

SUPERCRITICAL CO₂ PROCESSES FOR THE PRODUCTION OF NEW MATERIALS FROM NATURAL CARBOHYDRATE POLYMERS

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Drying and antisolvent precipitation were found to be potential applications of supercritical carbon dioxide (scCO₂) for converting natural polysaccharides such as cellulose and hemicelluloses into value-added products.

Based on the Lyocell process, ultra light-weight aerogels consisting of a large, interconnected system of meso and macro pores were obtained from commercial pulps and derivatized cellulose. Main process steps are: (1) Preparation of a cellulose solution in molten *N*-methylmorpholine-*N*-oxide monohydrate (NMMO·H₂O) at 110-120°C and casting the viscous mass into moulds, (2) regeneration of the cellulose aiming at the preservation of the cellulose dissolution structure upon extracting the solidified cellulose/NMMO bodies with, e.g., ethanol and (3) drying of the lyogels using scCO₂. The field of potential applications for the novel materials seems to be large and ranges from biomedical applications up to their utilization as catalyst support.

Supercritical carbon dioxide can be also used as an anti-solvent for controlled precipitation of hemicelluloses from dimethyl-sulfoxide (DMSO) and DMSO / water mixtures. The obtained nano- and micro-structured xylan and mannan agglomerates whose chemical constitution is hardly altered under the mild conditions of scCO₂ anti-solvent precipitation, can be used for example in encapsulation of active compounds, as slow release agents, or as chromatographic separation materials. Furthermore, there is some evidence that scCO₂ anti-solvent precipitation is a suitable measure for purifying hemicelluloses in terms of a reduced lignin content.

INTRODUCTION

Cellulose and hemicellulose represent the most important share amongst the class of natural carbohydrate polymers [1]. Apart from using these polymers as feedstock for the production of biofuels and other chemicals, their utilization for designing novel materials increasingly attracts interest. The trend towards renewable resources also claims the use of green solvents like supercritical carbon dioxide but direct processing of natural polymers by supercritical carbon dioxide is limited by the low miscibility of these substances. However, drying and anti-solvent precipitation using scCO₂ are two interesting applications in this field as the above mentioned low miscibility is a pre-requisite for applying these techniques.

Supercritical drying is regarded as a very gentle drying method and finds preferred use for converting lyogels into aerogels provided that the lyogel's solvent is miscible with scCO₂. Thus, this technique was found to be also applicable for drying cellulosic lyogels which were

obtained by regenerating cellulose from Lyocell dopes (solution of cellulose in NMMO) with ethanol or acetone [2-5]. Depending on the solvent used, supercritical drying can be performed at mild conditions [3] under which the cellulose macromolecules are neither oxidized nor hydrolyzed [4] and the fragile, highly-porous network structure is largely retained.

Supercritical CO₂ can also be used to precipitate polymers from solutions [6] via the supercritical-anti-solvent technique. This technique has already been applied to carbohydrate polymers [7] and was found to be a suitable technology for preparing hemicellulose particles with controlled morphology [8]. The principle of anti-solvent precipitation is based on the fact that a tertiary mixture of CO₂ with the respective solid (hemicelluloses) and an organic solvent is, depending on the CO₂ content or pressure, either homogeneous or splits into a solvent/CO₂ phase and a liquid phase which is rich in organic solvent and hemicellulose. A continued addition of CO₂ to the heterogeneous mixture leads to supersaturation in the polymer-rich liquid phase and finally to precipitation of hemicellulose particles.

In the present paper we communicate the effects of antisolvent precipitation on the morphology of the obtained xylan and mannan aggregates and on the purity of the products in terms of their lignin content.

MATERIALS AND METHODS

Cellulose Aerogels

Cellulose Aerogels were produced from different non-derivatised celluloses and pulps using the NMMO route. Solutions containing 3% and 6% cellulose were obtained by dissolving the corresponding amounts of cellulose in molten NMMO·H₂O the latter already containing an appropriate amount of the stabilizers propyl gallate and *N*-Benzyl-morpholine-*N*-oxide (NBnMO) [4]. The clear viscous melts were poured into cylindrical molds where the solutions solidified.

Regeneration of cellulose by extraction of the NMMO with an appropriate solvent and subsequent drying of the obtained lyogels are the two most sensitive steps in preparing cellulosic aerogels. Water or highly diluted aqueous solutions of NMMO are frequently used solvents for cellulose regeneration [5]. However, due to the low solubility of water in scCO₂, these solvents have to be replaced by more suitable ones such as ethanol prior to the final drying step.

For cellulose regeneration, the Lyocell molds (about 2 g) were placed in the tenfold amount of pure ethanol at room temperature. Even though regeneration could be also performed in a circulatory apparatus, regeneration in batch mode provided an opportunity to measure regeneration kinetics with a submersible UV/Vis probe.

After regeneration, the lyogels were transferred into a high pressure autoclave, which was quickly pressurized with scCO₂ to a pressure above the vapor pressure of ethanol in order to avoid uncontrolled drying. Then the autoclave was heated to 40°C and pressurized with scCO₂ to 100, 150 or 200 bar. After reaching the desired pressure, the outlet valve of the autoclave was opened and scCO₂ was flushed through the autoclave at constant pressure until the pores of the aerogel were free from the regeneration solvent. After slowly depressurizing the autoclave at constant temperature, the dried aerogels can be removed from the drying unit.

Mass and volume of the cylindrical gels were recorded after each preparation step. ESEM images were taken in order to get information about the pore structure of the aerogels. Specific surface area and porosity of the aerogels were obtained from nitrogen adsorption experiments at 77 K. Mechanical tests were performed on an electromechanical universal testing machine, equipped with a 500N load cell.

Supercritical Antisolvent Precipitation of Hemicellulose

Nano- and micro-structured hemicelluloses particles were prepared from birch xylan, oat xylan, and spruce mannan using an antisolvent-precipitation setup as shown in figure 1. The polysaccharides were dissolved in DMSO or water / DMSO mixtures at different temperatures up to 150 °C. Semi-continuous anti-solvent precipitation experiments were performed on a SF1 Supercritical Nucleation Equipment (Separex, France, see figure 1). Hemicellulose solutions were sprayed into an autoclave containing carbon dioxide at 40 °C and 150 bar.

ESEM images of the obtained particles were taken in order to get information about their morphology. Possible degradation reactions during the process were monitored by gel permeation chromatography, GC-MS and analysis of the carbohydrate composition.

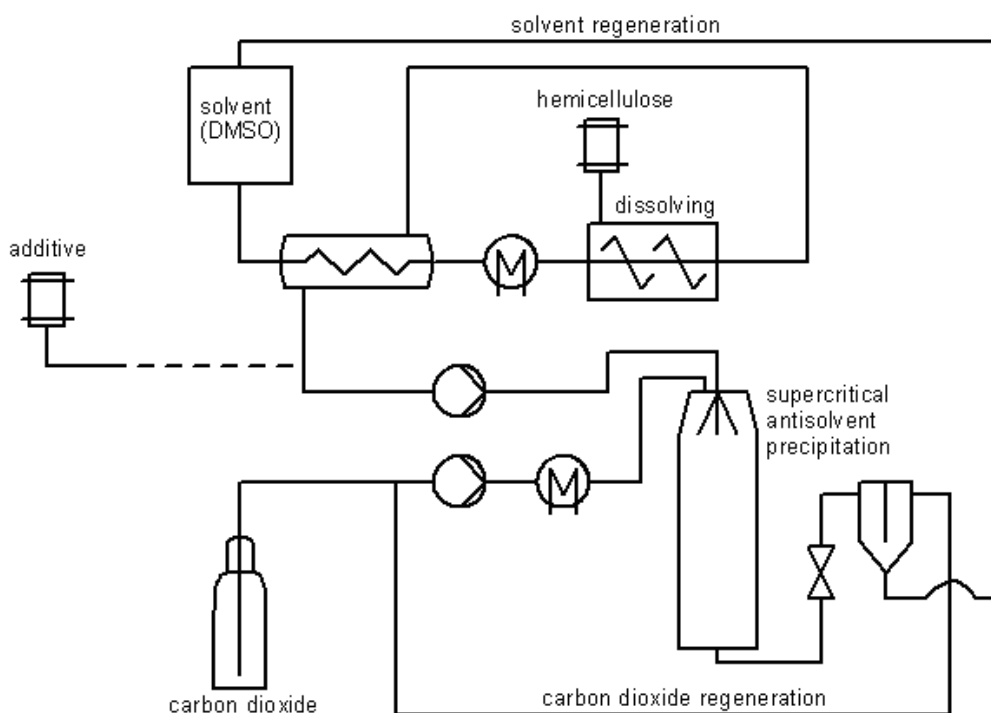


Figure 1: Schematic presentation of the Antisolvent-Precipitation Process

Prior to the precipitation experiments, the solubility of the particular hemicellulose samples in solvent / CO₂ mixtures at different pressure was investigated. A high pressure autoclave, equipped with a stainless steel frit at the bottom, was charged with hemicellulose solution to the half of his volume. The autoclave was then heated to 40 °C and pressurization was carried out stepwise over the bottom-valve to pressures ranging from 60 bar to 120 bar. After each pressurization step, a sample of the supernatant was taken and analyzed in an UV photometer.

RESULTS

Cellulose Aerogels

The preparation of cellulose aerogels comprises three steps: 1) Dissolving cellulose in NMMO·H₂O and casting the hot melt, 2) regeneration of cellulose from the solidified Lyocell dopes, and 3) drying of the obtained lyogels with supercritical CO₂ (figure 2, left). The resulting ultra light-weight aerogels consist of a large, interconnected system of meso and macro pores (figure 2, right) which make them attractive for many applications.

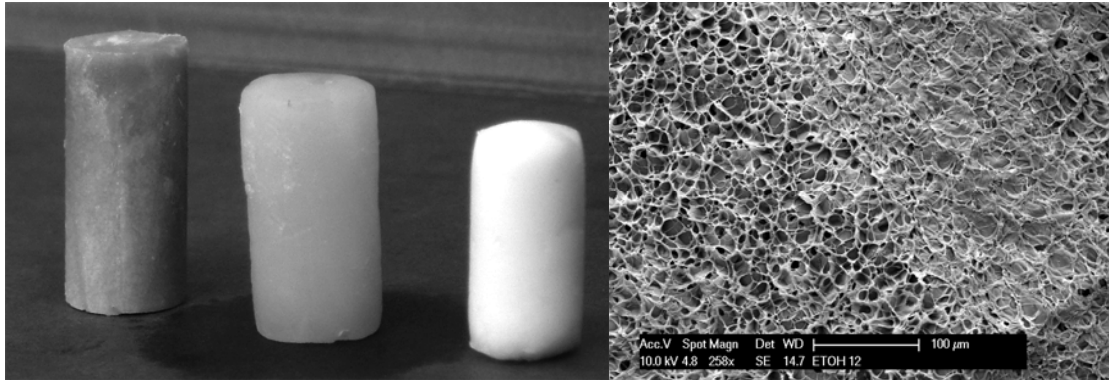


Figure 2: (l) products of the three cellulose aerogel – preparation steps (Lyocell mold, Alcolgel, Aerogel); (r) ESEM image of a typical cellulose-aerogel structure

The dimensional stability throughout the individual steps of aerogel preparation is a crucial pre-requisite for many potential applications. We found, that the extent of shrinking usually decreases with increasing molecular weight of the cellulose. On the other hand, cellulose solubility in NMMO decreases with increasing molecular weight. This leads to a longer dissolution time which, in turn, results in amplified oxidation and hydrolysis of the cellulose as NMMO is a strong oxidant.

Shrinking occurs in both extraction steps, the regeneration of cellulose and scCO₂ drying. While shrinking during scCO₂ drying was found to be comparatively independent of the type of cellulose, deformation during regeneration is strongly influenced by the cellulose type. Both, shrinking and swelling have been observed during the regeneration step, either homogeneously involving the whole body or locally, the later leading to strong deformations of the molds.

Shrinking during scCO₂ drying was found to be independent of pressure, as long as the pressure is above the critical point of the mixture solvent/scCO₂. An important parameter during scCO₂ drying is the flow direction of the drying medium during the flushing phase. While drying in a downward flow gave good results regarding the pore structure and drying time, drying in an upward flow yielded partially collapsed pores on the surface and required longer drying time.

Furthermore, it was found that the kinetics of the two extraction steps differed distinctly. The effective diffusivity of NMMO which is important for cellulose regeneration from the Lyocell dopes with ethanol was found to be one order of magnitude lower than the effective diffusivity of ethanol for supercritical drying (see figure 3). Thus regeneration is the limiting

step regarding dimensional stability as well as kinetics in the course of cellulose-aerogel preparation.

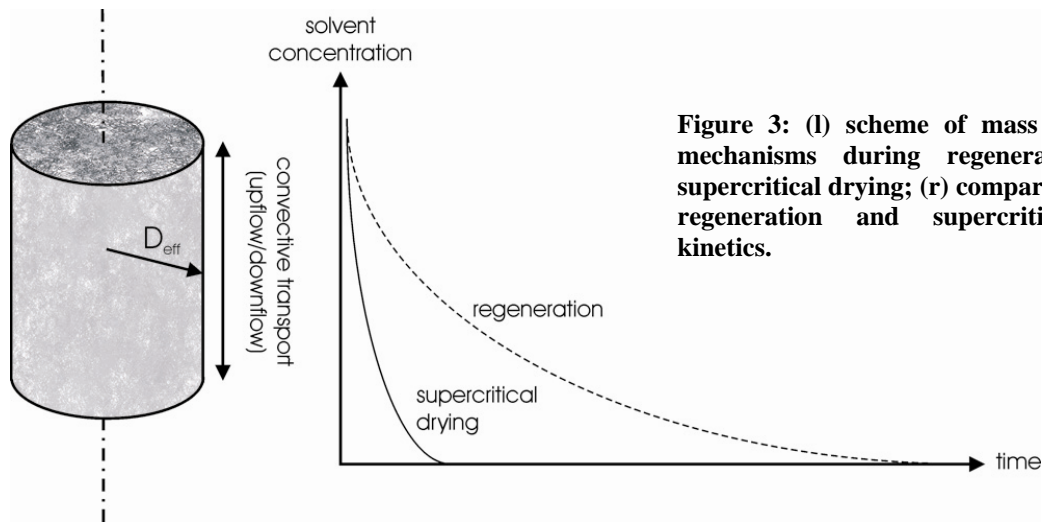


Figure 3: (l) scheme of mass transport mechanisms during regeneration and supercritical drying; (r) comparison of the regeneration and supercritical-drying kinetics.

Supercritical Anti-solvent Precipitation of Hemicellulose

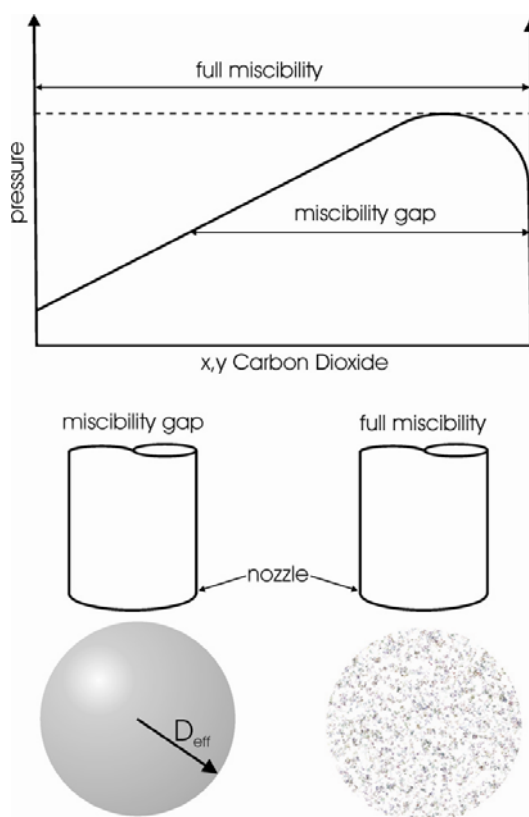


Figure 4: Mass transport during antisolvent precipitation with and without miscibility gap

The supercritical anti-solvent process was used to precipitate different hemicellulose-polymers from DMSO and DMSO/water (90/10, v/v) mixtures. DMSO was either pre-heated to 70 °C or mixed with 10 % (v/v) water in order to make it a suitable solvent for hemicelluloses. As xylans and mannans are not soluble in water, precipitation from DMSO/water mixtures takes place at the same pressure as from pure DMSO.

Supercritical anti-solvent precipitation of hemicellulose can be performed at conditions where $scCO_2$ and the respective solvent are either partially or fully miscible. In case of partial miscibility, droplets are formed and mass transfer within the droplets controls precipitation and thus particle morphology (figure 4). If the pressure is high enough to gain full miscibility, the extent of supersaturation is the only controlling factor and very small particles can be obtained.

The presence of water leads to additional mass transfer resistance even at pressures where DMSO and $scCO_2$ are fully miscible. Precipitation at low pressure or in the presence of water thus gives large, spherical particles whereas very small particles can be obtained if the pressure is above the miscibility gap (figure 5).

Supercritical anti-solvent precipitation was found to be not only a suitable tool for preparing hemicellulose particles of controlled size and morphology but also a potential measure for hemicelluloses purification. There is some evidence from Curiepoint Pyrolysis GC/MS and ^{13}C HR-MAS NMR studies of different hemicelluloses precipitates that scCO_2 anti-solvent precipitation reduces their lignin content.

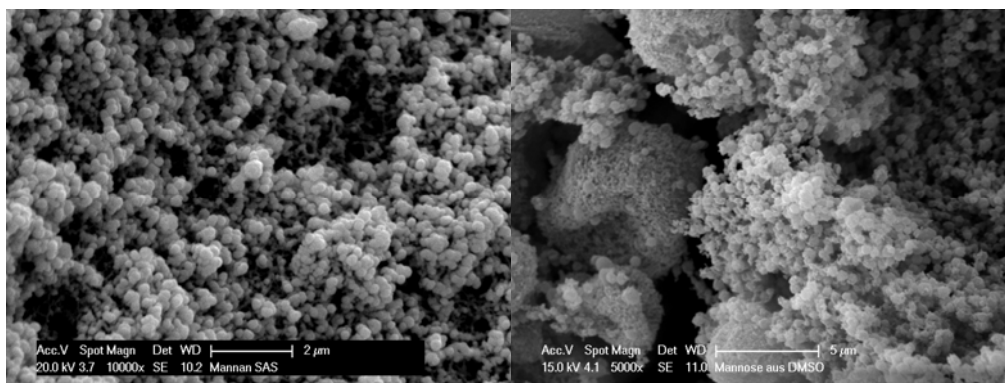


Figure 5: Mannan precipitated from a DMSO/water mixture (90/10, v/v) at pressures beyond the critical pressure (left); and below the critical pressure (right)

CONCLUSION

Supercritical drying and supercritical anti-solvent precipitation were found to be suitable techniques for converting natural polysaccharides such as cellulose or hemicelluloses into value-added biomaterials. Thus, cellulosic lyogels can be converted into ultra light-weight cellulose aerogels by scCO_2 drying. Improving the dimensional stability of the aerogels throughout the extraction steps is still challenging and will be subject to further studies. Hemicellulose particles of controlled size and morphology on the other hand can be obtained by scCO_2 anti-solvent precipitation. Purification of hemicelluloses from residual lignin is a beneficial side-effect of supercritical anti-solvent precipitation.

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