Acid-catalysed conversion of cellulosic biomass into value added small molecules

Thesis submitted in fulfilment of the requirements

for the degree Doctor of Philosophy

at

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Faculty of Science

School of Mathematical and Physical Sciences

by

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Certificate of original authorship

I, Iurii Bodachivskyi declare that this thesis, is submitted in fulfilment of the requirements for the award of Doctor of Philosophy, in the Faculty of Science at the University of Technology Sydney.

This thesis is wholly my own work unless otherwise referenced or acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

This document has not been submitted for qualifications at any other academic institution.

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Statement and list of papers

This *thesis by compilation* originates from the published and accepted works.

1. Bodachivskyi, I.; Kuzhiumparambil, U.; Williams, D.B.G. Acid-catalyzed conversion of carbohydrates into value-added small molecules in aqueous media and ionic liquids. *ChemSusChem* **2018**, *11*, 642–660.
2. Bodachivskyi, I.; Kuzhiumparambil, U.; Williams, D.B.G. A systematic study of metal triflates in catalytic transformations of glucose in water and methanol: identifying the interplay of Brønsted and Lewis acidity. *ChemSusChem* **2019**, *12*, 3263–3270.
3. Bodachivskyi, I.; Kuzhiumparambil, U.; Williams, D.B.G. Metal triflates are tunable acidic catalysts for high yielding conversion of cellulosic biomass into ethyl levulinate. *Fuel Process. Technol.* **2019**, *195*, 106159.
4. Bodachivskyi, I.; Kuzhiumparambil, U.; Williams, D.B.G. Acid-catalysed conversion of carbohydrates into furan-type molecules in zinc chloride hydrate. *ChemPlusChem* **2019**, *84*, 352–357.
5. Bodachivskyi, I.; Kuzhiumparambil, U.; Williams, D.B.G. 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. *Catal. Sci. Technol.* **2019**, *9*, 4693–4701.
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7. Bodachivskyi, I.; Kuzhiumparambil, U.; Williams, D.B.G. High yielding acid-catalysed hydrolysis of cellulosic polysaccharides and native biomass into low molecular weight sugars in mixed ionic liquid systems. *ChemistryOpen* **2019**, *8*, 1316−1324.
8. Bodachivskyi, I.; Kuzhiumparambil, U.; Williams, D.B.G. Catalytic valorization of native biomass in a deep eutectic solvent: a systematic approach towards high yielding reactions of polysaccharides. *ACS Sustainable Chem. Eng.* **2020**, *8*, 678–685.
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10. Bodachivskyi, I.; Kuzhiumparambil, U.; Williams, D.B.G. Chapter 2, Biomass processing via acid catalysis. In *Biomass valorization: sustainable methods for the production of chemicals*; Ravelli, D.; Samori, C., Eds.; Wiley. *Accepted*.

Statement of contribution of authors

Iurii Bodachivskyi (graduate research student) developed methodology, conducted research, including experimental work, data collection and data analysis (except for size exclusion chromatography-analysis), and drafted all manuscripts. Prof. D. Bradley G. Williams (principal supervisor) and Dr Unnikrishnan Kuzhiumparambil (co-supervisor) supervised Iurii Bodachivskyi's research activities, provided conceptual advice, and revised all manuscripts. Charlotte J. Page, Dr Simon F. R. Hinkley and Dr Ian M. Sims (co-investigators) performed size exclusion chromatography-analysis and revised the manuscript No. 9, 'Dissolution of cellulose: are ionic liquids innocent or non-innocent solvents?'

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Abstract

Acid-catalysed conversion of carbohydrates into organic building block molecules is a promising way to create renewable replacements for fossil fuel-based products. Despite this promise, it is presently not known how to usefully and economically convert native non-food-competitive cellulosic materials into sustainable carbon zero fuels and chemicals in high yields and with low losses. With the aim to remove the blockage towards the biorefinery, this project systematically studies the acid-catalysed transformation of cellulosic (poly)carbohydrates and provides innovative methods to efficiently convert raw, unrefined biomass into value added derivative products.

To explore catalytic reactions of cellulosic polysaccharides, this work starts with model transformations of monomer glucose under the action of Lewis acidic metal trifluoromethanesulfonates (metal triflates), Brønsted acids or combined Lewis/Brønsted acid catalysts in water and methanol. The work underscores the notion that metal triflates are highly tunable catalysts, which under optimised conditions can selectively convert glucose into disaccharides and oligosaccharides, fructose, methyl glycosides, or methyl levulinate. The tunable acidic catalyst systems are further employed in the high-yielding transformation of microcrystalline cellulose into ethyl levulinate in ethanol. The pretreatment of raw and unrefined cellulosic biomass with a biobased deep eutectic solvent affords similarly efficient transformation thereof into ethyl levulinate.

In parallel, the project interrogates the valorisation of cellulosic biomass in ionic liquids. Firstly, it researches zinc chloride hydrates with a molecular formula $ZnCl_2 \cdot nH_2O$ (n = 2.5–4.5) as solvent-catalyst media for the production of low molecular weight saccharides and furan type molecules. It defines the preferred reaction conditions to select furyl hydroxymethyl ketone and furfural, or low molecular weight saccharides and 5-(hydroxymethyl)furfural, from the processing of cellulosic materials. In addition, the work employs a co-solvent system, comprising 1-butyl-3-methylimidazolium chloride and the deep eutectic solvent choline chloride/oxalic acid for the selective depolymerisation of cellulosic biomass into derivative monomer sugars and water-soluble oligoglucans. It separately probes the reactivity of native polysaccharides in the neat deep eutectic solvent and identifies preferred conditions for the direct transformation of structurally branched polysaccharides into monosaccharides and furans, simultaneously providing fine cellulosic powder. The unreacted cellulose may be further beneficiated into additional useful chemicals, optimising towards total use of the biomass.

Finally, the work targets a deeper understanding of the dissolution, recovery, and characterisation of cellulose in various classes of ionic solvents. It combines the obtained knowledge of the processing of cellulose in the abovementioned ionic systems, providing practical recommendations for their use in cellulose refinery.

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