

Oxidative Esterification of Hydroxymethylfurfural in a Wall-Coated Catalytic Microchannel Reactor

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Highlights

- Oxidative esterification of HMF was studied in a catalytic microchannel
- Full conversion and high yields were obtained at unprecedented short residence times
- The reaction was found to proceed through a Langmuir–Hinshelwood mechanism

Introduction

5-hydroxymethylfurfural (HMF) is a biomass-derived molecule of high interest, as it is a platform molecule for various bio-derived products to replace their petrochemical counterparts. In particular, the oxidation of HMF to 2,5-furandicarboxylic acid (FDCA) has received a lot of attention, as FDCA is a monomer to produce a biopolymer that can replace and outperform PET. 2,5-dimethylfuran dicarboxylate (DMFDCA) is an alternative to FDCA and is more preferred for polymerization due to its high solubility in various solvents and facile separation/purification [1]. However, its production has not been studied as well as FDCA, due to the explosive nature of methanol/O₂ mixtures used in oxidative esterification of HMF to DMFDCA.

In this study, HMF conversion to DMFDCA was studied in a microchannel reactor as it provided the opportunity to conduct the experiments at a much lower explosion risk. The conversion was carried out in Au/SiO₂ wall-coated microcapillaries where a parametric study was performed to gain an understanding of how the reaction proceeds. Based on the experimental results, a reactor model was developed and, for the first time in literature, a kinetics model was proposed for the reaction.

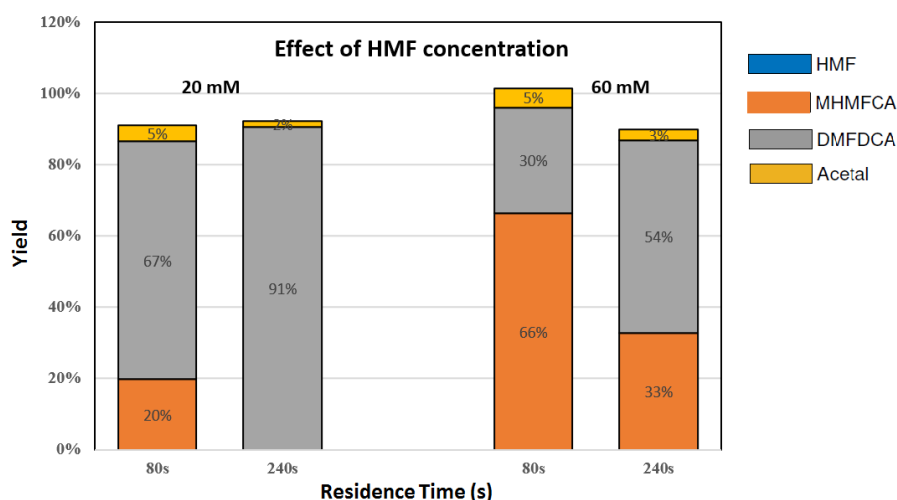


Figure 1. (a) effect of HMF concentration at 110 °C, 30 bar, 3 G/L, 2 mM KOCH₃.

Results and Discussion

The experiments were successfully performed in the continuous catalytic microchannel reactor. The coated catalyst, Au/SiO₂, turned out to maintain its high activity during an extended time-on-stream of 50 hrs. The results showed that not only it is feasible to safely perform the oxidative esterification in flow, but also complete HMF conversions and high yields of DMFDCA can be achieved at unprecedented short residence times of less than 5 min (Figure 1). Higher temperatures, residence times and base (KOCH₃) concentrations improved DMFDCA yields, however they also boosted the parallel undesired HMF degradation to humins. The reaction rate remained unaffected varying oxygen partial pressure from 6 to 30 bar. A higher gas-to-liquid ratio increased the yield, most likely due to better wetting of the channels. Finally, a reactor model was developed and the kinetics information was extracted. This work provides a clear example where microreactors are promising alternative to conventional reactors specially when it comes to reactions that require an explosive mixture of reactants/solvents. Other than that, their excellent heat and mass transfer properties enable conducting kinetic studies to gain a better understanding of the reactions and identify the key factors for an optimized reactor design and process intensification.

References

1. Li, F., *et al.*, “Aerobic oxidative esterification of 5-hydroxymethylfurfural to dimethyl furan-2,5-dicarboxylate by using homogeneous and heterogeneous PdCoBi/C catalysts under atmospheric oxygen”, *Green Chemistry*, **20**, p.p. 3050-3058 (Jun. 2018).
2. Delparish, A., *et al.*, “Towards coupling direct activation of methane with *in situ* generation of H₂O₂”, *Catalysis Science and Technology*, **9**, p.p. 5142-5149 (Sep. 2019).