Conversion of D-Fructose to 5-(Hydroxymethyl)furfural: Evaluating Batch and Continuous Flow conditions by Design of Experiments and In-line FT-IR Monitoring.

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Abstract

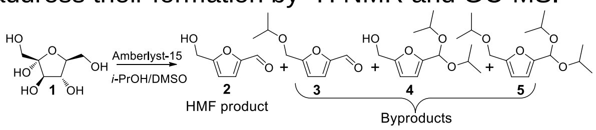
Conversion of Fructose to HMF was evaluated in batch and continuous flow conditions using Design of Experiments and in-line FT-IR monitoring.

Introduction

New bio-based chemicals and processes have motivated both academic and industrial segment in the last decade. In particular, the production of furfural and its derivatives such as 5-(Hydroxymethyl)furfural (HMF) has aroused and encouraged several groups due its potential conversion to feedstocks for bulk chemicals, polymers, solvents, and fuels.[1] Furthermore, HMF was listed as one of the 10 most important compounds that can be obtained from the biomass by the US Department of Energy[2].

Results and Discussion

Initially, the dehydration of Fructose (**1**) to HMF (**2**) was evaluated in batch using solid acid-catalyst Amberlyst-15 in alcohol/DMSO as solvent system. Among the alcohols evaluated (MeOH, EtOH, *i*-PrOH, and *t*-BuOH), *i*-PrOH afforded better selectivities and yields for HMF synthesis. However, since three different by-products could be formed when *i*-PrOH is used as solvent (**Scheme 1**), these compounds were synthetized from HMF in order to address their formation by ^{1}H NMR and GC-MS.



Scheme 1. Dehydration of Fructose to HMF and its potential by-products.

Having these compounds in hand, batch conditions were evaluated by DOE using *i*-PrOH/DMSO as solvent. In a full factorial design, temperature, time, catalyst loading, and amount of DMSO were the factors evaluated by the Design-Expert® software. Selected results are shown in **Table 1**. In summary, the temperature seems to play the major influence in this process, since the yield increased from 48 to 71% at a higher temperature. In Addition, the *i*-propyl ether **3** was the only by-product detected by ^{1}H NMR and GC-MS analysis of the crude reaction.

Table 1. Selected results for the dehydration of Fructose to HMF in batch.

Temperature (°C)	DMSO (% v/v)	Catalyst (mol%)	Time (min)	HMF[a] (%)	3[a,b] (%)
80	15	30	240	48	0.6
120	15	30	240	71	4.0
80	15	10	60	10	0.4
120	15	10	60	55	0.7

[a] Determined by ^{1}H NMR analysis using internal standard.[b] Single byproduct observed

We next turned our attention to continuous flow conditions. Temperature and residence time were evaluated in a full factorial design and temperature again showed the major contribution. For this process, HMF could be obtained in up to 95% yield in a short residence time (only 11 minutes). In order to demonstrate a long-time production of HMF and also to evaluate the recyclability of the acid resin, a continuous experiment was performed using in-line FT-IR monitoring. Gratifyingly, no process deviation was observed during this time and selectivity/yield maintained stable over 24 hours (**Figure 1**).

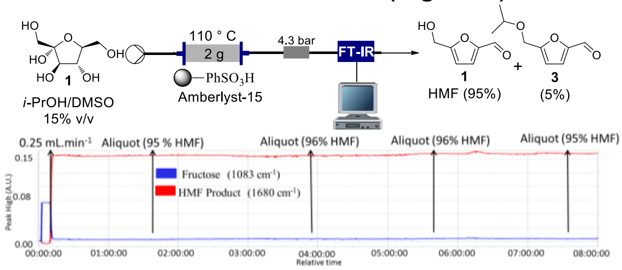


Figure 1. ConcIRT profile of HMF production by continuous flow conditions

Conclusion

In summary, an effective process for HMF production from Fructose was developed using *i*-PrOH/DMSO as solvent and Amberlyst-15 in a fixed-bed reactor. The yield increased from 71% in batch to 95% under continuous flow conditions and the system was stable over 24 hours, which could be confirmed by in-line FT-IR monitoring.

Acknowledgments

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