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SUPPLEMENTARY INFORMATION

The effect of pretreatment on methanesulfonic acid-catalyzed hydrolysis of bagasse to levulinic acid, formic acid, and furfural

Darryn W. Rackemann*, John P. Bartley, Mark D. Harrison and William O.S. Doherty

Centre for Tropical Crops and Biocommodities, Queensland University of Technology, Brisbane, Australia

*Corresponding authors

Postal address: GPO Box 2432, 2 George St, Brisbane, QLD 4001, Australia.

d.rackemann@qut.edu.au

Table S1 Levulinic acid and furfural yields from acid-catalyzed reaction of bagasse

Catalyst (M)	Feed (wt%)	Temp. (°C)	Time (min)	Furfural (mol%[a])	Formic acid (mol%[a])	Levulinic acid (mol%[a])	Solids (wt% feed)
0.1	3.68	160	20	33.7	3.6	0.2	58.9
0.1	3.68	160	40	51.4	0.0	0.0	59.9
0.1	1.84	160	60	95.5	11.8	4.2	62.5
0.1	3.68	160	80	62.6	7.5	2.1	54.0
0.3	3.68	180	20	46.0	64.7	48.3	38.6
0.3	3.68	180	30	41.0	64.4	49.1	37.4
0.3	3.68	180	40	18.5	76.9	56.5	40.9
0.1	1.84	200	20	64.7	62.8	51.4	48.1
0.1	1.84	200	60	16.3	85.8	62.1	36.3
0.5	1.84	200	20	9.2	73.0	59.5	21.1
0.5	1.84	200	60	0.0	58.8	59.1	40.1
0.06	3.68	180	40	78.2	17.4	9.8	45.1
0.3	3.68	180	40	18.5	76.9	56.5	40.9
0.75	3.68	180	40	3.0	72.7	59.9	44.0
0.5	3.68	160	20	67.4	9.6	4.3	54.0
0.5	3.68	180	20	19.8	73.1	55.7	38.5
0.5	3.68	200	40	0.0	55.1	52.7	40.5
0.3	2.30	180	40	33.5	73.5	63.5	38.2
0.3	2.63	180	40	30.3	73.3	57.7	38.4
0.3	3.46	180	40	37.8	68.6	58.6	40.9
0.3	3.68	180	40	18.5	76.9	56.5	40.9
0.3	3.77	180	40	30.0	72.6	52.3	40.1
0.3	4.19	180	40	14.6	74.1	53.6	46.6
0.2	3.68	180	20	84.8	35.9	28.2	28.8
0.2	3.68	180	20	76.4	39.6	31.6	29.4
0.2	3.68	180	20	84.1	36.2	28.4	47.5
0.2	3.68	180	40	54.6	68.5	58.6	39.5
0.5	1.84	200	20	7.4	68.3	52.9	39.3
0.5	1.84	200	20	14.3	74.9	61.8	39.4

[a] Based on pentose/hexose sugar content (anhydro-correction).

Note: Differences between duplicate results were ± 6.4% for furfural, ± 11.3% for formic acid, ± 8.3% for levulinic acid and ± 2.5% for solid residue.

Table S2 Levulinic acid, furfural and solid yields from acid-catalyzed reaction of various types of cellulosics

Sample	0.1 M MSA, 180 °C, 20 min (2 wt% feed)			0.3 M MSA, 180 °C, 40 min (3 wt% feed)			0.5 M MSA, 200 °C, 20 min (3 wt% feed)		
	Furfural yield (mol%[a])	Levulinic acid yield (mol%[a])	Solids (wt% feed)	Furfural yield (mol%[a])	Levulinic acid yield (mol%[a])	Solids (wt% feed)	Furfural yield (mol%[a])	Levulinic acid yield (mol%[a])	Solids (wt% feed)
Cellobiose				n.d.	58.8	11.0	n.d.	63.4	15.2
Avicel				n.d.	56.9	14.7	n.d.	57.3	25.4
Solka-Floc	n.d.	5.7	39.2	n.d.	57.7	16.8	n.d.	61.2	21.1
IL	66.3	7.6	50.7	n.d.	63.0	18.8	0.0	60.2	22.7
EG	73.0	10.0	42.6	14.9	57.8	21.2	2.7	60.0	26.8
Soda low lignin	88.3	6.7	55.8	26.9	68.9	29.6	10.3	76.8	24.6
Soda med lignin	72.2	8.5	46.1	34.0	61.5	31.1	6.4	64.6	34.7
Soda high lignin	73.7	6.6	51.8	34.6	61.0	31.6	14.3	67.7	36.7
Bagasse	87.8	4.5	55.3	35.6	62.2	43.4	14.3	61.8	39.4
Acid	62.1	13.4	68.7	29.3	60.3	50.1	0.0	63.2	48.0

[a] Based on pentose/hexose sugar content (anhydro-correction). n.d. not detected.

Note: errors ± 10% for furfural, ± 11% for levulinic acid, and ± 12% for solid residue.

Table S3 RSM model for levulinic acid and furfural yields from soda low lignin pulp

Factors		Levulinic acid			Furfural		
		Coded factor	F value	P-value	Coded factor	F value	P-value
Model/Intercept	a_0	67.66	13.42	< 0.0001	-25.79	42.99	< 0.0001
Acid Conc.	a_1	39.00	13.19	0.0015	-77.88	42.09	< 0.0001
Feed Conc.	a_2	2.77	0.08	0.7868	-55.96	15.31	0.0012
Temp	a_3	25.70	47.11	< 0.0001	-91.75	12.63	0.0026
Time	a_4	1.13	0.10	0.753	-67.71	10.76	0.0047
Acid*Feed	a_{12}	30.48	3.10	0.0922	-72.64	21.13	0.0003
Acid*Temp	a_{13}	-22.18	18.51	0.0003	-18.40	32.73	< 0.0001
Acid*Time	a_{14}	-16.39	6.71	0.0167	-	-	-
Feed*Temp	a_{23}	-	-	-	-69.53	4.71	0.0453
Feed*Time	a_{24}	-	-	-	-59.97	4.61	0.0475
$Acid^2$	a_{11}	-22.16	43.47	< 0.0001	11.52	4.69	0.0459
$Temp^2$	a_{44}	-25.55	34.75	< 0.0001	-	-	-
$Time^2$	a_{55}	16.89	13.17	0.0015	22.89	22.03	0.0002
		Adjusted R^2		0.7951	Adjusted R^2		0.9417
		Predicted R^2		0.4911	Predicted R^2		0.8875
		Adequate precision		13.523	Adequate precision		19.959
		Lack of fit		0.149	Lack of fit		0.404

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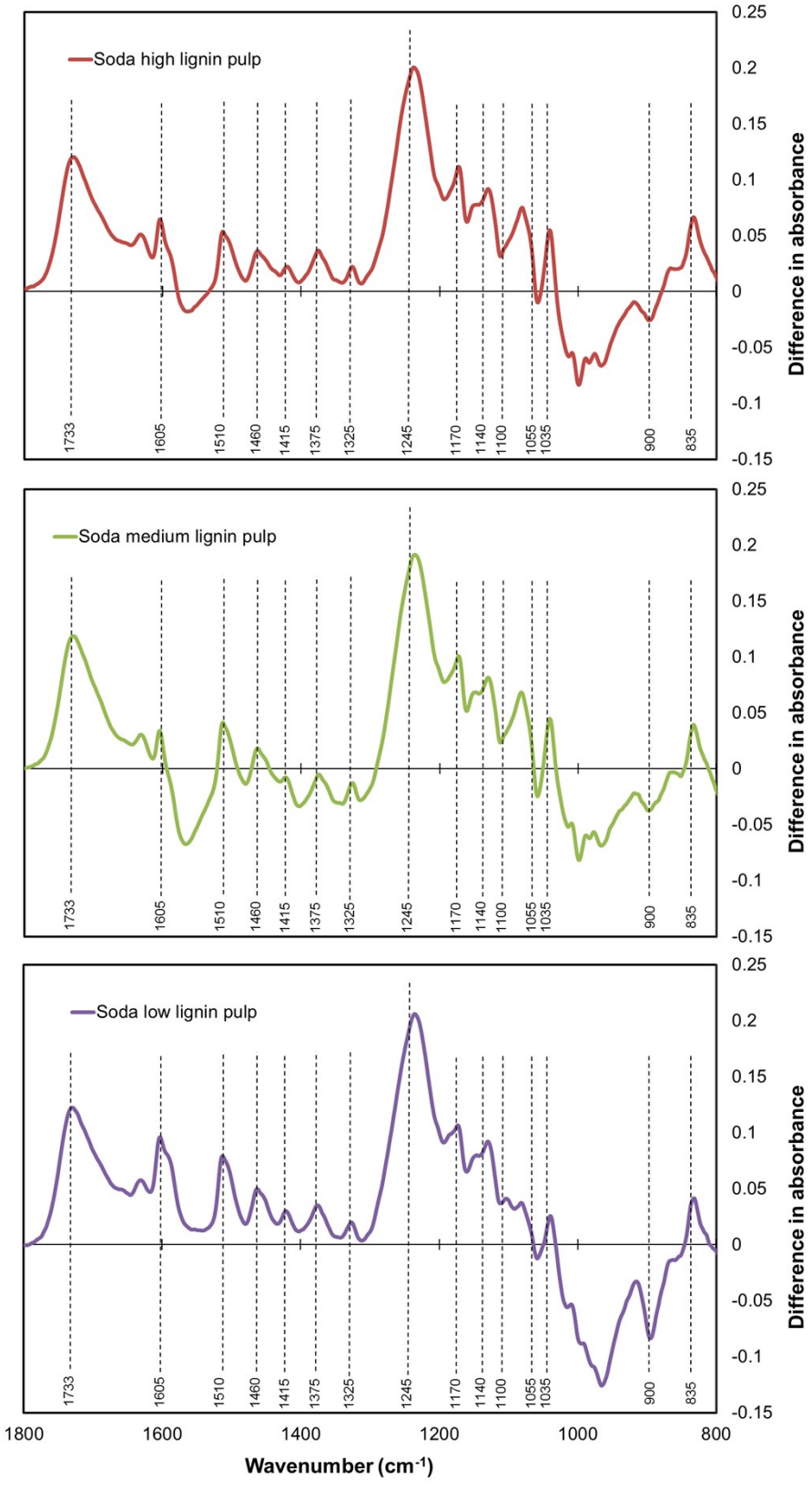

4 **Fig. S1. FTIR difference spectra (compared to bagasse) of the pulp (fiber) after soda**
5 **high lignin, soda medium lignin and soda low pretreatment**

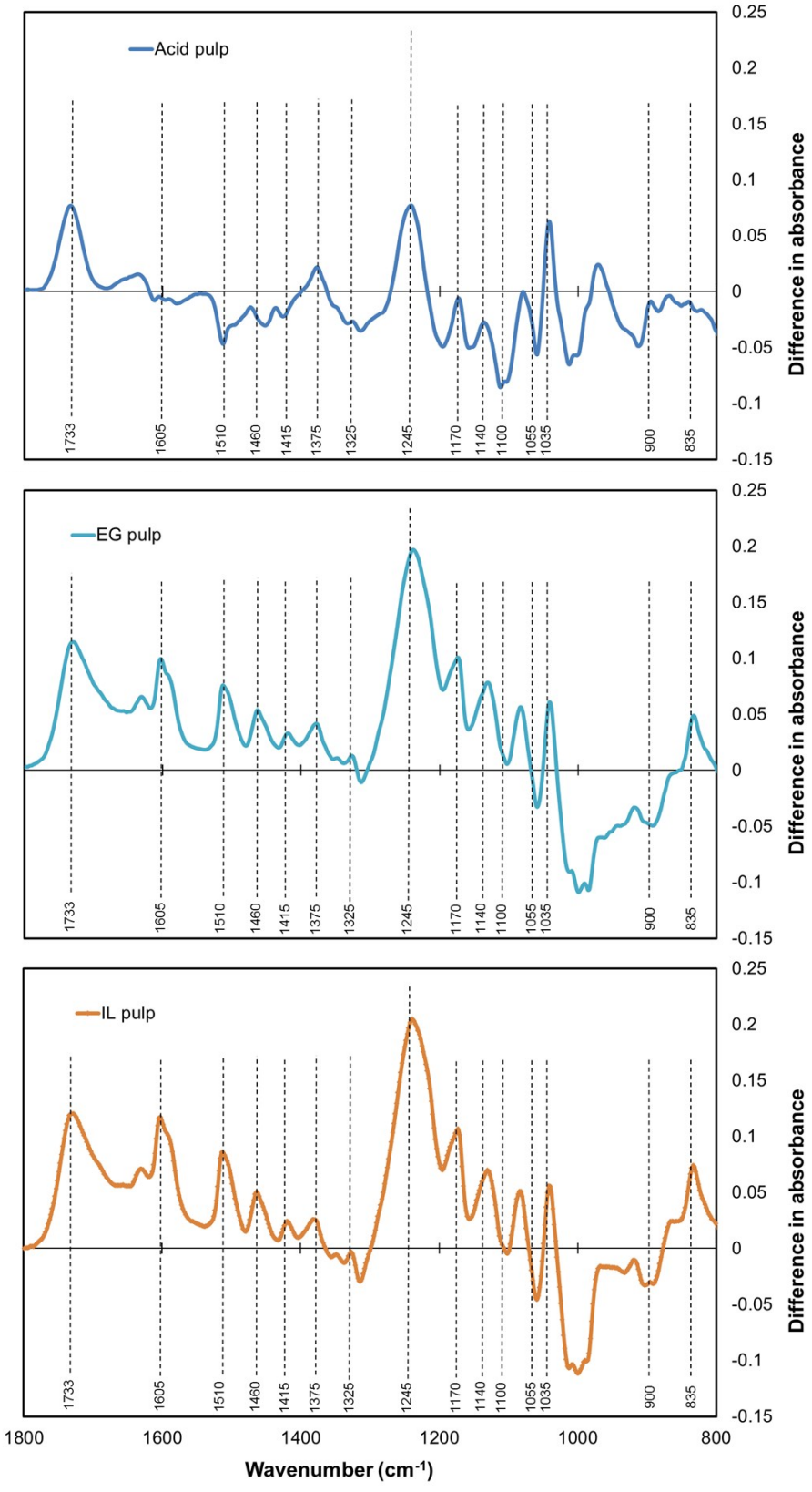

Fig. S2. FTIR difference spectra (compared to bagasse) of the pulp (fiber) after acid pretreatment, EG pretreatment and IL pretreatment

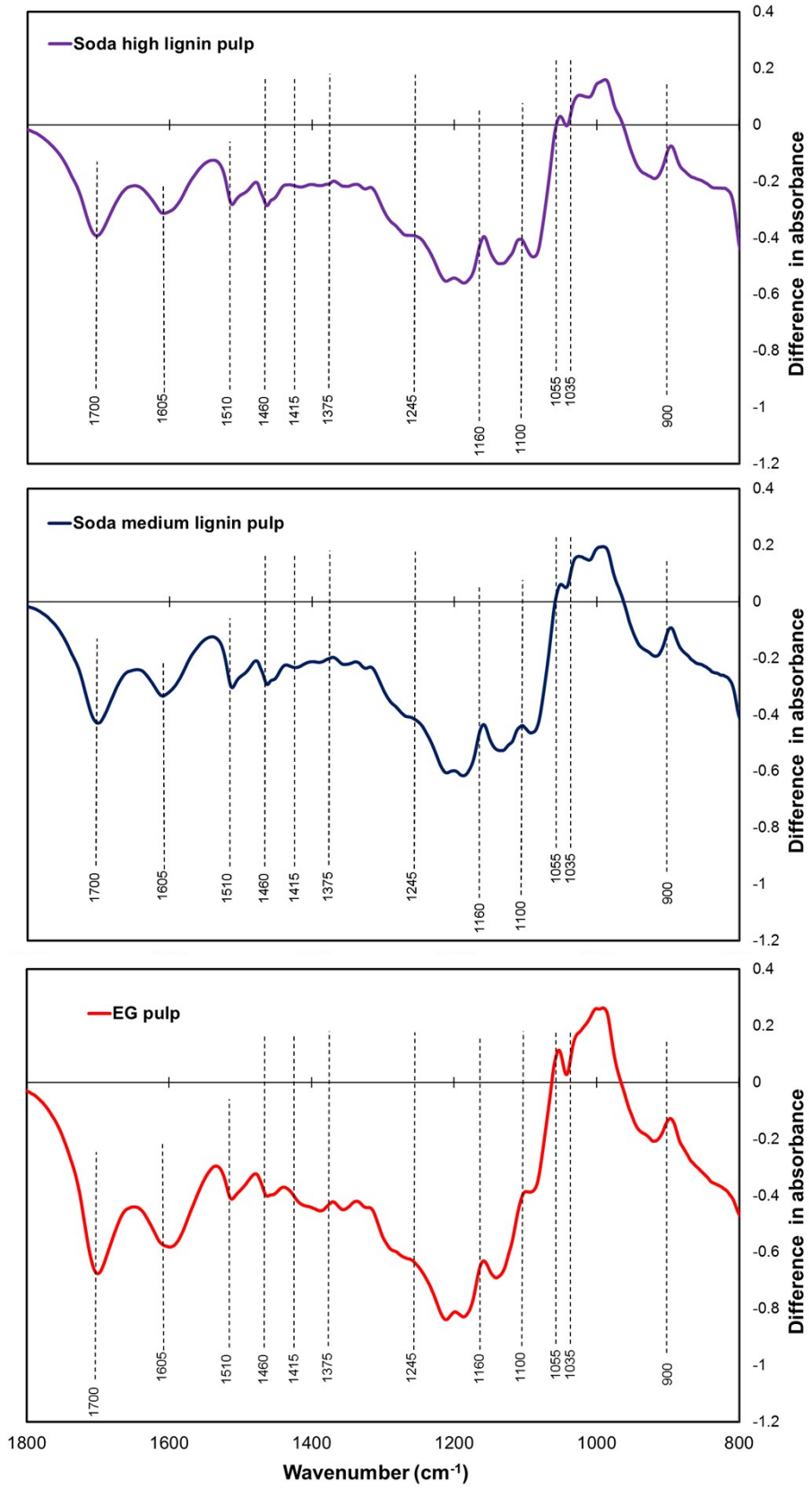

Fig. S3. FTIR difference spectra of acid hydrolysis residues (3 wt% feed, 0.3 M MSA, 180 °C, 40 min) compared to feed material for soda high lignin, soda medium lignin and EG pulps

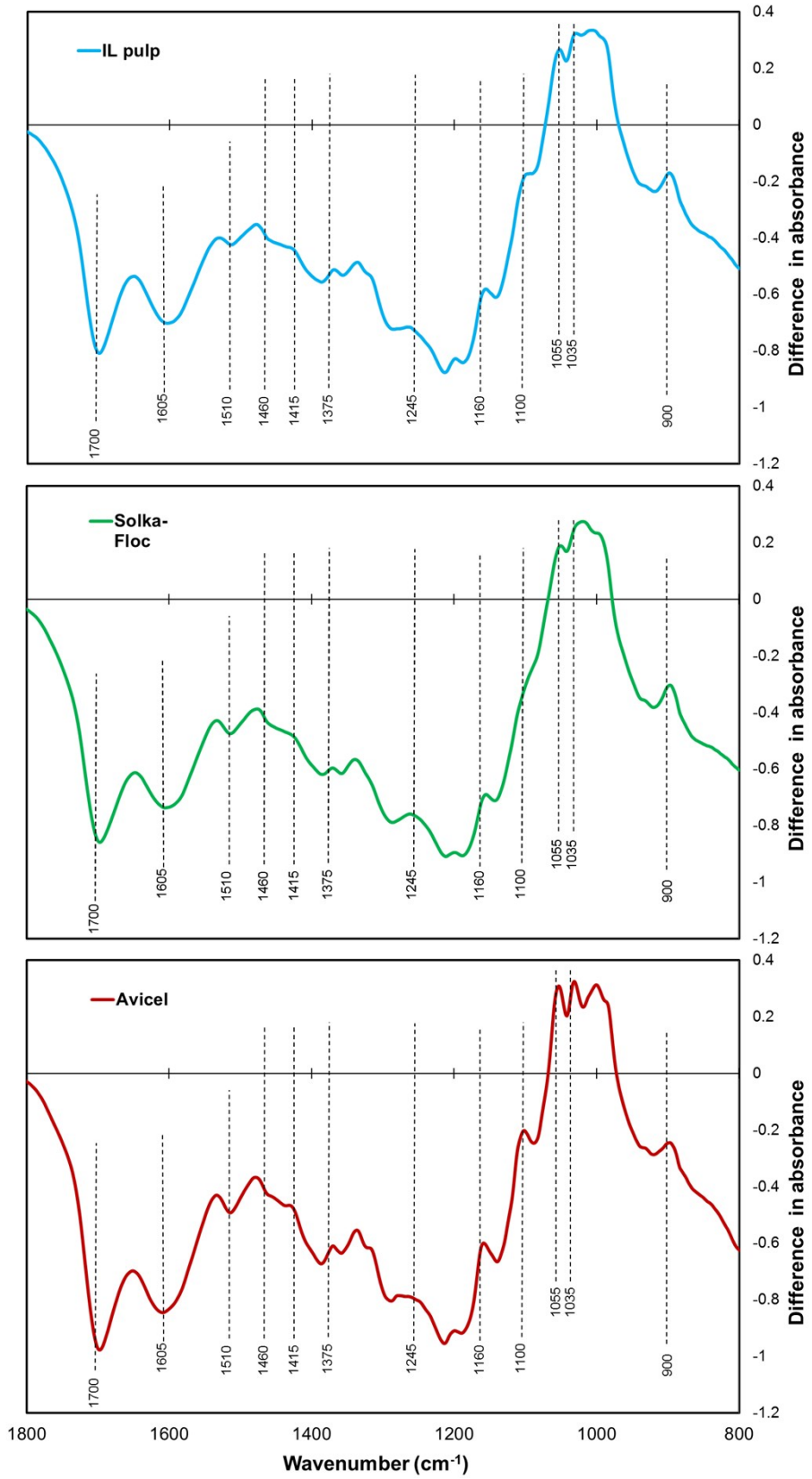

Fig. S4. FTIR difference spectra of acid hydrolysis residues (3 wt% feed, 0.3 M MSA, 180 °C, 40 min) compared to feed material for IL pulp, Solka-Floc and Avicel

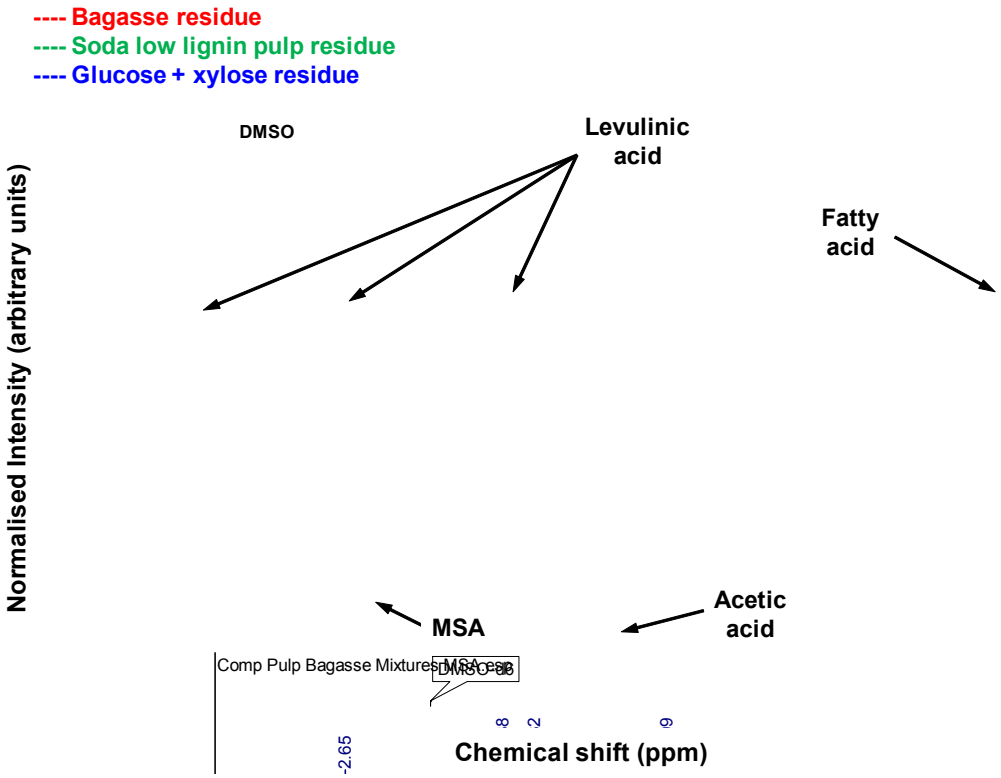

Fig. S5. Proton NMR spectra of the aliphatic region of acid hydrolysis residue of biomass (3 wt% feed, 0.3 M MSA, 180 °C, 40 min)

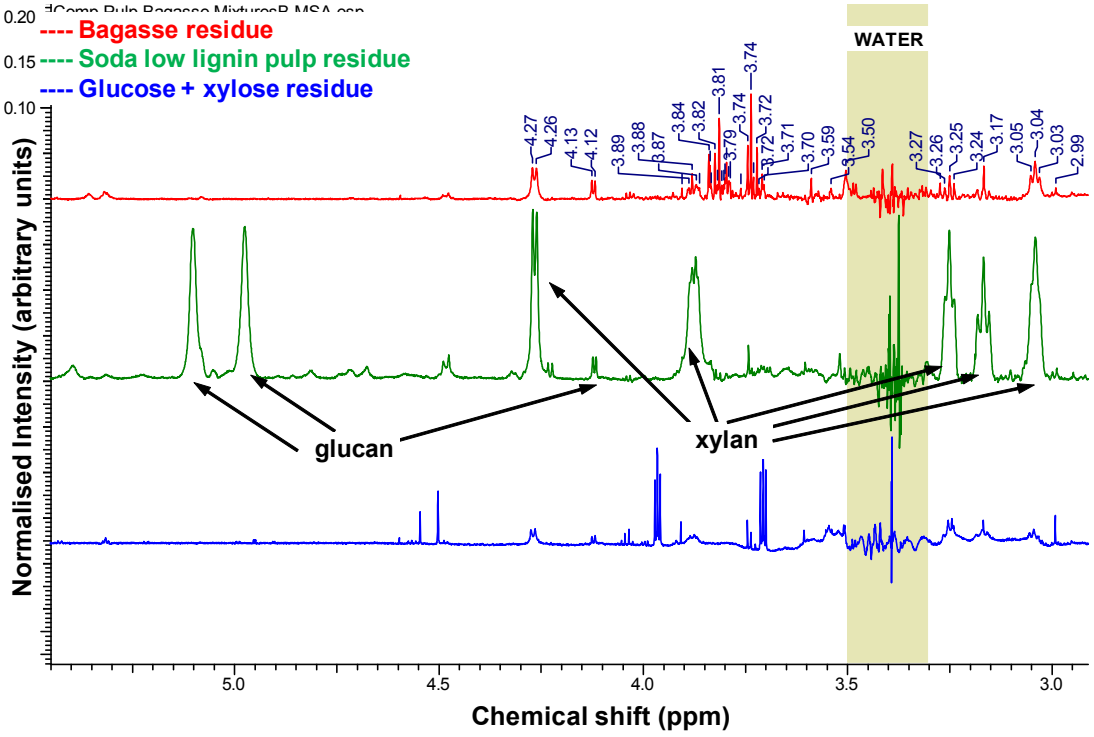

Fig. S6. Proton NMR spectra of the anomeric region of acid hydrolysis residue of biomass (3 wt% feed, 0.3 M MSA, 180 °C, 40 min)

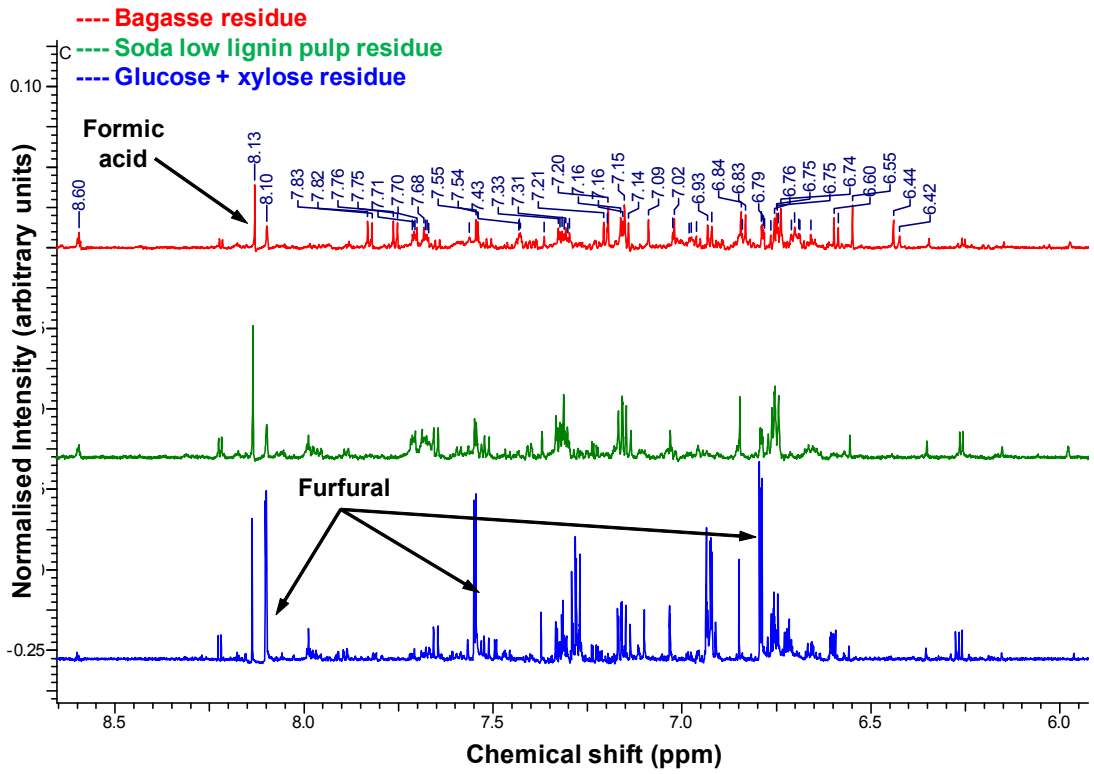

Fig. S7. Proton NMR spectra of the aromatic region of acid hydrolysis residue of biomass (3 wt% feed, 0.3 M MSA, 180 °C, 40 min)

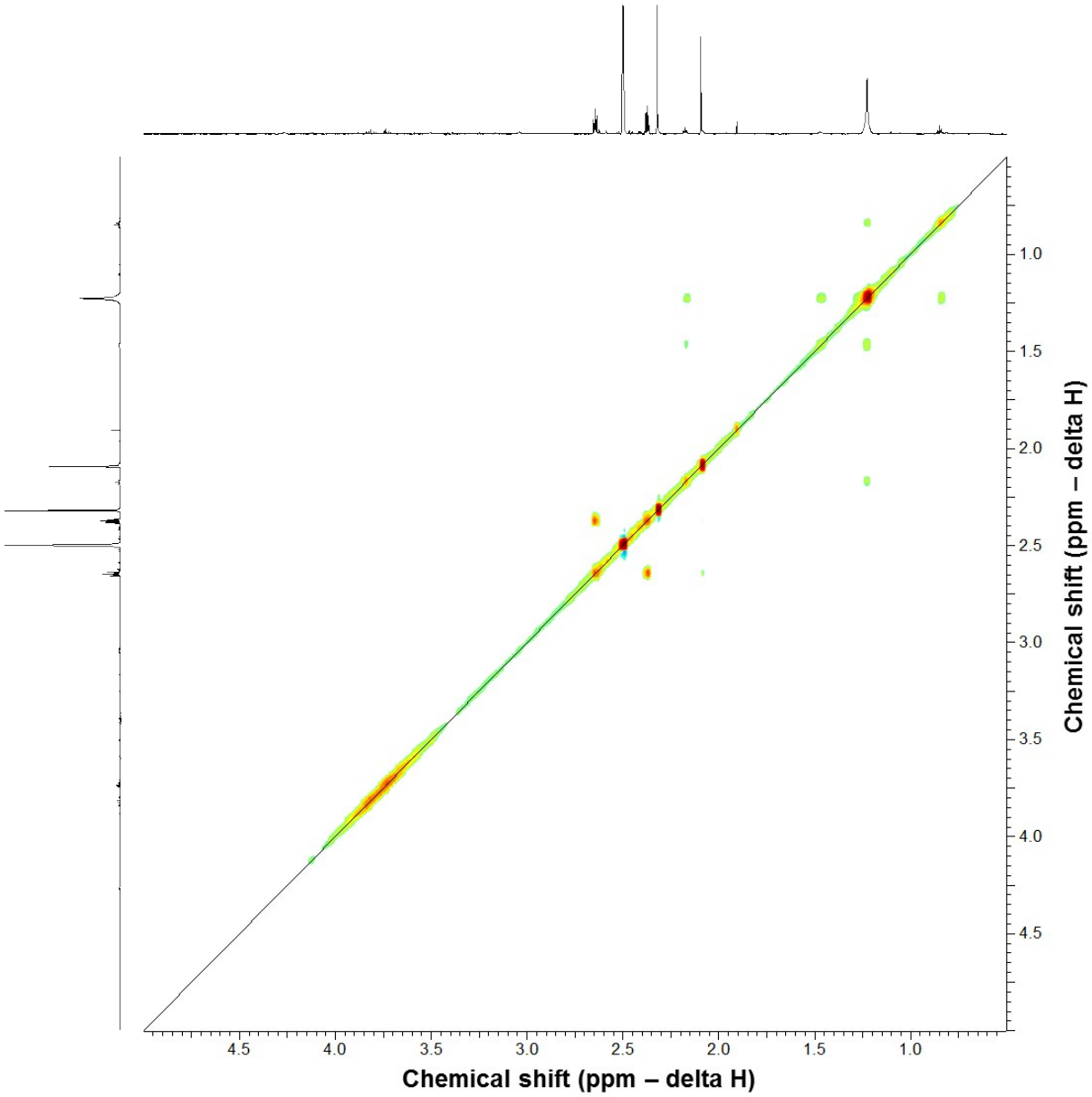

Fig. S8. COSY NMR spectrum of the acid hydrolysis residue of bagasse (3 wt% feed, 0.3 M MSA, 180 °C, 40 min)

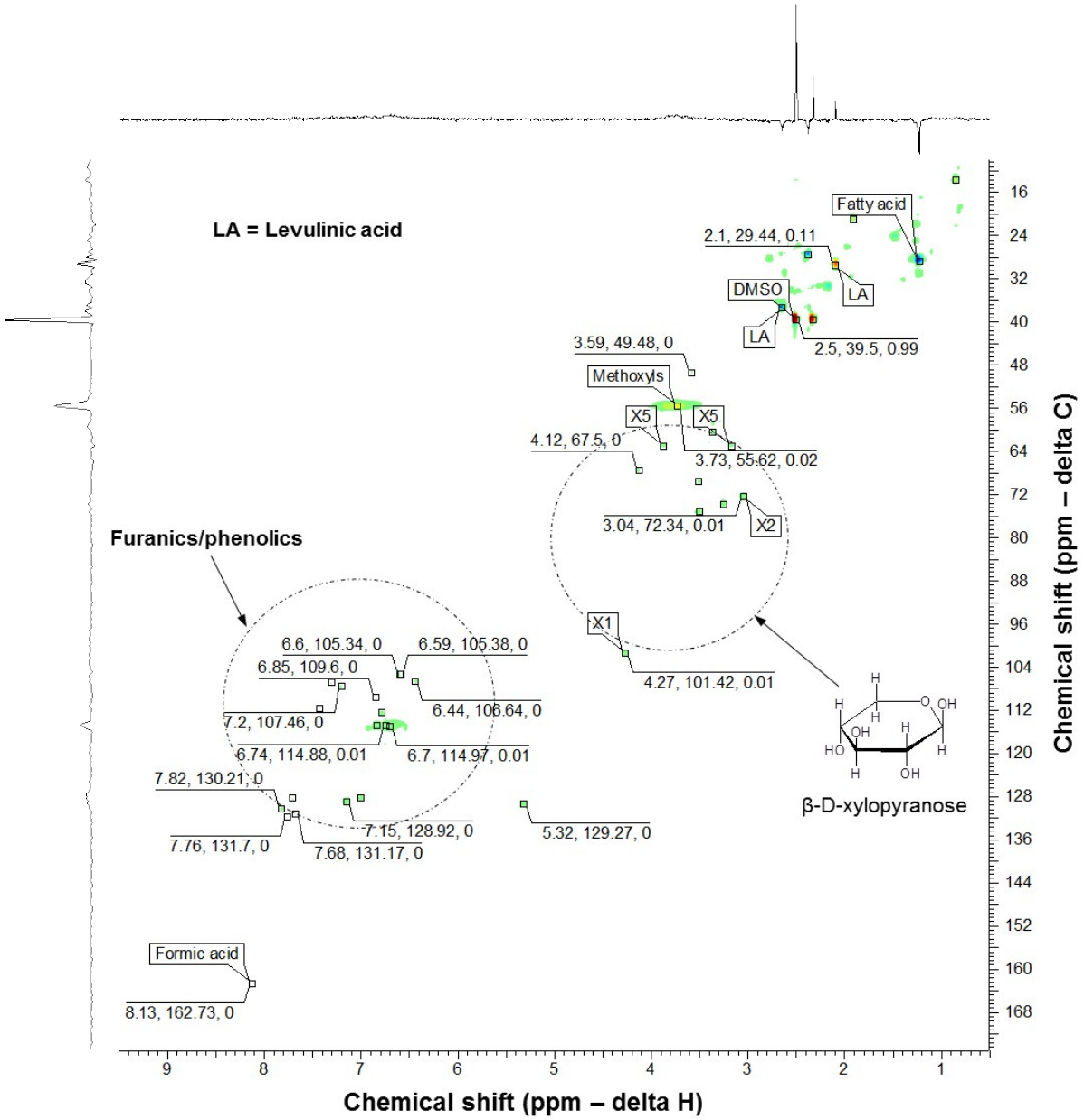

Fig. S8. HSQC NMR spectrum of the acid hydrolysis residue of bagasse (3 wt% feed, 0.3 M MSA, 180 °C, 40 min)