Techno-economic comparison of centralized versus decentralized biorefineries for two alkaline pretreatment processes

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Abstract

In this work, corn stover subjected to ammonia fiber expansion (AFEX™) pretreatment or alkaline pre-extraction followed by hydrogen peroxide post-treatment (AHP pretreatment) were compared for their enzymatic hydrolysis yields over a range of solids loadings, enzymes loadings, and enzyme combinations. Process techno-economic models were compared for cellulosic ethanol production for a biorefinery that handles 2000 tons per day of corn stover employing a centralized biorefinery approach with AHP or a de-centralized AFEX pretreatment followed by biomass densification feeding a centralized biorefinery. A techno-economic analysis (TEA) of these scenarios shows that the AFEX process resulted in the highest capital investment but also has the lowest minimum ethanol selling price (MESP) at \$2.09/gal, primarily due to good energy integration and an efficient ammonia recovery system. The economics of AHP could be made more competitive if oxidant loadings were reduced and the alkali and sugar losses were also decreased.

Keywords: AFEX, AHP, pretreatment, enzyme hydrolysis, biorefinery, techno-economic analysis.

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Introduction

Over the past years the quest for energy security has led to the search for alternative sources of fuels, and as a response to this, liquid biofuels such as corn starch and sugar cane-derived bioethanol and plant oil-derived biodiesel have emerged as alternatives to fossil fuels. Corn ethanol is the predominant biofuel produced in the United States; but its future growth is now sharply limited, given that ethanol production now consumes over one-third of the U.S. corn crop and that the blend wall of 10% of U.S. domestic gasoline has been reached (Bujanovic et al., 2004). An alternative approach to producing liquid biofuels is from lignocellulose or the cell walls of plants involves a chemical pretreatment followed by enzymatic hydrolysis of the cell wall polysaccharides to monomeric sugars and fermentation to a metabolite such as ethanol. These renewable liquid biofuels generated from lignocellulosic biomass offer the potential to achieve a lower net greenhouse gas generation relative to fossil-derived fuels and contribute to rural economic development (Souza et al., 2015). Identified challenges to the widespread deployment of cellulosic biofuels include technological challenges such as feedstock logistics (Hess et al., 2009), solids handling during pretreatment and hydrolysis (Lamers et al., 2015), and mixed sugar fermentation in the presence of inhibitors (Sato et al., 2014), while economic challenges include a substantially higher capital cost per unit of biofuel produced relative to sucrose or starch-derived biofuels (Humbird et al., 2011).

A diverse range of pretreatment chemistries have been investigated over the past several decades (Ong et al., 2014), while all of the recently built cellulosic ethanol plants use either dilute acid or hydrothermal pretreatment, with the exception of DuPont's Nevada, Iowa plant, which employs a dilute aqueous ammonia pretreatment. Pretreatment technologies under investigation at the Great Lakes Bioenergy Center (GLBRC) include alkaline pretreatments such as Ammonia Fiber Expansion (AFEXTM) pretreatment (Dale, 1986) and alkaline hydrogen peroxide pretreatment (AHP) (Banerjee et al., 2012). In the AFEX process, biomass with different moisture content (20-60% dry weight basis) is contacted with gaseous ammonia at approximately 1:1 (kg/kg) ammonia to biomass loading, temperatures between 40 and 120°C and residence times between 10 to 60 min followed by rapid pressure release (Balan et al., 2010). During pretreatment, ammonolysis and hydrolysis reactions cleave the ester crosslinks between cell wall biopolymers (Chundawat et al., 2010; Chundawat et al., 2011), while the sudden

pressure release also relocates lignin onto the biomass surface resulting in four to five fold improvements in the hydrolysis yields (Jin et al., 2013).

AHP pretreatment employed as a one-stage delignifying pretreatment has been demonstrated to be highly effective at improving the subsequent enzymatic hydrolysis yields of grasses such as corn stover, wheat straw, and switchgrass (Banerjee et al., 2012; Banerjee et al., 2011; Gould, 1984; Li et al., 2012). For conventional AHP pretreatment, biomass is treated with H_2O_2 at ambient temperature and pH 11.5 which primarily targets the removal of cell wall lignin. However, a drawback limiting economic efficacy of this as a one-step process is that H_2O_2 loadings of greater than 0.10 kg per kg biomass must be employed to realize any incremental improvement over low temperature NaOH-only pretreatment (unpublished data), presumably due to non-productive oxidation of lignins already solubilized by the alkali. We've recently adapted a two-stage pretreatment whereby alkali pre-extraction using NaOH at mild temperature and low alkali loadings is followed by solid-liquid separation to remove a fraction of the pre-extraction liquor. This pre-extraction liquor contains inorganics derived from the pretreatment and organics solubilized from the biomass that include extractives, acetate, *p*-hydroxycinnamic acids, lignins, and xylan. Options for utilization of this stream include concentration and combustion for generation of process heat and alkali recovery, recovery of soluble cell wall biopolymers for further valorization, utilization as a carbon source for anaerobic digestion, or animal feeds. This pre-extraction is followed by a second stage AHP delignification at low H_2O_2 loadings (Liu et al., 2014). This approach substantially improves the sugar hydrolysis yields (>95% hydrolysis yields of glucose) from corn stover at low enzyme loadings (15 mg protein per g biomass) and requires relatively low alkali loadings for pre-extraction (< 100 mg NaOH per g biomass at 80°C), and substantially lower H_2O_2 loadings in the subsequent AHP pretreatment step (25 mg H_2O_2 per g biomass) than a comparable single-stage AHP pretreatment (Liu et al., 2014). This approach can be considered as comparable to the existing commercial practice of soda pulping of non-woody agricultural residues followed by oxygen delignification or bleaching (Mohta et al., 1998). Recently constructed commercial lignocellulosic biorefineries employing these conversion pathways in the U.S., Europe, and Brazil operate at the scale of 12-30M gal ethanol per year (Davison et al., 2015), processing from 65,000 to 375,000 dry tons of biomass per year (~200 to 1000 dry tons per day). It is envisioned that large, centralized biorefineries may need to operate at the scale of up to 2000 tons per day to obtain greater benefit from the capital

investment due to economies of scale (Humbird et al., 2011). Decentralized biomass aggregation and pre-processing facilities feeding larger centralized biorefineries have also been proposed as solutions to the challenges associated with feedstock logistics (Egbendewe-Mondzozo et al., 2013). As one example, decentralized, depot-scale pre-processing employing AFEX pretreatment and densification via pelletization could provide feedstock-associated benefits that include increased bulk density by 8-10 fold, facilitating transportation, storage, and subsequent year-round supply as well as decreasing the sensitivity to supply chain disruptions and potentially yielding a product with additional applications (e.g., a high-digestibility ruminant feed) (Campbell et al., 2013; Lamers et al., 2015).

Techno-economic analysis (TEA) has been applied to compare AFEX with other pretreatments such as dilute acid, ammonia recycle percolation (ARP), liquid hot water and lime (Eggeman & Elander, 2005; Kazi et al., 2010), while recently the economic benefits of decentralized AFEX pretreatment and pelletization have been assessed (Campbell et al., 2013; Lamers et al., 2015; Sarks et al., 2016). While no TEA has been done for AHP pretreatment, other work has investigated the integration of alkaline pre-extraction followed by dilute acid pretreatment of corn stover and identified economic benefits associated with this two-stage process (Tao et al., 2012). As such, the scope of this work includes both an experimental assessment of the effects of enzyme and solids loading on enzymatic hydrolysis yields for AFEX and AHP pretreated corn stover and a TEA for these two pretreatments in a biorefinery processing 2000 tons of corn stover per day to ethanol. For the AFEX pretreatment a decentralized biorefinery approach was used, where the biomass is pre-processed and pretreated at depots and then sent to a centralized biorefinery for saccharification and fermentation. The AHP pretreatment on the other hand was modeled in a centralized biorefinery scheme. The costing of equipment required for enzymatic hydrolysis, fermentation, ethanol recovery and waste water treatment was performed based on the NREL model (Humbird et al., 2011). Results obtained from the enzymatic hydrolysis of the pretreated biomass at different solid and enzyme loadings determines the minimum ethanol selling price (MESP) for both processes. Finally, a sensitivity analysis investigated the relationship between the costs of the biomass, alkali, oxidant, and alkali recovery on the MESP. As a result, we have identified the MESP required for each of these pretreatments and have also identified bottlenecks for both the pretreatment process that must be

addressed in order to develop cost-effective pretreatment processes at commercial-scale biorefinery facilities.

Methods

Biomass

Low cob corn stover (*Zea mays* L. Pioneer hybrid 36H56) was used for both pretreatments. The biomass was grown and harvested in 2009 on Field 570-C Arlington Research Station, (Arlington, WI) and milled to pass a 5-mm screen (Circ-U-Flow model 18-7-300, Schutte-Buffalo Hammermill, LLC). The composition of the untreated biomass was determined using NREL/TP-510-42618 (Crocker, 2008).

Pretreatment

AFEX pretreatment of the corn stover was conducted at 100°C with a 1:1 ammonia to biomass loading and 60% moisture (dry basis) for 30 minutes residence time in a packed bed reactor system as reported previously (Campbell et al., 2013). AHP pretreatment with alkaline pre-extraction of corn stover was performed in a stationary stainless steel vessel with initial mixing only. Pre-extraction was performed at 80°C for 1 hour using 80 g of NaOH with 1 kg of biomass and a total liquid volume of 5 L (20% w/v). Following pre-extraction, the resulting slurry was press-filtered through a filter cloth whereby 70% of the pre-extraction liquor was removed. The residual insoluble solids with 30% of the pre-extraction liquor entrained were subjected to a subsequent AHP delignification treatment according to (Liu et al., 2014). AHP delignification was performed at a solids concentration of 23.2% (w/w) for 24 hours at approximately 23°C using an oxidant loading of 25 mg H₂O₂ per g original biomass, and the initial pH was adjusted to 11.5 using 100 mL of 5 M NaOH. Insoluble mass loss and composition analysis following each stage of the pretreatment were assessed.

Enzymatic hydrolysis

Enzymatic hydrolysis of the pretreated substrates was performed in 100 mL baffled shake flasks at 50°C and 250 rpm using an optimal combination of commercial enzymes including Cellic CTec2 and HTec2 (Novozymes, Bagsværd, DK) and Multifect Pectinase (DuPont Danisco, Rochester, NY). The pH was maintained between 4.8 and 5.0 during the hydrolysis by using 3M HCl. Three mass ratios of different commercial enzyme mixtures

(CTec2:HTec2:Pectinase) were evaluated in order to determine the optimum enzyme combinations of enzymes for each pretreated biomass at a 20% w/w solid loading condition. These included, cocktail 1 (33:33:33), cocktail 2 (50:25:25), and cocktail 3 (70:15:15). Total protein content of the enzyme cocktails was measured by the Bradford Assay (Sigma-Aldrich). Following hydrolysis, monomeric sugar concentrations were determined by HPLC using the Aminex HPX-87H (Bio-Rad, Hercules, CA, USA) equipped with a guard column (Micro-Guard Cation H⁺, Bio-Rad). The mobile phase consisted of 5 mM H₂SO₄ at a flow rate of 0.6 mL/min (Banerjee et al., 2012). As xylan, galactan, and mannan co-elute, the quantified “xylan” represents these three sugars, although non-xylan hemicelluloses are anticipated to comprise less than 2% of the mass of the cell wall or an order of magnitude less than xylan (Templeton et al., 2009). Enzyme cocktail 2 was identified as the optimal enzyme mixture for AFEX-treated biomass and cocktail 3 was selected for AHP. After selecting the optimal enzyme mixture, glucose and xylose hydrolysis yields were assessed for each of the pretreated materials through a design of experiments covering the range of solids loadings (15 to 25%), enzyme loadings (7.5 to 30 mg/g glucan) and incubation times (24 to 120 hours). Parameter significance and model selection were determined using Design Expert 6.0 (Statease, Minneapolis, MN).

Mass balance calculations

An overall mass balance for both pretreatment and enzymatic hydrolysis steps performed by assessing mass loss and composition following each of the stages in pretreatment, while soluble monomeric and oligomeric sugars in pretreatment liquors and hydrolysates were determined by HPLC as described previously (Uppugundla et al., 2014). Monomeric sugars were quantified using a Bio-Rad Aminex HPX-87H high-performance liquid chromatography (HPLC) column using 5 mM sulfuric acid as mobile phase. Oligomeric sugar was quantified by treating the hydrolysate using dilute acid using standard analytical procedure followed by analysis using Bio-Rad Aminex HPX-87H HPLC column. Oligomeric sugars are calculated by subtracting sugars produced before and after acid hydrolysis using appropriate sugar recovery standards. Mass loss following hydrolysis, composition following hydrolysis, and soluble lignin were determined by difference from quantified values. Experimental data for hydrolysis yields and empirical correlations for hydrolysis yield as a function of enzyme loading and solids loading are presented as Supplemental Materials (Supplemental Table A.1).

Biorefinery model

The MESP required for both pretreatments was evaluated considering a 2000 U.S. ton/day biorefinery and a 10% IRR. To perform the economic evaluation a modified version of the 2012 NREL model (Humbird et al., 2011) developed in Aspen Plus (Aspen Tech, Burlington, MA, USA), was used where either two-stage AHP pretreatments replaced the dilute acid pretreatment originally modeled or, for the AFEX case, the unit operations associated with pretreatment were removed to consider utilization of AFEX-pretreated pellets generated off-site at regional processing depots. All monetary values reported in this work are in 2012 US dollars.

In the case of AFEX, a decentralized biorefinery or “depot” configuration was assessed, where the biomass is shipped from the farms to a local depot (approximately 5-10 miles distant from the farms) where up to 200 tonne/day of biomass are AFEX-pretreated and then sent to the biorefinery to produce ethanol. In this scheme, the price of the biomass at the biorefinery included both the purchase cost (\$60 per tonne) and the AFEX processing and transportation from the depot (additional \$60 per tonne). This last price was determined by calculating the capital investment and the operation costs required to set up the depots and by considering a 20 year lifetime for the equipment (Lamers et al., 2015). Thus within the biorefinery model no equipment or operating costs related to the AFEX pretreatment were assessed since these were essentially part of the delivered cost of the biomass.

For the AHP process, a “centralized biorefinery” configuration was analyzed, whereby the biomass was transported directly from the farm to the biorefinery. The price of the biomass at the biorefinery was considered to be \$60 per tonne accounting for the harvesting and transportation of the corn stover. The capital investment and the operating costs related to the pretreatment were included in the biorefinery economic model by using the material and energy balances obtained from the simulation in Aspen Plus to size the equipment and determine the amounts of raw materials and water required. Considering that the price of biomass will be a function of the distance transported, delivered feedstock price differences between the centralized versus the decentralized biorefinery scenarios are considered in a sensitivity analysis with respect to minimum ethanol selling price.

The installed cost of the equipment used in the pretreatment area was calculated through equipment sizing and equations reported in the literature (Couper et al., 2009). The remaining process areas in the NREL model (ethanol recovery, wastewater treatment, storage, boiler and utilities) were sized using the six tenths rule and the mass balances obtained from Aspen Plus. In both cases the installed costs of the equipment required for enzyme production were eliminated, assuming instead that the enzymes were purchased from an outside vendor. In addition to the production of ethanol, heat and power are produced through the combustion of unhydrolyzed solids. The following chemical, biomass, and enzyme costs, and electricity selling price were used in the model calculations (in 2012 dollars): NH_3 at \$530/tonne, H_2O_2 at \$530/tonne, NaOH at \$380/tonne, H_2SO_4 at \$87/tonne, lime at \$107/tonne, biomass at \$60/tonne, AFEX depot processing at \$60/tonne, cellulase at \$3600/tonne, hemicellulose at \$4500/tonne, and electricity at \$0.0572 per kWh. For ethanol fermentation, it was assumed that 99% of the glucose and 90% of the xylose were converted to ethanol at a metabolic yield of 0.46 g ethanol per g glucose or xylose.

Results and Discussion

Impact of Solids and Enzyme Loading on Hydrolysis Yields

Both enzyme loading and solids loading during enzymatic hydrolysis are known to substantially impact hydrolysis yields (Hodge et al., 2008), capital costs and water use. In this work, the effects of solid and enzyme loadings used during enzymatic hydrolysis for both pretreatments were assessed and the fitted responses for total monomeric sugar yields (i.e., total monomeric glucose and xylose per maximum possible) are plotted in Figure 1. These results are the model predictions based on experimental results. Experimental data used to build these models are available in Supplemental Table A.1, with the average glucose-to-cellobiose ratio of these yields of 97:3 and the average xylose-to-xylooligomers of 76:24. Both pretreatments are effective at achieving more than 80% total sugar yields following enzymatic hydrolysis for a range of solids and enzyme loadings with the obvious trends of increasing yields in response to increasing enzyme loadings, increasing hydrolysis times, or decreasing solids. These conversions are comparable to previously-demonstrated yields for the two-stage AHP process (Liu et al., 2014), and for AFEX pretreatment utilizing these pretreatment conditions in a packed-bed reactor (Campbell et al., 2013). Increasing the solids loadings during hydrolysis decreases the

glucose hydrolysis yields the most at lower enzyme loadings for both pretreatments (Figure 1). The substantial hygroscopic properties of pith parenchyma cells in corn stover and particularly AHP-pretreated corn stover (Williams & Hodge, 2014), limits both the level of the solids during these processes and the water removal efficiency during solid-liquid separations. AFEX-pretreated biomass could be processed at higher solids loadings, as seen for AFEX-pretreated switchgrass, which was substantially less hygroscopic than AHP-pretreated switchgrass while achieving comparable hydrolysis yields (Williams & Hodge, 2014).

In order to achieve these high hydrolysis yields, AFEX-pretreated biomass requires more hemicellulase enzymes and pectinases than does AHP. This might be related to the fact that AFEX does not alter the overall biomass composition and does not involve the removal of lignin unlike AHP (Figure 2). For AHP pretreatment, some lignin and polymeric xylan are solubilized and removed by the alkaline pre-extraction step. However, even though AHP requires less hemicellulases within the enzyme cocktail it also may entail a higher loss of hemicellulose sugars during the solid liquid separation performed after the alkaline pre-extraction. In comparison to AFEX where no sugars are lost for fermentation, the AHP pretreatment results in up to 25% loss of the xylan and up to 5% loss of the glucan after the alkali pre-extraction step, affecting downstream ethanol production. However, the energy contained in these sugars is recovered as electricity following either combustion of black liquor or anaerobic digestion and co-generation of energy using biogas employing the organics-containing process water streams.

Material balances on pretreatment and hydrolysis

Experimentally determined mass balances for pretreatment and hydrolysis using the AFEX and AHP processes are shown in Figure 2. These results highlight three important differences in these pretreatment approaches that have important implications for the process. Firstly, lignin and xylan are partially solubilized during pre-extraction for the AHP process, with the consequence that their energy value is recovered during combustion within the ethanol production process rather than combustion as a fermentation-derived liquid fuel. Secondly, different strategies are employed for base recovery; namely, volatilization and recompression of anhydrous ammonia for AFEX pretreatment versus liquid phase concentration and re-causticization for AHP pretreatment. Thirdly, the use of a volatile weak base (i.e., ammonia)

versus a strong base (i.e., NaOH) results in substantial differences in the separations required; solid-liquid for AHP pretreatment versus solid-vapor for AFEX.

AFEX is a dry-to-dry process and does not result in bulk compositional changes (Figure 2). Instead, a structural rearrangement of cell wall polymers and cleavage of cell wall ester compounds occurs. During the pretreatment cell wall decomposition products including amides and lignin-derived phenolics are generated and then redeposited on the outer cell walls as the ammonia used in the process vaporizes. This results in cell wall polysaccharides that are more accessible to cellulolytic enzymes (Chundawat et al., 2011; Ong et al., 2014)

AHP, on the other hand, uses lower chemical loadings than AFEX with 80 mg NaOH per g biomass, resulting in the partial solubilization of lignin (approximately 75% solubilization) and xylan (approximately 25% solubilization) from the cell wall. Lower NaOH loadings compared to traditional soda or soda-AQ pulping of graminaceous biomass (where NaOH loadings may be 2 orders of magnitude higher (e.g., 5:1 liquor to biomass ratio at 180 g/L NaOH), are possible due to the high selectivity observed for lignin removal versus xylan removal which is desirable for biofuels processes utilizing xylose. Results in Figure 2B show that 2.2 g lignin removed per g xylan are removed in the pre-extraction stage or 2.1 g/g across both stages, comparable to our previous work (Liu et al., 2014). We previously demonstrated that most NaOH used at these low loadings is consumed during pretreatment.

Integration of ammonia or alkali recovery

Recovery of the ammonia used in AFEX is shown in (Figure 3). In this process the reactor is depressurized in order to volatilize the ammonia, while the reactor is subsequently subjected to steam stripping in order to remove the residual ammonia embedded in the biomass. The steam stripped ammonia is passed through a condenser to remove the water before being reused. The volatilized and steam-stripped ammonia is then compressed and recycled into the process. Over 97% of the ammonia applied is recovered for reuse by this process.

For alkaline pre-extraction followed by AHP post-treatment, a fraction of the mostly neutralized alkali used in the pre-extraction is removed in the liquid stream following solid-liquid separation. This stream offers the potential for several alkali, energy, and water recovery options. Three cases were evaluated for the recovery of the NaOH used in the alkaline pre-extraction (Figure 3). These include no recovery, which was evaluated in order to determine if

the recovery alternatives proposed would be economically as well as environmentally beneficial. Chemical recovery of the alkali was considered as separate cases for concentration, combustion, and chemical recovery from either just the pre-extraction stage or both pre-extraction and AHP pretreatment (Figure 3). For this, a recovery boiler is employed after the multiple-effect evaporators to simultaneously generate heat from the solubilized organics and recover the NaOH as Na_2CO_3 . The Na_2CO_3 is subsequently sent to a re-causticizing plant where NaOH is regenerated. The cost associated with the recovery boiler used in the causticization process was determined based on prices reported in the Humbird et al. report (Humbird et al., 2011), the kiln was sized and priced based on the literature (Loutfi et al., 1991). Sulfur-free black liquors for example, can be combusted in a lower capital cost fluidized bed recovery boiler which operates at a lower temperature and can utilize 35-40% solids (w/w) (Doherty & Rainey, 2006; Grace, 1987) compared to >70% solids required for a Kraft recovery boiler. This system may not only reduce the capital investment represented in the Kraft boiler but also reduce the energy requirements for the concentration of the black liquor in the evaporation system (Chovau et al., 2013). The soda recovery boiler capital cost in the AHP model is calculated utilizing the cost utilized in the NREL model (Humbird et al., 2011) and scaled according to the total organic solids fed to the boiler as determined from the Aspen simulation. The “six-tenths rule” was applied to scale the cost and a market conversion was applied to convert the capital cost to 2015 US dollars. The cost of the boiler along with other unit operations associated with AHP chemical recovery (e.g., evaporators, causticizer, etc.) were separated from the pretreatment installed cost and accounted for separately in their own chemical recovery/boiler area. A summary of capital costs for these 3 scenarios are presented in Figure 4.

Comparison of scenarios

AFEX makes use of the volatility of ammonia to its advantage and thus has a relatively simple process for ammonia recovery. The ammonia recovery process for AFEX has been improved over the years (Eggeman & Elander, 2005; Laser et al., 2009; Sendich et al., 2008). Recently, Balan et al. developed a new system using gaseous ammonia absorption onto subsequent packed beds of biomass followed by a steam or inert gas stripping step (Balan et al., 2015). Subsequently, Campbell et al. developed a method of recovering and reusing ammonia in a packed bed reactor system. At least 97% of the ammonia catalyst used can be recycled through

this process (Campbell et al., 2013). Furthermore, this new recovery strategy is expected to reduce the equipment costs by eliminating the use of an ammonia recovery column and a large compressor which were required in previous configurations. This case is what is considered in the decentralized depot-scale pretreatment and densification considered in this work.

For the AHP process, the two recausticization scenarios for chemical recovery includes a loss of either 42% (single-stage recovery) or 12% (two-stage recovery) of the NaOH used as incomplete washing of alkali-pretreated pulps is employed during solid-liquid separation between process stages (Figure 2). Additionally, all of the H_2O_2 applied is consumed during pretreatment, increasing the raw material costs associated with the process. Furthermore, by sending part of this stream through the causticization system some of the solubilized sugars would be sent to the recovery boiler rather than to fermentation. Specifically, removing only the first stream results in loss of 16.5% of the xylan and 5% of glucan, while removing a second stream results in loss of 26.5% of the xylan and 9% of the glucan.

A summary of the key outputs of the different scenarios is presented in Table 1. As can be seen by the MESP calculated for the different processes (Table 1) alkali recovery has a considerable effect on the economics of the AHP processes. The cases with higher MESP in the AHP pretreatment are associated with configurations with no alkali recovery. Of the configurations evaluated for recovering NaOH, the one with the highest alkali recovery (Table 1) was the causticization process in which NaOH was recovered from both the pre-extraction and the AHP process. While this high recovery efficiency comes with a higher capital investment when compared to the other processes evaluated, this scenario also yields the lowest MESP as a consequence of this improved recovery efficiency. Chemical recovery has been thoroughly studied within the context of the chemical pulping industry; this has allowed for high recovery efficiencies for the process. However this process has its drawbacks in the high cost of the boiler system required for the combustion of the black liquors. Recently other alternatives have appeared for recovering alkali from black liquors, including the direct alkali regeneration system (DARS), which involves a direct causticization of the black liquor with ferric oxide, recovering alkali through hydrolysis of the sodium ferrite. Not only can this process operate with less concentrated black liquors (50% solids) but can handle the presence of silica impurities within the stream (Naqvi et al., 2010). The water use presented in Table 1 considers only the water used in the pretreatment area, although recovered water that could be used as “backset” is accounted

for in this value. This includes for the AFEX case 0.210 kg H₂O / kg biomass recovered during ammonia recycle and for the AHP cases that 80% of the water in the pretreatment liquor is recovered, while 20% containing the majority of the volatile organics (i.e., the “foul condensate fraction”) is sent to wastewater treatment. It should also be considered that additional water will need to be re-added to the pretreated biomass for the subsequent enzymatic hydrolysis and fermentation as the AFEX-pretreated biomass at the depot needs to be dried prior to pelleting, while the water in the AHP-pretreated biomass can be used downstream.

In general, the recovery efficiency for the AHP system is affected by the amount of water used in the process, due to the evaporation costs involved in the process. After solid-liquid separation, the solubles (inorganic and organic) are recovered in a dilute solution that requires concentration through multiple effect evaporators before being sent to the combustion and chemical recovery processes, which increases the capital cost associated with the AHP system. Moreover a cooling tower and additional wastewater treatment are required in order to recover this water and re-use it in the system, which also add to the energy requirements.

The capital investment for the AFEX pretreatment is higher when compared to the AHP scenarios. That is, \$25.6M for AFEX (based on the ten 200-ton per day depots based on Lamers et al (Lamers et al., 2016)) versus \$9.76 M to \$17.21M for the AHP scenarios in a 2000-ton per day centralized biorefinery. This high cost is associated with the higher pressures of operation required in the AFEX system, which in turn requires higher capital costs for the reactor system as well as the fact that the AFEX reactors are operating at 10% of the scale of the AHP case, which benefits from economies of scale. The AHP pretreatment on the other hand, requires milder operating conditions that reduce the capital cost associated with the equipment. Nonetheless, the alkali losses negatively impact the operating costs of the AHP system, decreasing its profitability. Additionally, the by-product credits obtained from the generation of electricity through the combustion of unhydrolyzed solids are higher for AFEX than for AHP, probably due to the higher lignin content of these solids after the AFEX pretreatment wherein no lignin is removed, as well as the higher energy requirements observed within the water treatment system for the AHP process, due to the use of much more water in comparison with the AFEX process.

The no-alkali recovery approach produces the highest MESP at a value of \$2.73 per gallon, but with the lowest capital cost as shown in [Table 1](#). Alkali recovery scenarios were considered

for a single pretreatment effluent stream (alkali pre-extraction), or both pretreatment effluent streams (alkali pre-extraction and AHP). Table 1 shows that although the associated capital costs are higher for these scenarios as more evaporator capacity is required in order to recovery the NaOH from the pretreatment liquors, a decrease in MESP is obtained when compared to the no-alkali recovery scenario. Single stream re-causticization produces an MESP of \$2.53 per gallon, while concentration and re-causticization of both pre-extraction and pretreatment liquors yields an MESP of \$2.27. Moreover, Table 1 also shows that NaOH recovery lowers the MESP even with higher thermal energy requirements (albeit higher thermal energy recovery can be obtained). For this chemical recovery to occur multiple-effect evaporation is needed to remove water and increase the solids content of the pretreatment effluent streams. It should be noted that this water can be recovered and integrated into other parts of the biorefinery. For example, the single stream NaOH recovery scenario can recover up to 64% of the pretreatment process water, while NaOH recovery from pre-extraction and pretreatment can recover 73%. This considers the 20% of the organics-enriched condensate that must be purged to prevent the potential buildup of organics. The AFEX pretreatment thus uses a higher capital investment during upstream processing (the pretreatment itself) to provide a higher ammonia recovery and facilitating the downstream processing. AHP uses a simpler approach upstream, by operating at milder temperatures and pressures, but has a more complex process downstream in order to recover the catalyst used.

Sensitivity Analysis

The sensitivity analysis done for both the AHP and AFEX processes show that the biomass cost is a key factor influencing the MESP compared with the base recovery efficiency and the cost of the base (Figure 5). Feedstock cost is one of the major components contributing to the cost of production of ethanol; it is dependent on the availability of the biomass as well as the radius of collection. A continuous supply of low cost raw material over the year greatly enables ethanol production at a competitive price. One way to facilitate this is through densification that can generate a stable feedstock intermediate that is amenable to storage. When comparing the effect of the cost of the chemical inputs for both processes (NaOH for AHP and ammonia for AFEX) it can be observed that clearly the sensitivity is strongly impacted by both the chemical input and its recovery (Table 1). This is due to the lower base recovery efficiency for the AHP

process, which implies higher requirements for alkali to be supplied in the make-up stream. The AFEX process on the other hand, despite using a more expensive pretreatment catalyst, is not as dependent on catalyst cost because of the high efficiency of its recovery. The H₂O₂ cost also impacts the MESP in the AHP process, however its influence is not as great as that of NaOH since the quantities required are not as high as the amounts of NaOH required.

Conclusions

The MESP for AFEX is mainly affected by the high capital investment required. The capital investment is lower for AHP, however the greater use of water (and its evaporation) and the loss of alkali in the design case presented in this study increase the capital cost of the plant and the MESP. Unlike AHP, AFEX has relatively simple downstream processing that allows for greater than 97% catalyst recovery. AHP economics on the other hand are affected by sugar losses during the alkali extraction step. The lowest MESP for the AHP pretreatment scenarios was obtained for the recovery of NaOH from both pre-extraction and pretreatment, while the overall lowest MESP was for AFEX pretreatment.

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Figures

Figure 1: Response surface for total sugar conversion (glucan plus xylan per initial) during enzymatic hydrolysis for (A) AFEX and (B) AHP pretreatment as a function of initial insoluble solids, enzyme loading, and time

Figure 2: Mass balances on sugars and lignin for (A) AFEX and (B) AHP as well as visible macroscopic differences between pretreated biomass

Figure 3: Summary of key unit operations and process inputs in the pretreatment area for the biorefinery model

Figure 4: Equipment capital cost for the pretreatment and chemical recovery area and MESP for the AHP pretreatment scenarios in 2012 US dollars

Figure 5: Sensitivity analysis for the impact on MESP of operating costs, including (A) biomass cost and ammonia cost and recovery for AFEX pretreatment and (B) biomass cost and pretreatment variables for AHP pretreatment

Table 1: Model estimates for electricity produced, thermal requirements, thermal energy produced and catalyst recycle and recovery percentage for AFEX and AHP based on process assumptions.

Pretreatment and catalyst recovery	Electricity kWh/Mg Biomass	Thermal Requirement GJ/Mg Biomass	Thermal Recovery	Alkali Recovery %	Water Use kg/kg biomass	Capital Cost \$ x 10 ⁶	MESP \$/gal
AFEX	45	2.00	-	98 %	1.03	\$25.6	\$2.09
AHP							
No Recovery	10.96	1.51	0.92	0	6.35	\$9.76	\$2.73
Re-causticization from pre-extraction	13.60	2.18	2.28	46.6 %	4.16	\$14.87	\$2.53
Re-causticization from pre-extraction and AHP	13.60	2.84	2.17	87.2 %	1.72	\$17.21	\$2.27

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5