Reverse Osmosis and Ultrafiltration of Corn Light Steep-Water Solubles

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ABSTRACT

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Evaporative concentration of light steep water from about 10 to 50% solids in corn wet milling uses a great deal of energy. Another more efficient process was investigated. Light steep water was separated by continuous centrifuge (45,200 × *g*) into light steep-water solubles (93% of total dry matter and 93% of total nitrogen) and centrifuged solids. Reverse osmosis (RO) at 1,360 kPa (200 psi) combined with ultrafiltration (UF) of light steep-water solubles yielded an RO permeate of 70% of the total volume, 8.8% of total nitrogen, 10% of total solids, and 13% of total ash of light steep-water solubles. At 5,440 kPa, RO combined with UF produced a permeate that had 80% of the total volume, with residuals of 0.11% of the total nitrogen, 0.23% of the total solids, and 0.24% of the total ash initially present in the light steep-water solubles. At 6,800 kPa, RO combined with UF resulted in a permeate of 84% of the total volume, 0.09% of total nitrogen, 0.18% of total solids, and 0.18% of total ash of light steep-water solubles. Thus, RO at 5,440 or 6,800 kPa, combined with UF, appears practical to process a large volume of corn light steep-water solubles into a small volume of potentially useful concentrate and a large volume of permeate suitable for reuse or safe disposal.

In conventional wet milling, corn is steeped in 0.1–0.3% sulfur dioxide solution at 48–55° C for 28–72 hr. Softened corn is then separated into germ, gluten, fiber, starch, and light steep water. The light steep water, containing about 10% solids, is usually concentrated in multiple-pass, steam-heated evaporators to heavy corn steep water or corn steep liquor having about 53% solids. Water is most efficiently removed by a mechanical vapor recompression type of evaporator, requiring approximately 230 kJ/kg water (Cicuttini et al 1983). In contrast, reverse osmosis (RO) consumes approximately 37 kJ/kg water; this low energy consumption makes RO attractive for the corn wet-milling industry, as steep-water evaporation is one of its largest energy users (Cicuttini et al 1983).

Ultrafiltration (UF) is essentially molecular filtration. The average pore diameter of a UF membrane ranges from less than 1 nm to about 10 nm. Water, which has an effective diameter of about 0.2 nm, can pass freely through all UF membranes. Glucose, with a molecular weight of 180 and a size of about 0.5 nm, can also pass through most UF membranes. Proteins and other large biological molecules are generally excluded. RO is similar to UF in that water is pumped through a membrane under pressure whereas solutes are excluded, but their mechanisms differ. The RO membrane does not have definable pores but has spaces between polymer fibers where a small volume of water in clathrate aggregates like ice can be taken up. Water molecules join the "icelike" aggregate on the concentrate side of the RO membrane under pressure and "melt" away at the permeate side so that there is an effective flow of water through the membrane. Molecules that are too large to fit through the membrane or that cannot conform to the clathrate structure, such as ions, are rejected in RO. Gregor and Gregor (1978) discussed UF and RO with synthetic membranes, and the application of these membranes to waste-water treatment and desalination.

RO and UF have also been used to process cereal stillage solubles. RO of corn stillage solubles, without prior UF to remove larger molecules, resulted in leakage of RO columns (Wu et al 1983), however. UF combined with RO was subsequently used to process stillage solubles from dry-milled corn fractions (Wu and Sexson 1985), sorghum (Wu and Sexson 1984), and barley (Wu 1986). Cicuttini et al (1983) also used RO to produce high-purity process water from light middlings (starch gluten suspension) in corn wet milling. This paper reports that UF combined with RO (at 1,360, 5,440, and 6,800 kPa) (200, 800, and 1,000 psi) processed corn light steep water efficiently into a small volume of concentrated solution and a large volume of dilute permeate suitable for discharge as water or reuse in a process stream.

MATERIALS AND METHODS

Corn Light Steep Water

Corn light steep water was supplied by Pekin Energy (Pekin, IL). The light steep water was centrifuged at 45,000 rpm (45,200 × *g*) in a model T-1 Sharples continuous centrifuge with a bowl having a 4.5-cm inside diameter. The solution that passed through the centrifuge was designated solubles, while centrifuged solids remained in the centrifuge bowl.

UF and RO

An OSMO Econo Pure RO unit (Osmonics, Inc., Minnetonka, MN) equipped with OSMO-112 Sepralators (1.0 m^2 spirally wound membrane, hold-up volume about 600 ml) was used for UF at 680 kPa and RO at 1,360 kPa. For UF, SEPA-O polysulfone (PS) or cellulose acetate (CA) membranes with a molecular weight cutoff (MWCO) of 1,000 for organic compounds were used. For RO of UF permeate at 1,360 kPa, a SEPA-97 CA membrane with a MWCO of 200 for organic compounds was used. The solution that passed through the membrane was called permeate, and that solution retained by the membrane was termed concentrate. The concentrate stream was circulated back to the initial solution for both UF and RO. Concentrate plus initial solution (subsequently called concentrate) and permeate were periodically sampled at equal intervals of permeate volume collected for analyses to monitor progress. The flow rate of UF permeate at room temperature was 7.6 L/(m^2/hr) for PS and 8.6 L/(m^2/hr) for CA membranes. The flow rate of RO permeate decreased linearly from 1.5 to 0.36 L/(m^2/hr) in 3.5 hr and then slowly decreased further to 0.30 L/(m^2/hr) in the next 3 hr. The hold-up fraction was obtained by draining the column under gravity. In addition, six wash fractions were collected by pumping approximately 1 L of distilled water through the system and draining each time. Material balance and percent recovery were based on the sum of permeate, concentrate, hold-up, and wash fractions. UF and RO continued until no concentrate was left in the container or when permeate flow was too slow to be practical.

A model UHPROLA-100 RO system (Village Marine Tec, Gardena, CA), equipped with an SW30-2521 module with 1.1-m^2 polyamide (PA) membrane (Filmtec, Minneapolis, MN), was used for production of RO permeate at pressures of 5,440 and 6,800 kPa. The PA membrane has a 98.6% minimum rejection for 3.2% NaCl solution (equivalent in ionic strength to sea water), but the manufacturer does not quote an MWCO value for organic

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molecules. The concentrate stream was circulated back to the initial solution, and samples of permeate and concentrate were periodically removed for analyses.

Analyses

Solids contents (dry matter) of solutions were determined in duplicate by pipetting known volumes into previously weighed crucibles, drying overnight in an air oven at 100° C and then for three days in a vacuum oven at 100° C, and weighing. Nitrogen contents were determined in quadruplicate by micro-Kjeldahl analysis, and ash was determined in duplicate by heating to 600° C (AACC 1983). Conductivity measurements were made by a Radiometer type CDM 2e conductivity meter with a CDC 104 cell.

For amino acid analysis, each sample was hydrolyzed for 24 hr by refluxing in 6*N* hydrochloric acid and evaporated to dryness in a rotary evaporator. The residue was dissolved in 0.2*N* sodium citrate buffer at pH 2.2, and a portion was analyzed with a Dionex D300 amino acid analyzer (Dionex Corp., Sunnyvale, CA). Data were computed automatically (Cavins and Friedman 1968).

RESULTS AND DISCUSSION

Nitrogen Content and Amino Acid Composition of Corn Light Steep-Water Solubles and Centrifuged Solids

Nitrogen contents of corn light steep-water solubles and centrifuged solids were 7.48 and 7.65%, respectively, on a dry basis. Corn light steep-water solubles accounted for 93% of the total weight and 93% of total nitrogen of corn light steep water on a dry basis. Ash contents of corn light steep-water solubles ranged from 17.3 to 18.8% (dry basis).

Amino acid analyses showed that corn light steep-water solubles and centrifuged solids (Table I) are both relatively rich in lysine, compared with corn. All nitrogen of light steep-water solubles was recovered as amino acids upon amino acid analysis. Steep-water solubles had lower asparagine + aspartic acid, glutamine + glutamic acid, alanine, isoleucine, leucine, tyrosine, and phenylalanine contents but higher glycine, cystine + cysteine, histidine, and arginine contents than centrifuged solids. Comparison of glutamine + glutamic acid, proline, tyrosine, and lysine contents of steep-water solubles and corn proteins (Table I) suggested that most proteins solubilized by sulfite steeping during corn wet milling were albumins and globulins.

Material Balance of UF and RO

Percent recoveries of nitrogen, solids, and ash for each UF and RO run were calculated from the sums of permeate, concentrate, hold-up, and wash fractions as a percent of the starting material. For UF, percent recoveries for the PS membrane were 98, 94, and 100 for nitrogen, solids, and ash, respectively. The corresponding recoveries for UF on CA membranes were 100, 102, and 108%, respectively. For RO, recoveries of nitrogen, solids, and ash were 96, 94, and 97%, respectively, for CA membranes, and 95, 103, and 99%, respectively, for PA membranes. Thus, all nitrogen, solids, and ash appear to be quantitatively recovered from all membranes in UF and RO, and no strong binding by membranes is indicated.

UF and RO at 1,360 kPa

Results from UF and RO of corn light steep-water solubles at 1,360 kPa are summarized in Table II. Each RO concentrate fraction was 100 ml, except fraction 10 was 194 ml for 1,360 kPa. For this and subsequent experiments, the smaller number in each range of nitrogen, solids, or ash concentration is for the first fraction, and the larger number is the corresponding value for the last fraction. Concentrations of nitrogen, solids, and ash in UF permeates were about two-thirds of the values in starting solubles, whereas those in UF concentrate were 50 to 100% higher than in the solubles. When UF permeate was used as feed solution for RO, the average concentrations of nitrogen, solids, and ash in RO permeate decreased by a factor of about five compared with UF permeate. However, nitrogen and solids concentrations of RO permeate increased rapidly with volume of RO permeate collected (Fig. 1), and the RO permeate flow rate decreased by five times. Further treatment of the 1,360 kPa RO permeate would be needed to reduce its nitrogen, solids, and ash concentrations to acceptable levels before it could be discharged from the premises.

UF and RO at 5,440 kPa

Because RO at 1,360 kPa of corn light steep-water solubles resulted in permeate still containing substantial amounts of nitrogen, solids, and ash, RO at 5,440 kPa was carried out (Table II). Solubles were first processed by UF, and the UF permeate then used for RO. Average concentrations of nitrogen, solids, and ash for the RO permeate at 5,440 kPa were 48 to 77 times lower than those at 1,360 kPa. Also, nitrogen and solids concentrations of the RO permeate at 5,440 kPa were very low from beginning until the

TABLE I

Amino Acid Composition of Corn Light Steep-Water Solubles, Centrifuged Solids and Corn Proteins[a]

Amino Acid	Light Steep-Water Solubles	Centrifuged Solids	Whole Corn[b]	Albumin[c]	Globulin[d]	Zein[d]	Glutelin[d]
Aspartic acid[e]	6.0	7.7	7.4	9.6	8.0	6.3	5.5
Threonine	3.6	4.1	4.0	5.5	3.9	3.2	4.2
Serine	4.7	5.0	5.3	5.1	5.9	5.4	5.6
Glutamic acid[f]	16.0	20.5	22.0	13.5	14.4	28.0	22.0
Proline	6.6	6.1	9.6	4.1	5.2	12.4	13.9
Glycine	5.1	3.8	4.1	6.6	6.1	1.5	4.6
Alanine	9.3	10.8	8.4	7.6	6.3	11.5	7.7
Valine	5.1	5.4	5.3	5.9	5.7	4.5	5.4
Cystine + cysteine	1.9	1.2	2.0	...[g]	2.7	0.5	2.0
Methionine	1.0	0.9	2.4	1.3	1.4	0.4	2.4
Isoleucine	2.8	4.1	3.8	3.4	3.5	5.4	3.3
Leucine	9.3	15.4	13.1	6.2	5.8	23.3	13.0
Tyrosine	3.2	4.8	3.8	3.3	3.6	6.0	5.7
Phenylalanine	3.2	5.0	4.2	4.0	4.9	9.5	5.1
Lysine	4.2	3.8	2.8	6.9	5.5	0.1	2.5
Histidine	2.7	2.0	2.9	2.6	3.9	1.4	4.6
Arginine	6.9	4.3	4.9	7.6	12.8	2.0	5.1

[a] Grams of amino acids per 16 g of nitrogen recovered. Tryptophan not determined.

[b] Wu and Sexson 1976.

[c] Paulis and Wall 1969.

[d] Boundy et al 1967.

[e] Includes asparagine.

[f] Includes glutamine.

[g] Not determined.

ninth fraction, when significant increases in nitrogen and solids concentrations were observed (Fig. 2). These increases in nitrogen and solids concentrations were accompanied by a drastic decrease in permeate flow rate—9.4 L/(m^2/hr) for the first eight fractions to 1.2 L/(m^2/hr) to 0.12 L/(m^2/hr) for the ninth and tenth permeate fractions. An optimal end point for RO at 5,440 kPa thus appears to be when solids and nitrogen concentrations reach 0.25 and 0.01 mg/ml, respectively, in the RO permeate. Termination at this point avoids a large drop in permeate flow rate. Using these conditions, concentrations of solids and nitrogen in RO concentrates reached 150 and 10 mg/ml, respectively.

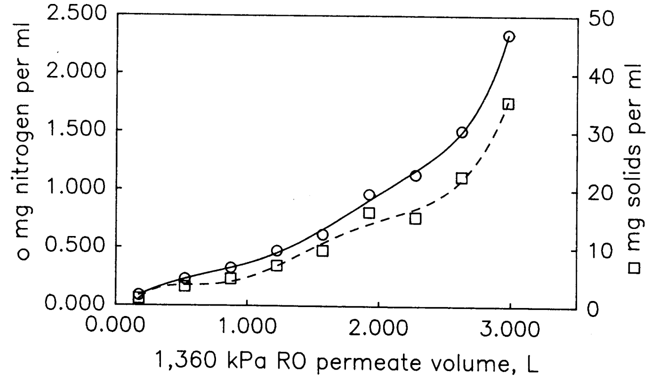

Fig. 1. Solids (-□-) and nitrogen (-o-) contents of permeate during reverse osmosis of corn light steep-water solubles at 1,360 kPa.

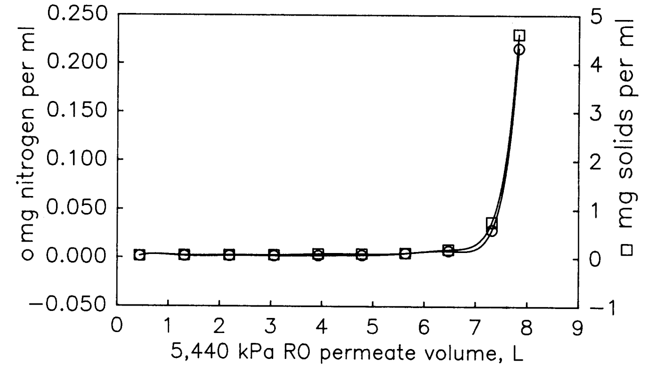

Fig. 2. Solids (-□-) and nitrogen (-o-) contents of permeate during reverse osmosis of corn light steep-water solubles at 5,440 kPa.

UF and RO at 6,800 kPa

Because a large decrease in permeate flow rate was observed near the conclusion of RO at 5,440 kPa, RO of UF permeate from corn light steep-water solubles was carried out at 6,800 kPa (the upper pressure limit of the instrument) (Table II). Average concentrations of nitrogen, solids, and ash of RO permeates at 6,800 kPa were lower than those at 5,440 kPa. Nitrogen and solids concentrations of RO permeate and RO concentrate at 6,800 kPa increased slowly at first but rapidly near the end (Figs. 3 and 4). However, the percentage increases of nitrogen and solids concentrations of RO permeate were much higher than those of RO concentrate. These rapid increases in nitrogen and solids concentrations were accompanied by decreases in RO permeate flow rate—18.8 L/(m^2/hr) for the first nine fractions to 3.5 L/(m^2/hr) for the tenth (last) permeate fraction. To avoid decreased permeate flow rate at 6,800 kPa, an optimal end point occurred at solids and nitrogen concentrations of about 0.3 and 0.01 mg/ml, respectively, after the ninth permeate fraction was collected. At this point the RO concentrate contained 143 mg of solids and 8.7 mg of nitrogen per milliliter.

Conductivity of RO Permeate and RO Concentrate

Solids and ash concentrations of RO permeate and concentrate are linearly related to conductivity at all three pressures. Correlation coefficients of conductivity versus ash and conductivity versus solids ranged from 0.969 to 0.999. Thus, conductivity can rapidly monitor solids and ash concentrations of RO permeate and of RO concentrate. Conductivity of cold tap water at room temperature (0.72 mS/cm) was less than that of RO permeate at 1,360 kPa (6.47 mS/cm) but higher than those of RO permeates at 5,440 kPa (0.28 mS/cm) and at 6,800 kPa (0.19 mS/cm).

Efficiency of UF and RO Procedures

Efficiency of UF and RO can be compared under conditions that maximize throughput of permeate while minimizing nitrogen, solids, and ash contents. Table III (columns 4–7) shows

TABLE II
Ultrafiltration and Reverse Osmosis of Corn Light Steep-Water Solubles

Material[a]	Volume (ml)	Nitrogen (mg/ml)	Solids (mg/ml)	Ash (mg/ml)
Solubles	5,150	7.69	95.4	16.8
Permeate (UF, PS)	4,810	4.90	61.6	12.4
Concentrate (UF, PS)	170	14.6	153	24.6
Permeate (RO, 1,360 kPa)	3,150	0.852	12.6	2.81
range, 9 fractions	350	0.089–2.34	1.20–35.2	0.21–8.28
Concentrate (RO, 1,360 kPa)	1,094	7.57	91.8	18.9
range, 10 fractions	100–194	4.52–11.5	56.4–131	11.9–27.3
Solubles	9,840	6.18	82.6	14.3
Permeate (UF, PS)	9,840	4.39	58.7	12.1
Concentrate (UF, PS)	233	17.6	205	29.8
Permeate (RO, 5,440 kPa)	7,928	0.011	0.26	0.053
range, 10 fractions	195–877	0.0016–0.216	0.036–4.61	0–1.55
Concentrate (RO, 5,440 kPa)	1,000	6.99	112	21.3
range, 10 fractions	100	4.10–12.2	59.2–214	11.1–41.2
Solubles	9,145	6.44	82.1	15.4
Permeate (UF, CA)	8,950	3.56	53.0	10.5
Concentrate (UF, CA)	205	24.3	264	52.2
Permeate (RO, 6,800 kPa)	7,525	0.0072	0.18	0.033
range, 10 fractions	607–773	0.0019–0.47	0.049–0.93	0–0.246
Concentrate (RO, 6,800 kPa)	977	5.86	88.9	17.2
range, 10 fractions	77–100	3.34–13.0	46.7–202	9.26–39.5

[a] UF = Ultrafiltration, RO = reverse osmosis, PS = polysulfone membrane, CA = cellulose acetate membrane.

TABLE III
Permeate from Ultrafiltration (UF) and Reverse Osmosis (RO) of Corn Light Steep-Water Solubles as Percentage of Original Material[a]

Process	Membrane[b]	Pressure (kPa)	Volume	Nitrogen	Solids	Ash
UF	PS	680	97	63	65	74
	CA	680	98	54	63	67
RO	CA	1,360	72	14	16	18
	PA	5,440	82	0.21	0.37	0.36
	PA	6,800	86	0.17	0.29	0.27

[a] Percent of corn light steep-water solubles for UF; percent of UF permeate for RO.
[b] PS = Polysulfone, CA = cellulose acetate, PA = polyamide.

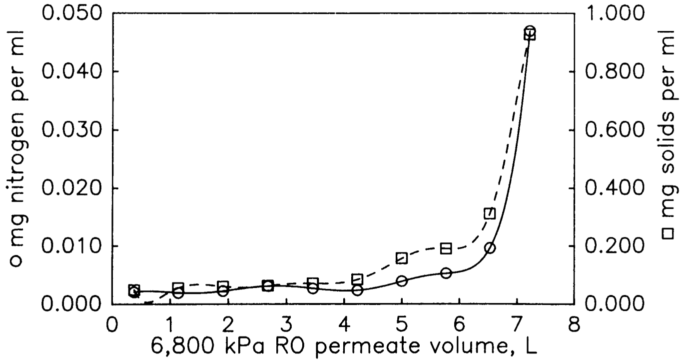

Fig. 3. Solids (-□-) and nitrogen (-o-) contents of permeate during reverse osmosis of corn light steep-water solubles at 6,800 kPa .

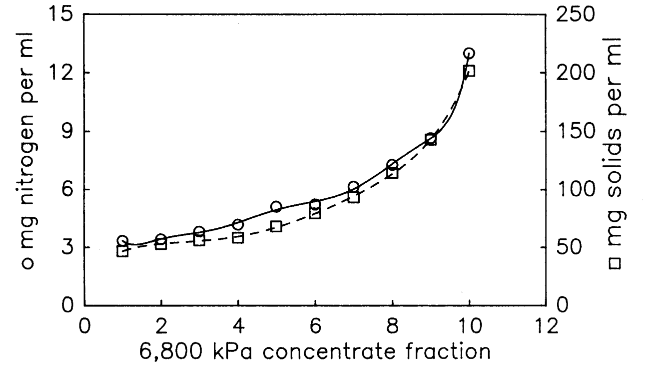

Fig. 4. Solids (-□-) and nitrogen (-o-) contents of concentrate fractions during reverse osmosis of corn light steep-water solubles at 6,800 kPa.

percentages of original material in permeate fractions, normalized for differences in the starting materials. The CA membrane was better than the PS membrane for UF, because it retained more nitrogen, solids, and ash. The RO permeate at 1,360 kPa accounted for 72% of the total volume, and contained 14% of total nitrogen, 16% of total solids, and 18% of total ash which came from the UF permeate. At 5,440 kPa, however, the RO permeate from corn light steep-water solubles accounted for 82% of the total volume, and contained only 0.21% of total nitrogen, 0.37% of total solids, and 0.36% of the total ash that had come from the UF permeate. At 6,800 kPa, the RO permeate contained a higher percentage of the total volume, and yet it had lower concentrations of nitrogen, solids, and ash compared to the permeate from the 5,440 kPa process. At 6,800 kPa, the RO permeate flow rate was also substantially higher than the flow rate at 5,440 kPa. Thus, a pressure of 6,800 kPa is recommended for RO of the UF permeate of corn light steep-water solubles.

CONCLUSION

Gregor and Jeffries (1979) reported that the total cost for equipment, power, and labor for combined UF and RO was $3.53 per 3,785 L of stillage treated, compared to $8.33 for fuel alone by the evaporative route. Thus, RO in combination with UF appears to be a practical method to process a large volume of corn light steep-water solubles into a small volume of concentrate and a large volume of permeate that can be reused for processing or safely discharged from the plant. CA membranes are better than PS membranes in UF processing, and RO at 6,800 kPa is better than that at 5,440 kPa because of the faster permeate flow rate and lower concentrations of nitrogen, solids, and ash in the permeate at higher pressure. However, RO at 5,440 kPa is far more efficient than and preferred over that at 1,360 kPa. Conductivity can rapidly monitor solids and ash concentrations of RO permeate and of RO concentrate or the end point in RO.

The small volume of combined concentrates from UF and RO at 6,800 kPa contained 99.8% of total nitrogen, 99.7% of total solids, and 99.7% of total ash of the corn light steep-water solubles, assuming that only the RO permeate is discarded (Table III). Thus, the amino acid composition of the combined UF and RO concentrates will be essentially the same as light steep-water solubles, which has enhanced lysine and sulfur amino acid contents compared to whole corn (Table I). Nitrogen recovery of light steep-water solubles upon amino acid analysis was 101%, showing that all nitrogen was from amino acids or proteins. Percent nitrogen of corn can be converted to protein by multiplying by 6.25 (Watt and Merrill 1963). The protein content of UF concentrate was 57.5% and that of RO concentrate at 6,800 kPa was 41.2% on a dry basis. Thus, the combined concentrates from UF and RO had both high protein contents and better amino acid compositions than corn. Processing of corn light steep-water solubles by combined UF and RO may, therefore, improve the economics of corn wet milling while providing potentially valuable food or feed products.

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