Electronic Supplementary Information (ESI)

One-pot Ionic Liquid Pretreatment and Saccharification of Switchgrass

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Table S1. Assignments of the lignin ^{13}C-^{1}H correlation peaks in the 2D HSQC spectra of switchgrass cell wall and residual solids

Label	δ_C/δ_H (ppm)	Assignment
MeO ($-OCH_3$)	55.6/3.73	C–H in methoxyls
A_α	70.9/4.71 and 4.83	C_α–H_α in β-O-4' substructure (**A**)
$A_{\beta(G)}$	83.4/4.27	C_β–H_β in β-O-4' substructures (**A**) linked to a G unit
$A_{\beta(S)}$	85.9/4.10	C_β–H_β in β-O-4' substructures linked (**A**) to a S unit
D_α	83.3/4.81	C_α-H_α in dibenzodioxocin substructures (**D**)
$S_{2,6}$	103.8/6.69	C_2–H_2 and C_6–H_6 in etherified syringyl units (**S**)
G_2	110.9/6.99	C_2–H_2 in guaiacyl units (**G**)
pCA_β and FA_β	113.5/6.27	C_β–H_β in *p*-coumarate (***p*CA**) and ferulate (**FA**)
G_5/G_6	114.9/6.72 and 6.94 118.7/6.77	C_5–H_5 and C_6–H_6 in guaiacyl units (**G**)
$H_{2,6}$	127.8/7.22	$C_{2,6}$–$H_{2,6}$ in *p*-hydroxyphenyl units (**H**)
p$CA_{2,6}$	130.1/7.45	C_2–H_2 and C_6–H_6 in *p*-coumarate (***p*CA**)
pCA_α and FA_α	144.7/7.41	C_α–H_α in *p*-coumarate (***p*CA**) and ferulate (**FA**)

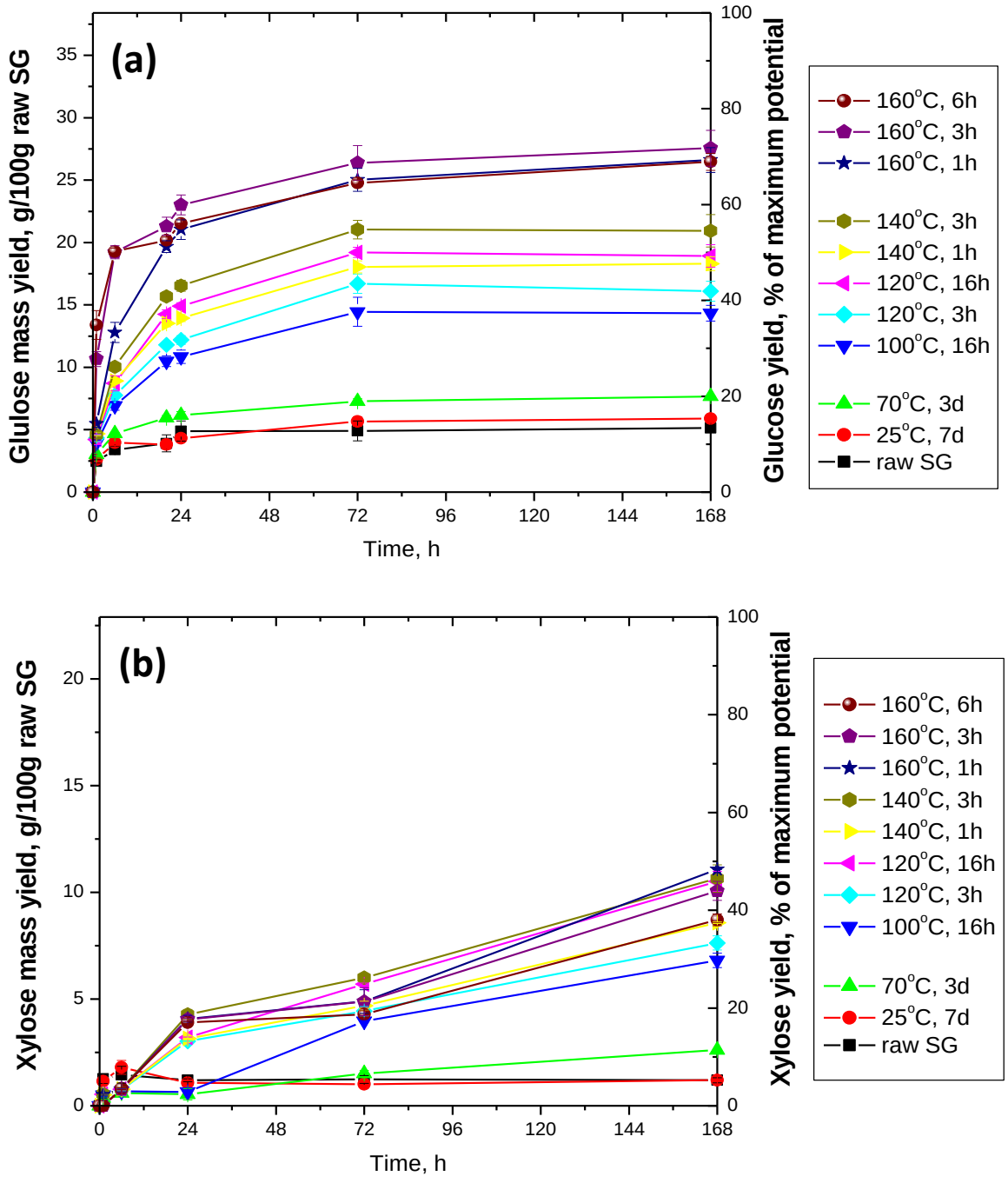

Figure S1 Glucose and xylose release during 168h one-pot pretreatment and saccharification with different pretreatment conditions. JTherm loading: 5.75 mg/g starting biomass.

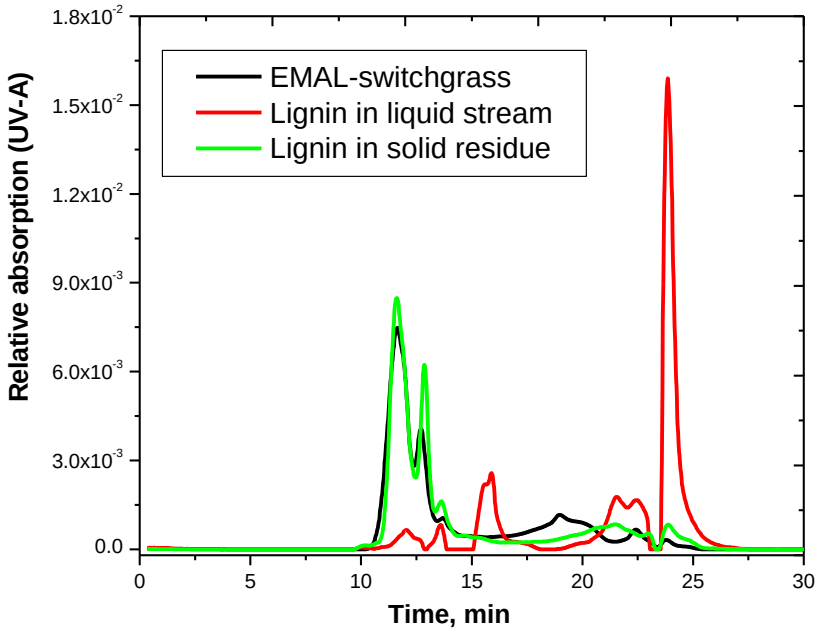

Figure S2 Elution profiles of lignin in remaining in the liquid stream and residual solids after one-pot ionic liquid pretreatment and saccharification of switchgrass.

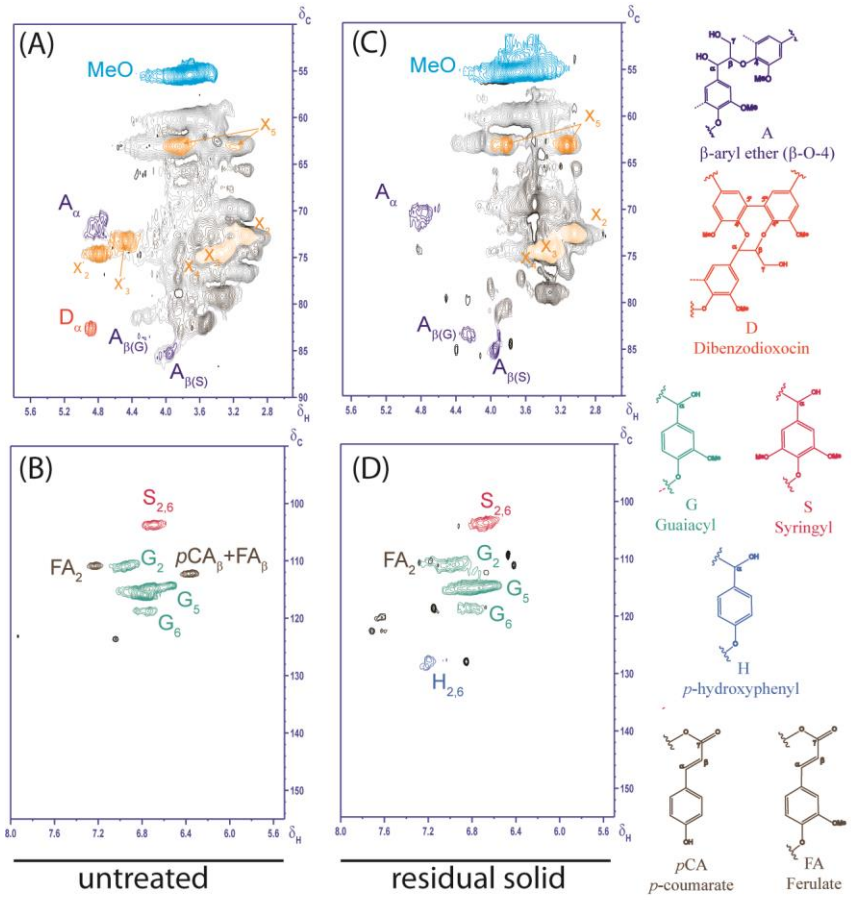

Figure S3 Side chain (δ_C/δ_H 50-90/2.5-5.8) and aromatic/unsaturated (δ_C/δ_H 90-155/5.5-8.0) regions in the 2D HSQC NMR spectra of untreated switchgrass (A and B) and residual (C and D).

IL recycle: We have demonstrated preliminary results for recycling [C_2mim][OAc] from "one-pot" hydrolyzate and reuse of the recycled IL for the next batch of "one-pot" pretreatment and saccharification. Briefly, "one-pot" hydrolyzate was subjected to liquid-liquid sugar extraction using the boronic acid complex as described in manuscript. The pH of the sugar-extracted hydrolyzate was adjusted to 6.8 using 1M hydrochloric acid (HCl) and passed through sequential filtration including: 20 μm Steriflip filter unit (Millipore, Billerica, MA) →0.2 μm PTFE syringe filter (Nalgene) →50 kDa →10 kDa → 3 kDa Amicon Ultra-15 Centrifugal Filter Units (Millipore, Billerica, MA). The filtered hydrolyzate was vacuum dried overnight with a lyophilizer (Labconco FreeZone 12, Kansas City, MO) and centrifuged at 3220 rcf for 10 min to remove any precipitates. IL recovery (%) was calculated based on the starting IL content in one-pot hydrolyzate. Water content of recycled IL was measured as ~9.7% using Karl Fischer titration method (Metrohm USA, Riverview, FL) and has been taken account into the calculation. After sequential filtration and vacuum evaporation, 90.8% IL, [C_2mim][OAc] was recovered. Some of the IL might be lost due to wetting of the membranes we used or during transferring. Further improvements in technology developed during scale-up could generate cost-effective IL recycle technologies that are greater than 98% effective.

Proton (^{1}H) NMR spectra of neat and recycled [C_2mim][OAc] samples were acquired on a Bruker AV-500 NMR spectrometer with 16 scans for each sample at room temperature. DMSO-d_6 was used for providing lock frequency and as an internal reference. ^{1}H NMR of recycled IL confirmed preservation of [C_2mim][OAc] in recycled IL as indicated by the presence of the triplet/quartet proton shift around 1.5 and 4.3ppm, as also showing in neat IL. The broadening of regions ~4ppm is probably due to the trace lignin or sugar residues in recycled IL (Figure S5). The recycled IL was used to pretreat switchgrass under identical conditions (160 ^{o}C, 3h, 10%

biomass loading) as with neat IL. Residual sugars in recycled IL have been subtracted during sugar yield calculation. Compared with neat IL, reuse of the recycled IL for the next batch of one-pot pretreatment and saccharification showed 93.5% and 89.2% of the original glucose and xylose yield, respectively (Figure S6).

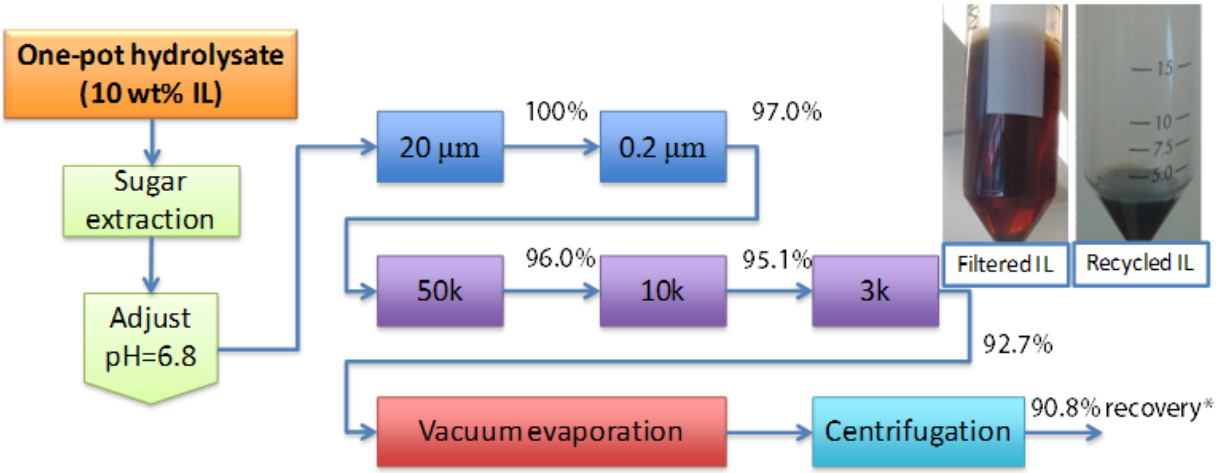

Figure S4 Ionic liquid recycle from "one-pot" hydrolyzate after liquid-liquid sugar extraction

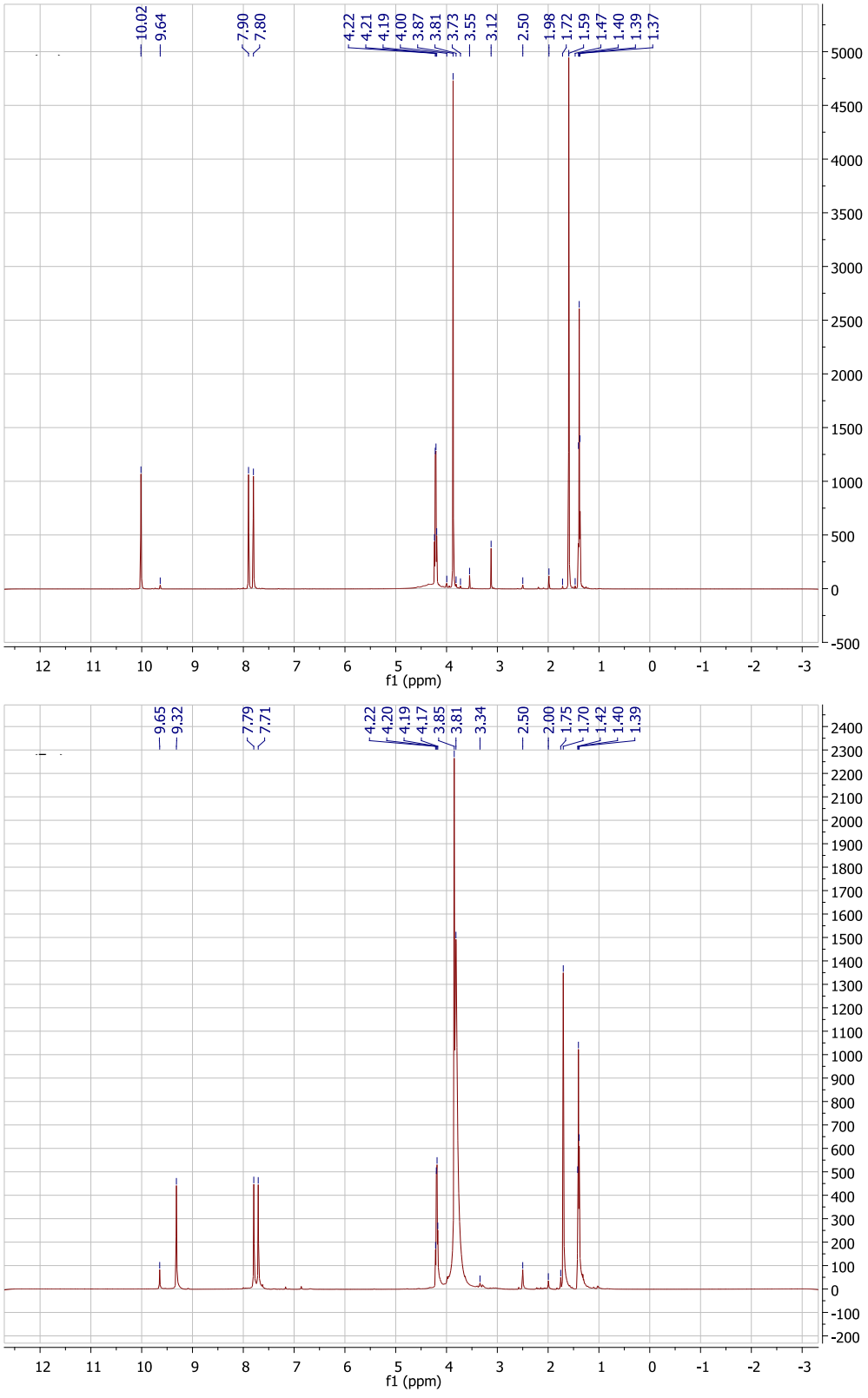

Figure S5. ^{1}H NMR for a) neat and b) recycled ionic liquid, [C_2mim][OAc].

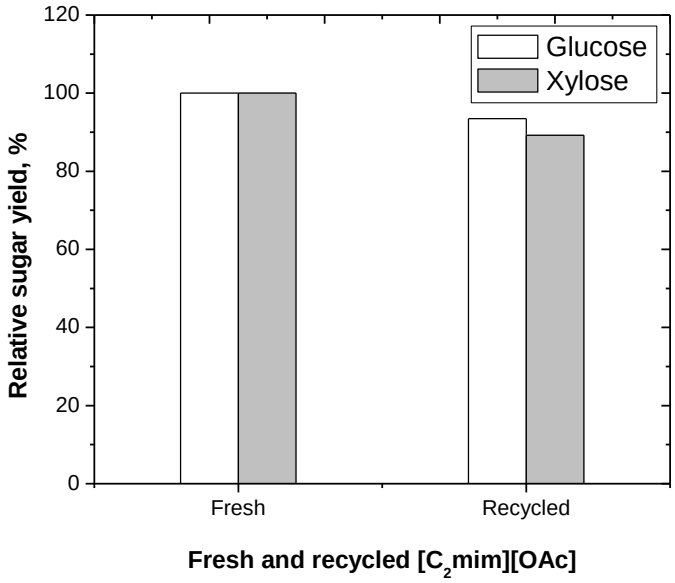

Figure S6. Sugar yields from one-pot pretreatment and saccharification using neat and recycled ionic liquid, [C_2mim][OAc].