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Effects of critical fluid lipid extraction on the gelatinization and retrogradation of normal dent cornstarch

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Abstract

Critical fluid extraction of native lipids from cornstarch using 80/20 (v/v) CO_2/ethanol and 100% ethanol was carried out in order to see what effects each solvent would have on the starch pasting profile. The results were compared with cornstarch defatted by refluxing with 75/25 (v/v) *n*-propanol/water. Pure ethanol extracted more native lipid than CO_2/ethanol, and extraction improved when the initial moisture content of the starch was increased from 10% to 19%. Granules became less swollen and less deformable with increased lipid extraction. Paste viscosity studies carried out at starch concentrations less than 8% yielded lower peak and setback viscosities of lipid-extracted cornstarch relative to native cornstarch. However, above 8% starch concentration, swollen granules were in more intimate contact, and the added rigidity caused by lipid extraction yielded much higher peak viscosities relative to the starch control. Lipid-extracted cornstarch samples at concentrations above 8% showed plateau rather than peak viscosities reflecting the limited swelling power of the granules, and the defatted samples displayed less viscosity breakdown due to their increased granule rigidity.
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1. Introduction

The extraction of native lipids from cornstarch can alter its physical properties and thus add to the many end-use applications for this abundant agricultural commodity. Supercritical CO_2 and CO_2/ethanol blends offer a convenient and non-toxic method for carrying out these extractions. The native lipid component of cornstarch contains mainly free fatty acids along with lesser amounts of phospholipids (Morrison, 1988; Morrison, Milligan, & Azudin, 1984). Linoleic, palmitic and oleic acids are the fatty acids present in the largest amounts. The solubility of lipids in supercritical CO_2 under different experimental conditions and the use of supercritical CO_2 as an extraction medium and as a technique for separating lipid mixtures have been extensively studied (e.g., Bamberger, Erickson, Cooney, & Kumar, 1988; Brunetti, Daghetta, Fedeli, Kikic, & Zanderighi, 1989; Chrastil, 1982; Hammam, 1992). Although supercritical CO_2 is a non-polar solvent, the ability of this solvent system to dissolve polar lipids can be enhanced by adding co-solvents such as ethanol.

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There are only a few reports on the treatment of starch and flour with supercritical fluids. Braga, Moreschi, and Meireles (2006) studied supercritical fluid extraction on ginger and tumeric tuber starches and saw subtle changes in the physical arrangement of the starch molecules by X-ray diffraction, but the authors did not correlate these results as a function of the native lipid. Hubbard, Downing, Ram, and Chung (2004) used supercritical CO_2 and CO_2/ethanol to extract non-starch free lipids from wheat flour as an alternative to the traditional Soxhlet extraction with non-polar solvents such as hexane. These workers did not consider the extraction of native lipids from starch granules. Koxholt, Altieri, Marentis, and Trzasko (2003) used extraction with supercritical fluids to remove off-flavors, odors and colors from starch but did not identify the native lipids removed by this process. Francisco and Sivik (2000) examined the gelatinization of cassava, potato and wheat starches in supercritical CO_2; however, they did not determine the extent of native lipid extraction under their experimental conditions.

In this study, ethanol was used as either a solvent or co-solvent for lipid extractions at elevated temperature and pressure. The pressure and temperature used were not above the critical point for ethanol, so this procedure will be designated critical fluid extraction (CFE) rather than supercritical fluid extraction. Native lipid fractions were extracted from normal dent cornstarch at two different moisture contents using CFE with ethanol or CO_2/ethanol as solvents. X-ray diffraction patterns, microscopy, birefringence images and pasting properties were used to characterize the extracted cornstarch granules. Pasting properties of extracted cornstarch samples were compared to those of cornstarch prior to critical fluid extraction and also to cornstarch which was extracted with 75% *n*-propanol/water to remove essentially all of the native lipid component.

2. Materials and methods

2.1. Materials

Normal dent cornstarch (pure food grade) was obtained from A.E. Staley Mfg. Co., Decatur, IL. This starch had a moisture content of approximately 10% (w/w) and was used as the control. Starch with higher moisture content was prepared by placing a pan containing 130 g of the same starch in a sealed Plexiglas chamber with a pan of distilled water for 24 h at room temperature (23 °C). This starch had a moisture content of approximately 19% (w/w). A saturated starch slurry containing roughly 43% moisture content was also tested, but this sample presented difficulties during critical fluid extraction that led to non-homogeneous samples which had not been evenly extracted. Moisture content was determined either by vacuum drying weighed starch samples at 100 °C or by using an HFT 2000 moisture analyzer (Data Support Co. Inc., Encino, CA). All starch weights are given on a dry weight basis. Heptadecanoic acid and lipid reference standard GLC-68A were supplied by Nu-Chek Prep, Inc., Elysian, MN. A standard solution of heptadecanoic acid was made by diluting a weighed amount of the solid with toluene.

2.2. Lipid extraction

Lipids were extracted from 2 g (dry weight) of cornstarch using refluxing 75/25 (v/v) *n*-propanol/water as described previously (Morrison, 1988; Peterson, Fanta, Adlof, & Felker, 2005). Critical fluid/pressurized solvent extractions were carried out on an ISCO Model 3560 SFE (ISCO Corp., Lincoln, NE) apparatus. Roughly 5 g of sample was weighed and added to the extraction cell between glass-fiber filter discs on the top and bottom of the cell. Samples were extracted at 80 °C at a pressure of 8000 psi for 20 min with a solvent flow rate of 1 mL/min. Two solvent systems were used: 100% ethanol and 80/20 (v/v) CO_2/ethanol. Initially, supercritical lipid extractions using 100% CO_2 were also carried out, but the extractions did not yield any detectable lipid (<0.01 mg), apparently due to very poor lipid extraction efficiency.

2.3. Lipid analysis

Extracted lipids were analyzed by gas chromatography after esterification to form fatty acid methyl esters. Since the lipids in these samples of cornstarch are primarily mixtures of free fatty acids and monoglycerides, a dual esterification procedure utilizing diazomethane and hydrochloric acid/methanol was used in order to differentiate these two species as outlined previously (Peterson et al., 2005).

A Varian 3900 (He carrier gas, FID detector) gas chromatograph controlled by Varian Star Chromatography Workstation software version 5.52 was used with a Supelco SP2380 column (30 m × 0.32 mm × 0.2 μm). For each run, column temperature started at 100 °C and rose 3 °C/min to a final temperature of 205 °C. Retention times for the esterified lipid peaks were identified using lipid reference standard GLC-68A (Nu-Chek Prep, Inc., Elysian, MN).

2.4. Starch pasting curves

Pasting curves were obtained using a TA AR2000 rheometer (TA Instruments, New Castle, DE) utilizing a starch pasting cell attachment. Samples were prepared either at 5% or 10% starch solids; approximately 1 or 2 g (dry weight) brought to 20 g total weight with deionized water. First, an initial mixing step at 750 rpm was applied for 30 s at 25 °C. Then, a linear temperature increase of 5 °C/min was applied until the sample reached 95 °C. During this step and for the remainder of the pasting profile, the mixing head rotated at 100 rpm. At 95 °C the sample was held for 5 min, and then the temperature was decreased linearly at 5 °C/min to 25 °C. For retrogradation studies, once 25 °C was reached, the sample was immediately subjected to an oscillatory time sweep test and oscillated at 0.5% strain for a minimum of 10 h.