Aqueous Conversion of Monosaccharides to Furans: Were we Wrong all along to Use Catalysts?

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Electronic supplementary information (ESI)

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Test of reproducibility

The reproducibility of the conducted experiments of saccharide conversion was investigated by dehydration of glucose experiments at 160 °C were performed in quadruplicates and results are presented in a Figure 1 below.

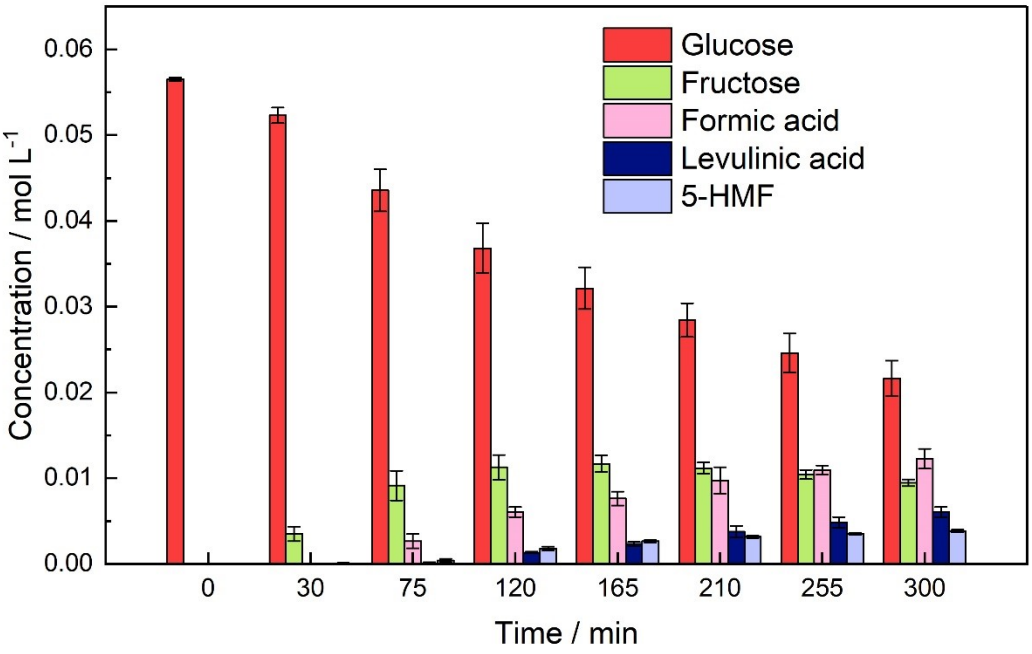

Figure 1: Reproducibility of glucose dehydration at 160 °C.

The influence of agitation rate

In order to exclude any possible limitation present due to mass transfer different stir speeds were tested for H-BEA catalyzed glucose conversion at 160 °C, Figure 2. The concentration of all quantified liquid products were within the experimental error, therefore mass transfer limitations can be excluded above the 200 rpm agitation rate.

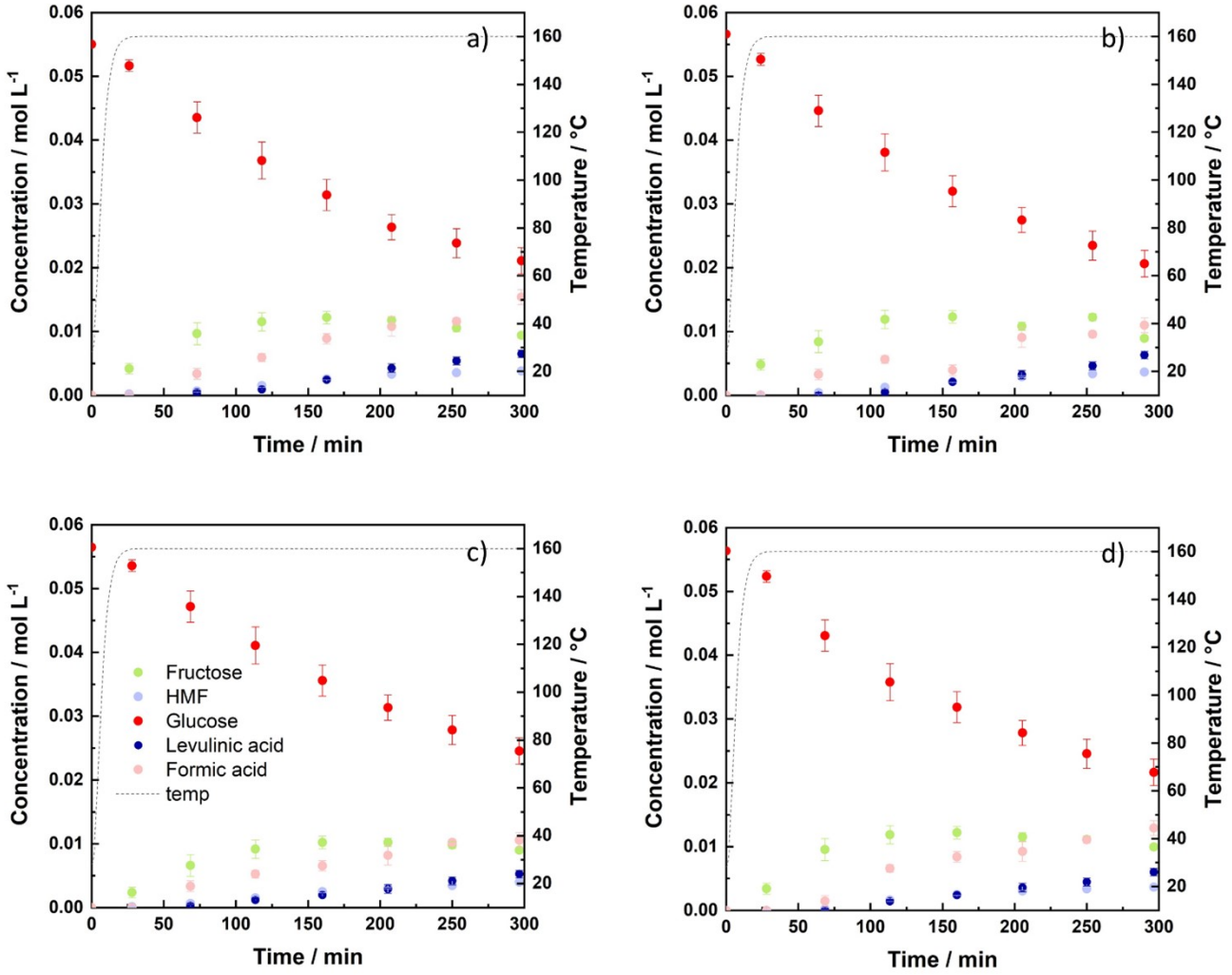

Figure 2: The influence of the agitation rate on dehydration of glucose over H-BEA zeolite at 160 °C, a) 200 rpm, b) 400 rpm, c) 600 rpm, d) 800 rpm.

Catalyst stability and characterization

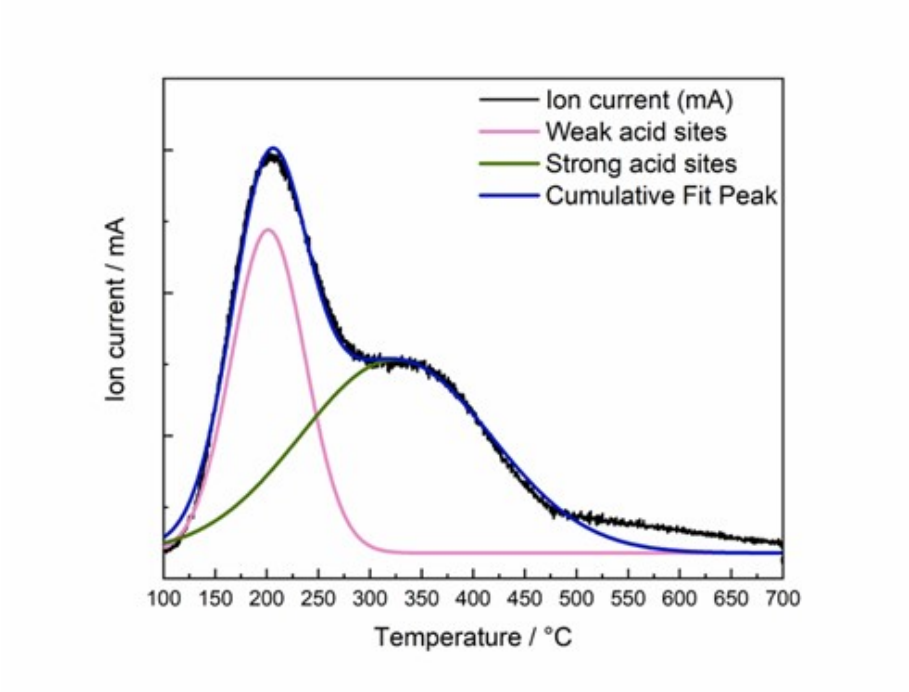

Figure 3: Characterization of H-BEA catalyst; Acidity NH3-TPD

Based on the scanning electron microscopy morphology of H-BEA zeolite was studied. It is depicted in the Figure 4, where the sphere shaped particles, typical for H-BEA type of zeolite, with the size of 200-400 nm can be observed [1]. The catalyst was pretreated in the furnace at 550 °C for 6 h. Scanning electron microscopy was also used when studying the catalyst deactivation, where observed sample of the catalyst was filtered and dried in the oven after the reaction conducted at 160 °C. We can observe severe deposition of carbon on the catalyst surface and it can be noticed as additional layer of coating on the catalyst surface. The carbon deposition was confirmed with total organic carbon analysis of filtered and oved dried catalyst, where carbon deposition occurred to be up to 7 wt. % of analyzed spent catalyst mass.

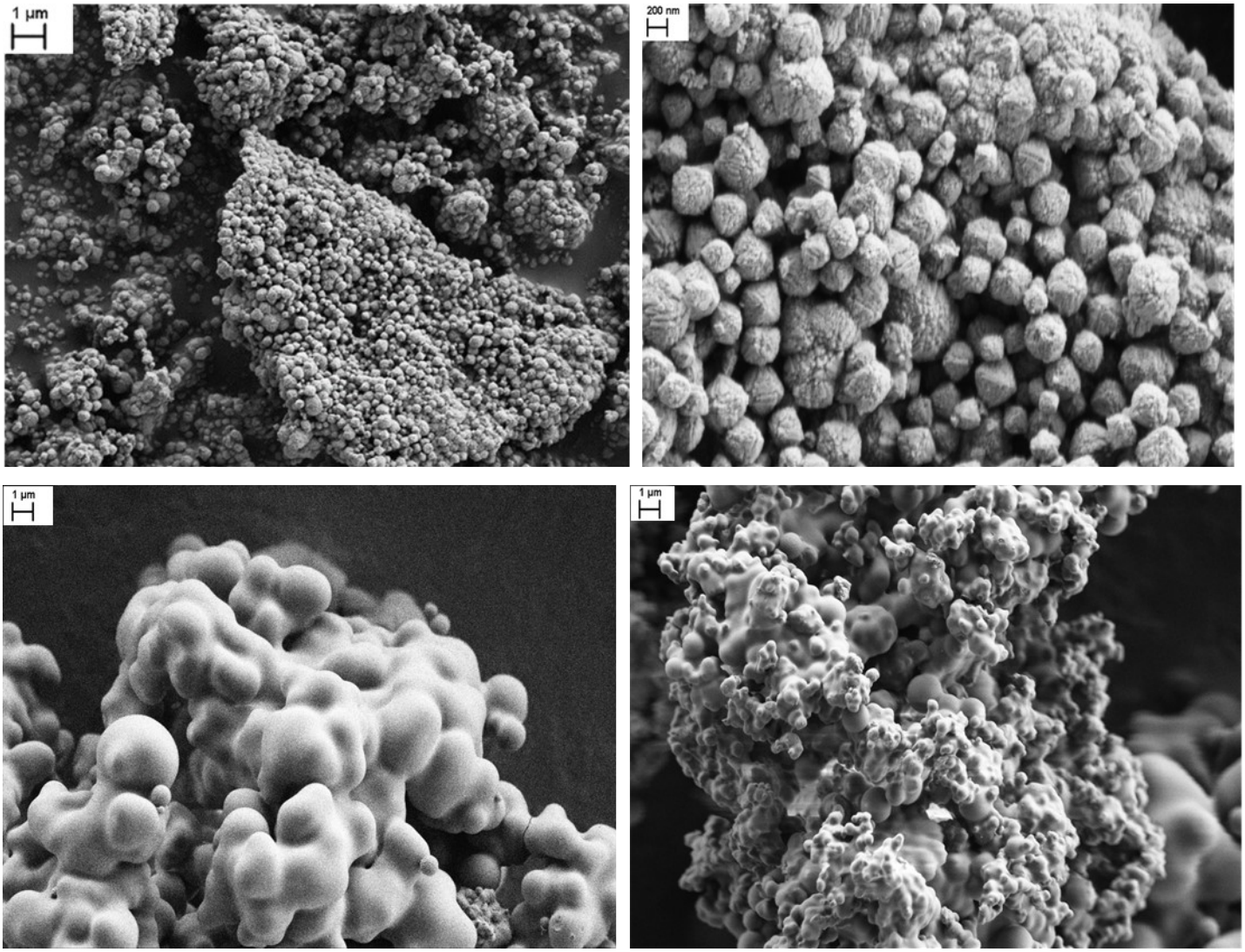

Figure 4: Morphology of fresh (top) and spend (bottom) H-BEA zeolite using scanning electron microscopy.

In order to characterize the catalyst and study catalyst deactivation after conducting the reaction at 160 °C, X-ray diffraction analysis was conducted on the fresh, spent and regenerated catalyst. The spent catalyst sample was collected after the reaction and dried in the oven, while regenerated sample was prepared using the calcined spent catalyst at 550 °C for 6 h. In the 2θ spectrum, we can observe decrease in the peaks significant for H-BEA zeolite at 22.5, 21.4 and 7.8 ° [1], Figure 4.

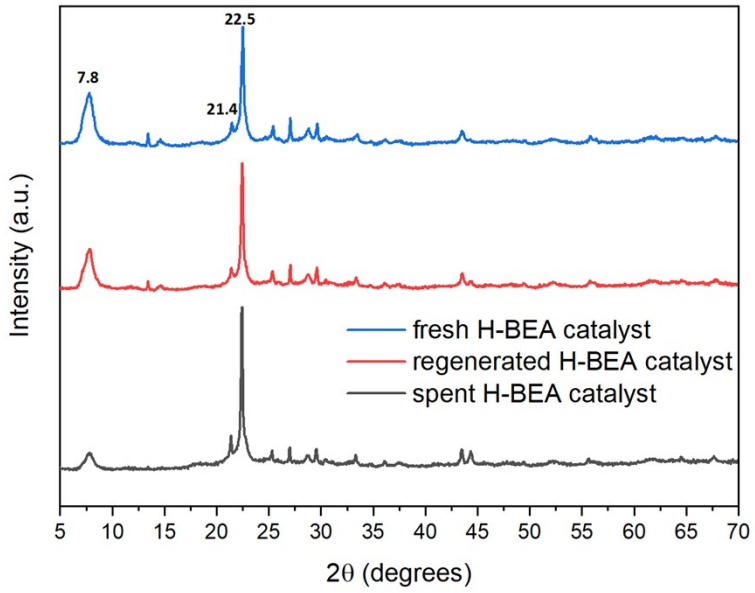

Figure 5: XRD of fresh, spend and regenerated H-BEA catalyst.

To confirm that homogenous and heterogeneous reaction steps are transpiring simultaneously and independent of each other additional experiments were required. Due to the zeolite induced change in pH in aqueous solution, some studies claim the possibility of homogeneously catalyzed dehydration due to the presence of H-BEA zeolite [2,3]. Two catalytic tests of cold Figure 5 b) and cold hot c) filtration were conducted to confirm the absence of zeolite induced homogeneous catalytic activity. Cold filtration proceeded in a way, where 500 mg of zeolite was suspended in 50 mL of water and left to stir for 24 h. H-BEA was than filtered of with 0.2 µm cellulose acetate filter and the filtrated aqueous solution (pH 5.9) was used as a solvent for the reaction of glucose (1 wt. % glucose solution dehydration at 160 °C, for 5 h). Furthermore, we conducted hot filtration of zeolite, where 600 mg of H-BEA suspended in 60 mL of water and treated in an autoclave for 5 h, at 160 °C. The zeolite was then filtered of and aqueous solution (pH 3.9) was as before mentioned used to conduct the reaction of glucose (1 wt. % glucose solution dehydration at 160 °C, for 5 h). The concentration profiles of 5-HMF and fructose during glucose dehydration under hydrothermal treatment, cold and hot filtration did not show any variations among each other's and no facilitated isomerization or rehydration to levulinic acid was detected. Therefore, both experiments confirmed no additional homogeneous activity H-BEA induced by the pH change.

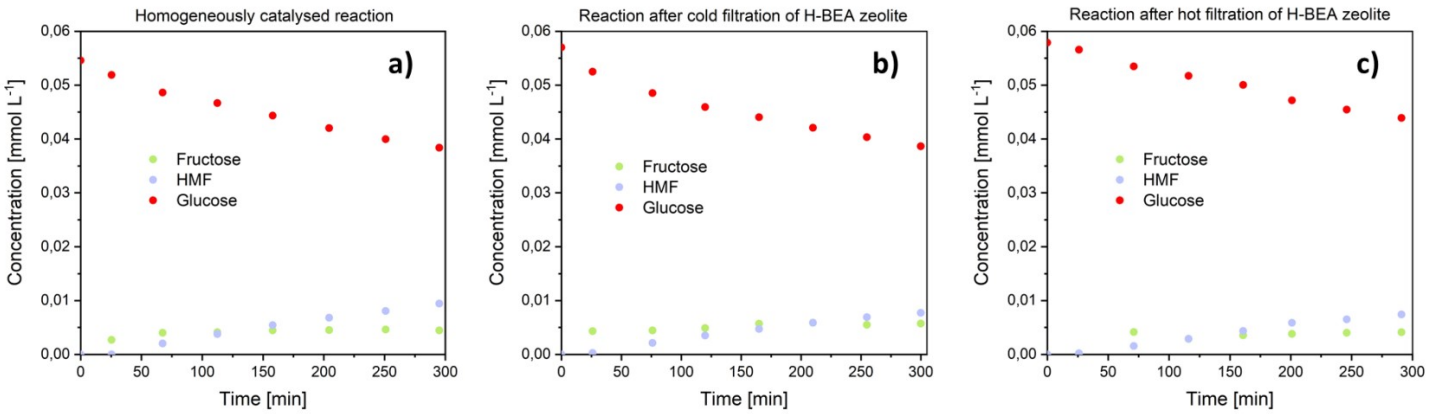

Figure 6: Glucose dehydration under a) hydrothermal conditions, b) after cold H-BEA zeolite filtration and c) after hot H-BEA zeolite filtration.

Identification and characterization of degradation product was performed using SEC and it is represented in the Figure 6. After glucose and xylose dehydration conducted under hydrothermal conditions without catalyst, insoluble residue was filtered of, dried and re-dissolved in THF. Obtained samples were later analyzed according to the protocol similar to [4], where identified species were found to have the molecular weight within the rage of 150 Da – 3000 Da.

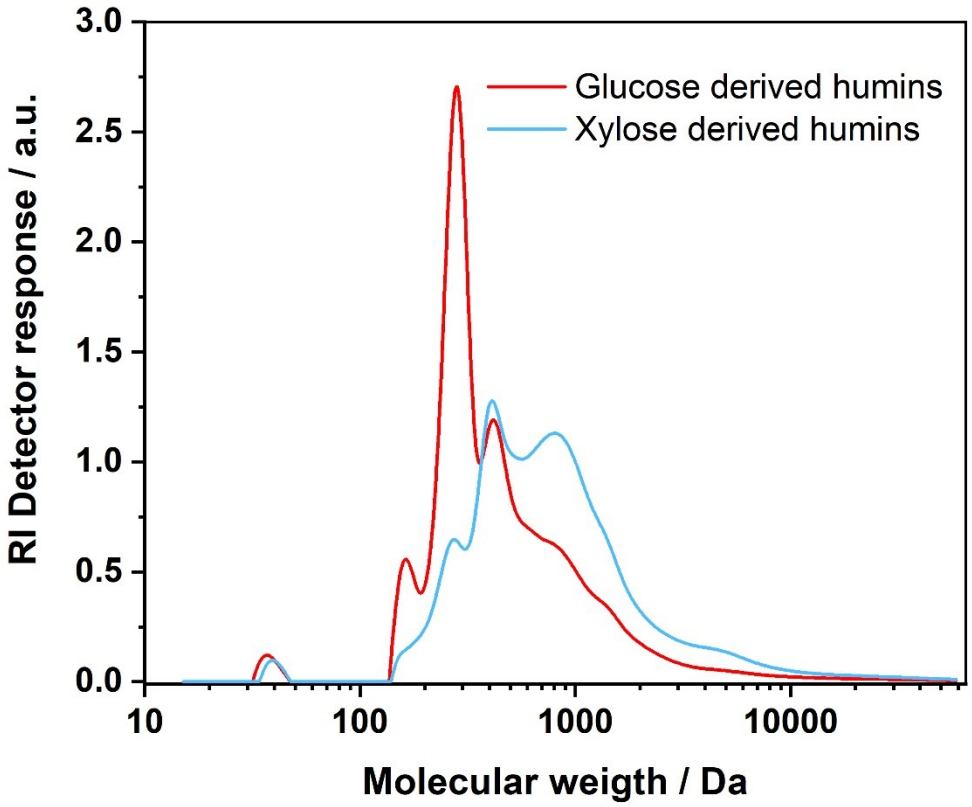

Figure 7: Molecular weight distribution of glucose and xylose derived humin.

Degradation of HMF and furfural in HLW in the absence of catalyst

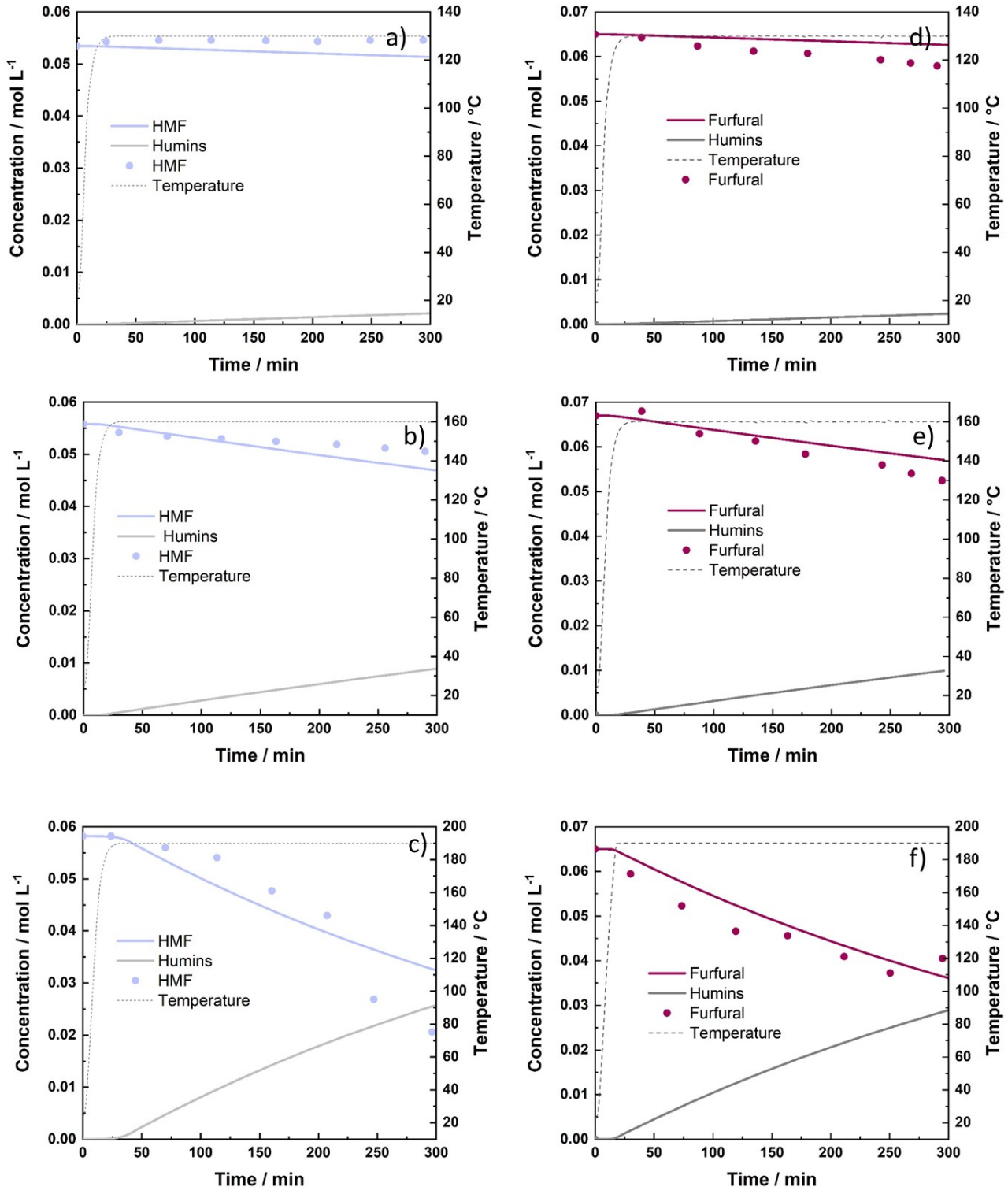

Figure 8: Influence of the temperature on the product distribution as function of the time for HMF degradation reaction in aqueous media without catalyst at four different temperatures a) 130 °C, b) 160 °C, c) 190 °C and furfural degradation in the same temperature range; e) 130 °C, f) 160 °C, g) 190 °C. Where symbols represent experimental points and lines corresponds to model • 5-HMF, • furfural, − humins, ----- temperature.

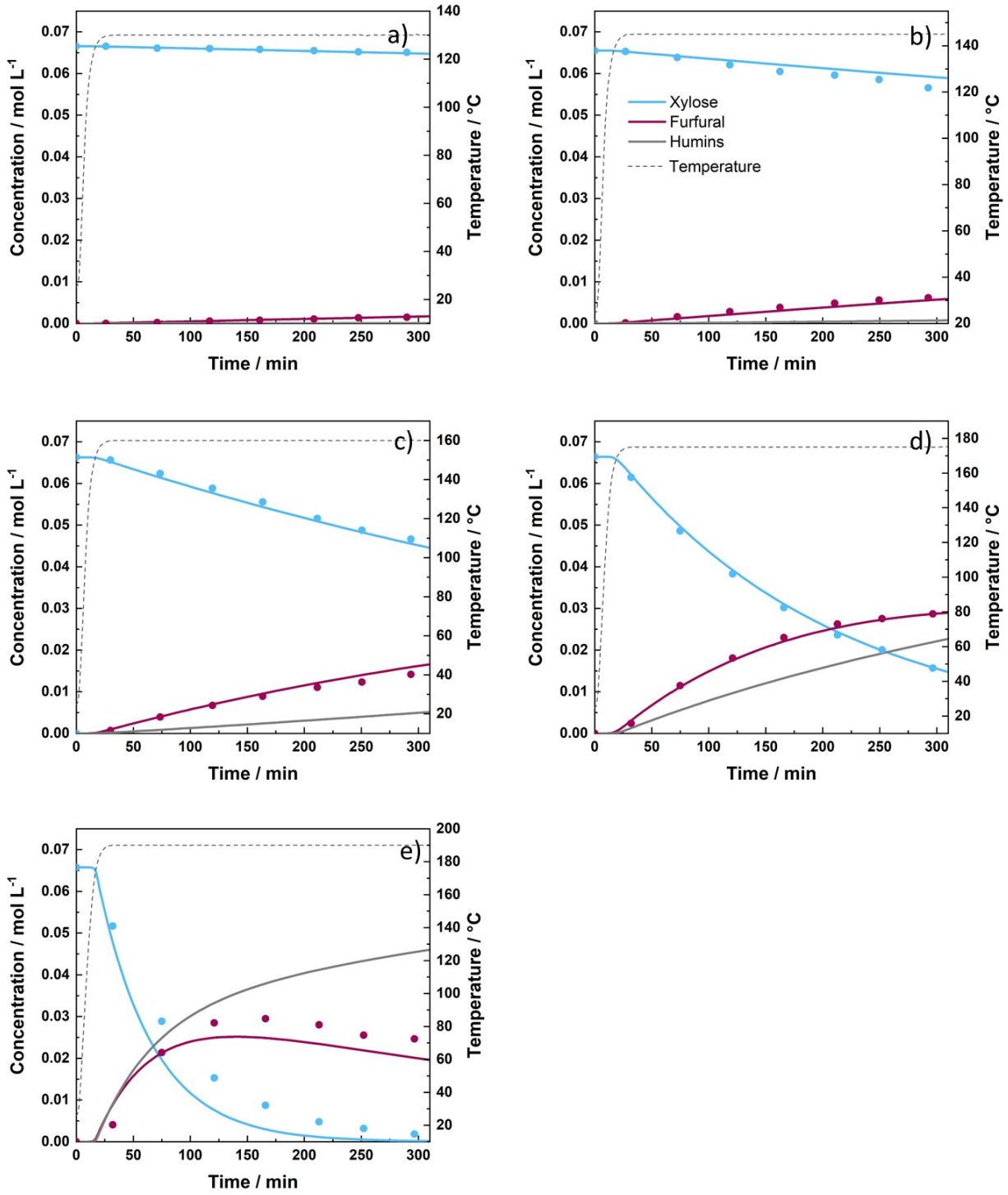

Figure 9: Influence of the temperature on the product distribution as function of the time for xylose dehydration reaction in aqueous media without catalyst at five different temperatures a) 130 °C, b) 145 °C, c) 160 °C, d) 175 °C and e) 190 °C. Where symbols represent experimental points and lines corresponds to model values • xylose, • furfural, – humins, ----- temperature.

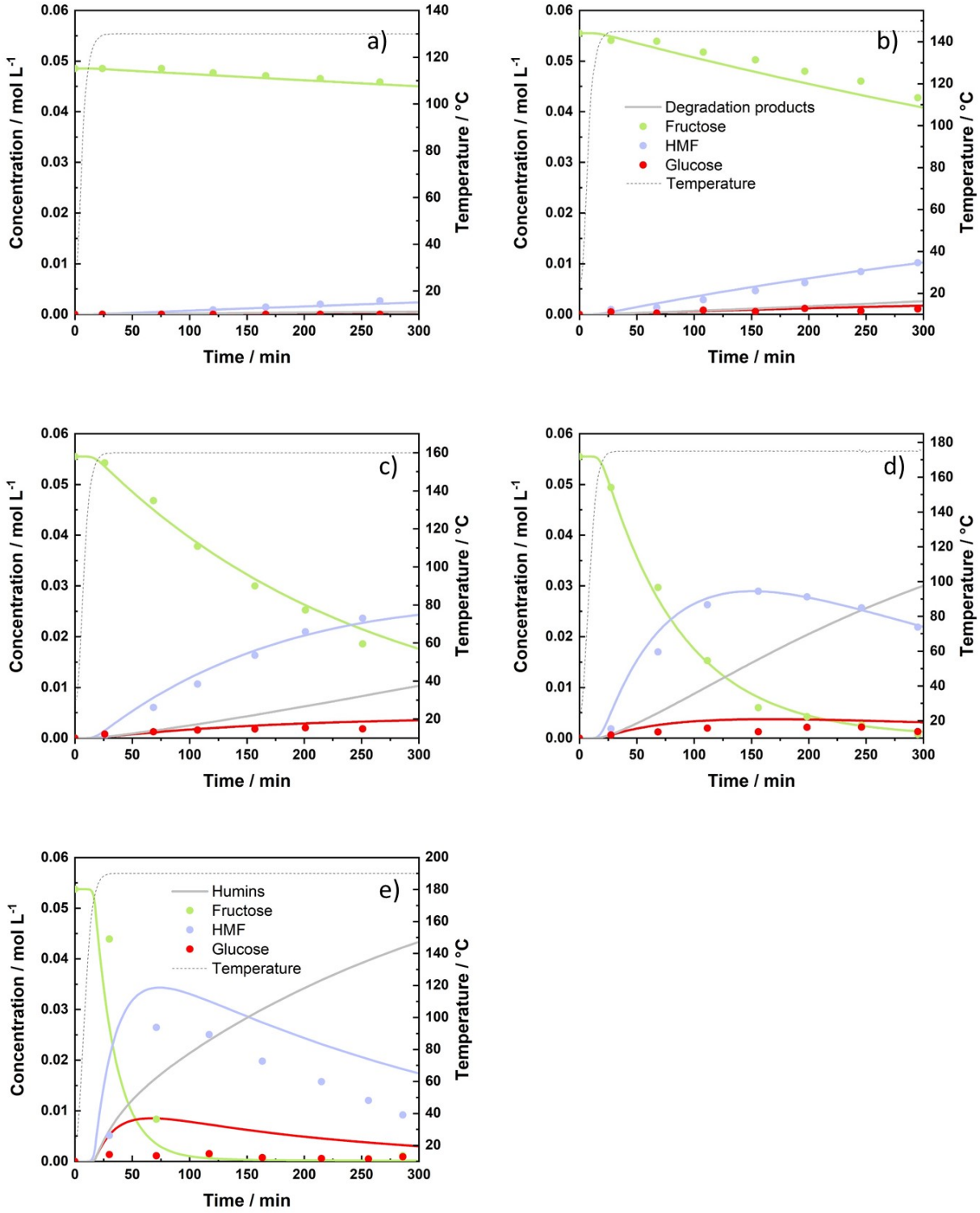

Figure 10: Influence of the temperature on the product distribution as function of the time for fructose dehydration reaction in aqueous media without catalyst at five different temperatures a) 130 °C, b) 145 °C, c) 160 °C, d) 175 °C. Where symbols represent experimental points and lines corresponds to model values • fructose, • 5-HMF, • glucose, – humins, ----- temperature.

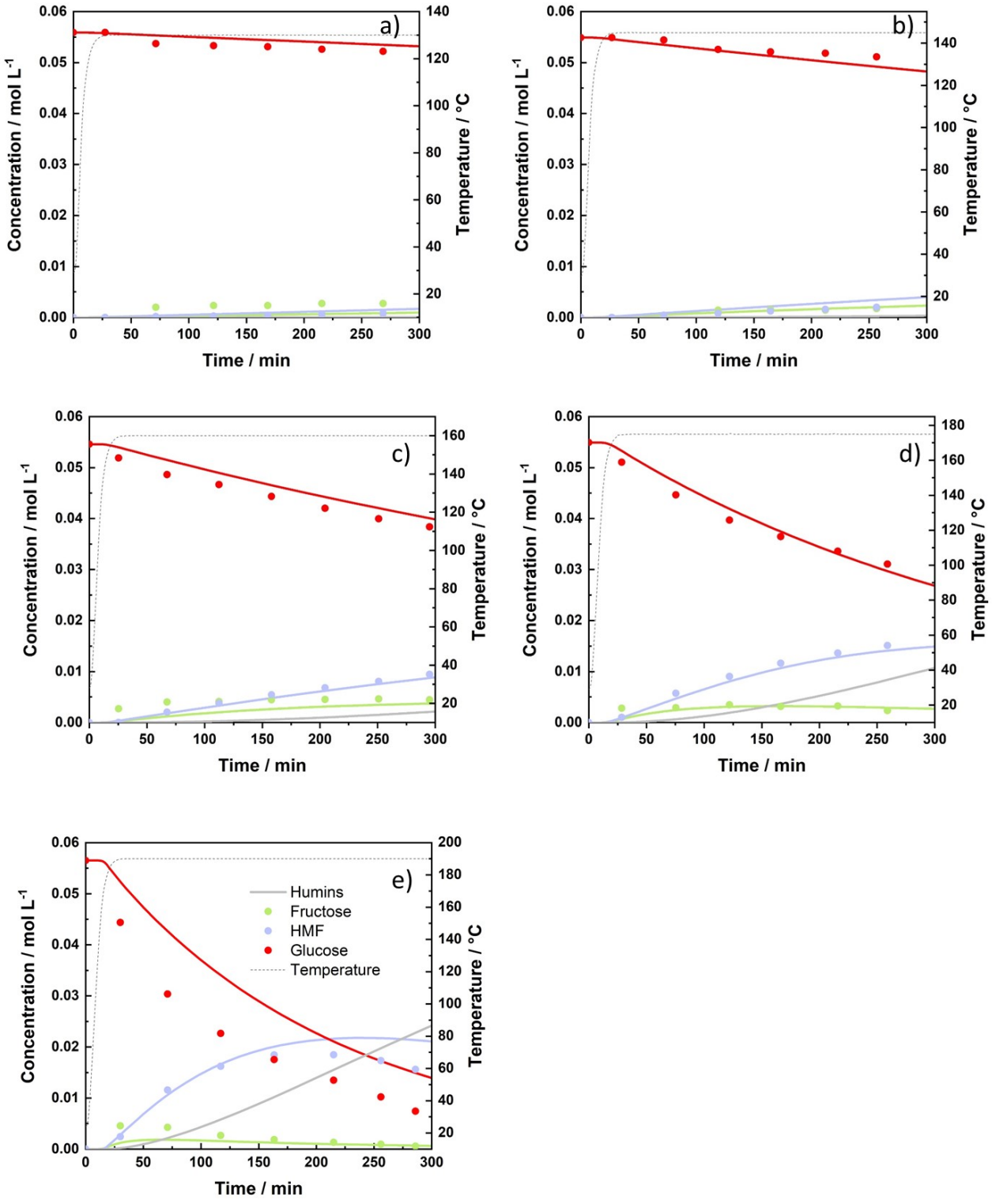

Figure 11: Influence of the temperature on the product distribution as function of the time for glucose dehydration reaction in aqueous media without catalyst at five different temperatures a) 130 °C, b) 145 °C, c) 160 °C, d) 175 °C, e) 190 °C. Where symbols represent experimental points and lines corresponds to model values • fructose, • 5-HMF, • glucose, − humins, ----- temperature.

Degradation of HMF and furfural in HLW in over H-BEA zeolite

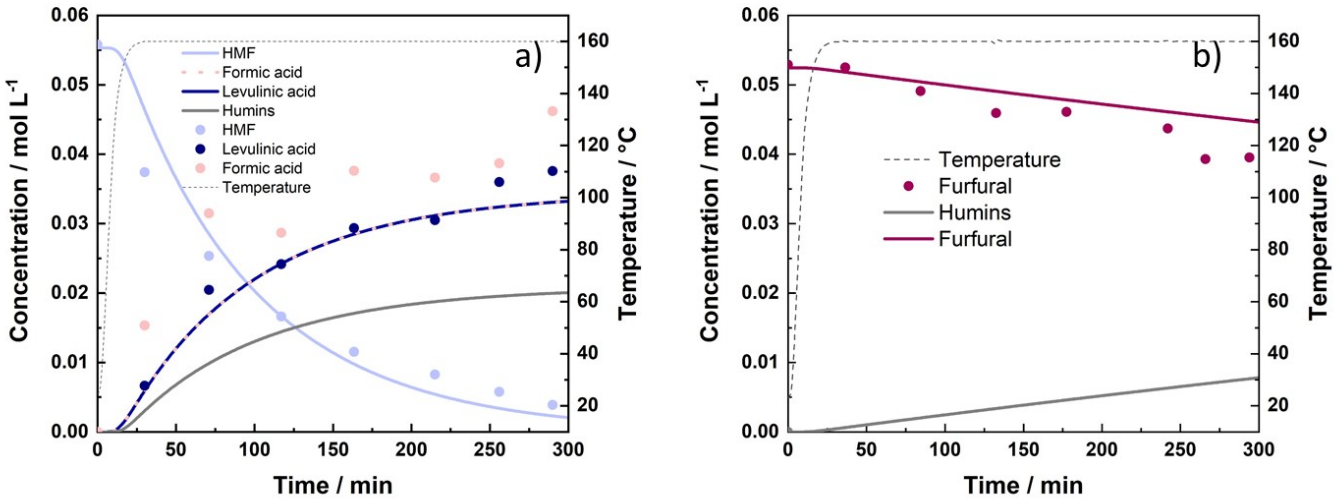

Figure 12: Degradation of a) HMF and b) furfural over H-BEA zeolite at 160 °C.

Stability of levulinic acid in HLW in over H-BEA zeolite

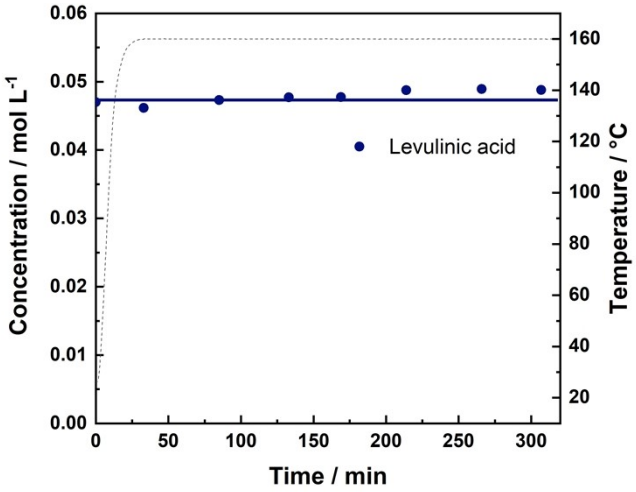

Figure 13: Stability of levulinic acid in the presence of H-BEA zeolite at 160 °C.

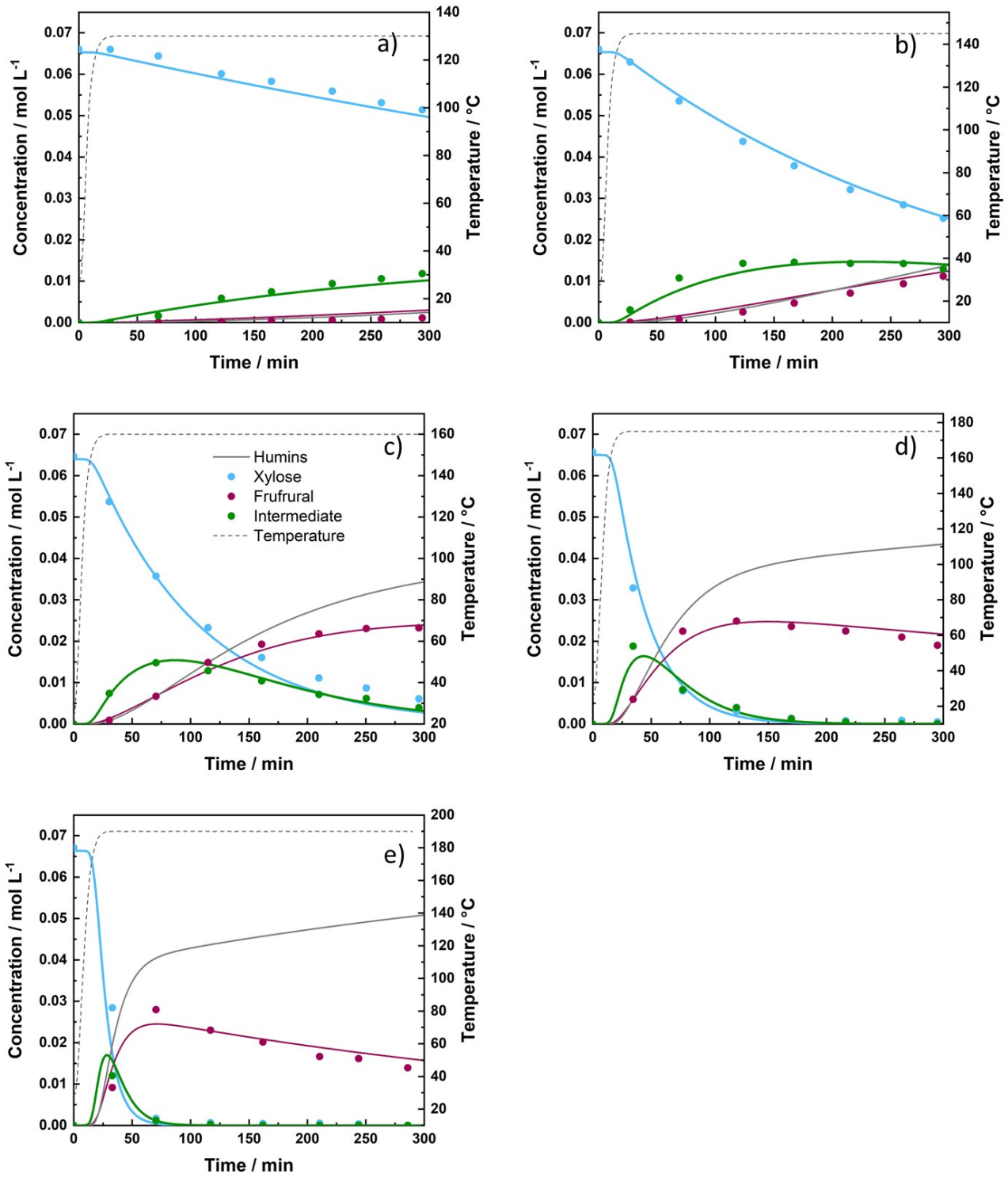

Figure 14: Influence of the temperature on the product distribution as function of the time for xylose dehydration reaction in aqueous media with catalyst at five different temperatures a) 130 °C, b) 145 °C, c) 160 °C, d) 175 °C and e) 190 °C. Where symbols represent experimental points and lines corresponds to model values • xylose, • intermediate • furfural, – humins, ----- temperature.

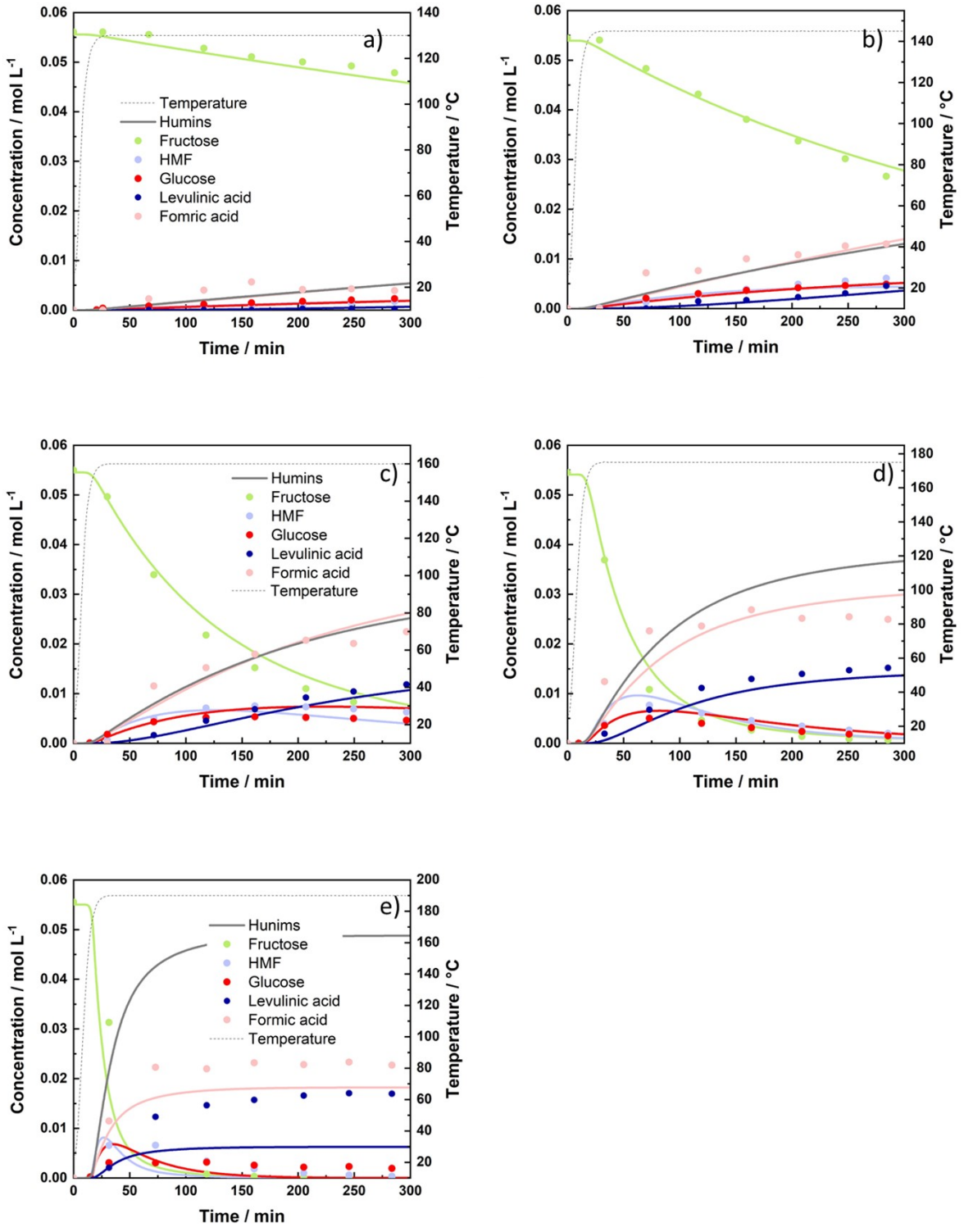

Figure 15: Influence of the temperature on the product distribution as function of the time for fructose dehydration reaction in aqueous media with H-BEA zeolite at five different temperatures a) 130 °C, b) 145 °C, c) 160 °C, d) 175 °C, e) 190 °C. Where symbols represent experimental points and lines corresponds to model values • fructose, • 5-HMF, • glucose, • levulinic acid, • formic acid, – humins, ----- temperature.

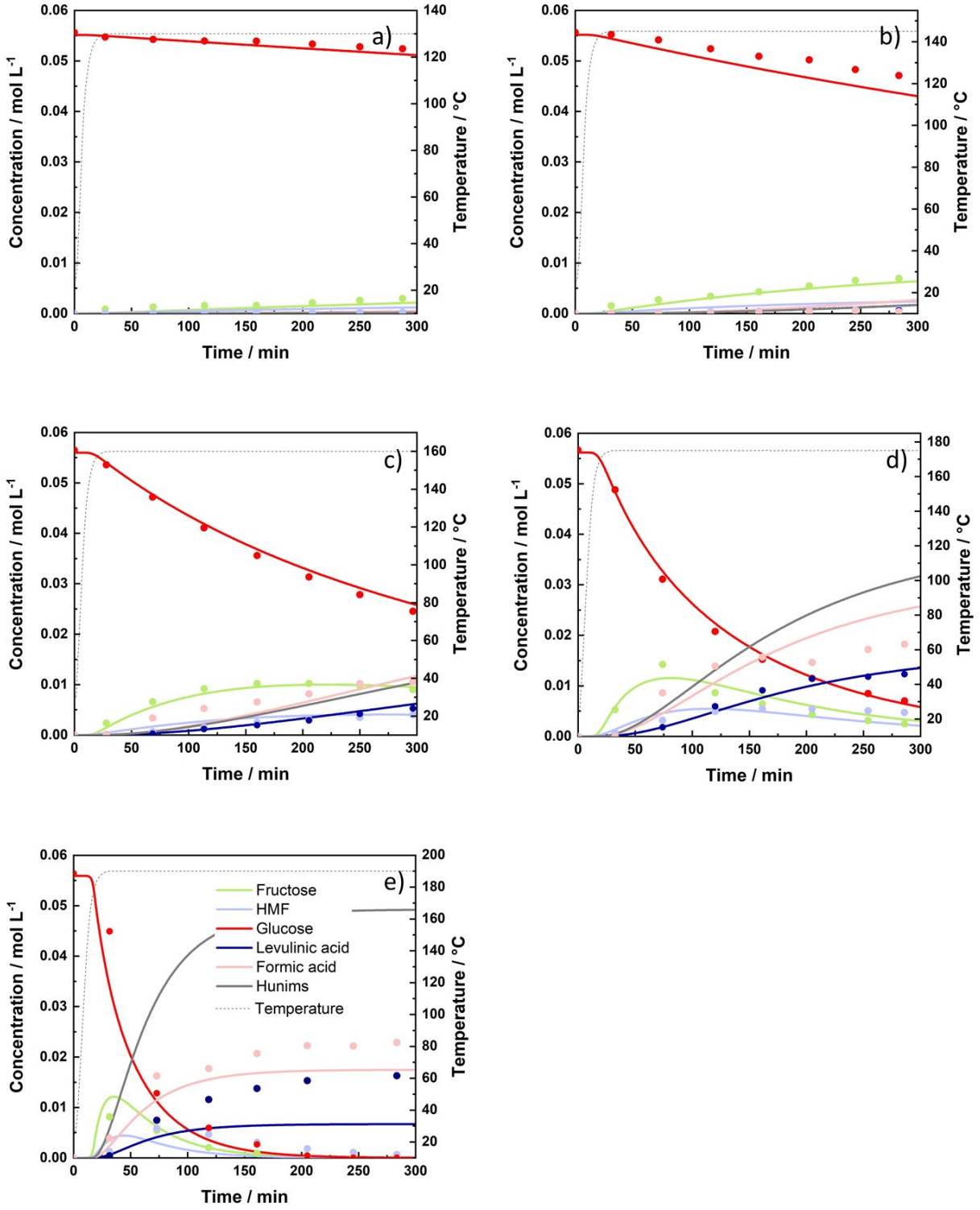

Figure 16: Influence of the temperature on the product distribution as function of the time for glucose dehydration reaction in aqueous media with H-BEA zeolite at five different temperatures a) 130 °C, b) 145 °C, c) 160 °C, d) 175 °C, e) 190 °C. Where symbols represent experimental points and lines corresponds to model values • fructose, • 5-HMF, • glucose, • levulinic acid, • formic acid, – humins, ----- temperature.

Summary of established kinetic models

Figure 17 demonstrates a summary of the combined established kinetic models for both homogeneously (dashed lines) and heterogeneously (solid lines) catalyzed xylose conversion. Reaction temperatures between 145 – 175 °C are presented. Figure 17a shows homogeneously and heterogeneously attained conversion of xylose as a function of time where, xylose conversion was shown to be considerably enhanced by H-BEA zeolite. The reversible isomerization step of xylose to xylulose/lyxose occurs exclusively in the presence of H-BEA zeolite and has not been detected in homogeneously catalyzed reaction, as seen in Figure 17b. Furthermore, it can be seen that H-BEA zeolite slightly increased furfural yield at the temperatures 145 °C and 160 °C, while a reaction temperature of 175 °C resulted in unimproved furfural yields but was reached in a significantly shorter reaction time compared to in the absence of catalyst, as displayed in Figure 17c. Similarly to xylose dehydration, Figure 18 demonstrates a summary of developed kinetic models of fructose dehydration in the presence and absence of H-BEA zeolite. Each individual graph is showing the evolution of identified substrates, products and intermediates as a function of time. Therefore, Figure 18a, c and e exhibits glucose, fructose, 5-HMF and LA concentration for the reaction dehydration with a fructose as a starting feedstock. Overall, 5-HMF rehydration towards LA was in the studied temperature range catalyzed solely by H-BEA and was not noticeable in homogeneously catalyzed reaction (Figure 18e). Analogously, Figure 18b, d, f exhibit kinetic models of glucose dehydration.

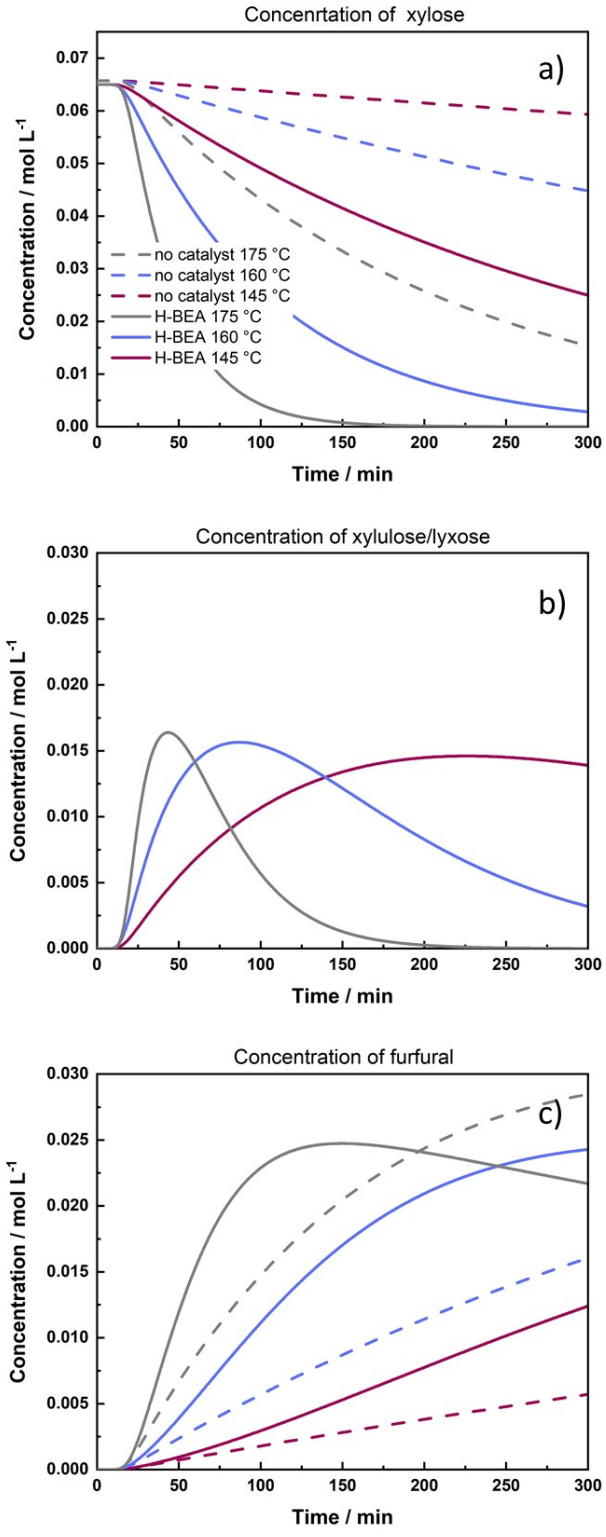

Figure 17: Modelled concentration of homogeneously --- and heterogeneously − catalyzed a) xylose b) xylulose/lyxsose, and c) furfural, at three different temperatures (•145, •160 and •175 °C).

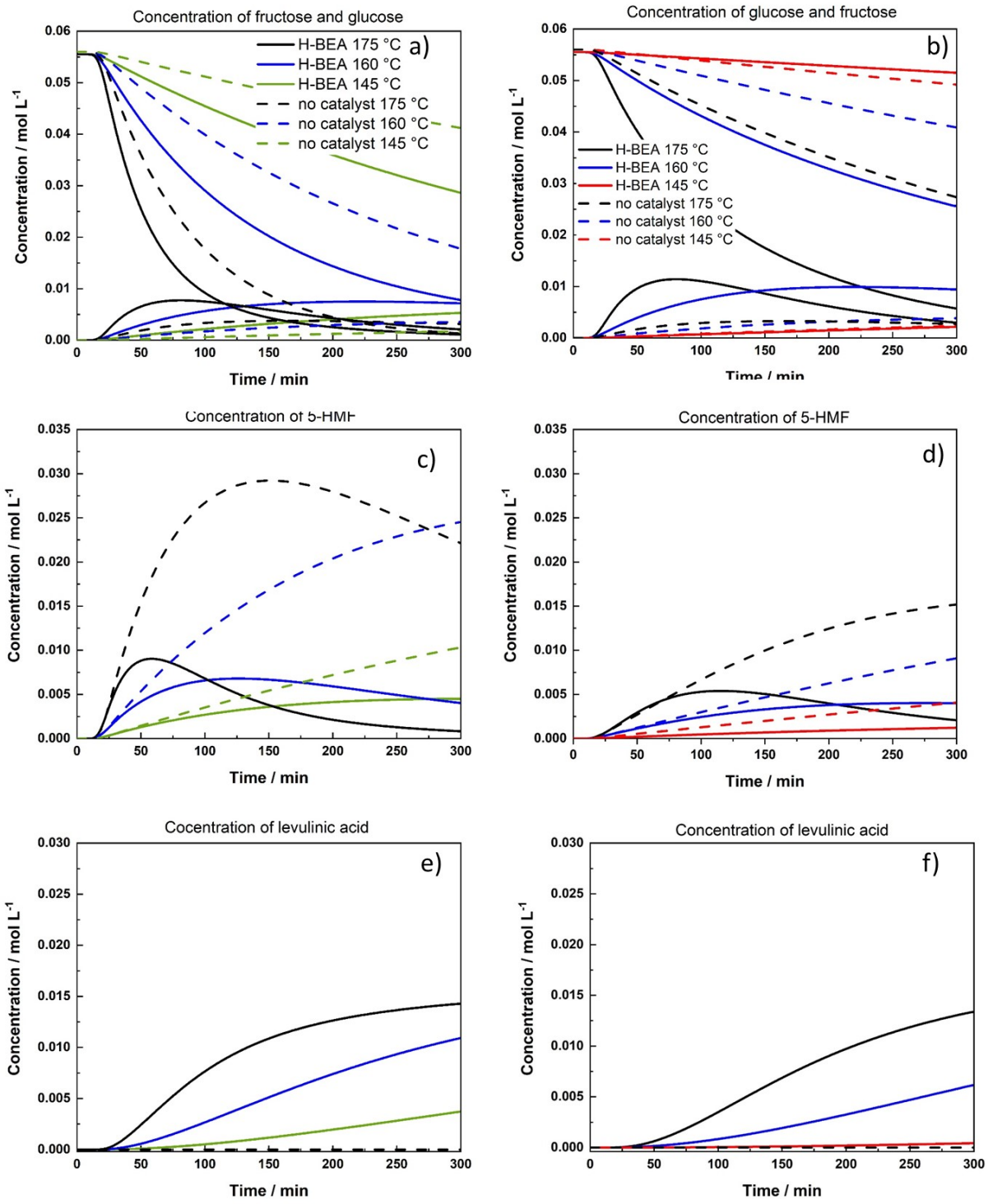

Figure 18: Modelled concentration of homogeneous --- and heterogeneous – fructose conversion with depicted concentrations of a) glucose and fructose, c) 5-HMF and e) LA, as well as glucose conversion with concentrations of b) glucose and fructose, d) 5-HMF and f) levulinic aicd at three different temperatures (•145, •160 and •175 °C).

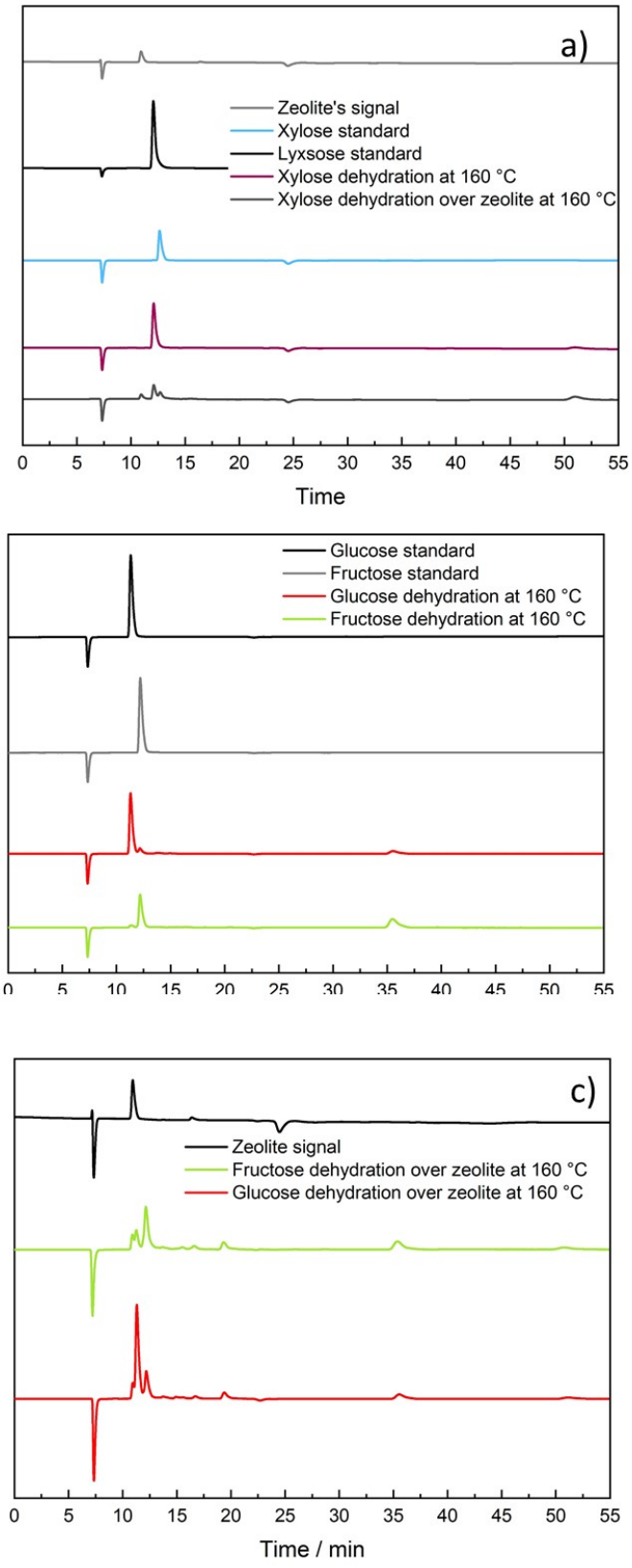

Figure 19: HPLC chromatograms obtained during a) homogeneous and heterogeneous xylose dehydration, b) homogeneous glucose/fructose dehydration and b) heterogeneous glucose/fructose dehydration.

References

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