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### Blending Municipal Solid Waste with Corn Stover for Sugar Production Using Ionic Liquid Process

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1                    **Blending Municipal Solid Waste with Corn Stover**  
2                    **for Sugar Production Using Ionic Liquid Process**

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20 **Abstract**

21 Municipal solid waste (MSW) represents an attractive cellulosic resource for sustainable fuel  
22 production. However, its heterogeneity is the major barrier to efficient conversion to biofuels.  
23 MSW paper mix was generated and blended with corn stover (CS). It has been shown that both  
24 of them can be efficiently pretreated in certain ionic liquids (ILs) with high yields of  
25 fermentable sugars. After pretreatment in 1-ethyl-3-methylimidazolium acetate  
26 ( $[\text{C}_2\text{C}_1\text{Im}][\text{OAc}]$ ), over 80% glucose has been released with enzymatic saccharification. We  
27 have also applied an enzyme-free process by adding mineral acid and water directly into the  
28 IL/biomass slurry to induce hydrolysis. With the acidolysis process in  
29 1-ethyl-3-methylimidazolium chloride ( $[\text{C}_2\text{C}_1\text{Im}]\text{Cl}$ ), up to 80% glucose and 90% xylose are  
30 released. There is a correlation between the viscosity profile and hydrolysis efficiency; low  
31 viscosity of the hydrolysate generally corresponds to high sugar yields. Overall, the results  
32 indicate the feasibility of incorporating MSW as a robust blending agent for biorefineries.

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34

35 **Keywords:** Mixed feedstocks, biomass pretreatment, municipal solid waste, paper mix, ionic  
36 liquid, acidolysis.

## 37 **1. Introduction**

38 Renewable energy technologies are being developed as new sources of fuels and power to meet  
39 our current and future energy needs. Lignocellulosic biomass is an important renewable  
40 source for production of biofuels and bio-products. Significant attention has been historically  
41 given to agriculturally-derived feedstocks; however a diverse range of wastes, including  
42 municipal solid wastes (MSW) also have potential to serve as feedstocks for the production of  
43 advanced biofuels due to its abundance and low cost (The Biomass Research and Development  
44 Board Report, 2008; Williams, 2007). Compared with the seasonal availability of agricultural  
45 wastes, MSW has the advantage of year-round availability, an established collection  
46 infrastructure and potential availability at negative cost (Williams, 2007). An efficient use of  
47 MSW would not only benefit biofuel industry but also reduce landfill disposal (Williams,  
48 2007). Recent reports projected that an estimated 44.5 million dry tons of MSW will be  
49 available in 2022 in the United States, among which paper mix is one of the major components,  
50 representing about 30% of total MSW (Environmental Protection Agency Report, 2010).  
51 Biomass feedstock costs remain a large contributor to biofuel production costs  
52 (Klein-Marcuschamer et al., 2010). The costs could be reduced by blending more expensive  
53 high quality feedstocks with lower cost, lower quality feedstocks such that the overall quality  
54 still meets specifications required by the biorefinery and the final costs are reduced (Thompson,  
55 2014).  
56 Among the various options of biomass pretreatment strategies, ionic liquid (IL) pretreatment  
57 with imidazolium-based ILs has been proven to be one of the most effective ways for biomass  
58 processing, primarily due to the efficient solubilization and perturbation of the major  
59 components of the plant cell wall, which makes the biomass structure amenable for  
60 downstream processing (Li et al., 2010; Sun et al., 2013; Xu et al., 2012). The conversion to  
61 sugars can be realized biologically by using commercial enzyme mixtures, or chemically by  
62 using mineral acid as a catalyst (Binder & Raines, 2010; Li et al., 2010). Enzymatic hydrolysis  
63 is frequently used for polysaccharide hydrolysis to monosaccharides after biomass  
64 pretreatment. However, the saccharification process takes as long as 2 to 3 days, and enzyme  
65 cost is the second highest contributor to material costs of the biofuel conversion process after

66 those associated with the feedstock input itself (Klein-Marcuschamer et al., 2010). Acidolysis  
67 in certain ILs has been reported as an enzyme-free process for biomass conversion (Binder &  
68 Raines, 2010). By using a direct injection of acid and water after IL pretreatment, both pentose  
69 and hexose are released from polysaccharides within 2-3 hours. The significant reduction of  
70 processing time would be a great benefit for biorefineries due to the increased productivity and  
71 significant cost reduction. In addition, there is no need for ionic liquid separation or  
72 solid-liquid separation before acidolysis. Our previous study showed up to 83% of glucose and  
73 99% of xylose liberation from switchgrass with the imidazolium chloride IL pretreatment  
74 followed by acidolysis (Sun et al., 2013). To date, there is no known published report on  
75 evaluating the performance of IL pretreatment for the processing of MSW and MSW blends. In  
76 this study, both enzymatic hydrolysis and dilute acid hydrolysis were evaluated in terms of  
77 sugar production from feedstock blends.

78

## 79 **2. Materials and Methods**

### 80 **2.1 Raw materials**

81 The paper waste materials, consisting of 15% glossy paper, 25% non-glossy paper, 31%  
82 non-glossy cardboard, and 28% glossy cardboard, were collected over the course of two weeks  
83 from one of the Idaho National Laboratory (INL) buildings and utilized to represent the MSW  
84 material in this study. The MSW paper material was shredded through a conventional office  
85 shredder and the cardboard material was cut into pieces with scissors. Each paper type was  
86 ground to 2 mm using a Thomas Scientific Model 4 Laboratory Wiley Mill (Thomas Scientific,  
87 Swedesboro, NJ). The corn stover was grown near Emmitsburgh (IA, USA) and was harvested  
88 in September 2010. Harvested corn stover was ground using a Vermeer BG480 grinder  
89 (Vermeer, IA, USA) designed for processing up to 4x4 ft bales. A 1-inch screen was used for  
90 these grinds. The MSW paper materials were then mixed with previously ground corn stover  
91 (CS) in different ratios. The IL [C<sub>2</sub>C<sub>1</sub>Im][OAc] (>95% purity) was purchased from BASF  
92 (Ludwigshafen, Germany). [C<sub>2</sub>C<sub>1</sub>Im]Cl (>97% purity) and 6 N hydrochloric acid were  
93 purchased from Sigma-Aldrich.

94

## 95 **2.2 Feedstock cost determination**

96 DOE has set a cost target of \$80/ton for feedstock delivered to the biorefinery. This target was  
97 developed to address barriers involved with commercializing logistics systems to be cost  
98 competitive with petroleum fuels. INL has developed several feedstock logistics models that  
99 calculate the costs associated with harvest and collection, storage, preprocessing, handling and  
100 transportation of feedstocks. The Biomass Logistics Model (BLM) simulating the flow of  
101 biomass throughout the entire supply chain and accounting for cost as different unit operations  
102 are applied. This model is used to evaluate supply chain designs in order to meet DOE targets.  
103 The BLM is an integrated model whose analytic engine is developed in the system dynamic  
104 software package Powersim<sup>TM</sup>. Additionally, the Least Cost Formulation Model (LCF)  
105 combines grower payment/access cost from the Billion Ton Update (BT2) with logistics costs  
106 from the BLM and feedstock quality characteristics from the Biomass Resource Library to  
107 estimate the total cost of feedstock to the throat of the biorefinery. The LCF model is  
108 developed in a simulation software package AnyLogic<sup>TM</sup>. The concept behind LCF is similar  
109 to the animal feed industry where the goal is to provide the least expensive combination of feed  
110 constituents (soybean meal, corn meal, etc.) while meeting nutrient requirements for desired  
111 animal growth. For example, the University of Georgia Athen's Windows User-Friendly Feed  
112 Formulation for Poultry and Swine (WUFFDA) model generates least cost animal feed  
113 formulations for desired feed ingredients. Where the feed industry pursues desired yield  
114 (animal weight gain) the biofuel industry's targets fuel production, both trying to minimize  
115 cost while maintaining performance. The LCF joins output of models and databases (BLM,  
116 BT2, Biomass Resource Library) to generate the delivered costs of feedstock formulations to  
117 direct research to help meet the \$80/ton target.

## 118 **2.3 Pretreatment in [C<sub>2</sub>C<sub>1</sub>Im][OAc] followed by enzymatic saccharification**

119 **Pretreatment** A 10% (w/w) biomass solution was prepared by combining 2 g of MSW or  
120 MSW/CS blends with 18 g of [C<sub>2</sub>C<sub>1</sub>Im][OAc] in a 50 mL Globe reactor (Syrris, UK). The  
121 reactor was heated to the desired temperature (140 °C, ramp time: 40 minutes) and stirred at  
122 300 rpm with a Teflon overhead stirrer. Following pretreatment, 60 mL of 95% ethanol was  
123 slowly added to the biomass/IL slurry with continued stirring. The mixture was transferred in  
124 to 50 mL Falcon tubes and centrifuged at high speed (14,000 rpm) to separate the solids.

125 Additional solids were collected from the supernatant by nylon mesh filtration (1 micron pore  
126 size), and the combined pretreated biomass was washed two additional times with 60 mL DI  
127 water to remove any residual IL. The solids were again filtered through 1 micron nylon mesh  
128 and stored at 4 °C for analysis.

129 **Enzymatic saccharification** Enzymatic saccharification of pretreated and untreated biomass  
130 was carried out at 50°C and pH 5.5 at 150 rpm in a rotary incubator (Enviro-Genie, Scientific  
131 Industries, Inc.) using commercial enzyme mixtures, Cellic® CTec2 (batch number  
132 VCN10001) and HTec2 (batch number VHN00001), obtained as a gift from Novozymes. The  
133 protein content of enzymes was determined by bicinchoninic acid (BCA) assay with a Pierce  
134 BCA Protein Assay Kit (Thermo Scientific) using BSA as protein standard. CTec2 has a  
135 protein content of  $186.6 \pm 2.0$  mg/mL, and protein content of HTec2 is  $180.1 \pm 1.8$  mg/mL  
136 protein (Socha et al., 2014). All reactions were conducted at 10% biomass loading by placing  
137 500 mg of biomass (dry weight) in a 25 mL centrifuge tube. The pH of the mixture was  
138 adjusted with 50 mM sodium citrate buffer (pH 4.8) supplemented with 0.02% (v/v)  $\text{NaN}_3$  to  
139 prevent microbial contamination. The total volume of 5 mL included a total protein content of  
140 20 mg protein/g glucan as determined by compositional analysis, with the volumetric ratio of  
141 CTec2:HTec2 = 9:1. Reactions were monitored by centrifuging 50  $\mu\text{L}$  aliquots of supernatant  
142 (5 min, 10,000 x g) in spin-filter centrifugal tubes with 0.45  $\mu\text{m}$  nylon filter at specific time  
143 intervals and measuring monomeric sugar concentrations by HPLC.

#### 144 **2.4 Acidolysis in $[\text{C}_2\text{C}_1\text{Im}]\text{Cl}$**

145 Biomass solutions were prepared by combining 3 g of biomass with 17 g  $[\text{C}_2\text{C}_1\text{Im}]\text{Cl}$  in a 100  
146 mL Globe reactor (Syrris, UK). The mixtures were programmed to be heated to different  
147 temperatures (120 °C, 140 °C, and 160 °C; ramp time: 30-40 minutes) and hold for 2 h. The  
148 solutions were then cooled down to the acidolysis temperature of 105 °C and acidolysis started  
149 after 15 min equilibration time. Acidolysis was performed following a procedure described  
150 previously (Sun et al., 2013). In summary, 2.07 mL 4 M HCl was added to the  
151 biomass- $[\text{C}_2\text{C}_1\text{Im}]\text{Cl}$  solution ( $t=0$ ) and with DI water added to give a  $\text{H}_2\text{O}$  concentration of 5%  
152 (w/w) of the total weight. More water (3.175 mL) was added at 10 min to get the targeted  
153 water concentration of 20%. Water was injected into the mixture starting from 15 min at the  
154 rate of 227.5  $\mu\text{L}/\text{min}$  for 45 min. Acidolysis was continued for a total of 2.5 h and stopped by

155 cooling down the reactor to room temperature. Time points were taken every 30 min during  
156 acidolysis to monitor sugar yield by HPLC.

## 157 **2.5 Analysis and characterization methods**

158 **Moisture analysis** Moisture content of pretreated biomass was quantified using a moisture  
159 content analyzer (Mettler Toledo, Model HB43-S Halogen) by heating to 105 °C and  
160 monitoring the mass until it remained constant.

161 **Biomass composition and sugar hydrolysate analysis** Compositional analysis before and  
162 after pretreatment was determined using NREL acidolysis protocols (LAP) LAP-002 and  
163 LAP-005 (Sluiter, 2004). Briefly, 200 mg of biomass and 2 mL 72% H<sub>2</sub>SO<sub>4</sub> were incubated at  
164 30 °C while shaking at 300 rpm for 1 h. The solution was diluted to 4% H<sub>2</sub>SO<sub>4</sub> with 56 mL of  
165 DI water and autoclaved for 1 h at 121 °C. The reaction was quenched by placing the samples  
166 into an ice bath before removing the biomass by filtration. Carbohydrate concentrations were  
167 determined from the filtrate by Agilent HPLC 1200 Series equipped with a Bio-Rad Aminex  
168 HPX-87H column and a Refractive Index detector, and acid insoluble lignin was quantified  
169 gravimetrically from the solid biomass after heating overnight at 105 °C.

170 **Rheology analysis** A stress controlled Malvern Kinexus Rheometer (Worcestershire, UK)  
171 with 40 mm diameter parallel plate geometry was used to measure the viscosity and phase  
172 angle of all materials. The materials were refrigerated immediately after treatments and  
173 thawed to room temperature prior to performing viscosity studies. All viscosity measurements  
174 were conducted at 25°C at varying shear rate from 0 to 150 s<sup>-1</sup>. Gap heights of 2 to 5 mm were  
175 set for acidolysis and pretreated solids, respectively, to engage the materials between the plates  
176 for accurate measurements. Care was taken to avoid air bubbles trapped in the sample. Also,  
177 bulging of the sample on the edges of the plates was ensured to avoid end effects. Clear drop in  
178 viscosity was observed with increasing shear rate in all samples. Accordingly, the tested  
179 portion of the samples were discarded and not re-used for further measurements due to lack of  
180 confidence in material integrity.

181

## 182 **3. Results and discussions**

183 **Least Cost Formulation for CS/MSW blends** Figure 1a shows predicted delivered feedstock

184 costs for corn stover from the LCF model assuming 2017 state of technology with projected  
185 supply chain costs and resource availability(INL/EXT-13-30342, 2013)(INL/EXT-13-30342,  
186 2013)(INL/EXT-13-30342, 2013). Areas shown in light blue are approximately \$80/ton,  
187 capable of meeting DOE targets, but only a few locations exist, all of which are in high  
188 productivity corn growing areas. To sustain a national scale biorefining industry, more  
189 locations need to be capable of meeting the DOE biomass cost target. INL has been exploring  
190 the concept of blending lower cost feedstock to reduce overall feedstock costs while  
191 maintaining quality specifications required by the biorefinery. The LCF model integrates  
192 individual feedstock logistics costs and grower payment/access fees from models developed  
193 previously (BLM, BT2) to determine the formulated cost for a blend in a given region of the  
194 U.S. Figures 1b and 1c show the delivered feedstock costs for CS:MSW blends of 80:20, and  
195 50:50. For the other blend ratios (90:10, 70:30, and 60:40) the costs are shown in Figure 1S.  
196 As can be seen, as the amount of MSW increases, more areas have feedstock available at  
197 \$80/ton or less including areas outside of the traditional Midwest Corn Belt. The high  
198 availability of MSW near large cities in the Midwest provides states like Illinois, Indiana, Ohio  
199 and Michigan with sufficient biomass resources to support biorefinery development.  
200 The other key aspect of blending is whether or not the blend meets quality specifications  
201 needed for efficient conversion. Using the CS and MSW compositions in Table 1, the various  
202 blends of corn stover and MSW would yield ash and sugar specifications shown in Table 2.  
203 Since the sugar composition (glucan + xylan) of the corn stover and MSW are very similar, the  
204 sugar compositions of the blends do not vary much. However, the ash changes from 3.8% for  
205 the 90:10 blend to 7.0% for the 50:50 blend. Although all of the blends meet the cost target,  
206 they may not all meet the required biorefinery specification target and those factors need to be  
207 considered as well. For example, if a biorefinery ash target was set at 5%, then only the 90:10  
208 and 80:20 blends should be considered. If that target could be relaxed, then more areas of the  
209 U.S. would have sufficient biomass.

210 **[C<sub>2</sub>C<sub>1</sub>Im][OAc] pretreatment** Reports using [C<sub>2</sub>C<sub>1</sub>Im][OAc] to pretreat biomass have  
211 typically used temperatures between 120-160°C and time intervals of 1-3 h to achieve high  
212 sugar yields. (Li et al., 2010; Sun et al., 2014) In the present study we chose 140 °C for 3 h to

213 get an initial evaluation of the convertibility of MSW or MSW blend (CS/MSW=1:1). Table 1  
214 shows compositional analysis before and after IL pretreatment. Three of the major plant cell  
215 wall components, glucan, xylan, and acid-insoluble lignin, were monitored before and after  
216 pretreatment. Solid recovery refers to the mass percentage of biomass (dry weight) recovered  
217 from the original biomass load. After washing, 72% of the corn stover, 77% of the CS/MSW  
218 (1:1) blend and 93% of the MSW was recovered. We hypothesize that the higher recovery of  
219 MSW is due to the high content of glucan in MSW and [C<sub>2</sub>C<sub>1</sub>Im][OAc] pretreatment mainly  
220 removes lignin and hemicelluloses (Sun et al., 2014). After pretreatment, the glucan loading  
221 increased with decreased lignin content for both CS and MSW/CS (1:1). After pretreatment of  
222 MSW, the compositions of the major components remain similar compared to the raw starting  
223 material. As shown in Figure 2, a significant amount of lignin (78%) initially present in the CS  
224 has been removed after pretreatment. However, only 9.2% lignin was removed from MSW.  
225 We attribute this difference to the nature of the lignin in these two feedstocks. For MSW, the  
226 paper mix has already gone through a pulping process that removed most of the lignin from the  
227 biomass, as verified by the compositional analysis of the starting material. The remaining  
228 lignin structure is thus expected to be more recalcitrant compared to the intact lignin in CS,  
229 thus more difficult to be removed.

230 To compare glucan digestibility, enzymatic hydrolysis of untreated and pretreated biomass was  
231 carried out using commercial enzyme cocktails, Novozymes Cellic® CTec2 and HTec2. For  
232 each sample, enzyme loadings were normalized to glucan content as determined by  
233 compositional analysis. Pretreated samples were used without drying, and solid loading (as 10%  
234 dry weight in the hydrolysis slurry) was calculated based on moisture content determined for  
235 each sample. Glucan and xylan yields after 72 h are plotted in Figure 3. After IL pretreatment,  
236 significantly faster saccharification rates and higher sugar yields were achieved for all the three  
237 feedstocks. All glucose yields (calculated based on the glucan present in pretreated biomass)  
238 were above 90% with final glucose concentrations reaching 50 g/L. Most glucan to glucose  
239 conversion was complete after 24 h of enzymatic hydrolysis. Xylan conversion was also  
240 significantly improved with relatively lower yields compared to glucose, primarily due to  
241 hemicellulose solubilization during pretreatment. The mass balance of the

242 pretreatment/hydrolysis process is shown in Figure 3. After pretreatment 78.1% lignin, 8.9%  
 243 xylan and 11.7% glucan was removed from CS; 5.9% lignin, 0.9% xylan and 15.2% glucan  
 244 was removed from MSW; and 58.8% lignin, 27.6% xylan and 7.1% glucan was removed from  
 245 MSW/CS (1:1) blend. More xylan removal and less glucan removal were unexpected with  
 246 MSW/CS blend compared to the two biomass feedstocks individually, which may be due to the  
 247 rheology change after blending with CS (discussed in later section). Overall, 82.5% glucose  
 248 yield and 43.4% xylose yield were obtained for CS; 81.9% glucose yield and 75.2% xylose  
 249 yield were obtained for MSW; and 84.0% glucose yield and 40.0% xylose yield were obtained  
 250 for MSW/CS blends (yields calculated based on the glucan or xylan in original biomass).  
 251 These results show that IL pretreatment is efficient for MSW as well as MSW/CS blends, and  
 252 the pretreated materials are readily to be converted to sugar using commercial cellulolytic  
 253 enzyme. Figure 2S showed the powder X-ray diffractograms

254 **Acidolysis in [C<sub>2</sub>C<sub>1</sub>Im]Cl** To test the feasibility of chemical conversion of MSW blends,  
 255 one-pot sugar conversion using mineral acid (HCl) has been carried out in the IL [C<sub>2</sub>C<sub>1</sub>Im]Cl.  
 256 [C<sub>2</sub>C<sub>1</sub>Im]Cl instead of [C<sub>2</sub>C<sub>1</sub>Im][OAc] was used for acidolysis process since there is no anion  
 257 exchange with the acid (HCl) used in the hydrolysis step. Different pretreatment temperatures  
 258 and blending ratios were attempted to test the effect of conversion. The results are shown in  
 259 Figure 4 and Table 1S. The sugar yields obtained after pretreatment and hydrolysis were  
 260 calculated using Eq. 1:

$$261 \quad \text{Yield \%} = \frac{C_{sup} \times M_{sup}}{W \times C \times f} \times 100\% \quad (1)$$

262 where,  $C_{sup}$  is the sugar concentration of the supernatant (w/w),  $M_{sup}$  is the mass of the  
 263 supernatant,  $W$  is the weight of the biomass,  $C$  is the percentage of glucan or xylan contained in  
 264 the biomass, and  $f$  is the factor to convert glucan or xylan to glucose or xylose (1.11 for glucan  
 265 and 1.136 for xylan). After pretreatment at 120 °C, neither MSW nor corn stover dissolved  
 266 well in [C<sub>2</sub>C<sub>1</sub>Im]Cl, resulting in low glucose yield (< 15%). Xylose yields are higher since  
 267 xylan is easier to dissolve compared to glucan (Sun et al., 2013). Based on these observations,  
 268 dissolution or swelling of the cell wall seems essential for the following hydrolysis step. With  
 269 increasing pretreatment temperature, the glucose yields after acidolysis increased dramatically

270 (13.5% to 69.6% for CS, 32.5% to 60.5% for CS:MSW=3:1, 37.3% to 73.5% for  
271 CS:MSW=1:1, and 12.5% to 74.7% for MSW). The sugar yields generally increase as a  
272 function of incubation time, with a maximum observed at 150 minutes. The increases in sugar  
273 yields are more significant after pretreatment at lower temperatures (i.e. 6.7% to 13.5% for CS  
274 pretreated at 120 °C vs. 67.5% to 69.6% for CS pretreated at 160 °C). For pretreated CS/MSW  
275 blends (3:1), the sugar yields were maximized after incubation for 90 (pretreated @ 160 °C) or  
276 120 (pretreated @ 140 °C) minutes. The highest glucose (80.6%) and xylose (90.8%) yields  
277 are obtained after pretreatment of MSW at 140 °C for 2 h. For the MSW/CS blends, the yields  
278 are observed to decrease overall, with highest sugar production of 79.4% for glucose and 64.1%  
279 for xylose with equal mass blending of MSW and CS and pretreated at 140 °C for 2 h. With  
280 more CS blended in (CS:MSW = 3:1) the sugar yields further decreases, and the optimal  
281 conditions obtained with pretreatment at 160 °C for 2 h and acidolysis for 90 minutes. Thus,  
282 with more CS blending into the feedstock, higher temperature pretreatment is preferred for  
283 glucose production while xylose yields dropped, possibly due to the degradation of xylose.  
284 Overall both MSW and MSW/CS blends can be efficiently converted to sugars through either  
285 chemical pathway (acidolysis) or biological pathway (enzymatic sacchrification). Both of the  
286 two approaches involve biomass pretreatment for the first step to overcome the biomass  
287 recalcitrance. The pretreatment efficiency is highly dependent on the pretreatment conditions  
288 such as temperature and time. Under the optimized conditions, the sugar yields of MSW for  
289 enzymatic hydrolysis is 81.9% for glucose and 75.2% for xylose; while 80.6% glucose and  
290 90.8% xylose yields are obtained for acidolysis. Thus, these two approaches have similar  
291 performance for sugar production from MSW and MSW/CS blends with acidolysis process  
292 superior in terms of xylose release.

293 **Rheology.** The rheological properties of pretreated MSW, CS, and MSW/CS blends from two  
294 IL pretreatment processes were assessed to gain further insight into the deconstruction process.  
295 Figure 5 shows the viscosity profiles of the biomass materials after  $[C_2C_1Im]Cl$  pretreatment  
296 (PT, Figure 5a) as well as  $[C_2C_1Im]Cl$  pretreatment and acidolysis (PT+AD, Figure 5b). The  
297 viscosities of the solids after  $[C_2C_1Im][OAc]$  pretreatment and washing with water (PT+WS)  
298 are shown in Figure 3S.

299 Upon  $[C_2C_1Im]OAc$  pretreatment and washing (PT+WS), MSW showed highest viscosity

300 compared to MSW/CS blends (1:1) and CS. Decrease of MSW reduces the viscosity by 62%  
301 (42.0 vs 16.1 Pa.s at 100s<sup>-1</sup>). Solids recovered from all samples of PT and PT+WS treatments  
302 behaved visco-elastic with a dominant elastic component (~10 degree Phase Angle). The  
303 solid-like behavior from biomass probably emanated from the polymeric form of cellulose  
304 after PT and PT+WS.

305 After [C<sub>2</sub>C<sub>1</sub>Im]Cl pretreatment, MSW (PT) showed higher viscosity levels than CS (PT) but  
306 both MSW/CS blends at 1:1 and 1:3 ratios (PT) showed similar and somewhat of an  
307 intermediate viscosity profile between those of MSW and CS. Although corn stover itself was  
308 not easily pretreated and saccharified, addition of corn stover in MSW helped lowering  
309 viscosity of the reaction mixture in the pretreatment stage, allowing better mass transfer  
310 between acid and dissolved cellulose, thus results in better hydrolysis of the convertible  
311 fraction as evidenced in high glucose release from 3:1 or 1:1 blending ratios after pretreatment  
312 at 120 °C for the MSW/CS blends (32.5% for the blend CS:MSW=3:1 and 37.3% for the blend  
313 CS:MSW=1:1 vs. 13.5% for CS and 12.5% for MSW). As expected, acidolysis step converts  
314 polymeric cellulose/hemicellulose to monomeric glucose/xylose and accordingly changes the  
315 rheological behavior as well. The viscosities of both CS and MSW dropped from 9.0 (CS, PT)  
316 and 78.5 (MSW, PT) to 0.51 (CS, PT+AD) and 0.30 Pa.s (MSW, PT+AD) at 100s<sup>-1</sup>. MSW  
317 after pretreatment and acidolysis has lower viscosity than CS, which can be correlated with  
318 their sugar conversions as MSW has the highest glucose and xylose release (80.6% for glucose  
319 and 90.8% for xylose) compared to CS that has much lower conversion (29.2% for glucose and  
320 55.8% for xylose). At this stage, the samples are very liquid-like (90 degree phase angle) and  
321 were pumpable beyond 6 Pa stress (yield stress). The most interesting results came from the  
322 sample of MSW/CS blends (PT+AD), where 1:1 blend (PT+AD) had the similar viscosity with  
323 CS (PT+AD); however, 1:3 blend (PT+AD) had the lowest viscosity level of 0.15 Pa.s at 100  
324 s<sup>-1</sup>. It is unclear why the blends' viscosity didn't follow the trend as their sugar releases, and  
325 merits further investigations.

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#### 329 **4. Conclusions**

330 MSW can be blended into corn stover (CS) providing lower cost biorefinery feedstock inputs  
331 that are easily pretreated using the IL pretreatment technology. After pretreatment in  
332 [C<sub>2</sub>C<sub>1</sub>Im][OAc], up to 84% glucose and 75% xylose are released. Pretreatment in [C<sub>2</sub>C<sub>1</sub>Im]Cl  
333 followed by acidolysis is also efficient with maximums of 80% glucose yield and 90% xylose  
334 yield. Although MSW gives the highest sugar yields, the viscosity of the slurry after  
335 pretreatment was high. Blending CS with MSW helps to decrease the viscosity making the  
336 mixture more transferable. The results suggest the great potential to use MSW for biofuel  
337 production while maintaining performance and lowering costs.

338

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347 **References**

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390 **Table 1.** Chemical composition<sup>a</sup> before and after IL pretreatment  
 391

Feedstock		Glucan, %	Xylan, %	Lignin <sup>c</sup> , %	Ash, %
Corn stover	raw	33.2±1.0	20.8±0.04	18.7±1.5	3.0±0.3
	pretreated	40.7±4.0	26.2±2.2	5.7±0.8	9.6±0.5
MSW paper mix	raw	55.8±5.0	10.0±1.4	11.9±0.3	10.9±1.3
	pretreated	52.6±7.2	11.0±1.1	12.0±1.7	6.8±0.3
CS/MSW (1:1)	raw	46.0±3.1	17.3±1.0	16.0±0.6	7.5±0.5
	pretreated	55.8±6.4	16.3±0.4	8.6±1.2	7.6±0.6

392 <sup>a</sup> Values represent the average and standard deviation of each component on the basis of dry  
 393 materials.

394 <sup>b</sup> Klason (acid insoluble) lignin based on NREL LAPs.

395

396 **Table 2.** Ash and sugar compositions of CS/MSW blends

CS/MSW	Ash (%)	Glucan (%)	Xylan (%)	Glucan+Xylan (%)
90:10	3.8	35.5	19.7	55.2
80:20	4.6	37.7	18.6	56.3
70:30	5.4	40.0	17.6	57.6
60:40	6.2	42.2	16.5	58.7
50:50	7.0	44.5	15.4	59.9

397 \* numbers in this table are the theoretical calculation based on the compositions of corn  
 398 stover and MSW paper mix

399 **Figure legends**

400

401 **Figure 1.** Delivered feedstock costs for a) corn stover, b) 80% CS and 20% MSW blend and  
402 c) 50% CS and 50% MSW blend

403

404 **Figure 2.** Mass balance of the pretreatment process followed by enzymatic hydrolysis.

405

406 **Figure 3.** Glucose (a) and xylose (b) yields before and after IL pretreatment and enzymatic  
407 saccharification.

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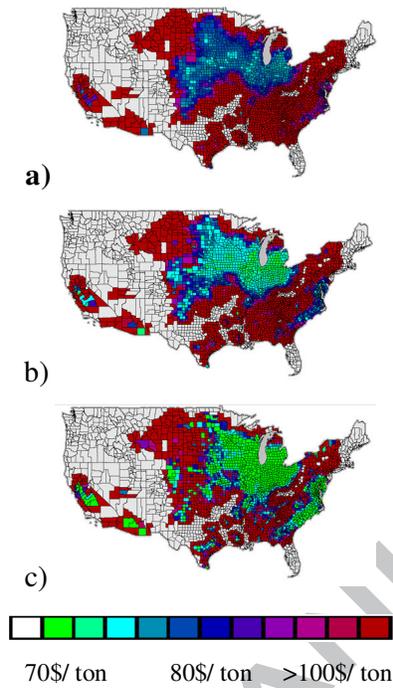
409 **Figure 4.** Glucose and xylose yields after pretreatment and acidolysis of corn stover (CS), municipal solid  
410 waste (MSW), and their blends with different ratios (1:1 and 1:3).

411

412 **Figure 5.** Viscosity profiles of municipal solid waste (MSW), corn stover (CS), and their  
413 blends from the [C<sub>2</sub>C<sub>1</sub>Im]Cl process, PT: after pretreatment at 140 °C, and PT+AD: after  
414 pretreatment at 140 °C followed by acidolysis at 105 °C.

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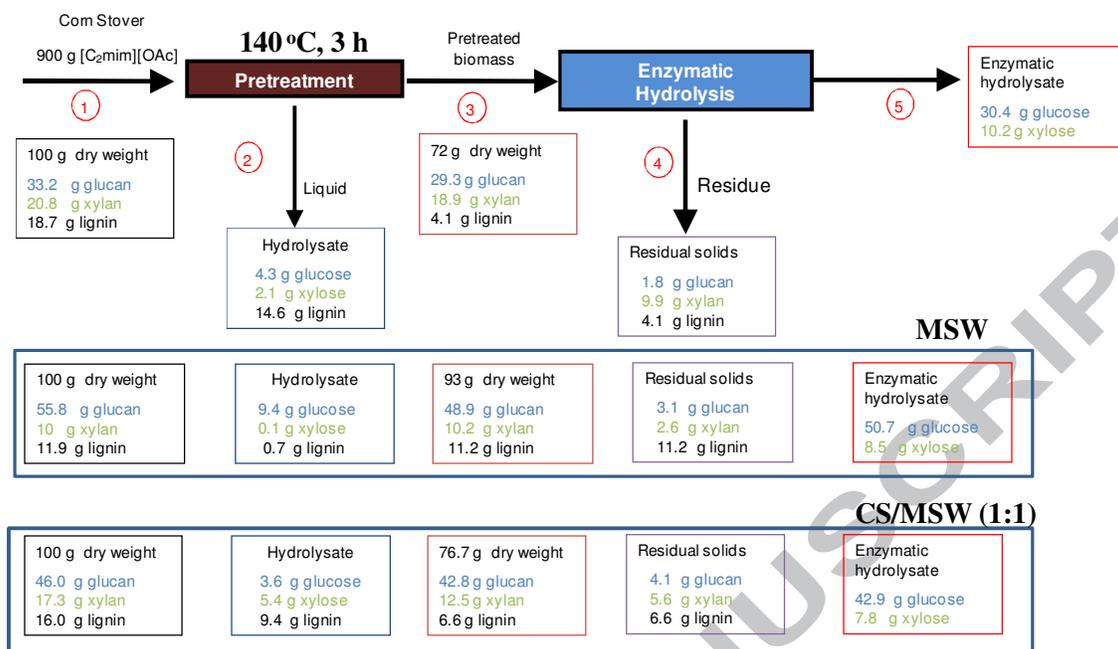
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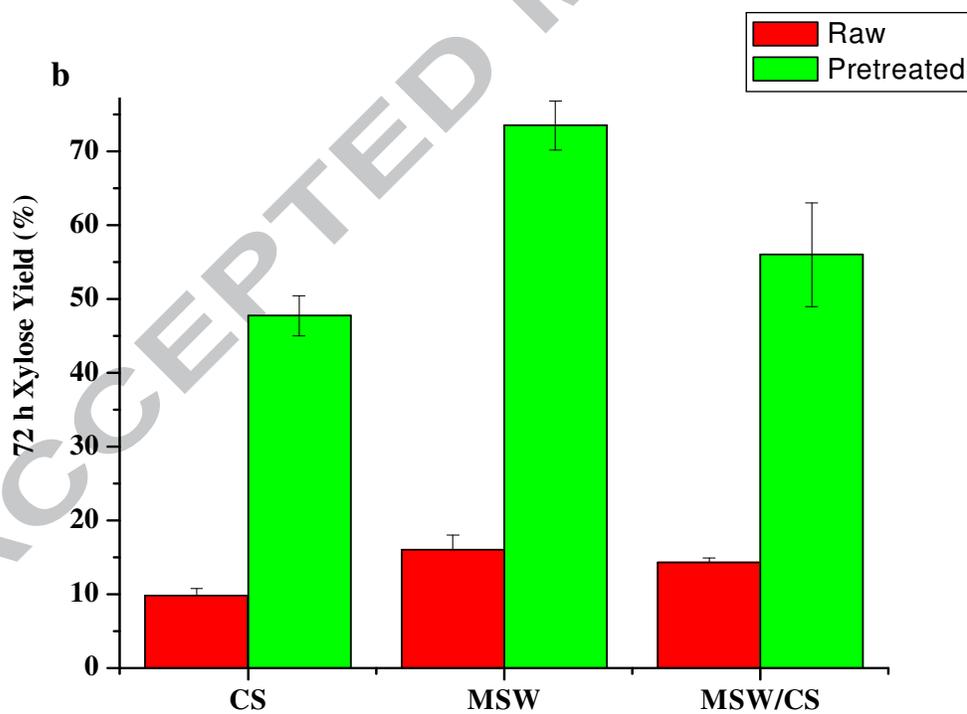
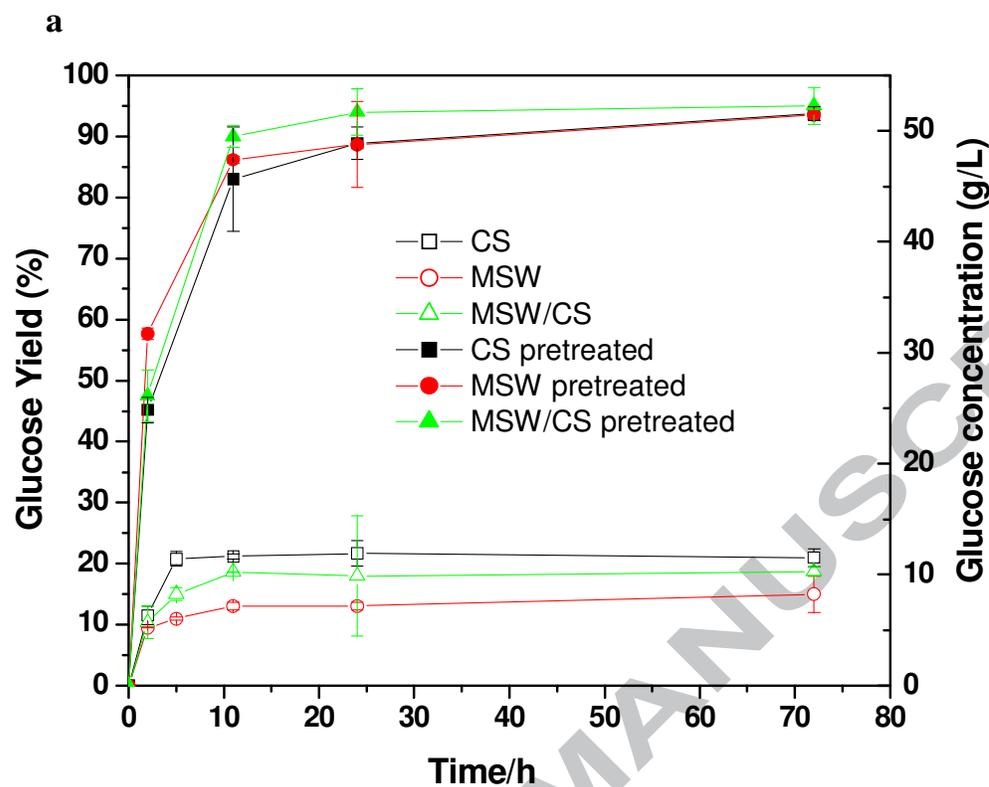
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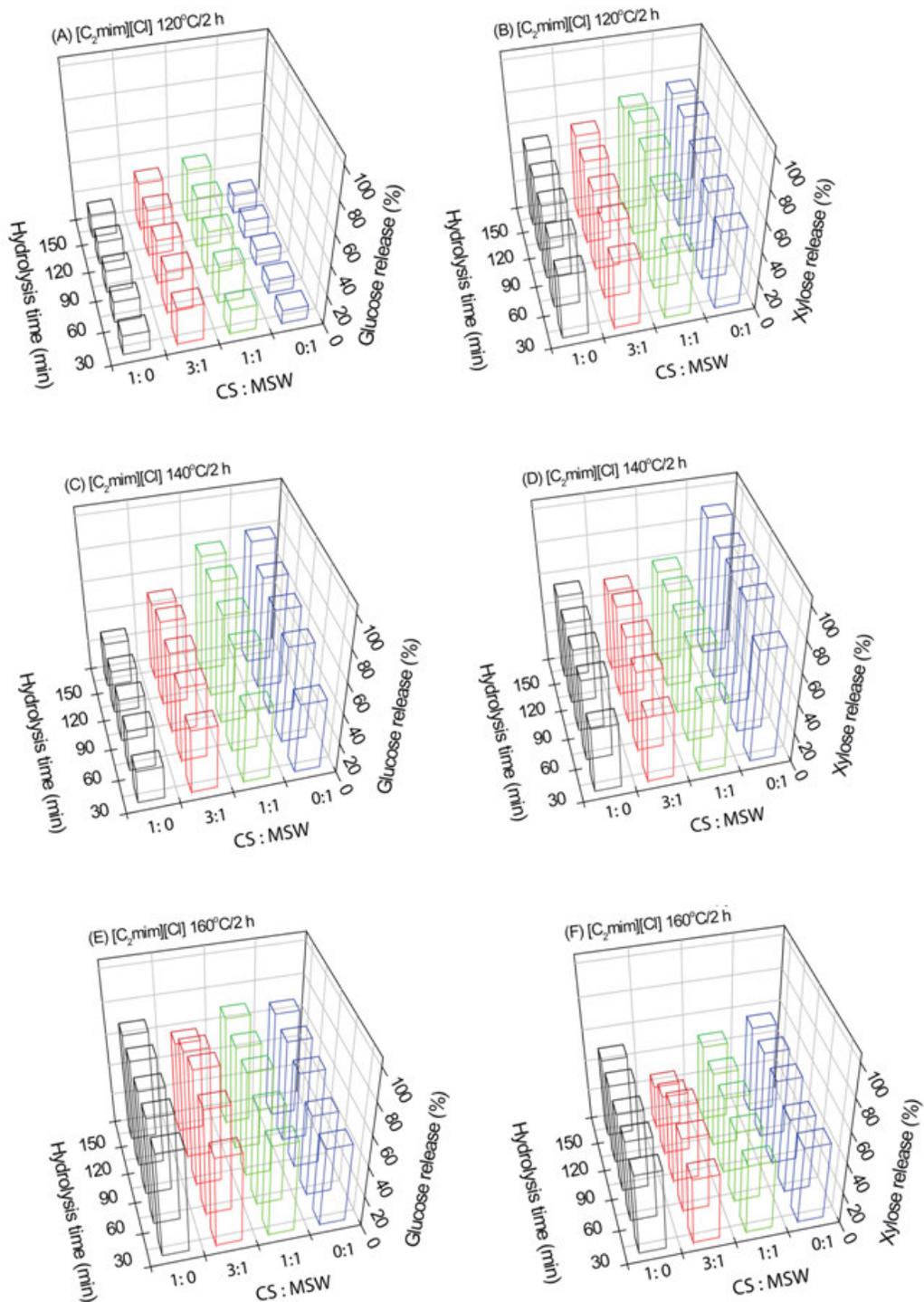
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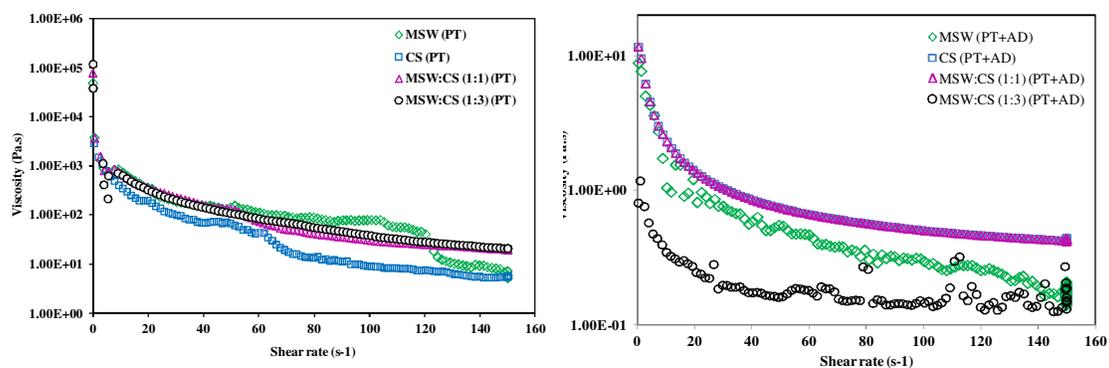
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428

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 434 pretreatment at 140 °C followed by acidolysis at 105 °C.

435

436

- 437      • Blending in municipal solid waste (MSW) decreases the feedstock cost
- 438      • MSW and its blends can be efficiently pretreated in certain ionic liquids
- 439      • Blending corn stover with MSW helps to decrease the viscosity

440

ACCEPTED MANUSCRIPT