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Manufacture of lignin microparticles by anti-solvent precipitation: Effect of preparation temperature and presence of sodium dodecyl sulfate

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ABSTRACT

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 hardened 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. Although the glass transition temperatures of dried lignins were in the range of 75–87 °C, depression of glass transition temperature in the presence of water during particle formation may be associated with the increasing agglomeration of particles with increasing temperature. Incorporating sodium dodecyl sulfate (SDS) in the water at temperatures of 20–60 °C inhibited agglomeration producing smooth, spherical, monodisperse particles in the range of 0.1–0.2 μm. However, SDS concentrations greater than 1% caused the formation of some larger particles. Once safety, consumer acceptance and aspects of functionality have been established, spherical particles in the 0.1–0.2 μm size range may have application as food industry fat mimetics, fillers or even as solid particle emulsifiers.

Industrial relevance

Increased biorefining of lignocellulosic feedstocks to produce bioethanol may lead to an abundance of lignin that could be well-utilised as a sustainable, non-caloric food ingredient. Microparticulation provides a route for the transformation of lignin into a useful food ingredient, on the basis that particles with suitable properties for use in food systems can be produced: notably, a particle diameter preferably between 0.1 and 25 μm, spherical shape and stability against aggregation.

1. Introduction

Microparticulate ingredients have wide-ranging use in the food industry. For example, microcapsules and microparticles can be used to incorporate ingredients, bioactives and other materials into foods. Encapsulation provides many benefits, including preventing nutritional losses, masking off-flavours and converting liquids into powders that are easier to handle (Desai & Jin Park, 2005). By using their small size and homogeneity to mimic the lubrication properties of fat droplets in a dispersed phase, microparticles have also been used as fat mimetics in emulsion based foods (Gómez, 2008; Setser & Racette, 1992; Singer, 1996). Furthermore, microparticles have been used as bulking agents, to replace solids in low-calorie and low-fat foods (Humphreys, 1996). Finally, microparticles, generally in the form of micro-rods, have been used as Pickering stabilisers for foams and emulsions (Campbell, Holt, Stoyanov, & Paunov, 2008; Campbell, Stoyanov, & Paunov, 2009; Wege, Dyab, Velev, & Paunov, 2007; Wege, Kim, Paunov, Zhong, & Velev, 2008).

For fat mimetic applications, in which microparticles are used to mimic the fat droplet, the microparticles must be insoluble in water. With diameters of only 0.1–3 μm, the particles are not detected individually, but rather as a smooth, creamy, fluid product that coats the mouth in a similar way to fat. In this way, fat droplets in emulsion-based foods can be replaced by equivalent phase volumes of microparticulate fat mimetics (Gómez, 2008; Setser & Racette, 1992; Singer, 1996). Although many fat replacing ingredients on the market have hydrophilic

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characteristics, hydrophobic microparticles may better mimic fat droplets (Jones, 1996). Hydrophobic microparticles exhibit less interaction with aqueous media and could potentially form films that provide a more fat-like mouth coating (Stark & Gross, 1994).

For any particles that are added to foods, particle size, shape, hardness and taste are important to consider. Hinton (1970) has suggested that the minimum particle size that can be felt by the palate is around 25 μm. Tyle (1993) observed that particle shape and hardness heavily influence the perception of different particle sizes, finding that particles as large as 80 μm are not perceived as gritty if they are either soft and spherical or relatively hard and flat. Conversely, for hard and angular particles, grittiness can become evident as particles exceed a size range of about 11–22 μm. Thus there seems to be an important interplay between particle size, shape and hardness. Taste is also critical; a major commercial drawback for LITA®, an ingredient produced by microparticulating zein protein from corn gluten meal, was its inherent flavour problems (Jones, 1996).

There is great potential for lignin to be used for the preparation of microparticulate ingredients for the food industry. Lignin is an aromatic heteropolymer found in the woody stems of hardwoods and softwoods and in all types of vascular plants (Sarkanen & Ludwig, 1971; Wool, 2005). The polymer is a high yielding by-product of lignocellulosic biorefining processes. It is likely to be both abundant and relatively inexpensive if biorefining flourishes as predicted. We suggest lignin could be well utilised as a food ingredient, provided that a form suitable for incorporation into foods can be produced.

Lignin is water insoluble and also relatively hydrophobic (Lora & Glasser, 2002). In its native form, lignin is non-digestible and since it is consumed naturally as part of some plants, it is also considered to be non-toxic. Calcium lignosulfonates (40–65) are already approved for use as food additives in New Zealand as carriers of fat-soluble vitamins and carotenoids in water based foods. Sodium lignosulfonates are approved processing aids. One of the many methods that can be used to remove lignin from feedstocks is organosolv pulping, which uses organic solvents at high temperatures for delignification (Lora, 2008). Organosolv lignin is known to consist of low molecular weight fragments and Baurhoo, Ruiz-Feria, and Zhao (2008) suggest that these fragments are digestible by both ruminant and monogastric animals. Thus unlike native lignin, organosolv lignin may be absorbed into the blood. It is unknown whether this lignin would have a caloric effect once absorbed. If no caloric effect exists, the insolubility and hydrophobicity of lignin indicate that microparticles of lignin could function as non-caloric colloidal particles in foods.

A technique based on anti-solvent precipitation may be an appropriate route for the preparation of lignin microparticles. In this technique, an organic solution containing the polymer of interest is added to an aqueous solution under shear. Through the removal of the organic solvent by either evaporation or extraction, polymer precipitation occurs and solid microparticles are produced. For example, Patel, Bouwens, and Velikov (2010), Zhong and Jin (2009) and Parris, Cooke, and Hicks (2005) sheared ethanol solutions containing dissolved zein into water, and then removed the ethanol to produce zein microparticles or nanoparticles. Asrar and Ding (2006) patented a method of producing lignin microparticles for the controlled release of agricultural actives using a solvent evaporation technique. The method produced lignin particles with an average size in the range of 5.6–7.3 μm, depending on the mixing speed used. Finally, numerous parameters can be altered when using the antisolvent precipitation method. These include mixing type and speed, polymer concentration, volume ratio of the dispersed and continuous phases, temperature, composition of the phases and the rate of solvent removal. Use of emulsifiers and stabilisers is also an option.

Temperature influences the rate of solvent evaporation during microparticle formation. Temperatures close to or above the boiling point of the dispersed phase solvent are suggested to increase the rate of solvent evaporation. Faster evaporation reduces the amount of shearing that the dispersion undergoes before the precipitation of solid microparticles, leading to larger microparticles with larger size distributions (Yang, Chia, & Chung, 2000; Yang, Chung, Bai, & Chan, 2000). On the other hand, Stark and Gross (1994) have suggested that smaller microparticles are formed if higher temperatures are used during the precipitation process. However, the maximum temperature is limited by the boiling point of the system and also by the solution properties of the polymer. Asrar and Ding (2006) have recommended that the temperature should remain at least 20 °C below the normal boiling point of the organic solvent.

Emulsifiers can influence particle size and stability by enabling the size of dispersed phase droplets to be better controlled (Asrar & Ding, 2006). Stabilisers can prevent the aggregation of particles by providing, for example, electrostatic or steric repulsion (Patel et al., 2010). Asrar and Ding (2006) found cellulose derivatives, particularly methylcellulose, to be useful emulsifiers for the preparation of lignin microparticles. Stark and Gross (1994) suggest that carboxymethyl cellulose, gum Arabic, sodium caseinate, lecithin, DATEM-esters, polysorbates and sodium dodecyl sulfate (SDS) can all be used effectively to stabilise zein microparticles. Thus there is a variety of emulsifiers and stabilisers that may be useful for the production of lignin microparticles.

The main focus of this study is to examine the influence of process variables on the size and shape of lignin microparticles. These variables include temperature during shearing and the presence and concentration of surfactant. Although Asrar and Ding (2006) have previously prepared lignin microparticles, we use fresh lignin still dissolved in its food-grade extracting solvent. The existence of the organosolv delignification process, possible without mineral acids, offers food-grade liquor and the potential to close-couple particle formation to the extraction in an efficient plant with solvent recycle. We aim to produce particles with suitable properties for use in foods. We are especially interested in the use of lignin microparticles as fat mimetics, but also for other applications such as fillers or solid particle emulsifiers.

2. Materials and methods

2.1. Materials

Lignin was extracted from chipped *Salix purpurea* and used in the form of extraction liquor containing 4.68 ± 0.04% solids. Lignin precipitated from this liquor was found to have a total lignin content of 96.5 ± 0.1% (w/w) as determined by acid insoluble and acid soluble lignin analyses on a dried sample. The remainder mostly comprised ash (1.65%), xylosyl sugars (1.78%) and glucosyl sugars (0.33%).

Absolute ethanol (analytical reagent grade, LabServ, Thermo Fisher Scientific New Zealand Ltd) was mixed with distilled water to prepare 60% (v/v) ethanol.

Sodium dodecyl sulfate (SDS) (BDH, VWR International Ltd, New Zealand) was used as received.

2.2. Methods

2.2.1. Lignin extraction

Lignin was extracted from chipped *S. purpurea* by heating the feedstock with 60% (v/v) aqueous ethanol to 195 °C in a stainless steel vessel (Parr 4767, Parr Instrument Company, Illinois) and holding the mixture at this temperature for 132 min. The extraction conditions were chosen based on earlier optimisation trials and are consistent with the range of conditions normally used for organosolv delignification. The extraction liquor containing the lignin was recovered after the vessel was cooled by filtering the vessel contents through glass wool to remove the wood chips. The extraction liquor was then stored at 5 °C until use.

2.2.2. Microparticle preparation

Microparticles were prepared using a method based on anti-solvent precipitation (Patel et al., 2010). To study the influence of preparation