beginning of this discussion, for the environmental temperature control in buildings. Actually, due to the recent strong increase of the number of publications concerning biochar-based composite PCMs, it is important to summarize the research results proposed by scholar literature.

PCMs and PCMs

Here, by writing "PCM" the meaning is Phase Change Material. However, among the literature about carbonaceous material, we can find that "PCM" means also Porous Carbonaceous

Material. Cheng et al., 2017, consider this kind of PCMs, mainly used as electrodes in electrochemical double-layer capacitors (EDLCs). The reason of this use is in the large surface area and porosity, besides a good charge conductivity, a low-cost and wide availability. Cheng and coworkers stress that to produce porous carbonaceous materials it is possible to use organic wastes. Hydrothermal carbonization (HTC) and pyrolysis are the two basic processes to modify the biomass wastes into PCMs (Hu et al., 2010, Wei et al., 2011, Kambo & Dutta, 2015).

In Cheng et al. we can find a discussion of HTC process, which offers a platform for producing a carbonaceous material with a surface decorated by abundant functional groups (Demir-Cakan et al., 2009). Then, Cheng et al. consider the fast pyrolysis by means of which biochar is obtained as a carbon raw material suitable to produce the porous carbonaceous materials. "Compared to the HTC method, fast pyrolysis is a solvent-free process that can be accomplished in seconds", tell Cheng et al.

Callegari and Capodaglio, (2018), are reporting that in 2012, the European Biochar Foundation (EBC), in its "Guidelines for a Sustainable Production of Biochar", stated that "a biochar's carbon content must be higher than 50% of the dry mass, while pyrolysed organic matter with a carbon content lower than 50% is classified as Pyrogenic Carbonaceous Material (PCM)". Therefore, Callegari and Capodaglio use PCMs to indicate the pyrogenic carbonaceous materials.

From now on, PCM means phase-change material.

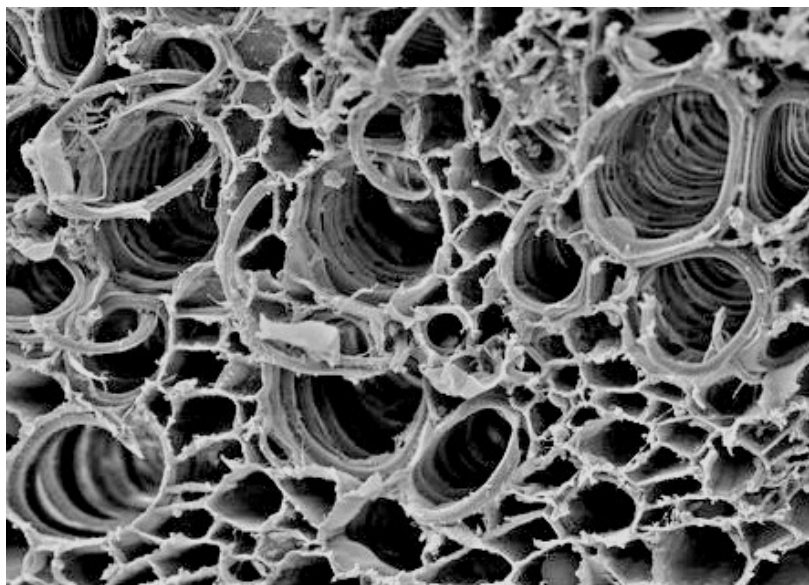


Figure 1. Structure of macropores in biochar is due to the vascular bundle of plants. In the figure, a detail of a scanning electron microscope image of a cross-section through a *Helianthus annuus* (sunflower). Courtesy Louisa Howard, Dartmouth College EM Facility. doi:10.7295/W9CIL40391, ark:/b7295/w9cil40391, <http://cellimagelibrary.org/images/40391>

Pores in biochar

Before discussing in detail the biochar-PCM composites, let us talk about the pores in biochar, that are present at micro-, meso- and macroscales. Lu and Zong, 2018, considered the structure of several biochars, derived from different feedstocks and pyrolysis conditions, in order to establish quantitatively the environmental serves of these materials. The potential of biochar as pollutant adsorbent, for instance, depends on its physical and chemical structures. The pore structure of biochar is also fundamental for many of its ecological serve roles, because the pores are suitable habitats for microbe and fungi communities (Lu & Zong, 2018).

In the study proposed by Lu and Zong the macroporous characteristics of biochar derived from different feedstocks were measured by means of nitrogen adsorption and the mercury intrusion porosimetry. Let us here report that Lu and Zong observed that the pore size distribution has 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 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. For what concerns the effect of pyrolysis conditions on the pores, they are largely depended on the used feedstocks (Lu & Zong, 2018).

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. Again, we find told that the nature of biomass feedstock and the temperature of pyrolysis are the factors influencing the pore structure. Moreover, Leng and coworkers suggest that the best candidate for biochar is the lignocellulosic biomass as wood and woody biomass in particular. The moderate pyrolysis temperatures used for biochar are also those suitable for the best development of the pore structure. Further improvement, according to Leng et al., 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, "broadly speaking", the macropores are generally good for the diffusion of substances, the mesopores are acting as channels for mass transfer and the micropores are a "trapping space", as told by Leng and coworker mentioning Chen et al., 2017. As we can see from SEM microscopy imaging, the biochar is rich of macropores. Having a relatively large aperture, the macropores are suitable for the microflora settlement (Quilliam et al., 2013). In biochar - Leng and coworkers are stressing - mesopores and micropores are suitable to store water and dissolved substances in it, that is these pores retain the supply substances for microbial metabolism (Brewer & Brown, 2012).

As previously seen, the substantial storage pores of biochar for environmental serves (microflora settlement) have a size ranging from from 0.5 μm to 50 μm . These pores are macropores. In fact, the porous materials have been IUPAC classified according to their pore sizes: microporous, less than 2 nm, mesoporous, from 2 nm to 50 nm, macroporous, greater than 50 nm (Fang et al., 2010). Pore size is generally the distance between two opposite walls of the pore and therefore the diameter in the case of cylindrical pores (Salamon, 2014). As given by Leng and coworkers, biochar possesses micropores, mesopores and macropores and therefore it is a natural structure with hierarchical porosity. Some chemical activation, as reported by Leng et al., is favorable to establish a true hierarchically porous structure. To see how pyrolysis conditions are influencing porosity and pore size distribution of biochar, the recent researches by Muzyka et al., 2022, are available (see the Figure 5 of the reference, which is giving the

percentage distribution of pores divided into micropores, mesopores and macropores according to pyrolysis conditions).

Let us now mention an example of production of "mesoporous biochar". It was obtained by pyrolysis of brewing industry wastes (Machado et al., 2020). The researchers propose the pyrolysis of malt bagasse to obtain simultaneously the mesoporous biochar and a bio-oil rich in palmitic acid. The best production of biochar was at 500 °C for 10 min. The resulting mesoporous character of biochar is relevant to be used as adsorbent. By means of a physisorption analysis based on the Brunauer-Emmett-Teller (BET) theory, 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). According to IUPAC classification, the solid material obtained by Machado and coworkers was a mesoporous material. Machado and coworkers summarize that the pyrolysis produced structural changes in the malt bagasse, giving a biochar "with a mesoporous and amorphous structure, and containing some cavities and functional groups in the surface" (Machado et al., 2020).

The importance of being mesoporous

As previously told, phase change materials can be involved in building elements for the latent energy storage. In the case of liquid-solid transition, the main drawback of the PCM is its leakage during the phase change. Another drawback is its generally poor thermal conductivity. In fact, a low thermal conductivity is disturbing the process of the thermal conversion. To support or, as it is also told, to "encapsulate" the PCM, the solid scaffolds of the biomass-derived porous carbons have been recently proposed as shape-stabilizers of the phase change materials (Bordoloi et al., 2022). In the article by Bordoloi and coworkers, we can find a study about the porous biochar for being used to give stability to organic PCMs. 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 researchers selected organic mixture material [savE OM35 PLUS](#) as PCM, with a nominal melting temperature of 35°C, latent heat 202 J/g. The experiments confirm biochar being good for PCM encapsulation. The observed highest heat of fusion obtained was of 99 J/g.

For what concerns the porosity of the biochar, Bordoloi and coworkers are stressing 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 capacity". 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).

Why are the micropores negatively affecting the storage? The answer given by Bordoloi et al. is as follow: "The *mesoporous structure* is the most preferred option as an encapsulating media 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". About this explanation, Bordoloi and coworkers are mentioning Khadiran et al., 2015.

Khadiran and coworkers tell that the previous work by Chapotard and Tondeur (1983) demonstrated 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 the PCM as a TES" is 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". These observations are coming from the theoretical and experimental results provided by Chapotard and Tondeur, 1983, Py et al., 2001, and 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 PCM, 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 PCM.

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 biochar is waste phoenix leaf biochar and organic PCMs are paraffin, stearic acid, and polyethylene glycol. In the 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 CO₂". Experiments tell that the biochar which is physically activated had "richer structural characteristics" than biochar, with a consequent enhanced encapsulation capacity for PCM (Lv et al. 2022).

According to SEM observations after the impregnation of biochar with PCM, Lv et al. concluded that "the *mesopores* of biochar were *almost filled*". Therefore, the biochar structure can effectively encapsulate the PCMs considered by the researchers, that is paraffin, stearic acid and polyethylene glycol. The researchers summarize their experimental investigation, telling that the structural features and surface functional groups interaction, mainly hydrogen-bonding and hydrophobic interaction, with other potential mechanisms that Lv et al. are not specifying, are impacting the encapsulation capacity and efficiency of "biochar encapsulated PCMs". A large specific surface area with the proper structural characteristics can increase the encapsulation of organic PCMs. But the encapsulation efficiency can also be reduced by the increase of surface functional groups, especially in the case of polymer polar substances, such as the polyethylene glycol (PEG).

Among the primary findings of Lv et al. researches 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.

Standard biochar, surface functional groups and stability

Atinafu et al., 2020b, proposed a discussion and experimental results about the "tuning surface functionality" of *standard biochar* and the possibility of increasing the capacity of energy storage for organic PCMs. The organic PCMs, among them esters, paraffin waxes, glycols and fatty alcohols and acids, are receiving an increasing attention over inorganic PCMs. The reason is because they are non-corrosive, nontoxic, and a low supercooling is observed. "In response to the call for fabricating highly value-added supporting materials and preventing seepage [leakage] of organic PCMs, biochars have been introduced for the adsorption of organic PCMs", it is told by Atinafu et al., mentioning Jeon et al., 2019a.

Biochar 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 (see please the references given by Atinafu et al.). Although several researches on biochar-based composite PCMs exist, 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, and Sedlak, 2018). To improve replication of experiments and for benchmarking investigations, in 2015 the United Kingdom Biochar Research Centre (UKBRC), University of Edinburgh, produced *standard biochar products* to be used by the scientific community. These biochar were used as reference material by various research centers (Mašek et al., 2018).

In the work by Atinafu et al., 2020b, we can find investigated biocomposites based on standard biochar provided by UKBRC and 1-dodecanol, that is lauryl alcohol, 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., 2020b). "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., 2020b).

Atinafu and coworkers used the polar 1-dodecanol and nonpolar dodecane for comparison. Before being used, the standard biochar was activated via heating at 105 °C in order to improve "their capillary force and pore characteristics". The organic PCMs resulted "encapsulated" in biochar by capillary force and surface tension. According to Atinafu and coworkers, the interaction between the functional biochar and organic PCMs is relevant to determine the thermal behavior of composite PCMs. For the oilseed rape standard biochar, the researchers measured a large specific surface area (77.6 m²/g) and large micro/mesopore proportions, which produced an enhanced capacity of loading PCMs. The energy storage was of 90.5 J/g (dodecane) and 73.6 J/g (1-dodecanol). The researchers are also stressing that "the strong confinement effect" due to the pore structure of biochars and the "highly sensitive functional group of 1-dodecanol played a key role in increasing thermal stability up to 53% compared with dodecane-based composites". 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 a large number of thermal cycles have been performed. Of course, this is especially important for latent heat and melting point after a repeated number of thermal cycles (Rathod, 2018).

Templating the pores

A specific porous network in biochar can be obtained by means of a template method, and actually we have biochar also used for obtaining ordered mesoporous carbon. As told by Leng and coworkers (2021), we have the possibility to integrate different methods to prepare a biochar with a specific designed porous structure. The activation is an "effective way to produce microporous biochar", but the template method is a "great candidate for the fabrication of mesoporous/macroporous biochar" as told by Leng et al., 2021. The shape and the order of the pores can be regulated by the used template method. As a consequence, "activating templated mesoporous/macroporous biochar is a *promising way* for the synthesis of *hierarchical porous biochar*" (Leng et al., 2022).

In the review by Liang et al., 2022, we can find illustrated the template method as a common method for synthesizing biochar. Again, it is stressed that the template method can adjust the structure of the pores in the carbon materials. It can be a hard or soft template method. In the hard template method, the used solid material must have an intrinsic rigidity and a given shape of the porous structure. The biomass is melted to have a carbon precursor that is poured into the template. Then the hard template is removed and a carbon material with a given pore structure obtained. Atinafu et al., 2018, used MgO as a template in a hydrothermal synthesis to convert dewaxed cotton into porous carbon material. This carbon material possesses some graphitic properties, with large mesopores. The soft template method is based on organic amphiphilic molecules (block copolymers and surfactants) as templates, where the interaction between template molecules and carbon precursors allows to form self-assembled systems having an ordered mesoporous structure. The template is removed by carbonization at a high temperature. The process is sketched in the Figure 2b by Liang et al. 2022, and there we have the pyrolysis to produce the mesoporous carbon from the mesophase of the hybrid material made of lignin and Pluronic F127. F127 is a copolymer surfactant also used for the production by soft templating of mesoporous silica materials (Sparavigna, 2022).

The review by Xi et al., 2020, is combining the large literature about the templating of carbon materials and "the idea of preparing high porosity biochar by template method". It is not just an idea, because in the article by Xi and coworkers we can find experimental results telling that, compared with biochar directly prepared by pyrolysis, the biochar prepared by the soft template method possesses a larger specific surface area and total pore volume. Moreover, the performance quality is better. In the soft template method, the lignin is the carbon precursor. According to Xi et al., among the templating agents, Pluronic F127 is providing a relatively large specific surface area and total pore volume, giving to the mesoporous biochar an "excellent pore size performance". Therefore, the proposal is that of using the lignin extracted from straw material as precursor and block polymer F127 as template, with an appropriate amount of a cross-linking agent and solvent. The "target" biochar material is obtained by pyrolysis carbonization, which is removing the template. The final product is characterized by an open pore structure, with pores having the features of the template. The structure of the pores in the mesoporous carbon can be controlled through the synthesis conditions.

Then, as in the case of the mesoporous silica materials, we have a new family of mesoporous materials, which are known as "hydrothermal mesoporous biochars" (HMCs), such as the HMC-800, obtained by a soft-template-assisted hydrothermal route using F127 and the biomass batatas as carbon precursor. HMC-880 is used for the removal of tetracycline from wastewater (Zheng et al., 2021).

PEG in pores

One of the best known ordered mesoporous carbon is the CMK-5, synthesized using the mesoporous silica material (SBA-15) as template and sucrose as carbon precursors (Jun et al. 2000). We can find it in Wang et al., 2012, as supporting material for *shape stabilized* PCMs based on polyethylene glycol (PEG). The two other materials considered by Wang and coworkers were the expanded graphite (EG) and the active carbon (AC). These materials have distinct influences on the phase change behaviors of PEG-based composites. The highest stabilized content of PEG is 70 wt% for AC and 90% for both EG and CMK-5. The study proposed by Wang et al. suggests that "pores with micrometer size", in this case those of the expanded graphite, "exhibit the same level of shape stabilization ability as the pores with nanometer size". Being the role of micrometer size pores in EG apparently different, let us consider the research in more detail.

In the introduction of the article by Wang and coworkers, the carbon based materials are presented as a highly attractive support for PCMs, because they have a low density, a good thermal conductivity, such as chemical stability. Their porous nature and large surface area can enhance the "shape *stabilization* capability and thus *minimize the loss of energy storage capacity*". AC, EG and CMK-5 are porous carbon materials but they have different pore structures, and the pore structure is influencing the stabilization ability of the PCM PEG. EG and AC have irregular pores but CMK-5 has an ordered hexagonal mesoporous structure. The pore sizes are also different. To determine the pore size distributions of AC and CMK-5 the Barret–Joyner–Halenda (BJH) method can be used, while the porosity of EG has been obtained by the mercury intrusion method. EG has pores which are orders-of-magnitude larger than those of AC and CMK-5. EG average pore diameter is of about 1.3×10^4 nm; AC and CMK-5 have similar average pore diameters, which are 4.0 nm and 3.5 nm respectively, but the pore volume of CMK-5 is twice as large as that of AC. Wang and coworkers give the following fundamental result; considering temperatures above the melting point of PEG, "there was *no leakage* when the content of PEG was 90 wt% for PEG/EG and PEG/CMK-5 composites and 70 wt% for the PEG/AC composite" (Wang et al.). Then, in spite of the quite different porosity, the behavior with respect to leakage in EG and CMK-5 is similar.

The expanded graphite EG based composite PCMs have been investigated by Zhang and Fang, 2006, Sarı and Karaipekli, 2009, Xia et al., 2010, Zhang et al., 2013, Liu et al., 2014, Fethi et al., 2015, Ren et al., 2020, Chriaa et al., 2021.

Xia and coworkers are explaining the preparation of EG for the absorption of paraffin. The raw material is the expandable graphite, produced by H_2SO_4 –graphite intercalation composites, giving a high expansion volume during heat treatment (Kim & Drzal, 2009). A commercial expandable graphite was subjected to heat treatment at 700 °C for 15 min; this heat-treatment is suitable for the complete expansion of the expandable graphite. During the thermal expansion, EG retains the same structural layer as natural graphite flakes, but it has inside different sizes of pores with very large specific surface area (Xia et al., 2010).

Shape Stabilized Phase Change Materials in general

In the review by Trisnadewi and Putra, 2020, shape stabilized PCMs for thermal energy storage are considered in general. The thermal energy storage (TES) can mitigate the increasing energy consumption, but TES requires improved PCM composites, able to store *large* amounts of thermal energy in *small* volumes. As previously told, the main problem of PCMs is the leakage during the phase change process: the solution is a shape stabilized PCM (SSPCM), that is a PCM in a supporting material. SSPCM can be obtained by vacuum impregnation, a method

producing a stable PCM, removing gas and moisture from the pores of the supporting material and then injecting PCM into it.

In the article by Zhang et al., 2006, the preparation and thermal performance of SSPCMs have been considered. At the time, the authors told that SSPCM is "a kind of *novel* PCM". The salient features are: large apparent specific heat, proper thermal conductivity, and the "keeping shape stabilized in the phase change process and no need for containers" (Zhang et al., 2006). After experimental investigation, Zhang and coworkers proposed a list of quite interesting conclusions for TES. Polymeric matrices have been used to shape stabilize the paraffin.

Pinecone biochar and palmitic acid

Biochar is a "porous carbonaceous material" suitable for encapsulating PCMs. Then, let us return to biochar/PCM composites.

In the introduction of their article of 2020, Das and coworkers start the discussion from the renewable solar energy and its main drawback, the intermittency. Consequently, a form of thermal energy storage is important. The surplus of the thermal energy generated by sunshine can be stored and PCMs are ideal materials to store and discharge energy by their phase change. And here, Das and coworkers stress the problems existing with PCMs. For instance, there is the already mentioned problem of liquid leakage during phase transitions, when the solid-liquid phase transition is used. The corresponding PCM must be contained to prevent leakage. To have an improved stability and performance of a PCM, Das and coworkers observe that it is better to have the supporting material in the form of a network from micro to macroscale, a material where the PCM can be 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. Therefore, the research had to consider the issues related to PCMs to obtain a suitable latent energy storage material. An interesting solution is the use of polymeric networks, such as in the high-density polyethylene composite and paraffin. Among the composites mentioned by Das et al., 2020, we can find zeolite ZSM-5 and polyethylene glycol (Li et al., 2018). The mesoporous ZSM-5 was the supporting material and a vacuum impregnation was used. The composite had a thermal conductivity increased by 200% with respect of that of pure polyethylene glycol.

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. "No chemical reactions happened between the two materials", are the researchers concluding. The palmitic acid is physically absorbed by the pinecone biochar. The thermal conductivity of the composite material increased of about 44%, with respect to that of the palmitic acid. 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).

The palmitic acid is "one of the ideal PCMs" and, according to Wan et al., has several merits such as chemical stability, large latent heat and a suitable fusing point. However, two disadvantages exist. One is its low thermal conductivity that disturbs the thermal conversion. The other problem is the leakage occurring during the phase change process. As told before, Wan et al. propose to solve these problems by the use of shape-stabilized PCMs (see the discussion in the article by Wan et al. and the literature mentioned there), in the form of the PB pinecone biochar. We have already seen that the thermal conductivity increases in biochar composites. It remains to detail the problem of the leakage. The researchers prepared

composites PA/PB-1, PA/PB-2, PA/PB-3, PA/PB-4 and PA/PB-5, with PA and PB with different mass ratios of 3:7, 4:6, 5:5, 6:4 and 6.5:3.5, respectively. The leakage test was made at 75 °C: no leakage were observed for PA/PB-1, PA/PB-2, PA/PB-3 and PA/PB-4. PA/PB-5 had a spot of leakage at 75 °C. According to Wan et al., the PB was competitive because of its large pore volume and specific surface area, features which are "beneficial for the PA/PB composite to preventing the leakage of melted PA in the phase change process" (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 then the biochar has a mesoporous structure. The presence of this mesoporous structure, 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. Accordingly, the results are used for proposing a novel and low cost biochar-PCM hybrid latent heat energy storage material. 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".

Microencapsulated PCMs or SSPCMs?

As we have previously seen, to avoid the leakage problem, solutions for stabilizing PCMs have been proposed, which can be subdivided in *true* encapsulation and shape-stabilized PCMs (SSPCMs). The shape-stabilization is based on the use of a porous material, such as the biochar that we are here discussing. Sometimes, the shape-stabilization is also defined as an "encapsulation", but the *true* encapsulation is based on the specific creation of a capsule shell for the PCM. The microencapsulated PCMs, or MicroPCMs, are consisting of 3 to 100 micron size particles made of a PCM core in a polymer shell (Dolez & Vu-Khanh, 2009). Today several commercial microencapsulated paraffin-based PCMs exist and had been tested for different applications (Giro-Paloma, et al., 2016, Castellón et al., 2006).

Castellón et al., 2006, consider microencapsulated PCM for building applications. The question is the following: is it possible to introduce PCMs into a cementitious material, to obtain structural–functional integrated thermal energy storage cementitious materials (TESCMs)? We can find a positive answer in the work by Yang et al., 2022a. But it is also observed that "TESCMs have not been widely applied in large-scale engineering and remain in a trial or test stage". The review by Yang and coworkers provides an overview of TESCMs for passive buildings. A commercial product is BASF Micronal DS 5038 X, made of purified paraffin in a highly crosslinked polymethylmethacrylate shell. The melting is at 25 °C and the solidification at 24 °C; heat of fusion 97 J/g. Micronal is one of the MicroPCMs considered for direct incorporation in cement-based materials (CBM) by Drissi et al., 2019. In the Figure 14 of the given reference, it is possible to see the test huts and the PCM sheets installed in the huts.

The Global Market Insight, April 13, 2022, announced that the "[microencapsulated paraffin phase change materials market size to be worth USD 370 million by 2028](#)". Can biochar be competitive?

Other biocomposites with mesoporous biochar

In Jeon et al., 2019a, we can find biocomposites made by using coconut oil impregnated biochars. The coconut oil is an organic PCM. Biochar are 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 shows a maximum latent heat storage capacity of 74.6 J/g and a low thermal conductivity of 0.030 W/mK. Then, LHSBCs "have a high latent heat storage capacity and thermal *insulation* performance". The Table 3 of the article by Jeon et al. gives the surface area and pore properties of biochar. The average pore diameter is ranging from 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, due to the fact that 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. Moreover, the low thermal conductivity of LHSBC is sufficient to provide insulation, when this material is applied for thermal insulation. Jeon and coworkers do not consider the low thermal conductivity as a problem for the performance of composite PCMs but an opportunity for the thermal insulation.

In a study proposed by Atinafu et al. (2020a), biochar that the researchers are specifically defining as "mesoporous biochar" was introduced as a support for PCMs. The used PCMs were different n-alkanes (dodecane, tetradecane, and octadecane). The n-alkanes were infiltrated in the spruce biochar by means of a vacuum impregnation method. The infiltration ratio was of about 50%. The researchers then consider biochar in thermal energy management systems. Among the biochar/n-alkane composites, that obtained from octadecane exhibited a high latent heat storage capacity of 91.5 kJ/kg, that is 15.7 % and 25.9 % respectively higher than that of dodecane and tetradecane-based composites. 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 large mesoporous ratio and the high specific surface area are relevant for composites with organic PCMs.

The morphology of the spruce biochar has been characterized by Atinafu and coworkers using SEM. The pristine biochar has a structured surface which is suitable for PCMs infiltration. The n-alkane is distributing itself homogeneously in the biochar. As explained by the researchers, the seepage is avoided by the capillary force and intermolecular interaction between biochar and organic PCMs, during the phase change process. The functional groups of biochar (such as –COOH and –OH) are anchoring and stabilizing the organic PCM via the hydrogen bonding. Then, the behavior shown by the biochar/PCM composites is consistent with the previously stable composite PCMs 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., 2019b).

Comparative analysis

Atinafu et al., 2021a, have proposed a comparative analysis of biochar and other forms of carbon, with respect to PCM loading in the thermal energy-storage capacities. 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 measured latent heat storage capacity was ranging from 53.3 J/g to 195.9 J/g. 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 *combined effect* on the

crystallinity of heptadecane in the composite PCMs" (Atinafu et al.). The four composite PCMs (carbon nanotube, CNT; expanded graphite, EG; biochar, BC; activated carbon, AC; heptadecane, HD) are the following: HD/BC, HD/AC, HD/CNTs, and HD/EG and the exhibited latent heat capacities are of 53.3 J/g, 85.4 J/g, 163.3 J/g, and 195.9 J/g, respectively. Then, the best latent heat is that of HD/EG (expanded graphite). All the composite PCMs exhibited a decrease in heat enthalpy when compared with the pure PCM. "This is due to the pore structure of the supporting materials that restrict the normal movement of the HD chain".

In another work by Atinafu et al., 2021b, 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 resulting PCM loading capacity of biochar, biochar-CNT, and CNTs reached about 51%, 71%, and 83% respectively. The latent heats are of 93.4, 127.3, and 152.3 J/g, respectively. The synthesis strategy proposed by Atinafu and coworkers is that of creating a platform to produce "biochar-based multifunctional PCMs" suitable for specific applications.

Eco-friendly for energy efficiency of buildings

Biochar is in general recognized as an environmentally friendly product and it is considered for being used in buildings too, where it can represent a solution to some environmental concerns. Luisa Cabeza, 2021, summarizes the literature on biobased phase change materials (PCMs) used in buildings. "When implemented in testing huts", biobased PCMs are performing as expected, "decreasing the energy needed for cooling buildings". Therefore, biochar/PCM composites, such as other materials, can enhance of the energy efficiency of buildings. The base is in the integration of common construction materials with latent heat storage biocomposites (Jeon et al., 2019c). These composites are prepared through the vacuum impregnation of the PCM into biochar. Biochar is environmentally-friendly and the used PCMs can be biobased materials too. Jeon and coworkers used numerical analyses to show that the latent heat storage biocomposites (LHSBCs) can reduce in an efficient manner the energy consumption of the reference building models. Experiments and simulations validate the claim that an LHSBC can be "a promising building material" (Jeon et al., 2019c).

Also Atinafu et al., 2020b, assume biochar as a "cheap, eco-friendly, and commercially available" material suitable to adsorb several organic and inorganic specific substances. As we have previously seen, the researchers produced composite PCMs based on standard biochar and organic PCMs, such as 1-dodecanol and n-dodecane. The synthesis of the composites is influenced by the biochar specific surface area and by the intermolecular interactions, because of the presence of hydroxyl group in the organic PCM.

By Song et al., 2020, we find stressed that the practical application requires a shape-stable phase change composite (PCC). The researchers produced a stable PCC by incorporating the polyethylene glycol, PEG, with a biomass-based porous carbon, created by freeze-drying and carbonization of the fresh towel gourd. The PCC obtained by the researchers had a high melting latent heat of about 164.3 J/g. Besides the use in energy-saving buildings, Song and coworkers are mentioning a possible use of PCC in protective textiles, for the solar thermal energy storage, and also for an "infrared stealth of military targets".

A review about the biomass-derived porous carbons composite PCMs for building energy efficiency has been proposed by Jiang et al., 2022. Again, in this review, we can find the problem of the leakage during the solid-liquid phase transition process and the poor thermal conductivity. The design and synthesis of shape-stabilized phase change materials, based on

biomass-derived porous carbons, is investigated by the review for active and passive energy-saving building systems. The study by Jiang and coworkers concludes that the shape-stabilized PCMs in buildings can reduce the temperature fluctuation of indoor air and, consequently, enhance the building energy efficiency. The same we can find in the research work by Kim et al., 2022, that investigated biochar and phase-change materials in artificial finishing stones.

After collecting data from recent publications, Jiang and coworkers conclude that shape-stabilized PCMs designed for buildings are mostly made by organic PCMs and porous materials as solid supports. Paraffin wax is the most used PCM (about 75% of the SSPCMs for buildings). Paraffin wax has a high latent heat energy, chemical stability and it is non-corrosive. The shape supporting materials are categorized into carbon-based, silica-based, and polymer-based. About 65% of the scaffolds is made of carbon-based porous materials. They have high thermal conductivity and durability, high specific surface, besides an excellent affinity with PCMs. From page 15 to page 19, the review is devoted to biochar. "The inherent nature of the high porosity and ample pore channel allows for efficient capture of PCMs" (Jiang et al., 2022).

Walnut and almond shells

The review by Jiang and coworkers, 2022, contains a large numbers of references about biomass-derived porous carbons for PCM to be used specifically for the building energy efficiency. Let us mention two of these biochar, those which have been 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. DSC measurements give melting temperatures of WSC/MP and AWSC/MP at 26.27°C and 26.65°C. Fusion enthalpy was 108.3 and 138.1 J/g, respectively. The proposed data are regarding leak-free composites (Hekimoğlu et al., 2021). Also 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.

Black magnetic biochar

In the recent review that we have already mentioned before, that by Liang et al. 2022, a section of the article is devoted to the use of biochar-based composite PCMs for the storage of solar energy in the form of thermal energy. The solar energy is stored as heat using the PCM, and then released when the thermal energy is required. Among the reported literature, we can find the article by Yang et al., 2019. These researchers used poplar wood powder to obtain carbonized wood flour (CWF), and then synthesized CWF-PCMs. Moreover, Fe₃O₄ nanoparticles have been introduced to prepare a composite able to improve the solar thermal efficiency of CWF-PCMs, because the Fe₃O₄ nanoparticles are adding - as told by Liang et al. - a "black appearance" to biochar so that the absorbed sunlight is increased. Liang and coworkers are also mentioning the work by Xie et al., 2020, that prepared a tankless solar water heater based on biochar-based composite PCMs.

For what concerns the article by Yang et al., 2019, let us stress that the composite is a "magnetic wood-based composite phase change material". The Fe₃O₄ nanoparticles provide magnetic property to the composite. Due to the magnetothermal effect, the composite "can be

heated under an alternating magnetic field". The magnetic wood-based composite PCM has a latent heat as large as 179 J/g.

Other experiments

Yang et al., 2022b, are proposing an *anisotropic* biochar supported PCM composite for solar-thermal energy conversion and storage. Hemp stems were converted into biochar possessing a three-dimensional multi-level *anisotropic* pores. The material is supporting PEG. The loading rate is about 88 wt% and latent heat 170.44 J/g. Tian et al., 2022, are proposing *anisotropic* reed-stem-derived biochar for paraffin wax, again for the solar-thermal energy conversion and storage. The loading is about 93 wt% and thermal energy storage capacity of 141.47 J/g.

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 systems (BTMS) for electric vehicles (Goud & Raval, 2022). Again, 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).

What about?

Let us conclude with the question "What about greener phase change materials?", that we can find in the title of a review about biobased PCMs by Okogeri and Stathopoulos, 2021. The authors consider that paraffins, which are the most analyzed organic PCMs, have many desirable properties but they are not environmental friendly being derived from petroleum, coal, or oil shale. There are green organic alternatives, according to Okogeri and Stathopoulos. Let us list some of them from the review: edible oils, non edible plant oils and waste cooking oils. These oils have many good properties being non corrosive, with a low vapor pressure. Moreover, their melting point is related to the length of the carbon chain and then the PCM features can be tailored according to this length. Their thermal conductivity is low, but we have

previously learned that, used in biochar, the composite usually shows an increase of thermal transport. To have an eco-friendly composite, the shape-stabilizing scaffold needs to be environmental friendly too, and we have seen that biochar is perfect for this role.

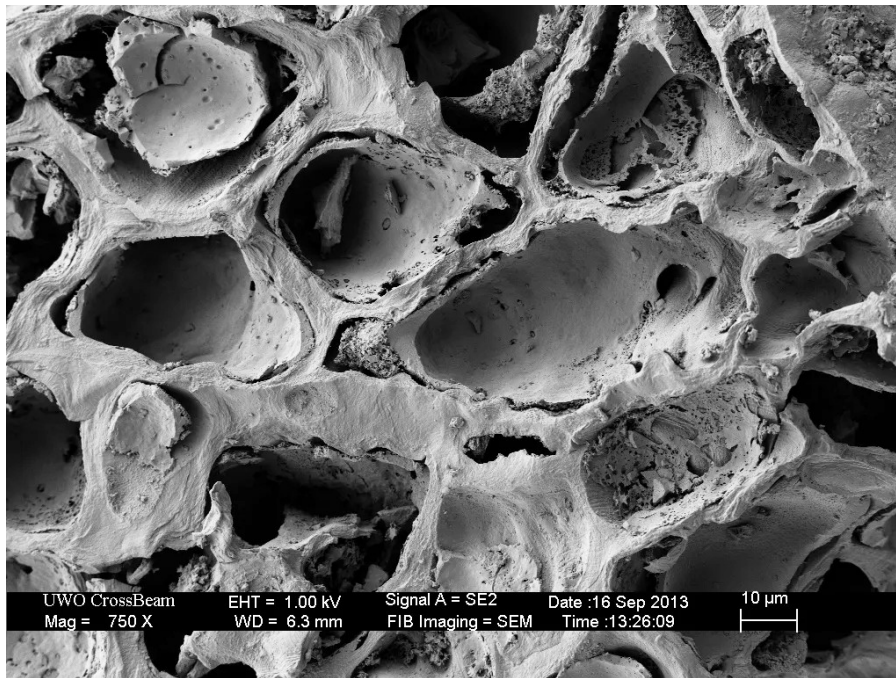


Figure 2. Scanning electron microscope image of roast ground coffee. Courtesy Todd Simpson, UWO Nanofabrication Facility, CC license, www.flickr.com/photos/zeissmicro/12695783353/

We have seen before the palmitic acid used as PCM in the pinecone biochar (Wan et al., 2019), and palmitic acid is the principal constituent of the refined palm oil. But we have also considered the work by Machado and coworkers, 2020, that proposed the pyrolysis of malt bagasse to obtain simultaneously mesoporous biochar and a bio-oil rich in palmitic acid. This bio-oil could be a good substitute of the refined palm oil in preparing a biochar composite PCM which we can consider totally bio-based and eco-friendly, because using only biomass waste.

And what about coffee? From the 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, Giorelli & 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 tell 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 yield 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 could have biochar to be used as a scaffold of the palmitic acid from coffee bio-oil, so to have another coffee biochar composite PCM, a further eco-friendly composite for thermal applications. And, besides pinecones and coffee grounds, we could continue with several other examples.

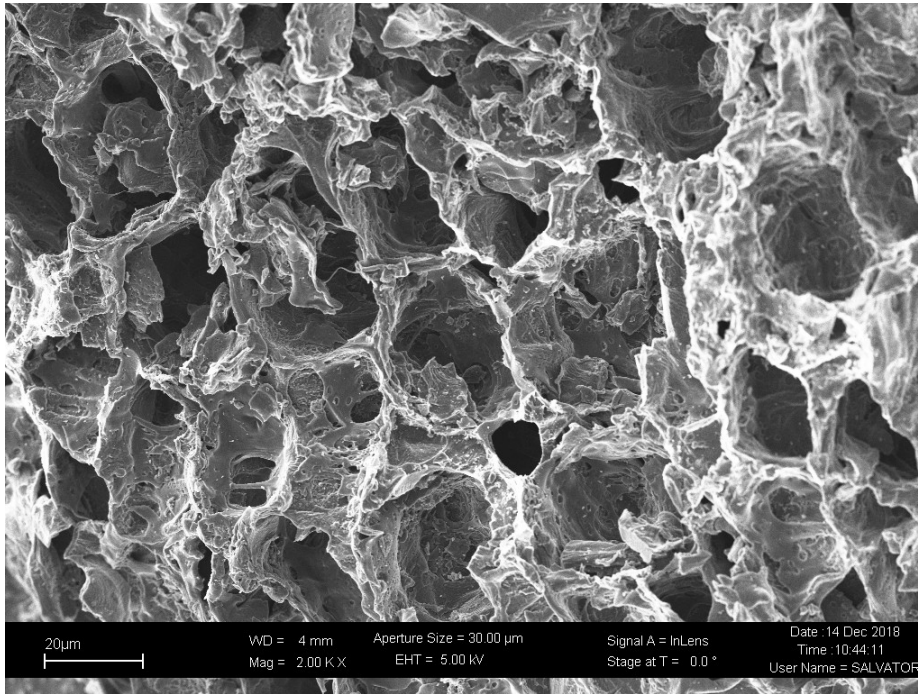


Figure 3. Scanning electron microscope image of biochar from ground coffee. Courtesy Mauro Giorcelli, Department of Applied Science and Technology, Polytechnic University of Turin, Italy. Discussion about this biochar is given in Giorcelli and Bartoli, 2019.

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