Electronic Supplementary Information

Design of a combined ionosolv-organosolv biomass fractionation process for biofuel production and high value-added lignin valorisation

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1 Experimental procedure

1.1 Pretreatment solvent compositions:

For *Miscanthus* pretreatments

Table S1 Solvent compositions for *Miscanthus* pretreatments with ethanol at 120 °C at a 1:10 biomass loading

Sample ID	Absolute Ethanol (g)	Ionic liquid [TEA][HSO_4] (g)	Water (g)
Control (IonoSolv)	0	8	2
Ratio 1	1	8	1
Ratio 2	2	8	0
Ratio 3	3	7	0
Ratio 4	4	6	0
Ratio 5	5	5	0
Ratio 6	6	4	0
Ratio 7	7	3	0
Ratio 8	8	2	0

Table S2 Solvent compositions for *Miscanthus* pretreatments with butanol/acetone at 120 °C at a 1:10 biomass loading

Sample ID	Absolute butanol/acetone (g)	Ionic liquid [TEA][HSO_4] (g)	Water (g)
Control (IonoSolv)	0	8	2
Ratio 1	2	8	0
Ratio 2	4	6	0
Ratio 3	6	4	0
Ratio 4	8	2	0

For pine pretreatments

Table S3 Solvent compositions for pine pretreatments with [DMBA][HSO_4] and ethanol, at 170 °C at a 1:10 biomass loading

Sample ID	Absolute Ethanol (g)	Ionic liquid [DMBA][HSO_4] (g)	Water (g)
Control (IonoSolv)	0	8	2
Ratio 1	2	8	0
Ratio 2	4	6	0
Ratio 3	8	2	0

- Mass loading pretreatments for *Miscanthus* were carried out with an ethanol to IL ratio of 4 : 6 g/g, at 120 °C.
- Mass loading pretreatments for pine were carried out with an ethanol to IL ratio of 4 : 6 g/g, at 170 °C.

1.2 Pretreatment procedure

All pretreatments were performed in triplicate. For each sample, 1.07 g of air dried *Miscanthus* or 1.05 g of air dried pine was mixed with 10 g of IL-ethanol/water mixture in a pressure tube (*Miscanthus*) or an autoclave reactor (pine), the exact weight of biomass added was recorded and the corresponding weight on an oven dried basis was calculated using the biomass moisture content obtained on the same day as the pretreatment was conducted. For *Miscanthus*, pretreatment was conducted in an oven at 120^{o}C for 8 hours, while pine pretreatments were carried out at 170 °C for 80 minutes. The cooked biomass (pulp) was cooled to room temperature before the pulp washing step. The pulp washing and lignin recovery steps were the same for both feedstocks.

The pulp was washed with 40 mL of absolute ethanol, and the suspension was transferred into a 50 mL Falcon centrifuge tube. For each tube, the mixture was well vortexed and left to settle for at least 1 hour before being vortexed again. The tube was then centrifuged for 50 minutes at 3000 rpm. The dark brown supernatant was decanted into a pre-labelled round bottom flask. This washing process was repeated another three times. All the supernatants were combined, and the remaining pulp was transferred into a cellulose thimble and further washed with 150 mL of boiling ethanol for 24 hours via a Soxhlet extraction process. The thimble containing pulp was then left in the fume hood to dry overnight.

The ethanol wash left from the Soxhlet extraction was combined with the previous washes and evaporated under reduced pressure. A brown solid containing both dried IL and extracted lignin was then obtained. 30 mL of distilled water was added into the round bottom flask to dissolve the IL, leaving the lignin as a solid. The suspension was then transferred into another 50 mL Falcon centrifuge tube, well vortexed, and then left for 60 minutes before being vortexed again. The tube was finally centrifuged, and the supernatant was decanted. The water washing process was repeated another three times.

The air-dried pulp was recovered from the cellulose thimble, weighed, and had its moisture content determined in order to obtain the oven-dried weight. The lignin was freeze-dried and weighed to obtain the lignin recovery yield.

1.3 Pulp compositional analysis

For each pulp sample, one compositional analysis sample was prepared. The acid-insoluble and acid-soluble lignin contents, ash content and sugar contents were determined. The equipment used were an analytical balance (details can be find in Experimental), 105 °C oven (VWR Venti-Line 115), muffle oven (Nabertherm with Controller P330), autoclave (Sanyo Labo ML5 3020U), pH meter (VWR SB70P), and UV-Vis spectrometer (Perkin Elmer Lambda 650 with STD detector module).

Air dried pulp (300 mg on an oven-dried basis) was weighed, transferred into a 100 mL Ace pressure tube, and 3 mL of 72 vol% sulfuric acid was added. The tube was placed in a 30 °C water bath, the acid-pulp mixture was stirred with a Teflon rod every 15 minutes for 1 hour, making sure the acid was well mixed with the pulp. The mixture was diluted with 84 mL distilled water, sealed, autoclaved for 1 hour at 120 °C and cooled for another hour to 80 °C. The compositional sample was then filtered through a pre-weighted ceramic crucible in order to separate the solid residue from the aqueous filtrate containing acid soluble lignin and sugar. 70 mL of the filtrate was collected and transferred into two 50 mL Falcon tubes for HPLC and UV analysis. For HPLC analysis, 20 mL of filtrate was neutralized with calcium carbonate until the pH value reached 5. The mixture was left to settle no more than 5 minutes, and 1 mL of the liquid phase was collected using a syringe and filtered through a 0.2 µm PTFE syringe filter into an HPLC vial and submitted for analysis.

All the solid residues were washed with hot distilled in the filtering crucible, which was dried in at 105 °C overnight, weighed (after being cooled in a desiccator for 20 minutes), and then ashed to constant weight in a muffle oven with a maximum ashing temperature of 575°C. The crucible containing ash was weighed (after being cooled in a desiccator for 20 minutes).

In total, three masses were recorded: the empty crucible, the crucible with acid-insoluble lignin and ash, and the crucible with ash only. The acid-insoluble lignin and ash contents were calculated from equations 1 and 2:

$$AIL(\%) = \frac{(m_{AIL\,+\,ASH} - m_0) - (m_{ASH} - m_0)}{m_{oven\ dried\ pulp}} \times 100\% \qquad \text{(eq. 1)}$$

$$Ash(\%) = \frac{m_{ASH} - m_0}{m_{oven\ dried\ pulp}} \times 100\% \qquad \text{(eq. 2)}$$

where m_0 is the mass of the empty crucible, $m_{AIL\,+\,ASH}$ is the mass of the crucible with acid insoluble lignin and ash, m_{ASH} is the mass of the crucible with ash only, $m_{oven\ dried\ pulp}$ is the mass of the compositional sample on oven dry basis (300 mg).

Filtrate samples were analysed by UV-Vis spectroscopy in order to determine their acid-soluble lignin contents. Two UV absorbance readings at a single wavelength 240nm were recorded. The average reading was used in equation 3 to calculate the acid soluble lignin content:

$$ASL(\%) = \frac{UV_{average} \cdot Volume_{filtrate}}{m_{oven\ dried\ pulp} \cdot \varepsilon \cdot l \cdot d} \times 100\% \qquad \text{(eq. 3)}$$

where $UV_{average}$ is the average reading of the UV absorbance, $Volume_{filtrate}$ is 86.73 ml, $m_{oven\ dried\ pulp}$ is the mass of compositional sample on oven dry basis (300 mg), ε is the absorptivity, 12 L/g cm for miscanthus and 25 L/g cm for pine, l is the path length of the cuvette in cm (1 cm), and *d* is the dilution factor of the filtrate sample (the filtrate was diluted to ensure a UV absorbance in the range of 0.7 to 1.0).

The HPLC analysis quantifies pulp sugar contents for both hexose and pentose sugars (glucose, xylose, arabinose, galactose, mannose). HPLC analysis was performed on a Shimadzu HPLC system with an AMINEX HPX-87P Column (BioRad, 300 x 7.8 mm) and an RI detector. Purified water (resistivity 18 MΩ) was the mobile phase (0.6 mL/min), the column was set to 85 °C with a flow rate of 0.6 mL min^{-1}, and the acquisition time was 20 min. Sugar calibration standards were also prepared and run for the analysis. Standards with concentrations of 0.1, 1, 2 and 4 mg mL^{-1} of glucose, xylose, mannose, arabinose and galactose and an 8 mg mL^{-1} sugar standard only containing glucose were employed. The sugar contents of compositional samples can be obtained according to equation 4:

$$Sugar(\%) = \frac{C_{HPLC} \cdot V \cdot corr_{anhydro}}{SRC \cdot m_{oven\ dried\ pulp}} \cdot 100\,\% \qquad \text{(eq. 4)}$$

where SRC stands for Sugar recovery coefficients (calculated as in equation 5), C_{HPLC} is the sugar concentration recorded by HPLC, V is the initial solution volume in mL (10.00 mL for the sugar recovery standards and 86.73 mL for the samples), $m_{initial\ weight}$ is the mass of the sugars used for preparing sugar recovery standards, $corr_{anhydro}$ is the correction for the mass increase during polymeric sugars hydrolysis and $m_{oven\ dried\ pulp}$ is the mass of compositional sample on oven dry basis (300 mg).

Sugar recovery standards for the compositional analysis procedure were prepared as 10 mL aqueous solutions close to the expected sugar concentration of the samples, transferred to pressure tubes, and 278 µL 72 % sulfuric acid was added. The pressure tubes with the sugar mixture were sealed and autoclaved. The sugar recovery coefficient was determined using equation 4. Two series of sugar recovery coefficients used in the pulp sugar content calculations are listed in **Table 4**.

$$SRC = \frac{C_{HPLC} \cdot V}{m_{initial\ weight}} \qquad \text{(eq. 5)}$$

Table S4 A list of recovery sugar standards and anhydrous correction values used in *Miscanthus* and pine compositional analysis

Sugar	Sugar recovery standards (*Miscanthus*/pine)	Anhydrous correction
Glucose	0.949/0.98	0.9
Xylose	0.878/1.08	0.88
Galactose	0.878/1.29	0.9
Arabinose	0.878/0.79	0.88
Mannose	0.878/0.86	0.9

1.4 Pulp saccharification assay

For each pulp sample, one saccharification sample was prepared. 100±10 mg of air-dried pulp was weighed, recorded, transferred into a 25 mL Sterilin tube, and the oven-dried weight was calculated. Three samples using untreated biomass were prepared for comparison Three enzyme-only samples were also run with 100 µL of distilled water, to correct for any sugar residues in the enzyme-buffer solutions. An enzyme-buffer mixture with two additional antibiotic solutions was prepared as the saccharification stock solution. Each saccharification sample was mixed with 9.9 mL of stock solution containing 5 mL sodium citrate buffer (100 mM, pH 4.8), 40 µL tetracycline solution (10 mg/mL in 70 % v:v ethanol and 30 % v:v distilled water), 30 µL cycloheximide solution (10 mg/mL in 100 % distilled water), distilled water (4.81 mL for *Miscanthus*, 4.78 mL for pine) and Novozymes experimental enzyme mixture Cellic® CTec 2led (20 µL for *Miscanthus*, 50 µL for pine). All samples were sealed and placed in a Stuart Orbital Incubator (S1500), incubated for 7 days at 50 °C and 250 rpm. After the incubation, 1 mL of the saccharification mixture was collected and filtered for each sample. All filtered samples were analysed on the Shimadzu HPLC system with an RI detector and an Aminex HPX-87P column (BioRad, 300 x 7.8 mm) with purified water (resistivity 18 MΩ) as mobile phase (0.6 mL/min). The column temperature was 85 °C and the acquisition time was 20 min. Sugar calibration standards were also prepared and run for the analysis. As for the compositional analysis, standards with concentrations of 0.1, 1, 2 and 4 mg mL^{-1} containing glucose, xylose, mannose, arabinose and galactose and an 8 mg mL^{-1} standard containing only glucose were employed.

2 Saccharification and compositional data for pulp

2.1 Saccharification and compositional data for *Miscanthus* pretreated with different organic solvent-[TEA][HSO_4] mixtures

Table S5 A list of compositional and saccharification key indicators for *Miscanthus* fractionation process using a mixture of ethanol and [TEA][HSO_4]

wt% of ethanol in pretreatment solvent	glucan recovery[a]	hemicellulose removal[a]	lignin recovery yield[a]	delignification[a]	saccharification yield[a]
0[b]	95.0	96.2	65.3	79.7	75.7
10	94.8	85.0	56.3	87.6	84.7
15	94.7	86.1	54.3	86.7	83.7
18	97.0	85.8	53.6	86.7	82.4
30	94.9	82.2	54.5	89.0	84.5
40	90.1	79.3	52.8	87.7	85.3
50	90.5	75.1	48.1	80.3	82.7
60	88.7	69.6	43.0	82.3	85.0
70	91.8	52.0	47.5	70.5	81.4
80	93.6	25.9	33.1	45.9	45.3

[a] The yield is presented in percentages of the theoretical maximum, relative to untreated biomass

[b] The pretreatment with 0 % ethanol content represents the ionoSolv process where the pretreated biomass is subjected to the ethanol pulp washing step

Table S6 A list of compositional and saccharification key indicators for *Miscanthus* fractionation process using a mixture of butanol and [TEA][HSO_4]

wt% of butanol in pretreatment solvent	glucan recovery[a]	hemicellulose removal[a]	lignin recovery yield[a]	delignification[a]	saccharification yield[a]
0[b]	90.4	91.4	66.3	70.1	65.8
20	97.5	80.8	86.6	81.5	84.6
40	92.1	77.0	71.6	79.8	85.2
60	93.0	67.1	66.5	66.6	80.2
80	97.1	34.6	61.8	53.0	51.1

[a] The yield is presented in percentages of the theoretical maximum, relative to untreated biomass

[b] The pretreatment with 0 % butanol content represents the ionoSolv process where the pretreated biomass is subjected to the butanol pulp washing step

Table S7 A list of compositional and saccharification key indicators for *Miscanthus* fractionation process using a mixture of acetone

wt% of acetone in pretreatment solvent	glucan recovery[a]	hemicellulose removal[a]	lignin recovery yield[a]	delignification[a]	saccharification yield[a]
0[b]	85.8	93.0	50.7	55.5	53.5
20	99.9	83.0	63.6	59.1	55.6
40	96.2	74.5	62.6	57.3	51.4
60	90.4	73.2	54.0	39.7	50.1
80	91.0	61.9	41.0	41.4	34.4

[a] The yield is presented in percentages of the theoretical maximum, relative to untreated biomass

[b] The pretreatment with 0 % acetone content represents the ionoSolv process where the pretreated biomass is subjected to the acetone pulp washing step

and [TEA][HSO_4]

2.2 Saccharification and compositional data for *Miscanthus* fractionated by an ethanol-[TEA][HSO_4] mixture with a 40 wt% ethanol at different solid to liquid loadings

Table S8 A list of compositional and saccharification key indicators for *Miscanthus* fractionation process using an ethanol-[TEA][HSO_4]

wt% biomass to solvent loading	Glucan recovery[a]	hemicellulose removal[a]	lignin recovery yield[a]	Delignification[a]	Saccharification yield[a]
10	96.3	62.5	60.2	86.8	86.7
20	95.0	52.3	32.2	81.3	86.8
30	96.0	42.0	22.6	70.5	77.7
40	93.2	37.9	15.4	73.7	74.6
50	95.8	36.7	12.2	70.8	71.4

[a] The yield is presented in percentages of the theoretical maximum, relative to untreated biomass

mixture with 40 wt% ethanol content with five different biomass loadings

2.3 Saccharification and compositional data for pine pretreated with different ethanol-[DMBA][HSO_4] mixtures

Table S9 A list of compositional and saccharification key indicators for pine fractionation process using a mixture of ethanol and [DMBA][HSO_4]

wt% of ethanol in pretreatment solvent	glucan recovery[a]	hemicellulose removal[a]	lignin recovery yield[a]	delignification[a]	saccharification yield[a]
0[b]	83.5	97.6	85.2	70.0	62.6
20	89.4	86.0	71.1	80.3	74.5
40	89.4	75.1	52.7	67.0	70.0
80	99.3	53.1	12.3	10.5	5.5

[a] The yield is presented in percentages of the theoretical maximum, relative to untreated biomass

[b] The pretreatment with 0 % ethanol content represents the ionoSolv process where the pretreated biomass is subjected to the ethanol pulp washing step

2.4 Saccharification and compositional data for pine fractionated by an ethanol-[DMBA][HSO_4] mixture with a 40 wt% ethanol at different solid to liquid loadings

Table S10 A list of compositional and saccharification key indicators for pine fractionation process using an ethanol-[DMBA][HSO_4] mixture with 40 wt% ethanol content with three different biomass loadings

wt% biomass to solvent loading	glucan recovery[a]	hemicellulose removal[a]	lignin recovery yield[a]	delignification[a]	saccharification yield[a]
10	90.9	74.0	52.7	70.0	70.0
30	95.9	73.0	54.2	57.4	37.1
50	96.3	66.1	43.8	45.0	17.5

[a] The yield is presented in percentages of the theoretical maximum, relative to untreated biomass

2.5 A comparison of saccharification result for pine fractionated by [DMBA][HSO_4] using different fractionation apparatus

Table S11 A list of saccharification data for pine [DMBA][HSO_4] pretreatment using different pretreatment apparatuses with different

For hydrothermal autoclave reactor[a]		For pressure tube[a]	
Pretreatment time (min)	**Saccharification yield**	**Pretreatment time (min)**	**Saccharification yield**
40	41.8	**30**	62.6
60	48.5	n/a	n/a
80	64.2	n/a	n/a
100	46.3	n/a	n/a
120	43.3	n/a	n/a

[a] All pretreatments were conducted in triplicate and the average sugar yield was listed

pretreatment durations

2.6 Substrate enzymatic digestibility of *Miscanthus* pretreated with different organic solvent-[TEA][HSO_4] mixtures

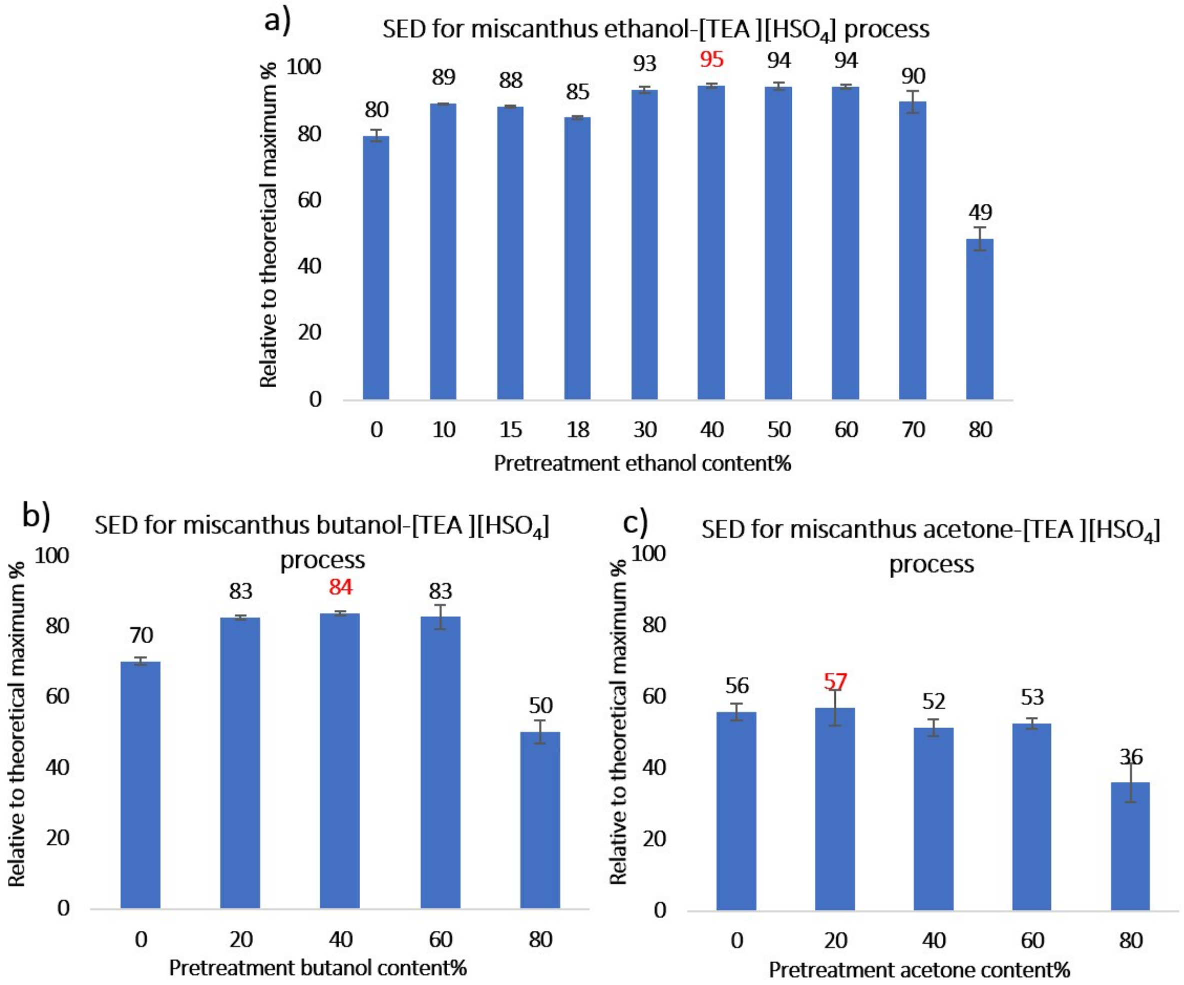


Figure S1 calculated substrate enzymatic digestibility (SED) for miscanthus pulps obtained from various organic-IL hybrid pretreatment processes a) ethanol-IL process b) butanol-IL process c) acetone-IL process

2.7 Substrate enzymatic digestibility of pine pretreated with different ethanol-[DMBA][HSO_4] mixtures

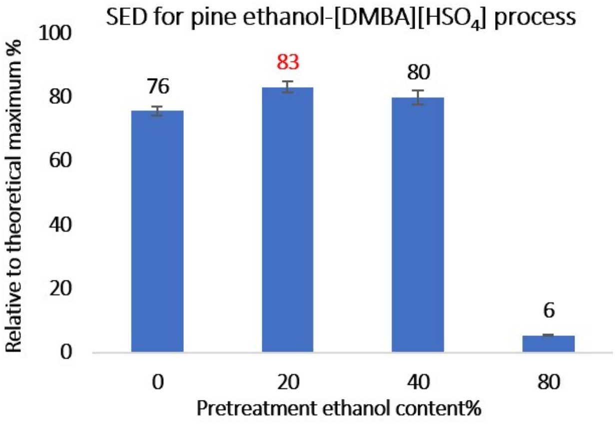


Figure S2 calculated substrate enzymatic digestibility (SED) for pine pulps obtained from various ethanol-IL hybrid pretreatment processes

3 Isolated lignin

3.1 S/G ratio of the lignin extracted from *Miscanthus*

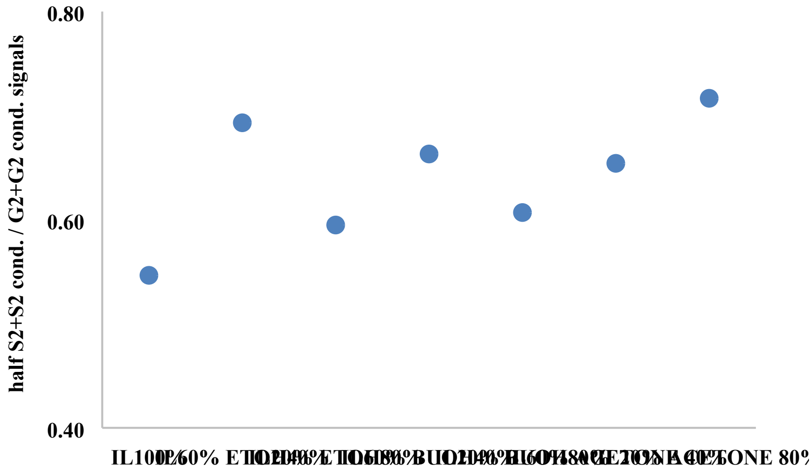


Figure S3 The calculated S/G ratio of the extracted lignin based on HSQC NMR spetra for lignin extracted from Miscanthus pretreated with different organic solvent-IL mixtures, organic solvent concentration ranged from 0 to 80 wt%, organic solvents used were ethanol, butanol, and acetone.

3.2 Dissolved lignin analysis for *Miscanthus* lignin fractionated by different organic solvent-[TEA][HSO$_4$] mixtures

Calculated Total Lignin in Solution (before lignin precipitation):

$$CTLS\left[\frac{mg}{g}\right] = \frac{(ASL + AIL)_{raw\ biomass}[mg] - (ASL + AIL)_{pulp}[mg]}{Solvent\ [g] + moisture\ [g]} \qquad \text{(eq. 6)}$$

Moisture correspond to the amount of water present in the biomass

Calculated Remaining Lignin in Solution (after lignin precipitation):

$$CRLS\left[\frac{mg}{g}\right] = \frac{(ASL + AIL)_{raw\ biomass}[mg] - (ASL + AIL)_{pulp}[mg] - lignin_{precipitated}[mg]}{Solvent\ [g] + moisture\ [g]} \qquad \text{(eq. 7)}$$

Error calculated by error propagation formula:

$$\frac{\partial}{\partial x}\left(\frac{x-a}{b+c}\right)=\frac{1}{b+c}$$

$$\frac{\partial}{\partial b}\left(\frac{x-a}{b+c}\right)=\frac{a-x}{(b+c)^2} \qquad \text{(eq. 8)}$$

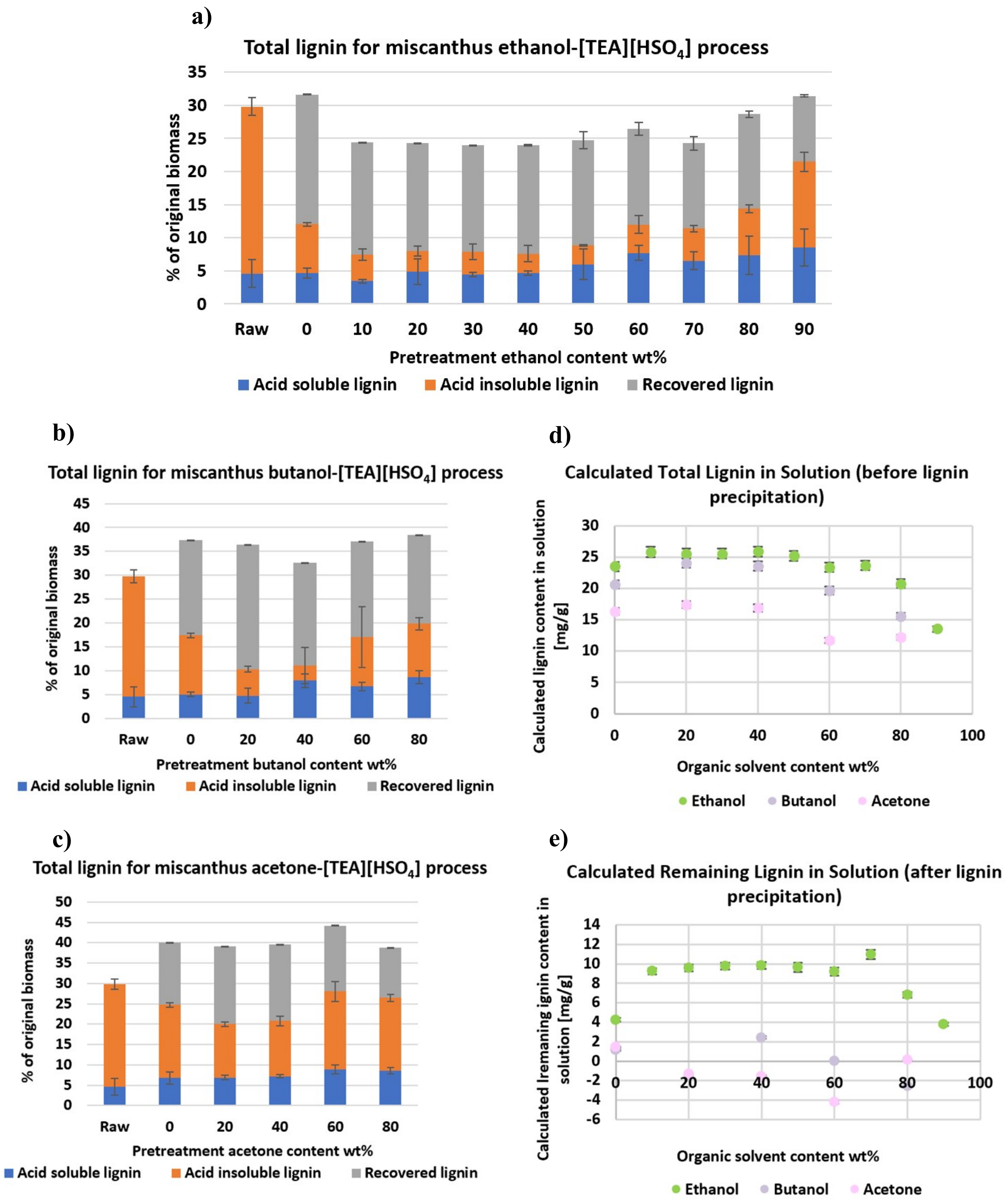


Figure S4 A comparison of total lignin content between raw and organic-IL pretreated miscanthus a) ethanol-IL pretreated pulps b) butanol-IL pretreated pulps c) acetone-IL pretreated pulps; and an analysis of lignin solubility in pretreatment solvents d) before the lignin precipitation and e) after the lignin precipitation

Pretreatment solvent composition	**IL100%**	**IL60% ETOH40%[a]**	**IL20% ETOH80%**	**IL60% BUOH40%[b]**	**IL20% BUOH80%**	**IL60% ACE40%[c]**	**IL20% ACE 80%**
G_2 peak integral intensity	46.5	65.1	77.3	73.1	83.1	48.7	65.2
$G_{2con.}$ [d] peak integral intensity	53.5	34.9	22.7	26.9	16.9	51.3	34.8
$G_{2con.}/G_2+G_{2con.}$ in %	**53.5**	**34.9**	**22.7**	**26.9**	**16.9**	**51.3**	**34.8**

[a] ETOH is short for ethanol

[b] BUOH is short for butanol

[c] ACE is short for acetone

[d] $G_{2con.}$ stands for condensed G_2 peak

3.3 The degree of condensation for isolated lignin

Table S12 Degree of condensation based on HSQC spectrum integrals for lignin extracted from miscanthus using different organic solvent-IL mixtures

Table S13 Degree of condensation based on HSQC spectrum integrals for lignin extracted from pine using different ethanol-IL mixtures

Pretreatment solvent composition	**IL100%**	**IL60% ETOH40%[a]**	**IL20% ETOH80%**
G_2 peak integral intensity	58.5	70.6	78.5
$G_{2con.}$[b] peak integral intensity	41.5	29.4	21.5
$G_{2con.}/G_2+G_{2con.}$ in %	**41.5**	**29.4**	**21.5**

[a] ETOH is short for ethanol

[b] $G_{2con.}$ stands for condensed G_2 peak

3.4 GPC analysis results for isolated lignin

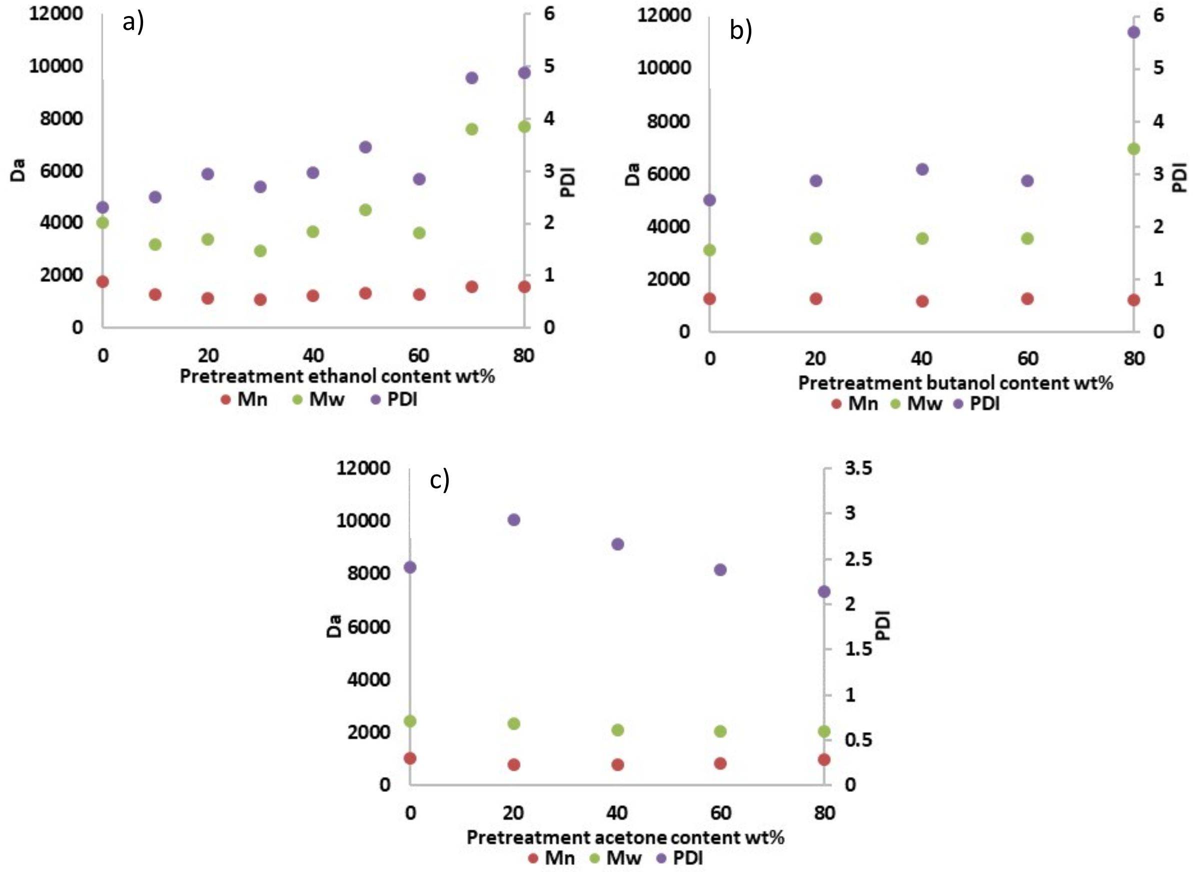


Figure S5 Average molar mass and polydispersity of lignin extracted with different organic solvent-IL mixtures a) ethanol-IL mixtures b)butanol-IL mixtures c) acetone-IL mixtures

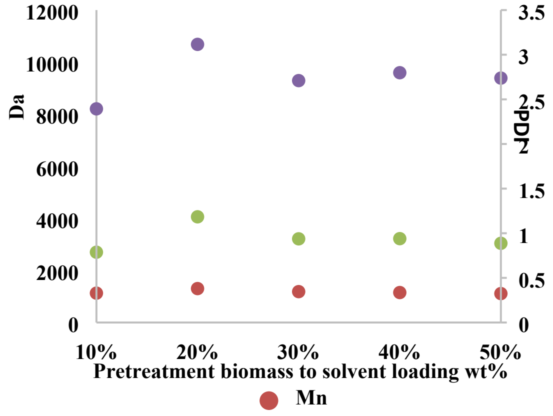


Figure S6 Average molar mass and polydispersity of lignin generated after pretreatments with different biomass loadings

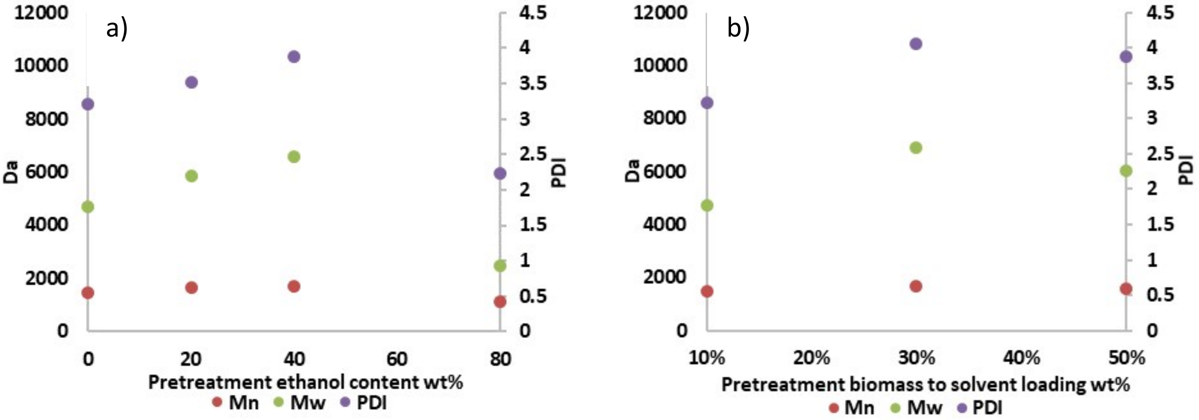


Figure S7 Average molar mass and polydispersity of lignin extracted from pine a) lignin extracted with different ethanol-IL mixtures a) extracted lignin generated after pretreatments with different biomass loadings.

4 Technoeconomic analysis of the Organosolv-ionoSolv process

The process for drying the IL has been modelled as a flash distillation, which is energy-intensive but simple, with minimum capital investment cost (CAPEX). The system was modelled in HYSYS V8.8 (thermodynamic package glycol package) with the following assumptions: I) the diluted solution contains 3 equivalents of water per equivalent of IL (on a mass basis) as per lab protocol, and II) the solution is dried to 20 wt% water for the IonoSolv case (0% organic solvent) and to 2 wt% for the other cases. The ionic liquid has been modelled as triethylene glycol (TEG). This compound have been chosen as it has a very high boiling point 289.5 °C (table S15). Despite the high boiling point and that operating temperatures remain below the boiling point (table S14), traces of TEG are found in stream 4. In the real system, it is expected that no IL will be present in stream 4 due to its very low vapour pressure. However, this should be confirmed experimentally. The heat capacity (C_p) for TEG is 3.052 kJ/kg/K, which is lower than the value determined experimentally for a similar ionic liquid triethylammonium hydrogen sulfate [TEA][HSO_4] 3.792kJ/kg/K°. As we are interested in the trend as opposed to the absolute energy consumption, the actual C_p value and the presence of TEG in stream 4, should not impact the conclusion of this analysis. The C_p value for [TEA][HSO_4] is higher than the reported C_p for an imidazole hydrogen sufate IL (1-ethyl-3-methylimidazolium hydrogen sulfate) 1.419 kJ/kg °C.

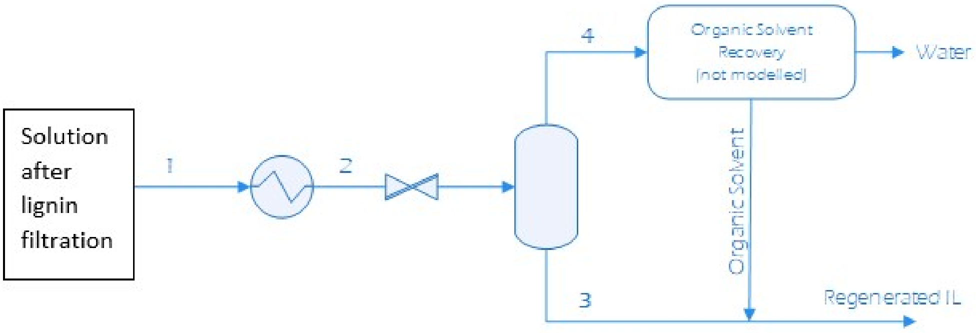


Figure S8. Simplified process flow diagram[1]

Table S14. Process conditions

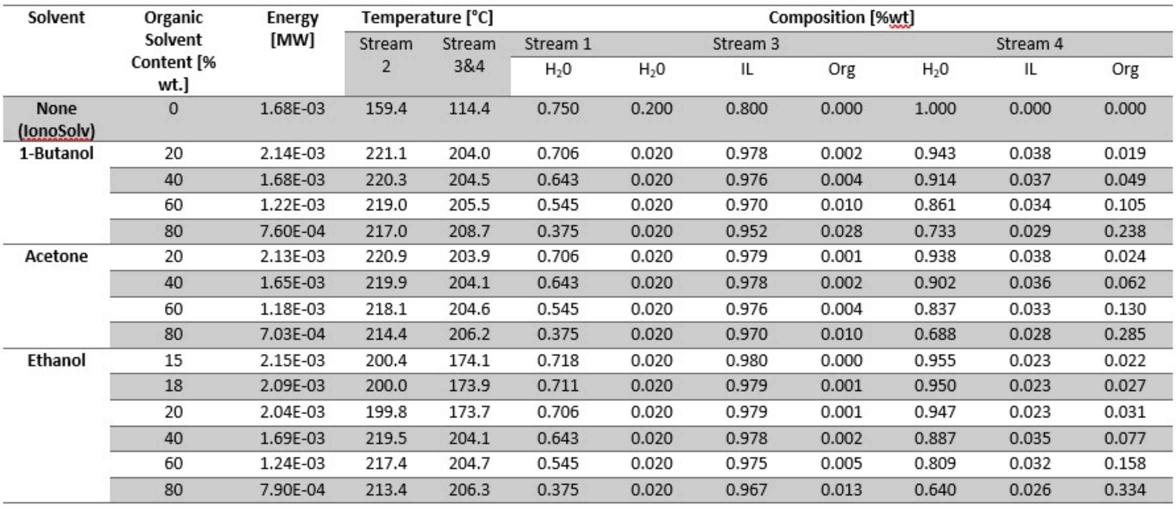
Stream	Temperature [°C]	Pressure [barg]	Remarks
1	25	4	Diluted IL for lignin precipitation
2	200-221 (*)	3.5	
3	174-209 (*)	0	Dried IL
4	174-209 (*)	0	Organic Solvent-water mixture

(*)Temperature is a function of the composition

Table S15. Compound properties predicted by HYSYS V8.8 with the thermodynamic package glycol package.

Compound	Molecular Weigh [g/mol]t	Mass Heat Capacity [kJ/kg °C]	Mass Heat of Vap. [kJ/kg]	Boiling Point [°C]
Acetone	58.1	2.022	512.1	56.1
1-Butanol	74.1	2.934	574.4	119.3
Ethanol	46.1	2.726	846.3	78.2
Water	18.0	4.217	2269.8	100.0
TEG	150.2	3.052	396.1	289.5

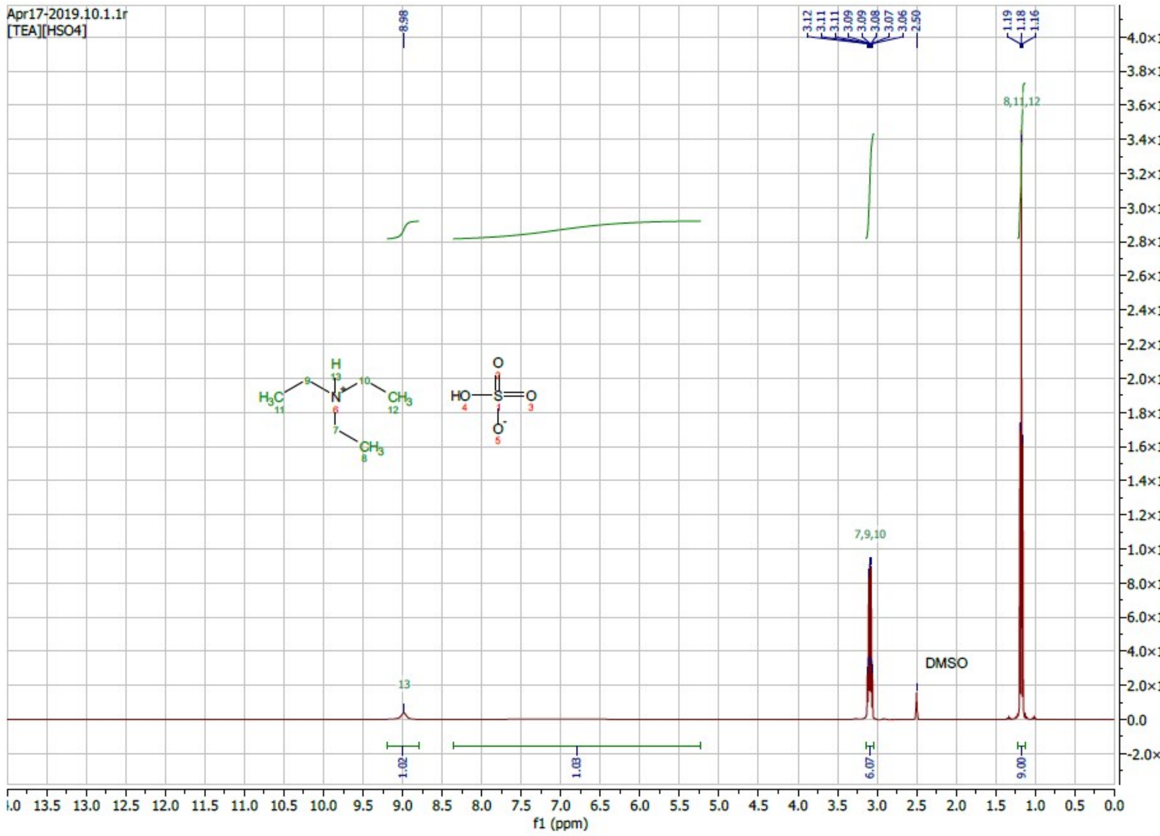
Table S16 Information about Simulation Results. Process conditions: Biomass flowrate: 0.1 kg/h and solvent flowrate 1 kg/h.



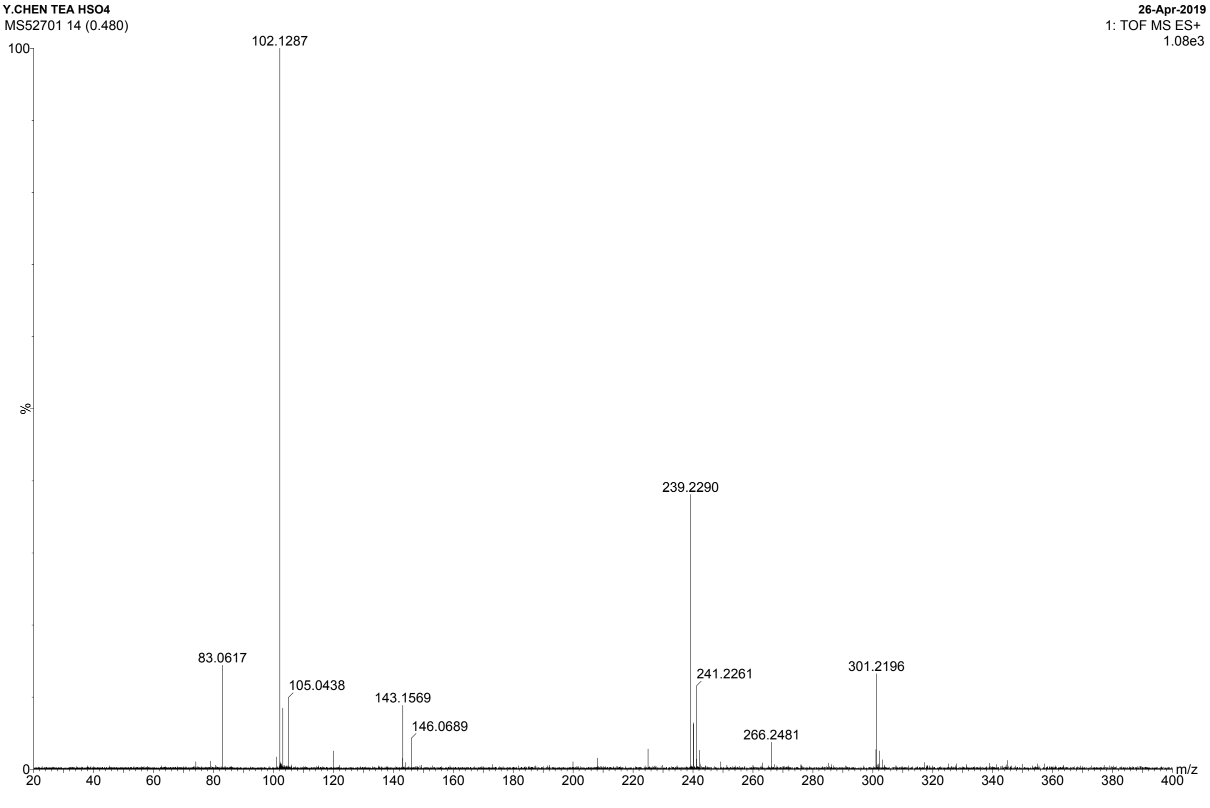
Solvent	Organic Solvent Content [% wt.]	Energy [MW]	Temperature [°C]		Composition [%wt]						
			Stream 2	Stream 3&4	Stream 1	Stream 3			Stream 4		
					H_20	H_20	IL	Org	H_20	IL	Org
None (IonoSolv)	0	1.68E-03	159.4	114.4	0.750	0.200	0.800	0.000	1.000	0.000	0.000
1-Butanol	20	2.14E-03	221.1	204.0	0.706	0.020	0.978	0.002	0.943	0.038	0.019
	40	1.68E-03	220.3	204.5	0.643	0.020	0.976	0.004	0.914	0.037	0.049
	60	1.22E-03	219.0	205.5	0.545	0.020	0.970	0.010	0.861	0.034	0.105
	80	7.60E-04	217.0	208.7	0.375	0.020	0.952	0.028	0.733	0.029	0.238
Acetone	20	2.13E-03	220.9	203.9	0.706	0.020	0.979	0.001	0.938	0.038	0.024
	40	1.65E-03	219.9	204.1	0.643	0.020	0.978	0.002	0.902	0.036	0.062
	60	1.18E-03	218.1	204.6	0.545	0.020	0.976	0.004	0.837	0.033	0.130
	80	7.03E-04	214.4	206.2	0.375	0.020	0.970	0.010	0.688	0.028	0.285
Ethanol	15	2.15E-03	200.4	174.1	0.718	0.020	0.980	0.000	0.955	0.023	0.022
	18	2.09E-03	200.0	173.9	0.711	0.020	0.979	0.001	0.950	0.023	0.027
	20	2.04E-03	199.8	173.7	0.706	0.020	0.979	0.001	0.947	0.023	0.031
	40	1.69E-03	219.5	204.1	0.643	0.020	0.978	0.002	0.887	0.035	0.077
	60	1.24E-03	217.4	204.7	0.545	0.020	0.975	0.005	0.809	0.032	0.158
	80	7.90E-04	213.4	206.3	0.375	0.020	0.967	0.013	0.640	0.026	0.334

5 NMR spectra for ionic liquids

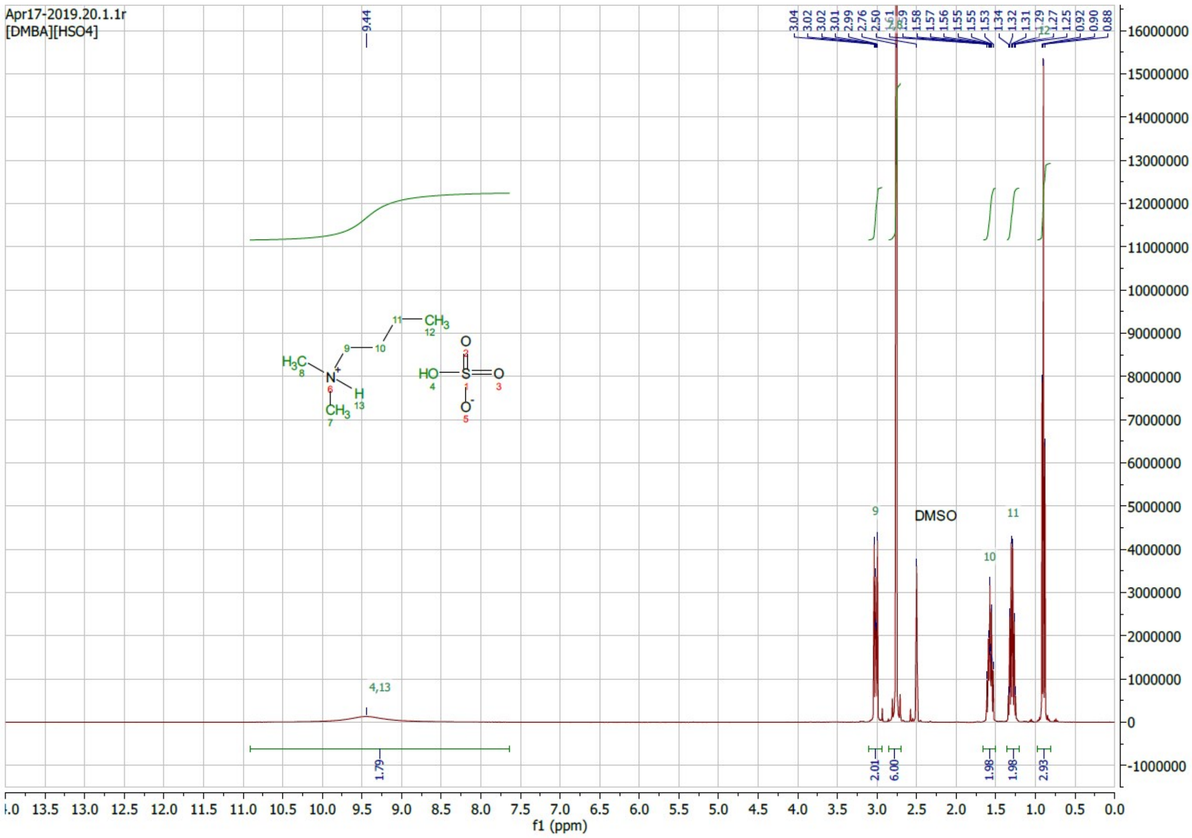
- ^1H NMR for [TEA][HSO_4]



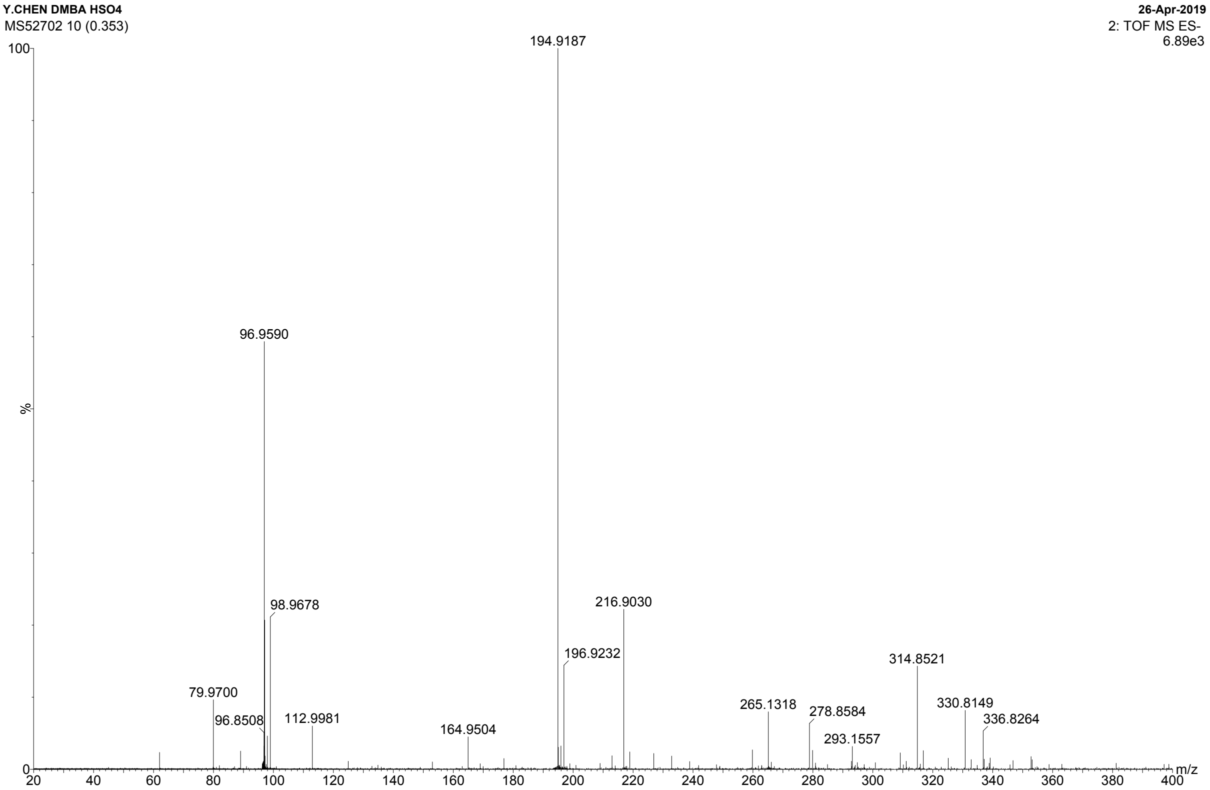
- Mass spectrum for [TEA][HSO_4]



- ^{1}H NMR for [DMBA][HSO_4]



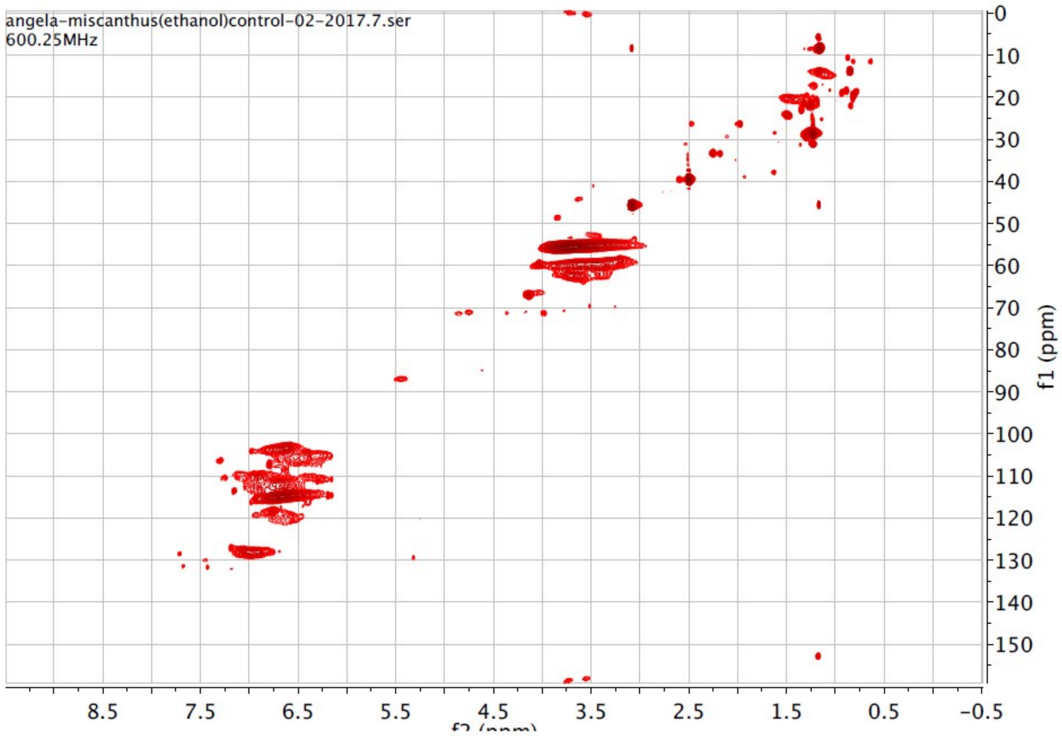
- Mass spectrum for [DMBA][HSO_4]



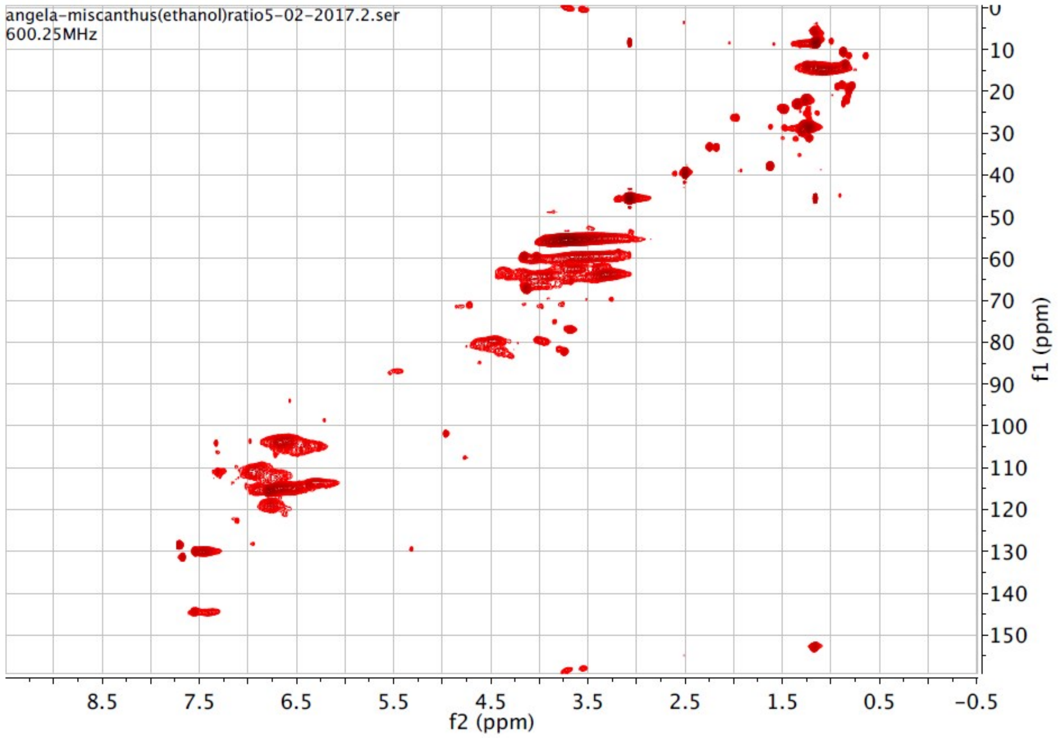
6 HSQC NMR spectra for isolated lignin

6.1 Lignin extracted from *Miscanthus*

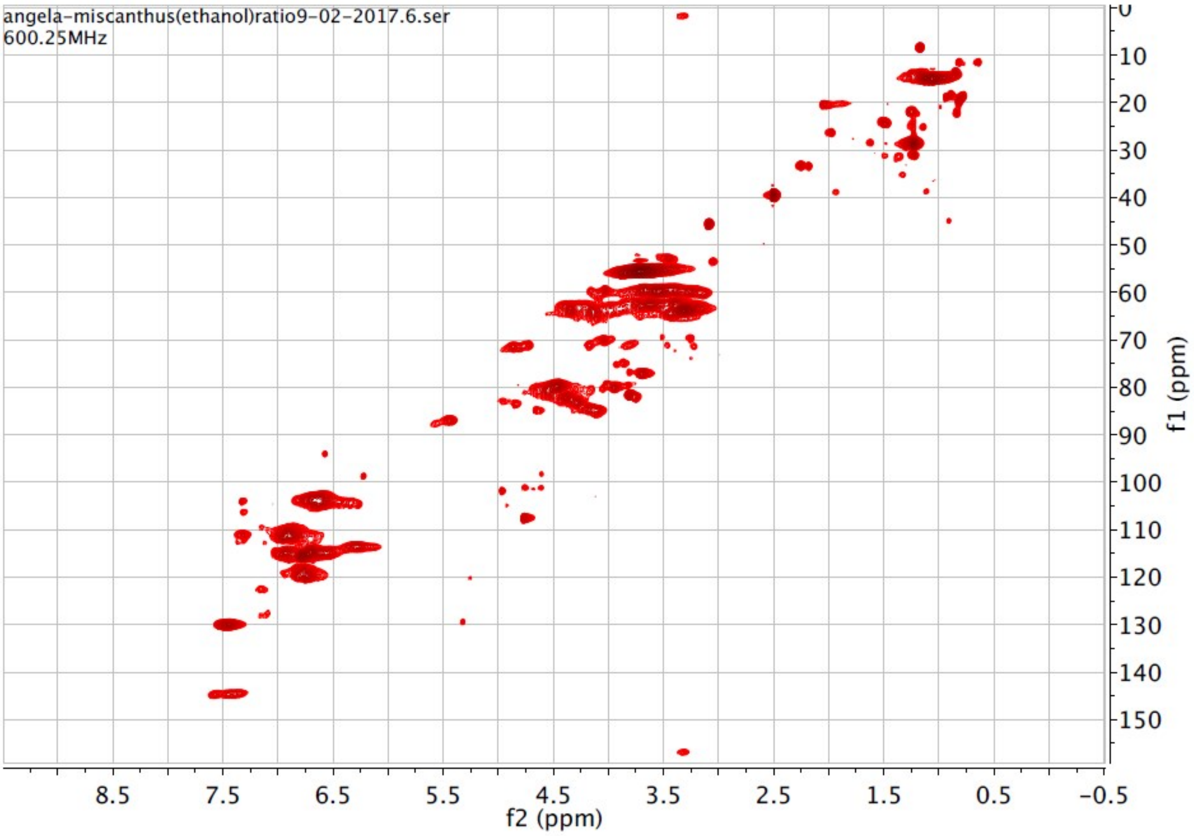
IL 100% a/b=1



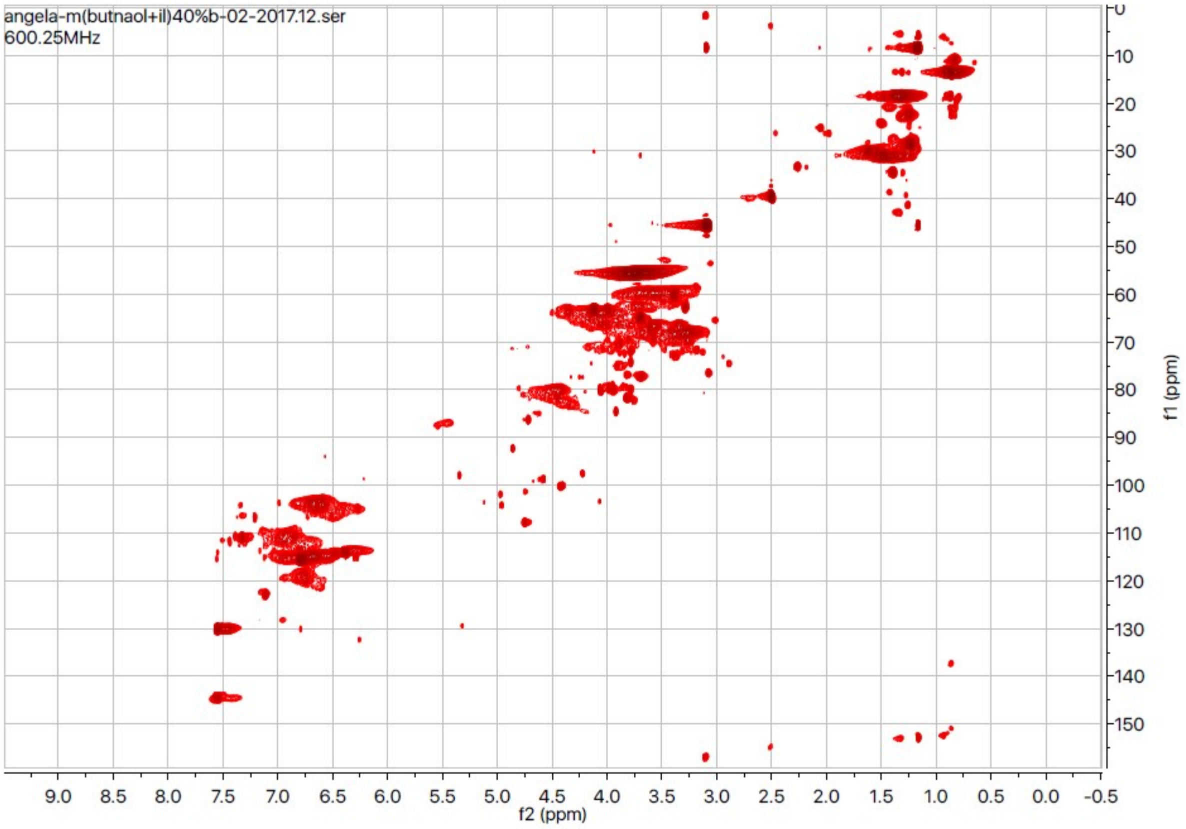
Ethanol 40% IL 60% a/b=1



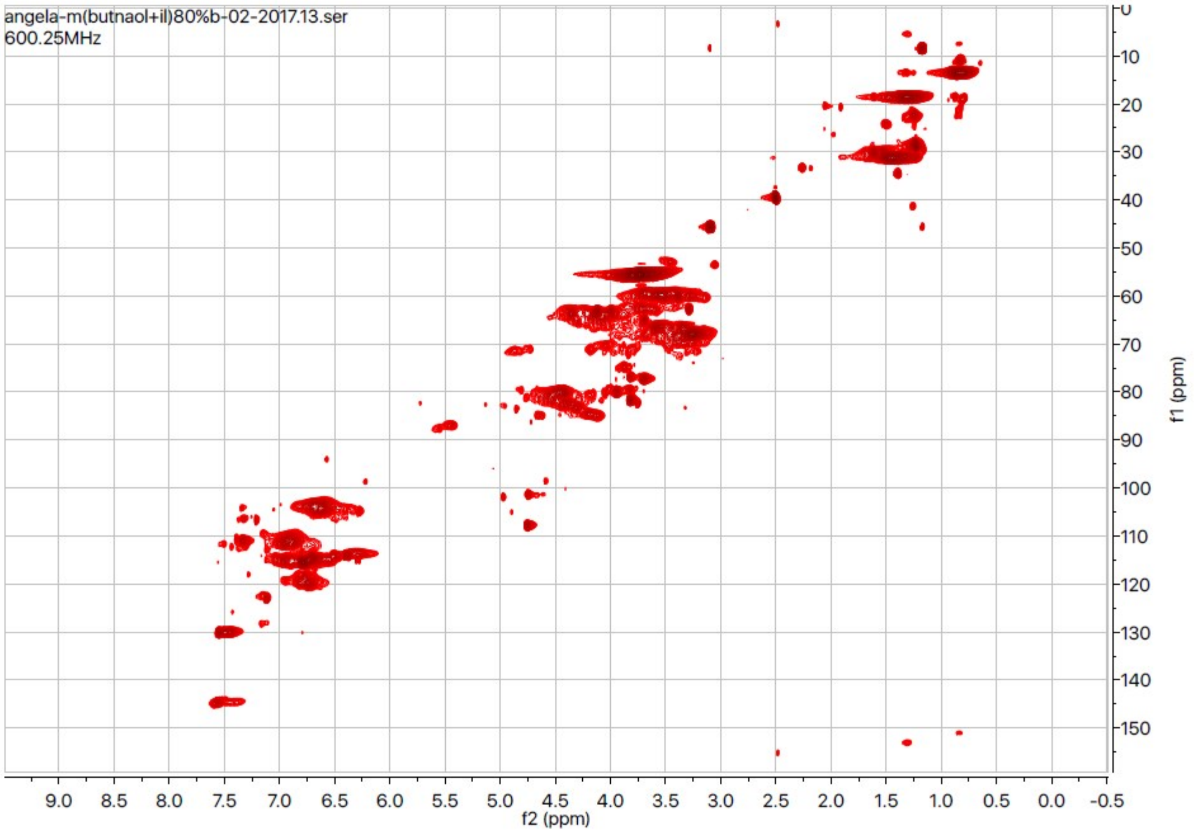
Ethanol 80% IL 20% a/b=1



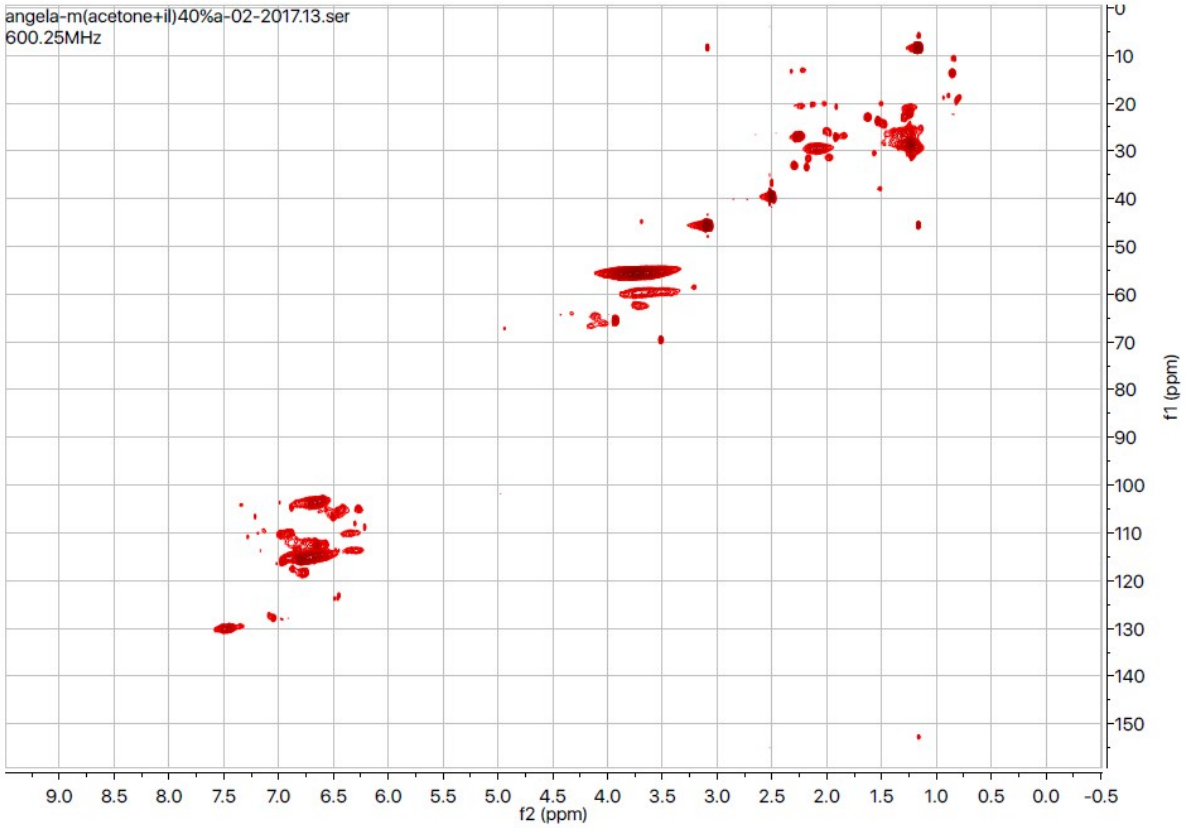
Butanol 40% IL 60% a/b=1



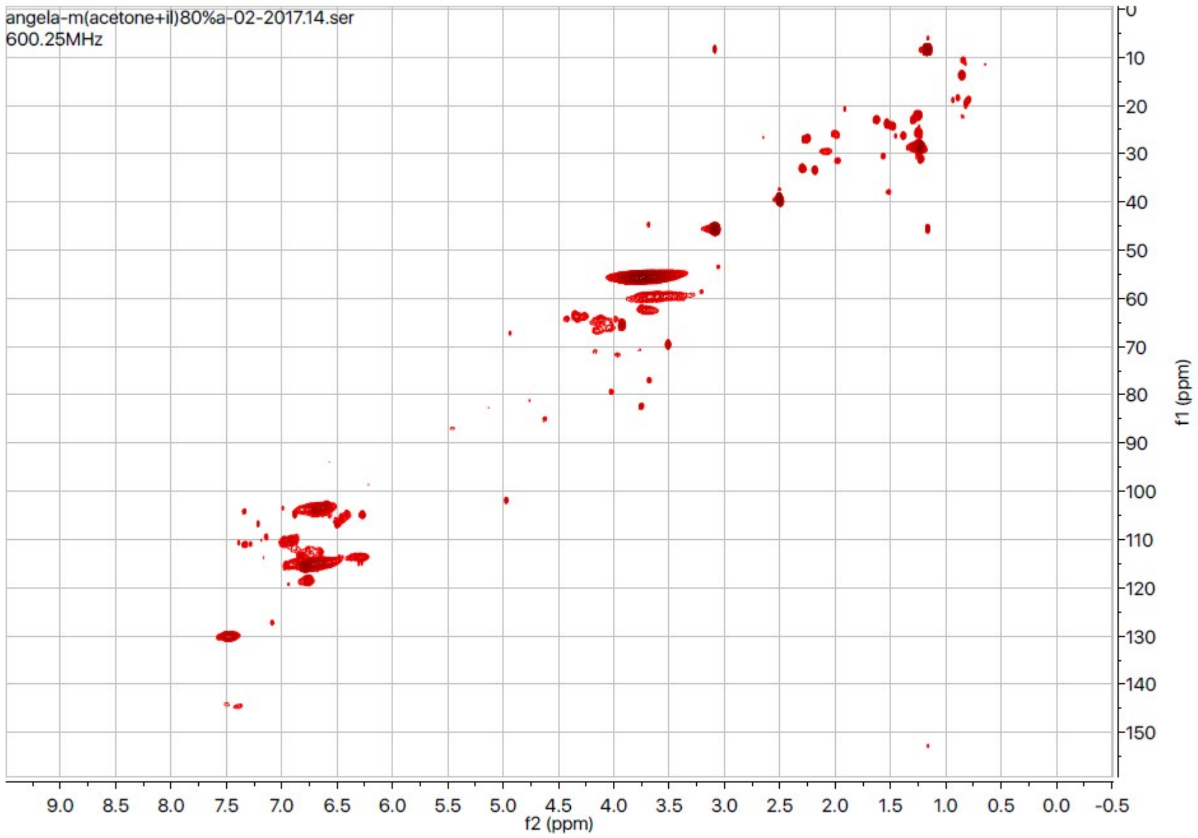
Butanol 80% IL 20% a/b=1



Acetone 40% IL 60% a/b=1

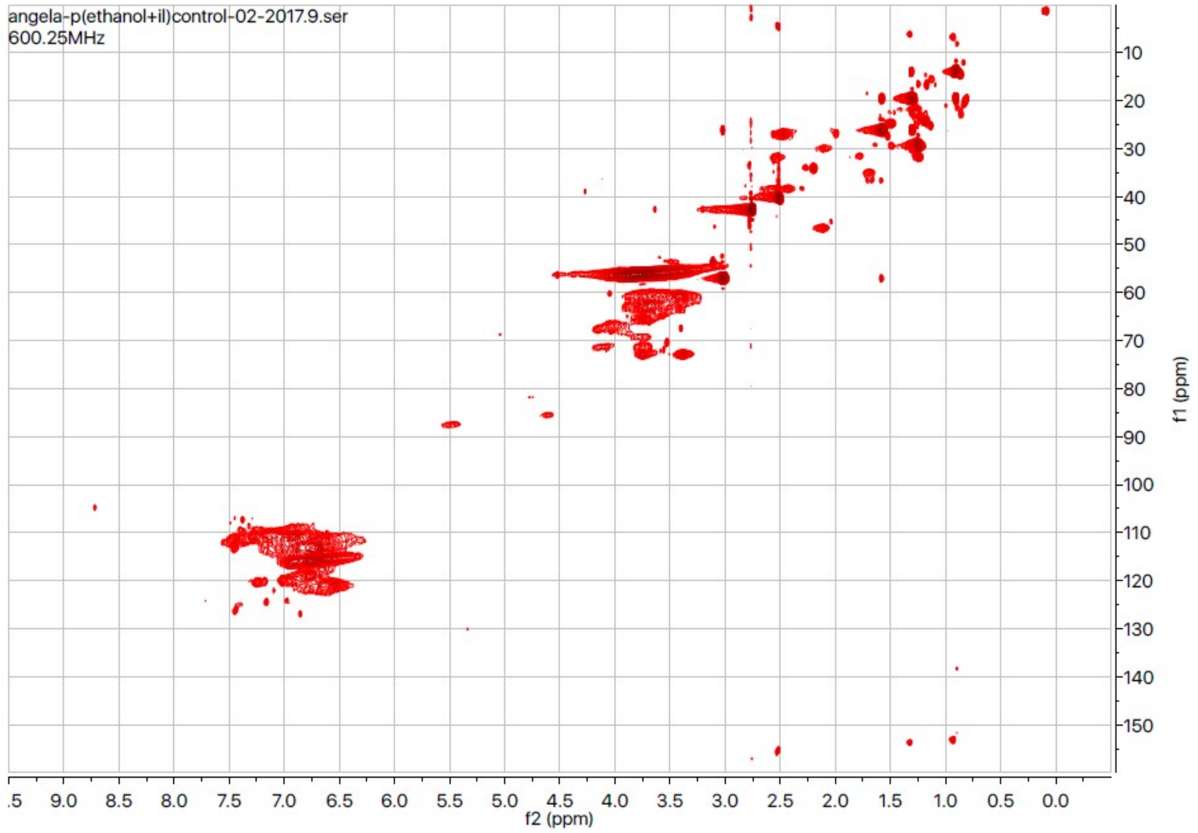


Acetone 80% IL 20% a/b=1

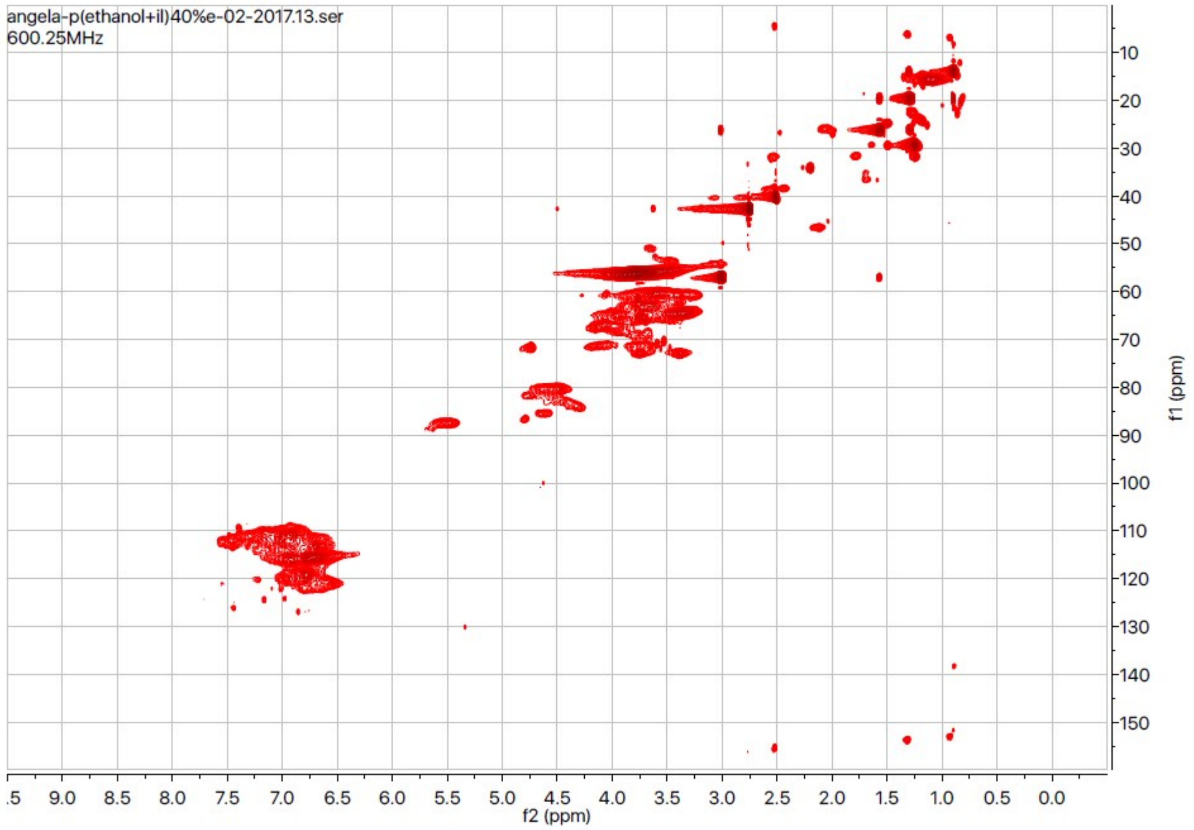


6.2 Lignin extracted from pine

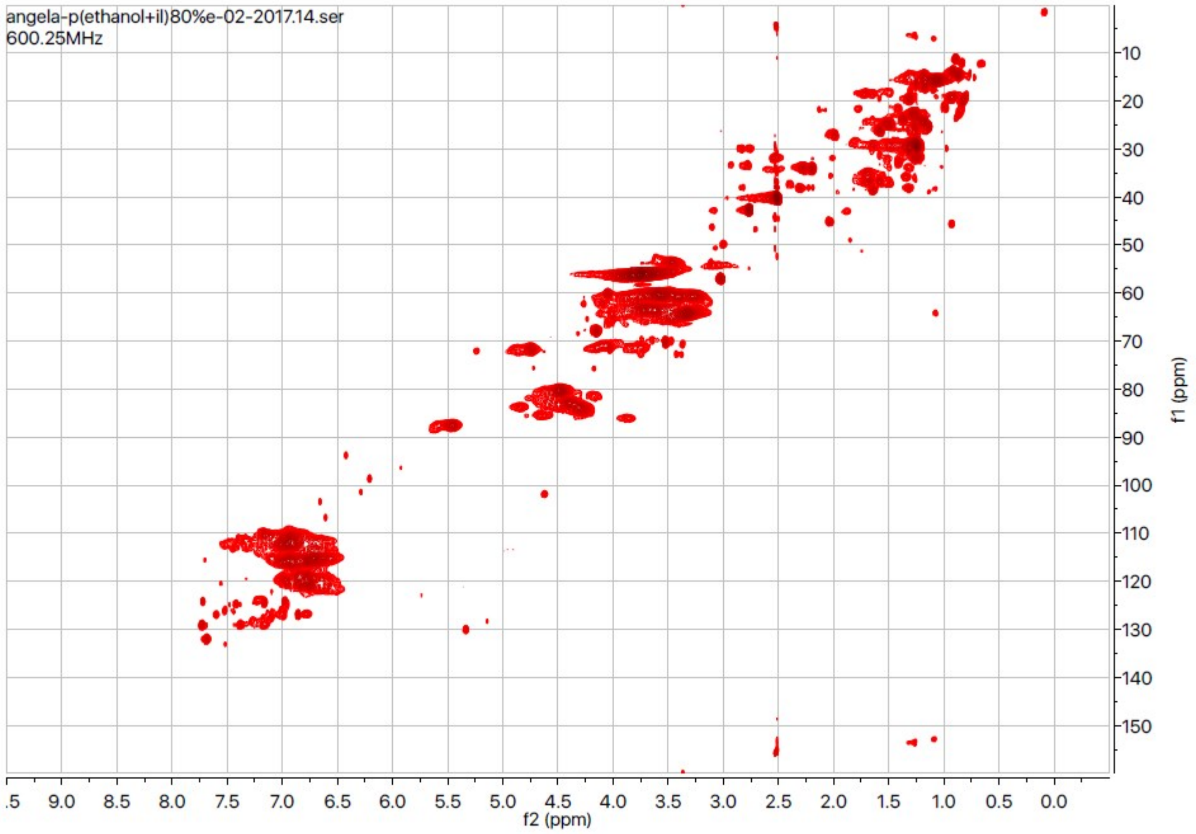
IL 100% a/b=1



Ethanol 40% IL 60% a/b=1



Ethanol 80% IL 20% a/b=1



7 References

1 A. R. Abouelela, F. V. Gschwend, F. Malaret and J. P. Hallett, in *Commercial Applications of Ionic Liquids*, 2019.