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Research paper

Scale-up of biomass conversion using 1-ethyl-3-methylimidazolium acetate as the solvent

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Abstract

This scale-up study demonstrated the feasibility of an ionic liquid (IL) pretreatment process at 40 kg scale, using the IL 1-ethyl-3-methylimidazolium acetate ($[C_2C_1Im][OAc]$) as the solvent. The pretreatment was followed by enzymatic hydrolysis through which the process efficiency for biomass conversion to monomeric sugars was determined. The results show that 43 wt% of switchgrass was dissolved in IL after 2 h of pretreatment at 160 °C with 15 wt% solid loading. A 120 h enzymatic hydrolysis of the pretreated switchgrass results in 96% glucan and 98% xylan conversion. $[C_2C_1Im][OAc]$ pretreatment has been successfully scaled up to 40 kg with improved sugar titers and yields relative to bench scale (6 kg). The mass flow of the overall process was established and the major scale-up challenges of the process were identified.

Keywords: Ionic liquid; 1-Ethyl-3-methylimidazolium acetate; Pretreatment; Scale up; Enzyme

1. Introduction

Ionic liquids (ILs) are a class of salts that are generally composed of organic cation and inorganic anion with melting points lower than 100 °C. There are approximately a thousand structures of ILs reported so far with one third of them commercially available. Unlike traditional solvents, ILs exhibit superior properties such as high thermal stability, minimal or no volatility, and recyclability at high yields [1]. Interestingly, some ILs can dissolve a wide range of biomacromolecules, such as cellulose, hemicellulose, silk fibroin, lignin, starch and zein protein, chitin/chitosan, wool keratin, etc. with high efficiency under certain conditions [2]. In addition, ILs have been used as solvents or catalysts for biomass pretreatment, showing high efficiency to overcome the natural recalcitrance of lignocellulosic biomass. This recalcitrance is mainly caused by cellulose crystallinity, presence of lignin, functional groups on hemicellulose, and interwoven linkages among these major components. To date, most IL-based processes of biomass conversion have been performed at lab-scale, the scalability evaluation and their impact on subsequent downstream processes is still lacking.

Common biomass pretreatment approaches such as those using dilute acid, dilute alkali ammonia, wet oxidation, steam explosion, organosolv, or irradiation, etc. can be selective for which feedstocks are most efficiently deconstructed [3,4]. However, IL-based pretreatments are usually feedstock agnostic and more broadly able to efficiently break down various feedstocks or blends. According to recent studies, IL-based biomass pretreatments are usually carried out in the temperature range of 50–160 °C at solid loadings of 5–20% [5–7]. Depending on the structures of the ILs, either cellulose

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alone or lignin together with hemicellulose are targeted during the pretreatment process. 1-ethyl-3-methylimidazolium acetate ($[C_2C_1Im][OAc]$) is one of the most effective ILs reported in biomass pretreatment [8]. Lab-scale studies (<1 kg) [9–11] on switchgrass pretreatment and process scale-up to the 6 kg level [12] have been reported. The challenges of optimization and scale-up of the $[C_2C_1Im][OAc]$ pretreatment process include biomass handling at high solid loading, high water use for washing of pretreated solids, formation of downstream fermentation inhibitors, lack of IL tolerance to downstream processes, etc. [12]. Lab-scale process designs may not be straightforward to transfer to a larger scale, in particular, the pretreatment and downstream conversion and upgrading processes may require redesign of suitable reactors and other equipment. Therefore, this study focuses on further scaling up the $[C_2C_1Im][OAc]$ pretreatment on switchgrass to a 40 kg batch in a 210 L customized pressure reactor [13]. Specifically, the reactor is corrosion resistant and equipped with a powerful helical impeller for efficient mixing. The data obtained from this study will identify the major scale-up challenges and point out research directions for further process development.

The significance of this development campaign lies in bridging the gap between lab and bench studies to pilot-scale implementation. The effect of $[C_2C_1Im][OAc]$ pretreatment on switchgrass at 40 kg scale and subsequent enzymatic saccharification were evaluated. Bottlenecks and major process challenges at larger scale were also addressed. Pinpointing current technical limitations will lead to better plan and design of further scaling, and a promising outlook in IL-related biomass conversion technologies.

2. Materials and methods

2.1. Feedstock and compositional analysis

Switchgrass was received from the Idaho National Laboratory. Switchgrass samples were milled and passed through a sieve with a mesh size of 2 mm. Received switchgrass was stored in plastic drums and placed in a cold room at 4 °C, with humidity maintained at 64–68%. Compositional analysis of switchgrass before and after each reaction was carried out using the two-step sulfuric acid hydrolysis procedure developed by National Renewable Energy Laboratory (NREL) [14].

Absorbance measurements of acid soluble lignin was taken at 205 nm using a UV−Vis spectrophotometer (Shimadzu UV-2401). Quantification of monosaccharides was conducted using a high-performance liquid chromatography (HPLC) system (Thermo Fisher Scientific, Ultimate 3000, Waltham, MA, USA), equipped with an electrochemical detector and an Aminex HPX-87H column (Bio-Rad, 300 × 7.8 mm, Hercules, CA, USA). The mobile phase was 5 mM sulfuric acid with a flow rate at 0.6 mL min^{-1} and column oven temperature at 65 °C. At least two parallel samples were used in all analytical determinations, and data are presented as the mean of replicates.

2.2. Ionic liquid pretreatment

The 1-ethyl-3-methylimidazolium acetate ($[C_2C_1Im][OAc]$, >97% purity) was purchased from BASF (Ludwigshafen, Germany). IL pretreatment was carried out in a 210 L customized Andritz thermochemical reactor (integrated by Harris Group Inc., R-100). This reactor, constructed of Hastelloy C-276, has an oil jacket and a temperature control unit (TEMPEST 2073-1110, Cleveland, OH, USA) to supply heat in the range of 10–232 °C. A helical impeller in the Andritz reactor was maintained at 50–75 rpm during pretreatment. Switchgrass was loaded to the reactor at 15 wt% solid loading (6 kg). 34 kg of $[C_2C_1Im][OAc]$ was pumped into the reactor at room temperature. Pretreatment was then performed at 160 °C for 2 h.

2.3. Ionic liquid removal by ethanol extraction

After 2 h of IL pretreatment, the temperature was decreased to 60 °C. Any pressure left in the reactor was vented. Then, 40 kg of ethanol (Sigma Aldrich, 95% purity, St. Louis, MO, USA) was slowly pumped into the reactor through the feed port to initiate precipitation. $[C_2C_1Im][OAc]$ was extracted from the switchgrass suspension by ethanol as the anti-solvent. After 1 h incubation with constant stirring, the slurry was then washed with 100 L of water. A lab blender (Waring Commercial, Model CB15, Torrington, CT, USA) was used to disrupt the precipitated solids. An additional 200 L of water was used to ensure residual $[C_2C_1Im][OAc]$ was removed from the switchgrass. Basket centrifugation (Western States, STM-2000, Fairfield, OH, USA) was then performed to separate the switchgrass solids and liquids. Washed solids were collected for the subsequent enzymatic saccharification. Presence of $[C_2C_1Im][OAc]$ was determined by conductivity measurement (Shimadzu UV-2401).

2.4. Enzymatic saccharification

Batch enzymatic saccharification was performed in a 50 L stirred tank reactor (IKA Works, Model SPP50, Inc., Wilmington, NC, USA), equipped with an anchor impeller and flow breakers to enhance mixing. The reaction was carried out at 50 °C for 120 h with 15 wt% solid loading based on dry weight of the pretreated switchgrass and a stirring rate at 40 rpm. Cellulase (Cellic® CTec2 with protein concentration: 190 mg mL^{-1}) and hemicellulase (Cellic® HTec2 with protein concentration: 174 mg protein/mL) enzyme cocktails were provided by Novozymes, Inc. (Davis, CA, USA). After pH adjustment to 5.0 with 6 N hydrochloride acid, the mixture of CTec2 and HTec2 was loaded at a fix ratio based on the cellulose content (54 mg CTec2/g cellulose, 6 mg HTec2/g cellulose) of the switchgrass. Samples were taken every 24 h to monitor sugar release. Basket centrifugation was performed after 120 h of saccharification to collect the switchgrass solids. Washed solids were collected for compositional analysis.

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3. Results and discussion

3.1. IL pretreatment

After 2 h pretreatment in [C_2C_1Im][OAc], the slurry had a dark brown color with the presence of biomass particles, indicating that switchgrass was not completely dissolved during the process. After washing and solid/liquid separation, 56.6 wt% of the starting switchgrass (6 kg) was recovered as solids. The other 43.4 wt% mass was owing to the dissolution of carbohydrate, lignin, and other extractives into [C_2C_1Im][OAc]. Inevitably, there was a small volume loss during the material transfer from the reactor to the receiving container, as well as during washing, drying and final collection. In comparison with the 6 kg scale experiment, Li et al., reported a 55.3 wt% solid recovery after 3 h [C_2C_1Im][OAc] pretreatment at the same solid loading (15 wt%) [12]. In this study, it was observed that [C_2C_1Im][OAc] extracted more xylan than glucan: 64 wt% of the xylan dissolved/degraded in the IL/liquid stream, while 96 wt% glucan remained in the recovered solids. In addition, the 2 h [C_2C_1Im][OAc] pretreatment resulted in a significant delignification of the switchgrass. About 48 wt% mass of total lignin from the original switchgrass feedstock was removed during the IL pretreatment and subsequent water washing step. The level of delignification is influenced by the type of IL, the severity of pretreatment reaction (temperature, duration), the initial lignin composition in the biomass, etc. IL-pretreated biomass is also rich in cellulose and hemicellulose, indicating that the pretreated biomass is suitable for glucose/xylose co-fermentation after enzymatic saccharification [15,16]. Methods and processes of recovering dissolved sugars from aqueous IL have been discussed in other studies [17].

3.2. IL recovery

In the biomass recovery process, 40 kg of ethanol was added to the slurry with constant agitation to ensure effective mixing. Dark colored (brown to black) precipitate formed immediately. Ethanol-induced flocculation of the regenerated biomass has been observed in milliliter scale experiments reported in other studies, but this phenomenon was exacerbated and made worse during this scale-up development campaign. This issue led to increased difficulty during solids recovery. To resolve this problem, 80 kg of water was added into the reactor and stirred for 2 h, to soak and dilute the solids. In this scale-up study, the use and performance of ethanol as the anti-solvent was unsatisfactory, even though it had worked well at small scale. A better solvent should be able to extract the IL and prevent the biomass from the formation of gel or large chunks. The following solid homogenization and extensive wash consumed considerable amount of water: 300 kg of water was used to remove excess IL, nearly 8 times of the batch total weight.

To lower the cost of IL pretreatment and reduce its environmental impact, IL recovery is particularly important. It is generally accepted that ILs must be recovered at levels >99% for large-scale industrial applications. This would require the ILs to be structurally stable under reaction conditions and/or easily regenerated from the pretreatment liquor. Techniques such as pervaporation [18], distillation, extraction, adsorption, membrane separation and induced phase separation have been discussed as feasible IL recycle methods (Mai et al., 2014). Developing efficient IL recycle processes may require a combination of multiple techniques.

3.3. Enzymatic saccharification

Pretreated switchgrass was loaded in the 50 L bioreactor at 15 wt% solid loading for enzymatic saccharification. Without drying, the moisture content of recovered switchgrass solids from pretreatment is high (about 70 wt% moisture content). In order to ensure high solid loading of pretreated biomass for high sugar titters in the hydrolysate, the amount of water used to dilute enzymes was very limited. However, given the effective mixing of the bioreactor (Fig. 1a), the product liquefied after 3 h of incubation. Fig. 1b shows the sugar release over time. During the 166 h incubation, HTec2 and CTec2 successfully converted the polysaccharides in the pretreated switchgrass to the monosaccharides glucose and xylose. The concentrations of glucose and xylose increased rapidly in the

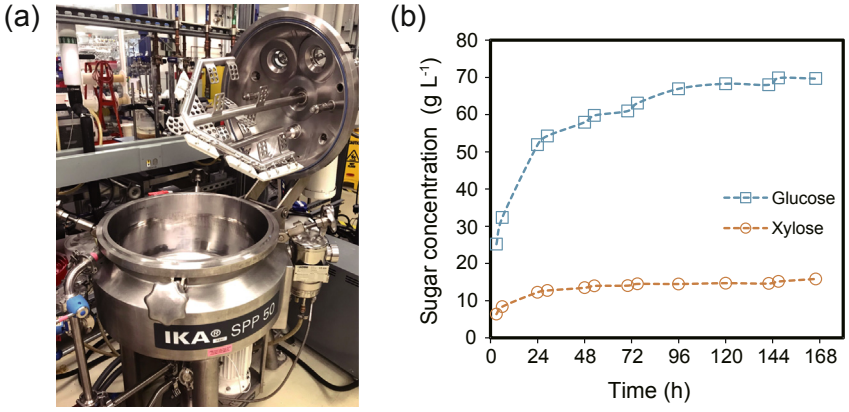

Fig. 1. (a) IKA SPP50 reactor used for enzymatic saccharification; (b) Sugar release data during enzymatic saccharification of [C_2C_1Im][OAc] pretreated switchgrass.

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Table 1
Composition of switchgrass (dry weight basis).

Feedstocks	Glucan (wt%)	Xylan (wt%)	Klason lignin (wt%)	Acid-soluble lignin (wt%)	Ash (wt%)
Raw SG	29.79 ± 0.00	22.32 ± 1.57	17.84 ± 0.32	1.96 ± 0.04	1.37 ± 1.07
After PT	50.57 ± 1.91	14.07 ± 1.14	16.48 ± 0.30	1.70 ± 0.01	0.96 ± 0.45
After ES	7.72 ± 0.19	2.15 ± 0.10	57.12 ± 2.01	2.40 ± 0.09	5.13 ± 1.30

first 24 h. After 24 h, glucose kept increasing at a lower rate while xylose concentrations remained relatively constant. By 166 h the glucose concentration reached 69.7 g L^{-1}, and xylose concentration reached 15.8 g L^{-1}. In the 6 kg scale performed by Li et al. they also observed rapid sugar release and reported sugar titers of 62.1 g L^{-1} for glucose and 15.0 g L^{-1} for xylose after 72 h saccharification [12].

The overall glucose conversion during enzymatic saccharification was 95.9% and xylose conversion was 98.3% calculated based on the glucan and xylan loadings in the pretreated biomass, indicating efficient [C_2C_1Im][OAc] pretreatment and very limited enzyme inhibition from the IL after extensive washing. The concentration of [C_2C_1Im][OAc] residue in the hydrolysate was measured as only 0.02 wt%. The resulting hydrolysate has been used to produce the jet-fuel precursor candidate D-limonene using an engineered IL-tolerant *E. coli* strain [19]. The *E. coli* DH1 *rcdA* mutant strain produced about 400 mg L^{-1} D-limonene in the presence of residual [C_2C_1Im][OAc]. No toxicity was observed when the strains were grown in hydrolysate-derived growth medium containing 12 mM [C_2C_1Im][OAc] compared to glucose-derived growth medium.

3.4. Composition of switchgrass before and after reactions

The composition of switchgrass could vary by region, age, harvest season, storage conditions and other factors. In this study, the average moisture content of raw switchgrass (Raw SG) was 9.21 wt%. As shown in Table 1, switchgrass has about 30 wt% glucan and 22 wt% xylan. Klason lignin and acid soluble lignin accounted for a total lignin of about 20 wt %. In other studies, similar [10] or higher [20–22]glucan content have been reported for different populations of switchgrass. After the IL pretreatment (After PT), the glucan content in recovered switchgrass increased to over 50 wt%, xylan content decreased to 14 wt%, with the lignin and ash content remaining similar. After enzymatic saccharification (After ES), less than 10 wt% of carbohydrate remained in solids and the materials was primarily rich in lignin with about 60 wt% lignin and 5 wt% ash. Fig. 2 shows the material morphology in each process.

3.5. Mass flow of the IL based conversion process

The mass flow of [C_2C_1Im][OAc] during pretreatment, enzymatic saccharification, and subsequent solid/liquid separation is summarized in Fig. 3. Initially, a reaction mixture was prepared by combining 6 kg of dry switchgrass (15 wt% solid loading) with 33.4 g of [C_2C_1Im][OAc]. The starting switchgrass contained approximately 1787 g glucan, 1339 g xylan, 1188 g lignin and 82 g ash. After the IL pretreatment at 160 °C for 2 h, about 3.7 wt% glucan, 63.7 wt% xylan and 48.0 wt% lignin in the original switchgrass were extracted by the IL and dissolved into the aqueous IL stream. Under the selected conditions, IL pretreatment preserved >95 wt% glucan in the

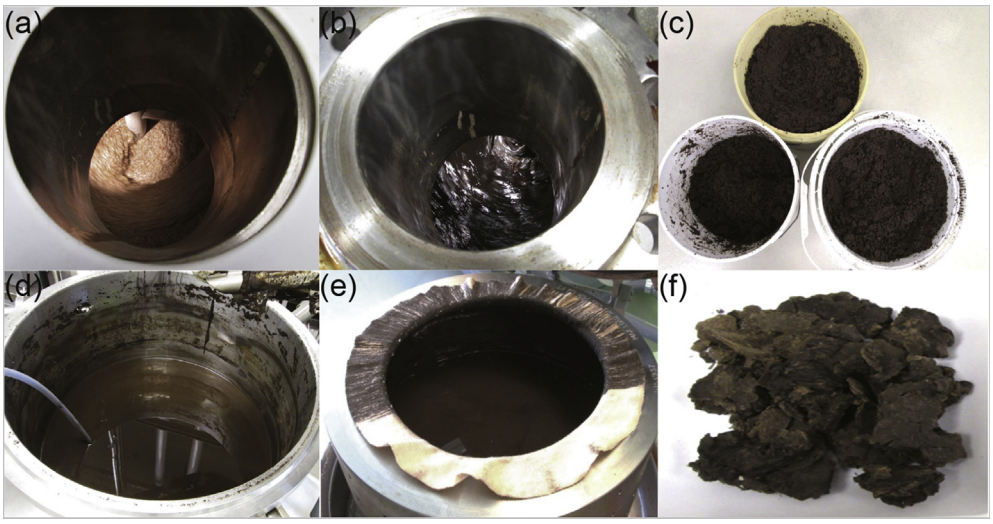

Fig. 2. (a) Morphology of switchgrass in each unit operation: switchgrass mixing with [C_2C_1Im][OAc]; (b) slurry after 2 h IL pretreatment; (c) recovered pretreated switchgrass; (d) hydrolysate after 166 h enzymatic saccharification; (e) captured wet solid during solid/liquid separation using a basket centrifuge; (f) dried switchgrass residue.

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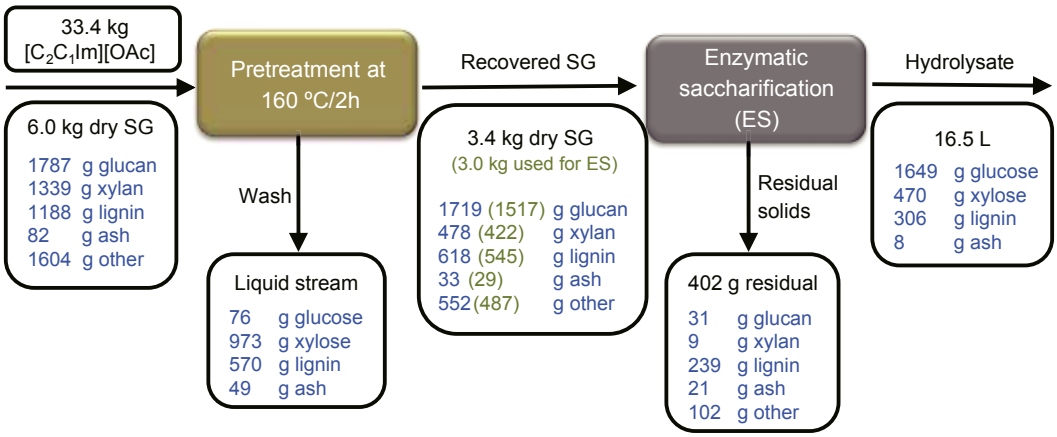

Fig. 3. Mass flow of [C_2C_1Im][OAc] pretreatment and enzymatic saccharification for switchgrass (SG).

pretreated switchgrass with >60 wt% xylan stripped off to the liquid stream.

The pretreated switchgrass was then rinsed with water to remove IL residue, and the washed switchgrass was collected for subsequent enzymatic saccharification. 3.4 kg (56.7 wt%) of pretreated switchgrass was recovered after washing, retaining 96.2 wt% of glucan, 35.7 wt% of xylan, 52.0 wt% of lignin and 40.2 wt% ash from the original switchgrass. Nearly half of the lignin was removed, which is beneficial for the following enzymatic hydrolysis. After 166 h enzymatic saccharification, 83.1 wt% of glucan and 30.7 wt% of xylan (based on carbohydrate content in the original biomass) were converted to monomeric sugars, and 25.8 wt% of original lignin was extracted to the hydrolysate. Lastly, pretreated switchgrass that had not been hydrolyzed by enzymes was separated from the hydrolysate through solid/liquid separation, and 402 g residue was obtained after drying. From the original switchgrass, about 1.7 wt% original glucan, 0.7 wt% original xylan, and 20.1 wt% original lignin were left unreacted in solid residue which is supposed to be the most recalcitrant portion of the plant cell wall. The mass balance also indicated some mass loss, likely due to the formation of other degradation products and mass during material handling (transfer, centrifugation, etc.).

3.6. Scale-up challenges

The combination of IL pretreatment and enzymatic catalysis has shown its advantage in being relatively feedstock agnostic, performing efficient delignification, converting biomass with high sugar yields and fast kinetics. However, challenges still exist prior to pilot scale demonstration. In general, biomass deconstruction and downstream conversion requires ILs to have excellent thermal stability, high extractability of the major biomass components (cellulose, hemicellulose or lignin), recyclability, and preferably low toxicity and low cost. As yet, there have been limited reports of IL-based pretreatment of biomass at larger scale (>1 L). The scale-up of IL-based biomass pretreatment is still in its early stage with numerous possibilities of IL structures and characteristics unidentified. In addition to the lack of knowledge on physicochemical properties and eco-toxicity, the expected difficulties of current process scale-up still exist in the material handling and product recovery.

Considering process economics, ILs have to be efficiently recycled and reused. The high production cost of ILs, relative to materials such as simple acid and base catalysts, is still one of the major impediments to IL utilization in cellulosic biorefineries [6]. Significant price differences (from 1 to 800 $/kg) exist in the IL market based on the IL structure and production scale [34]. The most influential factors that affect IL prices are industrial demand and prevailing scale of production. Identifying efficient and economically viable ILs is crucial for future research and commercialization. Researchers have made significant progress to date in this regard, including: reduction of the concentrations required for ILs and enzymes during biomass deconstruction [23,24], development of efficient IL recycling technologies [18,25], optimization of IL-tolerant enzyme cocktails [26–28], increasing solid loading during pretreatment and/or saccharification [29], employment of integrated systems approaches such as “one-pot” process configurations [30,31], development of more cost-effective ILs [32], and evaluation of process scale-up [33,34]. In IL manufacture, synthesis and purification are the major steps that affect IL properties. Solvent properties can also be tuned by selection of anions and cations for specific tasks. Lately, lignin and hemicellulose-derived compounds have also been used as starting materials for IL synthesis [35]. Some reported techno-economic analysis (TEA) models are useful to evaluate the economic impact of pretreatment processes and to identify process challenges or bottlenecks [36–39].

Generally, pretreatment processes always address and target high feedstock solid loadings to save solvent/catalyst cost and achieve high sugar titers. To date, there have been limited reports of potential ILs that can achieve high sugar yields with low IL/biomass ratio at lab scale. Most reported solid loadings have been in the range of 5–30 wt% and high purity and concentrations of ILs are needed. Based on our observation, the IL/feedstock slurry begins to challenge the reactor impeller and drive at solid loadings above 15 wt%.

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High purity ILs have a moderate to high viscosity at low temperatures compared to water-based solvents, which also contributes to torque burden. Thus, the appropriate reactor must be equipped with sufficient driving force to enable stirring the slurry with high solid loadings. Efficient mixing and mass/heat transferring are the keys to ensure even temperature of the slurry as well as to prevent biomass from overheating.

Moreover, the manufacturing material of the reactors, storage tanks, delivery and transport equipment such as pumps should be able to tolerate the pH of the ILs for long term usage, which could be highly acidic or basic especially at elevated temperatures. Some high quality stainless steel and alloy manufacturing equipment can meet this prerequisite. Studies on IL corrosion to metals are very limited. At high operating temperatures, the corrosion from ILs could be more severe. For example, a coupon testing of reactor metal has been carried out in a recent scale-up study of biomass pretreatments using two chloride-based ILs [33]. The study found that these ILs are more corrosive at elevated temperatures to hastelloy C-276.

The eco-toxicity and other hazards of most ILs remain unknown or unpublished and these chemicals will require environmental and occupational health and safety assessments for large scale process design. Furthermore, one of the general characteristics of ILs is their high electrical conductivity, which opened up their applications as electrolytes in batteries, double-layer capacitors or solar cells [40]. However, as a process solvent, the high conductivity of ILs can lead to electrical hazards. For example, ILs may penetrate into the electrodes, wires, circuit boards, and sockets if spilled, and the leakage of ILs to the electrical components may cause a short circuit or fire. From a safety standpoint, chemical resistant, heat resistant and waterproof cables should be considered in critical operating zones where IL exposure may occur.

It is reported that some ILs inhibit subsequent enzymatic saccharification and fermentation [41,42]. In the presence of ILs for biomass pretreatment, ILs can easily inactivate the enzymes [6]. Therefore, identifying ILs that can be tolerated by enzymes and fermentation microbes has become a new approach to the development of IL processes [31,43]. IL tolerance has also become a key factor in the genetic engineering of the strains that produce advanced bioproducts [44].

4. Conclusions

[C_2C_1Im][OAc] pretreatment of switchgrass has been successfully scaled up to 40 kg in this study. [C_2C_1Im][OAc] was proven to be efficient in delignification and has enhanced subsequent enzymatic saccharification in sugar conversions. High titers of fermentable sugars were obtained in the hydrolysate with limited presence of IL. Challenges and opportunities in the overall processes were discussed. Efforts are needed in the future to improve transitional processes such as material transfer, biomass recovery from aqueous IL stream, anti-solvent selection, IL recycling, and improvement of enzymes tolerance to ILs.

Conflict of interest

We declare that we have no conflict of interest.

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