Sonication Enhanced Cornstarch Separation

Yellow dent corn soaked in deionized water at 52°C for 24 h without addition of SO2 was wet-milled using a modified 100-g laboratory procedure employing ultrasound treatment at different points in the milling process and compared to conventional wet milling and milling-only corn. Starch yields from ultrasound treatments varied from 66.93 to 68.72% and were comparable to conventional wet milling (68.92%). The ultrasound treated samples produced 6.35 to 7.02 more percentage point starch compared to the milling-only corn. Compared to the starch from milling-only corn, the ultrasound-produced starches showed a significant increase in whiteness and decrease in yellowness that are comparable to starches produced by conventional wet milling. Ultrasound treatment after the second grinding produced the highest starch yield and the lowest protein content in the resulting starch. The ultrasound-treated starches exhibited different pasting properties as evidenced by higher paste viscosities.

Keywords: Starch separation; Sonication; Wet milling; Cornstarch; RVA

1 Introduction

Wet milling is the largest value-added non-feed use of corn that involves chemical, biochemical and mechanical operations to separate corn into relatively pure fractions of starch, gluten, germ and fiber [1]. Wet milling is also a time-consuming and energy- and capital-intensive process [2]. In conventional wet milling, the first operation is steeping, which softens the corn kernel and breaks the disulfide bonds within the protein matrix [3]. During steeping, corn kernels are soaked in a dilute sulfurous acid solution at 50–52°C for 24–48 h. The sulfur dioxide (SO2) cleaves disulfide bonds in the corn endosperm protein matrix that encapsulates starch granules, disperses the endosperm protein and enhances starch release [4]. The main objection to wet milling is the long steep time and the use of SO2, which is an environmental concern. Numerous research efforts have tried various approaches to reducing steep time and SO2 usage. These alternative wet-milling procedures include enzyme-assisted steeping [2] and milling [5, 6], high-pressure disintegration [7], alkali wet milling [8, 9] and sequential extraction [10].

Power ultrasound is sound waves in the frequency range of 20–100 kHz with a sound intensity of 10 to 1,000 W/cm². When ultrasonic waves pass through a liquid, this results in alternate rarefaction and compressions and bubbles or cavities can be formed if the amplitude of the waves is high enough. This phenomenon is known as cavitation. The collapse of bubbles creates localized high pressure that disrupts cell membranes and causes the cell wall to break down [11]. On the other hand, the stable cavitating bubbles interacting with the acoustic field generates strong micro-streaming and high shear. These mechanical actions of sonication have been studied for enhancing various biological and biochemical separation operations. Ebringerová et al. [12] used ultrasound to assist the extraction of immunologically active xylan from corncobs and heteroxylan from corn hulls. They did not observe noticeable changes in functional properties of the biopolymers. Salisova et al. [13] and Vinatoru et al. [14] tested sonication as a means to extract low molecular substances from plant materials and argued that the increase in extraction of organic compounds was due to disruption of cell walls and enhanced mass transfer between interfaces of bio-components. Mason [15] documented a study using ultrasound to treat rice grains in which surface erosion and particle size reduction resulted in shorter cooking and gel times.

Only a few studies have used ultrasound to separate biological components in corn processing and none has examined the effect of sonication on the quality of the resulting cornstarch. In an attempt to enhance rice starch isolation, Wang et al. [16] found that power ultrasound treatment resulted in high starch recovery but at a slightly higher residual protein content. Yang et al. [17, 18] used an acoustic-assisted process to treat corn kernels soaked in water to enhance corn pericarp separation without pro-
ducing any starch. They observed a reduction in the affinity between the pericarp and the endosperm, which is dependent on frequency and power intensity. In a study to recover starch from slurries of degemem corn flour and hominy feed, Zhang et al. [19] tested power ultrasound as a means for starch-protein separation with degemem corn flour and hominy feed, which are reasonably high in starch and may be a source of non-sulfate treated starch. Five treatments were used to produce starch from degemem corn flour and hominy feed slurries (10% solid): control, ultrasound only, ultrasound followed by fine grinding, fine grinding followed by ultrasound, and fine grinding only. The starch recovery from the corn flour was 37.1% for the control, and yields from ultrasound treatments were 65.5 to 67.0%, a 76.5 to 80.6% increase compared to the control. Similarly, starch yields from the hominy feed by ultrasound treatments were 45.4 to 45.8%, a 54.9 to 56.3% increase compared to the control. Comparing with the total starch contents in the two products, ultrasound treatments recovered 97.3 to 99.5% total starch from the degemem corn flour and 97.8 to 98.9% from the hominy feed. The objectives of this study were to determine the technical feasibility of using power ultrasound to fractionate corn without addition of sulfate, and to study the properties of the resulting starch.

2 Materials and Methods

2.1 Treatment procedures

Yellow dent corn samples (100 g) of a single commercial hybrid were soaked in deionized water at 52°C for 24 h without the addition of SO₂ or other chemicals. For comparison, samples were milled with a laboratory SO₂ procedure [20] and named “conventional” in subsequent analyses. Four ultrasound treatments were performed in duplicate using a VC-750 ultrasound processor (20 kHz, Sonics & Materials, Inc., Newtown, CT, USA) (Fig. 1):
1. **No ultrasound (UST-0).** The same procedure was used as the 100-g conventional wet milling, but without use of SO₂. This treatment is also termed “milling-only treatment”.

2. **First grind followed by ultrasound (UST-1).** The soaked corn was milled in 200 mL water using a Waring blender (Dynamic Corp. of America, New Hartford City, CT, USA). The slurry was washed into a beaker with 250 mL water, and treated for 30 min by the ultrasound processor with a setting of 100% amplitude and power input of 120 W. A relatively low temperature (< 40°C) was maintained during sonication via a jacket cooling system. After the ultrasound treatment, the slurry was drained into a #7 (2.83 mm) sieve placed in a bucket to remove the germ and coarse fiber. Further separation was done according to the 100-g milling process.

3. **Ultrasound followed by second grind (UST-2).** After the first grinding, sieving, shaking and washing out of the germ and coarse fiber (the same procedures as the conventional milling process), the slurry was allowed to sit for 30 min. The top layer of the slurry was decanted and the precipitate slurry left in the bottom layer was transferred into the sonication container. The slurry (total volume — 600 mL) was treated for 30 min using the ultrasound processor with the same operation setting as UST-1. The slurry was finely ground in a mill (Quaker City model No. 4-E; the Straub Co., Warminster, PA, USA). After the slurry was passed through the mill, the decant water was used to wash the mill and was retained with the resulting slurry, and the milled slurry was collected in a small bucket. Further processing was done following the 100-g milling process.

4. **Second grind followed by ultrasound (UST-3).** As in the conventional milling process, the slurry was finely ground in the mill. The slurry was allowed to sit for 30 min. The top layer of the slurry was decanted and the precipitate slurry left in the bottom layer was transferred into the sonication beaker. The slurry (total volume — 600 mL) was treated for 30 min using the ultrasound processor with the same operation setting as UST-1. After ultrasound treatment, the slurry was washed with the decant water and transferred into a labeled bucket. Further processing was done according to the 100-g milling process.

5. **Fine fiber slurry treatment with ultrasound (UST-4).** As in the conventional milling process, the fine fiber left on the #200 (74 μm) sieve was transferred into the sonication beaker after the second grinding and washing, and reconstituted into a slurry with the decant water to make a total volume of about 600 mL. The slurry was treated for 30 min using the ultrasound processor with the same operation setting as UST-1. After ultrasound treatment the slurry was re-separated by washing it through the #200 sieve. The filtrate was incorporated into that from the previous sieving. Further processing was done according to the 100-g milling process.

### 2.2 Proximate analysis

Moisture contents of starch samples were measured using a forced-air oven at 135°C for 2 h according to AACC method 44–15A [21]. The collected fiber and gluten were dried in a forced-air oven for 24 h at 50°C, and then transferred into another forced-air oven at 135°C for 2 h for dry matter content determination. The yields of fractions (starch, fiber and gluten) were determined as percentages of initial sample dry weight. The total starch content of the products was measured using a starch assay kit (SA-20, Sigma, Co., St. Louis, MO, USA). The protein content was analyzed using a combustion method at the Identity Preserved Grain (IPG) Laboratory (Illinois Crop Improvement Association, Inc., Champaign, IL, USA). The oil content was determined at the IPG laboratory according to AACC method 30–25 [21].

### 2.3 Color determination

The color of starch samples was determined with a Spectrocolorimeter (Hunter Lab MiniScan, Hunter and Assoc., Reston, VA, USA), which gave the tristimulus color scale L, a, and b (L is the degree of lightness; a and b denote a two-color coordinate, with a the red-green axis, and b the yellow-blue). All starch samples were run with triple replications. Only L and b values were compared in this study.

### 2.4 Starch pasting properties

Pasting properties of the resulting starch were measured using a Rapid Visco-Analyser (RVA) (Newport Scientific Pty. Ltd., Warriewood, Australia). A commercial regular cornstarch (S-4126, Sigma, Co., St. Louis, MO, USA), which is a product produced with a conventional wet-milling method, was used as a reference. Each starch sample (2.5 g, 14% moisture, wet basis) was mixed with 25.0 mL deionized water in an aluminum RVA sample canister. A programmed 23.0 min heating and cooling cycle was used, where the sample was held at 50°C for 1 min, heated to 95°C in 7.5 min, held at 95°C for 5 min, cooled to 50°C in 7.5 min, and then held at 50°C for 2 min. Starch pasting parameters compared were from pasting curves, which included the highest viscosity of the paste after gelatinization, the peak viscosity (PV); the shear-thinned viscosity of the paste, the hot-paste viscosity
(HPV) (the pasting viscosity after holding at 95°C); and the final viscosity (pasting viscosity at the end of holding at 50°C), the cool-paste viscosity (CPV).

2.5 Statistical analysis

Analysis of Variance (ANOVA) and correlation analyses were carried out using the Statistical Analysis System Version 6.13 for Windows (SAS Institute, Cary, NC, USA). Comparison of means was performed using the least significant difference (LSD) test.

3 Results and Discussion

3.1 Yields of fractions and starch recovery

Total dry matter recovery (TDMR) is the total weight of the dry fractions divided by the original weight of the sample. The TDMR for the conventional wet-milling process was 99.63%, and for ultrasound treatments, 97.05 to 97.21% (Tab. 1). The slight decreases in TDMR for the ultrasound treatments might be due to some losses of dry matter during sample transferring from the ultrasound treatment container to those for milling procedures. However, no significant difference in TDMR was observed among the different treatments.

Starch yields from ultrasound-treated samples were 66.93 to 68.72%, comparable to the yield from the 100-g conventional wet milling (68.92%). The ultrasound treatments produced 6.35 to 7.02% more starch compared to milling only (UST-0). Very little difference in germ yields was observed among different treatments. From Tab. 1, gluten yields for the ultrasound treatments (10.42–11.54%) were slightly higher than in the conventional wet-milling process (9.25%), but were significantly higher compared with UST-0 (7.54%). Slight differences in fiber yields were observed among the ultrasound treatments, and between the ultrasound and conventional wet-milling process. Wide variation in total fiber yields was observed between UST-0 and other treatments. The total fiber yield for the UST-0 was 20.28%, about twice that of other treatments. Our experiment suggested that the lower starch yield for the UST-0 might be due to more starch left in the fine fiber fraction, compared to other treatments. This can be seen from the data of UST-4 in which by treating only the fine fiber slurry with ultrasound, a starch yield of 68.70%, a 7.00% increase of starch yield compared with UST-0 (61.70%), was achieved. Dowd [22] used additional milling to recover starch from corn fiber and found milling for four times can recover up to 21.2% starch from the fiber which corresponds to an increase in overall starch yield of about 1.3%. Obviously, sonication treatments used in this study are more effective than the physical milling process in further separating starch from the small protein-starch complexes of the fine fiber fraction.

In addition to a difference in the starch yield between the UST-0 and the conventional wet milling process, slight differences can also be found among the ultrasound treatments applied at different stages in the milling process. The difference in fraction yields may be due to the particle size difference in the slurry resulting from grinding. The effect of ultrasound is attributable mainly to a phenomenon called cavitation [15], which refers to the formation, growth, and implosion of tiny gas bubbles in a liquid when ultrasound travels through it. A liquid system with homogenous and small solid particles allows higher cavitation activity than one with non-homogenous and larger particles [23]. In the milling process, the second grinding further broke down the particles in the slurry, produced a slurry with finer particles, and thereby enhanced cavitation activity to facilitate better starch-protein separation (UST-3).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fiber</th>
<th>Germ</th>
<th>Gluten</th>
<th>Starch</th>
<th>TDMR²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fine</td>
<td>Coarse</td>
<td>Total</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Conventional</td>
<td>7.58b¹</td>
<td>4.12a</td>
<td>11.70b</td>
<td>5.88a</td>
<td>68.92a</td>
</tr>
<tr>
<td>UST-0</td>
<td>16.80a</td>
<td>3.47ab</td>
<td>20.28a</td>
<td>5.65a</td>
<td>67.10b</td>
</tr>
<tr>
<td>UST-1</td>
<td>7.59b</td>
<td>3.85ab</td>
<td>11.44b</td>
<td>5.45a</td>
<td>10.42a</td>
</tr>
<tr>
<td>UST-2</td>
<td>7.48b</td>
<td>4.23a</td>
<td>11.71b</td>
<td>5.90a</td>
<td>10.76a</td>
</tr>
<tr>
<td>UST-3</td>
<td>6.32ac</td>
<td>3.38b</td>
<td>9.70b</td>
<td>5.59a</td>
<td>11.33a</td>
</tr>
<tr>
<td>UST-4</td>
<td>5.88c</td>
<td>3.60ab</td>
<td>9.48b</td>
<td>5.64a</td>
<td>11.54a</td>
</tr>
</tbody>
</table>

1. Values with the same letter in the same column are not significantly different (P < 0.05).
2. Total dry matter recovery.
3.2 Starch color and protein content

Notable variation in protein content and color of starch was found among the starch resulting from different treatments (Tab. 2). The UST-0 treatment produced a starch with the highest protein content. Ultrasound treatments before the second grinding (UST-1, UST-2) produced starches with protein content comparable to that from the conventional wet-milling process (control). UST-3 produced a starch with the lowest protein content, which is 26.9% lower compared with UST-0 and 24.0% compared with the conventional wet milling process. The starches treated with ultrasound showed a comparable level of \( L \)-values (whiteness) and \( b \)-values (yellowness) to that by the conventional wet milling process. Compared with the starch from UST-0, all the ultrasound-produced starches showed a significant increase in whiteness and decrease in yellowness. As shown in Tab. 2, except for the yellowness (\( b \) value) reading for the UST-4 treatment, low protein content in the starch samples usually corresponds to a relatively low \( b \) value and hence a less yellowish color. Our data on the fraction yield, starch color, and protein content suggest that ultrasound could be used to effectively disrupt the bonds in the corn endosperm protein matrix that encapsulates starch granules so as to enhance starch-protein separation.

Tab. 2. Protein content and color of cornstarches from different treatments.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Protein [%]</th>
<th>( L^b )</th>
<th>( b^c )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional</td>
<td>0.50a</td>
<td>92.81a</td>
<td>6.78b</td>
</tr>
<tr>
<td>UST-0</td>
<td>0.52a</td>
<td>90.77b</td>
<td>7.56a</td>
</tr>
<tr>
<td>UST-1</td>
<td>0.47a</td>
<td>92.76a</td>
<td>6.11bc</td>
</tr>
<tr>
<td>UST-2</td>
<td>0.46a</td>
<td>92.81a</td>
<td>5.82c</td>
</tr>
<tr>
<td>UST-3</td>
<td>0.38b</td>
<td>92.58a</td>
<td>5.80c</td>
</tr>
<tr>
<td>UST-4</td>
<td>0.39ab</td>
<td>91.72b</td>
<td>6.76b</td>
</tr>
</tbody>
</table>

a) Values with the same letter in the same column are not significantly different \((P<0.05)\).
b) \( L \) = whiteness, \( b \) = yellowness.

3.3 Pasting properties of starch

The starches from both non-ultrasound treatment and ultrasound treatments exhibited slightly different characteristics as shown by the RVA curves (Fig. 2). The pasting parameters of starches treated with different methods and at different stages of a 100-g milling process are listed in Tab. 3. Generally, starches from ultrasound treatments had a higher pasting viscosity than did starch from the conventional wet-milling process. CPV was increased more than PV and HPV by ultrasound treatments. Increased CPVs suggest that the paste could be more resistant to shearing, and form a more rigid gel after cooling down. Small differences in pasting curves can also be observed among samples treated with ultrasound at different process stages. In ultrasound treatments, intense agitation of starch granules in the slurry was generated by sonication and localized spots of very high temperature and pressure were generated by cavitation activities. These conditions might lead to configurational modifications of the granular structure, which could be in the forms of diffuse erosion or pitting of the starch granules as observed by Degrois et al. [24]. Further studies are needed to characterize the possible configurational changes in ultrasound-treated starches.

Tab. 3. Pasting properties of corn starch from dry milling products by ultrasound treatments.a.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>PV(^a) [mPa s]</th>
<th>HPV(^a) [mPa s]</th>
<th>CPV(^a) [mPa s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional</td>
<td>1399</td>
<td>922</td>
<td>1480</td>
</tr>
<tr>
<td>UST-0</td>
<td>1613</td>
<td>1142</td>
<td>2010</td>
</tr>
<tr>
<td>UST-1</td>
<td>1600</td>
<td>1117</td>
<td>2000</td>
</tr>
<tr>
<td>UST-2</td>
<td>1548</td>
<td>1064</td>
<td>1941</td>
</tr>
<tr>
<td>UST-3</td>
<td>1568</td>
<td>1029</td>
<td>1900</td>
</tr>
<tr>
<td>UST-4</td>
<td>1598</td>
<td>1064</td>
<td>2033</td>
</tr>
</tbody>
</table>

a) PV = peak viscosity; HPV = hot-paste viscosity; CPV = cool-paste viscosity.

4 Conclusion

Ultrasound treatment effectively enhanced starch-protein separation in a wet-milling process. Ultrasound treatment also resulted in noticeable changes in the pasting properties of the resulting starches. The results reported in this
study demonstrate that ultrasound-assisted starch-protein separation is a technically feasible process. The economic feasibility needs to be evaluated in future studies.

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References


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