

Accepted Manuscript

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

Ning Sun, Feng Xu, Noppadon Sathitsuksanoh, Vicki S Thompson, Kara Cafferty, Chenlin Li, Deepti Tanjore, Akash Narani, Todd R. Pray, Blake A. Simmons, Seema Singh

PII: S0960-8524(15)00273-4
DOI: <http://dx.doi.org/10.1016/j.biortech.2015.02.087>
Reference: BITE 14660

To appear in: *Bioresource Technology*

Received Date: 12 December 2014
Revised Date: 20 February 2015
Accepted Date: 21 February 2015

Please cite this article as: Sun, N., Xu, F., Sathitsuksanoh, N., Thompson, V.S., Cafferty, K., Li, C., Tanjore, D., Narani, A., Pray, T.R., Simmons, B.A., Singh, S., Blending Municipal Solid Waste with Corn Stover for Sugar Production Using Ionic Liquid Process, *Bioresource Technology* (2015), doi: <http://dx.doi.org/10.1016/j.biortech.2015.02.087>

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.



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

3
4 Ning Sun,^a Feng Xu,^{a,b} Noppadon Sathitsuksanoh,^a Vicki S Thompson,^c Kara Cafferty,^d
5 Chenlin Li,^e Deepti Tanjore,^e Akash Narani,^e Todd R. Pray,^e Blake A. Simmons^{a,b} and Seema
6 Singh^{*a,b}

7
8 ^aDeconstruction Division, Joint BioEnergy Institute, Lawrence Berkeley National Laboratory,
9 Berkeley, CA, USA

10 ^bBiological and Materials Sciences Center, Sandia National Laboratories, Livermore, CA,
11 USA

12 ^cIdaho National Laboratory, Biological and Chemical Processing Department, Idaho Falls, ID,
13 USA

14 ^dIdaho National Laboratory, Environmental Engineering and Technology, Idaho Falls, ID,
15 USA

16 ^eAdvanced Biofuel Process Demonstration Unit, Lawrence Berkeley National Laboratory,
17 Berkeley, CA, USA

18
19

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.

33

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 [C₂C₁Im][OAc] (>95% purity) was purchased from BASF
92 (Ludwigshafen, Germany). [C₂C₁Im]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 PowersimTM. 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 AnyLogicTM. 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 [C₂C₁Im][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 [C₂C₁Im][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 ± 2.0 mg/mL, and protein content of HTec2 is 180.1 ± 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) 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 μL aliquots of supernatant
142 (5 min, 10,000 x g) in spin-filter centrifugal tubes with 0.45 μm 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 H_2O 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% H₂SO₄ were incubated at
164 30 °C while shaking at 300 rpm for 1 h. The solution was diluted to 4% H₂SO₄ 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⁻¹. 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 exists, 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 **[C₂C₁Im][OAc] pretreatment** Reports using [C₂C₁Im][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 [C₂C₁Im][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 [C₂C₁Im]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 [C₂C₁Im]Cl.
 256 [C₂C₁Im]Cl instead of [C₂C₁Im][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 [C₂C₁Im]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⁻¹). 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 [C₂C₁Im]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⁻¹. 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⁻¹. It is unclear why the blends' viscosity didn't follow the trend as their sugar releases, and
325 merits further investigations.

326

327

328

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 [C₂C₁Im][OAc], up to 84% glucose and 75% xylose are released. Pretreatment in [C₂C₁Im]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

339 **Acknowledgments**

340 The enzyme mixtures used in this study were obtained as a gift from Novozymes. This work
341 was supported by funding from the DOE Energy Efficiency and Renewable Energy's
342 BioEnergy Technology Office. The portion of the work conducted by the Joint BioEnergy
343 Institute was supported by the Office of Science, Office of Biological and Environmental
344 Research, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

345

346

347 **References**

348

349

350

351

352

353

354

355

356

357

358

359

360

361

362

363

364

365

366

367

368

369

370

371

372

373

374

375

376

377

378

379

380

381

382

383

384

385

386

387

388

389

1. Binder, J., Raines, R. 2010. Fermentable sugars by chemical hydrolysis of biomass. *PNAS*, 107, 4516-4521.
2. Environmental Protection Agency Report, 2010. Renewable Fuel Standard Program - Regulatory Impact Analysis p53.
3. INL/EXT-13-30342. 2013. Feedstock Supply System Design and Economics for Conversion of Lignocellulosic Biomass to Hydrocarbon Fuels
[https://inlportal.inl.gov/portal/server.pt/gateway/PTARGS_0_6663_148104_0_0_18/Feedstock%20Joule_Biochem%20Design_Draft_Final_v2%20\(4\).pdf](https://inlportal.inl.gov/portal/server.pt/gateway/PTARGS_0_6663_148104_0_0_18/Feedstock%20Joule_Biochem%20Design_Draft_Final_v2%20(4).pdf) Last accessed 10/06/2014.
4. Klein-Marcuschamer, D., Oleskowicz-Popiel, P., Simmons, B.A., Blanch, H.W. 2010. Technoeconomic analysis of biofuels: A wiki-based platform for lignocellulosic biorefineries. *Biomass Bioenergy*, 34, 1914-1921.
5. Li, C., Knierim, B., Manisseri, C., Arora, R., Scheller, H.V., Auer, M., Vogel, K.P., Simmons, B.A., Singh, S. 2010. Comparison of dilute acid and ionic liquid pretreatment of switchgrass: Biomass recalcitrance, delignification and enzymatic saccharification. *Bioresour. Technol.*, 101, 4900-6.
6. Sluiter, A. 2004. Determination of structural carbohydrates and lignin in biomass. National Renewable Energy Laboratory (NREL) Analytical Procedures.
7. Socha, A.M., Parthasarathi, R., Shi, J., Pattathil, S., Whyte, D., Bergeron, M., George, A., Tran, K., Stavila, V., Venkatachalam, S. 2014. Efficient biomass pretreatment using ionic liquids derived from lignin and chemically. *PNAS*, 111, E3587-E3595.
8. Sun, N., Liu, H., Sathitsuksanoh, N., Stavila, V., Sawant, M., Bonito, A., Tran, K., George, A., Sale, K.L., Singh, S. 2013. Production and extraction of sugars from switchgrass hydrolyzed in ionic liquids. *Biotechnol. Biofuels*, 6, 1-15.
9. Sun, N., Parthasarathi, R., Socha, A.M., Shi, J., Zhang, S., Stavila, V., Sale, K.L., Simmons, B.A., Singh, S. 2014. Understanding pretreatment efficacy of four cholinium and imidazolium ionic liquids by chemistry and computation. *Green Chem.*, 16, 2546-2557.
10. The Biomass Research and Development Board Report, 2008. Increasing Feedstock Production for Biofuels: Economic Drivers, Environmental Implications, and the Role of Research.
http://www.esd.ornl.gov/eess/8_Increasing_Biofuels_Feedstock_Production.pdf. Last accessed 2/12/15.
11. Thompson, V.S.R., Allison E., Sun, Ning; Singh, Seema; Simmons, Blake A. 2014. Assessment of municipal solid waste as a blend feedstock to lower biomass feedstock costs. 36th Symposium on Biotechnology for Fuels and Chemicals. April 28-May 1, 2014, Clearwater Beach, FL.
12. U.S. Department of Energy. 2011. U.S. Billion-Ton Update: Biomass Supply for a Bioenergy and Bioproducts Industry. R.D. Perlack and B.J. Stokes (Leads), ORNL/TM-2011/224. Oak Ridge National Laboratory, Oak Ridge, TN. 227p.
13. Williams, R.B. 2007. Biofuels from Municipal Wastes- Background Discussion Paper
<http://energy.ucdavis.edu/files/05-13-2013-2007-cbc-biofuels-from-municipal-solid-waste-background-paper.pdf> Last accessed 2/12/15.
14. Xu, F., Shi, Y.-C., Wang, D. 2012. Enhanced production of glucose and xylose with partial dissolution of corn stover in ionic liquid, 1-Ethyl-3-methylimidazolium acetate. *Bioresour. Technol.*, 114, 720-724.

390 **Table 1.** Chemical composition^a before and after IL pretreatment
 391

Feedstock		Glucan, %	Xylan, %	Lignin ^c , %	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 ^a Values represent the average and standard deviation of each component on the basis of dry
 393 materials.

394 ^b 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.

408

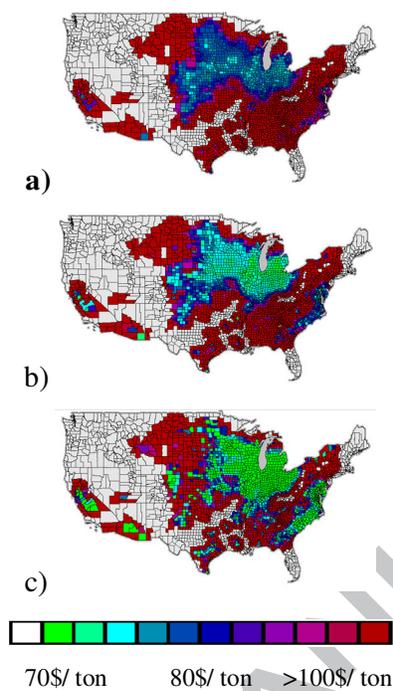
409 **Figure 4.** Glucose and xylose yields after pretreatment and acidolysis of corn stover (CS), municipal solid
410 waste (MSW), and their blends with different ratios (1:1 and 1:3).

411

412 **Figure 5.** Viscosity profiles of municipal solid waste (MSW), corn stover (CS), and their
413 blends from the $[C_2C_1Im]Cl$ process, PT: after pretreatment at 140 °C, and PT+AD: after
414 pretreatment at 140 °C followed by acidolysis at 105 °C.

415

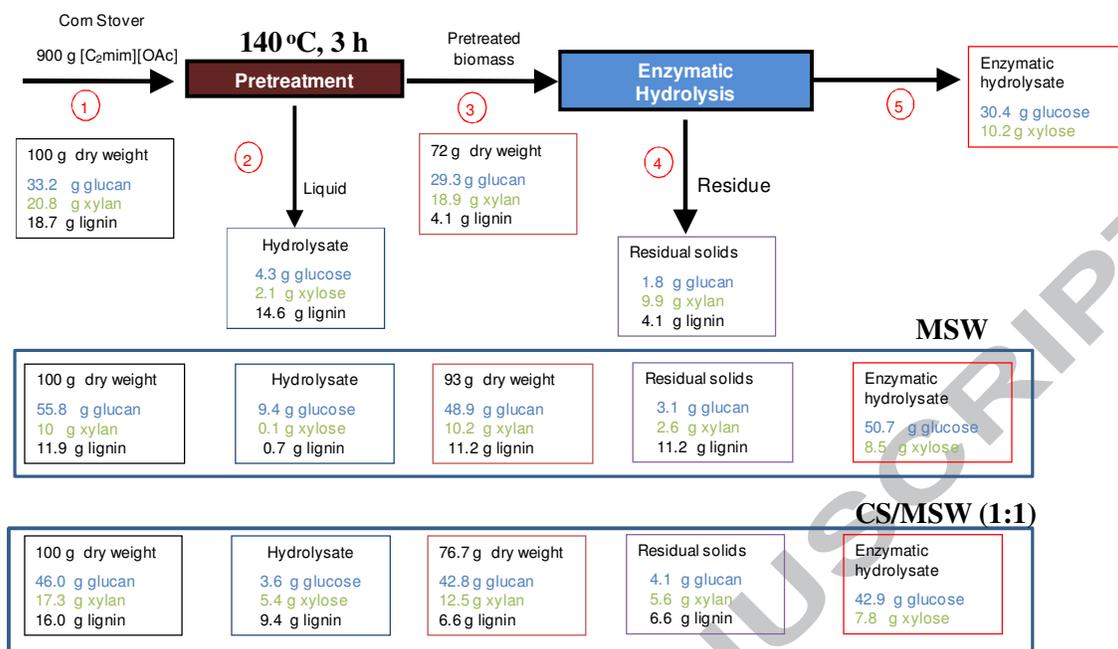
416



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

418 c) 50% CS and 50% MSW blend

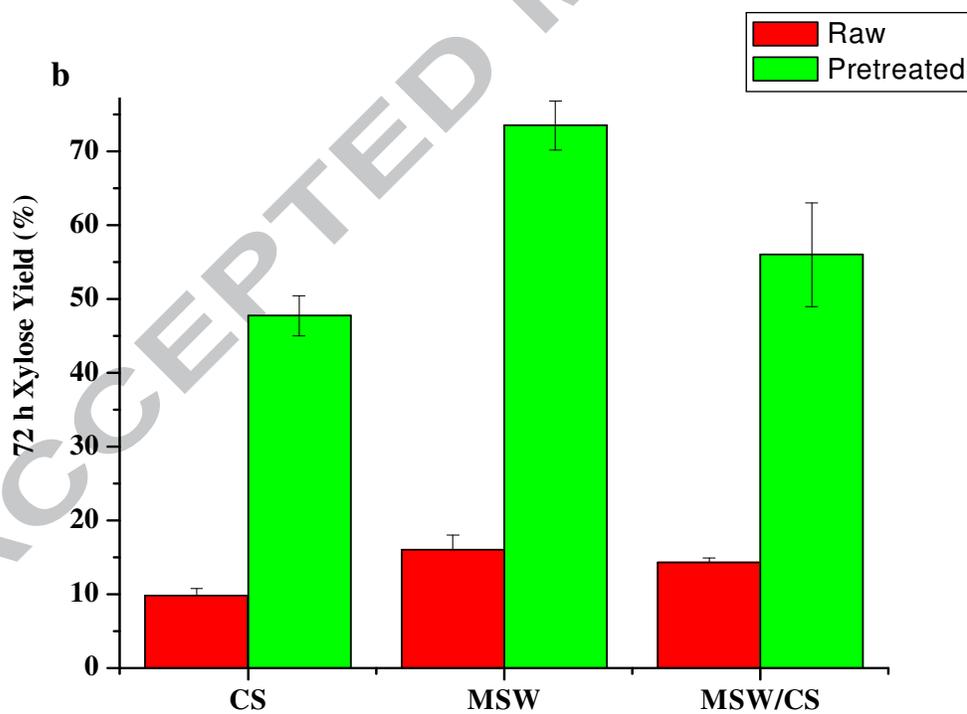
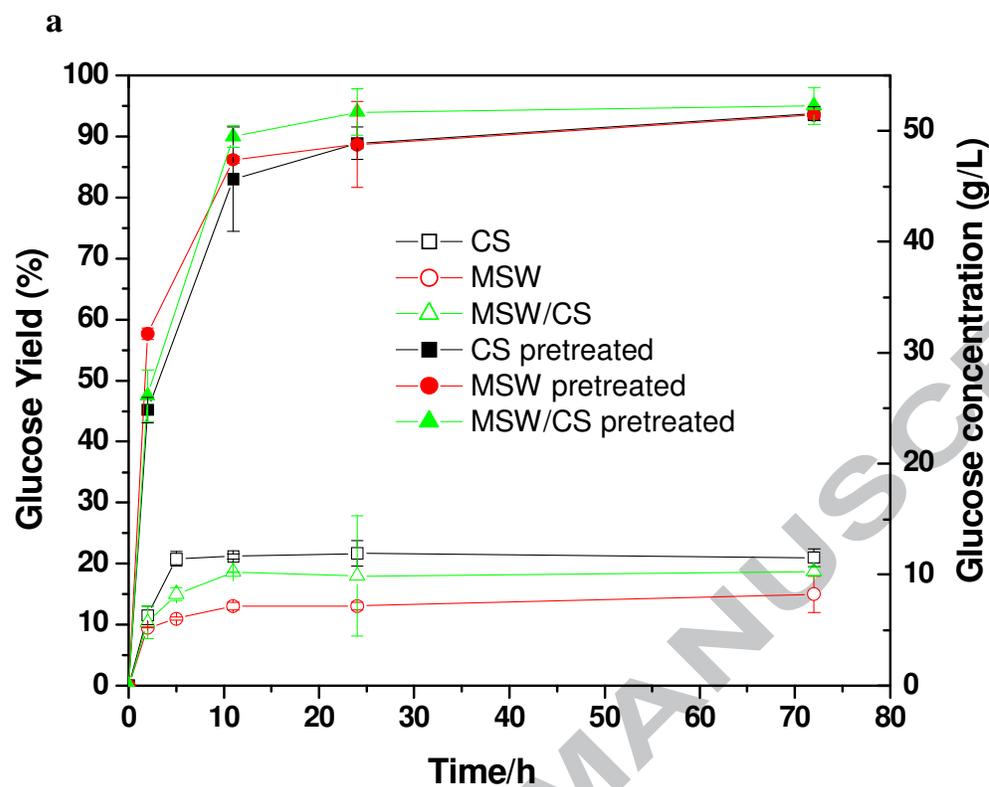
419



420
421
422

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

423



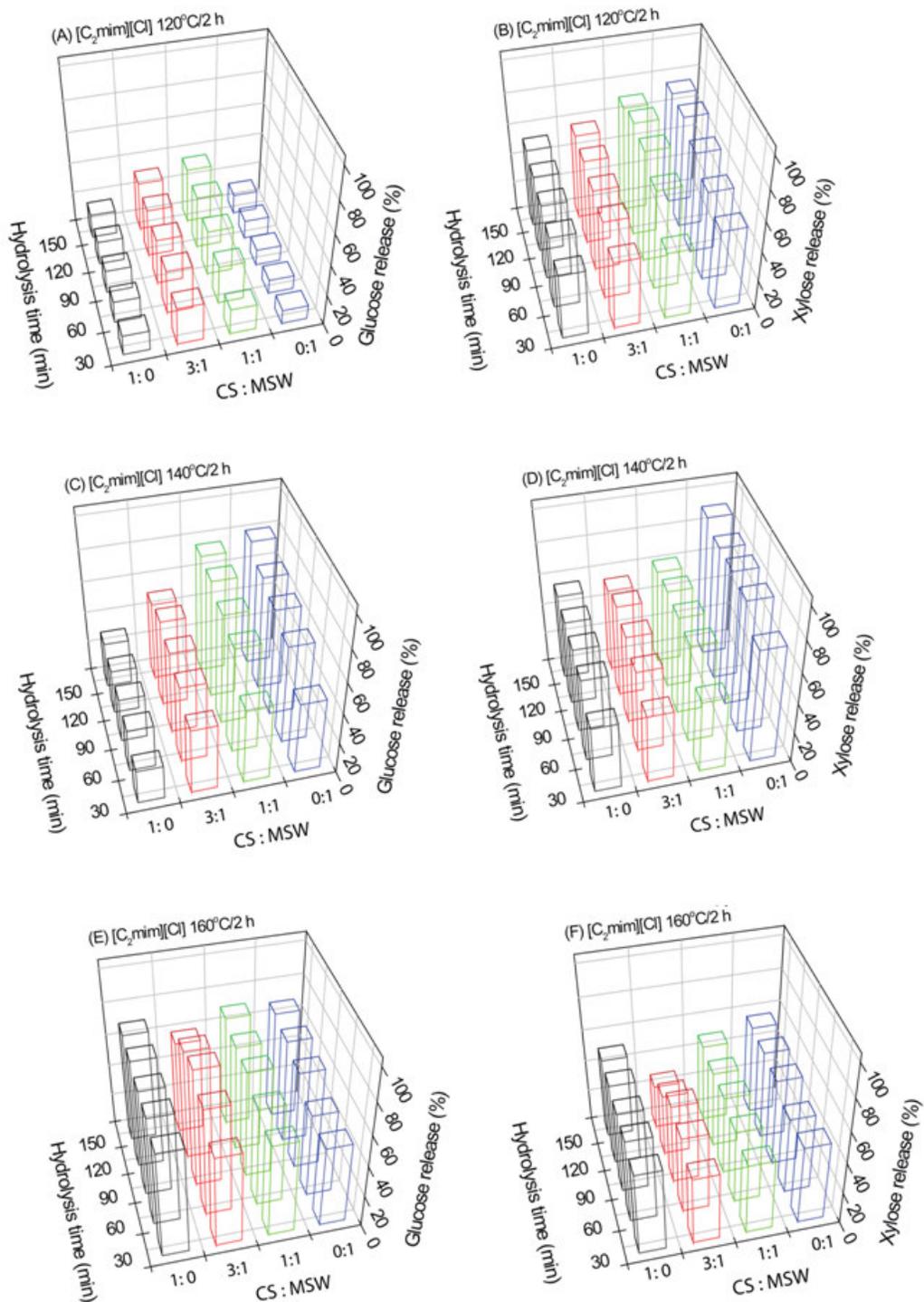
424

425

426

427

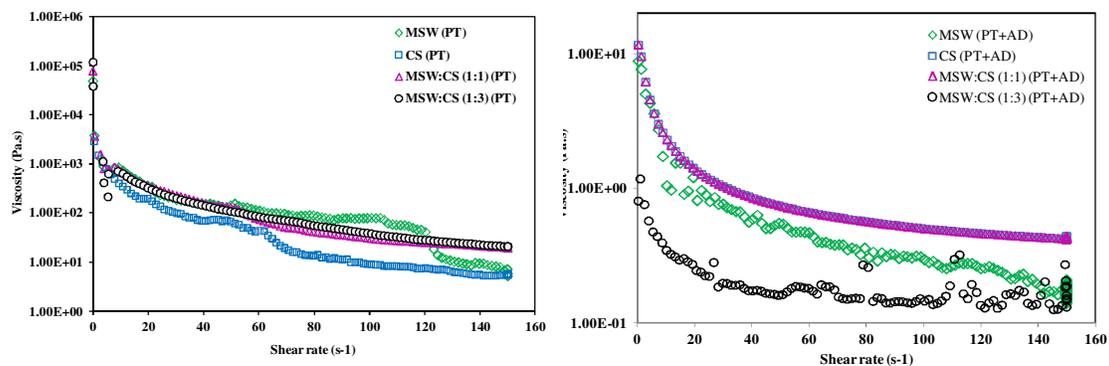
Figure 3. Glucose (a) and xylose (b) yields before and after IL pretreatment and enzymatic saccharification.



428

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

431



432 **Figure 5.** Viscosity profiles of municipal solid waste (MSW), corn stover (CS), and their
 433 blends from the $[C_2C_1Im]Cl$ process, PT: after pretreatment at 140 °C, and PT+AD: after
 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