Recovery of Stillage Soluble Solids from Corn and Dry-Milled Corn Fractions by High-Pressure Reverse Osmosis and Ultrafiltration

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ABSTRACT

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High-pressure reverse osmosis (RO) combined with ultrafiltration (UF) was used to separate stillage solubles from corn and dry-milled corn fractions into small volumes of concentrated solutions and large volumes of permeates suitable for reuse. The UF permeate at 680 kPa (100 psi) contained 23–60% of total nitrogen and 38–65% of total solids of the stillage solubles. The UF permeate was used as the feed solution for RO. The RO permeate at 6,800 kPa (1,000 psi) contained 0.32–1.3% of the total nitrogen, 0.13–0.41% of total solids and 77–86% of total volume of the UF permeate. The percentage of nitrogen and solids from stillage solubles that can be economically recovered by combined UF and RO at 6,800 kPa (assuming only the amount of nitrogen and solids in the RO permeate is discarded) is 99.6–99.9% and 99.8–99.9%, respectively. Conductivity of the RO permeate at 6,800 kPa was lower than that of tap water. UF and high-pressure RO methods developed for stillage solubles from corn and dry-milled corn fractions may encourage increased use of distillers' grains from corn and corn fractions while reducing the total cost of the alcohol process.

Corn is most commonly used for commercial ethanol production by fermentation in the United States (Morris 1983). Fermentation of ground corn to make ethanol produces a protein-rich material (stillage) after ethanol is distilled. The stillage that contains 5–10% solids is screened or centrifuged to remove most suspended insoluble solids, and the remaining soluble fraction containing 2–4% solids usually is evaporated to a syrup, which is marketed as-is or dried with the solids from screening or centrifugation. The most efficient evaporator requires approximately 230 kJ/kg water (Cicuttini et al 1983).

Ultrafiltration (UF) is an efficient process for separating solutions by solvent flow through a membrane. Particles larger than the specified membrane cutoff are quantitatively retained, but solutes smaller than the membrane pores pass through with the solvent. Reverse osmosis (RO) also can concentrate solutions by removing water by means of a membrane that is more permeable to water than to ions and other dissolved matter (Gregor and Gregor 1978). In RO, the solution is pumped at high pressure across the membrane to overcome the osmotic pressure that resists the migration of water. Because no evaporation of water is involved in UF or RO, energy consumption, which is approximately 37 kJ/kg of water (Cicuttini et al 1983), is much lower than in concentration by heating. The total cost for equipment, power, and labor for combined UF and RO is $0.93 per 1,000 L of stillage treated compared with $2.20 for fuel costs alone by the evaporative route (Gregor and Jeffries 1979).

Several studies have already explored the applications of RO for processing dilute solutions. Sheehan and Greenfield (1980) reviewed methods for handling distillery waste water. Sheu and Wiley (1983) used RO for preconcentration of apple juice, Agbevavi et al (1983) concentrated whole milk by RO for cheddar cheese production. Lawhon and Lusas (1984) reported on UF and RO methods for protein isolation from oilseeds. Wu (1987a) reported the recovery of stillage soluble solids from hard and soft wheat by RO and UF. Wu et al (1983), Wu and Sexson (1985), and Wu (1987b) found combined UF and RO at 1,360 kPa (200 psi) to be an attractive method to separate stillage solubles from corn and dry-milled corn fractions into a large volume of permeate with low nitrogen and solids contents and a small volume of concentrate with high nitrogen and solids contents. This paper reports the large improvement of efficiency for processing stillage solubles from corn and dry-milled corn fractions by combined UF and high pressure RO at 6,800 kPa (1,000 psi), compared with UF and RO at 1,360 kPa used previously.

MATERIALS AND METHODS

Fermentation and Fractionation of Stillage

Wu et al (1983, 1985) gave the details of fermentation of ground corn and dry-milled corn fractions to ethanol, and of the fractionation of resulting stillage after ethanol is distilled. Each medium was fermented in duplicate in a 20-L stainless steel, temperature-controlled, jacketed fermentor equipped with stirrers. α-Amylase converted starch to soluble dextrins, glucoamylase hydrolyzed dextrins to glucose, and yeast converted glucose to ethanol. Steam was used to distill ethanol from the fermentor. Filtration through cheesecloth under suction separated stillage into distillers' grains (remaining on cheesecloth) and thin stillage. Centrifugation (45,200 × g) separated the thin stillage into a solid fraction (centrifuged solids) and stillage solubles. Figure 1 is a schematic diagram of the fermentation, fractionation of stillage, and UF and RO recovery processes.

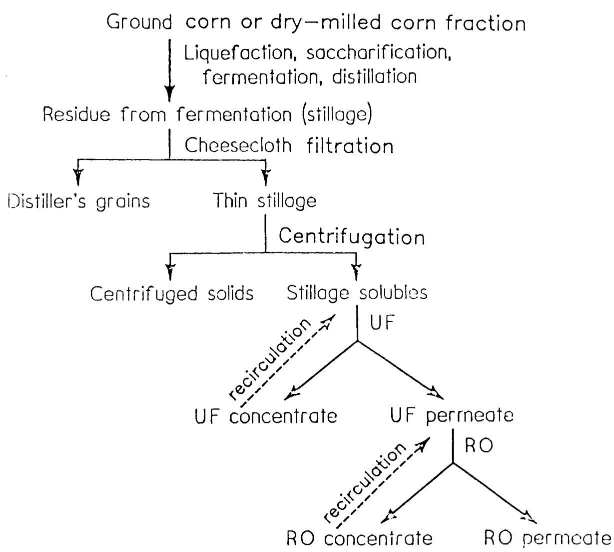

Fig. 1. Schematic diagram of fermentation, stillage fractionation, and ultrafiltration and reverse osmosis recovery processing of corn or dry-milled corn fractions.

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UF and RO

An OSMO Econo Pure RO unit (Osmonics, Inc., Minnetonka, MN) equipped with OSMO-112 Sepralators (1.0 m^2 membrane, hold-up volume about 600 ml) was used for UF at 680 kPa. SEPA-O polysulfone or cellulose acetate membrane for UF had a molecular weight cutoff of 1,000. Permeate was the solution that passed through the membrane, and concentrate was the solution retained by the membrane. The concentrate stream was recirculated back to the initial solution. The flow rate of UF permeate at room temperature was 15 L/(m^2/hr) for ground whole corn stillage solubles using the polysulfone membrane, and 12–18 L/(m^2/hr) for stillage solubles from dry-milled corn fractions using the cellulose acetate membrane. Draining the column at end of UF gave the hold-up volume. Approximately 1 L of distilled water was then pumped 4–6 times through the system; draining each time yielded wash fractions. The sum of permeate, concentrate, hold-up, and wash fractions permitted calculation of material balance and percent recovery.

A model UHPROLA-100 RO system (Village Marine Tec., Gardena, CA) equipped with an SW 30-2521 module with 1.1 m^2 polyamide membrane (Filmtec, Minneapolis, MN) with a molecular weight cutoff of 100 was used for RO of UF permeate at 6,800 kPa. Samples of permeate and concentrate were periodically analyzed to follow RO progress. The flow rate of RO permeate was 18–26 L/(m^2/hr) at room temperature. The hold-up volume of the membrane module was 605 ml. Pumping 2 L of distilled water through the system seven times and draining each time resulted in wash fractions. Material balance and percent recovery included the sum of permeate, concentrate, hold-up, and wash fractions.

Viscosity

Viscosity measurements on clear solutions (UF permeates, RO permeates and RO concentrates) were made with Cannon no. 50 and no. 75 viscometers with flow times of about 230 and 130 seconds for water, respectively. The viscometers were in a constant temperature bath at 25.1°C.

Viscosities of stillage solubles and UF concentrates (both with suspended solids that settled out on standing) were measured with a Brookfield model LVF Synchro-Lectric viscometer with U.L. adapter for low viscosity (Brookfield Engineering Laboratories, Stoughton, MA) at 60 rpm, and with a Haake Rotovisco RV 100 viscometer equipped with a 500 head (Haake Buchler Instruments, Inc., Saddle Brook, NJ) at room temperatures. The viscosity values were corrected to 25.1°C.

Relative viscosity was calculated as the ratio of flow time of solution to that of water or the ratio of Brookfield reading (after correction for windage and temperature) to that of water.

Analyses

AACC methods 46-13 and 08-03 (AACC 1983) were used to determine nitrogen by micro-Kjeldahl analysis (in quadruplicate) and ash by heating to 600°C (in duplicate). Known volumes were pipetted into previously weighed crucibles (in duplicate), dried overnight in an air oven at 100°C, then dried for three days in a vacuum oven at 100°C, and weighed to indicate solids contents (dry matter) of solutions. A Radiometer CDM 2e conductivity meter with a CDC 104 cell revealed conductivity of stillage fractions at 27°C.

RESULTS AND DISCUSSION

Material Balance

The amounts of nitrogen, solids, and ash in permeate, concentrate, hold-up, and wash fractions indicated percent recoveries based on stillage solubles for UF and on the UF permeate for RO. Average recoveries of nitrogen, solids, and ash were 99, 96, and 104%, respectively, upon UF of stillage solubles from corn and dry-milled corn fractions. The average recoveries of nitrogen, solids, and ash were 101, 102, and 101%, respectively for RO of UF permeates from stillage solubles of corn and dry-milled corn fractions. Near-quantitative recoveries indicate no strong binding of corn protein or solids to UF and RO membranes. The average amounts of nitrogen, solids, and ash in hold-up and wash fractions were 51, 39, and 26%, respectively, for UF and 81, 81, and 81%, respectively, for RO.

UF and RO of Stillage Solubles from Corn and Dry-Milled Corn Fractions

Tables I–V summarize UF and RO results for stillage solubles from corn and dry-milled corn fractions (amounts of nitrogen, solids, and ash in hold-up and wash fractions are not included in

TABLE I
Ultrafiltration and Reverse Osmosis of Ground Whole Corn Stillage Solubles[a]

Material[b]	Volume (ml)	Nitrogen (mg/ml)	Solids (mg/ml)	Ash (mg/ml)
Stillage solubles	4,495	0.679	31.8	4.21
UF Permeate	4,030	0.278	13.4	3.30
UF Concentrate	178	1.78	80.2	4.25
RO Permeate	3,149	0.0012	0.034	0.0059
range, 10 fractions	310–325	0.0010–0.0017	0.015–0.071	0.001–0.013
RO Concentrate	629	0.330	14.0	3.92
range, 9 fractions	69–70	0.212–0.516	9.36–20.8	2.43–5.57

[a] In addition to permeate and concentrate fractions, hold-up and wash fractions were also collected and analyzed for material balance and percent recovery.
[b] UF = Ultrafiltration; RO = reverse osmosis.

TABLE II
Ultrafiltration and Reverse Osmosis of Corn Grits Stillage Solubles

Material[a]	Volume (ml)	Nitrogen (mg/ml)	Solids (mg/ml)	Ash (mg/ml)
Stillage solubles	8,078	0.860	20.0	1.64
UF Permeate	7,580	0.554	11.5	1.79
UF Concentrate	200	2.19	54.2	2.47
RO Permeate	6,406	0.0039	0.043	0.0027
range, 9 fractions	487–746	0.0025–0.0084	0.024–0.090	0–0.0085
RO concentrate	911	0.934	20.1	3.15
range, 9 fractions	100–111	0.484–1.79	10.5–37.6	1.50–6.32

[a] UF = Ultrafiltration; RO = reverse osmosis.

TABLE III
Ultrafiltration and Reverse Osmosis of Corn Flour Stillage Solubles

Material[a]	Volume (ml)	Nitrogen (mg/ml)	Solids (mg/ml)	Ash (mg/ml)
Stillage solubles	4,350	0.391	61.3	2.27
UF Permeate	4,210	0.115	41.4	1.60
UF Concentrate	144	1.21	81.6	2.77
RO Permeate	3,157	0.0019	0.069	0.0002
range, 10 fractions	175–340	0.0007–0.0072	0.024–0.150	0–0.0011
RO concentrate	738	0.113	51.6	1.91
range, 9 fractions	60–118	0.076–0.173	31.8–78.7	1.20–3.24

[a] UF = Ultrafiltration; RO = reverse osmosis.

TABLE IV
Ultrafiltration and Reverse Osmosis of Corn Degerminator Meal Stillage Solubles

Material[a]	Volume (ml)	Nitrogen (mg/ml)	Solids (mg/ml)	Ash (mg/ml)
Stillage solubles	4,000	0.717	28.2	6.09
UF Permeate	3,830	0.197	11.5	4.34
UF Concentrate	240	1.99	59.3	9.36
RO Permeate	3,084	0.00077	0.056	0.017
range, 10 fractions	285–327	0.00062–0.0010	0.019–0.105	0.004–0.039
RO Concentrate	602	0.236	15.3	5.00
range, 10 fractions	60–62	0.122–0.369	9.52–24.5	3.13–7.79

[a] UF = Ultrafiltration; RO = reverse osmosis.

Tables I–V). Concentrations of nitrogen and solids in UF permeate were 25–64% and 40–68%, respectively, of those of stillage solubles. UF also removed large suspended particles from stillage solubles, resulting in clear permeates suitable for subsequent RO. The nitrogen, solids, and ash concentrations of the RO permeates were 0.01–1.6% of those of UF permeates. In Tables I–V, the lower "range" numbers for nitrogen, solids, and ash concentrations are generally for the first fractions, and the higher numbers for the last fractions. Concentrations of nitrogen and solids increased from two- to 17-fold in the RO permeates and increased two- to fourfold in the RO concentrates during RO.

Efficiency of Various UF and RO Procedures

Percentages of original volume, nitrogen, solids, and ash in UF and RO permeates indicate process efficiency. Ideally, permeates should maximize volume and minimize nitrogen, solids, and ash concentrations. Table VI shows the percentage of original material in permeate fractions. UF permeates of stillage solubles from corn and dry-milled corn fractions had 90–97% of total volume, 23–60% of total nitrogen, 38–65% of total solids, and 62–92% of total ash of the original stillage solubles. The 1,360 kPa RO permeate contained 4.6–21% of the total nitrogen, 4.5–30% of total solids, 3.4–37% of total ash, and 70–92% of total volume of the UF permeate. However, the 6,800 kPa RO permeate had 0.32–1.3% of the total nitrogen, 0.13–0.41% of total solids, 0.01–0.33% of total ash, and 77–86% of the total volume of the UF permeate. Thus, a fivefold increase in RO pressure reduced total permeate nitrogen from 14- to 23-fold, solids from 35- to 73-fold, and ash from 112- to 340-fold.

Solids and ash concentrations of RO concentrate were found to be linearly related to conductivity (significant at the 0.01 level) (data not shown). More dilute RO permeates exhibited a less-significant relationship. The correlation coefficients of conductivity versus milligrams of solids per milliliter of RO permeate for corn stillage solubles and for conductivity versus milligrams of ash per milliliter of RO permeate for corn hominy feed stillage solubles were significant at the 0.06 and 0.10 levels, respectively. The correlation coefficients of conductivity versus milligrams of solids per milliliter of RO permeate for corn grits stillage solubles, corn flour stillage solubles, and corn degerminator meal stillage solubles and of conductivity versus milligrams of ash per milliliter of RO permeate for corn degerminator meal stillage solubles were significant at the 0.01 level. Solids and ash concentrations of RO concentrate and permeate of wheat stillage solubles were also linearly related to conductivity (Wu 1987a). Thus, conductivity can rapidly and accurately monitor solids and ash concentrations of RO concentrates and some RO permeates. These measurements indicate that the solids and ash concentrations of 6,800 kPa RO permeates are significantly lower than that of tap water (0.061–0.18 mS/cm, compared with 0.72 mS/cm).

TABLE V
Ultrafiltration and Reverse Osmosis of Corn Hominy Feed Stillage Solubles

Material[a]	Volume (ml)	Nitrogen (mg/ml)	Solids (mg/ml)	Ash (mg/ml)
Stillage solubles	2,980	0.865	34.7	7.90
UF Permeate	2,840	0.212	13.8	5.10
UF Concentrate	261	1.88	56.6	9.19
RO Permeate	2,168	0.0014	0.048	0.016
range, 8 fractions	195–287	0.0009–0.0016	0.027–0.063	0.011–0.029
RO Concentrate	480	0.219	14.4	4.92
range, 8 fractions	60	0.148–0.309	9.67–21.1	3.14–7.70

[a] UF = Ultrafiltration; RO = reverse osmosis.

TABLE VI
Ultrafiltration and Reverse Osmosis Permeate Volumes and Compositions of Corn and Corn Fractions Stillage Solubles[a]

Stillage Solubles/ Membrane[b] (pressure)	Volume	Nitrogen	Solids	Ash
Corn				
UF	90	37	38	70
RO (6,800 kPa)	80	0.34	0.20	0.15
RO (1,360 kPa)[c]	71	18	30	37
Corn grits				
UF	94	60	55	92
RO (6,800 kPa)	86	0.60	0.32	0.13
RO (1,360 kPa)[d]	85	12	9.2	5.8
Corn flour				
UF	97	28	65	68
RO (6,800 kPa)	77	1.3	0.13	0.010
RO (1,360 kPa)[d]	85	21	15	21
Degerminator meal				
UF	96	26	39	68
RO (6,800 kPa)	83	0.32	0.41	0.33
RO (1,360 kPa)[d]	92	19	9.0	7.2
Hominy feed				
UF	95	23	38	62
RO (6,800 kPa)	80	0.53	0.28	0.24
RO (1,360 kPa)[d]	70	4.6	4.5	3.4

[a] Numbers in last four columns indicate percent of stillage solubles for UF and percent of UF permeate for RO.
[b] UF = Ultrafiltration; RO = reverse osmosis.
[c] Wu et al (1983).
[d] Wu and Sexson (1985).

Viscosity and pH

The relative viscosities of RO permeates (0.99–1.02) were very close to that of water. Relative viscosities of UF permeates (1.10–1.38) and RO concentrates (1.07–1.38) were higher than water. Stillage solubles had relative viscosities of 1.24–1.99, but the UF concentrates had the highest relative viscosities (1.67–4.60) of all solutions. Measurements made with a Haake viscometer with a wider range of shear rate showed that the solutions were Newtonian. Thus, the viscosities of RO permeates and concentrates, UF permeates and concentrates, and stillage solubles will not cause any problem in processing.

The pH of stillage solubles ranged from 2.6 for corn grits to 3.9 for hominy feed. In general, the pH values of UF concentrate, UF permeate, RO concentrates, and the last fractions of RO permeates were very close (within 0.1) to those of respective stillage solubles. The pH values of the first RO permeate fractions were about one unit higher than the respective stillage solubles, probably as a result of the very low buffering capacity present.

CONCLUSIONS

UF combined with high-pressure RO is a practical method to process stillage solubles from corn and dry-milled corn fractions. A large volume of dilute solution can be separated into a small volume of concentrate and a large volume of permeate that can be reused or safely discarded. RO at 6,800 kPa is significantly more efficient than that at 1,360 kPa (Wu et al 1983, Wu and Sexson 1985).

This method may improve the economics of ethanol production from corn and dry-milled corn fractions, while providing valuable food-grade products or feeds. For example, Tsen et al (1982, 1983) used corn distillers' dried grain flour as an ingredient in bread and cookies. Cost-effective UF and high-pressure RO may therefore encourage increased food use of corn-derived distillers' grains while reducing the total cost of the alcohol production process.

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