GREENWIN INTERNATIONAL CONFERENCES GREEN CHEMISTRY - WHITE BIOTECHNOLOGY - 5TH EDITION
09/05/2019
GOSSELIES, BELGIQUE

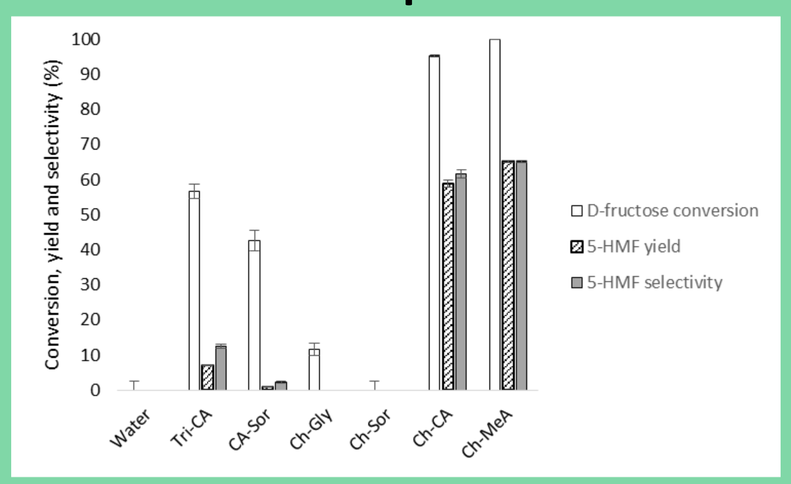
Production of 5-hydroxymethylfurfural from D-fructose in low-transition-temperature mixtures enhanced by chloride anions and low amounts of organic acids

Thibaut Istasse[a], Antoine Hospied, Lauris Bockstal, Prof. Aurore Richel
Laboratory of Biomass and Green Technologies, Gembloux Agro-Bio Tech-University of Liège, 5030-Gembloux, Belgium
[a]thibaut.istasse@uliege.be

Context:

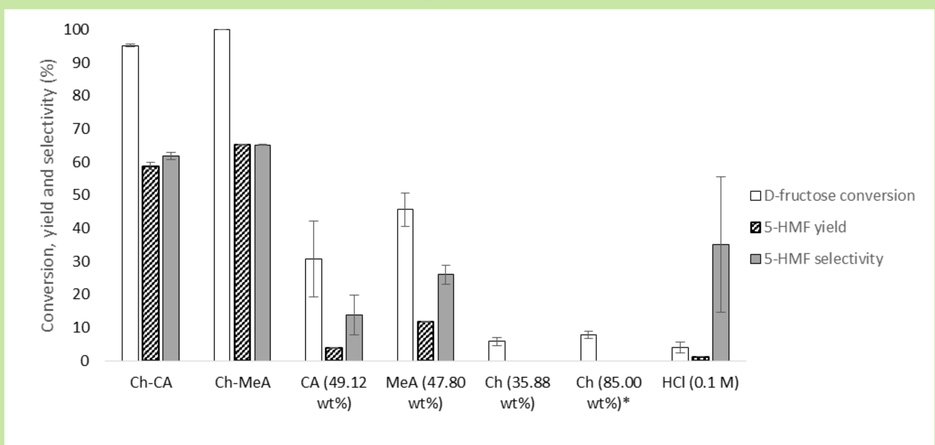
- **5-hydroxymethylfurfural (5-HMF) is a dehydration product of hexoses with an interesting potential as a platform molecule for biobased plastics, fuels and solvents synthesis.**
- **The most efficient media able to generate this building block are biphasic systems containing DMSO or ionic liquids but such media are usually expensive.**
- **Low-transition-temperature mixtures (LTTMs) composed of natural and biodegradable substances are a cheaper alternative to ionic liquids and also possess a tunable catalytic activities.**
- **The potential of some LTTMs to produce 5-HMF from D-fructose was explored in this work at temperatures lower than 100°C.**

Selection of LTTMs components:



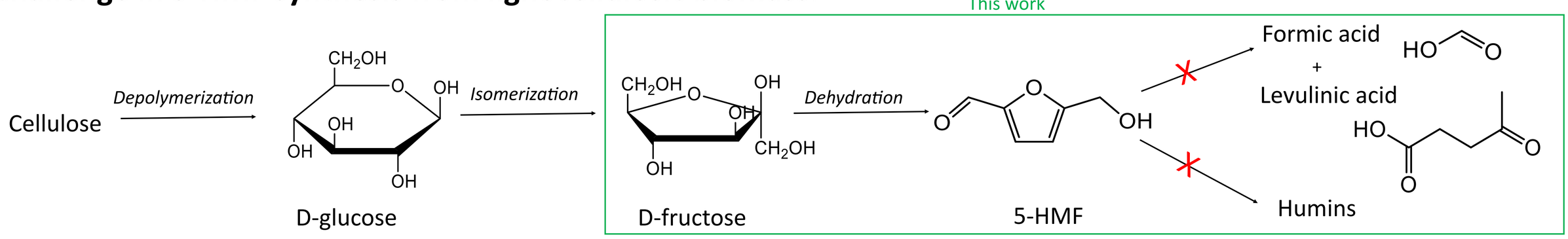
Several LTTMs were prepared using natural components or derivatives such as citric acid (CA), maleic acid (MeA), trimethylglycine (Tri), choline chloride (Ch), sorbitol (Sor) and glycerol (Gly). Only combinations of acids and choline chloride seem to be effective to produce 5-HMF at 90°C (2 hours).

LTTMs vs individual components solutions:

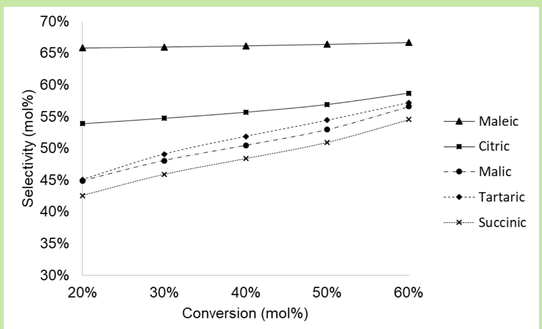


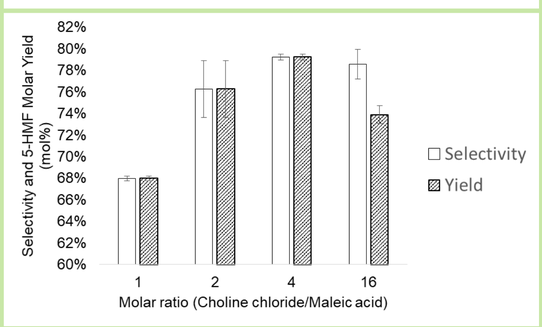
Concentrated solutions of individual components weren't able to catalyze the dehydration reaction as selectively as LTTMs, showing their unique catalytic properties. A hypothesis to explain these results is the inhibitory effect of water on the reaction. The aqueous phase was suspected to greatly limit 5-HMF formation at moderate temperatures by inducing higher activation energy for the second dehydration step of D-fructose to 5-HMF.

Challenge in 5-HMF synthesis from lignocellulosic biomass:



Acidic LTTM component effect:

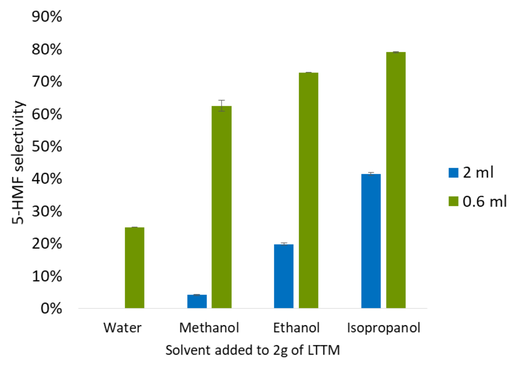


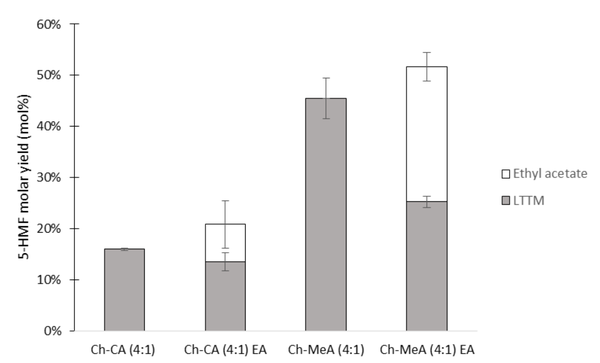


Different organic acids with close chemical structures were compared in choline chloride based LTTMs. While the selectivity achieved with malic, tartaric and succinic acids slightly increased with D-fructose conversion, it was observed that citric and maleic acids were nearly as selective at low D-fructose conversion as at high conversion.

If the acidic components is required to catalyze the dehydration reaction, it could also favor side reactions. Experiments at different choline chloride/acid ratio demonstrated that reducing the acid proportion could greatly enhance selectivity for 5-HMF.

Water effect and 5-HMF extraction:





Replacing water by different organic solvents in LTTMs greatly improves selectivity towards 5-HMF and enables its synthesis at a temperature of only 60°C rather than 90°C. In another experiment, 5-HMF could be extracted from the LTTM phase with ethyl acetate. This last experiment showed that the choice of the acidic component is as crucial for selectivity as for 5-HMF extraction and purification steps.

Conclusion:

Choline chloride and organic acids have a synergic effect on D-fructose dehydration to 5-HMF. Maleic and citric acids are especially selective as acidic components of LTTMs even at early conversion of D-fructose, which suggests that they can limit side reactions favored by a high monosaccharide concentration. The choline chloride/acid ratio and the water content of the LTTM are crucial parameters. Low amounts of organic acid as well as limited presence of water during the dehydration reaction enable to achieve a 80% 5-HMF yield at only 60°C.

Reference:

Istasse, T. , Bockstal, L. and Richel, A. (2018), Production of 5-Hydroxymethylfurfural from D-Fructose in Low-Transition-Temperature Mixtures Enhanced by Chloride Anions and Low Amounts of Organic Acids. ChemPlusChem. . doi:10.1002/cplu.201800416

This work is financially supported by the Walloon Region and the European Regional Development Fund (project: BIOMAT, portfolio: Low Carbon Footprint Material)