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Enzymatic hydrolysis suspension cross-flow diafiltration using polysulfone hollow fiber module

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ABSTRACT

Glucose and enzyme in a high concentration enzymatic hydrolysis suspension were separated using hollow fiber cross-flow diafiltration. The operating condition effects on the filtration performance are discussed. Over 86% of the enzymes were retained using a 10 kDa polysulfone membrane. Most glucose molecules penetrated through the membrane into the filtrate. The major filtration resistances are due to the cake formation on the membrane surface and enzyme blocking in the membrane pores in addition to the appreciable virgin membrane resistance. The cake mass is correlated with the drag force ratio tangential to the filtration directions and the average specific cake filtration resistance is expressed as a power-function of the transmembrane pressure with a cake compressibility of 0.3. The empirical equation related the resistances due to internal membrane fouling to the operating conditions established by conducting experimental data regression. The filtration flux can be estimated accurately by substituting the results calculated using the empirical equations into the basic filtration equation. An increase in cross-flow velocity or transmembrane pressure leads to higher filtration flux. The filtration flux increases ca 2-fold as the cross-flow velocity increases from 0.3 to 1.5 m/s under a transmembrane pressure of 60 kPa. The filtration flux increases over 3-fold as the transmembrane pressure increases from 20 to 100 kPa. Two kinds of modified operating methods are used to improve the filtration flux. A pulse feeding method may increase the filtration flux by 25%, while the step-increase pressure method improves the filtration flux by over 34%. Forming a thin cake under low pressure in the early filtration period has great potential to significantly mitigate membrane pore blocking and enhance filtration flux.

1. Introduction

The increasing fossil oil price and climate and environmental concerns have accelerated bio-ethanol development in recent years. In order to avoid food competition with humans and animals the next generation bio-ethanol feedstock are based on cellulosic biomass instead of sugar or starch plants. In such processes cellulose is hydrolyzed enzymatically in a saccharification step to produce sugars for the following ethanol fermentation. Many researchers and engineers have paid more attention to the efficiency and cost of enzymatic hydrolysis. The monomeric sugars produced by cellulose and hemicellulose degradation during enzymatic hydrolysis require removal from the system to minimize the product inhibition effects and improve enzyme activity [1–5]. An efficient membrane separation method is satisfactory for achieving such demand due to accurate membrane selectivity. A hybrid hydrolysis system coupled with a membrane unit in either side-stream or submerged mode facilitates continuous hydrolysis operation and increases the sugar yield by recovering enzymes and unused feedstock [3].

Abels et al. [5] reviewed the development of membrane processes used in biorefinery applications in the past decade and concluded that membrane technology can enhance the enzymatic conversion of cellulose to glucose. Mameri et al. [2] studied the enzymatic saccharification of olive mill solid residue in an ultrafiltration membrane reactor. The cellulose substrate conversion attained 45% in 14 h using a membrane bioreactor. Twenty-four hours was required when using a batch reactor because of the sugar inhibition effects. The produced sugars were separated by the membrane to decrease the inhibition effects and increase the sugar yield. Gan et al. [3] used an integrated membrane reactor for enzymatic cellulose hydrolysis. The cellulose substrate conversion reached as high as 53% during continuous operation with simultaneous product removal. A batch reactor cellulose hydrolysis

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system reached only 35%. Bélafi-Bakó et al. [6] studied continuous cellulose hydrolysis using an enzyme, *Celluclast* 1.5 L®, and a tubular membrane reactor for glucose separation. A composite membrane, constructed using a non-woven technical textile layer, was used to retain the cellulose and enzyme, while the glucose permeated through the membrane. They achieved 70% cellulose conversion in the membrane reactor with continuous sugar removal. Yang et al. [7] studied sugar production using rice straw enzymatic hydrolysis. A tubular reactor coupled with an ultrafiltration membrane was used for sugar separation. They concluded that the hydrolysis rate and sugar yield were significantly improved due to the continuous removal of inhibitory products. Zhao et al. [8] modified a 0.2 μm alumina membrane using three organic compounds and separated cellulose acid hydrolysis mixtures using microfiltration. They found that a thicker membrane manufactured for longer polymerization time produced lower filtration flux in the early filtration period but could effectively mitigate membrane fouling. The filtration flux of the modified membrane was kept at 80% of the original value after three backflushing cleaning cycles. Hwang et al. [9] used three kinds of flat sheet membranes to separate the reducing sugars produced in enzymatic hydrolysis using rice straw as feedstock. Over 70% filtration resistances in the cross-flow diafiltration were caused by the membrane internal fouling when a 0.025 μm membrane made of mixed cellulose ester was used. The virgin membrane resistances were dominant using two kinds of regenerated cellulose (RC) membranes. They concluded that the sugar purification was more effective using a 10 kDa RC membrane, operating under higher transmembrane pressures. Echavarria et al. [10] used ultrafiltration for separating glucose and recovering the enzyme from pectin hydrolysis effluents. They found that the enzymes still expressed 62.2% initial activity even after 4 filtration cycles if the glucose was continuously removed.

Diafiltration is used frequently for separating micro-solutes from a solution using a membrane as the filter medium. It has been used increasingly in food, beverage, biotech and pharmaceutical industrial processes. When an enzymatic hydrolysis suspension is filtered the enzymes and cellulose debris are retained, while the sugars are washed through the membrane. Membrane fouling caused by membrane pore blocking and/or cake formation may lead to drastic flux attenuation during diafiltration. Therefore, mitigating membrane fouling is important for achieving improved operating efficiency. After the separation of residual cellulose debris using a microfiltration (which is discussed in another paper), glucose in a high concentration enzymatic hydrolysis suspension was removed in this study with the enzyme recovered and recycled using cross-flow diafiltration. The filtration resistances due to cake formation and membrane internal fouling were analyzed to estimate the filtration flux under various conditions. The operating condition effects on enzyme rejection and glucose yield are discussed. Two kinds of modified operating methods were used to improve the filtration flux.

2. Materials and methods

An enzyme for cellulose hydrolysis, *Celluclast*® 1.5 L, with a molecular weight range of 22–95 kDa was purchased from Novozymes in Denmark. Glucose with a molecular weight of 180 Da was manufactured by Sigma Co. in the USA (Ca. #: 50–99-7). The enzyme and glucose were dissolved into an acetic buffer solution to prepare a pH 5.5 solution to simulate the hydrolysis suspension after residual cellulose substrate removal. A ratio of 150 unit *Celluclast* per gram cellulose source and a glucose concentration of 10 kg/m^3 were used. The components, concentrations and pH in this model suspension were fit in with those in enzymatic hydrolysis suspensions in previous studies [5,9]. A hollow fiber membrane module manufactured by GE Healthcare (Ca #: UFP-5-C-3 MA) was used for diafiltration. Each fiber in the module had an inner diameter of 5×10^{-4} m and a length of 0.3 m. The overall module filtration area was 1.4×10^{-2} m^2. The membrane was made of polysulfone with a hydrophobic surface and had a mean molecular weight cut-off of 10 kDa. The hollow fiber membrane was soaked in 25 wt% ethanol aqueous solution for 24 h, rinsed with distilled water and the air bubbles in the module driven out before the experiments.

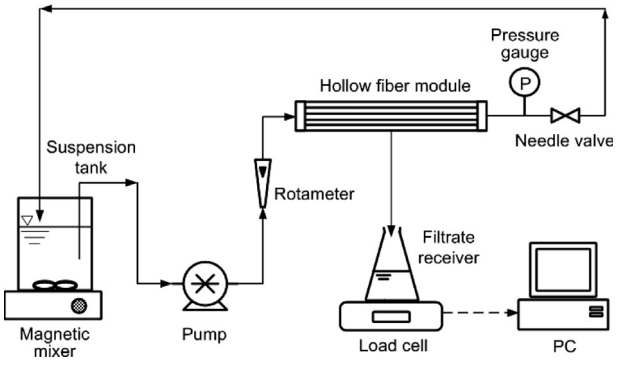

Fig. 1. A schematic diagram of the cross-flow diafiltration system.

Cross-flow diafiltration experiments were carried out using the hollow fiber membrane module. A schematic diagram of the diafiltration system is shown in Fig. 1. The suspension was prepared and stirred uniformly using a magnetic mixer. The suspension temperature was kept at 20 °C. The cross-flow velocity was adjusted and measured using a rotameter, while the transmembrane pressure was adjusted using a needle valve and indicated on the pressure gauge. The filtrate was collected into a filtrate receiver and weighed using a load cell. The filtrate weight data during filtration was recorded on a personal computer. The same amount of distilled water was added into the suspension tank once 20 ml filtrate was collected. The *Celluclast* and glucose concentrations in the filtrate were determined using the optical methods of Ratanakhanokchai et al. [11] and the standard dinitrosalicylic acid (DNS) method [12], respectively. When an experiment was terminated the membrane was cleaned using a backflush of distilled water for 2 h. The membrane was then soaked in a 25 wt% ethanol aqueous solution and ultrasonic cleaning was performed for 1 h.

Cross-flow diafiltration was also carried out in a two-parallel-plate filter [9], in which a flat sheet membrane made of mixed cellulose ester, with a mean pore size of 0.025 μm, to understand the cake formation process on the membrane surface under various operating conditions. The cake mass at pseudo-steady state was weighed after experiments.

3. Results and discussion

3.1. Filtration resistances

The filtration resistances in a filtration process may be due to the concentration polarization layer, R_{cp}, filter cake, R_c, internal membrane fouling, R_{if}, and virgin membrane, R_m. The basic filtration equation based on the resistance-in-series model can be written as

$$q_s=\frac{\Delta P}{\mu(R_t)}=\frac{\Delta P}{\mu(R_c+R_{cp}+R_{if}+R_m)} \quad (1)$$

where q_s is the pseudo-steady filtration flux, ΔP is the transmembrane pressure, μ is the fluid viscosity and R_t is the overall filtration resistance. The filtration resistances mentioned above