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Assessing the environmental impacts and water consumption of pretreatment and conditioning processes of corn stover hydrolysate liquor in biorefineries

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A B S T R A C T

In biorefinery procedures, pretreatment and conditioning of lignocellulose substrates are considered critical to enhance yields and rates of transformation. These processes use large volumes of water and chemicals, impacting the sustainability and economics of the biorefinery industry. In this study, we evaluate four pretreatment and conditioning process scenarios for removing acidic impurities from corn stover hydrolysate liquor, i.e., overliming, ammonia addition, two-stage treatment and membrane separations. The environmental impacts of these processes were determined using a life cycle assessment (LCA). Moreover, both the water and carbon footprints were estimated by considering energy and materials consumption. The results indicate that ammonia addition, two-stage treatment and membrane separations reduce environmental impacts in comparison to overliming. Integrated membrane separations exhibited the lowest water consumption (i.e., 2.5 L/kg-biomass) and carbon footprint (i.e., 6.2 g CO_2/kg-biomass). In membrane separations, acidic impurities can be selectively recovered by electrodeionization as value-added products or reuse as process chemicals. Based on the LCA results, an integrated solution for hydrolysate pretreatment and conditioning is proposed as a cleaner and more sustainable process for the biorefinery industry.

1. Introduction

Conservation and protection of water resources is a global concern in response to potential impacts of climate change, growing population, energy demand, and food production. According to the U.S. Geological Survey [1], water withdrawal refers to water removed or diverted from a ground or surface-water source for a specific purpose, for example, thermoelectric power, irrigation, or public supply. Water consumption is the part withdrawn that is not returned to the source catchment area. It occurs when water evaporates, transpires and returns to another catchment area or the sea, is incorporated into processes or products, or consumed by humans or livestock [1,2]. It was estimated that global freshwater withdrawals for energy production in 2010 was about 583 billion m^3[3]. Water and energy are inextricably linked. In one case, energy-related water use is expected to rise as to increase with increasing global production of biofuels [3]. Increased water withdrawals and subsequent discharge downstream at higher temperatures can be detrimental to ecosystems, aquatic life and human health, increasing potential environmental impacts. Rising water temperatures decrease efficiency when the withdrawn water is used for cooling. Therefore, both the environmental impact and water footprint should be evaluated and assessed for energy production process, notably for bioenergy.

The U.S. Department of Energy's Bioenergy Technologies Office considers conversion of lignocellulose biomass to hydrocarbon fuels and biobased products a core pathway to reduce global greenhouse gas (GHG) emissions [4]. Several studies have assessed the environmental benefits and impacts of the entire biorefinery, such as life-cycle energy use and GHG emissions [5], fertilizer/energy intensity of feedstock production [6] and consumptive water

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use [3]. The results indicate that the bioethanol production from corn stover can reduce GHG emissions by 90–103%, compared to petroleum gasoline [5]. In bioethanol production, pretreatment and conditioning of lignocellulose substrates are critical processes to enhance yields and rates of transformation [7]. Pretreatment breaks down the lignin structure and also disrupts the crystalline structure of the cellulose and hemicellulosic fractions to monomeric sugars. A variety of pretreatment processes have been investigated, such as liquid hot water [8], dilute acid [9–11], two-stage treatment (alkali extraction followed by dilute acid) [12], green liquor [13], black liquor [14], ionic liquid [15] and steam explosion [16,17]. The dilute-acid method using sulfuric acid is one of the most common. Dilute acid creates challenges detrimental to downstream processing, including (1) the acidification of hydrolysate liquor by sulfuric acid or organic acids that inhibit enzymatic hydrolysis and fermentation; and (2) the formation of the inhibitory compounds to subsequent enzymatic hydrolysis and fermentation. The fermentation inhibitors include organic acids (e.g., acetic acid, syringic acid, and *p*-hydroxybenzoic acid), aldehydes (e.g., furfural, hydroxymethyl furfural (HMF), and vanillin) and other compounds [10]. Detoxification of the pretreated hydrolysate is an essential step for successful fermentation [18]. Several detoxifying (or conditioning) methods have been developed, such as overliming [10,11], ammonia addition [10,12] and membrane separations [19].

Pretreatment and conditioning processes normally result in extensive use of water and chemicals. Table 1 presents the process water consumption of a typical biorefinery for converting lignocellulosic biomass to bioethanol using dilute acid pretreatment and ammonia conditioning. More than half of the process water was consumed in the pretreatment and conditioning processes, while approximately 35% of process water was consumed in the boiler feed and cooling system, under which the produced steam and/or vapor was mainly used for the pretreatment process. This evidence indicates that the water intensity of pretreatment and conditioning processes should be a key performance indicator in the entire biorefinery. To enhance biofuels production performance, breakthroughs in water management are required in processing technologies (i.e., blue water footprint), thereby decreasing the operating cost and carbon footprint towards a cleaner production [20].

Despite rapid development in process design and evaluation, only a few studies focused on the environmental impact assessment of pretreatment processes. For example, Adom et al. [21] evaluated the fossil energy consumption and GHG emissions impact for dilute acid pretreatment and ammonia fiber expansion. Several critical environmental impact issues, including chemical and water consumption, for these pretreatment and conditioning processes have not been addressed comprehensively in the literature. In this study, we evaluate the life-cycle environmental impact of four scenarios for corn stover hydrolysate pretreatment and conditioning. We report on the water and carbon footprints of these scenarios. Based on the LCA results, we propose a sustainable water- and energy-efficient strategy for integrated hydrolysate conditioning.

2. Materials and methods

2.1. Scope of work and scenario set-up

To critically assess the impacts and benefits of various pretreatment and conditioning processes for biomass hydrolysate, we conducted a comparative LCA of several commonly used methods including overliming (as a baseline), ammonia addition, the two-stage method, and integrated membrane separations. A total of four scenarios was established, as briefly described in Table 2.

Scenario 1 (S1, dilute acid followed by overliming): The biomass is pretreated using dilute sulfuric acid (1.1%) at high temperature (190 °C) and pressure (12.1 atm) for 2 min. After that, the hydrolysate slurry is filter-pressed (i.e., pneumapress) to obtain the liquid portion, and left behind the solid cake. The liquid portion then is “overlimed” to pH 10 by adding lime for a period of time. Finally, pH adjustment, precipitation of gypsum, and slurrying occur, where the gypsum is filtered out and the acid-removed hydrolysate liquid is mixed again with solid cake and dilution water (to control acetic acid concentration). The technical information and process data were mainly extracted from the experiments reported in the literature [11,22].

Scenario 2 (S2, dilute acid followed by ammonia addition): The biomass is first pretreated with dilute sulfuric acid (1.1%) for 5 min, and then processed in “oligomer conversion” step to convert most of the xylose oligomers to monomeric xylose without generating significant additional degradation products. After that, the hydrolysate slurry was cooled by dilution water, and sent to ammonia conditioning reactor, where the pH of slurry was raised from 1 to 5–6. The technical information and process data were obtained from the literature [23].

Scenario 3 (S3, two-stage pretreatment followed by ammonia addition): The biomass is processed and catalyzed in an alkaline deacetylation step using dilute sodium hydroxide to solubilize and remove acetate and other non-fermentable components. Deacetylation can significantly improve conversion of oligomeric to monomeric xylose. After that, the deacetylated solution was drained and treated with dilute sulfuric acid catalyst at a high temperature for a short time. Afterwards, ammonia is added into the pretreated slurry to raise its pH to ~5 for subsequent enzymatic hydrolysis. The technical information and

Table 1
Process water consumption of a typical biorefinery for biochemical conversion of lignocellulosic biomass to ethanol (in the case of dilute acid pretreatment and ammonia conditioning).[a]

Process[b]	Unit operation	Process water (kg/h)	Ratio (%)
Pretreatment	Plug screw feeder	140,850	26.9
Conditioning (ammonia addition)	Addition tank	150,310	28.7
Cellulose production fermentation	Media-prep tank	11,419	2.2
Rectification distillation	Vent scrubber	26,836	5.1
Cooling system	Cooling tower	155,041	29.6
Sterile water and CIP system	CIP system	145	<0.001
Particulate removal and FGD	Lime slurry system	3579	0.7
Boiler feed water preparation	Boiler	35,284	6.7
Total		523,464	100.0

[a] Process information was based on a dry-biomass capacity of 83,334 kg/h [23].
[b] CIP = clean in place; FGD = flue gas desulfurization.