

Hydrothermal formose reaction

Moderate temperature experiments, NMR and GC data

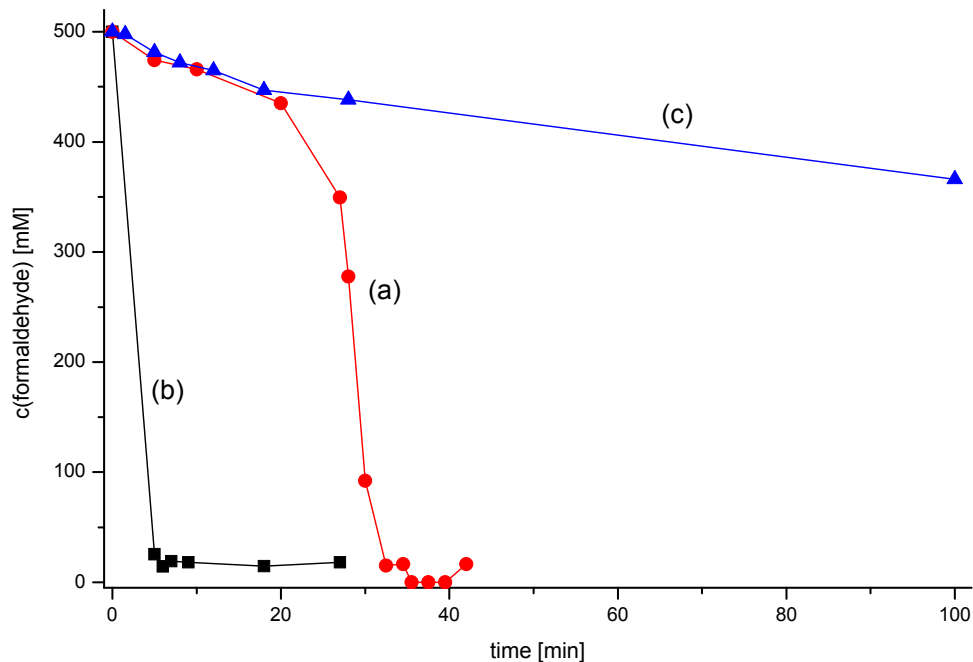


Fig. 1S: Conversion of 0.5 M formaldehyde at 60 °C in a) 0.05 M Ca(OH)₂; b) 0.05 M Ca(OH)₂ with 1 mol% glycolaldehyde and c) 0.1 M NaOH with 1 mol% glycolaldehyde.

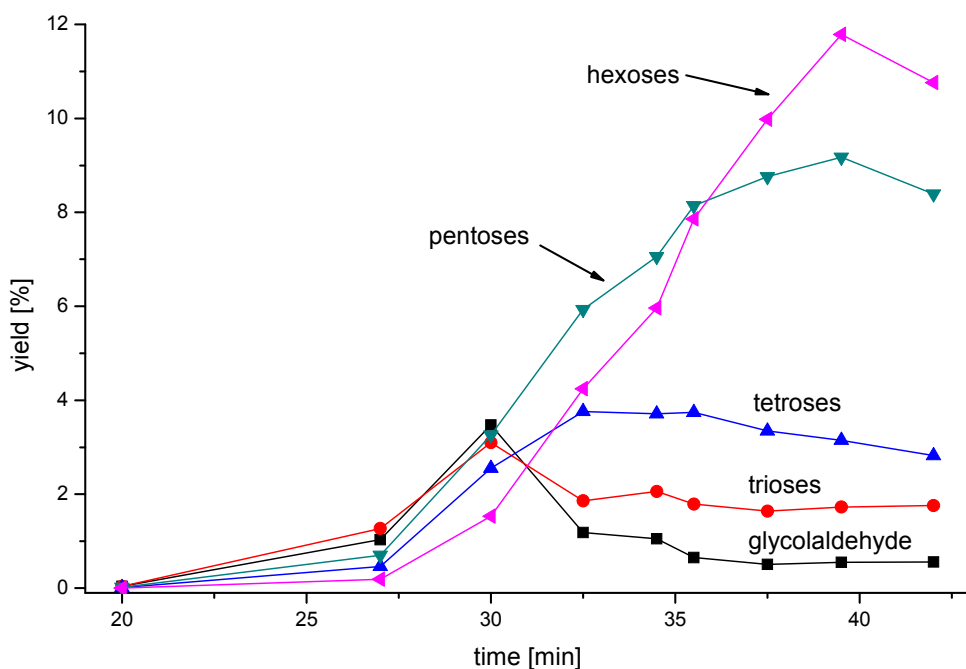


Fig. 2S: Kinetics of carbohydrate formation at 60 °C of 0.5 M formaldehyde in 0.05 M Ca(OH)₂ without initiator.

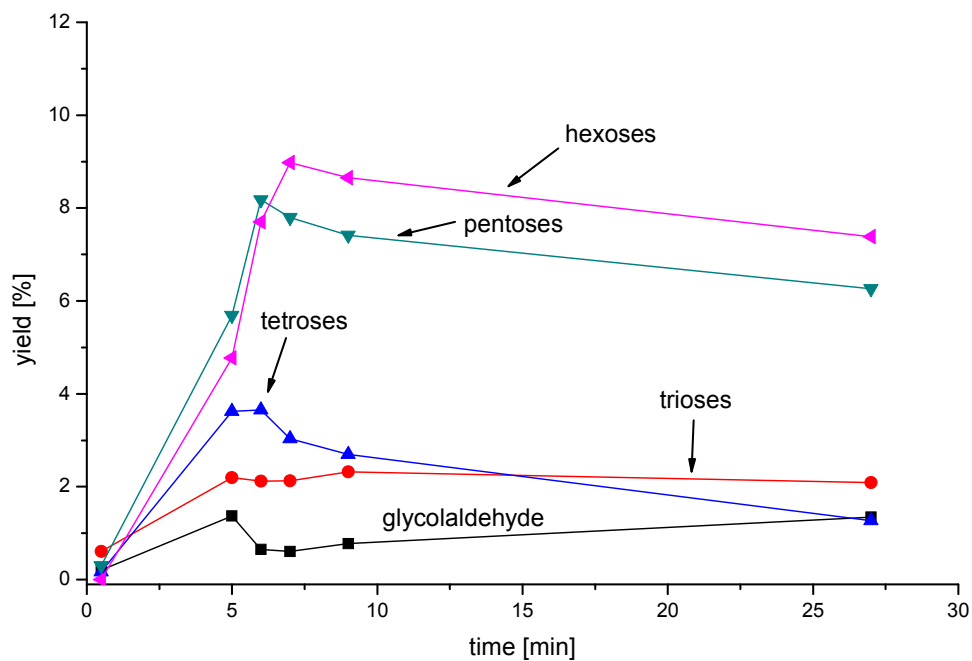


Fig. 3S: Kinetics of carbohydrate formation at 60 °C of 0.5 M formaldehyde in 0.05 M Ca(OH)₂ with 1 mol% glycolaldehyde as initiator.

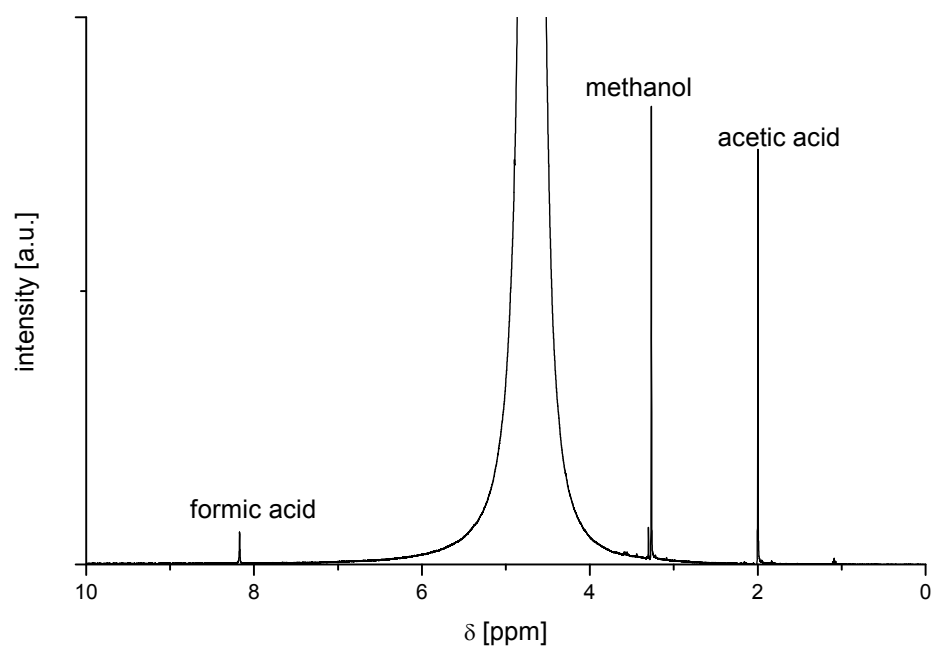


Fig. 4S: ¹H-NMR spectrum of the hydrothermal formose reaction of 0.5 M formaldehyde in 0.1 M acetic acid just shows the Cannizzaro products methanol and formic acid; reaction time 5.8 minutes at 200 °C and 100 bar.

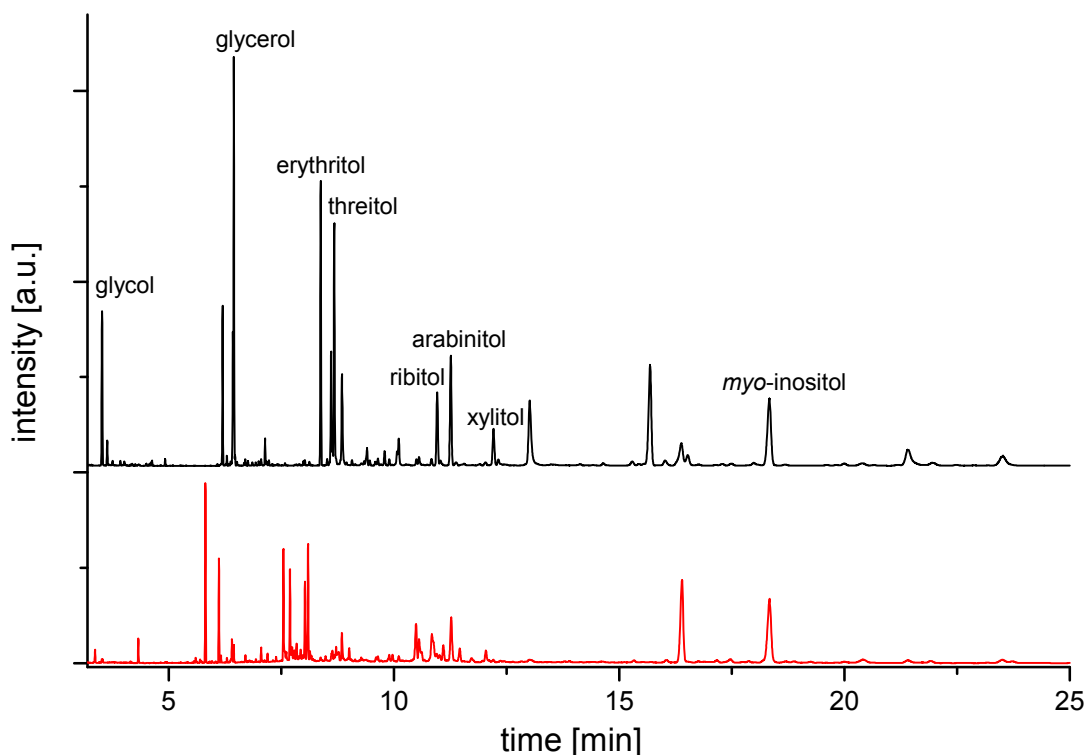


Fig. 5S: GC traces of a 0.5 M formaldehyde solution in 0.1 M K_2HPO_4 reacted for 0.81 min at 200 °C and 100 bar; upper chromatogram was obtained after reduction with $NaBH_4$ and acetylation, lower one is from a directly acetylated reaction mixture. Only marginal amounts of sugar alcohols are present after reaction.

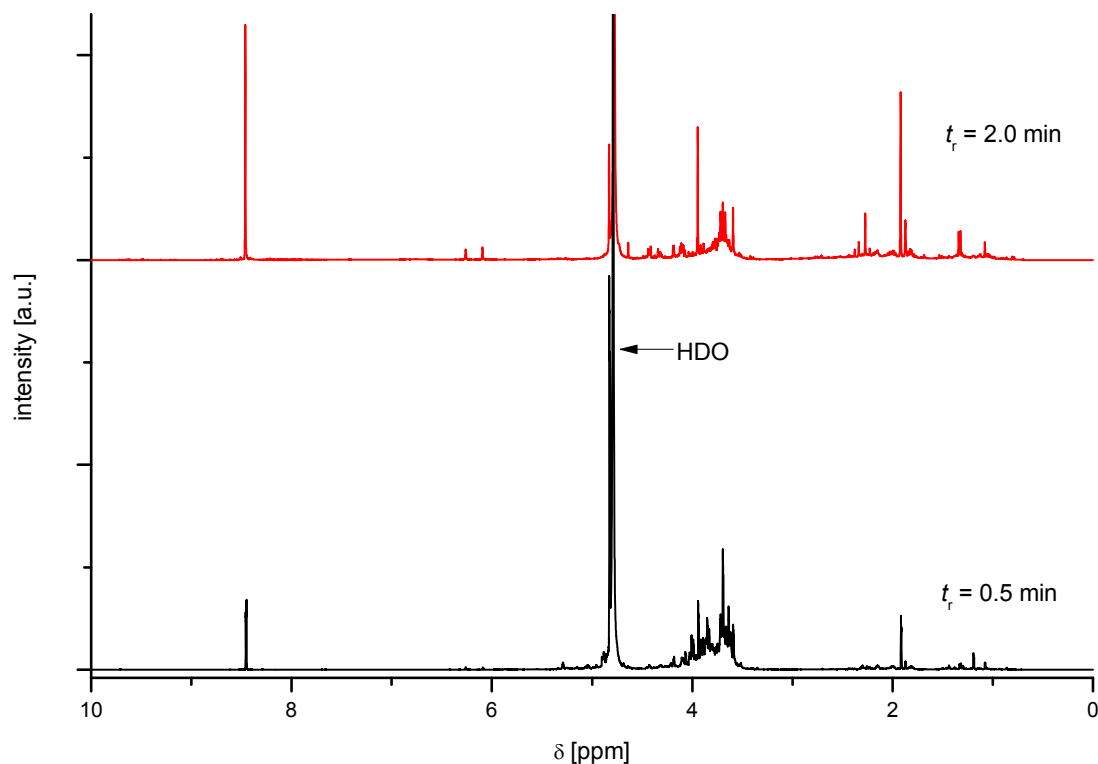


Fig. 6S: 1H -NMR spectra of a formose reaction with 0.5 M formaldehyde in 0.1 M $NaHCO_3$ at 200 °C and 100 bar with 1 mol% dihydroxyacetone added. The lower spectrum was obtained after 0.5 min reaction time, around the yellowing point and the upper one after 2 min; spectra recorded in D_2O .

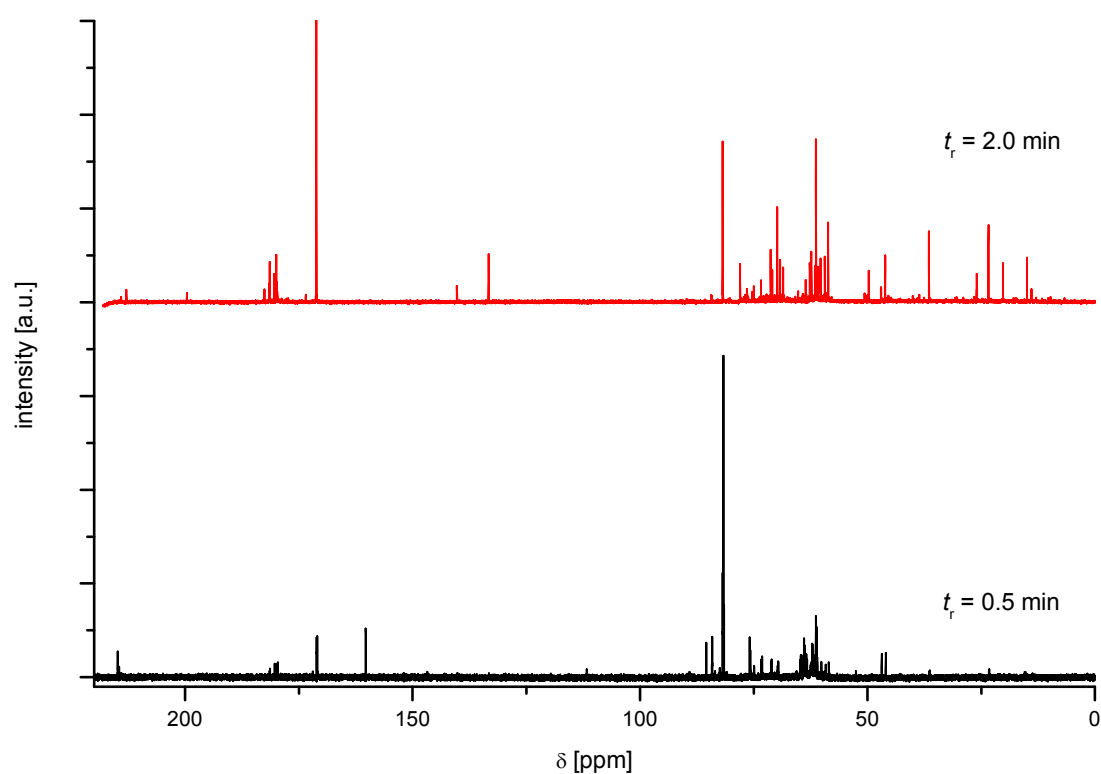


Fig. 7S: ^{13}C -NMR spectra of a formose reaction with 0.5 M formaldehyde in 0.1 M NaHCO_3 at 200 °C and 100 bar with 1 mol% dihydroxyacetone added. The lower spectrum was obtained after 0.5 min reaction time, around the yellowing point and the upper one after 2 min; spectra recorded in D_2O .

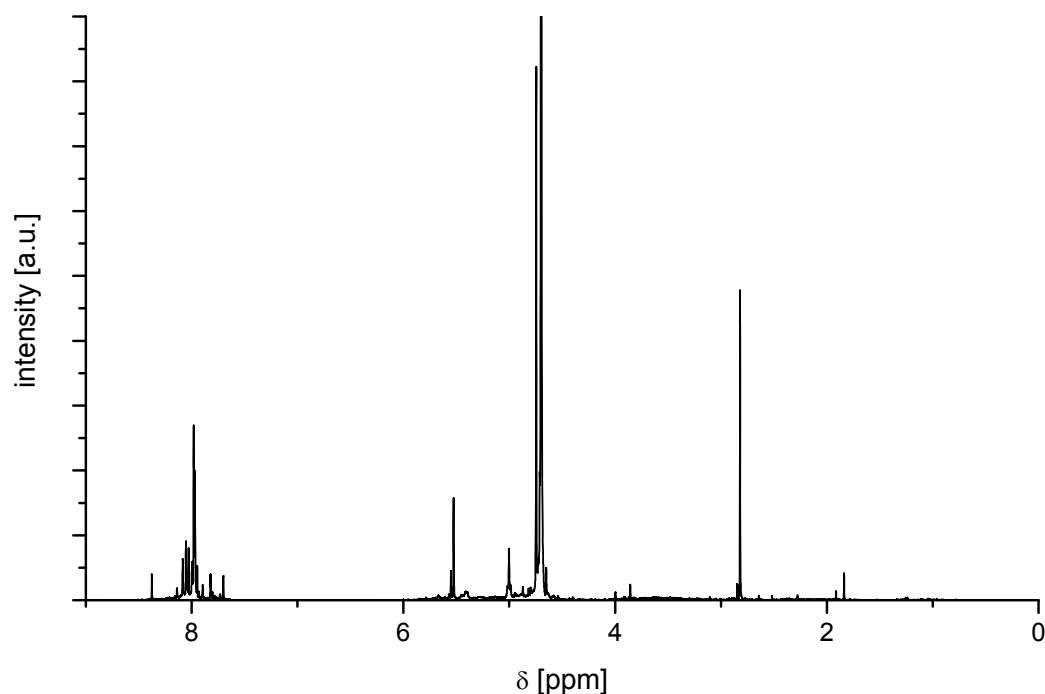


Fig. 8S: ^1H -NMR of the reaction of 0.5 M formaldehyde with 0.1 M adenine at 200 °C and 100 bar for 5.2 minutes lacks of peaks corresponding to carbohydrates; recorded in D_2O

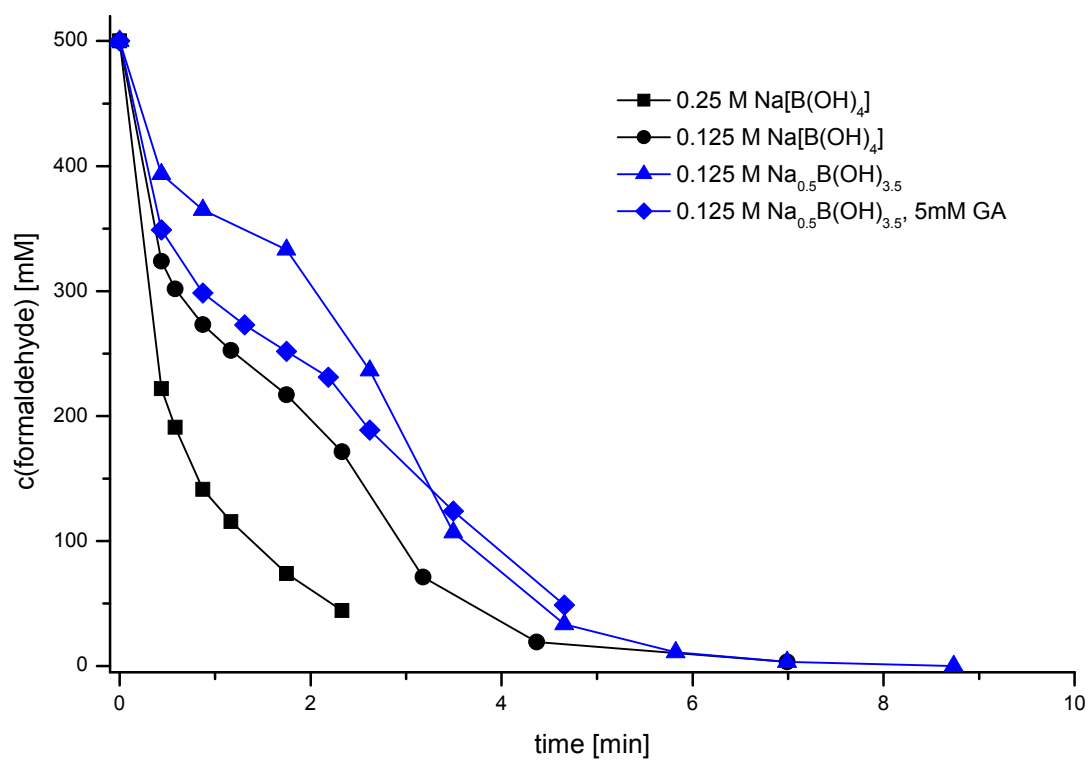


Fig. 9S: Conversion of 0.5 M formaldehyde at 200 °C and 100 bar in presence of borate (black curves) and borate buffer (blue curves).