Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Supplementary Materials for

CO_2 enabled process integration for the production of cellulosic ethanol using bionic liquids

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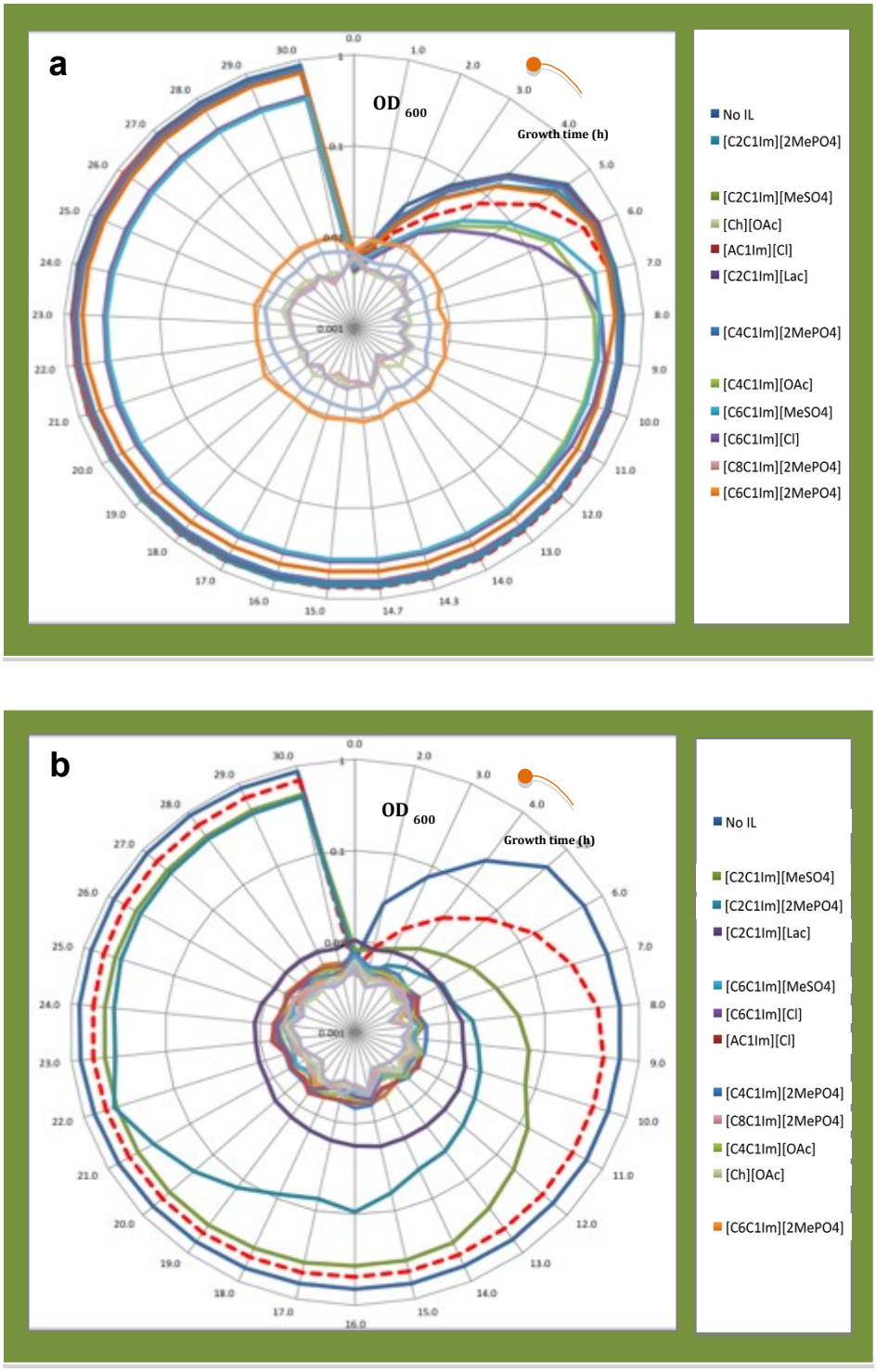

Figure S1. Toxicity screening of fifteen ILs on *Saccharomyces cerevisiae* strain BY4741 at (A) 0.6 wt% and (B) 5 wt% IL.

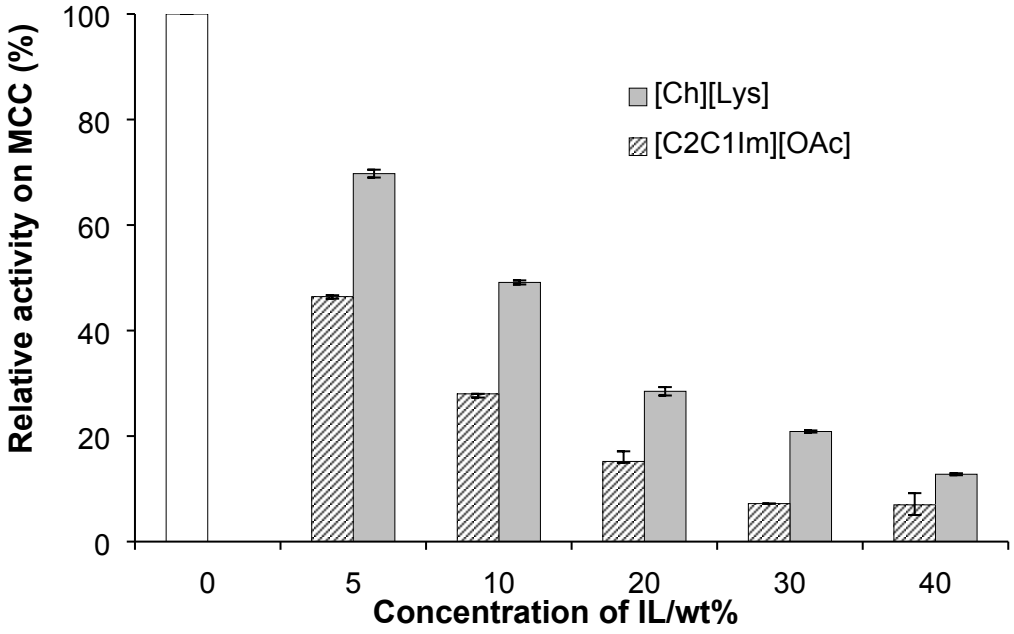

Figure S2. Inhibition of IL concentration to the hydrolysis of microcrystalline cellulose (MCC) by commercial enzyme cocktails. Conditions: pretreatment, MCC 50 mg, liquid 1.5 mL, 140 °C, 1h; saccharification, 30 mg CTec2+HTec2 protein/g Avicel, 50 mM citric buffer, pH 5, 50 °C, 72 h.

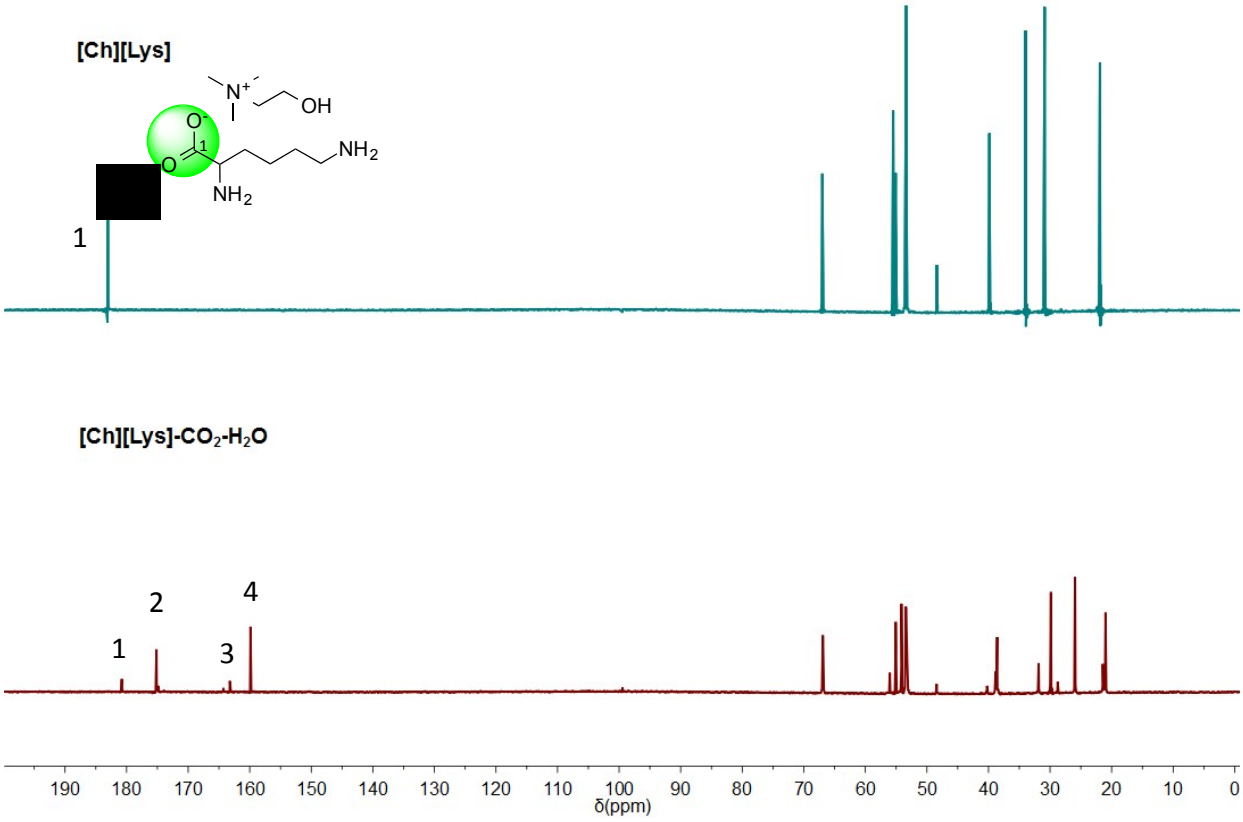

Figure S3. ^{13}C NMR (150 MHz, DMSO-*d6*, 298K) spectra of [Ch][Lys] before (top) and after CO_2 absorption (bottom). ^{13}C NMR spectra of [Ch][Lys] shows one signal for carbonyl carbon (1, top spectra). Upon CO_2 absorption the ^{13}C NMR spectra of [Ch][Lys] shows four signals for carbonyl carbon (1-4, bottom spectra), which are indicative of different IL-H_2O-CO_2 complexes.

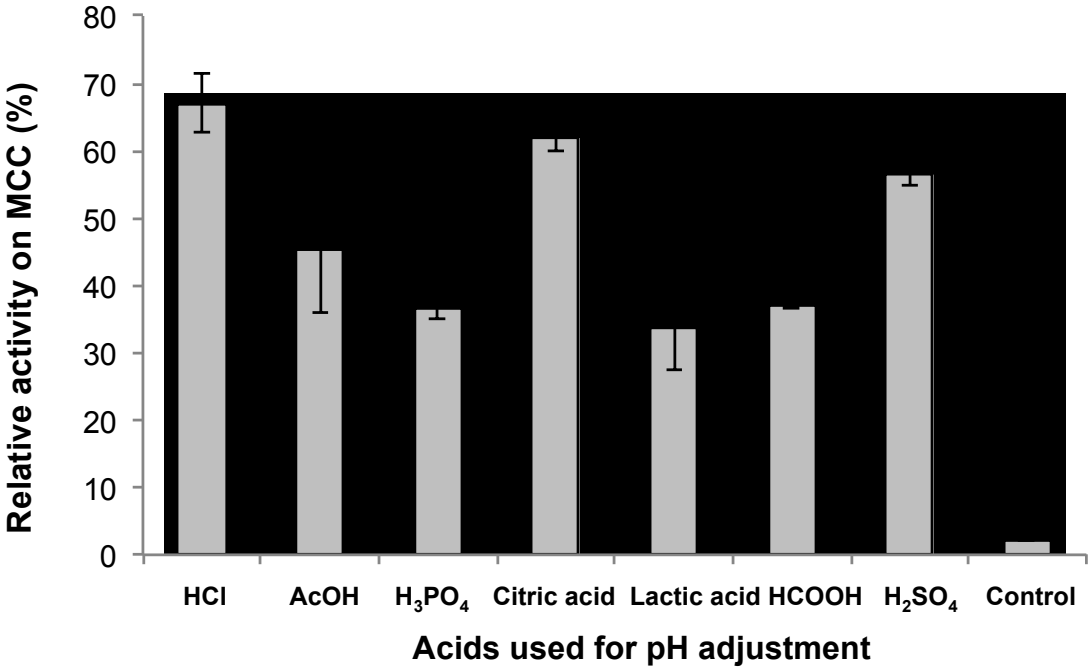

Figure S4. Effect of acid-induced pH adjustments on enzymatic hydrolysis of MCC. Conditions: MCC (50 mg), liquid 1.5 mL, [Ch][Lys] (5 wt%), 30 mg CTec2+HTec2 protein /g Avicel, 50 mM citric buffer, pH 5.0, 50 °C, 72 h.

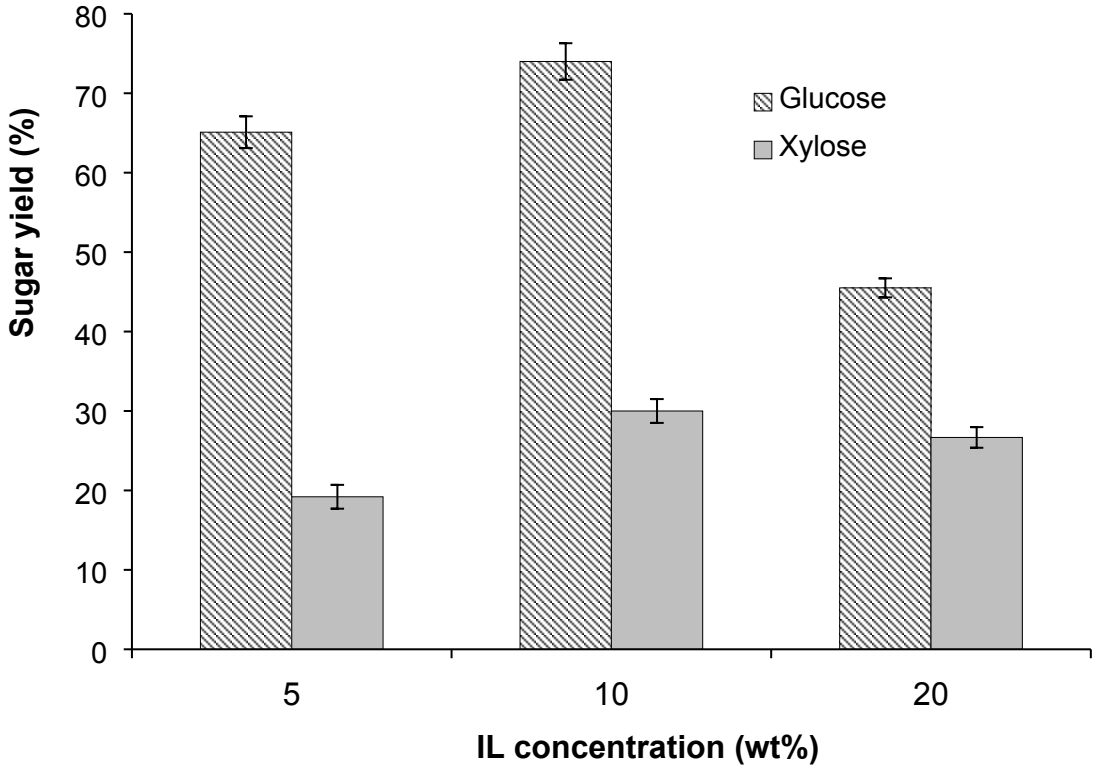

Figure S5. Comparison of sugar yields using different concentration of [Ch][Lys] for both pretreatment and saccharification process. Conditions: pretreatment, 10 wt% switchgrass loading, 5 (10 or 20) wt% [Ch][Lys], 85 (80 or 70) wt% H_2O, 140 °C, 1h; Saccharification, 10 mg CTec2+HTec2 protein /g SG, 50 °C, 72 h and 1 MPa CO_2.

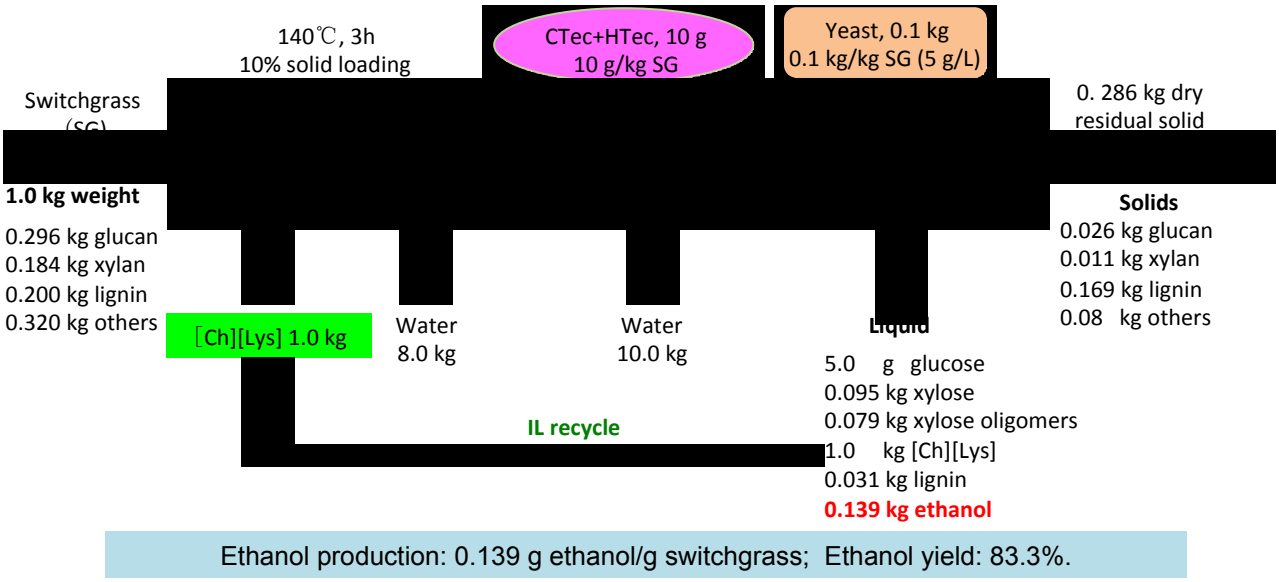

Figure S6. Overall mass balance of the integrated process using [Ch][Lys], carbon dioxide, commercial enzyme cocktail and wild type yeast *S. cerevisiae*.

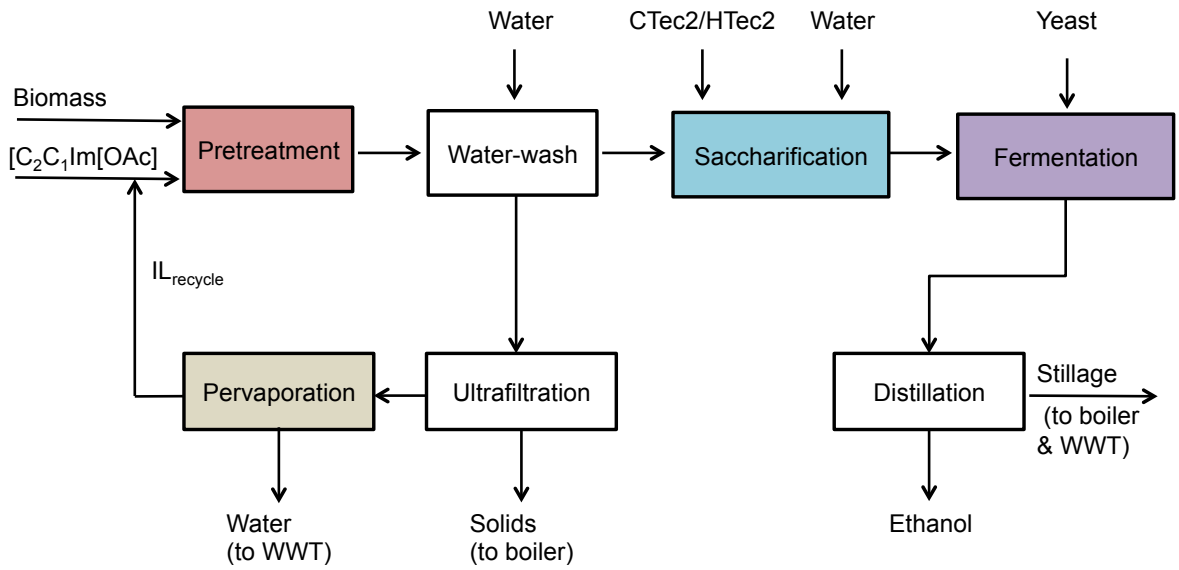

Figure S7. Simplified block flow diagram of water-wash process configuration.

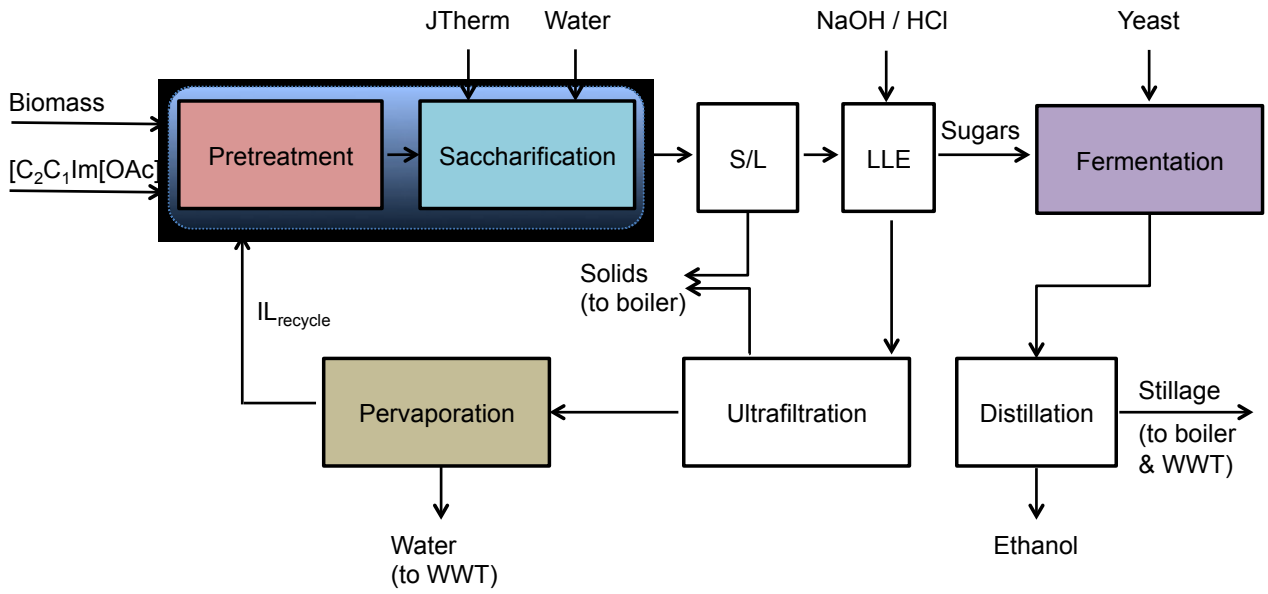

Figure S8. Simplified block flow diagram of JTherm process configuration with liquid-liquid extraction (LLE) to recover sugars from hydrolysate.

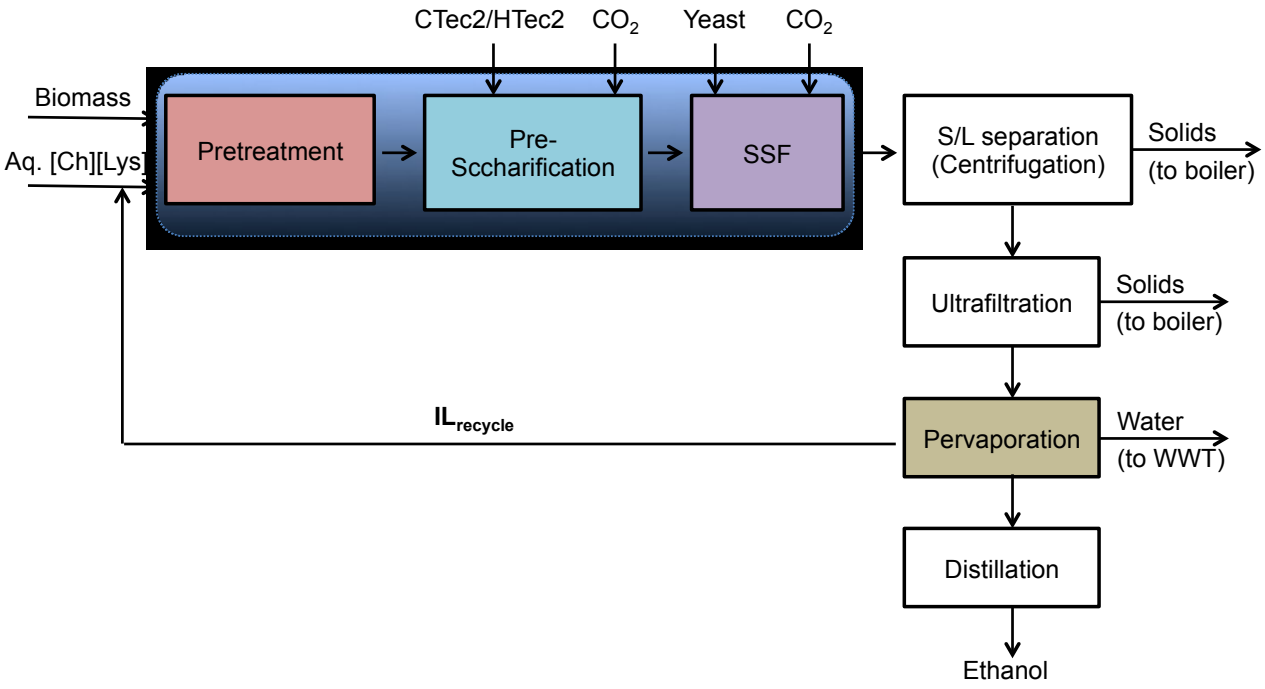

Figure S9. Simplified block flow diagram of integrated CO_2 process configuration.

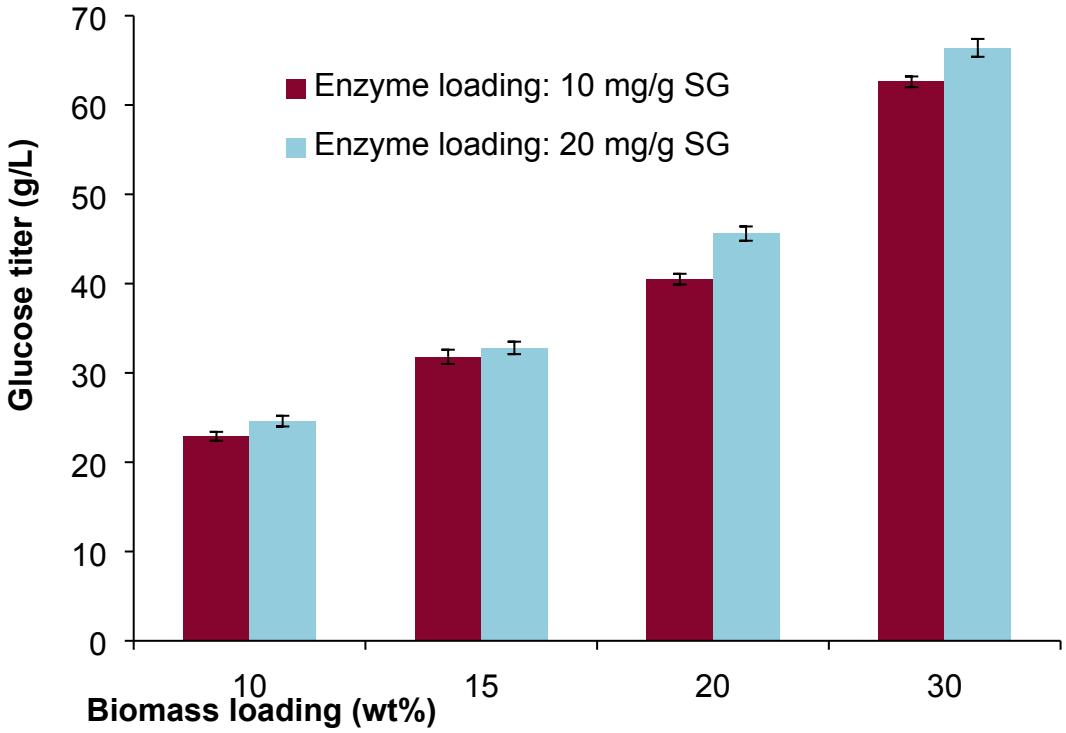

Figure S10. Effect of biomass and enzyme loading on glucose titer.

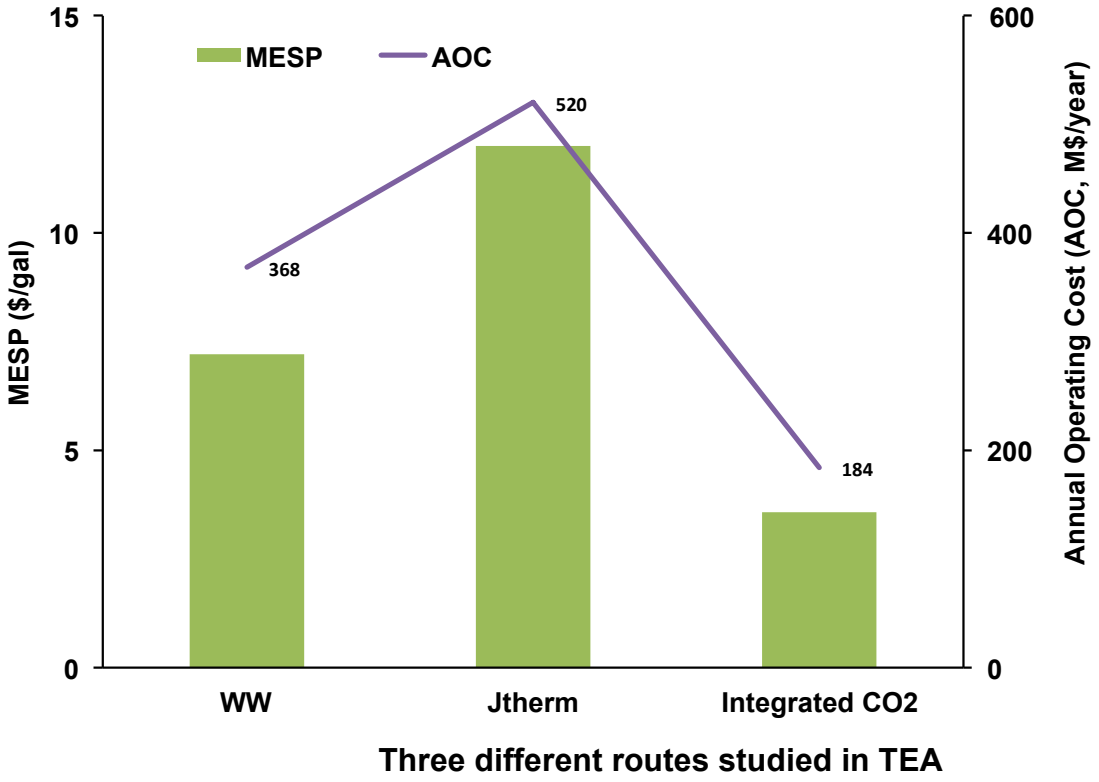

Figure S11. Minimum selling price (MESP) and annual operating cost (AOC) for the WW, JTherm, and integrated CO_2 schemes.

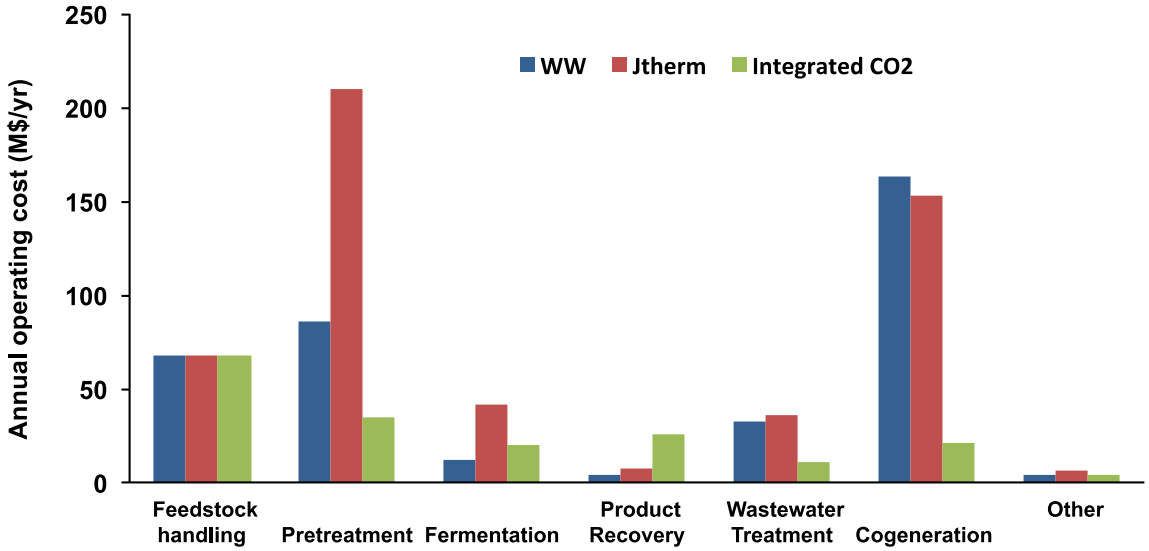

Figure S12. Detailed section-wide cost breakdown for the WW, JTherm, and integrated CO_2 routes.

Table S1. Calculated acidity of [Ch][Lys] with CO_2 and water molecules and local chemical reactivity descriptors of terminal and side chain N atoms.

	Calculated Acidity (eV)	f_k^-	
		Terminal	Side
[Ch][Lys] $(H_2O)_2$	2.3	0.142	0.039
[Ch][Lys] (H_2O) (CO_2) (side)	2.36	0.291	0.007
[Ch][Lys] (H_2O) (CO_2) (ter.)	2.7	0.015	0.065
[Ch][Lys] $(H_2O)_2$ $(CO_2)_2$	2.7	0.017	0.026

Table S2. Chemical composition of dominant components in the switchgrass studied and solid recovery.

	Solid recovery/%	Glucan /wt%	Xylan/wt%	Lignin/wt%
Untreated SG	/	32.2±0.1	20.0±0.1	21.8±0.2
10% IL, 1h	65.8	44.7±0.7	24.0±1.2	9.2±0.2
10% IL, 3h	63.2	47.8±0.7	23.6±1.0	9.2±0.3
90% IL, 1h	45.7	62.3±0.7	24.0±0.3	6.5±0.1

Pretreatment conditions: 10% biomass loading, [Ch][Lys], H_2O (0 or 80%), 140 ℃.

Table S3. Key process and economic data for the three scenarios studied in the TEA

Process configuration	WW[a]	JTherm[b]	Integrated CO_2

Biomass processed (dry MT/day)	2000	2000	2000
Biomass price ($/dry ton, delivered at plant-gate)	80	80	80
Pretreatment			
IL used	$[C_2C_1Im][OAc]$	$[C_2C_1Im][OAc]$	[Ch][Lys]
IL price ($/kg)[c]	10	10	2
IL purity (wt% of IL in aqueous IL solution [IL:H_2O])	90	100	13.5
Biomass loading (wt%)	20	20	20
IL recovery (%)	99.9	99.9	99.9
Water loading (mass ratio between fresh water and biomass in water-wash step in WW route)	20	N/A	N/A
Loss of glucan in water-wash step (wt% of initial glucan)	5	NONE	NONE
Loss of xylan in water-wash step (wt% of initial xylan)	24	NONE	NONE
Hydrolysis			
Configuration	SHF	SHF	SSF
Enzyme type	CTec2/HTec2	JTherm	CTec2/Htec2
Enzyme price ($/kg protein)[d]	4.29	10	4.29
Enzyme loading (mg/g glucan)	20	20	20
Operating pressure (atm)	1	1	20 (~2 MPa)
Operating temperature (C)	50	70	50
Operating time (hr)	72	72	24 (pre-hydrolysis)
Glucan-to-glucose conversion (%)	90	90	90
Xylan-to-xylose conversion (%)	90	90	90
Sugar losses during extraction (%)	N/A	5	N/A
Fermentation			
Co-fermentation of glucose and xylose	YES	YES	YES
Glucose-to-ethanol conversion (%)	90	90	90
Xylose-to-ethanol conversion (%)	90	90	90
Xylose-to-ethanol conversion (%)	90	90	90
Operating pressure (atm)	1	1	20 (~2 MPa)
Opiating temperature (C)	32	32	32
Operating time (hr)	72	72	72

[a]based on (Bai, Wang et al. 2013, Cruz, Scullin et al. 2013, Konda, Shi et al. 2014, Shi, Balamurugan et al. 2014, Li, Tanjore et al. 2015)

[b](Konda, Shi et al. 2014, Shi, Balamurugan et al. 2014)

[c]price of ILs is assumed to reflect on the fact that the choline based ILs use cheaper raw materials and require simpler synthesis methods. For instance, according to the information available in the open literature (e.g., www.alibaba.com), both choline hydroxide and lysine (i.e., the primary raw materials used to synthesize [Ch][Lys]) can be purchased for about $700-$1500/MT (depending on the supplier, quality and order quanity). Moreover, the synthesis of [Ch][Lys] is fairly simple and doesn't require extensive concentration/purification steps as the OP-CO_2 process uses aqueous IL. Therefore, a price of $2/kg of [Ch][Lys] is a reasonable estimate in this preliminary TEA. Furthermore, a sensitivity analysis around IL price (varying from $1 to $10/kg) is conducted.

[d]price of enzyme is assumed to reflect that the novel enzymes (JTtherm) are likely to be more expensive compared to the commercial enzymes (CTec2/HTec2)