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Development of Food-grade Microparticles from Lignin

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Abstract

An opportunity presented itself to develop a new food ingredient from the wood biopolymer lignin. Lignin is set to become a high-yielding and inexpensive by-product of lignocellulosic biorefining processes. The aromatic heteropolymer is water insoluble, relatively hydrophobic, non-digestible in its native form, and also considered to be non-toxic. Retention of these properties in isolated lignin may enable a microparticulate food ingredient, with particular use as a fat mimetic, to be developed.

Lignin was extracted from shrub willow using an organosolv pulping procedure. A reactor vessel suitable for pulping under organosolv conditions was obtained, modified and commissioned. Using central composite design, an ethanol concentration of 60% (v/v), extraction time of 132 minutes and extraction temperature of 195°C were found to extract lignin of the highest yield and purity. The total lignin content of lignin extracted from chipped, untreated willow under these conditions was 96.53 ± 0.10% (w/w).

An anti-solvent precipitation technique was explored for the ability to produce lignin microparticles. An aqueous-organic solution of lignin was dispersed into a much larger volume of water, whereby leaching of organic solvent from the dispersed phase into the water resulted in progressive precipitation of the lignin solute, ultimately producing a suspension of solid microparticles. Temperature and addition of surfactant were investigated as a means of controlling particle properties. Increasing initial water temperature between 4 and 80°C produced increasingly large agglomerates of uniform sub-micron primary particles, increasingly fused into monolithic masses. Faster removal of ethanol, hydrophobic interactions or an increase in rate of diffusion limited coalescence may be responsible for the increased fusion at higher temperatures.

Incorporating the ionic surfactant sodium dodecyl sulfate (SDS) or cetyltrimethylammonium bromide (CTAB) in the water at temperatures of 20-60°C during anti-solvent precipitation produced spherical, monodisperse lignin particles in the range 0.1-0.2 μm. However, concentrations of these surfactants greater than 1% (w/v) caused aggregation of primary particles, probably due to bridging between bilayers of surfactant at high concentration. The non-ionic surfactants Tween 20 and sucrose ester were unable to prevent particle fusion at the 60°C preparation temperature, indicating that the electrostatic repulsion between particles coated with SDS and CTAB is important to stability.

The ability to manipulate the size of SDS-stabilised particles using added salt and adjustment of pH was determined. The electrostatic mechanism of stabilisation by SDS was confirmed by the ability of added potassium chloride and calcium chloride to destabilise lignin particles. Measured particle size increased with the concentration of added salt, due to either greater fusion of lignin during particle formation or to aggregation of primary particles, depending on whether the salt was added before or after particle formation. Decreasing the pH of the suspension of particles to 1.5, which is lower than the pKa of SDS, caused primary particles to aggregate. For destabilisation with salt and pH, generally only the relative volumes of particles in two modal distributions (~0.1-2 μm and ~1-100 μm) appeared to change. This indicates that the ability to control particle size may be limited by aggregation kinetics. Adjustment and control of pH throughout particle formation may enable the preparation of particles in the intermediate size range, such as narrowly distributed 1-10 μm particles. The ability to prepare particles of various and controlled size is important for maximising industry applications.

To highlight a possible application of food-grade lignin microparticles, the performance of particles as Pickering stabilisers of oil-in-water emulsions was evaluated. A literature method of emulsion formation involving the redispersion of dried lignin particles and various pH-modification steps, and a method using lignin in the form of freshly prepared microparticle suspensions were explored. Both methods produced emulsions stable to coalescence for five months of chilled storage, although the pH-modification method produced slightly smaller (D[3,2] of 2.7-11.9 μm) oil droplets than the fresh suspension method (D[3,2] of 11.6-31.2 μm). It may be possible in the future to produce smaller emulsion droplets by using a higher energy emulsification technique and by utilising sub-micron lignin particles, rather than ~10 μm particles.

Three main areas in which work could be carried out to move this project forward have been identified. These areas are:

1. Lignin characterisation – including molecular weight, chromatography to determine lignin fragment types and contact angle.
2. Control of particle size – including the investigation of more food-grade surfactants, ultrasonic mixing and controlled pH changes during anti-solvent precipitation.

3. Food applications – including further investigation into Pickering emulsions, foam stabilisation and fat mimetic applications.

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