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Efficient Kinetic Measurements in the Micro-reactor via In-line Raman Spectroscopy

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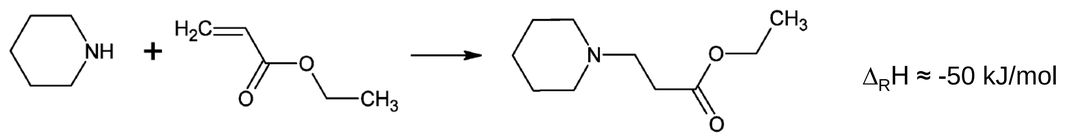
INTRODUCTION

- Investigation of kinetic chemical reactions via the application of in-line Raman spectroscopy in micro-reactors
  - Clearly defined reaction conditions in the micro-/ millichannel
  - Investigation of rapid and exothermic reactions
  - Substantial time and material savings by avoiding extra work steps (quench, sample preparation, offline analyses)
- Michael addition as an exothermic example reaction with known kinetics [1]
- Transient operating mode for production of a dwell-time gradient [2]
  - Rapid recording of time conversion curves at different measurement points in the reactor channel
  - Application of parameter screening for reaction optimization

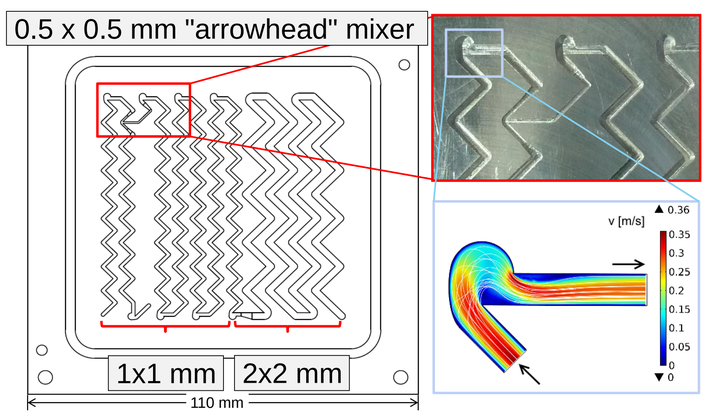


$\Delta_R H \approx -50$ kJ/mol

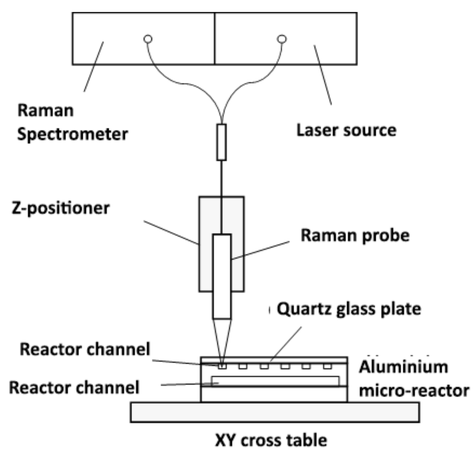
Piperidine **Acrylic acid-ethyl ester** **3-piperidino-propionic acid-ethyl ester**

MEASUREMENT METHOD

- Aluminum/glass plate reactor
  - High mixing efficiency and narrow dwell-time distribution
  - Rapid dissipation of reaction heat (regulated via cooling channels)
  - Optimized measurement points in the channel
  - Increasing channel cross-section

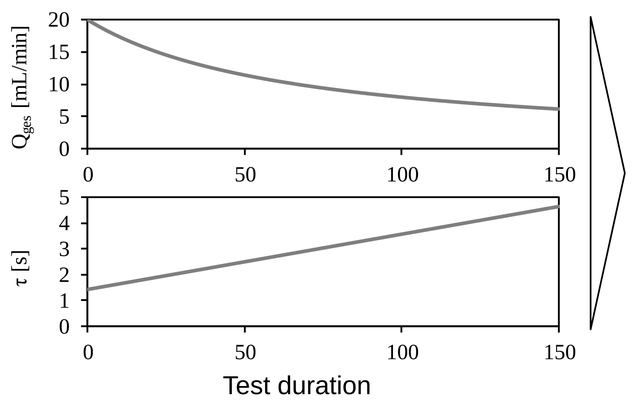


Channel design of the aluminum/glass microreactor, CFD simulation of the flow rate at a measurement point (10 mL/min; Re = 164)



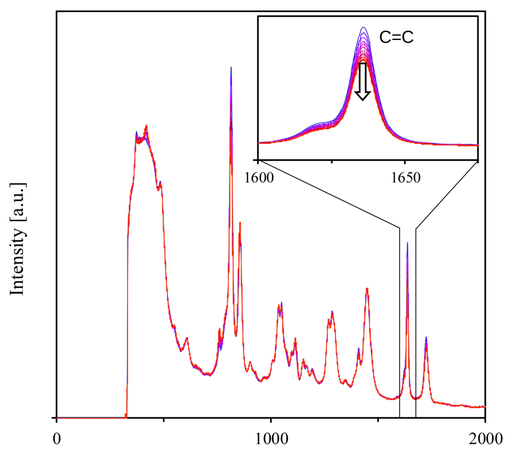
Experimental setup for the in-line-Raman measurements in the microreactor

- Measurement methods
  - **Measurements in stationary state**
    Variation in volume flow (2 – 20 mL/min) and measurement points
  - **Measurements with dwell-time gradients**
    Targeted reductions in flow volume to produce a linear dwell-time increase



Time progression of the volume flow and dwell time over the test duration with continuous measurement at the 6th measurement point

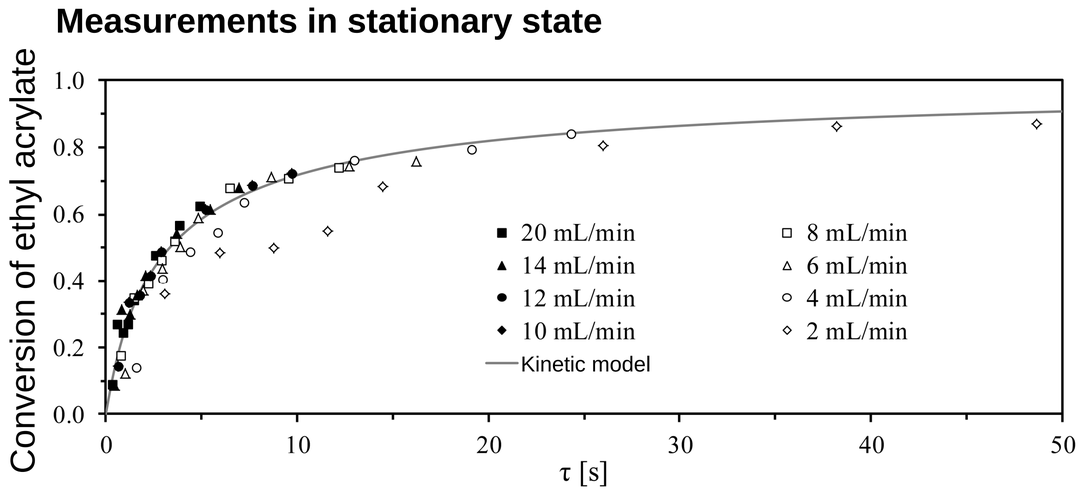
Dwell time τ(t): Dwell time spent, between mixing and measuring point,by the fluid element which is located at the measurement location at that point in time



Raman spectra of reaction mixture with continuous measurement during the dwell-time range (τ = 0.9 s to τ = 2.6 s)

RESULTS

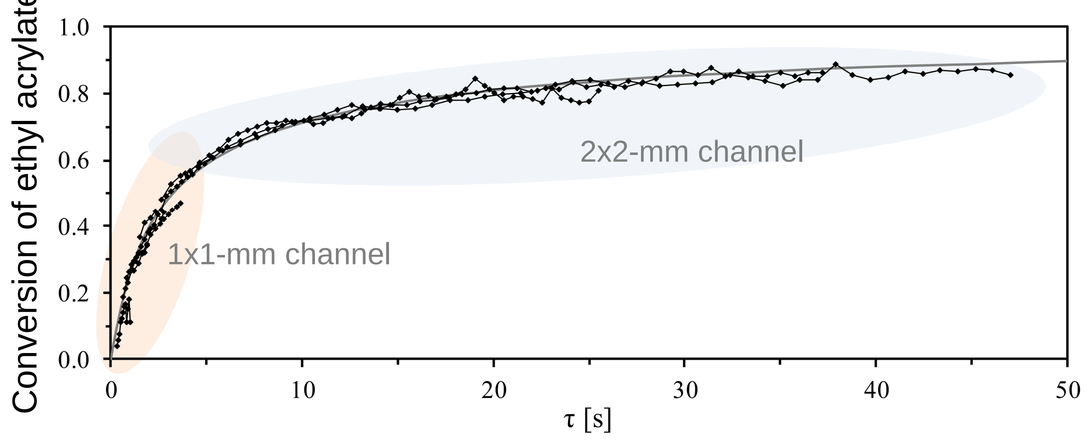
Measurements in stationary state



Comparison of ethylacrylate conversion in stationary operating mode, determined at 7 measurement points with the kinetic model of the reaction [1]

- Good agreement with kinetic model (based on tests with quench and GC offline analytics [1])
- Deviating measurement results at low-volume flow rates (< 6 mL/min)
- Minimal Reynolds number ($Re_{min} \approx 100$) to achieve short mixing time and high Bodenstein numbers (Bo ≈ 100)

Measurements with dwell-time gradients

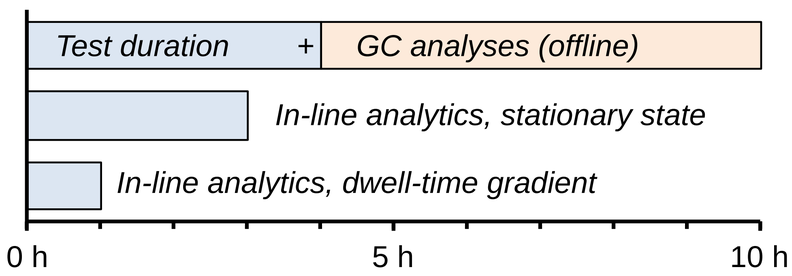


Comparison of ethylacrylate conversion in transient operating mode, determined via gradient measurement at 7 measurement points with the kinetic model of the reaction [1]

- Measurements with limited Re-range (100 – 330, $Re > Re_{min}$)
- Wide dwell-time range (0.4 – 48.6 s)
- High data density (200 data points, total test duration < 1h)

CONCLUSION

- Efficient method for rapid kinetic determination and parameter screening (influence of temperature, catalyst, etc.)
- Collecting a large conversion range via variation of measurement points at different channel cross-sections
- Saving time and materials via in-line analytics with dwell-time gradients
  - Additional time savings possible via motorized positioning table or measurement at several measurement points (multiplexer)



Assessment of required experimental time for time conversion curves with min. 30 data points

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Literature

[1] Schwolow, S., Heikenwälder, B., Abahmane, L., Kockmann, N., Röder, T., 2014. Kinetic and scale-up investigations of a Michael addition in microreactors. Org. Process Res. Dev. 18 (11), 1535–1544.
[2] Moore, J.S., Jensen, K.F., 2014. "Batch" Kinetics in Flow: Online IR Analysis and Continuous Control. Angew. Chem. 126 (2), 480–483
[3] Schwolow, S., Braun, F., Rädle, M., Kockmann, N., Röder, T., 2015. Fast and Efficient Acquisition of Kinetic Data in Microreactors Using In-Line Raman Analysis. Org. Process Res. Dev., accepted paper.