

Zein Batch Extraction from Dry-Milled Corn: Cereal Disintegration by Dissolving Fluid Shear

L. C. Dickey,^{1,2} M. F. Dallmer,¹ E. R. Radewonuk,¹ N. Parris,¹ M. Kurantz,¹ and J. C. Craig¹

ABSTRACT

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Corn particles were extracted in an agitated vessel with a 4:1 mass ratio of 70% ethanol to corn for periods of 1–6 hr at ambient temperature. The extract solution was filtered and centrifuged to remove suspended particles after extraction and then diluted to 40% ethanol to precipitate extracted solute. Measurements of the mass of suspended particles separated by centrifugation indicate that mixing the corn particles with the ethanol dissolves and weakens the protein between cells and between starch granules within cells near the particles' surface. Under the conditions of this study, corn particles release starch granules more rapidly than the protein bodies

dissolve, as indicated by analysis of the centrifuged particles. The diffusion coefficient for ethanol solution in corn was estimated and compared with a coefficient derived from a fit of the trend in the rate of release of fine particles from the milled corn. The diffusion coefficient of pure zein in a stagnant 70% ethanol solution was estimated from the measurement of weight loss by a ball of zein. Analysis of the ambient temperature protein extraction rate indicates that 2-mm particles exhibit more convective mass transfer than 20- μ m particles.

New nonfood, protein-rich coproducts can be produced from the material generated incidentally to ethanol production from corn. About half of the protein content of corn, zein is water-insoluble but soluble in mixtures of lower molecular weight alcohol and water, and it can be purified by a sequence of alcoholic solution extraction steps. Modest amounts of relatively pure zein extracted from corn gluten are now sold for edible coating use. Zein's water-insolubility makes it highly suitable for nonfood coating uses (Lai 1997) if it can be extracted and purified at a sufficiently low cost.

Extraction of zein from corn, rather than gluten, would be compatible with both dry-grind and wet-milling plants. High starch purity is not necessary for ethanol production, therefore steeping to ensure a thorough removal of protein from the starch may also not be necessary, especially if corn oil can be separated without steeping. It is also likely that extraction of zein and oil will increase starch hydrolysis rates beyond those of a comparable conventional dry-grind process. It has recently been demonstrated that if the oil is removed using 95% ethanol, and zein is subsequently removed from the deoiled corn using 65% ethanol, both extractions at 65°C (Cao et al 1996), the remaining corn can be converted to glucose at high yield. Simulated countercurrent zein extraction of flaked corn, previously deoiled by sequential extraction with 95% ethanol, using 45% ethanol and 55% 0.1M NaOH (v/v) (Hojilla-Evangelista et al 1992), showed that good yields could be obtained with a 15:1 mass ratio of solvent to corn.

Several studies of protein extraction from seeds (Oomah 1994, Liadakis 1995, Lampart-Szczapa 1996) have been published but they describe water-soluble proteins. In these cases, conserving solvent is unimportant when compared to protein recovery and purity. Water-to-meal mass ratios as high as 30:1 are cited as optimal. Overall yield was reported but not rate information necessary for equipment sizing and process cost estimating. Examination of traditional zein extraction methods shows that a major element of the cost is solvent recovery. Therefore, use of a minimal amount of alcoholic extraction solution will be an important feature of any new,

large-scale process. Zein has a reported solubility of 15 g/L (2.0% w/v) in 70% alcohol (Augustine 1987). A higher value was reported recently (Fu and Weller 1996). Even at the highest cited solubility, solvent reclamation is a major part of the cost of zein extraction. The extraction rate can be improved by reducing the size of the corn powder. Finer powders can be difficult to separate from some liquids, but miscible displacement of water by alcohol from compacted fine solids has been demonstrated (Dickey and Tayter 1984). After extraction, the liquid extract will be diluted to ≤ 40 wt% of ethanol, allowing the zein and extracted corn oil to co-precipitate.

Separation of the zein and oil may not be necessary for some product uses. We found that the precipitated mixture forms continuous, strong films on the wall of a centrifuge. To separate zein and oil, it would be only slightly more complicated to remove the corn oil in a preliminary step using an ethanol solution of $\geq 90\%$ in which zein is less soluble, and then extract the zein with 70% alcohol (Chen and Hoff 1987). The diluted extract can be filtered or centrifuged from the precipitate and recycled at a modest cost using the associated ethanol plant's distillation facilities. This strategy is shown in Fig. 1.

The zein proteins are found in "zein bodies" of ≈ 1 μ m distributed uniformly throughout the cytoplasm of endosperm cells between starch granules of 5–35 μ m (Device 1961). The spherical zein bodies are assembled by the rough endoplasmic reticulum membrane and the zeins are packed in an orderly arrangement (Lending 1989). The protein bodies in cells from the central part of the kernel are larger and contain mostly α -zeins, whereas the bodies in the outer, subaleurone layers of cells contain mostly γ - and β -zeins.

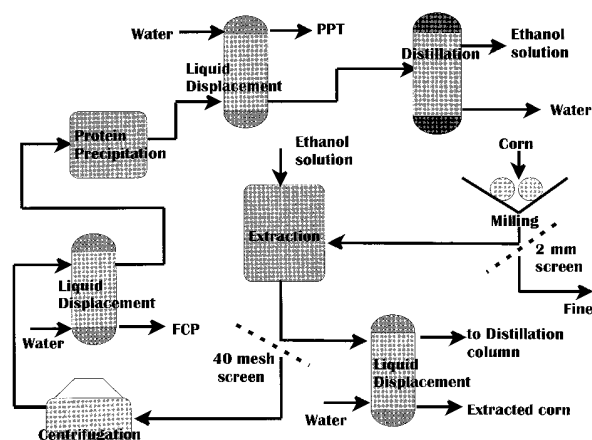


Fig. 1. Diluted extract filtered or centrifuged from precipitate and recycled at distillation facilities.

¹ U.S. Department of Agriculture, Agricultural Research Service, Eastern Regional Research Center, 600 East Mermaid Lane, Wyndmoor, PA 19038-8598. Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by the USDA implies no approval of the product to the exclusion of others that may also be suitable.

² Corresponding author. Phone: 215/233-6640. Fax: 215/233-6795. E-mail: Ldickey@arserrc.gov

Corn kernels can be mechanically separated into soft and hard endosperm fractions (Robutti 1997). Samples of corn from six U.S. genotypes were dry-milled and sifted on 1- and 0.5-mm sieves. The ratio of hard (>1 mm) to soft (<0.5 mm) mass per kernel ranged from 2.7 to 3.7. Dombink-Kurtzman and Bietz (1993) showed three times more 19- and 22-kDa zein in the hard endosperm; the 27-kDa γ -zein was twice as abundant in the soft endosperm fraction. The coarse, hard fraction contains slightly less than twice as much zein overall as the soft fraction.

A patented process (Kampen 1992) for corn protein extraction cites wet attrition milling the corn to $\approx 20 \mu\text{m}$ followed by extraction in two steps: 1) heated alkaline solution to remove glutelins (including glutelin-2 which is now considered a zein, although it is only extractable when a sulfide bond reducing agent is used); and 2) ethanol extraction of zein. The process seems to be much more expensive than conventional dry-milling because concentrated ethanol is needed to extract the wet-milled corn and, as with any ethanol extraction, nearly all of the extract must be recovered from the extracted, milled corn particles.

In response to what is perceived as an opportunity to develop a better use of the corn protein left over from dry-milling ethanol plants (DDG/DDGS), the USDA-ARS is developing a lower cost corn protein extraction method. Unlike conventional zein extraction methods, this process will use dry corn rather than corn gluten as feed. Unsteeped corn can be milled to optimize extraction. A small fraction of 20- μm corn flour is produced as a by-product during commercial (feed) milling of corn to a standard 2-mm particle size with a rotating disc mill. This article describes experiments made to determine the effect of size on extraction for these two convenient size fractions of milled corn.

MATERIALS AND METHODS

The viscosity of solutions of zein in 70% ethanol were measured using a Cannon-Fenske viscosimeter (Cannon Instrument Co., State College, PA), size 100, constant = 0.0145, held in a temperature-controlled bath at 20°C. Zein Z-3625 from Sigma Chemical Co. was used without further purification.

The protein content ($N \times 6.5$) was determined by the micro-Kjeldahl method (AACC 1995, AOAC 1995).

Two corn fractions (0.02 mm of corn flour and 2 mm of fine-cut corn) produced by a commercial feed mill using a counter-rotating, ribbed disc mill were used for extraction tests. Before disc milling, the corn was cracked with a roller mill and the pericarp was removed by aspiration. The dehulled corn was then milled to a median size of 2 mm (measured by shaking 50 lb of corn through a stack of sieves (95% of the mass was between 6- and 14-mesh (3.66- to 1.57-mm opening size) and weighing the fractions. A corn flour is

coproduced with the fine cut corn and separated at the mill by screening. The flour had a median size of 13.9 μm (80% of the mass between 13.2 and 25.0 μm). The particle size distribution of the corn flour and extraction products was measured (API Aerosizer-LD, Amherst Process Instruments, Hadley, MA) using a density of 1.23 for the protein products and 1.30 for the corn flour. Dried corn fines were removed by centrifugation from the extract solution before dilution.

Milled corn and 70% ethanol was mixed in a 189-L (50-gal) kettle with two counterrotating agitators powered through concentric shafts (Hamilton Kettles, Fairfield, OH); the drive shafts rotated at 2.5 rpm. All extractions starting with fresh corn and liquid used 10 kg of corn and 40 kg of liquid. Previously extracted corn or extract was reused with fresh corn and the fresh material mass was reduced to match the reused material, maintaining the mass ratio of liquid to corn at 4. After mixing for the selected period, the extract was drained from the corn and pumped through a 40-mesh (0.5-mm opening size) screen to a 104.8-mm tubular-bowl centrifuge (Sharples Corp., Philadelphia, PA) rotating at 15,000 rpm. The centrifuge generates 13,200 $\times g$. The temperature of the extract liquid was measured and is listed in Table I. Fine corn particles (FCP) that were small enough to pass through the rest of the corn and the filter were separated from the extract by the centrifugation; the efficiency depended on the flow rate. A minimum flow rate of 27 kg/hr (60 lb/hr) resulted in >99.5% separation of suspended FCP (as determined by recentrifugation of the centrifuge); 99% of the FCP were removed at 75 kg/hr. Thorough removal is necessary for product purity because the extract solution contains a low solute mass: 1% of the FCP (left in the extract) will be 11% of the final product mass.

After FCP removal, the centrifugate was diluted to 40% ethanol by adding tap water and held 16–20 hr at 3°C. The chilled suspension was then centrifuged at 68 kg/hr (150 lb/hr) and the separated solid (PPT) was dried, weighed, and analyzed.

For a 1-hr extraction, the 40% ethanol centrifugate was diluted to 20%, held in a chilled tank overnight, and centrifuged to determine the amount of zein and other solute left in solution after the initial precipitation process.

Batches of 2- and 0.02-mm corn were extracted with 70% ethanol for contact periods of 1–6 hr. One extraction for each size feed was made in which corn that had been extracted for 1 hr was extracted with fresh 70% ethanol for 2 hr. The centrifuge feed rate was reduced for the finer feed extractions because there was more FCP to remove from the extract.

A 1-hr 4:1 extraction was made; the extract suspension was centrifuged, and the centrifugate used to extract a second, slightly smaller mass of corn, keeping the original 4:1 liquid to corn mass ratio.

To estimate the extent of solvent absorption in the corn particles, 495 g of the 2-mm milled corn, sieved to remove particles

TABLE I
Extraction Products from Corn

Particle Size	Mixing			CFR ^a (kg/hr)	FCP ^b		Solid 2 ^c	
	Mass (kg)	Time (hr)	°C		Mass	Protein	Mass	Protein
20- μm	10	1	28	89	328	0.016	44	0.471
20- μm	8.1	2 ^d	29	67	285	0.028	39	0.429
20- μm	10	2	19	75	495	0.025	45	0.477
20- μm	10	6	20	70	782	0.021	60	0.516
2-mm	10	1	21	50	1,820	0.041	83	0.481
2-mm	10	1	24	30	2,395	0.042	98	0.518
2-mm	10	1	16	26	2,334	0.035	103	0.352
2-mm	5.8	2 ^d	19	26	1,099	0.037	45	0.338
2-mm	10	6	20	26	2,924	0.044	130	0.430
2-mm	10–9	2 ^e	19	26	4,964	0.044	214	0.400

^a Centrifuge feed rate.

^b FCP = fine corn particles. Product weight (g) and weight fraction protein are the sum of two separate centrifugings of the extract solution.

^c Product weight (g) and weight fraction protein determined after final dilution step.

^d Corn feed had already been extracted for 1 hr and then mixed for 2 hr with fresh liquid.

^e Extract solution was reused to extract a second batch of corn, both 1-hr extractions.

<0.7 mm, was added to 2,000 g of 70 wt% ethanol and mixed for 1 hr. The mixture was drained through the 0.7-mm screen and held on the screen, enclosed within a plastic bag to prevent evaporation, and allowed to continue draining over a weekend.

To estimate the absorption of ethanol solution in zein, a 2.5-cm diameter ball was made by dissolving 9.6 g of commercial zein in 70% ethanol, drying it to ≈50% solid content, and rolling by hand. The ball dried by evaporation in ambient air for five months. After drying, the ball was immersed in 38.4 g of 70% ethanol in a beaker covered with a parafilm layer to retard evaporation (at 20°C) and stirred gently with a magnetic bar for 1 hr at 20°C. The ball was then removed from the beaker, drained of liquid, and weighed.

RESULTS AND DISCUSSION

The extraction experiments (data in first four rows of Table I), showed little dependence of protein content of the precipitate (PPT) on centrifugation feed rate. Thus, the mass of FCP in the precipitate was only slightly dependent on the centrifuge feed rate. It was nearly all removed by centrifugation. When the centrifugate from the precipitated 40% (diluted) extract was diluted again to 20% ethanol, the resulting precipitate solids weighed <10% of the PPT; the second precipitate was 75% lipid and 12% protein.

These results and size measurements of FCP are consistent with cell separation during extraction. Soluble corn components, which began as cytoskeletal compounds, as well as the compounds composing the endosperm cell membrane (Clare 1996) and zein found in the zein bodies, end up as interstitial layers between the starch granules of fully developed corn kernels. The membrane proteins dissolve or weaken when exposed to ethanolic solvent, but the liquid also diffuses into the zein bodies and starch granules. Based on the ratio of solvent to zein required by zein's low solubility, zein dissolution within the particles must lag behind ethanol solution permeation. We expect that, at most, a small fraction of the zein dissolves while confined within the particles; if it did it would have a slow diffusive process to the bulk liquid, initially counter to the flow of liquid into the particle. When the outer layer of cells loosens sufficiently, due to the dissolution of some intercellular constituents and swelling of others, they can separate from the particles as FCP. Fresh solvent then contacts soluble compounds near the newly formed cavity on the particle and FCP surfaces. The soluble constituents of the FCP are exposed to liquid convection, and zein dissolution begins.

Table I data are consistent with this process. FCP mass increases with the time of extraction and the mass fraction of nonstarch components in FCP also increases with time. This second trend is due to the reduction of free liquid solvent needed to dissolve nonstarch material on the FCP as more of it is absorbed by the corn particles.

Milling of the corn did not produce a significantly different measured protein content for the two fractions: 2-mm corn had $6.3 \pm 0.7\%$ protein, 20- μm corn had $5.9 \pm 0.2\%$ (based on measurements of three batches). The fine fraction was not composed only, or mostly, of clean starch granules despite its small size.

The rate of liquid penetration into a particle depends on endosperm permeability and liquid composition that vary within the kernel and within and between particles. It seems reasonable that the rate of liquid diffusion into a corn particle could control the rate at which the outer layer of cells ablates from particles and disintegrates into starch granules with protein and other debris on their surfaces.

The results of 2-hr extractions with fresh batches of 70% ethanol of corn that had already been extracted for 1 hr are listed in Table I. They are also depicted at the 3-hr point in Fig. 2 (PPT recovery). The fine corn fits roughly with the plot of recovery versus time for the single extractions, whereas the use of the fresh solvent practically doubled the PPT yield for the 2-mm corn. These results show that the bulk liquid composition had a much different effect

on further extraction after 1 hr for different corn size fractions. The fine particle extraction was little changed for protein dissolving from the particles' surface. The increased rate for the 2-mm particles was probably due to the dissolution within the particles that continued while the particles were drained of the initial liquid and fresh solvent was added to the mixing tank. The liquid change may also have added some additional shearing, speeding up particle disintegration.

An extraction (Table I) reused liquid from a 1-hr extraction to extract a second batch of dry-milled corn. The PPT recovery indicates that the ethanol solution was not effectively saturated after the first extraction. Almost the same mass of protein and lipid was extracted from the second batch of corn. This suggests that the rate-slowing seen generally in extractions is due to depletion of extractable material located in the outer part of the corn particles rather than depletion of the liquid's solvent capacity.

Ethanol Diffusion in Corn Particles

The self-diffusion coefficient (D_s) for the 70% ethanol solvent can be estimated from the values for ethanol and water cited by Sek (1996). Based on the measured specific gravity, 0.8677, the molecular volume of a 70% ethanol mixture at 20°C is $3.62 \times 10^{-2} \text{ m}^3/\text{kmol}$; the measured viscosity is 2.40 cP. With these values, the D_s value was calculated numerically from Sek's formulas to be $7.3 \times 10^{-10} \text{ m}^2/\text{sec}$. For comparison, the D_s of water at 20°C is $22 \times 10^{-10} \text{ m}^2/\text{sec}$. The minimum diffusion (D) coefficients for a liquid in a partly permeable solid can be estimated according to the volume blocked (Mackie 1955):

$$D/D_s = [(1 - N_p)/(1 + N_p)]^2 \quad (1)$$

where N_p is the volume fraction of insoluble polymer, mainly starch. Although more accurate free-volume theories are available, their use depends on information presently unavailable. Estimating the soluble volume fraction in a solvent-saturated particle to be the protein fraction 0.1, D/D_s from the preceding equation is 0.0028. The liquid may permeate the starch and fiber but it will not dissolve them. Dissolution in the germ will not influence the breakdown of the endosperm. Liquid absorbed in these parts of the particles is lost to the protein-extraction process.

With $D_s = 7.3 \times 10^{-10} \text{ m}^2/\text{sec}$:

$$D = 2 \times 10^{-12} \text{ m}^2/\text{sec} \quad (2)$$

through corn containing 70% alcohol solution.

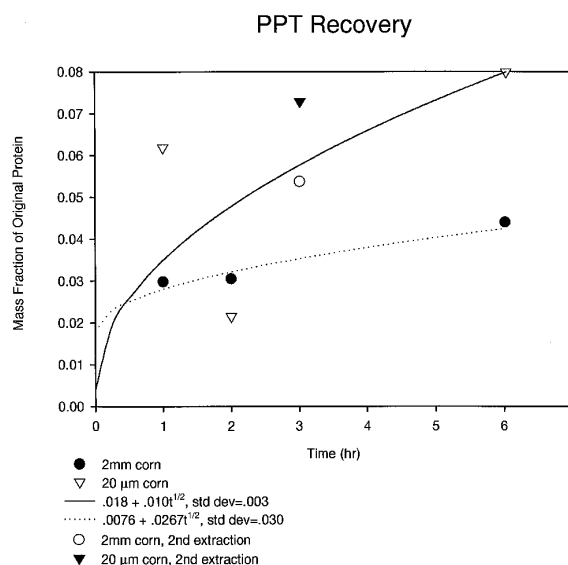


Fig. 2. Trends of experimental masses of protein content of the precipitate (PPT) recovery.

Water diffusion (to and from a vapor) through agricultural materials, including corn, has been measured. For example, Tolaba et al (1990) measured the diffusion rate of water through corn germ and endosperm and calculated a coefficient using a spherical model of a (dehulled) kernel with constant boundary conditions and an infinite Biot number, where the Biot number is the ratio of mean transfer at the interface to the mass transfer in the particle interior. The 50°C diffusion coefficient was 7.7×10^{-11} m²/sec. A more detailed measurement of water diffusion into corn by Muthukumarappan and Gunasekaran (1994) determined the diffusion coefficient dependence on temperature, endosperm type (hard or soft), and moisture content. Coefficients calculated from their model for 25°C and 90% rh were 1.6 and 1.1×10^{-11} m²/sec for soft and hard endosperm, respectively, and 4.9 and 3.4×10^{-11} m²/sec for soft and hard endosperm, respectively, at 50°C, which was slightly lower than the Tolaba drying rate estimate.

For simple Fick's law diffusion from a homogeneous isotropic sphere, Laplace transform methods (Carslaw and Jaeger 1946, Crank 1979) have been used successfully to model water transport out of corn (Shivhare 1994). Considering liquid diffusion as a factor in the loosening of the outer cell layer, the short time approximation of the expression for mass of solute extracted from a particle (M_t) as a fraction of the total mass in a particle (M_∞) is sufficiently accurate. Using 2×10^{-12} m²/sec for the diffusion coefficient estimated above:

$$M_t/M_\infty = 6/r (D_t/\pi)^{0.5} = 6 \times 10^{-6}/r (2/\pi)^{0.5} t^{0.5} \quad (3)$$

where t = time (sec) and (for 2-mm particles) r = particle radius (1.0×10^{-3} m).

$$M_t/M_\infty = 3 \times 10^{-3} t^{0.5} = 0.02 t^{0.5} \quad (4)$$

with t = time (hr).

The trends of experimental PPT masses and FCP mass fractions were fit to $a + b \times t^{0.5}$, as shown in Fig. 2 and Fig. 3, respectively. The FCP fit (Fig. 3) has a constant (b) coefficient about twice the estimate for the diffusion limited expression (Eq. 4). A higher coefficient for the extraction would result if FCP were released during the extraction.

The 20- μ m particles are about the same size as the FCP particles removed from the extract by centrifugation, and may consist of a substantial fraction of nondecomposable starch granules. The larger constant term for the fit of the 20- μ m particle runs (shown in Fig. 2) is probably due to a greater number of fine particles in the fine milled corn fraction initially.

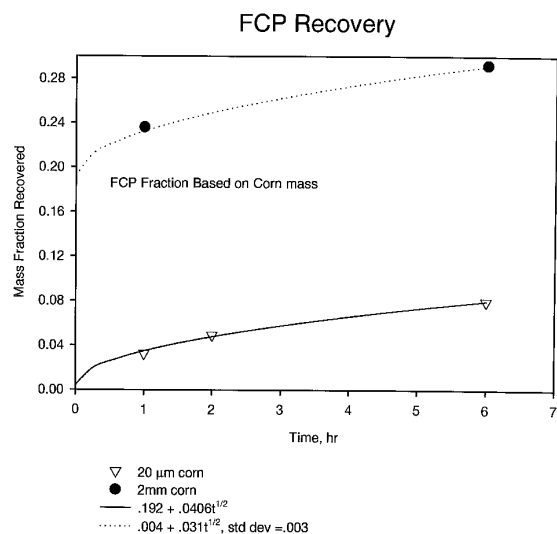


Fig. 3. Trends of experimental masses of fine corn particles (FCP) recovery.

Unmixed Extraction Results

Weight loss due to evaporation during the zein ball dissolution experiment was 0.6 g, 1.6 g of zein dissolved producing a liquid concentration of 3.8% (w/v), about twice as high as the value obtained by Augustine (1987). The ball absorbed no more than 0.38 g of liquid during the dissolution test, indicating that the liquid permeation front was not much ahead of the (shrinking) ball surface. The measured dissolution rate from the solid zein ball is equivalent to a permeation rate of 3×10^{-8} m²/sec, much higher than the expected rate for liquid diffusion.

The PPT mass plotted in Fig. 2 shows a slower increase than the plot of FCP, suggesting that, for the conditions used, dissolution of zein, even from the surface of free starch granules, limits the extraction rate. The protein mass fraction of PPT is fairly constant (0.06 ± 0.004) for the extractions listed in Table I, which suggests that protein dissolution is limited to the outer layers of the corn particles. The indicated initial mass fraction separated values for the PPT plot corresponds to protein that dissolved after the mixing stopped while the extract was drained from the corn and, at a much lesser rate, while the FCP were being centrifuged from the extract.

The corn particles are roughly spherical, and if the extraction rate per unit surface were the same for particles of different size, the extraction rate for a constant mass of corn should be inversely proportional to particle diameter. From the 1-hr extractions in Table I (PPT), the measured rates were 21 g/hr for the 2-mm particles and 36–51 g/hr for the 20- μ m particles. The smaller particles are only twice as extractable, not the 100 times expected from the increased surface area. Protein flux per unit of solid surface was 0.02 g/hr – m² for the small particles and 0.86 for the 2-mm particles. Both are considerably below the ≈ 300 g/hr – m² for the 2.5-cm ball. The flux from the corn, as a fraction of the zein ball flux, is lower than the mass fraction of zein in the corn. The lower rate per unit surface for the smaller particles is contrary to the usual expectation for particles this size, if the laminar film on the particle surface is about the same size as the particle (Nagy and Blicke 1984). Therefore, the measured rates suggest that the mixing was inadequate to keep the liquid film containing the highest concentration of zein on the corn particles as thin as required for maximum extraction rates. The mixing conditions, agitation, and masses of liquid and solid were the same for both 2-mm and 20- μ m corn extractions. The main difference in the extractions was due to dependence of agitation intensity on particle size.

Extraction mass transfer resistance comprises liquid penetration into the particle, dissolution of the soluble particle components, diffusion of those components in the absorbed liquid, and transfer from the particle surface into the bulk liquid. Interfacial mass transfer resistance is the simplest to control, and when it limits the overall rate, the rate can be increased by increasing agitation intensity (to increase convection at the surface) or by reducing particle size (to increase solid-liquid interface). There is a lower limit to beneficial particle-size reduction. Below the limit, smaller size will effectively reduce the agitation intensity because of reduced particle inertia.

In an earlier study (Russell and Tsao 1982), batches of degerminated grits of various size ranges were extracted using 55% ethanol. Those authors concluded that the rate limit was the transport of zein out of the endosperm. This earlier study achieved mixing of the particles in 8.8:1 and 10:1 liquid-to-solid mass ratios in shaken culture tubes and a 1-L agitated glass reactor. They concluded that external mass transfer was a minor factor in the extraction rate of the grits. The long-term protein fraction extracted from the 105- μ m grits by Russell and Tsao (1982) was 0.2. This corresponds to our estimate of the protein fraction at the grits' surface, assuming a protein layer surrounds the ≈ 100 20- μ m starch granules comprising each grit, suggesting that little extraction of the interior of the grits occurred.

Estimate of Peclet Numbers for Extraction

The measured protein fluxes from the corn particles can be used to estimate Peclet numbers for the extractions. Peclet number (Pe)

is the ratio of mass transported by convection to the mass transported by diffusion:

$$Pe = Uh/D \quad (5)$$

where U is the flow rate between particles at distance h from the particle surface, and D the diffusion coefficient of zein in the solution. Pe values range from 0 for a stagnant suspension or a suspension of particles so small that they move with the fluid and are hydrodynamically indistinguishable from fluid molecules, to ∞ for a perfectly mixed mixture, with no concentration difference between the liquid at the particle surface and the bulk liquid, and therefore instantaneous transfer from the solid to the liquid.

For ideal solutions at infinite dilution, the binary liquid diffusion coefficient of a particle or large molecule, can be calculated from the Stokes-Einstein equation (Probstein 1989):

$$D = kT/(6\pi\eta r) \quad (6)$$

where η is the solution viscosity, k is the Boltzmann constant, T is temperature, and r the hydrodynamic radius of the (spherical) atom being transported. The relation holds pretty well for liquids near the triple point. The radius of a water molecule calculated from D , η , and Eq. 6 (Egelstaff 1994) varies only from 0.11 to 0.12 nm from freezing up to the normal boiling temperature. To estimate D for zein, a molecular radius is needed. A detailed study (Rothfus 1996) of the residue sequences for several corn and wheat proteins show an average monomeric volume for whole zeins to be 143 \AA^3 . On this basis, 22-kDa zein with 266 residues has a molecular volume of 38 nm^3 . Zeins are regarded to be cylindrical in shape with a length-to-width ratio of 2:1 (Argos 1982). Taking the long axis $\approx 5.8 \text{ nm}$ as the hydrodynamic radius, the 20°C diffusion coefficient for 22-kDa zein in 70% ethanol ($\eta = 2.8 \times 10^{-3} \text{ N sec/m}^2$) calculated from Eq. 6 is $1.3 \times 10^{-11} \text{ m}^2/\text{sec}$. The mass flux of protein dissolving (j^*), which should model the fluxes calculated from the experimental extraction rates (unmixed extraction results) can be estimated from the approximation for channel flow (Probstein 1989):

$$j^* = 0.5 C_{\text{sat}} D (U/hDd)^{1/3} \quad (7)$$

where C_{sat} is the saturated concentration of zein next to the particle surface, and d is the flow length estimated to be the particle diameter. Equations 5 and 7 can be combined to provide a means of calculating Pe from the measured and estimated values:

$$Pe = (2j^*/C_{\text{sat}}D)^3 (h^2 d) \quad (8)$$

where $C_{\text{sat}} = 50 \text{ g/m}^3$ (estimate based on the ball dissolution experiment).

From Eq. 8 for the 2-mm particle extractions, $j^* = 0.86 \text{ g/hr m}^2$, $d = 2 \text{ mm}$, $h = 0.5 \text{ mm}$:

$$Pe = 2 \times 10^8$$

For the 20- μm particle extractions, $j^* = 0.02 \text{ g/hr m}^2$, $d = 20 \mu\text{m}$ and $h = 0.5 \times 10^{-2} \text{ mm}$:

$$Pe = 0.0025$$

The comparison indicates that the 20- μm particles exhibit much less convective mass transfer, and that considerable agitation intensity would be required to increase convective flux from them to match that of diffusion.

CONCLUSIONS

Measurements of fine particles separated by centrifugation (FCP) from a filtered slurry of milled corn extracted with 70%

ethanol indicated that mixing the corn particles causes them to shed FCP. An estimated rate coefficient of release of FCP from the milled corn based on liquid permeation into the corn protein was half the coefficient derived from a fit of a plot of FCP mass and extraction time. This difference is consistent with a significant effect of the FCP release during extraction. After FCP separation, the extract was diluted to 40% ethanol to precipitate extracted solute (PPT) and centrifuged. The corn particles released FCP more rapidly than protein dissolved, as indicated by variation of the FCP and PPT masses with time. The FCP rate measurements from 2-mm particles were fit to an expression based on simple diffusion, and the coefficient (0.03/0.5 hr) was close to an estimate (0.02/0.5 hr) based on the diffusion coefficient for 70% ethanol in corn determined from published correlations. The PPT rate measurements are not simply modeled as diffusion-controlled since the rate of extractable protein generation depends on the rate FCP production. Comparison of estimated Peclet numbers for the small and large particles indicates that the larger particles have higher mass transfer rates, due to convection, at the particle surface.

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