Lignocellulosic ethanol production without enzymes – Technoeconomic analysis of ionic liquid pretreatment followed by acidolysis

Piotr Oleskowicz-Popiel [a,b,1], Daniel Klein-Marcuschamer [a,b], Blake A. Simmons [a,b,c], Harvey W. Blanch [a,b,d,*]

[a] Joint Bioenergy Institute, 5885 Hollis St., Emeryville, CA 94608, United States
[b] Lawrence Berkeley National Laboratory, Physical Biosciences Division, 1 Cyclotron Road, Berkeley, CA 94720, United States
[c] Sandia National Laboratories, Biomass Science and Conversion Technology Department, Livermore, CA, United States
[d] University of California Berkeley, Department of Chemical Engineering, CA 94720, United States

HIGHLIGHTS

- The economics of lignocellulosic ethanol without the use of enzymes was studied.
- The process is based on acidolysis and sugar extraction.
- The model is intended to guide scientists in addressing key technical challenges.
- Through process optimization, the MESP could be lowered from $8.05/gal to $4.00/gal.

GRAPHICAL ABSTRACT
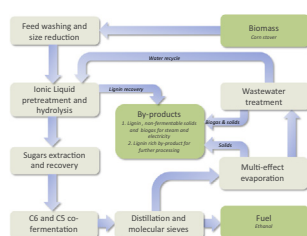
ABSTRACT

Deconstruction of polysaccharides into fermentable sugars remains the key challenge in the production of inexpensive lignocellulosic biofuels. Typically, costly enzymatic saccharification of the pretreated biomass is used to depolymerize its cellulosic content into fermentable monomers. In this work, we examined the production of lignocellulosic recovery, a process that does not require the use of enzymes to produce fermentable sugars. In the base case, the minimum ethanol selling price (MESP) was $8.05/gal, but with improved performance of the hydrolysis, extraction, and sugar recovery, the MESP can be lowered to $4.00/gal. Additionally, two scenarios involving lignin recovery were considered. Although the results based on current assumptions indicate that this process is expensive compared to more established technologies, improvements in the hydrolysis yield, the sugar extraction efficiency, and the sugar recovery were shown to result in more competitive processes.

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1. Introduction

There is a growing interest in renewable, non-fossil transportation fuels to address an increasing number of environmental, strategic, and economic problems. Production of lignocellulosic biofuels provides one possible route to address these problems, and ethanol in particular is among the most intensively investigated (Datta et al., 2011). Lignocellulosic biomass is abundant, and most importantly, renewable: growing plants consume CO_2 during photosynthesis, while the gas is returned to the atmosphere as the biofuel is combusted. Haberl et al. (2011) predict that the

* Corresponding author. Address: Department of Chemical & Biomolecular Engineering, 201 Gilman Hall, University of California Berkeley, Berkeley, CA 94720, USA. Tel.: +1 (510) 642 1387; fax: +1 (510) 643 1228.
   E-mail addresses: piotr.oleskowicz-popiel@put.poznan.pl (P. Oleskowicz-Popiel), DKlein@lbl.gov (D. Klein-Marcuschamer), BASimmons@lbl.gov (B.A. Simmons), blanch@berkeley.edu (H.W. Blanch).
[1] Present address: Poznan University of Technology, Faculty of Civil and Environmental Engineering, Institute of Environmental Engineering, Piotrowo 3A, 60-965 Poznan, Poland. Tel.: +48 61 665 3662.

bioenergy potential on agricultural areas in 2050 might be – after subtracting the area needed for food, feed, and fiber – in the order of 100 EJ per year, compared to total fossil fuel (coal, oil, natural gas) use of 453 EJ in 2008 (Haberl et al., 2011).

Production of ethanol via biological conversion of lignocellulosic materials is accomplished, in general, by (1) pretreatment of the biomass, (2) hydrolysis of the hemicellulose and cellulose polysaccharides into monomers and (3) fermentation of the monomers into ethanol (Kumar and Murthy, 2011). Typically, enzymatic saccharification of the pretreated biomass follows to depolymerize the cellulose and hemicelluloses into fermentable sugars. Alvira et al. (2010) stated that the main goal of pretreatment is to increase the enzyme accessibility to cellulose during the hydrolysis step, emphasizing the importance of the enzyme-dependent step. Cellulase enzymes are, however, quite expensive and contribute significantly to the final cost of the biofuel (Klein-Marcuschamer et al., 2012).

Alternatively, after pretreatment, mineral acid at low concentrations (e.g. 5% HCl) can be used to hydrolyze the polysaccharides into monosaccharides without the need of enzymes. To recover the sugars, a liquid–liquid extraction can be employed, where the sugars are transferred into a water-immiscible organic phase through the formation of a complex with lipophilic boronic acid compounds. This reaction is reversible and sugars can be recovered from the organic phase by stripping with dilute acid (Brennan et al., 2010). The main advantages of this process are the possibility of forgoing the use of enzymes, of recovering a relatively pure stream of monomeric sugars from the pretreated biomass, and of separating the lignin. The latter can offer significant economic benefits: the lignin might have different applications, for instance, as a binder, dispersant, emulsifier, or as a blending agent in commodity plastics (Lee et al., 2008).

Deconstruction of polysaccharides into fermentable sugars remains the key challenge in the production of inexpensive lignocellulosic biofuels and significant research has focused on pretreatment (Chandra et al., 2007), which refers to the "disruption of the naturally-resistant carbohydrate–lignin shield" (Yang and Wyman, 2008). Ionic liquid (IL) pretreatment is a relatively new technology that offers several advantages, in particular, its ability to effectively decrystallize cellulose, rendering it extremely susceptible to enzymatic hydrolysis. As indicated by its name, this pretreatment is based on organic salts that remain in liquid state below 100 °C (Rogers and Seddon, 2003). ILs are not only known to dissolve cellulose (Swatloski et al., 2002; Zhu et al., 2006) and lignin (Sun et al., 2009; Pu et al., 2007; Fort et al., 2007), but also hard- and softwoods, switchgrass (Li et al., 2010) and corn stover (Li et al., 2011). An overview of ILs suitable for dissolution of lignocellulosic materials is given in (Mäki-Arvela et al., 2010).

Typically, the IL pretreatment process includes dissolution of biomass at a temperature range of 110–160 °C for 0.5–6 h, depending on the IL. Although the exact mechanism for the dissolution of cellulose is not entirely known, the phenomenon has been ascribed to the disruption of the inter- and intra-molecular hydrogen bonding of cellulose, while new hydrogen bonds are formed between the carbohydrate hydroxyl protons and the anions of the IL (Sun et al., 2009). Biomass dissolution is followed by addition of an anti-solvent (such as water, ethanol or other solvents with hydrogen bonding capacity) that precipitates the biomass from solution. A previous technoeconomic study of an IL pretreatment-based biorefinery (Klein-Marcuschamer et al., 2011) concluded that lignin is an important by-product and the revenue derived from it could have a substantial impact on the profitability of the process.

In this work, we modeled the production of lignocellulosic ethanol via IL pretreatment followed by acidolysis and sugar extraction with naphthalene-2-boronic acid (N2B). The process model is based on a previous model, initially developed based on dilute acid pretreatment (Klein-Marcuschamer et al., 2010), and later modified to study IL pretreatment (Klein-Marcuschamer et al., 2011). The primary aim of the current study was to develop a model to evaluate the process configuration with IL pretreatment followed by acid hydrolysis, sugar extraction, and recovery. Furthermore, the purpose of this work was to identify possible process bottlenecks and necessary future research activities to lower the cost of biofuel production by this novel route. We performed a sensitivity analysis spanning the current status of the technology and the required future developments. Finally, a lignin recovery technology based on kosmotropic salt phase separation was modeled in order to identify the impact of processing and selling the lignin on the economic feasibility of the biorefinery.

2. Methods

2.1. Process description

An overview of the ethanol production process with acid hydrolysis and sugar extraction with N2B is illustrated in Fig. 1. The process model was developed based on previous versions, presented and described in (Klein-Marcuschamer et al., 2010, 2011); compared to the previous models, changes were centered in the pretreatment section and the parameters for the new section were obtained from Refs. Brennan et al. (2010) and Griffin and Shu (2004). The plant was assumed to work 330 days per year and process approx. 2000 MT of corn stover per day (priced at $60/tonne (Klein-Marcuschamer et al., 2010)) The composition of the corn stover is shown in Table 1. After the biomass is shredded, it enters the pretreatment reactor along with the IL (priced at $2.50/kg (Klein-Marcuschamer et al., 2011)). The dissolution reaction has a residence time of 30 min and is carried at 120 °C with a solids loading of 15%. The effluent of the pretreatment reactor is mixed with 4 M HCl (the amount of solution is 10% of the biomass by weight) and directed to the hydrolysis reactor (residence time is 2.5 h), where water is added gradually to a final concentration of 43% wt. To recover the sugars, the stream is cooled to 70 °C and mixed at a ratio of 1:1 with an organic phase (hexane:octanol (85:15 by volume) containing 70 mM N2B). The organic phase was priced at $0.70/kg of solution based only on the price of N2B, $59/kg (quotation received from commercial suppliers). The bottom stream from the "sugar recovery" unit, rich in ionic liquid, is further processed to recover the IL. The recovery percentage needed for a process to be economically feasible was taken from (Klein-Marcuschamer et al., 2011) and assumed to be 99.6%. Though this assumptions on the IL recycle rate is speculative, it allows studying the advantages and limitations of the novel process without being overshadowed by a parameter that has been previously examined.

When studying the effect of lignin recovery and its use as a co-product, a three-phase separation investigated and described by Shill et al. (2011) was included in the model. This was done to better capture the cost of recovering the lignin, and not only the effect of selling it. During the separation process, an aqueous kosmotropic salt (tripotassium phosphate) solution is applied to form a three-phase system, which precipitates the biomass and forms phases rich in IL and rich in salt. The salt was assumed to be ~0.20$/kg based on a database from the Economic Research Service (2013). This separation system reduces the amount of water that requires evaporation from the recycled IL stream. Lignin, which is a valuable by-product, is also separated in this step.

The sugars (glucose, xylose), at this point still diluted in the organic phase, are extracted with 1 M HCl. The stream is then neutralized with NaOH and pumped to the fermentation section. The rest of the process continues as in the base model (Klein-Marcuschamer et al., 2010): both C5 and C6 sugars are used for ethanol production, and the required concentration of ethanol (99.5%) is achieved through two distillation columns and a
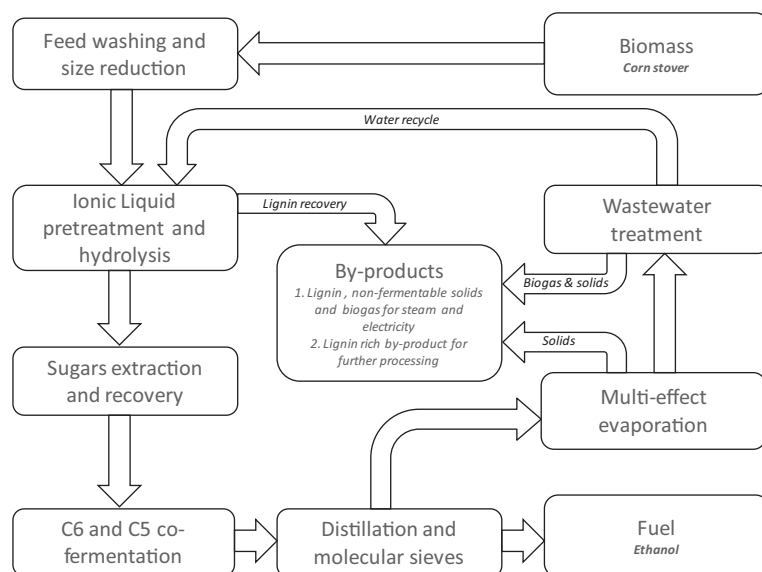
Fig. 1. Schematic view of a biorefinery. Lignocellulosic biorefinery employing IL pretreatment followed by acid hydrolysis, sugars extraction and recovery to produce fuel-ethanol.

Table 1
Corn stover composition.

Corn stover	(%)	Reference
Acetate (bound)	2.5	
Ash	4.4	Aden et al. (2002)
Cellulose	31.8	Klein-Marcuschamer et al. (2010)
Hemicellulose	17.9	
Lignin	15.3	
Other solids	13.1	
Water	15.0	

Table 2
Feed and product flow for the base case scenario.

Feed stream		Product and wastewater stream		
Raw materials	Flow rates (MT/day)	Products/byproducts	Flow rates (MT/day)	Purity (%)
Corn stover	2000	Ethanol	236	99.6%
IL	48	Biogas	149,050 m³	(62% of methane)
HCl	180 (4M) 2736 (1M)	Lignin (for combustion)	306	–
Water	16,465			

molecular sieve system. The stillage is sent through a series of multi-effect evaporators for partial dewatering. Some of the water is recycled and the rest, together with the effluent from the pretreatment processing, is treated in a wastewater treatment plant by means of anaerobic digestion, aerobic bio-oxidation, clarification, and filtration. The remaining lignin, non-fermented solids, and the methane produced during anaerobic digestion are used as fuel to produce steam. In order to meet electricity and heat requirements of the plant, an additional 14,640 m³ of methane are purchased per day. Feed and product flows for the base case are summarized in Table 2.

2.2. Process simulation and cost analysis

The process model was built with the aid of SuperPro Designer v8.5 (Intelligen, NJ, USA). Information on the processes presented was collected from various technical sources, research articles, and personal communications. Process flowsheets were constructed and the unit operations were parameterized, the

material and energy balances were solved, and the capital and operation cost were estimated using the software. The cost of equipment was calculated employing the power law estimation (Eq. (1)):

$$\text{Cost} = C_0 \times \left(\frac{Q}{Q_0}\right)^a \tag{1}$$

Where, C_0 is the base cost, Q is the capacity variable, Q_0 is the base capacity, and a is a correlating exponent. Base costs and capacities, as well as scaling exponents for each piece of equipment were taken from previous technoeconomic studies (Aden et al., 2002; Towler and Sinnot, 2008; Wooley et al., 1999; Klein-Marcuschamer et al., 2010, 2011), and updated to 2010 USD using the CEPCI index (Chemical Engineering, 2013). The complex mixture of acids and organic components present during sugar extraction and recovery could require changes to the metallurgy considered in this study, but more experimental data would be needed to determine such changes.

The total capital investment (TCI) was calculated as the sum of direct fixed capital (DFC), working capital, and start-up costs. The DFC is composed of direct cost (equipment purchase cost and installation, including piping, instrumentation, electrical, etc.) and indirect costs. The latter include engineering (0.25 of the direct cost) and construction (0.22 or 0.31 of direct costs, depending on the process section). Additionally, contractor's fee (0.07 of direct plus indirect costs) and contingency (0.03 of direct plus indirect costs) were added to calculate direct fixed capital costs. The depreciation period of 10 years and a discount rate of 10% were used in the analysis. The project lifetime was set to 25 years with a construction period of 18 months and startup period of 12 months. The minimum selling price of a product, as used in the present study, corresponded to a zero net present value of the project over its lifetime at the given discount rate. The base model and all the assumptions used to prepare it, which form the basis for the present analysis, can be freely accessed for non-commercial use at http://econ.jbei.org.

3. Results and discussion

3.1. Economic analysis

In the present study we modeled a process for lignocellulosic ethanol production based on IL pretreatment, acid hydrolysis,
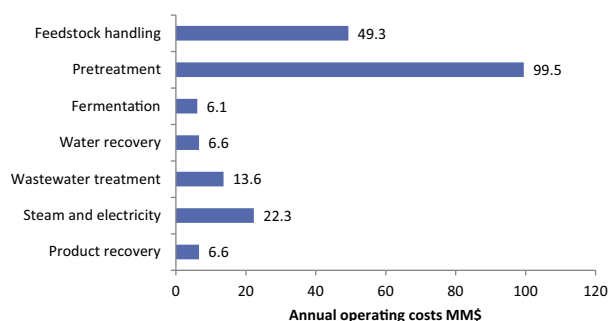
Table 3
Cost analysis for a base case.

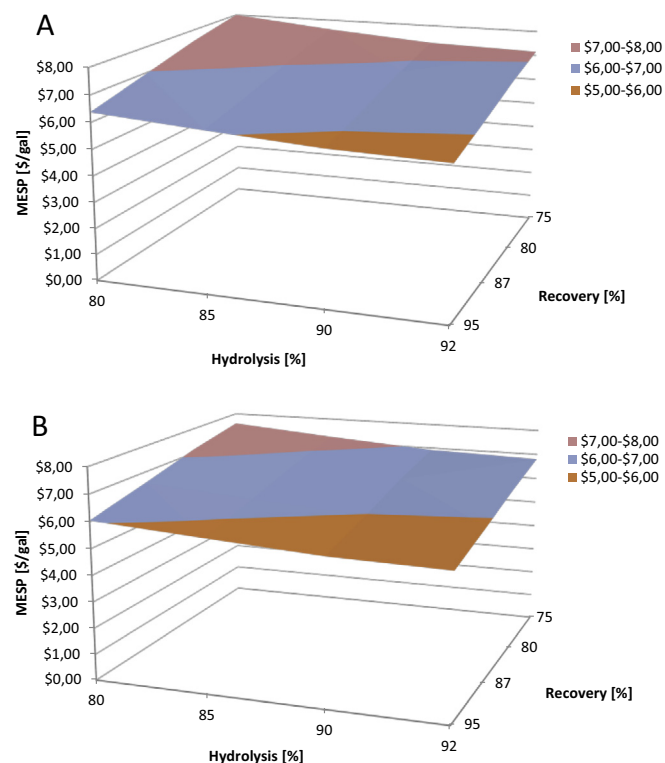| Type of cost	Value	Unit
Total Capital Investment	$366,000,000	
Total plant direct cost	$203,000,000	
Total plant indirect cost	$104,000,000	
Operating costs	$211,000,000	/yr
Operating costs by type		
Raw materials (total)	$103,000,000	/yr
Corn stover	$39,666,000	/yr
IL	$39,600,000	/yr
Chemicals (for pretreatment)	$13,741,000	/yr
Others	$9,083,000	/yr
Labor	$6,300,000	/yr
Facility	$72,000,000	/yr
Utilities (total)	$30,000,000	/yr
Std power	$29,200,000	/yr
Cooling water	$800,000	/yr
Corn stover consumption	560,000,000	kg/yr
Ethanol fuel	28,230,000	gal/yr
MESP	$8.05	/gal

MESP – minimum ethanol selling price.
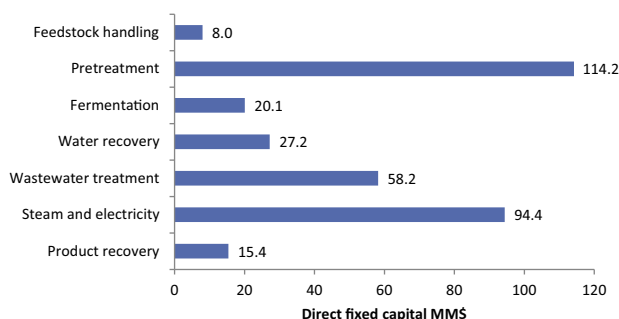
Fig. 2. Direct fixed capital breakdown for the base case scenario.

Fig. 3. Annual operating cost breakdown for the base case scenario.

Fig. 4. MESP for the studied process. Different yields of hydrolysis (80–92%), sugars extraction (91% and 98% on (A) and (B) figure, respectively), and sugars recovery (75–95%) are presented.

and sugar extraction. The base case results from the analysis are summarized in Table 3. The breakdown of the direct fixed capital and the annual operating costs are shown on Figs. 2 and 3, respectively. In the base case, the hydrolysis glucose yield equaled 80% (Brennan et al., 2010), the extraction efficiency was set to 91% (Brennan et al., 2010), and the sugar recovery to 75% (Griffin and Shu, 2004). The base case assumed the N2B was completely recycled, thus in this scenario the N2B raw material cost did not contribute to the MESP. The total capital investment of the investigated plant was slightly higher compared to previously reported processes (Klein-Marcuschamer et al., 2010, 2011). Even though the process did not employ saccharification tanks, which are quite large, it required additional equipment for acidolysis, sugar extraction and recovery (Fig. 2). More notable was the increase

in the annual operating cost (AOC), which was almost 70% higher compared to a process based on acid pretreatment followed by enzymatic hydrolysis (Klein-Marcuschamer et al., 2010). This increase was mainly due to the cost for raw materials, in particular the IL itself. Another factor contributing to the higher AOC was the power consumption (Fig. 3), as electricity was needed for stirring of the large hydrolysis reactors.

3.2. Process optimization

Because overall ethanol yield has been reported to be a key determinant in the economic viability of similar processes (Klein-Marcuschamer et al., 2010), three pretreatment steps that have a clear influence on yield were studied. These steps are hydrolysis, sugar extraction, and sugar recovery. The initial values were taken from existing literature (Brennan et al., 2010; Griffin and Shu, 2004) or were based on laboratory data. Further improvements to those three process steps were modeled to better understand their impact on the MESP (Fig. 4). The hydrolysis yield was varied from 80–92% and the sugar recovery was varied from 75–95%. In parallel, two sugar extraction efficiencies were considered, 91% and 98%. The most important parameter was found to be the hydrolysis yield, since this step is where cellulose and hemicellulose are depolymerized into simple sugars and therefore where the amount of sugars entering the rest of the process is determined. The extraction and sugar recovery efficiencies had similar effects on overall ethanol yield, and the improvement of these parameters was synergistic. In the base case (hydrolysis: 80%; sugar extraction: 91%; sugar recovery: 75%), the MESP was $8.05/gal, but this value decreased as the performance of the various stages was improved. For example, at a hydrolysis yield of 92%, a sugar extraction efficiency of 98%, and a sugar recovery rate of 95%, the MESP was reduced to $5.40/gal (Fig. 7). Further decrease in the
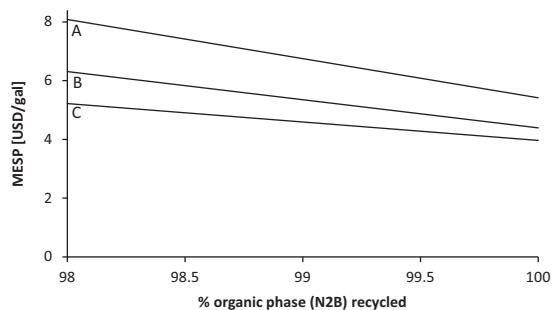
Fig. 5. Effect of organic phase recycle on MESP. A – 15% solids loading in the hydrolysis reactor, B – 20% solids loading in the hydrolysis reactor, C – 30% solids loading in the hydrolysis reactor. The organic phase price was estimated as $0.7/kg based on the price of N2B ($59/kg).
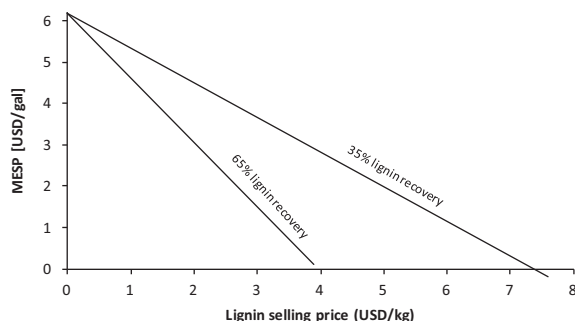
Fig. 6. Effect of lignin selling price on MESP at different rates of lignin recovery.

MESP could be achieved by increasing solids loading in the hydrolysis reactor. For instance, at 20% of solids, the MESP was $4.40/gal whereas at 30%, the MESP was $4.00/gal (Figs. 5 and 7).

Additionally, the effect of recycling the organic phase was considered. Fig. 5 illustrates that a high recycle rate is very important given the high price of the raw materials that form the organic phase and the large amounts of expensive N2B needed for extraction ($59/kg; see Section 2). This high flowrate was itself set by the experimentally-determined requirement of a 1:1 ratio of the IL phase to the organic phase, and future research should be conducted to determine whether lowering the use of the organic extractive solution is possible.

One of the main advantages of the pretreatment process here presented is that it does not require the use of enzymes. A recent study found that enzymes could contribute up to $1.47/gal to the cost of ethanol production (Klein-Marcuschamer et al., 2012). In our previous study (Klein-Marcuschamer et al., 2010), a process using dilute acid hydrolysis followed by an enzymatic hydrolysis, which is relatively established, was determined to have a MESP of $4.58/gal for a base case, with the enzyme cost assumed to be $0.35/gal of ethanol. Updating the enzyme cost to $1.47/gal would increase the MESP to $5.70/gal. This further justifies examining approaches to lower required enzyme loadings or forgo their use completely. IL pretreatment followed by sugar extraction is one such option, though it requires the use of other materials, some of which are also expensive. Given the chemical nature of the new raw materials, however, it is expected that they would be easier to recycle than enzymes would, encouraging further work in this area. Other improvements could also help in lowering the MESP e.g., increasing the solids loading in the IL reactor (Wu et al., 2011) or decreasing the volume of water needed for hydrolysis.

3.3. Lignin recovery

In addition to IL pretreatment and sugar extraction, lignin recovery was modeled based on a kosmotropic salt separation
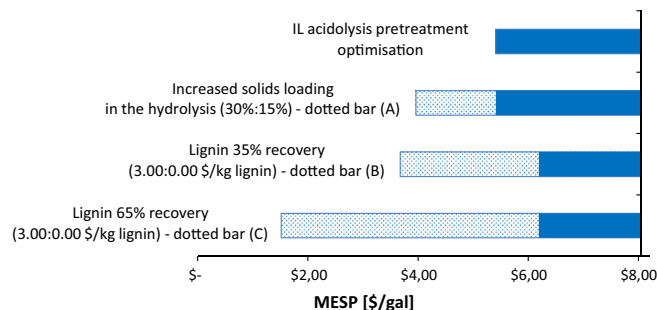
Fig. 7. Summary of the sensitivity analysis for IL acidolysis pretreatment optimization (solid filled bars) and additional MESP reduction through increased solids loading (dotted bar A) or lignin recovery (dotted bars B and C).

process described by Shill et al. (2011). For the lignin recovery exercise, we assumed the following parameters for the IL pretreatment: hydrolysis yield at 92%, sugar extraction efficiency at 98%, and sugar recovery rate at 95%. We considered two scenarios: 35% (Shill et al., 2011) and 65% (Klein-Marcuschamer et al., 2011) lignin recovery (Fig. 6). In those two scenarios, the organic phase recycle was set to 99.5%, and recycle of the kosmotropic salt solution was assumed to be 98%. In the case of 35% lignin recovery, the MESP could be lowered to the current market price of ethanol fuel ($2.10/gal – price for December 2011 from (Trading economics, 2013)) when lignin was priced at $4.87/kg. In the case of 65% lignin recovery, the ethanol became competitive with today's fuel price ($2.10/gal – price for December 2011 from (Trading economics, 2013)) when the lignin selling price was approximately $2.62/kg. Since currently envisioned uses of lignin for resins and polymers are likely to fall closer to $2–4/kg (Klein-Marcuschamer et al., 2011), lignin recovery rates of >~60% are needed. It should be noted that the kosmotropic salt recycle rate must still be proven. Shill et al. (2011), working with a similar three-phase tripostassium phosphate solution system, reported a recycle rate of 64%. With such a low recycling rate, even with a high lignin recovery (65%) and a high lignin price ($3.00/kg), the MESP ($8.10/gal) is significantly higher than current prices for transportation fuels. A summary of the sensitivity analysis is illustrated in Fig. 7. Lignin recovery required additional unit operations, hence the increased MESP (from $5.40 to $6.19/gal) when the lignin was priced at $0.00/kg, while the IL pretreatment parameters were held at the optimized level (hydrolysis yield of 92%, sugar extraction efficiency of 98%, and sugar recovery rate of 95%).

Market saturation issues become prominent at high lignin production and thus other uses for surplus of lignin, with larger overall markets, would be needed. Lignin-derived hydrocarbons could be used as fuels themselves, though at lower prices, requiring a higher lignin recovery from the pretreatment processes. Regardless of how this is accomplished, revenue from lignin could significantly benefit the economics of lignocellulosic biorefineries.

4. Conclusion

Although the results based on current assumptions indicate that the IL-based acidolysis process remains expensive compared to more established technologies (MESP $8.05/gal), improvements in the hydrolysis yield, the sugar extraction efficiency, and the sugar recovery rate were shown to result in more competitive processes (MESP $4.00/gal). The technical development of this novel process is in its infancy, and thus there is room for significant improvement in both the design and engineering of the process. The present technoeconomic model is intended to guide scientists in addressing the prevalent technical challenges and facilitate advances toward economic viability.

Acknowledgements

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