

5-Hydroxymethylfurfural production and extraction by solid acid-catalyzed fructose dehydration in supercritical CO₂-water two-phase system

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Biomass refinery is desired to be developed in near future because CO₂ emission should be reduced for keeping the balance of green-house gases effect and thus fossil resources for not only fuel but also chemicals must be replaced by the renewable carbon resources. One of the most applicable chemicals from carbohydrate is 5-hydroxymethyl furfural (HMF). Hydrothermal water is the green reaction field for this reaction. However, HMF is further reacted and the maximum yield of HMF is less than 50 mol% [1]. To increase the yield and selectivity of HMF from carbohydrate, it is considered that the produced HMF in hydrothermal water is simultaneously separated to inhibit sequential reactions of HMF into others. In this study, supercritical CO₂ (scCO₂) was chosen as a separation media and preliminarily partition coefficient of HMF between hydrothermal water and scCO₂ was studied. As a result, HMF partitioned into scCO₂ decreased with increasing temperature at constant pressure. To realize the simultaneous separation of HMF with scCO₂, reaction at lower temperature is favorable and a solid catalyst should be employed. Here, fructose conversion to HMF was conducted with Amberlyst 45 (A45) as a solid acid catalyst in a semibatch system with a CO₂ flow to know the effectiveness of the catalyst on HMF formation.

The aqueous solution of 5 wt% fructose 100 mL and the solid catalyst 5 g were loaded into the reactor (150 mL). The reactor was heated to 413 K. CO₂ was pumped into the reactor continuously at a flow rate of 2.67 g/min and 25 MPa. The composition of the reactant and the products in the reaction fluid was evaluated by HPLC. Figure 1 shows the reaction time dependence of the yield of the products and the unreacted fructose. As shown in Fig. 1, in the presence of A45, HMF was formed mainly at 60 min, but HMF was further converted into levulinic acid and formic acid. It is considered that HMF rehydration should be progressed because HMF extraction with scCO₂ was not enough and HMF recovery was insufficient because HMF was probably adsorbed on the surface of A45. At the reaction conditions, the recovered yield of HMF in the CO₂-phase was small and additional investigation should be necessary. To consider the desirable properties of solid catalyst, HMF adsorption on the surface of A45 was tested and it was revealed that HMF was selectively adsorbed at room temperature. Swift *et al.* suggested that a solid additive can act as a separation media of HMF from the reaction system [2], A45 was also functioned as the adsorption agent but the strong Br onsted acidity assisted HMF rehydration, which is an unfavorable reaction. By using scCO₂ and an acidity controlled solid additive, the partition of HMF not only between fluids but also between liquid and solid will be utilized to enhance HMF yield in near future.

Reference

- [1] H. Labauze, S. Camy, P. Floquet, B. B.-Mlayah and J.-S. Condoret, *Ind. Eng. Chem. Res.*, **58**, 92-100 (2019)
 [2] T. D. Swift, C. Bagia, V. Nikolakis and D. G. Vlachos, *AIChE J.*, **59**, 3378-3390 (2013)

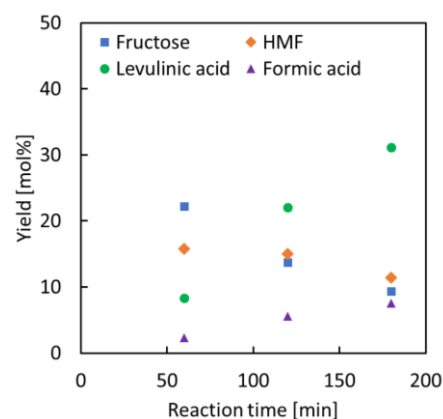


Figure 1 Result of HMF synthesis

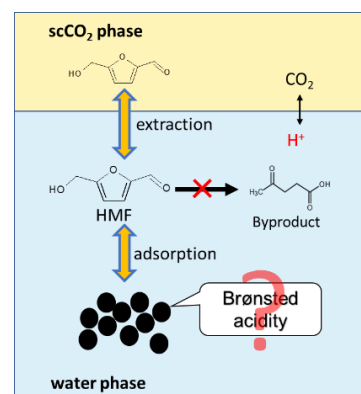


Figure 2 Inhibition of HMF rehydration