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Investigation of a submerged membrane reactor for continuous biomass hydrolysis

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ABSTRACT

Enzymatic hydrolysis of cellulose is one of the most costly steps in the bioconversion of lignocellulosic biomass. Use of a submerged membrane reactor has been investigated for continuous enzymatic hydrolysis of cellulose thus allowing for greater use of the enzyme compared to a batch process. The submerged 0.65 μm polyethersulfone microfiltration membrane avoids the need to pump a cellulose slurry through an external loop. Permeate containing glucose is withdrawn at pressures slightly below atmospheric pressure. The membrane rejects cellulose particles and cellulase enzyme bound to cellulose. Here proof-of-concept experiments have been conducted using a modified, commercially available membrane filtration cell under low fluxes around 75 L/(m^2 h). The operating flux is determined by the rate of glucose production. Maximizing the rate of glucose production involves optimizing mixing, reactor holding time, and the time the feed is held in the reactor prior to commencement of membrane filtration and continuous operation. Maximizing glucose production rates will require operating at low glucose concentration in order to minimize the adverse effects of product inhibition. Consequently practical submerged membrane systems will require a combined sugar concentration step in order to concentrate the product sugar stream prior to fermentation.

1. Introduction

Increasing world energy usage as well as increasing environmental concerns relating to greenhouse gas emission combined with limited fossil fuel reserves has led to considerable interest in the development of economical and energy efficient processes for sustainable production of fuels and chemicals (Huber et al., 2006). Plant biomass represents the only sustainable source of organic carbon (Wyman et al., 2004). Unlike 1st generation biofuels, production of 2nd generation biofuels from lignocellulosic biomass is far more complex. Development of new efficient separation and purification operations that lead to process intensification are essential for production of competitive 2nd generation drop-in biofuels. Membrane-based separation processes are attractive as they could lead to significant process intensification and hence reduced operating costs (Drioli et al., 2012).

Here we focus on hydrolysis of lignocellulosic biomass followed by fermentation. Fig. 1 is a schematic representation of a future lignocellulosic biomass to biofuel biorefinery. The main processing steps are shown. The first step involves receiving and storage of the lignocellulosic biomass. The biomass is usually shredded into an appropriate particle size and then pumped as a slurry to the pretreatment reactor. A leading technology for pretreatment is the use of dilute sulfuric acid at elevated temperatures (Schell et al., 2003; Shekiro et al., 2014). Dilute sulfuric acid has been shown to effectively hydrolyze the hemicellulose component of the biomass to its monomeric

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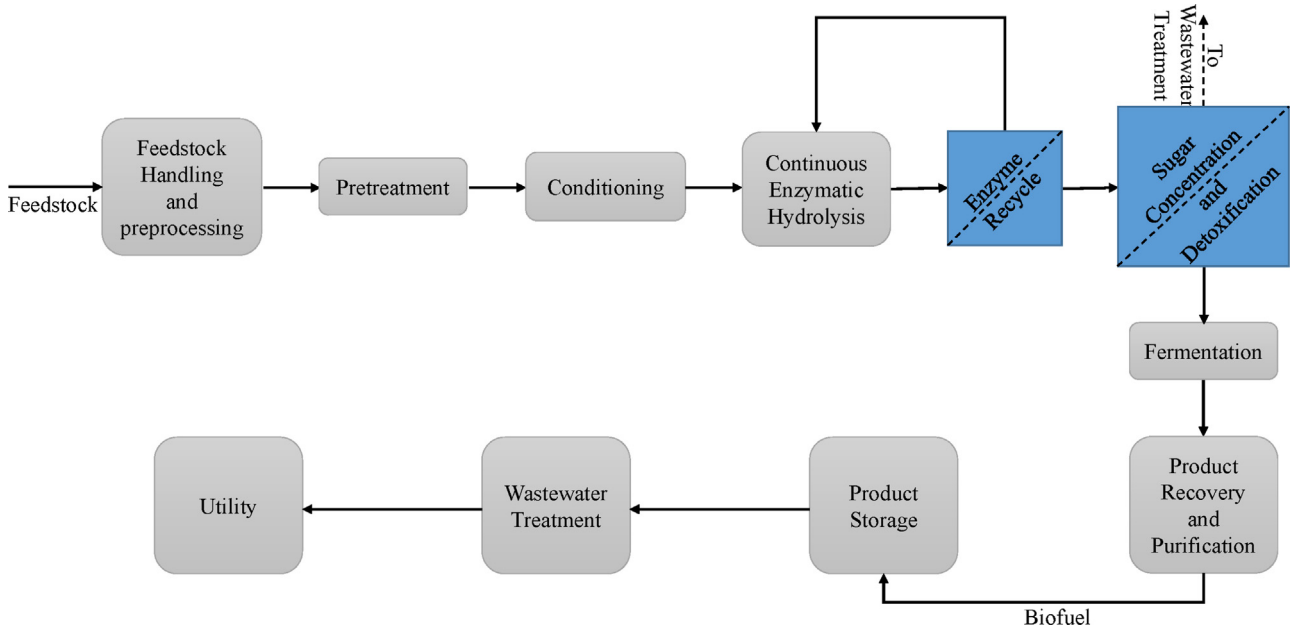

Fig. 1 – Schematic representation of a future lignocellulosic biomass to biofuel biorefinery. A possible continuous hydrolysis step with enzyme recycle has been included.

sugars as well as enhance the enzymatic digestibility of cellulose (Grzenia et al., 2012). After dilute acid pretreatment the pH of the hydrolysate is between 1 and 2. Further the presence of phenolics, acid soluble lignin, acetic acid and sugar degradation compound such as furfural (toxic compounds) in the hydrolysate can adversely affect the efficiency of the subsequent enzymatic hydrolysis and fermentation steps. Consequently the conditioning step adjusts the pH of the hydrolysate and sometimes removes toxic compounds.

Next, cellulose is typically enzymatically hydrolyzed to glucose in a batch process. A cocktail of cellulase enzymes is used to break down cellulose synergistically (Himmel et al., 2007). After enzymatic hydrolysis, the hydrolysate is fed to the fermentation reactor where the sugars are converted to the desired biofuel typically using microorganisms. Subsequent steps include product recovery, purification and storage. The purification operations used depend on the biofuel being produced. Given the large amount of water required to pump the lignocellulosic biomass slurry, water treatment and recovery are critical for an economically viable biorefinery.

This contribution considers the enzymatic hydrolysis step which is typically conducted in batch mode where the cellulase enzyme is used only once. However the cost of the enzymes has been an inhibitory factor for the commercialization of biomass conversion technology (Wyman, 2007). There is considerable variability in the cost and concentration of the cellulase enzyme that is considered to be economically viable. This variability stems from many factors, including feedstock type and delivery costs, the conversion technologies employed, and the price of the biofuels and bioproducts produced. The National Renewable Energy Laboratory suggests a cellulose loading of 20 mg enzyme/g cellulose (Humbird et al., 2011). This amount of enzyme accounts for ~16% ($0.35/gal ethanol) of the minimum ethanol selling price. The United States Department of Energy has set a goal of $0.12/gal ethanol, as the enzyme selling price (Humbird et al., 2011). These numbers highlight the importance of maximizing enzyme recycle and reuse. Increasing the usage efficiency of the enzyme is highly desirable. Thus development of a continuous enzymatic hydrolysis process where the cellulase enzymes may be reused is of considerable interest.

A further complication with batch hydrolysis of cellulose is that the conversion rate is often limited by product inhibition (i.e. inhibited by glucose and cellobiose). Using Celluclast, Novozymes A/S (Bagsvaerd, Denmark) cellulase enzyme, Andrić et al. (2010a) indicate that the presence of glucose significantly reduced enzymatic hydrolysis rates. Removal of glucose leads to increased glucose yields and rates of production. Combination of a membrane separation unit with a hydrolysis reactor could enable continuous removal of glucose and recycle of cellulase enzyme and residual cellulose. Here we focus on the development of a combined membrane separation unit and a hydrolysis reactor that could enable continuous enzymatic hydrolysis of lignocellulosic biomass.

Abels et al. (2013) provide an excellent review of membrane processes for biorefinery applications. Several studies (Henley et al., 1980; Alfani et al., 1982; Ohlson et al., 1984; Kinoshita et al., 1986; Bélafi-Bakó et al., 2006; Gan et al., 2002) have focused on the use of ultrafiltration membranes for continuous removal of glucose in the permeate. The retentate containing residual cellulase enzyme and cellulose is recycled to the enzyme reactor. Mores et al. (2001) have considered the use of sedimentation and microfiltration for recovery of cellulase enzyme. They indicate that by using 0.22 μm pore size membranes, 75% of the cellulase enzyme (46–100 kDa MW) could be recycled in active form due to the fact that the majority of the enzyme is bound to the biomass. The much lower pressures required for microfiltration (up to 100 kPa) is a significant benefit resulting in lower operating costs. Andrić et al. (Andrić et al., 2010b) provide several insights into the design of membrane bioreactors for enzymatic hydrolysis of lignocellulosic biomass. Since cellulose is insoluble, pumping high-solids concentration feed streams is problematic due to the high solution viscosity. Further membrane fouling is a serious concern at high solids loadings.

Carstensen et al. (2012) have reviewed the use of membranes for in situ product recovery. Two modes of operation exist: external loop membranes and submerged membranes.