Supporting Information

The role of the molecular formula of $ZnCl_2 \cdot nH_2O$ on its catalyst activity: A systematic study of zinc chloride hydrates in the catalytic valorisation of cellulosic biomass

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Abstract: The present work demonstrates a functionality of zinc chloride hydrate solvents in catalytic processing of cellulosic materials into value added small molecules. We conduct a systematic study of $ZnCl_2 \cdot nH_2O$ (n = 2.5–4.5) and its activity in varied model transformations based on refined saccharides and discover an optimal systems and conditions for the target catalytic processes. This enable the efficient and direct transformation of a range of low value substrates, such as lignocellulose and algal biomass, into significantly higher value chemicals, including small reducing saccharides, 5-(hydroxymethyl)furfural, furyl hydroxymethyl ketone and furfural.

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Supporting data

Table S1. The content of carbohydrates in cellulosic substrates[a]

Substrate	Glucans content (wt%)	Xylans content (wt%)
Hemicellulose (obtained from Corncob)	9	60
Algal sugars (obtained from *Ulva lactuca*)	63	0
Corncob	37	29
Wood chips (softwood)	48	18
Ulva lactuca	36	5
P. Cruentum	11	12

[a] The content of carbohydrates was established by standard analytical methods and is specified in wt% based on the dry substrate.[1,2] Other polysaccharides (despite glucans and xylans) were identified in trace amounts.

Table S2. Dissolution and regeneration of microcrystalline cellulose in/from $ZnCl_2 \cdot nH_2O$ (n = 2.5–3.5) [a]

Solvent	Mass loss (wt%)
$ZnCl_2 \cdot 2.5H_2O$	18
$ZnCl_2 \cdot 2.75H_2O$	17
$ZnCl_2 \cdot 3.0H_2O$	14
$ZnCl_2 \cdot 3.25H_2O$	11
$ZnCl_2 \cdot 3.5H_2O$	5
$ZnCl_2 \cdot 3.75H_2O$	5
$ZnCl_2 \cdot 4.0H_2O$	3
$ZnCl_2 \cdot 4.25H_2O$	0
$ZnCl_2 \cdot 4.5H_2O$	0

[a] Mass loss is specified in wt% based on cellulose input. Dissolution conditions: cellulose (50 mg), $ZnCl_2 \cdot nH_2O$ (5.000 g), 80 °C, 2.5 h.

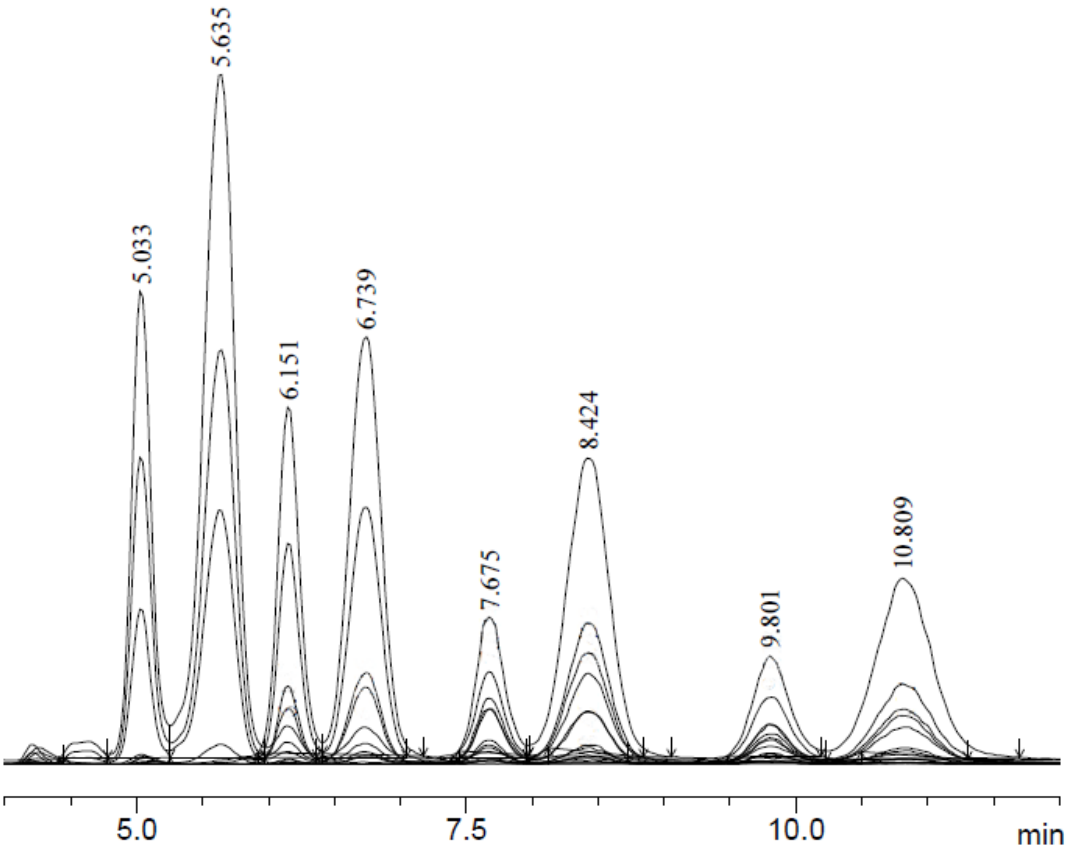

Fig. S1. LC-MS analysis of the recovered aqueous phase after the conversion of cellulose in $ZnCl_2 \cdot 4.5H_2O$ (transitions *m/z* 149.10 → 89.05, *m/z* 178.85 → 89.15, *m/z* 341.30 → 161.20, *m/z* 503.35 → 161.20 and *m/z* 665.25 → 503.10 were monitored). Peaks at retention time of 5.033, 5.635, 6.151, 6.739, 8.424 and 10.809 are appropriate to fructose, glucose, cellobiulose, cellobiose, cellotriose and cellotetraose respectively. Peaks at retention time of 7.675 and 9.801 are considered to be *keto*-isomers of cellotriose and cellotetraose, respectively.

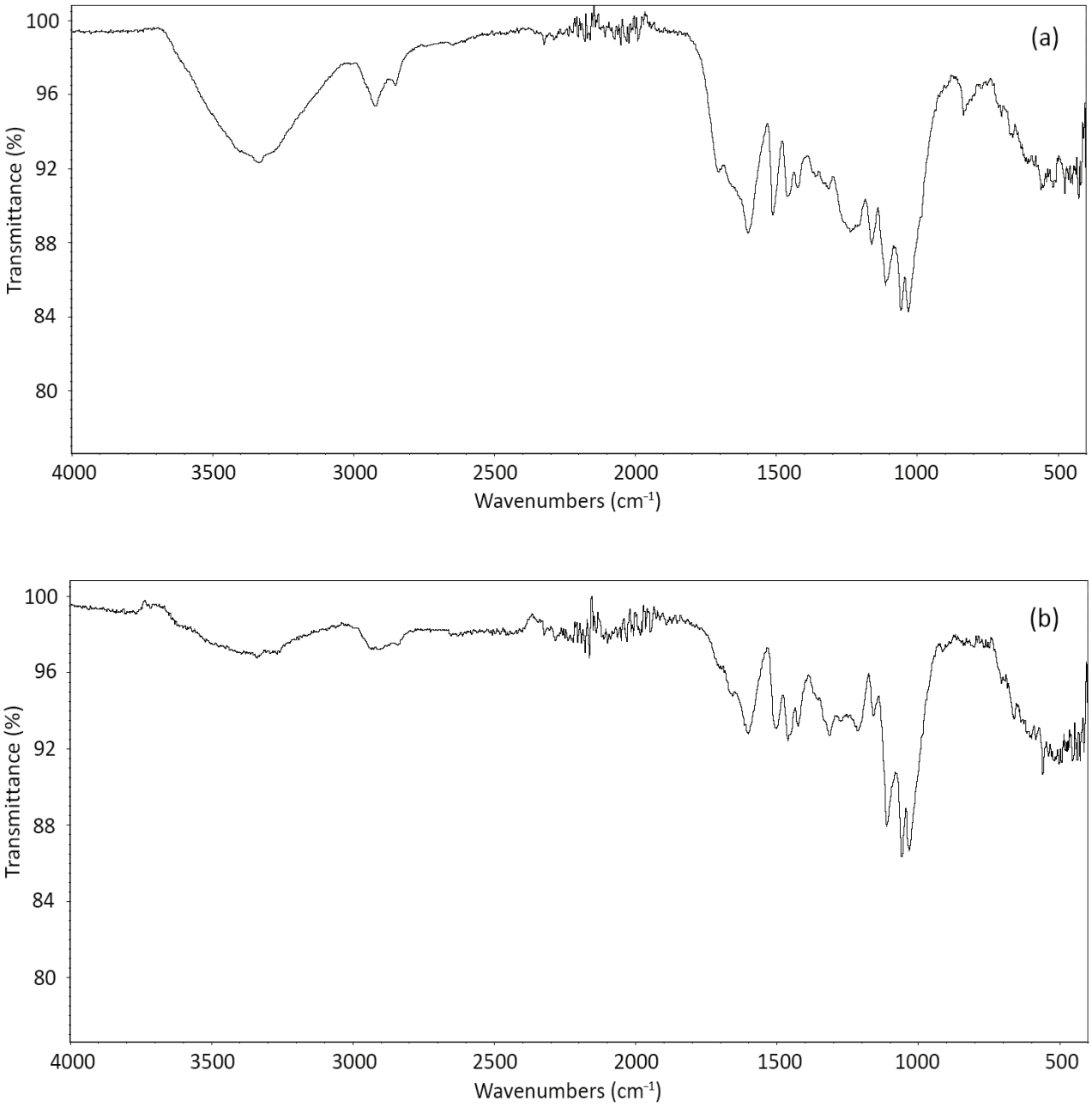

Fig. S2. IR spectra of lignin recovered after the acid-catalysed conversion of corncob (a) and softwood chips (b) in $ZnCl_2 \cdot 4.5H_2O$.

The assignment of IR spectra compares favourably with reported analytical data and is represented in Table S3.[3]

Table S3. Assignments of IR absorption bands of the recovered lignin[3]

Absorption bands for corncob lignin (cm^{-1})	Absorption bands for softwood lignin (cm^{-1})	Assignment
3335	3340	OH stretching
2922	2908	CH stretching of alkyl groups
1601, 1512, 1426	1601, 1501, 1425	Aromatic skeletal vibration
1460	1460	Aromatic methyl group vibrations
1360	1359	Aliphatic C–H stretch in CH_3
1315	1314	Syringyl ring breathing with C–O stretching
1160	1157	C–O stretch in ester groups
1111, 1056, 1031	1111, 1058, 1032	Aromatic C–H in-plane deformation

References

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