Obtaining Important Nitrogen-containing Platform Chemicals from the Valorisation of Chitin

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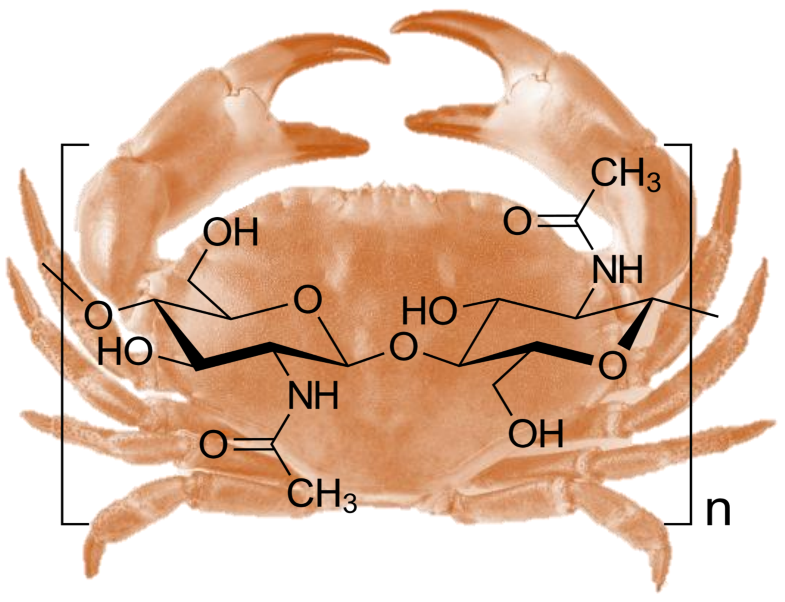

Figure 1. Structure of chitin (poly(β-(1-4)-N-acetyl-D-glucosamine)

Introduction

Chitin, a semi-crystalline biopolymer, is the most abundant source of biologically fixed N_2 (Figure 1). Chitin exists in the exoskeletons of arthropods, including crustacean shells, and in the cell walls of certain fungi.[1] Nearly 6 million tonnes of crustacean shell waste is generated annually, which is primarily used for low value applications or disposed of as part of municipal waste.[2] Most N-based chemicals are derived from NH_3 synthesised via the Haber-Bosch process.[3] This process accounts for around 1.5% of global greenhouse gas emissions and produces the most CO_2 of any chemical manufacturing process.[3] Hence the ability to convert chitin obtained from waste material could reduce demand for the environmentally harmful Haber-Bosch process.

Research Aims

- Explore the relationship between the solvent structure of ionic liquids (ILs) and the solubilisation and conversion of chitin, including the effect of IL mixtures
- The N-containing compound that is of particular interest is 3-acetamido-5-acetylfuran (3A5AF) a precursor used in the synthesis of nitrogenous compounds that are not derived from NH_3 (Figure 2)

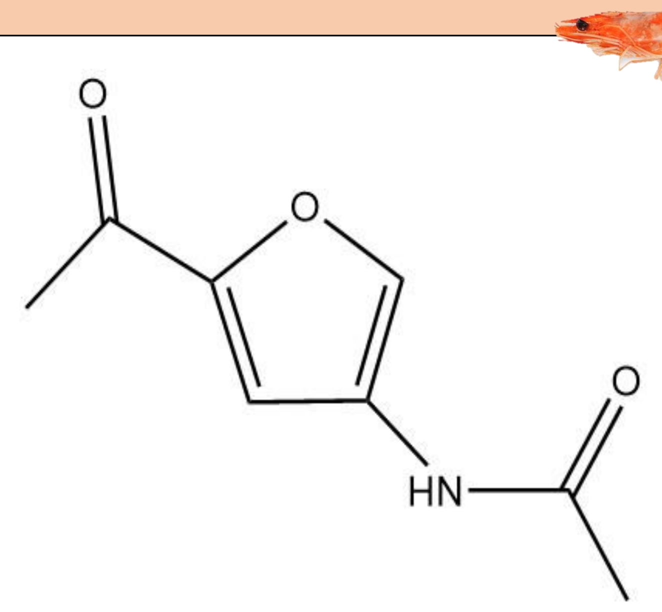

Figure 2. Structure of 3-acetamido-5-acetylfuran (3A5AF)

Methods

- Chitin (80 mg, 8 wt%), HCl (32.6 μL, 100 mol%) and BOH_3 (97 mg, 400 mol%) stirred in IL (1 g) at 180 ℃ for 1 h using conventional heating. Samples analysed by HPLC.
- Optimised conditions include lower chitin loading (5 wt%), HCl concentration (50 mol%) and temperature (120 ℃, 150 ℃)

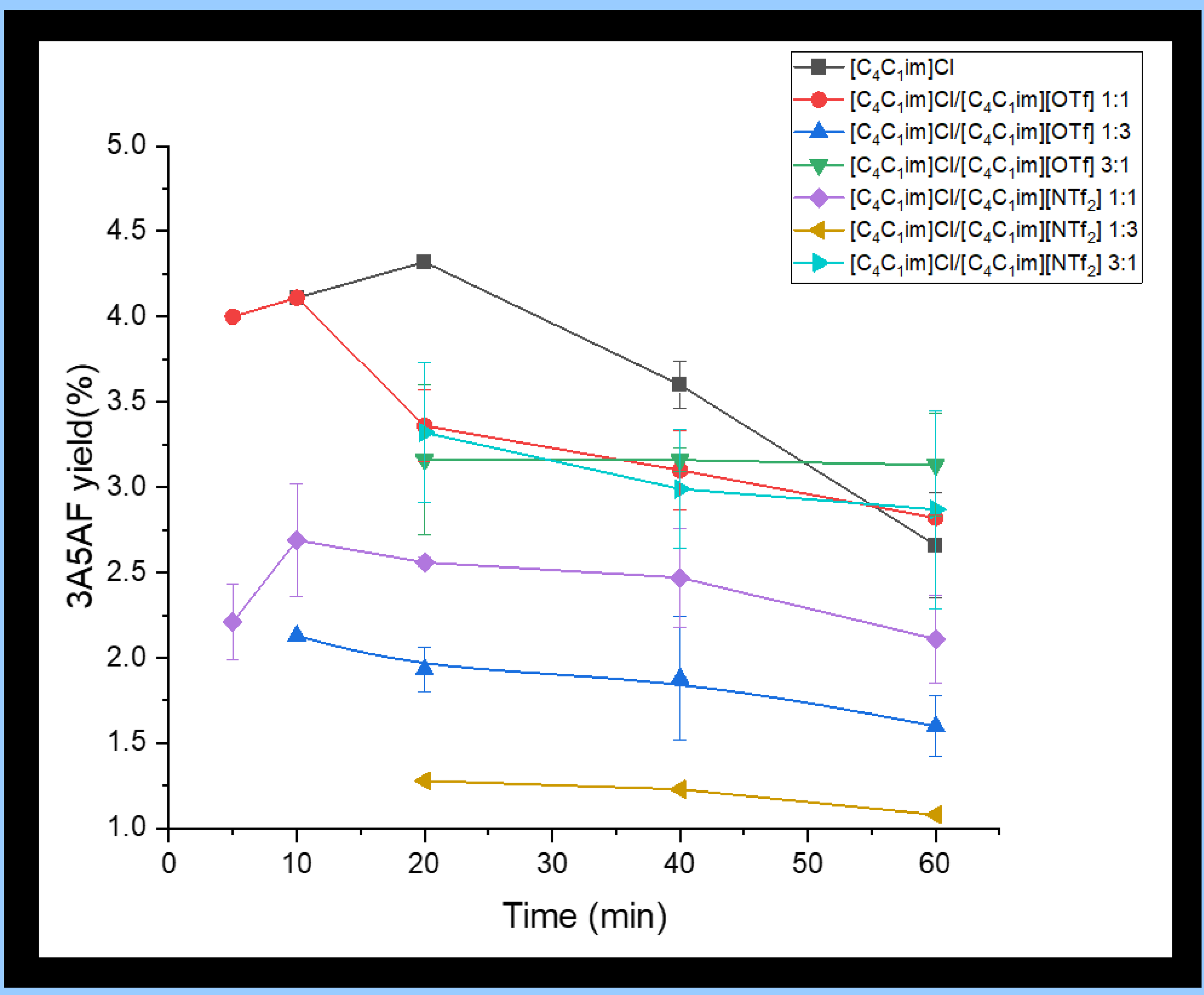

Figure 3. Yields of 3A5AF obtained from chitin conversion reactions performed in IL mixtures (400 mol% BOH_3, 100 mol% HCl, 180 ℃)

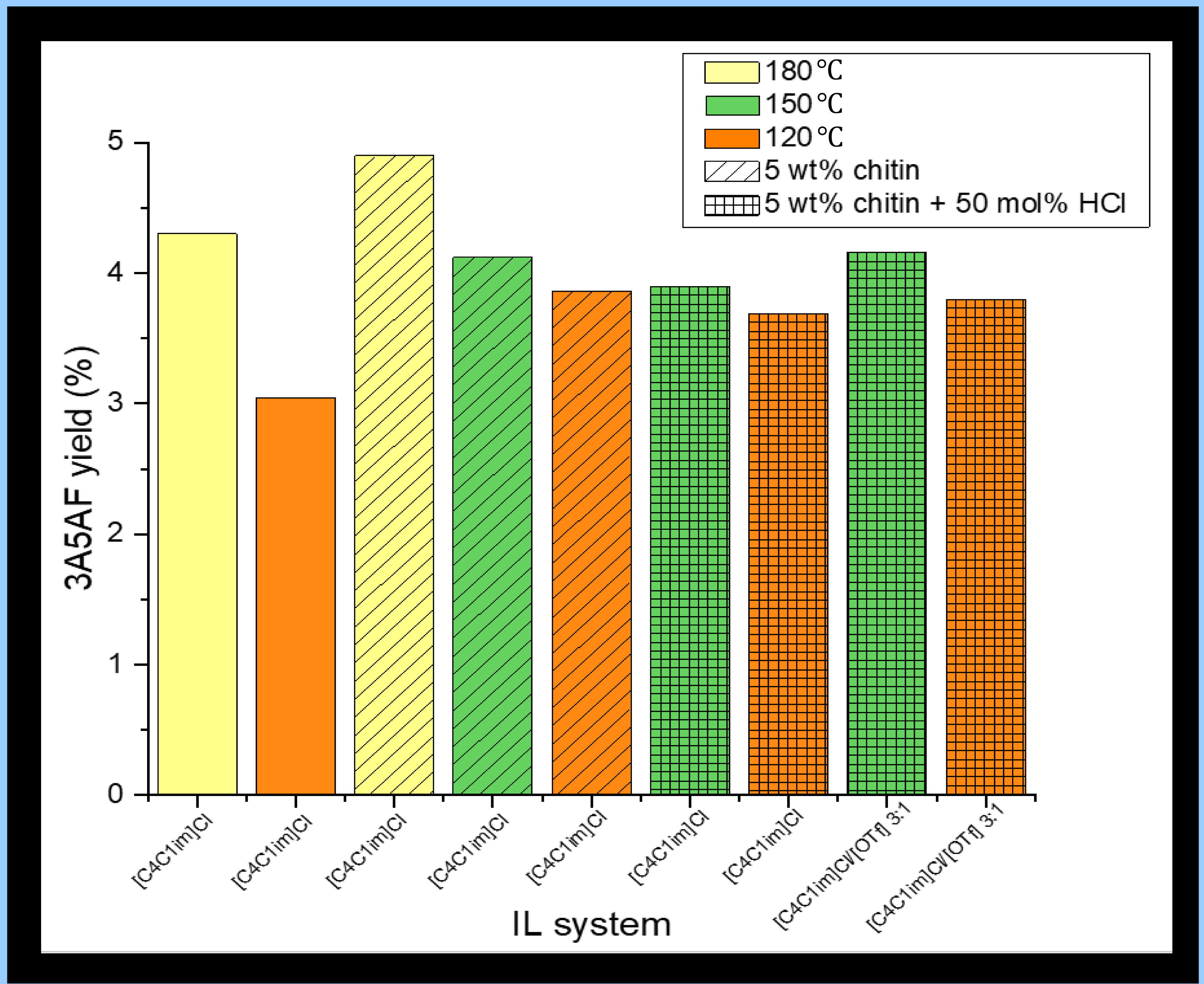

Figure 4. Highest yield of 3A5AF obtained from chitin conversion reactions performed in $[C_4C_1im]Cl$ and $[C_4C_1im]Cl/[C_4C_1im][OTf]$ mixtures under optimised conditions

Conclusions

- IL mixtures did not improve 3A5AF yields compared to pure $[C_4C_1im]Cl$, however the inclusion of more hydrophobic ILs may aid in preventing 3A5AF degradation
- Highest yield of 3A5AF was afforded in pure $[C_4C_1im]Cl$ with 5 wt% chitin after 10 min, which is most likely a result of improved chitin solubility within the IL
- Similar 3A5AF yields can be obtained at lower temperatures and acid concentration which is favourable from a green chemistry standpoint

Future Work

- Investigations into the effect of different reaction conditions in a wider range of ILs, including pyrrolidinium-based ILs
- Exploration of reactions using microwave heating and continuous product extraction methods to improve 3A5AF yields
- Identification of other unknown N-based products and potential product optimisation

Acknowledgements

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2. Chen, X.; Yang, H.; Yan, N. Shell Biorefinery: Dream or Reality? *Chem. Eur. J.* **2016**, *22* (38), 13402–13421.
3. MacFarlane, D. R.; Cherepanov, P. v.; Choi, J.; Suryanto, B. H. R.; Hodgetts, R. Y.; Bakker, J. M.; Ferrero Vallana, F. M; Simonov, A. N. A Roadmap to the Ammonia Economy. *Joule* **2020**, *4* (6), 1186–1205.

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