**Introduction**

Biomass includes all of the matter that can be obtained from photosynthesis, such as plants and agricultural and forestry wastes. Carbohydrates are major components of biomass, for example, the hexoses (e.g., fructose, glucose), disaccharides (e.g., sucrose) and polysaccharides (e.g., starches, cellulose, hemicellulose, and chitin).

5-Hydroxymethylfurfural (HMF), levulinic acid (LA), and γ-valerolactone (GVL)\(^{1,2}\) are all possible platform molecules\(^{3,4}\) for the production of renewable carbon-based products. We have been investigating the dehydration of fructose to HMF to gain a deeper insight into developing this potentially high-yielding carbohydrate conversion scheme.

**Results**

The HMF yield is highest at 130 °C, with higher temperatures causing hydration of HMF to levulinic acid, but also producing other unknown, highly-coloured side-products (humsins).

The reaction rate increases quickly over a small window of H\(_2\)SO\(_4\) concentration before causing decomposition of the products. The hydration requires an order of magnitude higher concentration of acid compared to the dehydration step.

**Experiment**

D-fructose

Acid catalyst, solvent

Microwave irradiation

HMF

A mixture of 1.88 g fructose, 1.67 mL of an acid catalyst such as 0.5 M HCl, and 10 mL GVL was heated to 130 °C for 10 minutes using a CEM Discover S microwave synthesis system. The heat-up and cool-down times were ca. 2 min and 15 min, respectively, so that “0” min at 130 °C still means that the reaction mixture is >100 °C for a significant period of time.

Other results (not shown) have established that yields of HMF are very competitive with other solvents under the same conditions.

A mixture of 0.25 g HMF, 1.5 mL H\(_2\)SO\(_4\) of varying concentrations, and 10 mL GVL as solvent, was heated to 100 °C for 10 min. In the same CEM Discover S microwave synthesiser.

Yields were calculated using \(^1\)H NMR with 80 s recycle delays, and with p-anisaldehyde as an internal standard. Although this is less precise than HPLC, no sample preparation is required. This has permitted us to detect significant quantities of the formate ester of HMF, which otherwise hydrolys辐 very easily.

**Conclusions**

HMF has been produced from fructose using microwave heating in high yields. The reaction is fast and reasonably selective, but separation of HMF from the by-products is very difficult. We have so far only investigated relatively few parameters of the reaction, but ongoing efforts will explore these much more widely, in particular focussing on the use of solid acids.

**Future Outlook**

The ultimate objective is to develop a high-yielding conversion of carbohydrates to GVL, via the in situ formation of HMF, LA, and formic acid, using some of the final product GVL as the solvent.

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**References**