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Ultrafiltration of Thin Stillage from Conventional and E-Mill Dry Grind Processes

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Abstract We used ultrafiltration (UF) to evaluate membrane filtration characteristics of thin stillage and determine solids and nutrient compositions of filtered streams. To obtain thin stillage, corn was fermented using laboratory methods. UF experiments were conducted in batch mode under constant temperature and flow rate conditions. Two regenerated cellulose membranes (10 and 100 kDa molecular weight cutoffs) were evaluated with the objective of retaining solids as well as maximizing permeate flux. Optimum pressures for 10 and 100 kDa membranes were 207 and 69 kPa, respectively. Total solids, ash, and neutral detergent fiber contents of input TS streams of dry grind and E-Mill processes were similar; however, fat and protein contents were different ($p<0.05$). Retentate obtained from conventional thin stillage fractionation had higher mean total solids contents (27.6% to 27.8%) compared to E-Mill (22.2% to 23.4%). Total solids in retentate streams were found similar to those from commercial evaporators used in industry (25% to 35% total solids). Fat contents of retentate streams ranged from 16.3% to 17.5% for the conventional process. A 2% increment in fat concentration was observed in the E-Mill retentate stream. Thin stillage ash content was reduced 60% in retentate streams.

Keywords Biofuels · Membrane filtration · Nutrient separation · Ethanol

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Introduction

Increased demand for ethanol as a fuel additive has resulted in rapid growth in ethanol production. Ethanol is made principally from corn in the USA and is blended with gasoline to increase octane rating and oxygen content. This may help reduce carbon monoxide and volatile organic compound emissions caused by methyl tertiary butyl ether, a fuel oxygenate derived from petroleum [1]. Wet milling and dry grinding are two large-scale fuel ethanol producing industries. Approximately 82% of fuel ethanol is produced by dry grind corn processing plants; the remaining 18% is produced by wet milling plants [2]. Dry grind plants require lower capital investment than wet milling plants [3]; most growth in the ethanol industry since 1998 has resulted from construction of dry grind plants. Ethanol production in the USA increased from 1.6 to 9.0 billion gallons from 2001 to 2008 [2].

Following fermentation, ethanol is removed by distillation and the remaining material, whole stillage, is centrifuged to produce thin stillage from wet grains (Fig. 1). Thin stillage contains 5% to 10% total solids. For a typical dry grind process, 6 to 7 L thin stillage is produced per liter ethanol. As fuel ethanol production increased, thin stillage production rate increased proportionately. Currently, the dry grind industry recycles 30% to 50% thin stillage as backset in the slurry tank (Fig. 1). Recycling at rates greater than 50% increased concentrations of low molecular weight organic compounds and inorganic salts which affected ethanol yields [4,5]. Therefore, a portion of thin stillage is diverted to evaporators to concentrate solids, mixed with wet grains, and dried to form distillers dried grains with solubles (DDGS). An issue associated with evaporative drying is fouling. Deposit formation on evaporator surfaces causes heat transfer resistance to increase. Time involved in cleaning of evaporators reduces operational efficiency. The presence of fouling in evaporators represents additional capital, energy, and labor costs [6,7]. About 55% to 60% of thermal energy of the plant is used for distillation and molecular sieve processes. The second largest thermal energy-consuming operations are evaporation and drying which

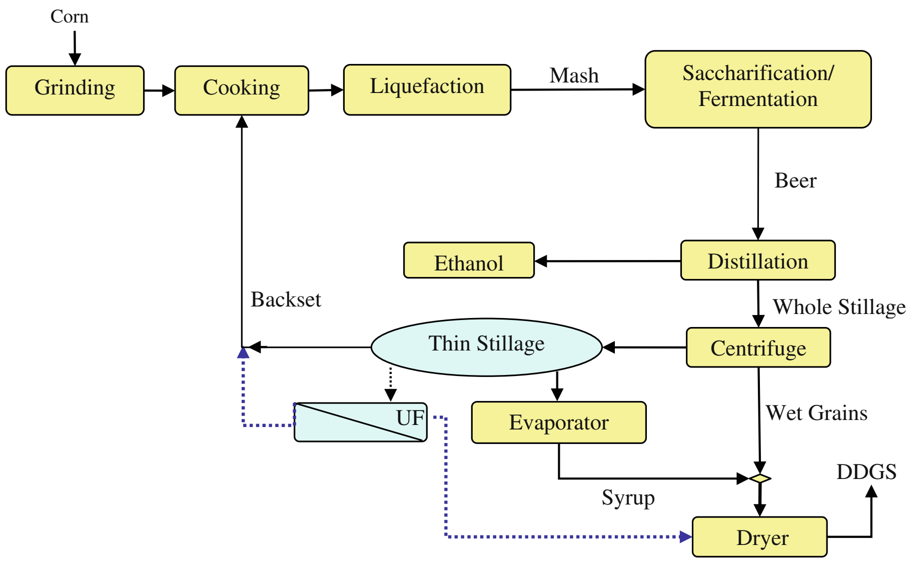

Fig. 1 Dry grind process with potential membrane application

account for 40% to 45% of thermal energy use and 30% to 40% of electrical energy use in the dry grind process [8]. Rausch and Belyea [9] suggested the need and importance of alternative methods of water removal from corn processing streams. Membrane technology is an alternative to evaporators in wet milling and dry grind industries for dewatering corn processing streams [10–13].

Membrane technology may provide an inexpensive and efficient means for dewatering and recycling thin stillage permeate in dry grind process. Membrane filtration was found to be useful in dewatering processing streams in the wet milling process [12–14]. In the dry grind process, effects of membrane separation on dewatering and evaporator fouling are not well-known. Only one study has been published on concentration of thin stillage using membranes [10].

Evaporation requires large energy inputs and may impact nutritional value of the resulting coproduct, DDGS. Using membranes, the permeate stream from membrane filtration could be recycled within the dry grind process and retentate could be further dried and fed to animals. Sequential filtration may provide new processing streams for process revenue that are not available using conventional centrifugation [15]. Ultrafiltration (UF) requires less energy (9 kJ/kg H_2O) than triple effect evaporation (1,300 kJ/kg H_2O) [9]. A potential application of membranes in the dry grind ethanol industry is shown in Fig. 1. The objectives of this study were to [1] compare filtration characteristics of thin stillage obtained from conventional and E-Mill processes and [2] evaluate solids separation and nutrient compositions of membrane filtered streams.

Materials and Methods

Experimental Material

Yellow dent corn 34N43 (Pioneer Hi Bred International, Johnston, IA, USA) obtained from the Agricultural and Biological Engineering Research Farm, University of Illinois at Urbana–Champaign was used to generate thin stillage using conventional and E-Mill dry grind processes. Corn samples were cleaned, packed in plastic bags, and stored at 4 °C. Whole corn kernel moisture content was measured using a standard 103 °C convection oven method [16].

During incubation and simultaneous saccharification and fermentation (SSF) steps, a granular starch hydrolyzing enzyme (GSHE; Stargen 001) and acid fungal protease (GC106) were added (both from Genencor International, Palo Alto, CA, USA). Active dry yeast (Fleischmann's Yeast, Fenton, MO, USA) was used to convert glucose to ethanol.

Conventional Dry Grind Process

A laboratory dry grind procedure described by Wang et al. [17] was modified with changes made during post-fermentation to obtain a thin stillage process stream (Fig. 2). Ground corn was slurried and incubated with GSHE and protease at 48 °C and pH 4.2 for 2 h. SSF was performed using GSHE, protease, and yeast at 30 °C and pH 5.5 for 72 h. Following SSF, ethanol was evaporated from beer at 90 °C for 3 h. Wang et al. [17] did not separate the thin stillage stream from wet grains and instead dried the whole stillage to form DDGS. In our study, remaining whole stillage was sieved using a sieve shaker (RX-86, W. S. Tyler, Mentor, OH, USA) equipped with a standard US No. 200 mesh screen (74 μm openings) for 1 h to produce thin stillage and wet grains fractions.

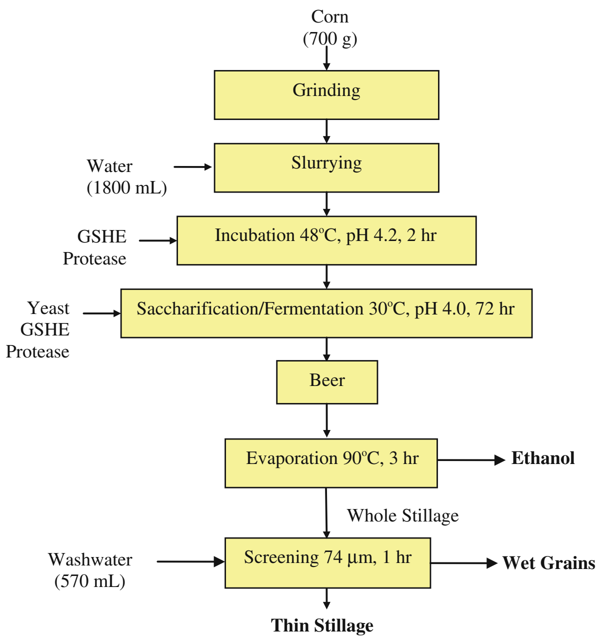

Fig. 2 Conventional dry grind process using granular starch hydrolyzing (*GSHE*) and protease enzymes based on [17]

E-Mill Dry Grind Process

The process outlined by Wang et al. [17] was followed with modifications (Fig. 3). As in the procedure of Wang et al. [17], corn was soaked in water followed by a first grind step to fractionate kernel components without damaging the germ. The resulting slurry was incubated with GSHE and protease, followed by skimming to recover germ and pericarp. The remaining material was finely ground and SSF was carried out using GSHE and protease. Ethanol was removed as in the conventional process. After endosperm fiber was separated using a standard US No. 100 mesh screen (150 µm openings), an additional step was performed to separate thin stillage and wet grains. The thin stillage separation process was similar to the conventional process. Thin stillage obtained from the two processes, dry grind and E-Mill, allowed characterization under controlled laboratory conditions.

Equipment

The conventional dry grind and E-Mill processes used the same equipment as in [17]. For membrane filtration, a stirred ultrafiltration cell (400 mL Amicon, model 8400, Millipore Corporation Bedford, MA, USA) was used for concentrating thin stillage (300 mL per batch). An argon gas cylinder was used to apply pressure to the stirred cell. A magnetic stir bar was used to simulate crossflow filtration. Two regenerated cellulose membranes (YM10 and YM100, Millipore Corporation, Bedford, MA, USA) with pore sizes of 10 and 100 kDa and effective membrane area of 41.8 cm^2 were used in the study. Permeate flux rates were determined by weighing permeate collected during a 2-min period using a stopwatch and expressed as liters per square meter per hour.

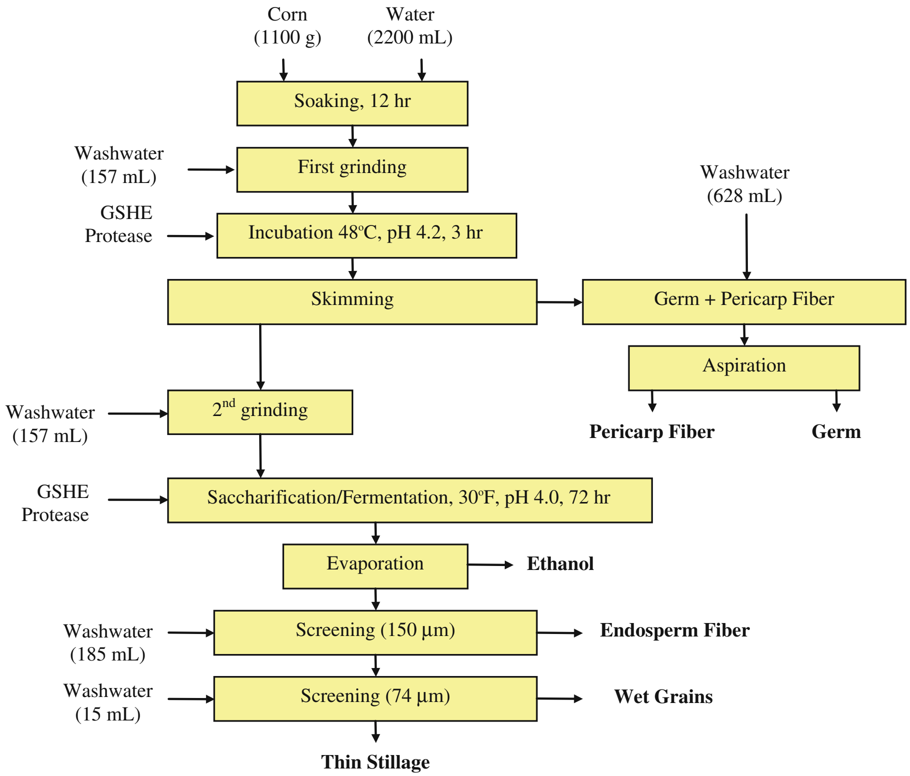

Fig. 3 E-Mill dry grind process using granular starch hydrolyzing (*GSHE*) and protease enzymes based on [17]

UF operating Conditions

Since separation by UF membrane is a pressure-driven process, the transmembrane pressure (TMP) plays an important role in determining membrane performance. To determine TMP for optimum permeate flux rates, pressure excursions were conducted at a range of 35 to 490 kPa using thin stillage produced from conventional dry grind process. Flux rates at higher pressures can be limited due to greater resistances at the boundary layer and other membrane surface phenomena [18]. Flux rates were measured as TMP was increased from 35 to 490 kPa, with increments of 35 kPa. Flux rates were measured at steady-state condition (i.e., 5 to 10 min after adjusting the pressure). Experiments were performed at room temperature (25±2 °C). Stirring speed was kept constant (300±20 rpm). Optimum TMP obtained were used for further filtration studies.

Flux Profiles

Thin stillage (350 mL) samples were concentrated at optimum TMP and operated in a batch concentration mode. Permeate flux rates and time were measured during concentration until material was exhausted. Both permeate and retentate samples were collected for analyses.

For each membrane (YM10 and YM100) and process type (dry grind and E-Mill), five replications were conducted.

Compositional Analysis

Total solids of membrane filtered streams were determined using a two-stage oven method [16]. Composition of thin stillage permeates and retentate streams obtained from conventional and E-Mill processes were analyzed for protein, fat, neutral detergent fiber (NDF), and ash content using standard methods [19] at the University of Missouri, Columbia. Each analysis was performed in duplicate. Some analyses of permeate compositions could not be determined due to insufficient sample quantity.

Experiment Design and Statistical Analyses

Using each of the two processes (dry grind and E-Mill) to obtain thin stillage, corn material was fermented and filtrations were performed with each UF membrane using five replicates. Statistical analyses were performed by using statistical software [20] using a significance level of $p<0.05$. Results were expressed as yield means and standard deviations. An analysis of variance procedure was performed to compare yield means of conventional and E-Mill processes for YM10 and YM100 membranes. The LSD method was used to determine if mean compositions of filtered streams with respect to processes and membrane types were different.

Results and Discussion

Pressure Excursions

For the YM10 membrane, increased pressure enhanced permeate flux rates up to 207 kPa. For the YM100 membrane, permeate flux rates increased from 25 to 69 kPa and then decreased with pressures above 69 kPa. Permeate flux for the membrane with larger pores attained a maximum flux rate (32 $L/m^2/h$) at 69 kPa at a lower TMP than the YM100 membrane. At TMP above the maxima attained, flux decreased with further increase in pressure. Therefore, optimum TMP for YM10 and YM100 membranes were 207 and 69 kPa, respectively. Operating pressures selected for membranes were similar to manufacturer recommendations.

Flux Profiles

In the thin stillage fractionation obtained from the conventional dry grind process, similar permeate flux rate profiles were observed for YM10 and YM100 membranes (Fig. 4). Rapid declines in permeate flux rates were observed during the first 10 min of filtration. This was attributed to a concentration polarization effect in which gradual deposition of a gel layer is formed on a membrane surface [18]. After this decline, permeate flux rates attained relatively steady state and continued for 2 h of operation. Mean permeate flux rates were 20 ± 1.5 and 18 ± 0.8 $L/m^2/h$ for YM10 and YM100 membranes, respectively. Since the YM10 and YM100 were membranes that can reject nominally 10 and 100 kDa solutes, YM100 pores may have become blocked due to presence of large molecular weight components, thus explaining the generally lower flux profiles for YM100.

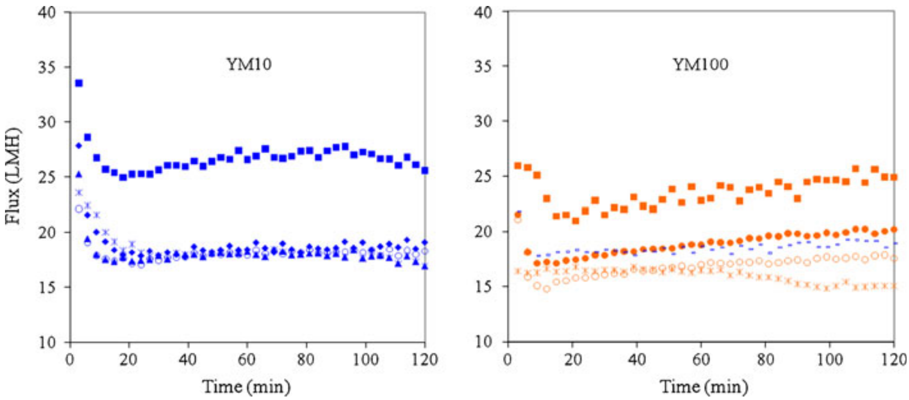

Fig. 4 Permeate flux rate (liters per square meter per hour) profiles for thin stillage obtained from the conventional dry grind process; transmembrane pressures for YM10 and YM100 membranes were 207 and 69 kPa, respectively

Permeate flux rate profiles for membranes were different for E-Mill thin stillage fractionation (Fig. 5). Higher protein content in E-Mill thin stillage may have increased YM100 membrane fouling. Mean permeates flux rates were 22±1.3 and 15.5±0.4 L/m^2/h for YM10 and YM100 membranes, respectively, after 30 min of operation. Both membranes followed similar trends and achieved a stable flux after an initial period of rapid decline.

Compositions of Membrane Filtered Streams

Total solids, ash, and NDF contents of input streams (conventional and E-Mill thin stillage) were similar within each process (Table 1). However, protein contents were higher in E-Mill and fat contents were higher in conventional thin stillage. Differences in fat contents were due to removal of the germ fraction, which contains nearly all kernel oil, before fermentation in the E-Mill process. For each thin stillage source, effects of membrane separation were evaluated to detect differences among initial material, permeate, and

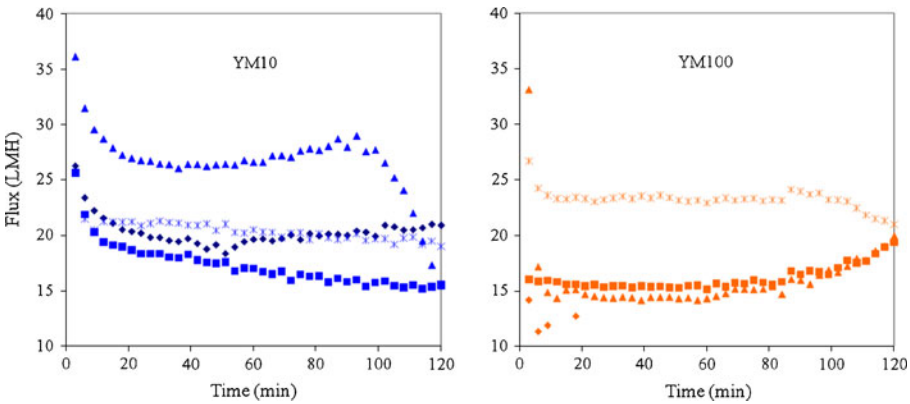

Fig. 5 Permeate flux rate (liters per square meter per hour) profiles for thin stillage obtained from the E-Mill process; transmembrane pressures for YM10 and YM100 membranes were 207 and 69 kPa, respectively

Table 1 Compositions of thin stillage and membrane filtered streams for YM10 and YM100 membranes (mean ± standard deviation)

Composition	Conventional		E-Mill	
	YM10	YM100	YM10	YM100
Total solids (%)				
Initial material	5.2±0.6ax	5.2±0.7ax	4.9±0.3ax	4.9±0.3ax
Permeate	2.1±0.2ay	2.3±0.2ay	2.3±0.3ay	2.4±0.3ay
Retentate	27.8±2.6az	27.6±1.8az	23.4±3.5abz	22.20±1.5bz
Protein (%db)				
Initial material	33.3±2.8ax	33.3±2.8ax	39.5±0.6bx	39.5±0.6bx
Permeate	15.5±2.3ay	15.6±3.1ay	22.8±2.6by	31.1±2.4by
Retentate	38.1±4.2abz	36.9±2.3ax	45.2±2.6bz	42.7±2.9bx
Fat (%db)				
Initial material	9.7±1.6ax	9.7±1.6ax	3.1±0.8bx	3.1±0.8bx
Permeate	ND	ND	ND	ND
Retentate (measured)	21.5±2.5ay	21.3±1.2ay	5.1±2.0bx	4.36±1.4bx
Retentate (calculated)	17.5±2.5ay[a]	16.3±1.2ay[a]		
Ash (%db)				
Initial material	6.3±0.7ax	6.3±0.7ax	6.7±1.1ax	6.7±1.2ax
Permeate[a]	14.4±1.2ay	14.1±1.2ay	12.6±0.9ay	12.6±0.9ay
Retentate	1.7±0.4az	1.8±0.3az	2.6±0.6az	2.6±0.6az
NDF (%db)				
Initial material	15.7±2.5ax	15.7±2.5ax	15.3±2.2ax	15.3±2.2ax
Permeate	ND	ND	ND	ND
Retentate	39.8±3.7ay	41.8±6.5ay	35.7±4.5ay	40.8±12.2ay

Means in same row (abc) and composition stream differ ($p<0.05$). Means in same column (xyz) and same composition stream differ ($p<0.05$)

ND insufficient material to conduct analysis

[a] Data calculated from mass balance based on composition of initial total solids and solid contents of retentates

retentate streams. Solids contents of thin stillage, permeate, and retentate were different for each process and membrane type. Retentate streams had the highest total solids contents followed by thin stillage and permeates. The YM10 membrane had protein content differences in all three streams for both processes, whereas the YM100 membrane had similar protein contents for initial thin stillage and retentate streams.

Total solids in retentate obtained from the YM10 membrane in conventional process was similar to the YM100 membrane but higher than retentates obtained from the E-Mill process for the same membranes (Table 1). Retentates obtained from processes had total solids contents ranging from 22.2% to 27.8%. Thin stillage from conventional dry grind had higher mean total solids contents compared to E-Mill thin stillage. Within each fractionation process, there were no differences detected in compositions of permeate streams between two membranes, i.e., YM10 and YM100 membranes had similar compositions in filtered streams. NDF and fat contents for permeate streams were not determined due to insufficient quantity of sample.

Observed fat concentrations in retentate were 21.5% and 21.3% in YM10 and YM100 membranes, respectively, whereas fat contents (calculated) were concentrated from 9.7% to 17.5% (db) in the conventional retentate stream. An imbalance was observed between measured and theoretical calculated values for conventional thin stillage stream (Table 1). The reason for this imbalance was not apparent. A 60% to 65% increase in fat concentrations was observed in E-Mill retentate streams. Ash content was reduced 60% in retentate streams of both processes for YM10 and YM100 membranes, respectively. This may be attributed to the solubility of minerals in the thin stillage stream, which allowed them to pass through the membranes. NDF concentrations were 2.5 times higher in retentate streams. While these results had been anticipated from general membrane filtration theory [18], no published data existed for these analytes.

Changes in the thin stillage stream composition may be a useful feature of membrane filtration. Syrup from conventional dry grind (Fig. 1) contained the highest element concentrations (e.g., K, P, S) among process streams [21]. Syrup is mixed with wet grains and dried to form DDGS. This coproduct has high concentrations of mineral matter. After potassium, phosphorus has the second highest concentration of elements present in corn and DDGS. High phosphorous concentrations in DDGS can become a cause of eutrophication if allowed to enter the environment [9]. Since a large portion of phosphorus is not available to the animal, it ends up in animal waste, causing disposal difficulties. Removal of ash from retentate could improve disposal issues; the permeate stream could be processed further to recover phosphorus and divert it to environmentally benign uses.

Conclusions

Permeate flux rates were higher for YM10 membrane (10 kDa) than for YM100 membrane (100 kDa). Total solids in retentate streams were similar to streams from commercial evaporators (25% to 35% total solids). Retentate streams produced after fractionation had higher protein, fat, and NDF contents and had lower ash contents. Retentate streams could be used as an ingredient in animal foods, and permeate streams could be processed further using membranes such as nanofiltration or reverse osmosis and recycled within the dry grind plant, thus helping to reduce process water requirements.

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