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SUPPLEMENTARY MATERIAL TO

Hydrothermal treatment of sugars to obtain high-value products

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KINETICS OF SUGAR DEGRADATION

The hydrolysis rates of lactose, glucose and galactose were found to be second-order reactions, which are presented with plots of c^{-1} value against the residence time at temperature of 250 °C in Fig. S-1A and B. The k values show that lactose underwent faster degradation at investigated subcritical water conditions than glucose and galactose. Further, glucose degraded faster than galactose. Khajavi *et al.* studied degradation kinetics of monosaccharides in subcritical water and showed that glucose degradation at short residence time followed first-order kinetics, but for longer time the first-order kinetics was not appropriate.[1] Further, Sasaki *et al.* showed that the hydrolysis rate of cellobiose followed second-order kinetics.[2]

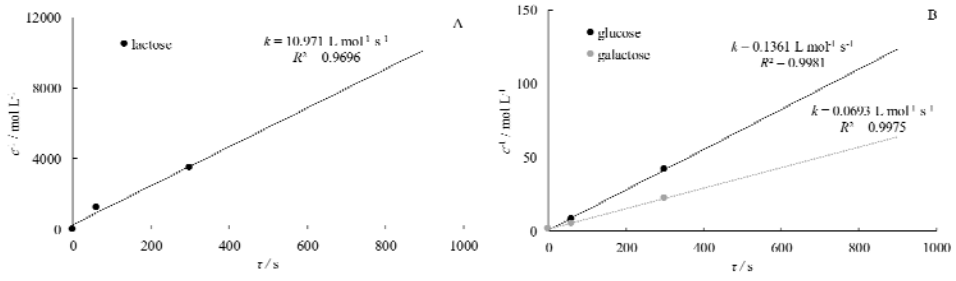

Fig. S-1. Plot of c^{-1} value against the residence time at 250 °C for second-order kinetics of: A – lactose degradation and B – glucose and galactose degradation.

5-HMF degradation is the first-order reaction, which is presented in Fig. S-2A and B, while furfural degradation in the case of fructose and xylose follows the

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second-order reaction, which is presented in Figure S-2C. The k values for 5-HMF degradation are similar for all sugars. The highest k values were obtained for 5-HMF degradation in the case of fructose (0.0045 s^{-1}) and galactose (0.0031 s^{-1}). Knowing that disaccharides are firstly hydrolyzed into monosaccharides and glucose is isomerized into fructose, it is obvious that 5-HMF degradation is slower in the case of these sugars. It is shown that fructose underwent fastest degradation compared to other monosaccharides, as well as 5-HMF in the case of fructose from which furfural was formed, thus the highest k (0.116 L mol^{-1} s^{-1}) value was obtained for furfural degradation in the case of fructose. The furfural degradation rate in the case of xylose hydrolysis was k = 0.0046 L mol^{-1} s^{-1}.

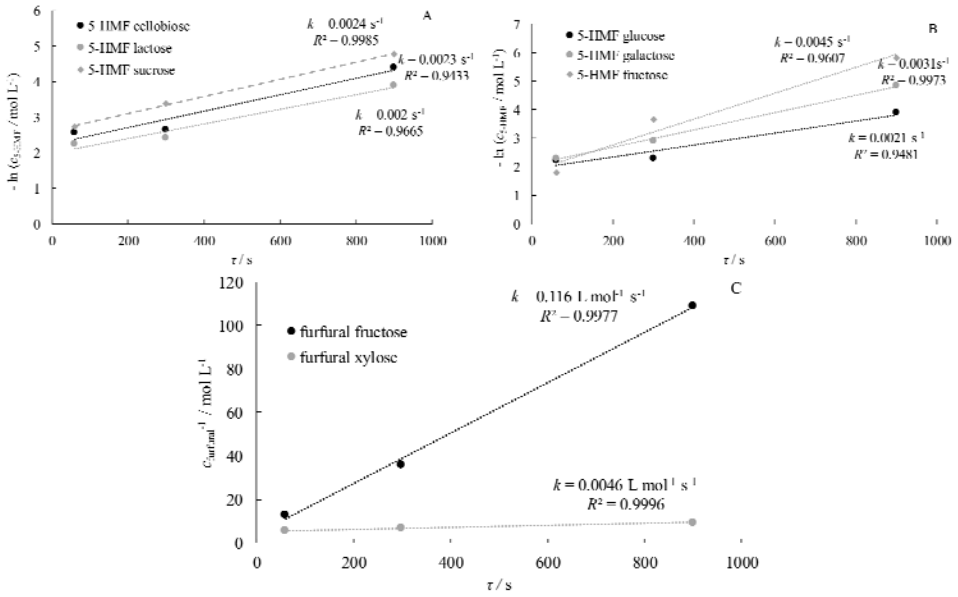

Fig. S-2. Plot of ln c value against the residence time at 250 °C for first-order kinetics of: A – 5-HMF degradation in the case of disaccharides and B – 5-HMF degradation in the case of monosaccharides; C – plot of c^{-1} value against the residence time at 250 °C for second-order kinetics of degradation of furfural obtained from xylose and fructose.

DEGRADATION MECHANISM OF SUGARS

Based on the results of HPLC analyses and literature data,[2–5] the proposed mechanism of sugar degradation is shown in Fig. S-3. Firstly, disaccharide hydrolysis is performed to obtain monosaccharides. For example, cellobiose degrades into glucose, which further isomerizes into fructose. Furthermore, sucrose degrades into glucose and fructose, while lactose, that consists of glucose and galactose rings, thus degrades into these two sugars. Glucose and fructose isomerize into each other. 5-HMF represents the main product of fructose degrad-

ation, but it can be obtained directly from glucose. By losing –CH_2O group, 5-HMF forms furfural, which represents the main product of xylose degradation. 5-HMF is an important platform chemical for the production of various organic acids, such as levulinic and formic acid. Glucose dehydration leads to the formation of 1,6-anhydroglucose, while hydrogenation can form sugar alcohol sorbitol. By the retro-aldol condensation reactions glycolaldehyde and erythrose and on the other hand glyceraldehyde and 1,3-dihydroxyacetone are formed. The dehydration of glyceraldehyde leads to the formation of pyruvaldehyde, which is further converted into lactic acid. Oxalic acid is also a product of glyceraldehyde. the hydrogenation of glucose can lead to the formation of sorbitol.

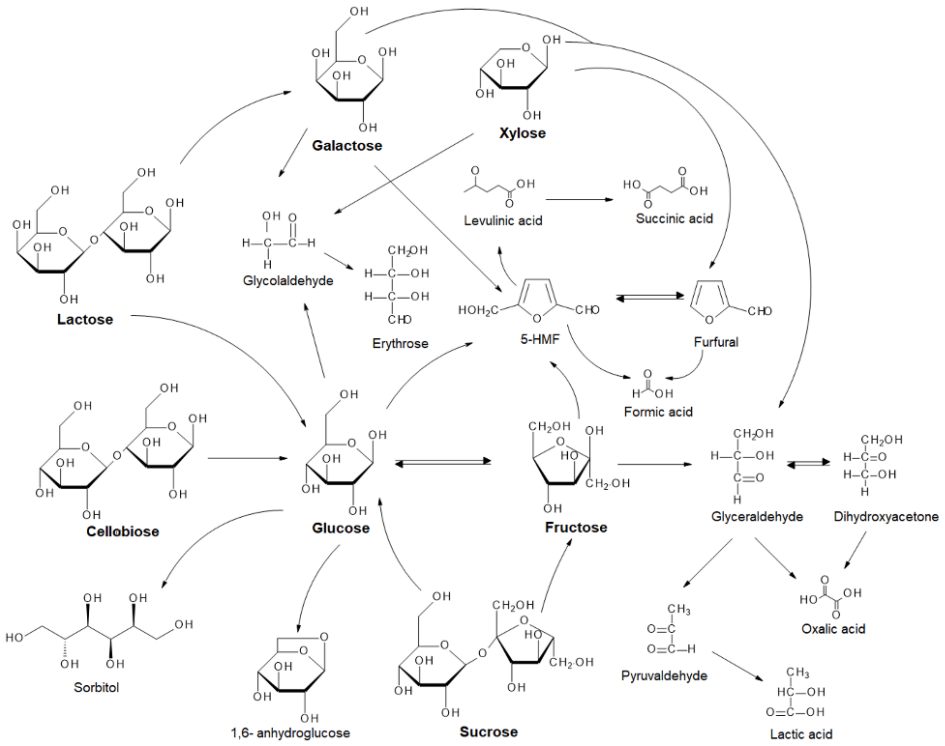

Fig. S-3. The proposed reaction mechanism of sugar degradation.

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