

## SUPPLEMENTARY INFORMATION

### **A facile method for the recovery of ionic liquid and lignin from biomass pretreatment**

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**Figure S1.** Cellulose precipitated from a 3.7 wt% solution in the IL 1-ethyl-3-methylimidazolium acetate by a 2.5:1 (v/v) of precipitation solvent:cellulose solution with a composition from region (f) (top) and region (b) (bottom) from Fig. 2. Cellulose and biomass precipitated using a solvent composition indicated by region (f) in Fig. 2 are easily filtered and do not form gel phase intermediates during precipitation.

|                                       | Percent, Extractives-Free Basis |       |          |        |     | % Ethanol<br>Extractives | % Water<br>Extractives | IL Content<br>% |
|---------------------------------------|---------------------------------|-------|----------|--------|-----|--------------------------|------------------------|-----------------|
|                                       | Glucan                          | Xylan | Arabinan | Lignin | Ash |                          |                        |                 |
| Corn Stover (CS)                      | 33.4                            | 24.9  | 3.8      | 17.2   | 3.6 | 3.3                      | 7.1                    | -               |
| CS glucan-rich product A <sup>†</sup> | 39.4                            | 24.8  | 3.9      | 11.3   | 2.5 | -                        | 18.9 <sup>†</sup>      | 2.7             |
| CS glucan-rich product B <sup>‡</sup> | 45.6                            | 25    | 4.8      | 9.5    | 1.7 | -                        | -                      | 0.17            |
| CS xylan-rich product <sup>†</sup>    | 12.8                            | 23.7  | 0.0      | 19.2   | 5.9 | -                        | -                      | 13.7            |
| CS lignin-rich product                | -                               | -     | -        | 37.6   | -   | -                        | -                      | -               |
| CS aliphatic-rich product             | 0*                              | 0*    | 0*       | -      | -   | -                        | -                      | -               |

'-' = Not Analyzed, '\*' = estimated from H<sup>1</sup> NMR

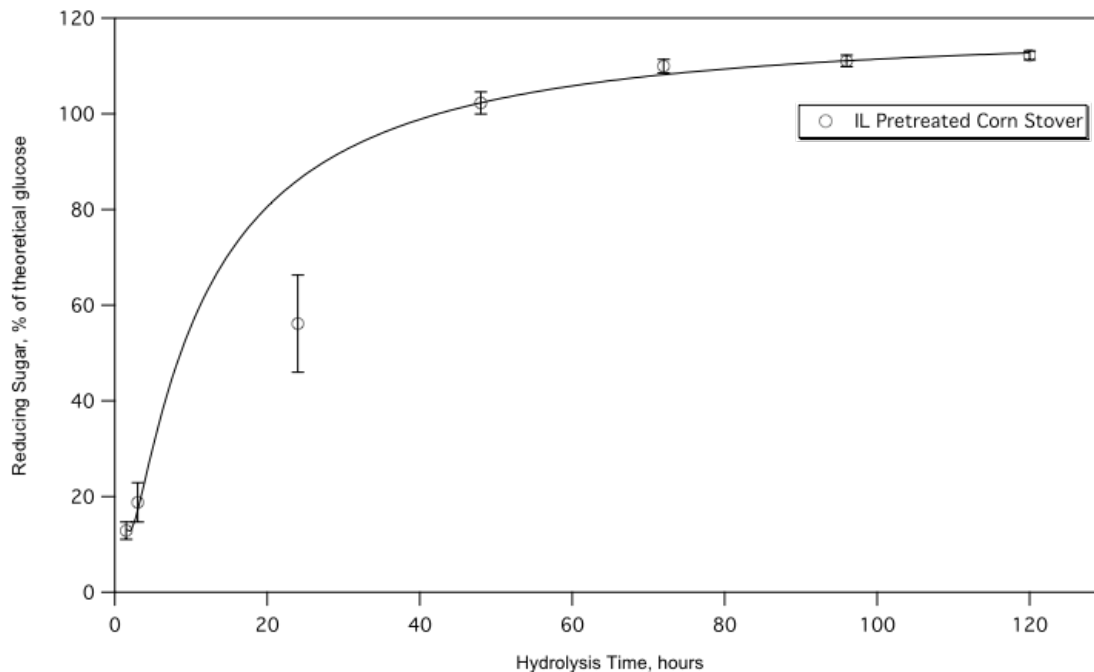
‡CS glucan-rich product B is CS glucan-rich product A after water washing

†CS xylan-rich product is the same as the CS glucan-rich product A water extractives

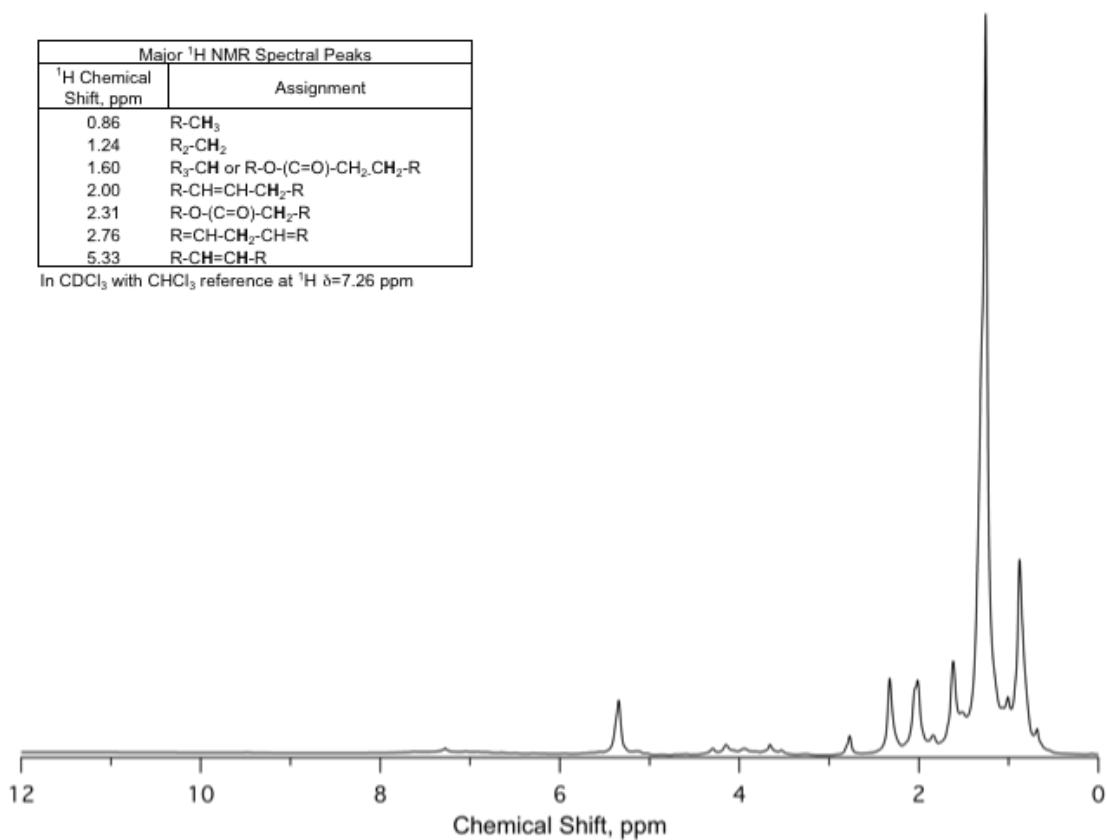
**Table S1.** Composition of corn stover and pretreated corn stover product fractions obtained from pretreatment with 1-ethyl-3-methylimidazolium acetate for 3 hours at 140 °C and subsequent recovery of the ionic liquid as described in the text.



**Figure S2.** Images of corn stover prior to (left) and after (right) ionic liquid pretreatment. Corn stover particle size is reduced by the pretreatment process and the choice of precipitation solvent and mixing method. Pretreated corn stover in these images was dried under vacuum from an ethanol-wet slurry.



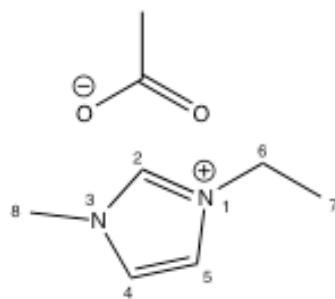
**Figure S3.** Reducing sugar obtained from the enzymatic hydrolysis of IL pretreated corn stover. Percent of theoretical glucose can be greater than 100% because of the presence of reducing sugars other than glucose released during hydrolysis. No xylanases were added during enzymatic hydrolysis reactions. Error bars represent standard deviation from two hydrolysis experiments, and the log-normal fit to the data was weighted by the standard deviation of the data and is drawn as a guide to the eye only.



**Figure S4.**  $^1\text{H}$  NMR spectra of Aliphatic-Rich Product. Spectra is of hexane soluble material only.



|                | IL, as-received           |           | IL, recovered             |                 | Assignment               |
|----------------|---------------------------|-----------|---------------------------|-----------------|--------------------------|
|                | $\delta_{\text{H}}$ , ppm | Intensity | $\delta_{\text{H}}$ , ppm | Intensity       |                          |
| IL Peaks       | 1.25                      | High      | 1.27                      | High            | -C(6)H <sub>3</sub>      |
|                | 1.50                      | High      | 1.56                      | High            | Acetate -CH <sub>3</sub> |
|                | 3.96                      | High      | 3.95                      | High            | -C(8)H <sub>3</sub>      |
|                | 4.25                      | High      | 4.26                      | High            | -C(7)H <sub>2</sub> -    |
|                | 8.27                      | High      | 8.12                      | High            | =C(5)H-                  |
|                | 8.44                      | High      | 8.27                      | High            | -C(4)H=                  |
| Impurity Peaks | 10.59                     | High      | 10.29                     | High            | -C(2)H=                  |
|                | 2.22                      | Low       |                           |                 |                          |
|                | 2.79                      | Low       |                           |                 |                          |
|                | 2.95                      | Moderate  |                           |                 | methanol                 |
|                | 3.28                      | Low       |                           |                 | ethanol                  |
|                | 6.63                      | Low       |                           |                 |                          |
|                | 7.20                      | Low       |                           |                 | ethyl imidazole          |
|                | 7.79                      | Low       |                           |                 | methylimidazole          |
|                |                           |           | 0.80                      | Moderate        | 2-propanol               |
|                |                           |           | 1.94                      | Moderate        | acetone                  |
|                |                           |           | 2.74                      | Low             |                          |
|                |                           |           | 3.23                      | Low             | ethanol                  |
|                |                           |           | 4.86                      | Moderate        | lignin                   |
|                |                           |           | 5.00                      | Low             |                          |
|                |                           |           | 5.14                      | Low             |                          |
|                |                           |           | 5.39                      | Low             |                          |
|                |                           |           | 5.49                      | Low             |                          |
|                |                           |           | 5.52                      | Low             |                          |
|                |                           |           | 5.59                      | Low             |                          |
|                |                           |           | 6.67                      | Low             | lignin                   |
|                |                           | 6.70      | Low                       | lignin          |                          |
|                |                           | 6.91      | Low                       | lignin          |                          |
|                |                           | 7.06      | Low                       | protein         |                          |
|                |                           | 7.18      | Low                       | ethylimidazole  |                          |
|                |                           | 7.75      | Low                       | methylimidazole |                          |
|                |                           | 8.60      | Moderate                  |                 |                          |



1-ethyl-3-methylimidazolium acetate

**Figure S5.** <sup>1</sup>H NMR signals in as-received and recovered ionic liquid (IL). Spectral positions are referenced to a DMSO internal standard with  $\delta_{\text{H}}$  2.49 ppm. Spectral assignments should be considered tentative and subject to confirmation.

| element  | IL content   | theoretical |
|----------|--------------|-------------|
| Carbon   | 53.76±0.22 % | 56.45%      |
| Oxygen   | 23.19±2.04 % | 18.80%      |
| Nitrogen | 15.19±0.20 % | 16.46%      |
| Hydrogen | 8.14±0.10 %  | 8.29%       |
| Chlorine | 843±346 ppm  | -           |
| Sodium   | 17±11 ppm    | -           |
| Calcium  | 14±6 ppm     | -           |
| Aluminum | 8±1 ppm      | -           |
| Nickel   | 5±1 ppm      | -           |

Element detection limits: <2 ppm, S  
 <0.05%, Br < 20 ppm

**Table S2.** Elemental composition of [C2mim][OAc] prior to use (as received from the manufacturer). Analysis was performed on three different IL lot numbers by Galbraith Laboratories, Inc. Knoxville TN.

| Observed |         |                    | Not Observed |                             |                            |
|----------|---------|--------------------|--------------|-----------------------------|----------------------------|
| IL #     | Cation  | Anion              | IL #         | Cation                      | Anion                      |
| 1        | C1mim   | dimethyl phosphate | 8            | C2mim                       | diethylphosphate           |
| 2        | C2mim   | acetate            | 9            | C2mim                       | methyl sulfate             |
| 3        | C2mim   | chloride           | 10           | C2mim                       | n-butyl sulfate            |
| 4        | C2mim   | dimethylphosphate  | 11           | C3mim                       | iodide                     |
| 5        | C2mim   | lactate            | 12           | C4mim                       | trifluoromethane sulfonate |
| 6        | C4mim   | chloride           | 13           | tributyl(methyl)phosphonium | methyl sulfate             |
| 7        | choline | acetate            | 14           | tetrabutylphosphonium       | chloride                   |
|          |         |                    | 15           | ethyltri(butyl)phosphonium  | diethylphosphate           |
|          |         |                    | 16           | N-butyl-3-methylpyridinium  | tetrafluoroborate          |

**Table S3.** Reversible phase formation test results for several ILs in the IL+water+methanol+acetone system. ILs #1-7 could be switched from a single phase solution to a two phase solution and then back to a single phase solution at least three times in series by minor additions of either water (to form a two phase solution) or methanol (to return to a single phase solution).

### Reversible phase formation testing method

Ionic liquids #1 (Aldrich, 671657), #2 (Aldrich, 51053), #3 (Aldrich, 38899), #4 (Aldrich, 671541), #5 (Aldrich, 669512), #6 (Fluka, 94128), #7 (Fluka, 73215), #8 (EMD, 4.90293), #9 (Aldrich, 18086), #10 (EMD, 4.90291), #11 (EMD, 4.90202), #12 (EMD, 4.90024), #13 (Cytec, Cyphos 108), #14 (Cytec, Cyphos 164), #15 (Cytec, Cyphos 169), and #16 (EMD, 4.90122) were tested as received from the manufacturer and without additional purification.

In a 13 X 100 mm (9 mL) screw-capped test tube, 1.0 g of the selected ionic liquid and 3.0 g of acetone were combined and mixed by manually shaking. For ILs that did not dissolve (if solid) or did not form a single-phase solution (if liquid), just sufficient methanol was added to the test tube to form a transparent, single-phase solution after mixing as indicated by an absence of a visible second phase or turbidity. To this single-phase solution, just sufficient water was added to induce the formation and coalescence of a second (denser) liquid phase that resulted in a distinct liquid layer on standing for 15 minutes or less. If a second phase was not observed by the addition water in any quantity, then reversible phase formation was indicated as 'not observed.' If a second liquid phase was observed, just sufficient methanol was added to the vial to again return the liquid to a single-phase state. This process was repeated by the sequential addition of water and methanol to form and dissipate a second liquid phase at least three times. ILs that formed reversibly switchable solutions a least three times in this test are listed in the 'Observed' column of Table S3.