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

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ABSTRACT

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 CO2/kg-biomass). In membrane separations, acidic impurities can be selectively recovered by electro-deionization 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.

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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 Water consumption is the part withdrawn that is not returned to the source catchment area.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 m³ [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
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 lignocellulosic 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 liquid 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 [18]. 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 xylene 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 processes were obtained from the literature [24].

Scenario 4 (S4, two-stage pretreatment followed by ammonia addition and membrane separation): The biomass is pretreated and conditioned using the two-stage process. After that, dilute acid is added into the hydrolysate slurry to raise its pH to ~5 for subsequent enzymatic hydrolysis. The technical information and processes were obtained from the literature [25].

Table 1

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

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.
Table 2
Four scenarios used for LCA regarding different pretreatment and conditioning processes to remove impurities from corn stover hydrolysate.

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Unit process/Process description</th>
<th>Engineering performance</th>
<th>Features</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1 (dilute acid + overliming)</td>
<td>C1: Dilute H₂SO₄ (1.1 wt%). Hydrolysis at 190 °C for 10 min&lt;br&gt;P1: S/L separation. Separator using pneumapress filter&lt;br&gt;C2: Overliming reactor. Vertical vessel with stirring for 1 h&lt;br&gt;C3: pH adjustment. Tank with stirring for 4 h to pH 4.5&lt;br&gt;P2: Gypsum separation. Hydrocyclone and rotary drum filter&lt;br&gt;P3: Slurrying tank. Slurrying with dilution water for 15 min</td>
<td>• H₂SO₄ removal: &gt;99.95%&lt;br&gt;• CH₃COOH removal: ~5.8%&lt;br&gt;• Furfural removal: ~0.4%&lt;br&gt;• HMF removal: 0%&lt;br&gt;• High sugar loss: up to 13%&lt;br&gt;• Long residence time: ~6.8 h</td>
<td>Pros:&lt;br&gt;• Low variable operating cost (lime is cheaper)&lt;br&gt;• High sulfuric acid removal ratio&lt;br&gt;Cons:&lt;br&gt;• Energy-intensive S/L separation&lt;br&gt;• Addition of chemicals&lt;br&gt;• Great number of unit operations&lt;br&gt;• Generation of toxic sludge&lt;br&gt;• Water required to control acetate levels&lt;br&gt;• Lower sugar titers</td>
</tr>
<tr>
<td>S2 (dilute acid + ammonia addition)</td>
<td>P1: Vertical presteamer. Operated at 165 °C for up to 10 min&lt;br&gt;C1: Dilute H₂SO₄ (1.1 wt%). Horizontal screw-feed reactor with short RT at 190 °C (18 mg acid/g dry biomass)&lt;br&gt;P2: Oligomer conversion. Stirring at 130 °C and 2.6 atm for 30 min (4.1 mg acid/g dry biomass)&lt;br&gt;C2: Ammonia conditioning. Raise pH to ~5 for 30 min</td>
<td>• H₂SO₄ neutralized: ~100%&lt;br&gt;• CH₃COOH removal: ~100%&lt;br&gt;• Furfural/HMF removal: ~15%&lt;br&gt;• HMF removal: N.A.&lt;br&gt;• Sugar retention: &gt;97%&lt;br&gt;• Median residence time: ~2.1 h</td>
<td>Pros:&lt;br&gt;• Elimination of S/L separation&lt;br&gt;• High miscibility with hydrolysate&lt;br&gt;• Reduced sugar loss&lt;br&gt;• Possible reduced nitrogen requirement in fermentation&lt;br&gt;Cons:&lt;br&gt;• Higher cost for ammonia (compared to lime)&lt;br&gt;• Require water to dissolve ammonia gas for pH adjustment&lt;br&gt;• Higher waste water treatment cost&lt;br&gt;Pros:&lt;br&gt;• Improvement in ethanol yields&lt;br&gt;• Acetyl groups are removed by NaOH during deacetylation&lt;br&gt;• Removal of lignin, ash, and other primarily non-fermentable components&lt;br&gt;• Lower sugar degradation products (furfural and HMF)&lt;br&gt;• Reduction of ammonia usage for neutralization&lt;br&gt;Cons:&lt;br&gt;• Higher cost for ammonia (compared to lime)&lt;br&gt;• Require water to dissolve ammonia gas for pH adjustment&lt;br&gt;• Higher waste water treatment cost&lt;br&gt;Pros:&lt;br&gt;• Simultaneous recovery of acetic and sulfuric acids&lt;br&gt;• Avoid chemical pH adjustment&lt;br&gt;• No waste gypsum generation&lt;br&gt;• Capable of continuous operation&lt;br&gt;Cons:&lt;br&gt;• Require additional electric power</td>
</tr>
<tr>
<td>S3 (two-stage method + ammonia)</td>
<td>C1: Deacetylation step. Soak in ~0.4% NaOH (pH 8–10) at 20% TS and 80 °C for 1 h with stirring (17 mg base/g dry biomass)&lt;br&gt;P1: Dewatered and drained&lt;br&gt;P2: Presteamers. Vertical steamer for 10 min&lt;br&gt;C2: Dilute sulfuric acid. Charge with dilute H₂SO₄ at 160 °C and 5.5 atm for 5 min, total solid loading ~30 wt% (9 mg/g dry biomass)&lt;br&gt;C3: Ammonia addition. Raise pH from 1 to ~5 for enzymatic hydrolysis</td>
<td>• H₂SO₄ recovery: ~99.5%&lt;br&gt;• CH₃COOH recovery: ~86.2%&lt;br&gt;• Furfural removal: ~40%&lt;br&gt;• HMF removal: ~25%&lt;br&gt;• Sugar retention: &gt;98%&lt;br&gt;• Short residence time: ~1 h</td>
<td>Cons:&lt;br&gt;• Higher cost for ammonia (compared to lime)&lt;br&gt;• Require water to dissolve ammonia gas for pH adjustment&lt;br&gt;• Higher waste water treatment cost&lt;br&gt;Pros:&lt;br&gt;• Simultaneous recovery of acetic and sulfuric acids&lt;br&gt;• Avoid chemical pH adjustment&lt;br&gt;• No waste gypsum generation&lt;br&gt;• Capable of continuous operation&lt;br&gt;Cons:&lt;br&gt;• Require additional electric power</td>
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<tr>
<td>S4 (dilute acid + membrane separations)</td>
<td>C1: Dilute sulfuric acid. Hydrolysis at high temperature for 10 min&lt;br&gt;P1: PF-MF, for collecting liquid fraction of hydrolysate&lt;br&gt;C2: RW-EDI. Selective removal of sulfuric and acetic acids in 1 h by applying different conditions (voltage and flow rate)</td>
<td>• H₂SO₄ recovery: ~99.5%&lt;br&gt;• CH₃COOH recovery: ~86.2%&lt;br&gt;• Furfural removal: ~40%&lt;br&gt;• HMF removal: ~25%&lt;br&gt;• Sugar retention: &gt;98%&lt;br&gt;• Short residence time: ~1 h</td>
<td>Pros:&lt;br&gt;• Simultaneous recovery of acetic and sulfuric acids&lt;br&gt;• Avoid chemical pH adjustment&lt;br&gt;• No waste gypsum generation&lt;br&gt;• Capable of continuous operation&lt;br&gt;Cons:&lt;br&gt;• Require additional electric power</td>
</tr>
</tbody>
</table>

Note: S/L: solid and liquid; PF-MF: pulse-flow microfiltration; RW-EDI: resin-wafer electrodeionization; C: chemical treatment process; P: physical treatment process. RT: residence time. HMF: 5-hydroxymethyl furfural; N.A.: value is not available.

2.2. System boundary and data inventory

In this study, the environmental impacts of the conditioning processes were quantified using LCA by Umberto 5.6, which follows the LCA method described in the ISO 14040:2006 and ISO 14044:2006 [24,25]. A total of four scenarios for various pretreatment and conditioning processes were established in the LCA. Fig. 1 shows a framework of the system boundary for the four scenarios, which incorporates biomass feedstock handling through hydrolysate conditioning prior to the enzymatic hydrolysis and fermentation. The detailed boundaries for all scenarios in Umberto can be found in Fig. S1 (see Appendix A). Since all scenarios were dealing with the same lignocellulose biomass input, the transport of biomass feedstock was not included in the system boundary. The life-cycle impacts of scenario 1 were regarded as a baseline throughout this study. In addition, the operating conditions of pretreatment processes (i.e., dilute sulfuric acid) in scenario 4 were considered from the conventional overliming in scenario 1 to

process data were mainly extracted from experiments reported in the literature [12].

Scenario 4 (S4, dilute acid followed by membrane separations): The liquid fraction of dilute acid pretreated hydrolysate slurry was collected continuously by pulse-flow microfiltration (PF-MF) process, and sent to resin-wafer electrodeionization (RW-EDI) for selectively removing ionic impurities, such as acetic and sulfuric acids, from the liquid fraction. In the RW-EDI process, relatively lower voltage and higher flow rate were applied first to remove sulfate preferentially over acetate ions. Once the sulfate in hydrolysate reached a targeted concentration, operating conditions were adjusted to remove acetate at a relatively higher voltage and lower flow rate. The acid-removed liquid fraction is then slurried with the retentate from the PF-MF for a continuous liquid-filtration and acid-extraction cycle. The acid-removed slurry was sent for substantial fermentation process. The technical information and process data were gathered from the literature [19,39].
determine the difference of environmental impacts due to the conditioning.

Table S1 (see Appendix A) presents the inventory data of the four scenarios, including key information regarding treatment condition and performance, and amounts of material and energy consumption. In this study, the functional unit of each scenario was 1 kg of dry biomass (DB) treated and hydrolyzed. The system boundary consists of all inputs (e.g., energy, raw materials and auxiliary agents) and outputs (e.g., products, emissions, brine and solid wastes). In addition, the uses of chemicals (e.g., sulfuric acid, ammonia and sodium hydroxide), tap water, steam, and electric power were included in the LCA. In Umberto modulus, a balance for material and energy flows could be drawn up for calculating and analyzing the investigated system boundary. The detailed description of LCA methodology and Umberto modules utilized in the cases of power generation, membrane separations, and chemical production were presented in our previous studies \[26,27\]. For example, the generation of electricity in the LCA was extracted from the ecoinvent database, and modified according to the 2015 statistics in U.S. Energy Information Administration \[28\], i.e., "electricity, low voltage, at grid [US]", which consisted 33.2% of coal-fired power, 32.7% of natural gas power, 19.5% of nuclear power, 6.1% hydroelectric power and 6.7% other renewable sources (excluding hydroelectric and solar). Moreover, the production of chemicals (such as sulfuric acid and sodium hydroxide) is considered from a cradle-to-gate approach, e.g., feedstock extraction, transport, manufacturing and waste disposal.

2.3. Environmental impact assessment

The environmental impacts of a process or product can be assessed by midpoint impact (i.e., a problem-oriented approach describing environmental themes) and endpoint impact (i.e., a damage-oriented approach expressing a consistent and concise view of ecosystem and human health effects). In this study, ReCiPe midand endpoint (E, A) in ecoinvent 2.2 database were applied for quantifying the environmental impacts of each scenario in Umberto. A total of ten midpoint impact indicators, i.e., WDP (water depletion potential), GWP (global warming potential), FEP (freshwater eutrophication), HTPinf (human toxicity), METPinf (marine eutrophication), MEP (marine ecotoxicity), PMFP (particulate matter formation), POFP (photochemical oxidant formation), TAP (terrestrial acidification) and TETP (terrestrial ecotoxicity), were determined for life-cycle impact assessment. In addition, both eco-system quality (EQ) and human health (HH) were selected as the endpoint impact indicators. The rest of midpoint (e.g., ozone depletion, radiation and agricultural land occupation) and endpoint (i.e., resource depletion) impact categories in ReCiPe were excluded from the analysis, because they did not exhibit significant difference among the scenarios. Due to the extensive water use in pretreatment and conditioning processes, different approaches to assessing the process water consumption were performed in this study. From the life-cycle point of view, both the direct and indirect water consumption for the pretreatment and conditioning processes could be evaluated from the WDP in midpoint impact assessment. The types of consumptive water resources considered in WDP include water from lakes, rivers, groundwater and any unspecified natural origin, as defined in the ReCiPe methodology \[29\]. However, to evaluate the effect of the process wastes (e.g., brine solution) on water pollution, the process water footprint should be conducted.

2.4. Determination of process water footprint (WF)

In this study, the process WF of the hydrolysate conditioning process is determined over the treatment process, which is defined as the volume of freshwater used to process or treat the hydrolysate per unit of time (i.e., m$^3$ h$^{-1}$). The WF comprises three major parts that is green, blue, and gray water footprints, as described in Eq. (1) \[2,31\]:

$$WF = WF_{green} + WF_{blue} + WF_{gray}$$ (1)

The green, blue, and gray water footprints were determined by collecting primary data related to direct process water/steam use, production of chemicals and electricity, and effluent pollutant load in each scenario. The definitions of green, blue, and gray water footprints are provided as follows.

1. Green WF: consumption of the precipitation on land that does not run off (rainwater insofar as it does not become run-off) or recharge the groundwater but is stored in the soil or temporarily stays on top of the soil or vegetation. In this study, the green WF is not considered because it is primarily relevant for agriculture and forestry \[2,31\], and is beyond the scope of this evaluation.

2. Blue WF: it refers to water usage (sometime refers to consumption) footprint, which is defined as the usage of surface and groundwater along the entire treatment process or product supply chain, as shown in Eq. (2). In this study, both the direct and virtual (indirect) water usage were considered.

$$WF_{blue} = DWU + VWU$$ (2)

where DWU and VWU are the direct and virtual water usage, respectively.

3. Gray WF: a hypothetical quantification of water pollution, which is defined as the volume of freshwater required to assimilate the load of pollutants to natural background concentrations or

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**Fig. 1.** System boundary of scenarios 1 (dilute acid + overliming conditioning), 2 (dilute acid + ammonia addition), 3 (two-stage treatment + ammonia addition) and 4 (dilute acid + membrane separation) for lignocellulosic hydrolysate.
existing ambient water quality standards, as shown in Eq. (3). Water quality parameters of the blowdown of processes, such as total dissolved solids (TDS), total suspend solids (TSS) and chemical oxygen demand (COD) were considered.

$$WF_{gray} = \frac{X_i}{C_{max} - C_{nat}}$$

where the $X_i$ (kg/h) is the load of the pollutant charged into a water body; $C_{max}$ (kg/m³) is the maximum acceptable concentration of the pollutant, e.g., ambient water quality standard; $C_{nat}$ (kg/m³) is the natural background concentration in the receiving body. In this study, the gray WF was calculated according to the guideline proposed by Franke, Boyacioglu [30].

3. Results and discussion

3.1. Evaluation of engineering performance: life-cycle data inventory

Table S2 (see Appendix A) summarizes the engineering performance of four scenarios with different pretreatment and conditioning processes. In the process conditions, as operating conditions, impurities removal efficiency and waste generation amounts. Overliming (in scenario 1) can effectively improve water microorganisms’ ability to ferment biomass sugars. In overliming, the pretreated hydrolysate is separated into washed solid and liquid fractions. The liquor and wash water are conditioned by “overliming” process, in which the pH increases from 1 to 10 with lime, and then readjusted to a pH of ~5 with additional sulfuric acid. In this way, one can image that additional number of unit operations (e.g., overliming tank, pH adjustment tank, settlement tank and separation devices) and long residence time were typically required. In addition, it was observed that a significant portion of sugars in hydrolysate (i.e., up to 13%) were lost in the overliming process due to high pH or pressed out with the gypsum sludge.

In scenario 2 (dilute acid followed by ammonia addition), sugar loss from hydrolysate can be avoided by the ammonia addition. Although ammonia is considerably more expensive than lime, the benefit of reduced sugar loss might make it more economically feasible. Nonetheless, the inhibitory compounds (acetate ions) are still present in the ammoniated biomass slurry. To overcome the above challenge, in scenario 3, a two-stage treatment, i.e., a decetylation process (sodium hydroxide pretreatment) prior to the pretreatment using dilute acid, was introduced. This can break bonds between lignin and carbohydrates, disrupt lignin structure, and make carbohydrates more accessible to enzymatic hydrolysis. Moreover, acetyl groups in the hemicellulose are liberated and removed as acetic acid by sodium hydroxide during deacetylation. This can greatly reduce inhibition from acetate, and improve hydrolysis and fermentation performance [12].

In scenario 4, membrane separations were utilized as the conditioning process for the hydrolysate after dilute acid pretreatment. It was noted that more than 99% sulfuric acid and up to 95% of acetic acid can be removed from the liquor [19]. At the same time, the furfural and HMF were removed by up to 40% and 25%, respectively. More than 98% of xylose was retained in the treated hydrolysate liquor, which was superior to other conditioning processes since the sugar loss in the overliming and ammonia-based processes was around 8–11.0% and 3%, respectively. Severe environmental impacts resulted from the gypsum sludge generated in overliming process can be avoided using integrated membrane separations. Furthermore, the hydraulic retention time of membrane separations was found to be relatively lower (i.e., ~1 h) than other processes. In other words, less area is needed for the membrane separations to achieve the same treatment capacity, compared to other processes.

3.2. Assessment on life-cycle environmental impacts

The environmental impacts of different pretreatment and conditioning processes for corn stover hydrolysate were evaluated, in terms of midpoint and endpoint impact assessments. Table S3 (see Appendix A) presents the details of process data on environmental impacts. Fig. 2 shows the midpoint impact of the four scenarios evaluated in this study, where each midpoint impact of overliming (S1) is used as the baseline (i.e., 100%). The results indicate that the processes (S2/S3/S4) generally offer lower environmental impacts, compared to the overliming process. For example, the potential of water resource depletion (i.e., WDP) in integrated membrane separations (scenario 4) exhibits the greatest reduction (i.e., ~64%) among all scenarios. It was noted that the WDP comprises both the direct and indirect water consumption for a process from the life-cycle point of view. The WDP can be compared to the results of water footprint for all scenarios (section 3.3), where the effect of process waste on water pollution was quantified.

In S4, a significant reduction of more than 83% and 96% was found in POFP and PMFP, respectively, and even a complete elimination in the impact of FEP and TAP500. These were mainly attributed by the water-efficient characteristic of the technique and the recovery of acetic and sulfuric acid, thereby avoiding the requirement of more wastewater treatment and potency of acidification to a natural water body. Moreover, the elimination of additional waste gypsum treatment after conditioning process is contributed to a great reduction in environmental impacts. Similar results were observed in both ammonia (S2) and two-stage (S3) processes because of their relatively lower water consumption compared to S1. However, the midpoint impacts of GWP500, METPinf, MEP, and TETPinf in scenario 4 were greater than that in S2 and S3, which was attributed to the fact that the membrane separations would consume additional electricity for movement of acid impurities. Furthermore, the improvement in HTPinfpin these promising processes was not significant, ranging between 30% and 40%. It was noted that, in membrane separations (S4), the environmental impacts caused from additional electricity consumption in the conditioning process can be compensated by the environmental benefits due to acid recovery and reduced uses of chemicals and water.
Fig. 3 presents the contribution of the main unit processes in pretreatment and conditioning to the environmental endpoint impacts, including EQ and HH, in terms of points. From the LCA results, conventional overliming (S1) exhibits the most significant environmental impacts, where the impacts on EQ and HH were $3.87 \times 10^{-3}$ and $6.75 \times 10^{-3}$ points, respectively. Among the unit operations in all scenarios, the impact of steam generation for the pretreatment was the greatest, contributing more than 78% and 65% in EQ and HH, respectively. Besides that, in S1, the impact of gypsum sludge disposal on HH was greater (i.e., 22.2%) than other unit processes. Moreover, the impact of lime production on EQ was considerable, i.e., 14.5%. In both S2 and S3, the main environmental issue in conditioning is the use of ammonia due to its substantial impact on both EQ and HH. Compared to the ammonia addition, the impact of NaOH and water uses on EQ and HH was found to be minor. In the case of S4, although additional electricity was required for separations, environmental benefits could be achieved by the recovery of acetic and sulfuric acids. Only membrane separations were found to offer negative net environmental impacts according to the endpoint assessment. It suggests that steam generation should be addressed next to further improve the environmental impacts of pretreatment.

3.3. Estimation of process water consumption

The WF of each scenario, including blue and gray WFs, was critically evaluated according to Eqs. (1)–(3). Fig. 4 shows the water usage footprints (i.e., blue WF) of different unit operation processes used in pretreatment and conditioning. The results indicated that the amounts of steam and water required in the pretreatment (dilute acid step) ranged from 14% to 74% in all scenarios. Compared to the results in the literature [32], for the entire biorefinery manufacturing process, the consumptive water of bioethanol from corn grain, stover and wheat straw was on an average of 31,132 and 139 L per liter biofuel, respectively, with extremely wide ranges.

The water usage for membrane separations was the lowest, approximately 2.54 L per kg-DB, where 73.4% of water used for steam generation in dilute acid pretreatment. Compared to the conventional overliming (~4.94 L per kg-DB), the total water usage for membrane separations can be reduced by almost a half in comparison to overliming. In overliming, the major water usage was liquid-solid separations (i.e., 30.8%). Moreover, a considerable amount of water, i.e., 17.9%, was utilized for hydrolysate neutralization in overliming. On the other hand, the water usage for ammonia addition and two-stage treatment was relatively lower than that overliming. In ammonia addition, 4.58 L of water was used for one kg-DB. Similarly, 4.25 L water was used per kg-DB processed by the two-stage treatment. However, both of these processes also required a great amount of water for hydrolysate neutralization. In two-stage treatment, a significant share of 86.2% in total water usage was found in ammonia addition step for neutralization. The above issue could be solved by applying membrane separations as the conditioning process, which was found to be a water-efficient technique for both dilute acid removal and pH adjustment because no further process water was required.

Besides the direct/indirect water usage (i.e., blue WF), the gray WF was determined by considering the process blowdown in all scenarios. The maximum acceptable concentration of TSS and COD was referred from the National Recommended Water Quality Criteria [33], while the maximum acceptable concentration of TDS in surface water was referred from the European Economic Community [34]. Fig. 5 shows the results of both blue and green WFs among the four different treatment processes. The results indicated that the WF for membrane separations was the lowest, e.g.
impurity separation using RW-EDI, the overall CO2 emissions can be potentially lower than other processes. It was noted that the gray WF was generally higher than blue WF in the pretreatment and conditioning processes, suggesting the end-of-pipe facilities should be included. In practice, the blowdown of existing processes is typically connected to a wastewater treatment plant or facilities should be installed. In practice, the blowdown of existing processes is typically connected to a wastewater treatment plant or facilities should be installed. In practice, the blowdown of existing processes is typically connected to a wastewater treatment plant or facilities should be installed.

3.4. Implication to carbon footprint

Process water consumption is one of the key performance indicators for energy production system. On the flip side, evaluation of greenhouse gas emissions is essential to achieve sustainable energy production. To propose a water-energy efficient process for biomass utilization, the carbon footprint (CF) of different conditioning processes for corn stover was evaluated by considering the process water use, chemicals addition, electricity consumption, product recovery, and sludge disposal. It was noted that the wastewater treatment process for brine solution from the pretreatment and conditioning processes was not included in the scope of CF calculation. In addition, chemicals used for the pretreatment and conditioning processes were considered from a cradle-to-gate approach in the LCA database. The end-of-life stage was included (i.e., a cradle-to-cradle approach), the CF of petrochemical-based chemicals will increase since they are not carbon-neutral materials.

As shown in Fig. 6, the membrane process associated with 33% acid recovery exhibited the lowest CF, i.e., 6.2 g CO2-Eq per kg-DB, among all processes. Although electricity was consumed for the impurity separation using RW-EDI, the overall CO2 emissions can be potentially balanced by recovering both acetic and sulfuric acids. In comparison, the CF of conventional overliming conditioning was about 22 g CO2-Eq per kg-DB, mainly attributed to the production of lime. The ammonia addition process presented a similar CF (~18.9 g CO2 per kg-DB) to the conventional overliming conditioning. In contrast, the two-stage design can significantly reduce the overall CF to 0.76 g CO2-Eq per kg-DB. Furthermore, it was found that the contribution of direct process water use on CF was not remarkable, i.e., less than 1%. Instead, the major contribution sources to CF were the uses of steam (the most significant in pretreatment process)), electricity and chemicals, which could be reduced by several strategies such as a district energy supply system, renewable energy, and waste recovery, reuse, and utilization.

3.5. Portfolio solution for hydrolysate pretreatment and conditioning

In general, a cost-effective biorefinery process requires less downstream inhibitors, low cost of pretreatment, and ease of operation and maintenance. In this study, four different scenarios for corn stover hydrolysate after dilute acid pretreatment, i.e., overliming, salt addition, two-stage treatment, and membrane separations, were evaluated. In the conventional methods, the acid impurities were normally removed from hydrolysate into (watery) waste streams, which should be coped with the entire process. In the integrated membrane separation, the acidic impurities (e.g., sulfuric and acetic) and inhibitory compounds (such as furfural and HMF) can be selectively separated and concentrated by adjusting applied voltage and feed flow rate for different operation times. The acetic acid rich stream could be recovered as a value-added co-product due to its high purity achieved by RW-EDI. The sulfuric acid can be recycled to the dilute acid pretreatment process, thereby reducing the demand for sulfuric acid.

Compared to overliming, the two-stage treatment exhibited a relatively lower water consumption of 86%, and a great carbon footprint reduction (i.e., down to 34%). However, integrated membrane separations with dilute acid pretreatment seems to be more promising due to its significant environmental and economic benefits. According to the LCA, the process water usage and CF for membrane separations can be reduced by 48.8% and 71.8%, respectively, in comparison to overliming. From the thermodynamic point of view, the separation of dissolved ions from bulk solution using electrochemical methods (such as RW-EDI) is more energy efficient than the separation of bulk water from concentrate solution (such as reverse osmosis). It suggests that integrated membrane separations (PF-MF and RW-EDI) should be a green process for conditioning and detoxifying the biomass hydrolysate.

Our analysis indicates that an integrated pretreatment/conditioning process (Fig. 7) can improve water and energy efficiency, and enhance environmental sustainability. Since the membrane separations (PF-MF and RW-EDI) exhibits the lowest process water consumption and carbon footprint, it should be the best available unit process for conditioning permeates. The dilute sulfuric acid

![Fig. 5](image1)

**Fig. 5.** Comparison of blue and gray water footprints (WFs) in each scenario.

![Fig. 6](image2)

**Fig. 6.** Carbon footprints of different conditioning processes including overliming, ammonia addition, two-stage treatment, and integrated membrane separations (in the case of 33% acetic acid recovery).
pretreatment was selected as the pretreatment process due to the potential for sulfuric acid recovery by RW-EDI. Nevertheless, the steam use in pretreatment should be supplied from a district energy system or other process waste (including waste heat) utilization. After pretreatment, the hydrolysate will be processing through the PF-MF for liquid and solid separations. The pH of the hydrolysate can also be adjusted via RW-EDI without water addition. Moreover, acid impurities in hydrolysate such as sulfuric and acetic acids can be efficiently removed and recovered, which is beneficial to the subsequent enzymatic fermentation. It was thus concluded that the integrated dilute acid and membrane separation process should be the preferred method of pretreatment and conditioning for biomass hydrolysate.

4. Conclusions

Four different conditioning processes for corn stover hydrolysate were evaluated using a life cycle assessment. The fermentation inhibitory compounds in hydrolysate liquor can be effectively removed by membrane separations, i.e., pulse-flow microfiltration (PF-MF) and resin-wafer electrodeionization (RW-EDI), without additional sludge generation. Compared to overliming, the other processes exhibited relatively lower environmental endpoint impacts on ecosystem quality and human health. In addition, the amount of water used for pH adjustment and/or neutralization of acid hydrolysate in overliming, ammonia addition, and two-stage treatment could be avoided by applying membrane separations. It was thus concluded that the integrated membrane separations (PF-MF/RW-EDI) should be a cleaner production process for biomass hydrolysate conditioning.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.energy.2016.09.109.

Nomenclature

Acronyms
COD chemical oxygen demand
CF carbon footprint
DB dry biomass
DWU direct water usage
EQ eco-system quality
FEP freshwater eutrophication
GHG greenhouse gas
GWP global warming potential
HH human health
HMF 5-hydroxymethyl furfural
HTPinf human toxicity
LCA life cycle assessment
MEP marine eutrophication
METPinf marine ecotoxicity
PF-MF pulse-flow microfiltration
PMFP particulate matter formation
POFP photochemical oxidant formation
RW-EDI resin-wafer electrodeionization
TAP terrestrial acidification
TDS total dissolved solids
TETPinf terrestrial ecotoxicity
TSS total suspend solids
VWU virtual water usage
WDP water depletion potential
WF water footprint

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