Reverse Osmosis of Soluble Fraction of Corn Stillage[1]

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ABSTRACT

Reverse osmosis of a soluble fraction of corn stillage with 1.1% solids in a laboratory unit yielded 76% of the initial volume as permeate, which contained only 4.6% of total solids and 3.2% of total nitrogen of the soluble fraction. Conductivity of the permeate was 68% that of tap water, but it increased with solubles content of the stillage. Soluble fractions of stillage from fermentations using recycled stillage solubles contained much higher salts than ordinary stillage. On reverse osmosis, this fraction (with 4.4–6.6% solids) yielded 56–62% of original volume as permeate, which contained 10–18% of the total solids and 3.2–10% of the total nitrogen of the soluble fractions. Ultrafiltration before reverse osmosis extends the concentration range for reverse osmosis.

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When corn is fermented to make alcohol, a residue (stillage) that contains 5–10% solids remains after alcohol is distilled off. The stillage is screened or centrifuged to remove most of the suspended insoluble solids. The remaining soluble fraction with 2–4% solids content is usually evaporated to a syrup, which is then marketed as-is or dried with the solids from screening or centrifugation. Considerable energy and cost are involved in drying the soluble fraction, but discarding it would result in a serious pollution problem.

Reverse osmosis separates water from a solution by means of a membrane that is more permeable to water than to ions and other dissolved matter (Gregor and Gregor 1978). 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 reverse osmosis, energy consumption is much lower than in concentration by heating. Little published information is available on reverse osmosis and ultrafiltration of the soluble stillage fraction. Gregor and Gregor (1978) discussed ultrafiltration and reverse osmosis with synthetic membranes and the application of these membranes to such industrial tasks as waste-water treatment and desalination. A comprehensive review of methods for handling distillery waste water was made by Sheehan and Greenfield (1980). Gregor and Jeffries (1979) reported that the total cost for equipment, power, and labor (but not for interest) for a combination of ultrafiltration and reverse-osmosis methods was $3.53 per 1,000 gal of stillage treated, as compared to $8.33 for fuel costs alone by the evaporative route. Wu et al (1981) reported that the soluble fraction of corn stillage consists of relatively small molecules of less than 10,000 molecular weight. This article reports the result of ultrafiltration and reverse osmosis on corn stillage solubles as an energy-saving alternative to drying.

MATERIALS AND METHODS

Corn Stillage

Yellow dent corn (U.S. grade no. 2) was ground in a Fitzpatrick Homoloid model J.T. mill through a 1.6-mm round-hole perforated screen to yield 30% between 12 and 20 mesh, and 33% each between 20 and 40 mesh and through 40 mesh. The 4% loss in weight was a combination of materials lost in the mill, the air, and the screen, and of moisture loss during milling. Ground corn (2,356 g) was dispersed in 5,000 ml of tap water in a 20-L stainless-steel, temperature-controlled, jacketed fermentor equipped with stirrers; pH of the slurry was adjusted to 6.2, and 6 ml Miles Taka-therm α-amylase was added. The temperature was maintained at 90°C for 1 hr to gelatinize and degrade starch to soluble dextrins. Then, 1,560 ml tap water was added, temperature was cooled to 60°C, pH was adjusted to 4.0, and 18 ml of Miles Diazyme L-100 glucoamylase added to hydrolyze the dextrins to glucose for 2 hr.

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[2]The mention of firm names or trade products does not imply their endorsement or recommendation by the U.S. Department of Agriculture over other firms or similar products not mentioned.

The mixture was cooled to 30° C and adjusted to pH 4.5, and 500 ml of yeast inoculum made from 9 g of Fermivin dry yeast (G. B. Industries), and nutrient was added to convert glucose to alcohol. The fermentation was halted at 66 hr.

Alcohol was distilled from the fermentor by steam, and the stillage was filtered through cheesecloth under suction. The thin stillage that passed through the cheesecloth was centrifuged at 45,200 × *g* with a model T-1 Sharples continuous centrifuge. The solution that passed through the centrifuge (centrifugate) is called soluble fraction of stillage or stillage solubles. The centrifuged solid that remained in the bowl of the centrifuge was not used in this experiment. Recycled stillage solubles were obtained in a similar manner, except that stillage solubles from the prior fermentation were used instead of tap water for nine successive fermentations.

Reverse Osmosis and Ultrafiltration

An OSMO Econo Pure reverse-osmosis machine (Osmonics, Inc., Minnetonka, MN) equipped with OSMO-112 Sepralators (51-mm diameter, 660-mm length, with an 11-sq-ft membrane) was used for reverse osmosis and ultrafiltration. The Sepralators are enclosed in pressure vessels. The membrane is spirally wound into the Sepralator with permeate carrier and mesh spacer separating channels, giving a high membrane area-to-volume ratio. For reverse osmosis, SEPA-97 membrane was used. This membrane has a molecular weight cutoff of 200 for organics, 94–97% sodium chloride rejection, and a nominal pore size of 5 Å. For ultrafiltration, SEPA-0 membrane with 0–10% sodium chloride rejection, a molecular weight cutoff of approximately 1,000 for organics, and a nominal pore size of 15 Å was used. Solution was pumped through the membrane under pressure (200 psi for reverse osmosis and 100 psi for ultrafiltration). The solution that passes through the membrane is designated permeate. The solution that is retained by the membrane is termed concentrate. For reverse osmosis, about 9 L of solution was used. The concentrate stream was circulated back to the initial solution, and the permeate stream was collected. It was desirable to circulate the concentrate stream back to the initial solution to reduce the concentrate volume, because the rate of permeate flow was much slower than the concentrate flow. Only a small fraction of the original solution could be collected as permeate if the concentrate stream was not combined with initial solution. Samples of permeate and concentrate plus initial solutions (designated as concentrate subsequently) were taken at various intervals for analyses. For some more concentrated solutions, ultrafiltration was used to reduce the solids content before the permeate from ultrafiltration was used as initial solution for reverse osmosis. The holdup volume of each Sepralator is about 600 ml.

This Osmonics machine does not have a control for constant temperature. Although both reverse osmosis and ultrafiltration experiments were performed at room temperature, the temperature of the solution rose during processing. Water loss from evaporation during processing occurred. The volume loss depended upon the room temperature, the length of time during processing, and whether a fan was needed to cool the motor so that the motor would not shut off automatically when temperature rise exceeded a certain limit. To minimize the volume loss during processing, the initial feed solution at refrigerator temperature was usually used for reverse osmosis and ultrafiltration. The initial volume before processing is equal to the sum of permeate volume, concentrate volume, evaporation loss, holdup volume of the machine, and any loss if leakage occurred. A reasonably accurate calculation can be made from the initial volume, permeate volume, and the composition of initial and permeate solutions.

Analyses

Nitrogen content was determined by micro-Kjeldahl, and ash was determined by heating to 600° C, as detailed in AACC methods 46-13 and 08-03 (AACC 1976). Solids content (dry matter) of solution was determined by pipeting into a previously weighed bottle or crucible a known volume, and drying overnight in an air oven at 100° C and then for three days in a vacuum oven at 100° C and weighing. Nitrogen determinations were made in triplicate or quadruplicate, and solids content and ash content determinations were in duplicate.

Conductivity measurements were made on stillage fractions by a Radiometer type CDM 2e conductivity meter with a CDC 104 NS cell (Radiometer America, Westlake, OH). The temperature of each solution was recorded, and the conductivity was then corrected to 20° C for comparison. Relative conductivity of 0.100*N* KCl solution between 20 and 30° C was used for the temperature correction factor. Since electrolytes have a temperature coefficient of approximately 2% per Centigrade degree, the conductivity value at a specified temperature is desirable for comparison.

RESULTS AND DISCUSSION

Reverse Osmosis of Stillage Solubles

Table I shows the result of reverse osmosis of stillage solubles. Permeate was collected at 500-ml intervals, and about 100 ml of concentrate was removed from the concentrate fraction remaining when each permeate fraction was collected. Reverse osmosis was stopped when the feed solution was nearly exhausted. Figure 1 shows nitrogen and solids contents of concentrate during reverse osmosis as a function of volume of concentrate. A decrease in nitrogen and solids contents of about 20-fold was observed in the permeate compared with the content of stillage solubles. The nitrogen and solids contents of both permeate and concentrate increased slowly with reverse osmosis until near the end, when rapid increase occurred. The permeate and concentrate at the termination of reverse osmosis had much higher nitrogen and solids contents compared with the average of all permeate and concentrate fractions collected earlier (Table I). Ash content of dried stillage solubles was 19.7%. Permeate accounts for 76% of original volume, 4.6% of total solids, and 3.2% of total nitrogen. Conductivity of permeate was 0.51 millimho/cm at 20° C, compared with tap water's value of 0.75. Since conductivity is a measure of electrolyte (mostly salt) concentration, lower

TABLE I
Reverse Osmosis of Stillage Solubles[a]

	Volume, ml	N, mg/ml	Solids, %
Stillage solubles	9,900	0.265	1.13
Permeate, total	7,500	0.011	0.069
Permeate, end	500	0.028	0.173
Concentrate, total	1,800	0.564	2.64
Concentrate, end	400	1.19	5.64

[a] Permeate accounts for 76% of original volume, 4.6% of total solids, and 3.2% of total N. Conductivity of permeate was 0.51 millimho at 20° C (tap water 0.75 millimho). Ash content of stillage solubles was 19.7%, dry basis. In addition to the permeate and concentrate, holdup volume in the machine and water loss from evaporation during processing also contributed to the initial volume.

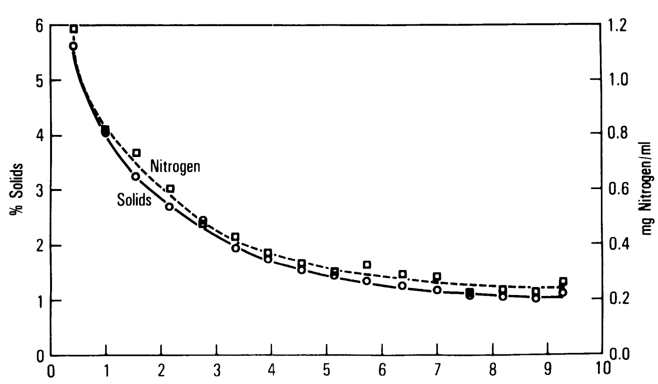

Fig. 1. Solids (-o-) and nitrogen (-□-) contents of concentrate during reverse osmosis of corn distillers' solubles with 1.13% solids.

conductivity of permeate compared with tap water indicates less salt in permeate and better quality than tap water. The permeate can be used as water without further treatment, and no evaporation or heating is needed.

Reverse Osmosis of Recycled Stillage Solubles

Since the result of reverse osmosis of stillage solubles in Table I was very favorable, recycled stillage solubles with much higher nitrogen, solids, and ash contents were tried (Table II). Permeate was collected at 500-ml intervals, and 100 ml of concentrate was removed when each permeate fraction was collected. Reverse osmosis was stopped when the pressure vessel leaked because of excessive pressure buildup. Percentage solids of concentrate and permeate during reverse osmosis is shown in Fig. 2. Permeate accounts for 56% of original volume, 9.8% of total solids, and 3.2% total nitrogen. Concentration of nitrogen and solids of the permeate was reduced about two- and sixfold, respectively, compared with recycled stillage solubles. The nitrogen and solids content of permeate and concentrate fractions increased slowly at first but rapidly near the end of reverse osmosis, so that the nitrogen and solids contents of both permeate and concentrate at the end were higher than the average value for permeate or concentrate (Table II). The limit of this reverse osmosis instrument was reached when concentrate attained 10% solids, and 29% of solids was ash.

Conductivity of each permeate fraction adjusted to 20°C was plotted against percentage solids or ash in Fig. 3. A linear increase of conductivity was observed with increasing percentage of solids. On the other hand, points for the plot for percentage ash as a function of conductivity showed more scatter, although the same general trend was observed. Conductivity as a function of percentage solids for concentrate fractions gave a smooth curve, whereas conductivity as a function of percentage ash resulted in a straight line with more scattering of points (not shown in Fig. 3). Conductivity as a function of percentage solids for other stillage solubles fractions also gave better correlations than conductivity as a function of percentage ash.

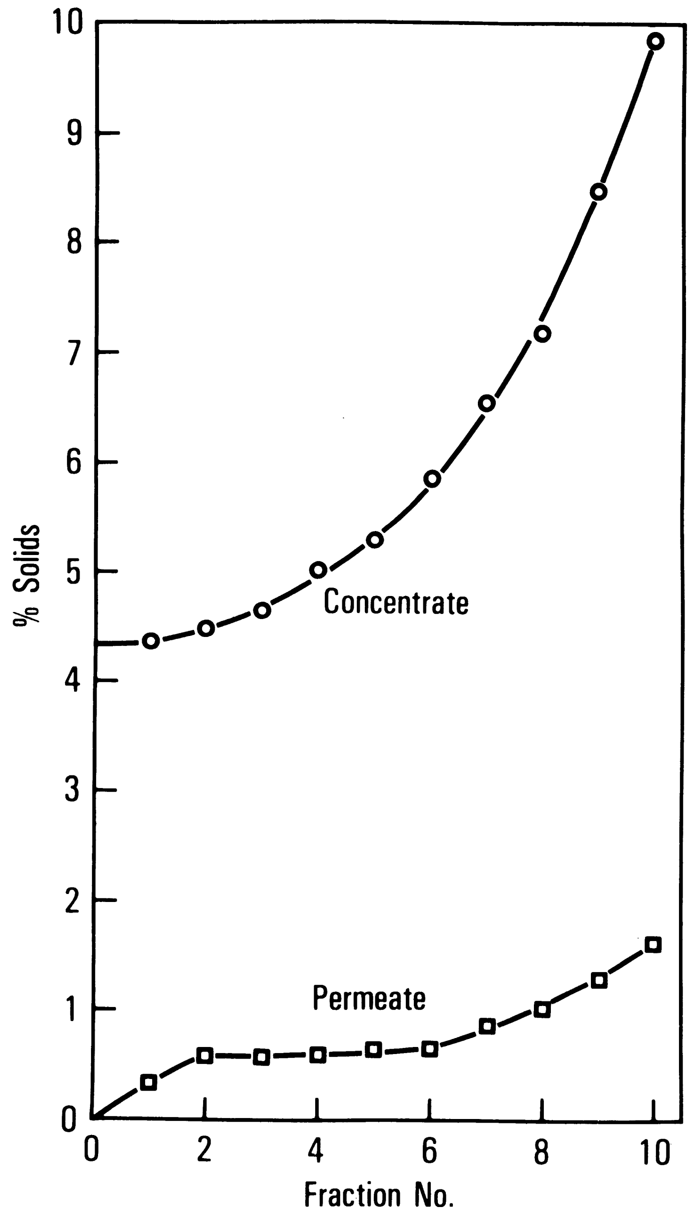

Fig. 2. Solids content of concentrate (–o–) and permeate (–□–) during reverse osmosis of recycled corn stillage solubles with 4.35% solids. Permeate fractions collected were 500 ml, except for fraction 10, which was 165 ml. When each permeate fraction was collected, 100 ml of concentrate was removed for analyses.

Ultrafiltration and Reverse Osmosis of Recycled Stillage Solubles

Because reverse osmosis of the recycled stillage solubles resulted in pressure vessel leakage caused by excessive pressure buildup, ultrafiltration before reverse osmosis was tried (Table III). The recycled stillage solubles were passed through an ultrafiltration membrane to remove larger particles, and ultrafiltration continued until the feed solution was nearly exhausted. Permeate from

TABLE II
Reverse Osmosis of Recycled Stillage Solubles[a]

	Volume, ml	N, mg/ml	Solids, %	Ash, % of dry matter
Stillage solubles	8,360	1.04	4.36	34.8
Permeate, total	4,670	0.059	0.76	78.1
Permeate, end	165	0.132	1.62	98.8
Concentrate, total	2,370	1.88	8.31	28.9
Concentrate, end	1,470	2.15	9.87	28.8

[a]Permeate accounts for 56% of original volume, 9.8% of total solids, and 3.2% of total N. In addition to the permeate and concentrate, holdup volume in the machine (630 ml), water loss from evaporation during processing, and leakage loss at end of this experiment also contributed to the initial volume.

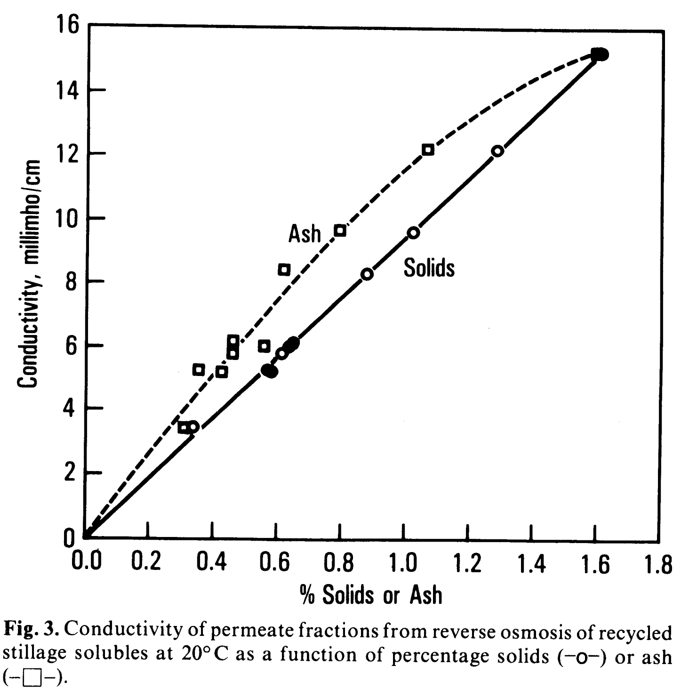

Fig. 3. Conductivity of permeate fractions from reverse osmosis of recycled stillage solubles at 20°C as a function of percentage solids (–o–) or ash (–□–).

TABLE III
Ultrafiltration and Reverse Osmosis of Recycled Stillage Solubles[a]

	Volume, ml	N, mg/ml	Solids, %	Ash, % of dry matter
Stillage solubles	7,000	1.54	6.63	32.9
Permeate (UF)	5,920	1.06	4.79	42.7
Concentrate (UF)	140	4.52	14.83	12.9
Permeate (RO), total	4,120	0.27	2.03	57.3
Permeate (RO), end	115	0.64	4.36	48.0
Concentrate (RO), total	980	1.58	7.54	37.5
Concentrate (RO), end	180	2.50	11.3	33.8

[a] Permeate from ultrafiltration (UF) accounts for 85% of orginal volume, 61% total solids, and 58% total N. Permeate (UF) was used as feed solution for reverses osmosis (RO) after 100 ml was removed for analyses. Permeate (RO) accounts for 71% of orginal volume, 30% total solids, and 18% total N of permeate (UF). In addition to the permeate and concentrate, holdup volume in the machine and water loss from evaporation during processing also contributed to the initial volume. The initial volume of ultrafiltration permeate for reverse osmosis was 5,820 ml.

TABLE IV
Ultrafiltration and Reverse Osmosis of Recycled Thin Stillage Through 100-Mesh[a]

	Volume, ml	N, mg/ml	Solids, %	Ash, % of dry matter
Thin stillage through 100 mesh	10,800	1.54	6.34	24.9
Permeate (UF)	10,510	0.73	3.81	35.6
Concentrate (UF)	190	8.28	21.3	6.9
Permeate (RO), total	6,660	0.14	1.22	66.4
Permeate (RO), Fraction 1	3,450	0.080	0.66	60.1
Concentrate (RO), total	2,040	2.05	10.4	33.1
Concentrate (RO), Fraction 1	100	1.00	5.46	41.1

[a] Permeate from ultrafiltration (UF) accounts for 97% of original volume, 59% of total solids, and 46% total N. Permeate (RO) accounts for 64% of original volume, 21% of total solids, and 13% of total N of permeate (UF). In addition to the permeate and concentrate, holdup volume in the machine and water loss from evaporation during processing also contributed to the initial volume. The initial volume of ultrafiltration permeate for reverse osmosis was 10,410 ml.

ultrafiltration (UF) accounts for 85% of the original volume, 61% of total solids, and 58% of total nitrogen. Permeate (UF) was then used as initial solution for reverse osmosis (RO) after 100 ml of the UF permeate was removed for analyses. Reverse osmosis was stopped when the feed solution was nearly exhausted. Permeate from reverse osmosis was collected at 500-ml intervals, and 100 ml of concentrate was removed when each permeate fraction was collected. Permeate (RO) accounts for 71% of total volume, 30% total solids, and 18% total N of UF permeate, or 60% of total volume, 18% total solids, and 10% total N of recycled stillage solubles. By combining ultrafiltration and reverse osmosis on recycled stillage solubles (Table III), a solution about 50% more concentrated in nitrogen and in solids than that in Table II can be processed without any leakage caused by excessive pressure buildup. No difficulty was encountered in ultrafiltration when the solids content of concentrate reached 15% and in reverse osmosis when solids content of concentrate reached 11%. It seems that when the larger solids were first removed by ultrafiltration, the resulting material can be processed at a higher concentration of solids in reverse osmosis. Apparently, we have not yet reached the upper limit of solids and ash concentrations that can be handled by a combination of ultrafiltration and reverse-osmosis methods.

Ultrafiltration and Reverse Osmosis of Recycled Thin Stillage

Thin stillage, the fraction that passed through cheesecloth, contains some suspended solids that clog up the 100-mesh screen filter in the reverse-osmosis machine. Thin stillage was passed through a 9XX silk screen (corresponds to 100-mesh screen) instead of using high-speed centrifugation to remove the small amount of suspended solids from thin stillage. Thin stillage through a 100-mesh screen was fed into an ultrafiltration column until the feed solution was nearly exhausted. Permeate solution from ultrafiltration accounts for 97% of original volume, 59% of total solids, and 46% of total nitrogen of thin stillage through a 100-mesh screen (Table IV). No difficulty was observed when the solids content of concentrate reached 21% at the end of ultrafiltration. Permeate from ultrafiltration was then used as feed solution for reverse osmosis after 100 ml was removed for analyses. Reverse osmosis was stopped when permeate flow rate dropped to 210 ml/hr from a maximum of 1,100 ml/hr. Permeate from reverse osmosis of ultrafiltration permeate (10,410 ml) accounts for 64% total volume, 21% of total solids, and 13% of total nitrogen of permeate from ultrafiltration. Alternatively, permeate from reverse osmosis of ultrafiltration permeate accounts for 62% of total volume, 12% of total solids, and 6% of total nitrogen of thin stillage through a 100-mesh screen. It appears, from data of Table IV, that by passing the thin stillage through a 100-mesh screen, a centrifugation step can be omitted to prepare the solution for ultrafiltration and reverse osmosis. However, there is a decline in permeate flow rate of the reverse osmosis step that may be caused by omitting the centrifugation.

CONCLUSION

This study demonstrates that 76% of original stillage solubles volume can be recovered as permeate with a quality better than tap water, based on conductivity. Recycled stillage solubles with higher solids and higher ash contents can also be processed with reverse osmosis or with ultrafiltration followed by reverse osmosis. The permeate from reverse osmosis accounts for 56–62% of the total volume, 10–18% of total solids, and 3–10% of total nitrogen of stillage solubles. Further processing of permeate from recycled stillage solubles, such as another reverse-osmosis cycle, is needed to reduce the conductivity of permeate to the level of tap water. The small volume of concentrate from reverse osmosis and ultrafiltration may be incorporated into feeds within liquid consumption limits of animals or may be dried with relatively little energy consumption, because only a small volume of concentrated solution is involved.

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