Modeling and Analysis

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Techno-economic analysis of a lignocellulosic ethanol biorefinery with ionic liquid pre-treatment

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Abstract: Lignocellulose dissolution in ionic liquids is a relatively new biomass pre-treatment technology that is receiving growing interest from the biofuels community as a route to provide readily-hydrolyzable holocellulose. Despite its proven advantages over other pre-treatment technologies – including feedstock invariance, high monomeric sugar yields over short saccharification times, and extensive delignification – there are several core issues that stand in the way of commercialization. These include the relative high cost of the ionic liquids themselves, a lack of knowledge in terms of process considerations for a biorefinery based on these solvents, and scant information on the coproducts this pre-treatment technology could provide to the marketplace. We present an initial techno-economic model of a biorefinery that is based on the ionic liquid pre-treatment technology and have identified, through a comprehensive sensitivity analysis, the most significant areas in terms of cost savings/revenue generation that must be addressed before ionic liquid pre-treatment can compete with other, more established, pre-treatment technologies. This report evaluates this new pre-treatment technology through the perspective of a virtual operating biorefinery, and although there are significant challenges that must be addressed, there is a clear path that can enable commercialization of this novel approach. © 2011 Society of Chemical Industry and John Wiley & Sons, Ltd

Keywords: techno-economic analysis; biofuels; ionic liquids; pre-treatment; biorefinery; lignin

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Introduction

Lignocellulosic biomass is the most abundant and renewable source of carbon on the planet – it has been estimated that between 600–800 million tons are available annually in the United States alone that have the potential to serve as sustainable feedstocks for bioenergy,[1] defined here as biopower and biofuel, production. Lignocellulosic biomass includes dedicated energy crops (e.g. switchgrass and Miscanthus), woody biomass (e.g. poplar and pine), milling residues, agricultural residues (e.g. corn stover, wheatstraw), municipal solid waste, manure, and other sources. The plant cell walls found in lignocellulosic biomass are complex structures composed of cellulose, hemicellulose, and lignin, and they are difficult to break down, or deconstruct, into their component polymers and monomers. This recalcitrance makes it more expensive and energy-intensive to convert lignocellulose into fermentable pentoses and hexoses (e.g. xylose and glucose) than the starches in feedstocks such as corn or sucrose in sugarcane.

One of the most critical needs that must be addressed in order for lignocellulosic biofuels to become commercially viable is a cost-effective and efficient biomass pre-treatment technology. It is estimated that, on a per-gallon basis, biomass pre-treatment represents the second-largest (19–22%) cost in biofuel production, after the feedstock (30–32%).[2,3] Several physical and chemical pre-treatment methods that exist today (dilute acid, ammonia fiber expansion, lime, steam explosion, autohydrolysis, and organic solvent) are being further developed to overcome the recalcitrance of lignocellulose to depolymerization, increase enzyme efficiency, and improve the yields of monomeric sugars from lignocellulose.

All of these pre-treatment technologies have advantages and disadvantages, and there is no biomass pre-treatment available today that can efficiently and cost-effectively process a diverse range of biomass feedstocks at high yields.[4] The most effective lime pre-treatment requires pressurized oxygen to be delivered at 1.4 MPa (200 psig).[5] Organic solvent pre-treatments typically require the presence of additional catalysts, and the solvents must be completely removed after use due to their inhibitory effect on downstream saccharification and fermentation (for an illustrative review, see Zhou *et al.*[6]). Dilute sulfuric acid pre-treatment effectively solubilizes the majority of the hemicellulose and small amounts of lignin, but at higher temperatures this pre-treatment also generates polysaccharide-degradation products that are known to be inhibitory to downstream fermentation organisms, which lowers the overall sugar yields obtained.[7,8] Steam pre-treatment can be applied to various types of materials, but the need of impregnating agents to improve yield results in some of the same shortcomings observed with dilute acid.[9,10] Ammonia fiber expansion (AFEX) appears to be an effective pre-treatment for corn stover and other agricultural residues, but it requires ammonia recycling and does not effectively pre-treat hardwoods and softwoods.[11,12]

Ionic liquids are a relatively nascent pre-treatment technology that holds great promise.[13,14] Ionic liquids were originally developed as a potentially 'greener' alternative to organic solvents. Out of the ~10 000 known combinations of anions and cations that comprise this class of solvents, relatively few are known to be able to dissolve biomass; most of these are typically liquids below 373 K (100^{o}C) and are based on an imidazolium cation. Ionic liquids have been shown to be very effective at pre-treating woody biomass,[15,16] switchgrass,[14,17] and agricultural residues.[18] The primary advantages of the ionic liquid pre-treatment are that it (i) enables the fractionation of lignin and polysaccharides into different output streams, and (ii) significantly disrupts the cellulose I polymorph.[17,19,20] This combination of effects generates a pre-treated material that can be easily hydrolyzed into monomeric sugars through saccharification when compared to other pre-treatment technologies.[14] The generation of a relatively pure lignin output stream, with controlled functionality based on processing conditions, also offers the potential of converting this material into a high-value coproduct.

For all of these advantages, ionic liquids currently suffer from clear and significant challenges that stand in the way of deployment and commercialization of this pre-treatment technology. These include the relative high cost of ionic liquids, the subsequent requirement of significant ionic liquid recovery and recycling, and the development of process technologies that enable effective use of the ionic liquids within a biorefinery. To date, there have been no reports that present the techno-economic impacts of the ionic liquid pre-treatment technology, and although it is commonly held that ionic liquids are currently too expensive, there is a lack of understanding from a process-engineering perspective that identifies operational targets for process improvement that would enable commercialization. We have developed a lignocellulosic ethanol biorefinery model, based on ionic liquid pre-treatment technology, which describes the cost impact of this approach on the minimum ethanol selling price (MESP). This analysis has identified several key unit operations and performance targets that would place the ionic liquid technology in a competitive position with other, more conventional pre-treatment technologies. Our results also indicate the singular importance of coproducts, in particular, lignin, to offset the costs of the ionic liquid pre-treatment technology. These results reinforce the conclusion that given specific process engineering and operational improvements, ionic liquids can be a viable technology in the biofuel marketplace.

Economics of an ionic liquid pre-treatment-based biorefinery

In order to study the major limitations for cost-effective biological production of ethanol using an ionic liquid (IL) pre-treatment process, we constructed a process model of a biorefinery based on a previously published flowsheet.[21] As certain ILs have been shown to be excellent solvents for lignocellulosic biomass, the dilute acid pre-treatment module of the flowsheet was replaced with the following unit operations: an IL biomass dissolution vessel where biomass is mixed with the IL solvent at 393 K (120°C) and atmospheric pressure (residence time was 30 min), an inline mixer powered by a progressive cavity pump where water is added to the IL/biomass mixture, a decanting centrifuge that separates the solids (most of the cellulose, part of the hemicellulose, and part of the lignin) from the IL, and an undefined IL processing operation that separates the lignin from the IL and recycles it back to the mixing reactor. The undefined section was added to provide flexibility in choosing a particular technology for IL separation and recycling, but it was priced based on the flow of material to the section (depending on the scenario, it represents between 30% and 60% of the equipment cost. This section was overpriced in order to be conservative, but its cost has limited impact in the overall economics). Saccharification (at 20% solids loading) is followed by adding 20 mg (0.5 FPU/mg)[22] of enzyme cocktail per gram of polysaccharide (i.e. cellulose and hemicellulose), with a residence time of 10 h and 85% conversion to monomers. The cost and enzyme loading was based on the assumptions and references of our previous model.[21] A further modification to that model is the elimination of the turbogenerator, since preliminary analyses revealed that including this unit operation downstream of the boiler negatively affected the MESP in most cases here studied. The fermentation yields were left as those for the previous model. Toxicity to ionic liquids has been investigated, but it seems to be highly dependent on the compound structure and the micro-organism tested (coincidentally, toxicity to *Saccharomyces cerevisiae* was comparatively low).[23]

As is evident from the above, and unlike our previous process model, we made projections of how a process based on IL pre-treatment technology will develop in the future. The motivation for this was to uncover the limitations stemming from IL use even if the non-IL-related bottlenecks are solved and to carry out a sensitivity analysis to establish the factors that are the primary drivers of cost in the proposed IL pre-treatment process technology. Therefore, we studied the sensitivity of the MESP (as defined previously[21]), to (i) IL loading, (ii) IL recycling, and (iii) IL cost, using optimistic assumptions for the rest of the process. To start the analysis, we simulated changes in IL/biomass (wt/wt) ratios between 1 and 10 at IL recycle rates between 94% and 99.6%. The cost of IL was changed between \$2.50 kg^{-1} and \$50 kg^{-1} (the range was chosen after discussions with IL manufacturers, considering the scale of this operation). A total of 80 combinations of the three variables were studied.

Sensitivity based on IL loading and recycling rate reveals a strong correlation of the MESP and makeup IL added to the process. This suggests that the main cost driver for the process is the amount of non-recycled IL, i.e. the IL that is lost during pre-treatment and follows the solid and non-volatile fraction of all downstream flows until it is ultimately burned in the boiler (Fig. 1). At a price of IL of \$50 kg^{-1}, for example, the cost increases perfectly linearly ($R^2 = 1.000$) with increasing amounts of non-recycled IL, regardless of whether the effect comes from an increase in IL loading or decrease in IL recycling.

The linear correlation is indicative of insensitivity of MESP to factors other than IL use, albeit IL recycling and loading affect the plant economics very differently. This is true in

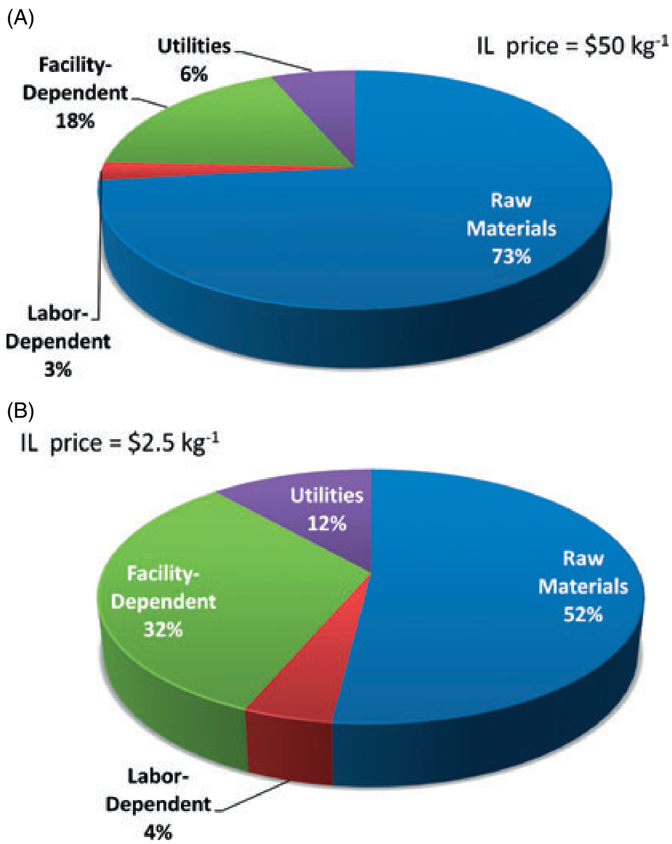

Figure 1. Distribution of the annual operating cost of the modeled biorefinery at two IL purchase prices, \$50 kg^{-1} (A) and \$2.5 kg^{-1} (B), for a process with a IL/biomass ratio of 1 and a recycle rate of 99.6%.

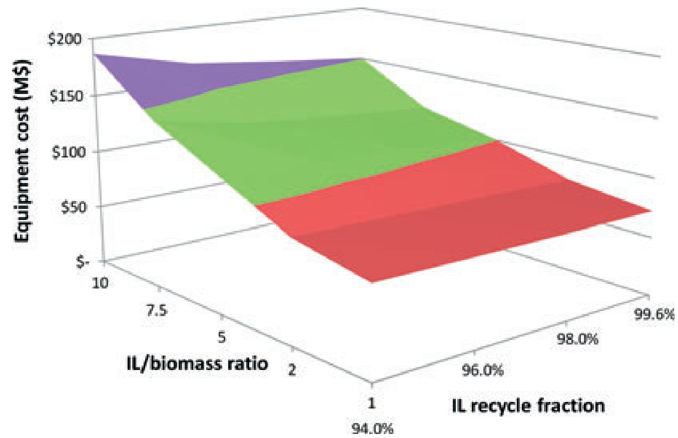

Figure 2. Equipment cost for the modeled biorefinery at different IL recycling rates and loadings. This cost does not include installation, construction, maintenance, or overhead.

particular of capital cost (Fig. 2). At constant IL loading, the recycle rate does not significantly affect the equipment cost, especially at low IL loading, because the overall size of the plant is not altered by the recycle rate (at least in this range). In contrast, IL loading affects the size of the plant, and at high IL loading, the recycle rate has a more pronounced effect in capital cost. At high IL loadings and low recycle, the IL processing and recycling section becomes less expensive compared to high recycle, but this is more than compensated by the larger size of the boiler. The reason is that the non-recycled IL flows to the boiler in this process flow configuration, so additional installed capacity is needed to dispose of it by burning. For instance, decreasing the recycle rate from 99.6% to 94% recycle at an IL/biomass ratio of 10 decreases the IL separation section capital costs from \$96M to \$93M, but increases the boiler costs from ~\$20M to ~\$60M. The caveat of this analysis is that it does not depend on the technology used for IL separation and recycling, which limits the realism in these numbers. However, the conclusions should not be overlooked: it is important to consider the economic implications not only of IL recycling, but, when required, of IL disposal as well.

The relationship between the MESP and the amount of non-recycled IL can be factored into IL loading and IL recycling effects. As expected, either low recycling or high IL loading increase the MESP, with less pronounced changes at higher recycle rates or lower IL loadings. As the IL cost decreases, the overall trend prevails, but the MESP is reduced. At an IL price of \$2.50 kg^{-1}, the MESP data indicate that an IL/biomass ratio of 2 or less, and a recovery of 97% or greater is required for an MESP of less than \$5 gal^{-1} (Fig. 3). In other words, technologies that reduce all three studied parameters (IL price, recycling, and loading) are needed to usher the adoption of this process technology.

How can the MESP be reduced?

The first and most obvious measure to reduce the MESP using the IL pre-treatment process is to decrease the IL purchasing price, because at high IL price, the technology is not economically viable even with a low IL loss (e.g. at an IL purchasing price of \$50 kg^{-1}, 99.6% IL recycle, and 1:1 IL/biomass loading, the MESP is >\$6 gal^{-1}). Furthermore, at high IL prices, this sole component is the largest contributor to the cost. At an IL/biomass ratio of 1:1 and a recycle of 99.6%, raw materials make up 73% of the total annual operating cost when the IL price is \$50 kg^{-1}, and

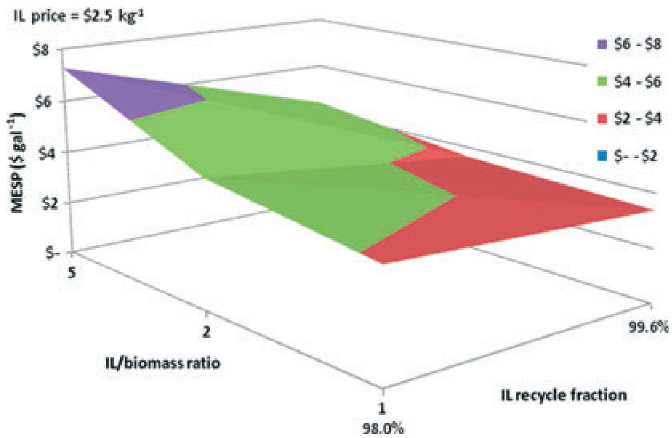

Figure 3. Minimum ethanol selling price at different IL recycling rates and loadings, corresponding to an IL purchasing price of $2.50 kg^{-1}.

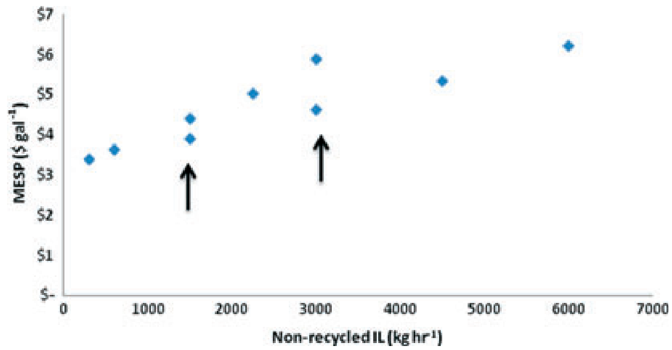

Figure 4. Minimum ethanol selling price at different rates of non-recycled (i.e. makeup) IL. The arrows indicate instances where the non-recycled IL rate is equal, even though it is achieved through a different combination of IL loadings and recycling rates.

the IL makes up ~64% of the raw material cost (~47% of the total). When the IL price is reduced to $2.50 kg^{-1} the contribution of raw materials drops to 52%, and the IL makes up ~8% (~4% of the total). In other words, at lower IL purchasing prices, other factors that affect the MESP become more obvious, even at constant non-recycled IL (Fig. 4). Discontinuities of MESP at constant amounts of non-recycled IL, indicated by arrows in Fig. 4, represent points in which IL loading and recycling can be differentiated as strategies for reducing production costs.

The results suggests that lowering IL loading is more important than increasing the IL recycle rate, and therefore should be targeted as the next most important step in reducing the high cost of this process. Savings from lowering IL loading stem from three main sources, in addition to the aforementioned trend of decreasing capital cost due to smaller equipment sizes at constant IL recycle. First, and most obvious, is the reduction in raw material costs associated with lower overall IL use. For example, at 94% IL recycle, the makeup IL feeding rate is 4500 kg hr^{-1} at an IL/biomass ratio of 1, and is 45 000 kg hr^{-1} at a ratio of 10. At $2.50 kg^{-1} of IL, this translates into IL costs of $90 and $900 million per year, respectively. The former figure is in line with the annual operating cost of a biorefinery based on dilute acid,[21] but the latter is too large in comparison. It is apparent that increasing IL recycle also reduces IL use, so this source of savings is shared in both strategies.

Second is the reduction in electricity use in the IL mixing reactor at lower IL loading. The power for mixing in this vessel was calculated from estimates of density, viscosity, mixing velocity, and agitator design according to established formulas.[24] As a basis for comparison, an IL/biomass ratio of 10 necessitates about 6-fold higher power than an IL/biomass ratio of 1 (~22 vs 3.6 MW). At the level of the entire plant, the former scenario uses ~320 GWh yr^{-1} of power, whereas the latter uses ~135 GWh yr^{-1} (both for the case of 94% IL recycle). Of the 185 GWh yr^{-1} difference between these two cases, ~145 GWh yr^{-1} come from the power use in the IL mixing reactor, or ~80% of the difference. This also implies that, although increasing IL recycling results in power savings in operations downstream of pre-treatment (e.g. by lowering the total amount of fluid in the system), these are small in comparison with the power use in the pre-treatment section itself.

Third, and often ignored, is the effect on working capital. Higher IL loading, as argued in the preceding two paragraphs, leads to higher operating costs. But this also means that there is a higher associated fixed cost for keeping the operation running. This is because a buffer investment is needed to ensure there are enough resources to start the operation initially and after irregular circumstances, such as unexpected maintenance due to equipment failure. Typically, and depending on the process, working capital provides between a few weeks and a few months of operating costs, and can add significantly to the total project investment at a time when the process has no revenue.

Reducing IL loading is more significant than increasing recycling, we have learned, but to what degree? As an example, consider a process that recycles 99.6% of the IL and has a 10:1 IL/biomass ratio versus one that recycles 96.0% but uses a 1:1 IL/biomass ratio. Even though both 'waste' the same amount of IL, the case of higher recycling is more than \$1.25 gal^{-1} more expensive than the case of lower IL loading. In the case of IL price of \$2.50 kg^{-1}, this difference is nearly 30% of the MESP (Fig. 4, right arrow). This effect is more significant at a lower IL price and disappears at high IL price, providing further evidence that minimizing IL price is a more important problem than variations in any of the other parameters studied here. A further reason why IL loading should be reduced is that IL recycle cannot continue indefinitely. It is likely that, whatever the process, recycle will not be able to perfectly separate IL from other constituents, leading to accumulation of impurities and changing the properties of the solvent. If that is the case, purchasing of fresh IL will lead to higher operating costs, and concomitantly to higher levels of working capital.

Revenue from lignin

Although the IL process is currently more expensive than others being developed for lignocellulosic biofuel production, it has the advantage of solubilizing and potentially functionalizing the lignin fraction, which can be further processed to valuable products. More research is needed to develop processes for lignin recovery from ILs, but studies suggest that recovery can be quite efficient (>90%)[25] (to be conservative, we assumed ~65% recovery). Potential uses for lignin, or lignin fragments derived from IL pre-treatment, include its use as a raw material for plastics and resins, which have a higher value compared to fuels (e.g. phenolic epoxy resins have typical values of ~\$4 kg^{-1}). We therefore considered the use of lignin as a possible source of revenue to offset the high cost of IL. If value can be obtained from the semi-pure mixture of lignin constituents flowing out of the pre-treatment process, this revenue stream can be used to offset the high IL cost. For comparison, consider that selling lignin based on its energy content would be ~\$0.30/kg if it were to displace natural gas at the plant (based on average natural gas prices used for the model[21]).

Using the same model, we observed that the MESP will decrease by ~\$1.50 gal^{-1} for every extra \$1 kg^{-1} that is added to the selling price of lignin. At high lignin selling prices, the MESP can be as low as zero, even when the IL purchasing price is \$50 kg^{-1} (depending on IL loading and recycling; Fig. 5). In other words, at high enough lignin selling prices, lignin becomes the main product while ethanol becomes a byproduct and, though selling this byproduct always brings revenue, the net present value (NPV) can be positive even at vanishing ethanol selling prices. Diversification of products being made at the biorefinery not only makes sense economically, but it is also a sound business strategy in a field with highly volatile markets. Although market size and saturation issues would have to be included to estimate the price of the lignin when supply from biorefineries is taken into account, the present analysis reveals that lignin coproducts could have a pronounced impact on the economics of the process.

It must be again noted that the process here presented does not detail the configuration of the IL processing and recycling section, thus the cost of equipment for this section – scaled so that the equipment cost is \$100M when the IL loading is 10:1 and all of it is recycled – could be deemed arbitrary. In order to ensure that changes in the capital cost for the IL recycling section do not affect significantly the MESP, we carried a separate analysis in which we varied the equipment cost of this section and recorded the effect on MESP. This revealed that roughly, an additional capital cost investment of ~\$20M adds ~\$0.10 gal^{-1} to the MESP for the plant designed. The need for higher investment in this section could arise from the desire to extract better quality lignin from the process, as it is also this section which would separate lignin from the IL. In that case, additional equipment

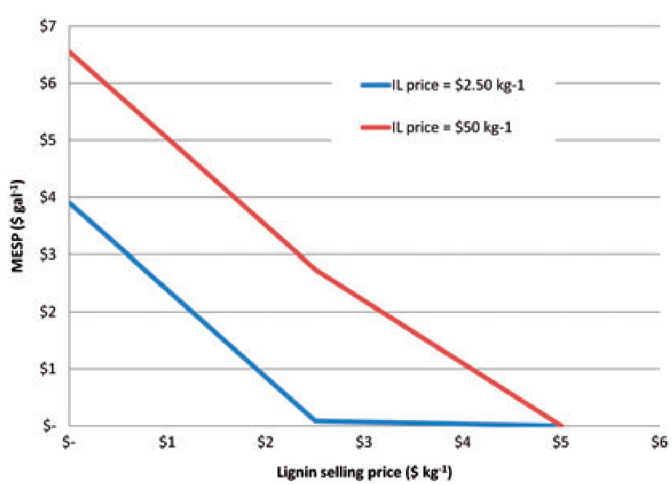

Figure 5. Effect of lignin selling price on MESP for the case of IL/biomass ratio of 1 and a recycle rate of 99.6%.

costs can be compensated by increasing the lignin selling price. As an illustrative example, adding ~\$100 million to the CAPEX (i.e. more than doubling the investment to this section) would be offset by selling the lignin for ~\$0.37 kg^{-1}.

Conclusions

We have constructed a process model for a lignocellulosic ethanol biorefinery that uses ILs for pre-treating biomass prior to enzymatic saccharification. By making projections about how the process will behave with improvements in technologies outside of IL use, we assessed the need for advances in three key areas: reducing IL cost, reducing IL loading, and increasing IL recycling. We demonstrated that reducing IL cost is most important, as other developments would have limited impact in the competitiveness of this process without lower IL costs. We showed that reducing IL loading is more important than increasing the rate of IL recycling, as it brings several simultaneous advantages. A few examples include lower capital cost, lower electricity use, and lower working capital required. We also showed that, while addressing the issue of IL use is as important as has been deemed to be by this and other studies, the issue of how to deal with the IL waste and the costs associated with doing so must also be addressed.

In addition, we used the process model to study the effect of selling lignin-derived products to offset the high cost of running this process. We showed that lignin can effectively lower the minimum selling price of the ethanol product to the point where the lignin becomes the principal revenue source for the biorefinery. We also showed that selling the lignin could be used to offset the investment costs associated with a section devoted to separating the IL and purifying the lignin coproduct.

The process model here presented is not meant to represent an existing industrial process, as there are no IL-based biorefineries to our knowledge today. We have therefore constructed a hypothetical virtual biorefinery without certain details that will have to be incorporated for a more accurate estimation of the economics of the process. What is certain, however, is that IL price, loading, and recycling, as well as selling of the lignin coproduct, will impact the feasibility of this process by different mechanisms, and it is not too early to study them and develop solutions. The performance advantages of the IL pre-treatment are significant and well documented, but unless the challenges and opportunities presented by this model can be effectively addressed, commercialization of the technology remains problematic. Tools such as this model can aid researchers in the field in elucidating these key challenges and opportunities and, thereby, guide the research needed to overcome the limitations that exist today.

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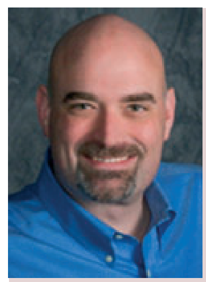

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