**Overcoming the Influence of HMF Reaction Mixture Constituents on Extraction Solvent Performance.**

André B. de Haan1

*1 Delft University of Technology, Chemical Engineering, Van der Maas Weg 9,*

*2629 HZ Delft, The Netherlands*

*\*Corresponding author: a.b.dehaan@tudelft.nl*

**Highlights**

* Effect of ionic liquid, deep eutectic solvent and fructose on HMF extraction by MIBK and 2-pentanol was evaluated.
* All reaction mixture constituents decreased extraction performance.
* Monovalent salts can overcome decreased solvent performance.

**1. Introduction**

HMF (5-hydroxymethylfurfural) is a promising bio-based platform chemical that is obtained from hexose dehydration and can be used to produce biofuels and various chemical products [1]. The hexose dehydration reaction is equilibrium limited, reversible and the HMF formed in this reaction can decompose into levulinic acid (LA) and formic acid (FA).



**Figure 1.** Reaction scheme for HMF formation.

In order to avoid HMF degradation, extensive research has been performed on biphasic systems wherein the catalytic dehydration reaction is coupled with direct extraction of the HMF into an organic solvent to increase the selectivity as well as conversion [2].



**Figure 2.** Comparison of various solvents for HMF extraction.

The focus of this work is a systematic study how the constituents of the reaction mixture affect the extraction performance of organic solvents. A solvent screening has shown that in addition to the widely studied solvent methyl isobutyl ketone (MIBK), 2-pentanol is a promising alternative with comparable selectivity but significantly higher distribution coefficient. Next to water and HMF the reaction mixtures typically contain the hexose substrate (glucose, fructose), salts, catalyst (acid) and co-solvents (DMSO, ionic liquids, deep eutectic solvents) [1]. All these constituents will influence the extraction performance (distribution coefficient, selectivity) of the solvent. However, while using these complex reaction mixtures in studying the effect on conversion and selectivity of the dehydration reaction, there are to our knowledge no studies that have systematically investigated the combined effect of these constituents on the solvent performance.

**2. Methods**

The study has been executed by determining liquid-liquid phase equilibrium data for the ternary systems HMF, water, and solvent (MIBK or 2-pentanol) at 313.15 K (40oC) and atmospheric pressure. Inorganic salts (NaCl, KCl, Na2SO4, KCl, K2SO4), [EMIM][BF4] as ionic liquid, 1:2 molar ratio mixture of choline chloride/urea as deep eutectic solvent and fructose were added to the aqueous phase. All data obtained were correlated using the NRTL model. The effects on solvent performance (HMF distribution coefficient and the selectivity) were derived from the LLE data.

**3. Results and discussion**

The results indicated that higher distribution coefficients are achieved in the 2-pentanol-HMF-water system compared to the MIBK-HMF-water system. On the other hand, the separation ability of MIBK is better than that of 2-pentanol. Adding up to 10 wt% inorganic salts to the system enhanced the distribution coefficient of HMF into the organic phase as well as the selectivity up to 2 times confirming the salting-out ability of the studied salts. The addition ionic liquid showed the opposite effect. At 30 wt% [EMIM][BF4] the HMF distribution coefficient as well as selectivity were reduced to 1/3 of the original value. This salting in effect is caused by the specific interactions between the HMF and ionic liquid that is known to increase the reaction selectivity by complexing with the hydroxyl groups of HMF. For the deep eutectic solvent a comparable effect as with the ionic liquid was observed. Also the introduction of fructose in the system reduced the HMF distribution coefficient and selectivity. Typically substrate concentrations up to 30 wt% are applied and at these conditions a significant decrease in solvent performance is observed. Finally it was observed that the presence of HMF and fructose in the system reduced the solubility of especially the divalent inorganic salts.

**4. Conclusions**

Overall monovalent salts like NaCl and KCl are the most suitable candidates to overcome the negative effects of co-solvents (ionic liquid, deep eutectic solvent) and hexose substrate on the solvent performance.

**References**

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