



Controlled precipitation and purification of hemicellulose from DMSO and DMSO/water mixtures by carbon dioxide as anti-solvent

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ABSTRACT

Anti-solvent precipitation of xylans and mannans from dimethylsulfoxide (DMSO) or DMSO/water mixtures, and subsequent drying with supercritical carbon dioxide (scCO₂) were developed into a useful technique for preparing spherical hemicellulose micro-particles. Depending on the type of hemicellulose, water content of DMSO, precipitation pressure and temperature, the particle size can be adjusted within a wide range from less than 0.1 to more than 5 μm. For example, fast super-saturation which can be achieved by applying supercritical conditions results in the formation of very small particles as mass transfer between the solvent DMSO and anti-solvent scCO₂ is reduced to a minimum.

Anti-solvent precipitation from aqueous DMSO (e.g., 10% water) allows for processing distinctly larger amounts of hemicelluloses compared to pure DMSO without the necessity of increasing the precipitation pressure. The formation of an additional inert aqueous phase increases the mass transfer resistance, which results in the formation of larger, stable agglomerates.

Curiepoint pyrolysis GC/MS, gel permeation chromatography (GPC) and analysis of the monosaccharide composition of both the parent hemicellulosic material and the corresponding precipitates demonstrated that hemicelluloses can be purified from residual lignin by supercritical anti-solvent precipitation with carbon dioxide without altering the structure of the biopolymers.

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1. Introduction

The concept of biorefinery as an integrated process based on the existing pulp mills gained more and more interest in the last years. Biorefineries are in principle comparable with oil refineries. However, in contrast to oil refineries which almost consist of fully optimized process-chains, biorefineries are still lacking complementary and optimized process steps. Exploring potential separation and formulation technologies and improving the overall techno-economic feasibility of biorefineries is thus still challenging [1]. Applications utilizing the green solvent carbon dioxide, such as in production of extractives, already joined the current spectrum of separation processes in the biorefinery sector [2].

Ethanol is one of the main products of biorefineries and significant progress has been made in the conversion of cellulosic and lignocellulosic biomass to ethanol [3]. Apart from production of biofuels, the utilization of byproducts like fats, lignin or hemicelluloses is of increasing importance as these byproducts significantly affect the feasibility of such concepts [4,5]. Especially if it succeeds

to utilize increasingly the hemicelluloses fraction of such lignocellulosic materials – which is in the limelight of the present study –, the effectivity and competitiveness of biorefinery processes would largely benefit. “When processes are implemented that allow for the entire plant (virtually any plant) to be chemically converted – economically – to chemicals or energy, the bio-based economy will truly have arrived”, was written by Davenport [6]. Having this in mind, the importance of searching for new separation and formulation technologies for biomass based products and byproducts of ethanol production becomes obvious.

Utilization of hemicelluloses is a big challenge, as this class of biopolymers represents the second most abundant biopolymer in the plant kingdom. Due to their properties, hemicelluloses have an immense application potential [7]. In conventional sulfite pulping processes, a large percentage of the hemicelluloses fraction becomes degraded to oligomers or monomers, which are dissolved along with lignin and are mostly used for energy production within the pulpmill. Hemicellulose in its native form is not soluble in water and extreme pH-values or additives are needed to dissolve small amounts of these polymers. Ebringerova and Heinze [8] found that DMSO or mixtures of DMSO and water are suitable hemicellulose solvents and several hemicellulose purification protocols using DMSO as a solvent have been proposed recently [9–11]. How-

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ever, there are some drawbacks of using DMSO for hemicelluloses purification, especially if this solvent is considered for large-scale applications: it is difficult to remove from isolated hemicellulose fractions due to its low vapor pressure, it is expensive and not environmental-friendly, and it might exert an oxidative effect when mixed with other agents, such as certain alkylating or acylating agents. Therefore, effective techniques are required for (a) quantitatively removing DMSO from purified hemicellulose fractions and (b) for recycling a high percentage of the used solvent.

A process which can effectively be used to precipitate and dry polymers from DMSO solutions is the gas anti-solvent process (GAS) [12,13]. The driving force behind this process is the addition of a gaseous anti-solvent to a polymer solution causing supersaturation of the polymer, especially under supercritical conditions. Depending mainly on the rate of super-saturation, particle size and morphology of the precipitates can be controlled to a certain extent. Even though a multitude of gases could be employed in the GAS process, carbon dioxide is the most extensively used anti-solvent next to water these days as it is cheap, largely inert and environmental-friendly [12]. Furthermore, the comparatively low energy input required for converting CO₂ into the supercritical state (and the ease of recyclability) makes this solvent very attractive for many applications such as the preparation of nanoparticles [14,15], polymer blends [16,17] and coatings for drug delivery [18,19].

The potential of using hemicelluloses as coating materials is well known [20,21], but requires the preparation of particles having largely uniform shape and diameter. In the present study we would like to communicate a procedure that allows for a controlled precipitation of xylans and mannans in the form of particles having defined structures. Furthermore, the effect of hemicellulose dissolution and anti-solvent precipitation at elevated temperature on the integrity of the biopolymer was studied by gel permeation chromatography and monosaccharide composition. Purification of the hemicelluloses in terms of reducing the residual lignin content was found to be an interesting side-effect of scCO₂ anti-solvent precipitation.

2. Material and methods

DMSO (>99.5%) was purchased from Roth (Germany) and carbon dioxide (>99.8%) was purchased from Linde (Austria). Xylan extracted from beech sulfite pulp (beech xylan) was kindly provided by Lenzing AG. Oat xylan and birch wood xylan were obtained from Roth (Germany). Spruce mannan was kindly provided by Abo Academy Turku, Finland. Mixed softwood Kraft lignin (INDULIN AT™, WESTVACO Co., USA) and spruce organosolv lignin (former Organocell GmbH, München, Germany) were used to study the dissolution behaviour of lignin in DMSO throughout the anti-solvent precipitation process.

2.1. Preparation of hemicelluloses solutions

Preparation of hemicelluloses solutions was performed by adding DMSO or DMSO/H₂O (90%, v/v) to an excess of hemicellulose, heating to 150 °C and stirring for 30 min. The solution was finally separated from non-dissolved hemicellulose by filtration. Using this procedure, hemicellulose concentrations of 1–5 mg ml⁻¹ were obtained.

2.2. Solubility of hemicelluloses

Solubility of hemicelluloses in DMSO upon dilution with supercritical CO₂ was studied in batch mode by measuring the optical density of solutions (OD 250 nm) at 10 different pressure levels covering the range from 0.1 to 15 MPa (repeat determination).

2.3. Batch mode

Batch mode experiments which were also used for studying the solubility of hemicelluloses in the binary mixture DMSO/CO₂ were performed using a high-pressure equipment consisting of an HPLC pump (TSP mini pump, Thermal Separation Products, USA) with cooled dual pistons and an empty 40 ml semi-preparative HPLC column (Alltech Grom GmbH, Germany) with a stainless steel frit at the bottom as batch cell. 20 ml of the saturated hemicellulose solutions (pure DMSO or DMSO/water mixtures) were placed in the batch cell and heated up to the respective temperature. After temperature equilibration, the column was pressurized up to 6 MPa with CO₂ at a flow rate of 5 g min⁻¹. After 15 min of equilibration time, a sample was taken from the solution and the pressure was increased to 7 MPa. After another 15 min the next sample was taken. Stepwise increase of system pressure and sampling was repeated up to a final pressure of 15 MPa. Finally, the supernatant was flushed out with scCO₂. The precipitate was dried with scCO₂ for 60 min.

Semi-continuous experiments were performed using high-pressure equipment (SF1, Separex, France). After pressurizing with CO₂ at a flow rate of 5 kg h⁻¹ and equilibrating (5 min) the atomisation vessel at 15 MPa and 40 °C, 200 ml of the saturated polymer solution was sprayed into the vessel at a flow rate of 2 ml min⁻¹. Hemicellulose particles were collected on a stainless steel frit at the bottom of the vessel. Removal of the supernatant liquor and drying of the precipitate was carried out as described above. DMSO was quantitatively recovered in a cyclone separator.

2.4. Gel permeation chromatography

Gel permeation chromatography (GPC) measurements used the following components: online degasser, Dionex DG-2410; Kontron 420 pump, pulse damper; auto sampler, HP 1100; column oven, Gynkotek STH 585; multiple-angle laser light scattering (MALLS) detector, Wyatt Dawn DSP with argon ion laser ($I_0 = 488$ nm); refractive index (RI) detector, Shodex RI-71. Data evaluation was performed with standard ASTRA and GRAMS/32 software.

Separation conditions were as follows – eluent flow: 1.00 ml min⁻¹; columns: four PL gel mixed A LS, 20 μm, 7.5 mm × 300 mm; injection volume: 100 μl; run time: 45 min; *N,N*-dimethylacetamide/lithium chloride (0.9%, w/v), filtered through a 0.02 μm filter, was used as mobile phase.

The amount of 25 mg of dry hemicellulose sample was weight to centrifuge tubes. The activation procedure consisted in subsequent steps of demineralised water and ethanol followed by removal of supernatant liquid. The samples were left in DMAc over night. The supernatant liquid was removed the other day and replaced by 2 ml of DMAc/LiCl 9% (w/v). The samples were left for dissolution overnight. Prior to measurement the samples were diluted (0.3 ml of sample solution:0.9 ml of DMAc) and filtrated.

2.5. Scanning electron microscopy

Scanning electron microscopy (SEM) was performed on a Phillips XL 30 ESEM instrument. All samples were sputtered with gold and mapped at an acceleration voltage of 10 kV.

2.6. Curiepoint pyrolysis GC/MS

Curiepoint pyrolysis GC/MS was performed using a CPP-40 pyrolyser (GSG, Germany) coupled with a GC 6890 and MSD 5973 (Agilent Technologies). 200 μg of the sample was pyrolysed at 600 °C for 10 s. GC/MS conditions were as follows: fused silica HP-5ms column (30 m, 0.25 mm, 25 μm), carrier gas: helium, 0.9 ml min⁻¹, inlet: 280 °C in split mode (1:20), oven program: 50 °C (5 min), then 5 °C min⁻¹ to 280 °C (15 min), auxiliary temperature:

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