

Towards a continuous synthesis of porous carbon xerogel beads

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Abstract

A continuous process for producing porous carbon xerogel beads has been developed. It consists in injecting a pre-cured aqueous solution of resorcinol and formaldehyde on top of a column filled with hot oleic acid. The latter is pumped on the top of the column and fed at the bottom, generating an upward flow that can be adjusted to match the terminal velocity of the settling beads. Thus, the bead residence time in the column can be adjusted to match the gelation time, allowing the beads to solidify before reaching the bottom of the vessel. The obtained beads are subsequently dried and pyrolyzed.

The developed experimental setup proved the continuous synthesis of porous carbon beads is possible. Nevertheless, the shaping process caused various texture changes of the porous carbon, which mainly yields macropores instead of micro and mesopores. This process also leads to the build-up of a denser skin around the beads.

Introduction

Carbon xerogels can be synthesized by condensing formaldehyde with resorcinol in water to obtain a gel that is subsequently dried and pyrolyzed¹. The texture of these materials can be tailored by adjusting the pH of the formaldehyde and resorcinol solution, through the addition of a base, such as Na_2CO_3 ². These materials have a high surface specific area, display a tailorable pore texture and are good conductors of electricity². Therefore, they can be used in a wide range of industrial applications as adsorbents^{3;4;5;6}, catalyst supports^{7;8;9;10}, and battery or fuel cell electrodes^{11;12;13;14;15;16}. The original process developed by Pekala^{1;17} is not applicable on a large scale because it involves long aging time of the gel and supercritical drying. Optimizations of this process proposed by Job et al.^{18;19} constitute a substantial improvement over the original process: the gels were, in this case, dried in air instead of supercritical conditions; however, the process still uses a batch molding manufacturing step, which is slow, discontinuous and cannot easily produce spherical shapes.

Spheres are indeed the shape of choice for packed beds in chemical reactors or filter cartridges because sphere packing has been extensively studied over the past few centuries²⁰. This shape ensures an excellent flowability of the material, thus making bulk handling more convenient at an industrial scale. Resorcinol-formaldehyde beads are most often produced by an inverse-emulsion process. The resorcinol-formaldehyde solution is dispersed under

vigorous stirring in an organic continuous phase such as cyclohexane containing surfactants^{21;22}. Monodisperse particle size distributions can be obtained by membrane emulsion^{23;24}. However, these techniques can only produce microspheres (1-500 μm) since larger droplets cannot form stable emulsions. Inverse-emulsion processes are also limited to batch production and the use of surfactants may interfere with the microsphere surface²⁵.

Another way of producing carbon xerogel beads would be to mill carbon xerogel monoliths and subsequently form the milled material into beads with the use of a binder. However, this technique is inherently discontinuous due to the batch-only production of xerogel monoliths. Besides this drawback, milling is a time-consuming process and inevitably leads to material losses due to the formation of fines. This process, although simple at laboratory scale, is not suitable for mass production.

Therefore, continuous synthesis processes of resorcinol and formaldehyde xerogels are set to be designed. The present work shows a proof-of-concept for the continuous production of bead-shaped carbon xerogels in a column reactor filled with hot oleic acid. These beads were characterized using nitrogen adsorption, mercury porosimetry, and scanning electron microscopy. The texture modifications caused by the forming process were highlighted and the beads synthesized by this process were compared (i) to monolithic carbon xerogels, i.e. carbon xerogels obtained from resorcinol-formaldehyde gels cured inside an ordinary lab vessel without any forming operation, (ii) to monolithic carbon xerogels synthesized in the presence of oleic acid and (iii) to carbon beads formed from milled carbon xerogel monoliths and sodium alginate as a binder.

Note that the device described herein is a proof-of-concept type reactor. The goal was not to reach a completely optimized process, but to demonstrate the feasibility of the continuous synthesis of carbon xerogel. It should be noted that the emphasis was logically put on the gel synthesis and shaping step, which is the step that should be continuous to design a fully continuous process from liquid precursors to porous carbon. The subsequent steps, i.e. drying and pyrolysis, can easily be performed continuously.

Experimental

Synthesis The innovative part of this work lies in the forming of resorcinol and formaldehyde gel beads which is achieved in the column reactor represented on Figure 1. The reactor is made up of two jacketed glass columns (A and B) supported by stainless steel parts: the top one and the bottom one. The top stainless steel part consists of a double funnel which is designed to ease the gel injection. It also has the oleic acid outlet and a hot water outlet. The bottom part is comprised of a descending duct equipped with an isolation valve (C), a bleed valve (D), and a bottom plug (E). The column A inner tube is 1000 mm long and 40 mm in diameter, whereas the column B inner tube is 1000 mm long and 20 mm in diameter. During operation, oleic acid was circulated upwards at 15 L/min in column A, using a centrifugal pump (F). In this configuration, the reactor contains about 2 L of oleic acid, which is constantly recirculated upwards in column A. Therefore, there is virtually no oleic acid consumption, although the

acid had to be replaced after a few weeks of use due to degradation (temperature-induced oxidation and possibly reaction with formaldehyde²⁶). Hot water was heated and pumped in the jackets of column A and B by a Julabo MW12 heating circulator. The oleic acid temperature was set to 80°C by circulating water at 94°C. The gel was injected through a 700 μm nozzle at the top of column A, 50 mm over the oleic acid level, thus forming spherical droplets of approximately 2 mm in diameter at a rate of about 3 droplets per second, corresponding to a flowrate of 45 mL/h. In this proof-of-concept configuration, the throughput is of course very low, but can be easily increased up to industrial production by (i) increasing the frequency of droplet formation and (ii) parallelizing injection nozzles. In these conditions, resorcinol-formaldehyde gel drops had a measured terminal velocity of 0.2 m/s. Note that the flowrate of the pump can be adjusted so that the beads are slowed down till their residence time in the column reaches 3 min. The size of the droplets could be adjusted by changing the nozzle size and the injection flowrate. Ultrasonic nozzles could potentially be used as well.

The beads were extracted either by using a stainless steel basket which was designed specifically for collecting the beads (and was inserted through column B to the bottom end of the reactor) or simply by quickly opening and closing the bleed valve D, once the beads had reached the bottom of the reactor. In other words, the beads were injected and formed in column A and subsequently sank to the bottom of column B which was used for bead collection only, either by using the bleed valve D or the collecting basket. When properly operated using the parameters above, the nozzle and the oleic acid circulation pump led to a very consistent residence time of the beads in the reactor. Therefore, all of the injected gel was turned into beads, leading to a polymer yield identical to cases where the gel is processed in emulsion batch or closed flask.

Oleic acid was chosen for its density (0.895 kg/L²⁷), its immiscibility in water²⁷ and its absence of reaction with water. Moreover, as the gelation time of RF gels is low at low pH (a few min at 80-90°C)¹⁸, the oleic acid was supposed to trigger the gelation on the surface of the beads so that they do not coalesce at the bottom of the reactor. Note, however, that reaction of oleic acid with formaldehyde²⁶ cannot be excluded even though after pre-curing the amount of remaining free formaldehyde should be low. Indeed, formation of methylol derivatives occurs just after mixing, leading to a quick depletion of the reactants, followed by a slower addition/polymerization phase²⁸. Since the drops were formed just before the gelation time, one can assume that a large part of formaldehyde has reacted; but oil ageing due to reaction remains plausible.

Gels were synthesized by polycondensation of resorcinol (Merck, for synthesis, $\geq 99\%$) and formaldehyde (Sigma-Aldrich, ACS grade, 37 wt.% in water, 10-15% methanol) in aqueous solution. The pH of the solution was adjusted by adding Na_2CO_3 (UCB, for analysis, $\geq 99.5\%$). In this kind of synthesis, the variables are the resorcinol/formaldehyde molar ratio (R/F), the resorcinol/ Na_2CO_3 molar ratio (R/C) and the molar dilution (D), i.e. the total solvent/reagents molar ratio. The variables R/F, R/C and D were respectively fixed at 0.5, 500 and 5.7. Reagents were separately preheated at 70°C, then mixed in a 250 mL stirred sealed flask. The flask was left unstirred at 70°C for pre-curing during 45 min. In these conditions, the gelation time is approximately 50 min^{19;29},

thus, after 45 min, the pre-cured solution was not gelled and could be handled as a liquid. The flask was quenched using tap water in order to slow down the gelation reaction and avoid any gelation in the nozzle that would instantly plug it. A third of the solution was then injected through a 700 μm nozzle at the top of the column reactor as described before. The second third was poured in a 250 mL flask containing 50 mL of oleic acid, the solution settled at the bottom of the flask while the oleic acid floated on the top. Finally, the last third was left in its original flask. This technique, summarized in Figure 2, produced three samples which could be compared to study the influence of the oleic acid alone vs. the influence of the bead forming process inside the column reactor.

When the xerogel beads were extracted from the column reactor, they were gelled enough so they did not stick together nor lost their shape. In other words, the gelation reaction had progressed at the surface of the beads so that their mechanical strength was sufficient to withstand pressure due to piling of the beads. This was obtained by carefully monitoring the pre-curing time, the oleic acid temperature, and the residence time of the beads in the reactor. However, they were still relatively soft and required extra curing for 72 h at 80°C in a sealed flask containing oleic acid. The other two samples, bulk gels with and without oleic acid, underwent the same treatment. After extra curing, the pressure was slowly decreased to 1200 Pa and the temperature was increased to 150°C for 48 h to dry the three samples. Finally, the three samples were pyrolyzed in a horizontal tube furnace flushed with nitrogen. The temperature program was 1.7°C/min to 150°C for 15 min then 5°C/min to 400°C for 60 min and finally 5°C/min to 800°C for 120 min. At the end of this process, three samples were produced: (i) a monolithic xerogel (MX) i.e. a carbon xerogel cured inside an ordinary lab vessel without any forming operation; (ii) a monolithic oiled xerogel (MOX) i.e. a carbon xerogel cured inside an ordinary lab vessel without any forming operation in the presence of oleic acid floating on the precursor solution; and (iii) xerogel beads (XB) of about 1 mm in diameter. This process is illustrated in Figure 2. The samples obtained during two production campaigns are discussed in the following paragraphs.

Moreover, in order to further discriminate the potential consequences of the counter current flow of oleic acid on the XB, static xerogel beads were also prepared. A resorcinol-formaldehyde solution similar to the one that was used for the XB synthesis was injected with a syringe at the bottom of a beaker containing oleic acid at 80°C. The droplets and the oleic acid were maintained at 80°C in the beaker and were kept still. The droplets were subsequently cured, dried, and pyrolyzed exactly as with XB. The new beads obtained are referred to as static xerogel beads (SXB). They are supposed to display evidence of the heat and oleic acid treatments, without the consequences of the counter-current fall in the column reactor.

For comparison with XB, beads made of milled carbon xerogel and sodium alginate as a binder were produced in parallel with the samples of MX, MOX, XB, and SXB. Alginates are polysaccharides present in the cell walls of brown algae. They are widely used as thickeners in the food industry or as enzyme immobilizers in the pharmaceutical industry³⁰. Alginate solutions can gel at room temperature in the presence of divalent cations such as Ca^{2+} . A solution of sodium alginate was prepared by dissolving 1 g of sodium alginate into 19 mL of water. A carbon xerogel

monolith with the same pore texture as that of the MX sample was milled in water with a Fritsch Pulverisette 02102 mill for 60 min. It was sieved at 45 μm and dried at 100°C for 48 h. 2 g of carbon powder were mixed with 6.8 g of ethylene glycol as a dispersing agent, following a previous study³¹, 2.5 mL of the alginate solution and 10 g of water. This carbon suspension was stirred manually then sonicated for 15 min. After sonication, the carbon suspension was injected using a syringe in a 250 mm deep glass vessel containing a 5 wt.% calcium acetate aqueous solution. The carbon suspension droplets hardened immediately when settling down in the liquid and did not aggregate at the bottom of the vessel. They were left in the calcium solution for 30 min for extra curing then were washed twice with water to remove the Ca^{2+} excess and twice with ethanol to decrease the capillary forces during drying and to prevent structural collapse. Drying was performed at ambient pressure at 100°C for 48 h. The beads were subsequently pyrolyzed in an horizontal tube furnace flushed with nitrogen with the same temperature program as the one used for the carbon xerogel monolith, i.e. 1.7°C/min to 150°C for 15 min then 5°C/min to 400°C for 60 min and finally 5°C/min to 800°C for 120 min. XABbp and XAB are used to designate bead samples obtained by the alginate route before and after pyrolysis, respectively, while the initial monolith is identified by MXA, i.e. monolithic xerogel for the alginate route.

Characterization Nitrogen adsorption measurements were carried out at 77 K with a Sorptomatic Carlo Erba Multisampler 190 and the isotherms were analyzed according to the BET theory and the method proposed by Lecloux³², which provided the Brunauer Emmett Teller specific surface area, S_{BET} , the micropore volume calculated by the Dubinin equation, V_{Dub} , and the total pore volume, derived from the adsorbed volume at saturation, V_{p} . Mercury porosimetry was performed using a Carlo Erba 2000 porosimeter between 0.01 and 200 MPa. The results were analyzed according to Washburn’s intrusion theory^{32;33} and to the pore collapse theory developed by Pirard et al.^{34;35}. The pore volume of pores larger than 7.5 nm, V_{Hg} , can be calculated with these theory. Pyrolyzed samples were directly observed with a Jeol JSM 840-A microscope. The samples were then split in two with a scalpel blade and observed again.

Results

The mass losses resulting from pyrolysis are given in Table 1. Alginate beads display the lowest mass loss, i.e. 16%, which is normal because the resorcinol-formaldehyde gel particles, which compose the beads, were pyrolyzed prior to bead forming. Xerogel beads undergo an average mass loss of 75%. Dry and oiled xerogel monoliths lost approximately 45% and 63%, respectively.

Nitrogen adsorption and desorption isotherms, measured at -196°C, of samples MX, MOX, XB, and XABbp are illustrated on Figure 3. Monolithic sample isotherms are a combination of type I and IV isotherms and thus are micro-mesoporous which coincides with the results found in previous studies^{2;18}. Micropores are those with a pore diameter < 2 nm, macropores are those with a pore diameter > 50 nm, and mesopores are between 2 and 50

nm. Xerogel bead isotherms are a combination of type I and II isotherms; therefore they are micro-macroporous. Finally, XABbp exhibit a micro-mesoporous texture similar to that of MX, but with a lower micropore volume. Mercury porosimetry was performed on samples MX, MOX, XB, XAB, and XABbp. The intruded mercury volume is represented as a function of pressure in Figure 4 a for samples MX, MOX, and XB and in Figure 4 b for XAB and XABbp. Similarly, the pore size distributions of these samples are shown in Figure 4 c and 4 d . Sample shrinkage due to crushing and mercury intrusion are observed in all the samples and they are discriminated by the sudden changes of slope highlighted on Figure 4 a and 4 b³⁵. These changes of slope at a given pressure represent the sudden increase of the mercury volume pushed into the material when intrusion occurs.

Thus, monolithic samples MX and MOX undergo crushing between 0.1 and 20-30 MPa, then mercury intrusion occurs until 200 MPa, which is the end of the pressure increase (Figure 4 a); their average pore size calculated from Washburn's equation, $d_{p,in}$, is 40 and 60 nm respectively (Figure 4 c). Note that this value corresponds to the constriction of the pores: in order to enter the porosity, the Hg pressure has to reach the value necessary to pass through these constrictions; once the value is reached, the Hg quickly fills the porosity. The pore size is thus somewhat underestimated by this technique, while nitrogen adsorption isotherms (type II, with the adsorbed volume tending to the infinity when p/p_0 tends to 1) show the presence of macropores. XB samples are crushed between 0.1 and 1 MPa, then mercury intrudes until 200 MPa, the end of the pressure increase (Figure 4 a); XB average pore size is 1000 nm (Figure 4 c). Finally, for alginate bead samples, mercury intrusion is observed at low pressure, starting at 1 MPa, and is probably coupled with crushing, then intrusion occurs again around 20 MPa (Figure 4 b). The pore size distribution of alginate beads appears to be bi-modal with 50 nm and 1 μ m pores (Figure 4 d). Sample shrinkage and mercury intrusion are discriminated by the sudden changes of slope, highlighted in Figure 4 a and 4 b³⁵. These changes of slope at a given pressure represent the sudden increase of the mercury volume pushed into the material when intrusion occurs.

Nitrogen adsorption measurements were analyzed to calculate the pore volume (V_p) of the saturated samples, the Brunauer Emmett Teller specific surface area (S_{BET}) and the Dubinin volume (V_{Dub}). In accordance with previous studies^{2;18;36;37}, the total void volume (V_v) was estimated as follows from nitrogen sorption and mercury porosimetry measurements :

$$V_v = V_{Dub} + V_{2-7.5} + V_{Hg} \quad (1)$$

where the Dubinin volume (V_{Dub}) represents the volume of the pores smaller than 2 nm, the inserted mercury volume (V_{Hg}) corresponds to pores with a diameter larger than 7.5 nm and $V_{2-7.5}$ is the volume of pores with a diameter range of 2 to 7.5 nm, estimated using the Broekhoff-de Boer method³². The latter was considered negligible ($< 0.1 \text{ cm}^3/\text{g}$) in our samples due to the micro-macroporous character of the materials. Results are summarized in Table 2. $d_{p,in}$ and $d_{p,ex}$ represent the pore size inside carbon xerogel particles and the pore size between the carbon xerogel particles in alginate beads, respectively.

Scanning electron micrographs show that the surface of the XB sample bead appears to be smooth and solid

whereas XAB are rough (Figure 5). The XB sample bead section displayed in Figure 6 shows the presence of a 5 μm thick skin which appears to be denser than the bead core, which is similar to monolithic carbon xerogels synthesized at low pH³⁸. Figure 7 compares the core texture of XB (a) and XABbp (b). XB presents a homogeneous texture whereas XABbp clearly displays fragments of milled xerogel bound together with alginate fibers, forming a heterogeneous structure. SEM pictures of XAB were also taken, although they are not shown here as they are similar to those of XABbp. This indicates that even after pyrolysis, the alginate fibers maintain their binding function. This is consistent with macroscopic observations as XAB retain their spherical shape and do not fall apart.

Discussion

The differences in mass loss during pyrolysis between samples MX, MOX, and XB are due to the amount of oil in each respective sample. The mass loss of MX matches the previous studies¹⁸ and is 19% lower than the mass loss of MOX, which contains the remaining oleic acid at its surface. The XB sample mass loss is higher than the MOX sample since the surface area to volume ratio is higher for small beads than for monoliths. The XAB sample displays a mass loss of 16% upon pyrolysis, however, the dry alginate mass represents only 6.25% of the total bead mass. The remaining 9.75% are probably due to water and ethylene glycol since the XAB beads were not extensively dried before pyrolysis.

The presence of oleic acid leads to: (i) a slight decrease of the specific surface area for monolithic samples (from 691 to 556 m^2/g) and (ii) a higher decrease of the specific surface area of beads samples (691 to 401 m^2/g). Moreover, the nitrogen adsorption and desorption isotherms show that the use of oleic acid generates micro-macroporous textures with lower surface area² instead of micro-mesoporous textures. These texture and specific surface area changes are more obvious for bead samples because the gel surface in contact with oleic acid is about 20 times higher for beads than for monolithic samples. XABbp sample displays the lowest specific surface area (241 m^2/g) whereas MXA has a specific surface area of 657 m^2/g ; this indicates that the milling-binding process probably damages the pores by sealing them with alginates residues, given that previous studies showed that the specific surface area is not significantly reduced by milling³⁹. Moreover, after subsequent pyrolysis, sample XAB displays a specific surface area of 624 m^2/g , which is almost similar to MXA (657 m^2/g). This confirms that the pores were obstructed by the alginate fibers in XABbp and were unblocked upon pyrolysis in XAB. The slight difference in specific surface area between MXA and XAB is probably due to different pore texture of the pyrolyzed alginate compared to the pore texture of the xerogel.

The presence of oleic acid reduced the pore, Dubinin and mercury intrusion volumes (V_p , V_{Dub} and V_{Hg}) for samples MX, MOX, and XB. Again, the influence is greater for beads than for monoliths and results for oiled samples correspond to results obtained with xerogels synthesized at a lower pH^{2;38}. Mercury porosimetry shows that beads

formed in oleic acid have 1000 nm macropores whereas original monoliths mainly have 50 nm mesopores. This result confirms that the presence of an organic phase containing oleic acid next to the resorcinol and formaldehyde aqueous solution favors the synthesis of macropores. Mercury intrusion measurements performed on XABbp samples display a bimodal pore size distribution with 40 and 650 nm pores. Pyrolysis leaves the 40 nm pores unchanged but widens the 650 nm pores to 1200 nm for XAB samples. The 40 nm pores clearly correspond to the milled carbon xerogel particle texture while the 650-1200 nm pores are the voids between the particles. These voids are partially filled with alginate fibers, which are partially eliminated upon pyrolysis thus widening 650 nm pores to 1200 nm. Note, however, that SEM pictures taken on the core of both the reconstructed alginate-containing beads (XABbp, Figure 7 (b)) and the same bead after alginate pyrolysis (not shown) cannot be distinguished from each other : the observed structure is quite similar.

Scanning electron microscopy confirms the previous observations: the XB core (Figure 7 (a)) is homogeneous and has a pore texture corresponding to that of a xerogel synthesized at low pH³⁸ while XABbp (Figure 7 (b)) clearly displays milled carbon xerogel particles bound together with alginate fibers. The main phenomenon highlighted by SEM is the presence of a smooth skin around XB samples which appears to be denser than the bead core (Figure 6). This skin was not observed in any other sample. The skin is about 5 μm thick and the actual homogeneous core texture approximately starts 15 μm away from the bead surface. The skin is obviously porous as no bead exploded during the degassing step prior to the nitrogen adsorption measurement. Gas transfer is possible either through cracks or through pores smaller than 10 nm. Whether this skin generates mass transfer limitations in the case of fluid circulation within the pore texture during a process such as catalysis or adsorption, is still to be determined. The skin aspect is not similar to that of the pyrolysis heat shrunk carbon xerogels; it seems to be chemically or mechanically caused by the forming process. The core texture is made up of interconnected microporous spherical particles similar to those observed in carbon xerogels prepared under low pH condition³⁸.

Proton migration from the oleic acid to the resorcinol and formaldehyde aqueous solution can occur and make the bead precursor solution more acidic, thus leading to such texture changes. However, the bead surface should be more impacted than their core due to the surrounding oleic acid during bead formation. Therefore, it seems that at least two phenomena are taking place simultaneously: (i) the global acidification of the bead, responsible for the core texture and (ii) the formation of the denser skin.

For investigating this phenomenon, the SXB were split with a razor blade and observed with a scanning electron microscope, with the same procedure as for XB. The resulting images are presented on Figure 8. These images show : (i) beads of a size comparable to XB, about 1 mm in diameter (Figure 8 (a)); (ii) a homogeneous inner texture from the core to the surface contrary to XB (Figure 8 (a) and (c)); (iii) a fluffy surface, rather different from the smooth surface of XB (Figure 8 (b)).

These phenomena could be explained by the mass transfer inside the forming beads during their counter-current fall in the column reactor. When a fluid droplet moves inside another fluid, convection streams appear in the

droplet. These convection movements have been widely studied in the field of liquid-liquid extraction and were observed, for example, by taking pictures of water droplets containing aluminium flakes free falling in castor oil (Figure 9 (a))⁴⁰, or by NMR measurements of the velocity field inside a silicone oil droplet maintained stationary by a water counter-current (Figure 9 (b))⁴¹. These convection phenomena increase the mass transfer between the droplet and the continuous phase and, in our case, could explain: (i) the XB texture, resulting from the acidification of the bead, due to the increased transport of H^+ from the continuous phase to the core of the droplet; (ii) the texture of SXB, unchanged because it did not undergo fall-induced convection; (iii) the fluffy surface observed on SXB (Figure 8 (b)) would be the consequence of the surface-only acidification of the bead, without any transport towards the core.

Moreover, the acidification of the droplets corresponds to the deprotonation of the oleic acid and thus to the transfer of H^+ from the continuous phase to the droplets. This transfer could be influenced by the vortices inside the droplets that would carry the H^+ towards the core, whereas the skin would be exposed to the conjugate bases (i.e. oleates) formed by the deprotonation of oleic acid. This situation, presented on Figure 10, would lead to a low pH at the core, due to the H^+ excess, and to a higher pH at the skin, due to less H^+ and oleates. Therefore, it could contribute to the skin phenomenon observed on XB.

Along with these vortices, droplets moving in a continuous phase undergo the formation of hard caps in low-velocity areas (Figure 9 (a)). The formation of hard caps is amplified by the presence of impurities, which tend to accumulate at the interface between the droplet and the continuous phase, thus interfering with the convection vortices^{42;43}. The impact of the presence of impurities at the interface would be particularly high in systems exhibiting high interfacial tension, such as aqueous liquids/nonpolar liquids⁴³, which is the case in the column reactor. The hard cap formation can have a serious impact on the heat and mass transfer between the droplet and the continuous phase⁴³. In our case, solid hardened resorcinol-formaldehyde residues from previous syntheses could have formed hard caps responsible for the skin phenomenon observed on XB.

Finally, two other hypotheses could explain this skin phenomenon. First, SAXS measurements performed during the synthesis of low-pH resorcinol and formaldehyde gels showed that the gel formation is driven by reaction-induced phase separation processes²⁹. The relative velocity of the beads in oleic acid can generate friction and shear stresses at the beads surface that could locally disturb the phase separation of the gel formation and lead to such skin phenomenon. Second, temperature has little influence on R/C=500 carbon xerogels when the synthesis is performed at a steady temperature¹⁸. However, the fast temperature changes occurring in this process (preheating, quenching and forming) can be responsible for this skin buildup which is a major consequence of this forming process and which requires further investigation.

Conclusion

Although the synthesis of resorcinol and formaldehyde xerogels has been thoroughly studied over the past two decades, continuous synthesis processes are still to be designed. The column reactor that was developed in this work proved that the continuous synthesis of porous carbon beads is possible in a way compatible with industrial applications and brought to light the main consequences of bead forming on the xerogel pore texture. By comparing the beads produced by this process with both regular carbon xerogel monoliths obtained in an ordinary lab flask and carbon xerogel monoliths obtained in an ordinary lab flask containing oleic acid, it was shown that the beads display pore textures similar to those observed in carbon xerogels prepared under low pH condition. They are homogeneous but show a denser skin which can be caused by: (i) the formation of convection vortices and hard caps; and/or (ii) the friction and shear stresses at the beads surface during the settling in the reactor; and/or (iii) rapid temperature changes during the forming process. This skin phenomenon requires further investigation.

Finally, the beads produced by this process were compared to beads made of milled carbon xerogel and sodium alginate as a binder. The latter display a bimodal pore size distribution corresponding to the initial texture of the milled carbon xerogel and to the voids between the particles. Moreover, these milled carbon xerogel and sodium alginate beads display a low specific surface area in comparison with the initial monolith before milling; this indicates that the milling-binding process damages the pores probably by sealing them with alginates residues.

It must be noted that the contact with oleic acid strongly modifies the final pore texture of the material, which somewhat hampers its control, easily performed in closed flasks. In order to prepare carbon xerogel beads with smaller and tuned pore size, the nature of the oil should probably be modified to avoid acidification of the core of the beads. This is the subject of current work in our research group.

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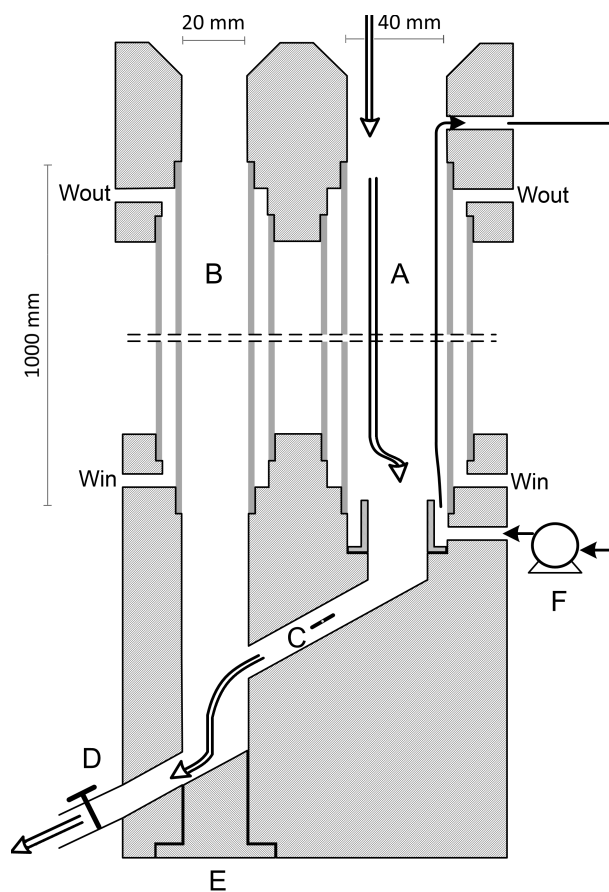


Figure 1: Column reactor for the forming of resorcinol-formaldehyde beads. Main column (A), auxiliary column (B), descending duct with isolation valve (C), bleed valve (D), bottom plug (E) and centrifugal pump (F). Oleic acid circulation ($\rightarrow$) and resorcinol-formaldehyde beads path ($\Rightarrow$). Hot water is circulated in the jacket : it enters the jacket at the bottom inlets marked Win and exits the jacket by the top outlets marked Wout.

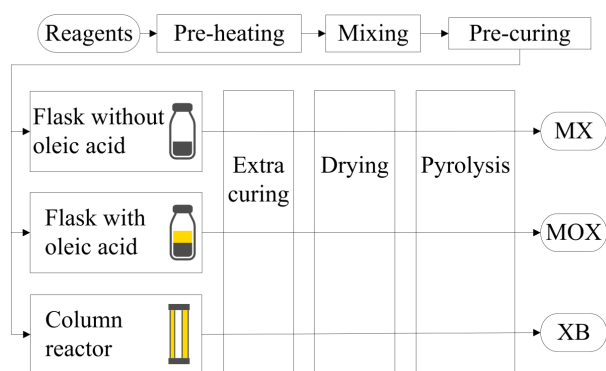


Figure 2: Xerogel sample synthesis process flowchart where MX is a monolithic xerogel, MOX is a monolithic oiled xerogel and XB are xerogel beads.

Table 1: Pyrolysis mass losses.

Sample name	Mass loss (%)
	± 0.01
MX	44.73 ± 0.94
XB	74.75 ± 3.48
MOX	62.48 ± 1.73
XAB	16.20

Average value and standard deviation obtained on several batches.

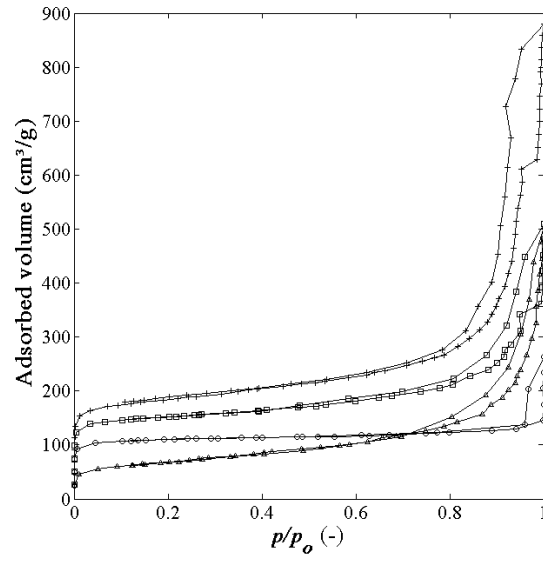


Figure 3: Nitrogen adsorption and desorption isotherms of samples MX (+), MOX ($\square$), XB ($\circ$) and XABbp ($\triangle$).

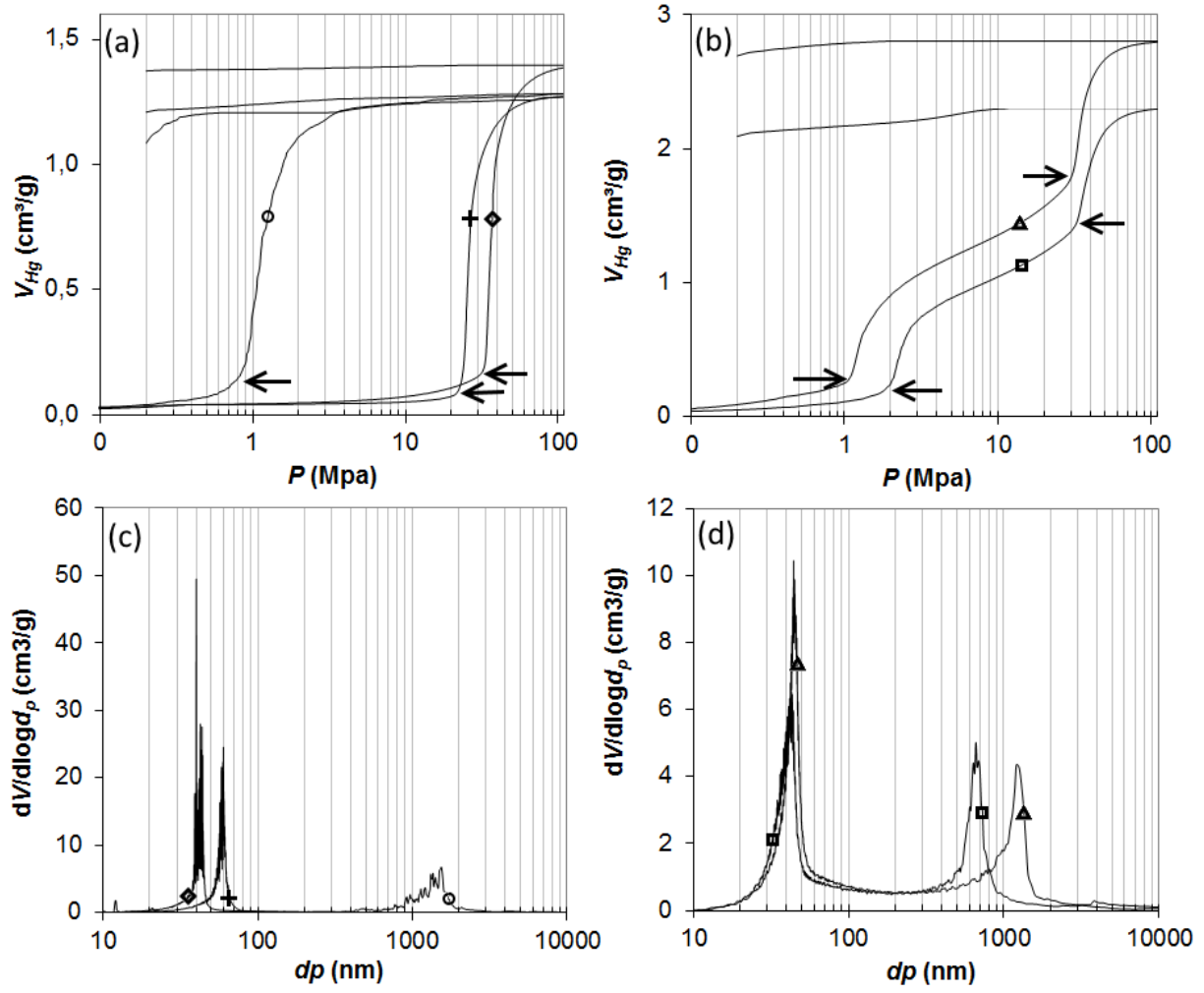


Figure 4: Mercury porosimetry of samples MX (+), MOX (◇), XB (○), XAB (△) and XABbp (□). (a) and (b): pore volume as a function of pressure. The arrows indicate the slope changes occurring when crushing stops and intrusion starts; (c) and (d): pore size distribution.

Table 2: Pore texture analysis.

Sample	V_p cm ³ /g ±0.05	S_{BET} m ² /g ±10	V_{Dub} cm ³ /g ±0.01	V_{Hg} cm ³ /g ±0.05	V_v cm ³ /g ±0.1	$d_{p,in}$ nm ±1	$d_{p,ex}$ nm ±50
MX	0.97	691	0.28	1.28	1.6	40	— ^(a)
MOX	0.56	556	0.24	1.21	1.5	60	— ^(a)
XB	0.23	401	0.18	1.21	1.4	1000 ^(b)	— ^(a)
MXA	1.56	657	0.27	1.48	1.8	45	— ^(a)
XABbp	0.77	241	0.10	2.10	2.2	40	650
XAB	1.59	624	0.25	2.56	2.8	45	1200

^(a) irrelevant measurement; ^(b) estimation for which the observational error is ±100. V_p is the pore volume at saturation, S_{BET} is the Brunauer Emmett Teller specific surface area, V_{Dub} is the Dubinin volume, V_v is the total void volume, estimated as follows : $V_v = V_{Dub} + V_{2-7.5} + V_{Hg}$ where V_{Dub} is the Dubinin volume, V_{Hg} the inserted mercury volume and $V_{2-7.5}$ is the volume of pores with a diameter range of 2 to 7.5 nm. $d_{p,in}$ and $d_{p,ex}$ represent the pore size inside carbon xerogel particles and the pore size between the carbon xerogel particles in alginate beads, respectively. $d_{p,in}$ and $d_{p,ex}$ were calculated from Hg porosimetry curves using Washburn's equation.

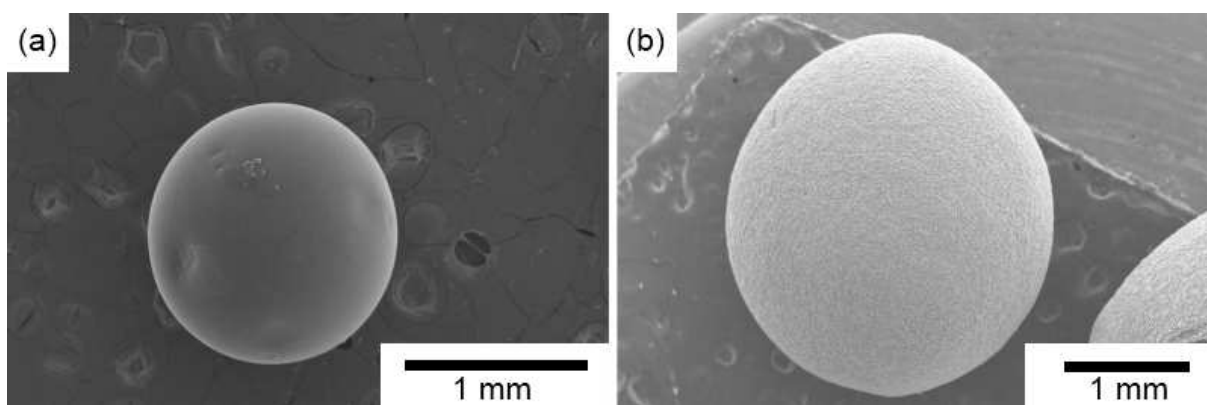


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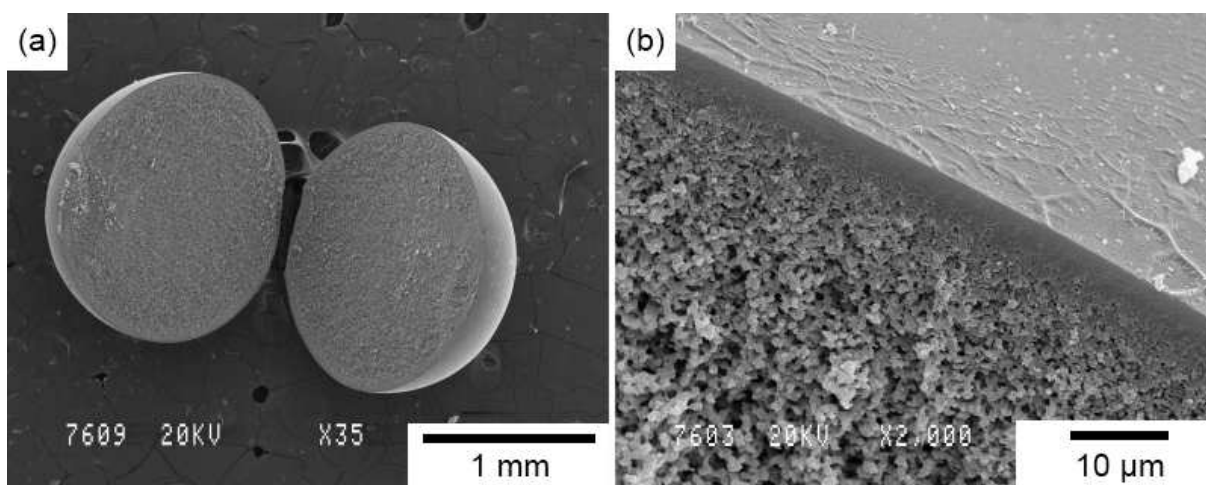


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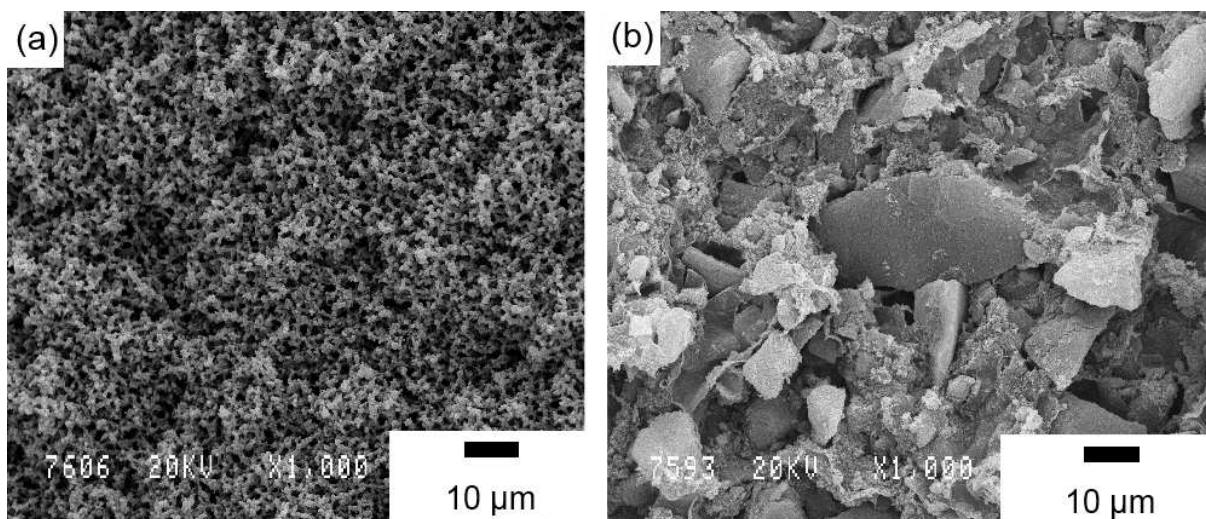


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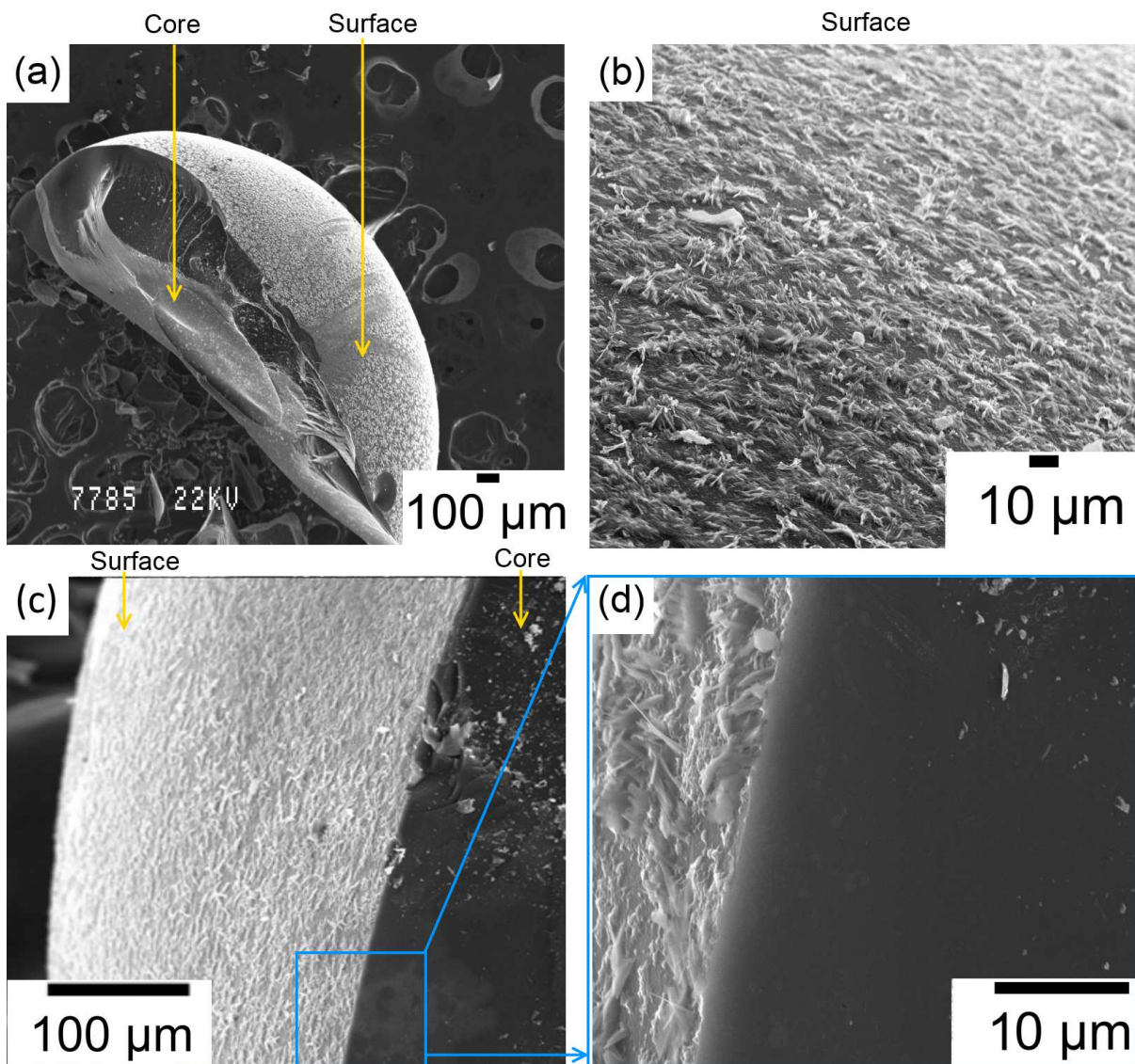


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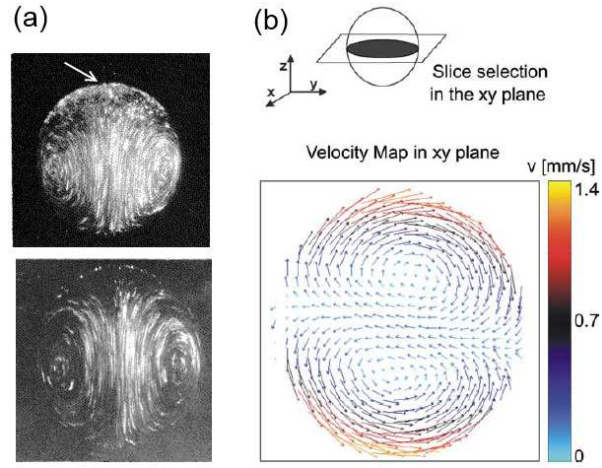


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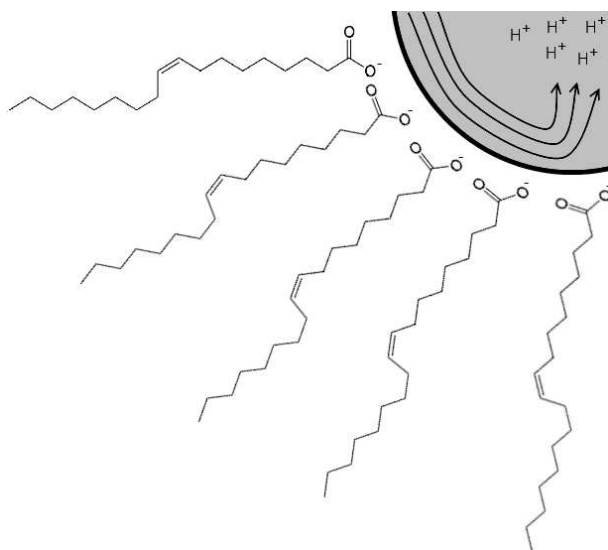


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