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Economic Evaluation of Isolation of Hemicelluloses From Process Streams From Thermomechanical Pulping of Spruce

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Abstract

Hemicelluloses, which are abundant in nature and have potential use in a wide variety of applications, may make an important contribution in helping relieve society of its dependence on petrochemicals. However, cost-efficient methods for the isolation of hemicelluloses are required. This article presents an economic evaluation of a full-scale process to isolate hemicelluloses from process water from a thermomechanical pulp mill. Experimental data obtained in laboratory scale were used for the scale up of the process by computer simulation. The isolation method consisted of two process steps. The suspended matter in the process water was removed by microfiltration and thereafter the hemicelluloses were concentrated by ultrafiltration, and at the same time, separated from smaller molecules and ions in the process water. The isolated hemicelluloses were intended for the production of oxygen barriers for food packaging, an application for which they have been shown to have suitable properties. The solution produced contained 30 g hemicelluloses/L with a purity (defined as the ratio between the hemicelluloses and the total solids) of approx 80%. The evaluation was performed for a plant with a daily production of 4 metric tonnes (t) of hemicelluloses, which is the estimated future need of barrier films at Tetra Pak (Lund, Sweden). The production cost was calculated to be € 670/t of hemicelluloses. This is approx 9 times lower than the price of ethylene vinyl alcohol, which is produced by petrochemicals and is currently used as an oxygen barrier in fiber-based packaging materials. This indicates that it is possible to produce oxygen barriers made of hemicelluloses at a price that is competitive with the materials used today.

Index Entries: Barrier film; economic evaluation; galactoglucomannan; hemicelluloses; ultrafiltration; thermomechanical pulp.

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Introduction

Lignocelluloses, i.e., celluloses, hemicelluloses, and lignin constitute approx 80% of the biomass on earth and could be utilized much more widely in the future. Hemicelluloses (i.e., heteropolysaccharides found in plant cell walls) may make an important contribution in helping relieve society of its dependence on petrochemicals, but cost-efficient methods for the isolation of hemicelluloses are required. Examples of potential applications of hemicelluloses are the production of barrier films *(1,2)* and hydrogels *(3)*, hydrolysis and fermentation to produce ethanol *(4)*, and as a feedstock for xylitol production *(5)*. The extraction of hemicelluloses from different raw materials has long been studied *(6–11)*. A promising hemicellulose source is the process streams in thermomechanical pulp mills. A method using membrane filtration to isolate hemicelluloses from process water from thermomechanical pulping of spruce has been developed in a previous study *(12)*. A screening of several different membranes was performed in this work to find the most suitable membrane material for this process.

The aim of the present study was to perform an economic evaluation of the isolation of hemicelluloses from process water from thermomechanical pulping of spruce. The purified and concentrated hemicelluloses were intended for the production of barrier films in fiber-based packaging materials. The dominating hemicellulose in spruce is *O*-acetyl galactoglucomannan, which has been shown to have suitable properties for the production of oxygen barriers intended for food packaging *(1)*. To enable an economic evaluation, experimental results are needed. Experiments were therefore performed in laboratory scale. The choice of membranes and operating conditions in the experiments was based on results from a previous investigation *(12)*.

Materials and Methods

Raw Material

The raw material was process water from thermomechanical pulping of spruce from Stora Enso Kvarnsveden Mill AB, Sweden. The process water was collected from the final dewatering step of the pulp. The pH of the process water was approx 4.6 and the amount of dissolved hemicelluloses, defined as oligo- and polysaccharides including acetyl groups, was around 0.5 g/L. The average molecular mass of the hemicelluloses in the process water was approx 10 kDa and the monosaccharide composition of the oligo- and polysaccharides was similar to that found in the hemicellulose galactoglucomannan.

Experimental Procedure

The method used to isolate hemicelluloses from the process water involves two steps: (a) pretreatment to remove solids by microfiltration and

(b) concentration and purification of hemicelluloses by ultrafiltration and diafiltration. The process was performed batch-wise with a starting volume of approx 1 m^3. All liquid streams were analyzed regarding oligo- and polysaccharide and acetyl concentration, to estimate the concentration of hemicelluloses. Monosaccharide content, total solids, and ash were determined to evaluate the purification efficiency.

Pretreatment

The process water was microfiltrated in a Vibratory Shear-Enhanced Processing (VSEP) unit (series L/P, New Logic, Emeryville, CA, USA) to remove the solids. The membrane stack consisted of 19 double-sided polytetrafluoroethylene membrane discs. The membrane pore diameter was 10 μm and the total membrane area was 1.57 m^2. The pump was a displacement pump (G-03, Wanner Engineering Inc., Minneapolis, MN). Microfiltration was carried out at a transmembrane pressure between 250 and 300 kPa and a temperature of 25°C. The vibration frequency was 50 Hz, which corresponds to the amplitude of 19 mm.

Concentration and Purification

Ultrafiltration and diafiltration were performed in a DDS 20 LAB module unit (Alfa Laval Corp., Lund, Sweden). In earlier work *(12)*, it was found that the ETNA01PP membrane (Alfa Laval) had good performance for ultrafiltration of the process stream. In the same study it was shown that a membrane with higher cutoff had better separation capability. The ETNA membranes are made of surface-modified polyvinylidene fluoride, which has been found to be very resistant to fouling *(13)*. Thus, two ETNA membranes with different cutoffs were compared: ETNA01PP (1 kDa) and ETNA10PP (10 kDa) (Alfa Laval). Two different membrane stacks were used, one with six double-sided ETNA01PP membrane discs with a total membrane area of 0.21 m^2 and one with eight double-sided ETNA10PP membrane discs with a total membrane area of 0.28 m^2. The pump was a displacement pump (D-25, Wanner Engineering Inc.) and the circulation flow rate was measured with a rotameter. The permeate flow was measured gravimetrically with a balance (FX-3000, A&D Company Ltd., Tokyo, Japan).

The average transmembrane pressure was 1.0 MPa and the temperature 50°C. The circulation flow rate was 5.2 L/min, which corresponds to a cross-flow velocity of 0.5 m/s. Two temperature-equilibrated diavolumes of deionized water were added at the same flow rate as the permeate flow during diafiltration. The number of diavolumes corresponds to the ratio between the volume of water added during diafiltration and the constant volume of feed solution in the system *(14,15)*. The membranes were cleaned with 0.5 wt% Ultrasil 10 (Henkel, Düsseldorf, Germany) at 50°C for 45 min and thoroughly rinsed with deionized water before the experiments.

Analysis

The ash content and total solids were determined according to the standardized methods of the National Renewable Energy Laboratory (NREL, US Department of Energy) *(16,17)*. The monomeric sugar composition and the concentration of oligo- and polysaccharides were analyzed by acid hydrolysis according to the standardized method of NREL *(18)*. Monomeric sugars were analyzed before and after acid hydrolysis and the oligo- and polysaccharide content was calculated from the difference in monosaccharide concentration before and after hydrolysis. Anhydro corrections of 0.9 and 0.88 were used for the hexoses and pentoses, respectively.

High-performance anion-exchange chromatography coupled with pulsed amperometric detection using an ED40 electrochemical detector (Dionex, Sunnyvale, CA) was used to analyze the monomeric sugars. The chromatograph was equipped with a gradient pump, (GP40, Dionex) an autosampler (AS50, Dionex), and a Carbo Pac PA10 guard and analytical column (Dionex). Millipore water with 2 m*M* NaOH was used as eluent at a flow rate of 1 mL/min, and the injection volume was 10 µL. D-mannose, D-glucose, D-galactose, D -xylose, and L-arabinose (Fluka Chemie AG, Buchs, Switzerland) were used as standards.

The acetic acid content was analyzed before and after acid hydrolysis and the concentration of acetyl groups in the hemicelluloses was calculated from the difference in acetic acid concentration before and after hydrolysis. The acetyl group concentration was multiplied by a factor of 0.98 to correct for the protonation. The acetic acid was analyzed using high-performance liquid chromatography equipped with a refractive index detector (Shimadzu, Kyoto, Japan) and an Aminex HPX-87H column (Bio-Rad, CA). Millipore water with 5 m*M* H_2SO_4 was used as eluent at a flow rate of 0.5 mL/min at 65°C. The injection volume was 20 µL. Acetic acid (Merck, Darmstadt, Germany) was used as standard. The hemicellulose concentration was defined as the sum of the concentrations of oligo- and polysaccharides and the acetyl groups.

Economic Evaluation

The investment and the operating costs for the isolation method were calculated to evaluate the profitability of the process. The annual repayment of the investment costs was calculated with the annuity method:

$$C_{\text{repayment}} = C_{\text{investment}} \times \frac{i \times (1+i)^n}{[(1+i)^n - 1]} \tag{1}$$

where $C_{\text{investment}}$ is the investment cost of the equipment, i is the interest rate, and n is the depreciation time in years. An interest rate of 8% and 10 yr of depreciation time were used. The calculations were based on 8500 operating h/yr and an electricity cost of 3¢/kWh, in accordance with the Swedish pulp and paper industry.

A feed concentration of 0.5 g/L of hemicelluloses was used in the calculations and the process was designed to handle a feed of 400 m^3/h, which corresponds to a production rate of approx 4 metric tonnes (t) of hemicelluloses/d. This is the estimated demand of hemicelluloses for the production of barrier films in fiber-based packaging materials at Tetra Pak (Lund, Sweden). The concentration of hemicelluloses required for barrier film production in industrial scale is today unknown. In this calculation, the concentration of hemicelluloses in the product was chosen to be 30 g/L.

Pretreatment

In the pulp and paper industry, drum filters are the standard method for removing fibers and solids from various process streams. One of the leading manufacturers of drum filters (Algas, Moss, Norway) suggested a drum filter with a 30-μm polyester cloth filter, based on their experience from similar applications. The drum filter had a net active filter area of 36 m^2, which would be sufficient to handle the design flow of 400 m^3/h according to the manufacturer. The energy demand of the filter is approx 21 kW. The recovery of hemicelluloses in the pretreatment step is expected to be very high because the content of suspended matter is very low. Therefore, a recovery of 100% was assumed in the calculations. In the laboratory experiments, removal of water insoluble matter was performed in a VSEP unit as a small-scale drum filter was not available. However, the quality of the water is expected to be equal irrespective of whether a VSEP unit or a drum filter is used for pretreatment.

Concentration and Purification

Owing to the results obtained from the experimental study the ETNA10PP was chosen for the economic evaluation. Spiral wound elements (8 × 38 in.) with 30 mil spacers with three elements per pressure vessel were chosen to be used in the full-scale ultrafiltration plant. The estimated lifetime of these membranes are 24 mo (according to the manufacturer). The temperature of the process water in the pulping process is 80°C. However, the upper temperature limit for the ETNA spiral wound elements is 60°C. The process water must thus be cooled, e.g., in a heat exchanger. The investment cost of a shell-and-tube heat exchanger with 200 m^2 surface area was calculated with Icarus Process Evaluator (Aspen Tech, Cambridge, MA). The price of the cooling water used in the heat exchanger was taken from the literature *(19)*.

The ultrafiltration plant was assumed to have multistage recirculation design with the same membrane area in all stages. This is the most common design for ultrafiltration plants regardless of application. The investment and operating costs of the membrane plant, was calculated for different number of stages. The cost for one extra stage was included in the

Table 1
Economic Data Used to Calculate the Investment and Operating Costs of the Ultrafiltration Plant

Costs	
Basic installation (€)[a]	50,000
Instrumentation, piping, and so on per stage (€)[a]	80,000
Membranes and housing (€/m²)[a]	150
Cleaning equipment (€)[b]	50,000
Membrane replacement (€/m²)[a]	50
Cleaning (€/yr)[c]	300,000
Maintenance[b]	2% of investment cost
Number of operators[c]	1
Labor cost (€/h)[c]	20

[a]Alfa Laval
[b]From ref. 15.
[c]Experience from the ultrafiltration plant at Stora Enso Nymölla mill.

calculations. This extra stage is necessary in the plant in order to be able to take one stage out of the operation for membrane cleaning and replacement, and still operate the ultrafiltration plant continuously. The calculations were based on membrane area and energy consumption of the ultrafiltration plant calculated by solving the mass balances in the process, i.e., the amount of hemicelluloses and process water entering and exiting each stage and the entire membrane plant. This was performed with the computer software Matlab (The Math Works Inc., Natick, MA). The flux in the different stages, i.e., as function of concentration, was obtained from experimental results. The energy requirement of the initial feed pump and the booster pumps was calculated for a plant operating at 1.0 MPa. The efficiency of the pumps was chosen to be 80% and the pressure drop in each spiral wound element was approximated to 0.08 MPa. Economic data were received from Alfa Laval, Stora Enso Nymölla mill (Sweden) and from estimates found in the literature *(15)*. These data are shown in Table 1.

Results and Discussion

Flux During Concentration of the Hemicelluloses

The concentration of total solids differed in different batches from the pulp mill. It was between 2 and 6 g/L, probably depending on how, and when, samples were withdrawn from the storage tank for process water. Although there was a variation in concentration of total solids in the raw process water, the pretreated process water had uniform properties with a concentration of total solids of 1.8 g/L, of which approx 30% was hemicelluloses. The pretreated process water was ultrafiltrated to increase both the purity and concentration of the hemicelluloses. The hemicelluloses

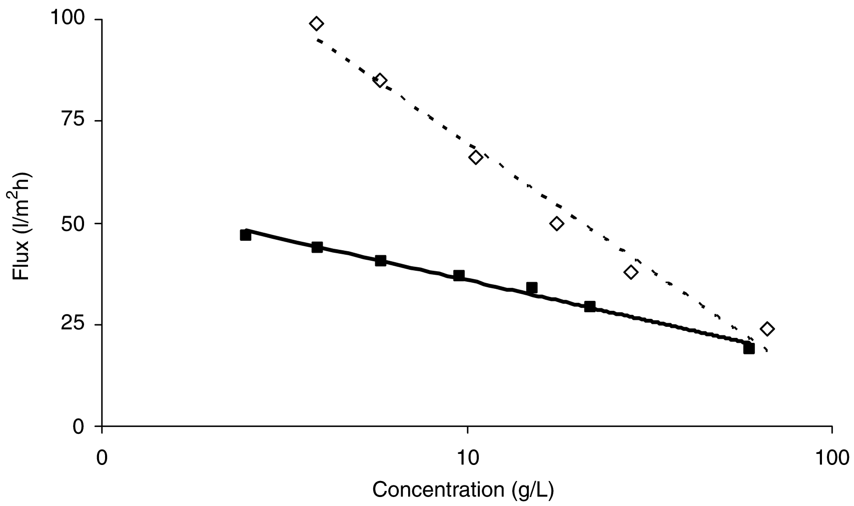

Fig. 1. Correlation between the flux and the concentration of hemicelluloses in the feed solution for the ETNA01PP (solid line) and ETNA10PP (dashed line) membranes.

were concentrated to 59 g/L with the ETNA01PP membrane and to 66 g/L with the ETNA10PP membrane. The retention of hemicelluloses was 98% for both membranes. The flux was significantly higher for the ETNA10PP membrane than for the ETNA01PP membrane, as shown in Fig. 1. The flux decreased as the hemicelluloses were concentrated in the feed. The relation between the flux and the concentration of hemicelluloses was determined by plotting the flux against the concentration on a logarithmic scale. The relation is linear, which is in accordance with the theory that states that this relation should be linear under limiting flux conditions *(20)*. This relation was used in the economic evaluation to calculate the flux in the different stages.

Purity During Concentration of The Hemicelluloses

Purity increases during concentration using ultrafiltration if the retention of the product is higher than the retention of other compounds *(15)*. In earlier work *(12)*, it was found that a hydrophilic membrane with a cut off of 5 kDa had better separation capability with respect to hemicelluloses and contaminants (salts and monosaccharides) than a hydrophilic membrane with a cut off of 1 kDa. Based on these results, it was expected that the purity (defined as the ratio between the hemicelluloses and the total solids) would increase faster during the concentration of hemicelluloses with ETNA10PP. This is verified by Fig. 2, which shows the purity as function of hemicellulose concentration.

The composition of the total solids in the process water changed drastically during concentration of the hemicelluloses. Table 2 shows the composition after pretreatment by microfiltration and after concentration to 66 g/L with ultrafiltration using the ETNA10PP membrane. The ash is partially

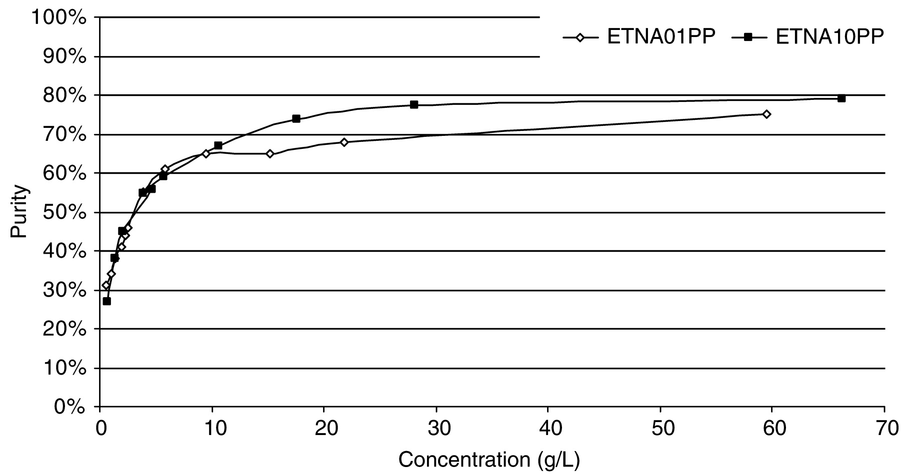

Fig. 2. The relation between the purity and the concentration of the hemicelluloses in the feed during ultrafiltration with the ETNA01PP and ETNA10PP membranes.

Table 2
Composition of the Process Water After Pretreatment by Microfiltration

	Hemicelluloses (g/L)	Monosaccharides (g/L)	Ash (g/L)	Other organic matter (g/L)
After microfiltration	0.7 (27%)	0.2 (6%)	0.8 (32%)	0.9 (35%)
After ultrafiltration	66.2 (79%)	0.3 (0%)	11.5 (14%)	5.8 (7%)

Composition expressed in grams per liter and percentage of total dry solids.

retained by the ultrafiltration membrane, which is somewhat unexpected. This is probably owing to ionic interactions with the hemicelluloses.

Diafiltration was investigated as a method to further increase the purity of the hemicelluloses after ultrafiltration. However, for the parameters used in the economic evaluation (the ETNA10PP membrane and a final hemicellulose concentration of 30 g/L), the purity was not increased significantly by diafiltration. Thus, diafiltration was not included in the economic evaluation.

Economic Evaluation

Pretreatment

The economic evaluation of the pretreatment step was performed based on the economic data received from the filter manufacturer Algas (*see* Table 3). The cost of pretreating a volume of process water corresponding to 1 t of product was calculated to be approx € 40.

Table 3
Economic Evaluation of the Pretreatment Step
with a Capacity of 400 m^3/h

Cost	€
Investment	
Equipment cost	280,000
Annual	
Capital cost	40,000
Energy cost	5000
Maintenance	20,000
Labor	0
Total annual costs	65,000
Cost of filtering a volume of process water corresponding to 1 t of product	40

A drum filter with a 30-µm polyester cloth filter manufactured by Algas was used.

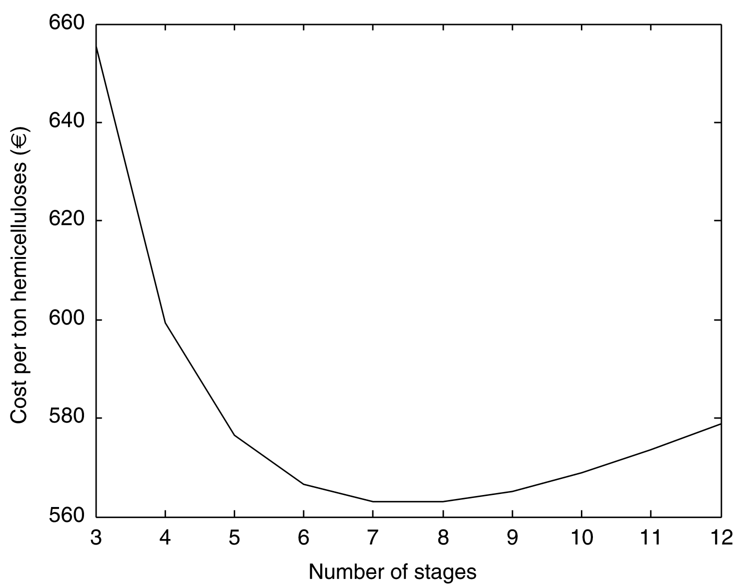

Fig. 3. The cost to concentrate 1 t of hemicelluloses to 30 g/L. The cost was calculated for a multistage ultrafiltration plant with varying number of stages.

Concentration and Purification

The cost for concentration by ultrafiltration varies with the number of stages in the ultrafiltration plant, as shown in Fig. 3. The optimal number of stages for minimizing the cost was found to be eight stages. The total membrane area of the plant was 4000 m^2 and the recovery of hemicelluloses was 89%. The total cost to heat exchange a feed corresponding to 1 t of product and to increase the hemicellulose concentration to 30 g/L in an ultrafiltration plant with eight stages is € 630, as shown in Table 4.

Table 4
Costs Associated With Cooling 400 m^3/h Process Water From 80 to 60°C and Ultrafiltrating to Increase the Hemicellulose Concentration to 30 g/L in an Ultrafiltration Plant With Eight Stages

Cost	€
Investment	
Heat exchanger including installation	210,000
Ultrafiltration plant	1,350,000
Total	1,560,000
Annual	
Capital cost	230,000
Cooling water (1.5 ¢/m^3)	85,000
Energy cost	40,000
Maintenance	30,000
Labor	170,000
Membrane replacement	100,000
Membrane cleaning	300,000
Total annual costs	955,000
Cost to heat exchange and concentrate 1 t of hemicelluloses	€ 630

There is a possibility that the future cost for ultrafiltration in a full-scale plant could be lower than calculated owing to the difference in operational conditions in the laboratory and the full-scale plant. First, in the laboratory study, the ultrafiltration was carried out at 50°C whereas the temperature in the full-scale ultrafiltration plant was set to 60°C. A higher temperature results in a higher flux through the decreased viscosity. Second, it is also probable that the flux would be higher in the spiral wound element than in the plate-and-frame module used in the laboratory, because the turbulence is greater in the flow channel of the spiral wound elements.

Total Cost of the Isolated Hemicelluloses

The total cost of producing a solution containing 1 t of hemicelluloses was calculated to be approx € 670. The market price of barriers with similar properties made of ethylene vinyl alcohol is around € 5800/t. These numbers are of course not directly comparable, but even if costs for additional treatment and handling, such as further concentration, transportation, and addition of chemicals to improve the properties of the barrier are added, it is most likely that the price for the hemicelluloses will still be very competitive. If the concentration of hemicelluloses required for barrier film production in industrial scale is higher than the value used in this study (30 g/L), further concentration is needed. This can be accomplished either by further treatment with ultrafiltration or by evaporation. Of these two alternatives, ultrafiltration is probably the more cost efficient alternative because the energy requirement of evaporation is significantly higher. However, to be able to perform the ultrafiltration to higher concentrations, further development of the method is necessary. An additional economic benefit when isolating hemicelluloses in the process water of thermomechanical pulp mills is that, the biological load on the sewage treatment plant will decrease when fibers and hemicelluloses are removed from the process water.

Conclusions

This study has shown the potential to isolate hemicelluloses from process streams from thermomechanical pulping at a competitive cost, even though the initial concentration of hemicelluloses is very low. Further research and development is of course required to implement this process, but the calculated cost is sufficiently low to leave a great margin to the price of barriers made of petrochemicals with similar properties, i.e., ethylene vinyl alcohol barriers. This process was designed for a thermomechanical pulp mill that produces 0.6 million t pulp/yr. The total Swedish production of mechanical pulp is more than 3 million t/yr and the worldwide production is above 30 million t/yr. This gives some idea of the amount of hemicelluloses available for isolation from thermomechanical pulp mills.

Acknowledgments

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