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Recovery of high value protein from a corn ethanol process by ultrafiltration and an exploration of the associated membrane fouling

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ABSTRACT

Biorenewable fuels hold tremendous potential in the continuing efforts toward a sustainable future. Within the biorefinery paradigm membrane operations have the potential to reduce processing costs, reduce water demands, and provide opportunities for valuable co-product recovery. Here, ultrafiltration has been evaluated as a separation operation within a traditional corn ethanol process to recover high value native and/or recombinant proteins prior to the fermentation. Different membrane materials and molecular weight cut-offs have been investigated to determine optimal conditions for yield, selectivity, and throughput. In addition, different modeling approaches, along with spectroscopic and microscopic analyses were completed to identify fouling mechanisms and the most problematic fouling constituents within a complex corn kernel extract. It was found that inorganic ash compounds may have been the most likely species fouling regenerated cellulose membranes, while protein and other organic compounds may have been more problematic when using a polyethersulfone-based chemistry. A smaller pore size (5 kDa) reduced the fouling rate for both membrane materials compared to a larger pore size (100 kDa). The molecular weight cutoff did not have a significant effect on protein yield or purity.

1. Introduction

The development of economical alternative liquid fuel sources is currently undergoing rapid expansion. With this growth, readily fermentable carbon sources originating from renewable feedstocks such as corn, sugar cane, switchgrass, forest waste, and paper have been investigated for production of ethanol and other biofuels. Ethanol production is a growing industry, generating 9 billion gallons in the United States in 2008 and over 10 billion gallons in 2009 [1]. Ethanol derived from corn kernels is currently the most common type of renewable fuel produced in the United States, and is produced by either a wet milling or dry milling process. The dry milling process is generally considered the less expensive route and thus the majority of current ethanol plants are constructed based on this design, as shown in Fig. 1 [2]. Advanced biofuels, such as butanol and "drop-in" gasoline substitutes, follow a very similar process; the only difference being the liquid fuel that is produced via fermentation following the pretreatment steps [3–5].

As shown in Fig. 1, following distillation for ethanol purification, the slurry stream containing solids is processed with a centrifuge and evaporator and separated into two streams: dry distiller's grain with solubles (DDGS) and thin stillage. Distiller's grains have a high protein content (27 weight percentage), in addition to fiber (8%), fats (10%), and ash (4.5%) [6]. However, due to the operating temperatures in the ethanol plant (especially distillation and drying), the corn protein may be significantly denatured during the process [7]. Thus, protein within the DDGS is degraded to the point that its primary use is as an inexpensive animal feed. If protein could be extracted upstream from the ethanol production portion of the process, minimal protein denaturing would be expected and the value of the protein would be significantly higher than in DDGS. Corn protein in this form could potentially be used as an additive in human food and drinks. Similarly, recombinant proteins (i.e., pharmaceutical products and industrial enzymes) have been produced in transgenic corn and could be easily extracted and purified prior to the fermentation of sugar [8,9]. The recovery of high value native or recombinant protein from corn would not only lead to potential high value co-products to improve plant economics, but would also help alleviate concerns associated the food versus fuel debate [10,11]. Referring to Fig. 1, protein extraction into an aqueous solution, followed by centrifugation and ultrafiltration could be inserted into the fuel production process directly after the grinding step, as shown within the dotted line box, to recover and purify

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the high value co-product. A sequential extraction process using ethanol to fractionate corn protein fractions has been developed previously, but filtration operations have not been evaluated in detail [32].

Membrane microfiltration and ultrafiltration are separation techniques that are currently used in many biotechnology, food, and pharmaceutical processes. These filtration operations are used to purify, concentrate, or separate products within complex process streams. Membrane operations have been investigated in many areas of the corn processing and ethanol production industries to optimize the design and reduce equipment and production costs. For instance, microfiltration has been studied to replace or enhance centrifugation and evaporation of thin stillage and to aid in the drying of DDGS without excessive heat and energy input [12]. Membrane technology has also been investigated within a closed loop recycle mode to the saccharification and/or fermentation steps to create a continuous membrane reactor in which cells are recycled, residence times are reduced, and ethanol product yield increased [13]. In addition, pervaporation has been coupled with the fermentation step to continuously remove the ethanol product, decreasing product inhibition of the fermenting cells. Similarly, pervaporation and membrane distillation have been investigated to replace the distillation step following fermentation in the ethanol plant and reduce energy consumption [14].

The two primary performance criteria during membrane processes are selectivity and productivity, both of which can be compromised due to membrane fouling. Fouling can be caused by complete pore blockage, intermediate pore blockage, standard blocking, and/or cake/gel filtration [15]. Membrane material and its associated surface charge, hydrophobicity, surface roughness, and pore size affect filtration selectivity, flux rates and membrane fouling characteristics [16]. Addition of a membrane operation step within a corn to liquid fuel process, or any bio-processing facility, have often been met with different degrees of success due to membrane fouling and membrane selectivity deficiencies. Here we evaluate the possibility of inserting a membrane separation into the corn ethanol process to recover high value native and/or recombinant proteins prior to the fermentation operation. Different membrane materials and molecular weight cut-offs have been investigated to determine optimal conditions for yield, selectivity, and throughput. In addition, using both a resistance model approach and a combined cake formation/pore blockage model, along with spectroscopic and microscopic analyses, we postulate the most likely fouling mechanisms and most problematic fouling constituents within a complex corn kernel extract.

2. Experimental

2.1. Corn kernel extract preparation

Ground whole kernel yellow dent corn (equivalent to the stream leaving the grinder in Fig. 1) was received from a regional corn mill (Lincoln, NE). The ground corn was prepared into solution using a ratio of 40 g of corn per 100 mL of de-ionized water and adjusted to a pH of 8.5 using sodium hydroxide. The extract was allowed to stir for a minimum of 30 min while continually monitoring and adjusting the pH to maintain pH 8.5. These conditions have been shown to be sufficient for high levels of native protein recovery from corn [17]. All corn extracts had a total protein concentration of 12.2 mg/mL ± 1.3 mg/mL. The solution was then centrifuged at 7000 rpm in a Beckman Coulter J series centrifuge in a 10.5 inch rotor (JLA-10,500) for 30 min. The resulting liquid was carefully decanted for use in filtration trials directly, or pre-filtered with a 0.22 μm syringe filter (Sigma–Aldrich, St. Louis, MO). Any solution

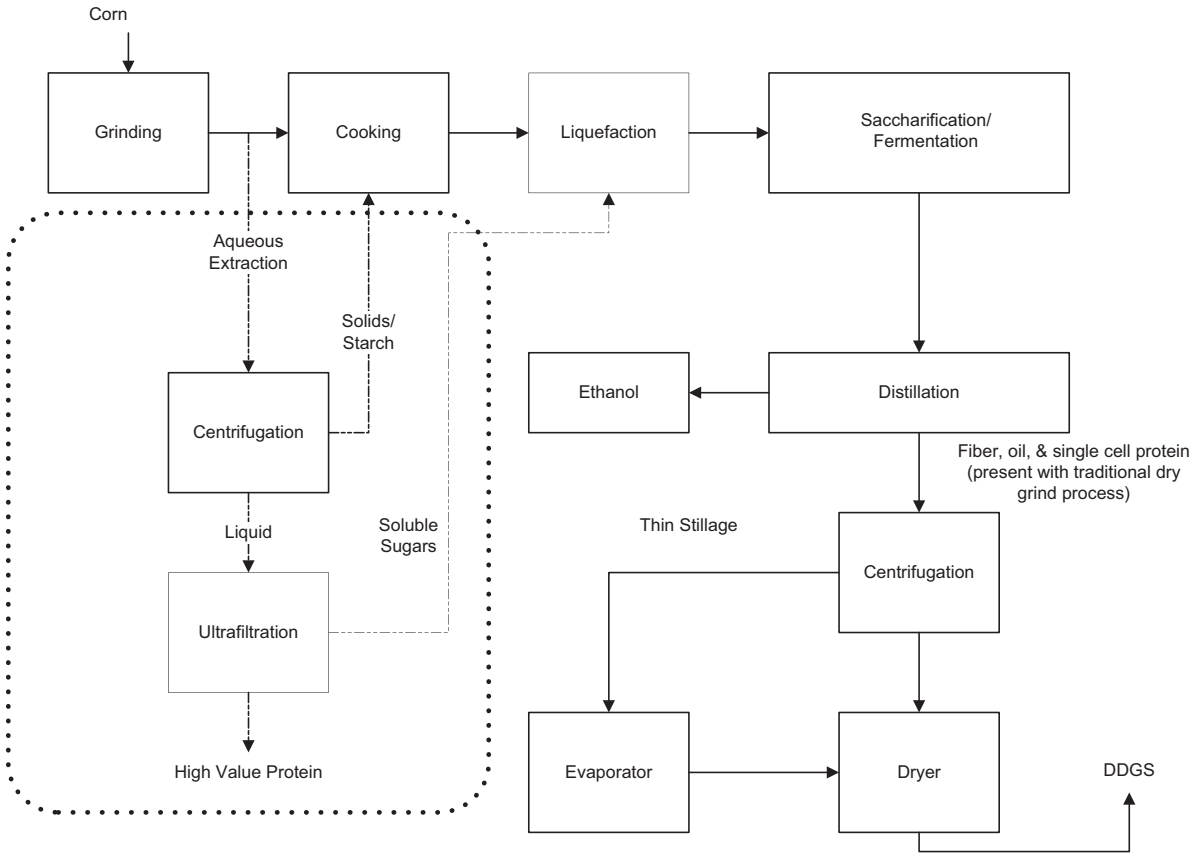

Fig. 1. Dry mill ethanol process with the addition of a high value protein extraction following grinding (the proposed new processing option is indicated by dotted line).