Reaction Monitoring in Chemical Engineering with Quantitative Online NMR Spectroscopy

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Eberhard Karls Universität Tübingen

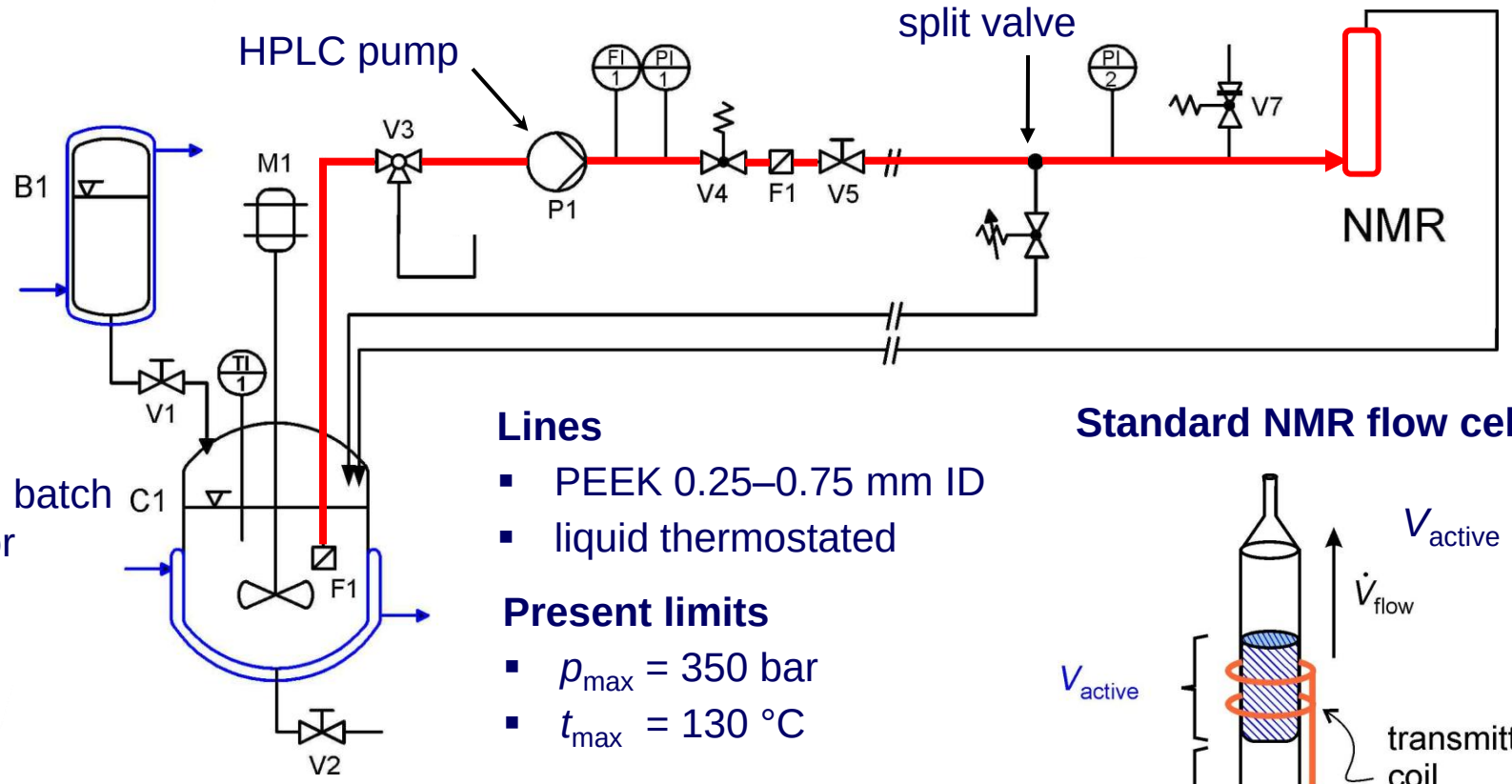
NMR Spectroscopy in Chemical Engineering

- Reaction and process monitoring and elucidation
  - ✓ qualitative and quantitative analysis
  - ✓ complex reacting mixtures
- Hyphenated NMR spectroscopy
  - ✓ non-invasive measurements
  - ✓ no change of:
    - temperature
    - pressure
    - sample composition
- Technical samples
  - ✓ deuterium-free
  - ✓ hazardous chemicals

NMR Laboratory & Group @ LTD

Hyphenation of Reactors with NMR Spectrometer

Typical set-up



Lines

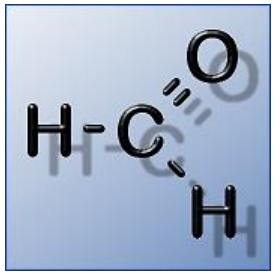
- PEEK 0.25–0.75 mm ID
- liquid thermostated

Present limits

- p_{max} = 350 bar
- t_{max} = 130 °C

Standard NMR flow cell

Formaldehyde



- Important C1 building block
- High reactivity
  - → large variety of formaldehyde-based products
  - → use in aqueous solutions
- Reactions in aqueous formaldehyde solutions

Formation of Methylene glycol

$$CH_2O + H_2O \rightleftharpoons HOCH_2OH$$

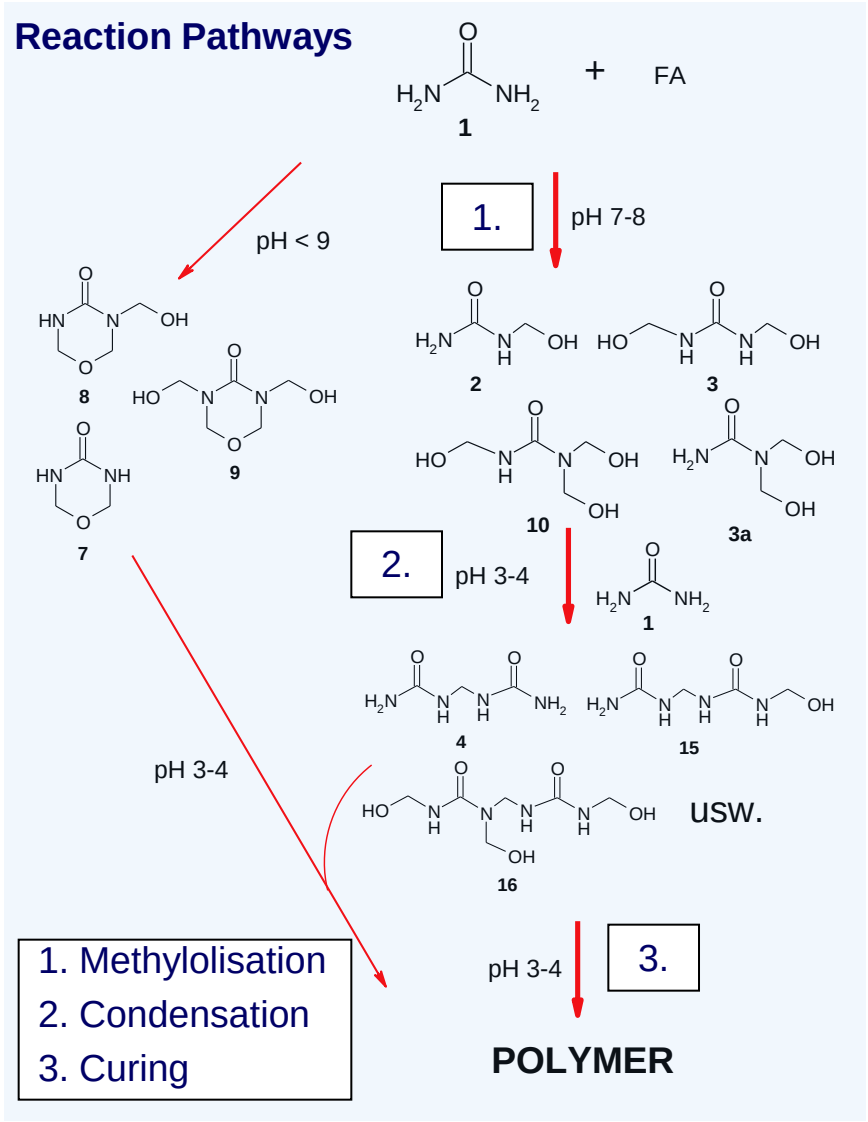
Formation of Poly(oxymethylene) glycols

$$HO(CH_2O)_{n-1}H + HOCH_2OH \rightleftharpoons HO(CH_2O)_nH + H_2O$$

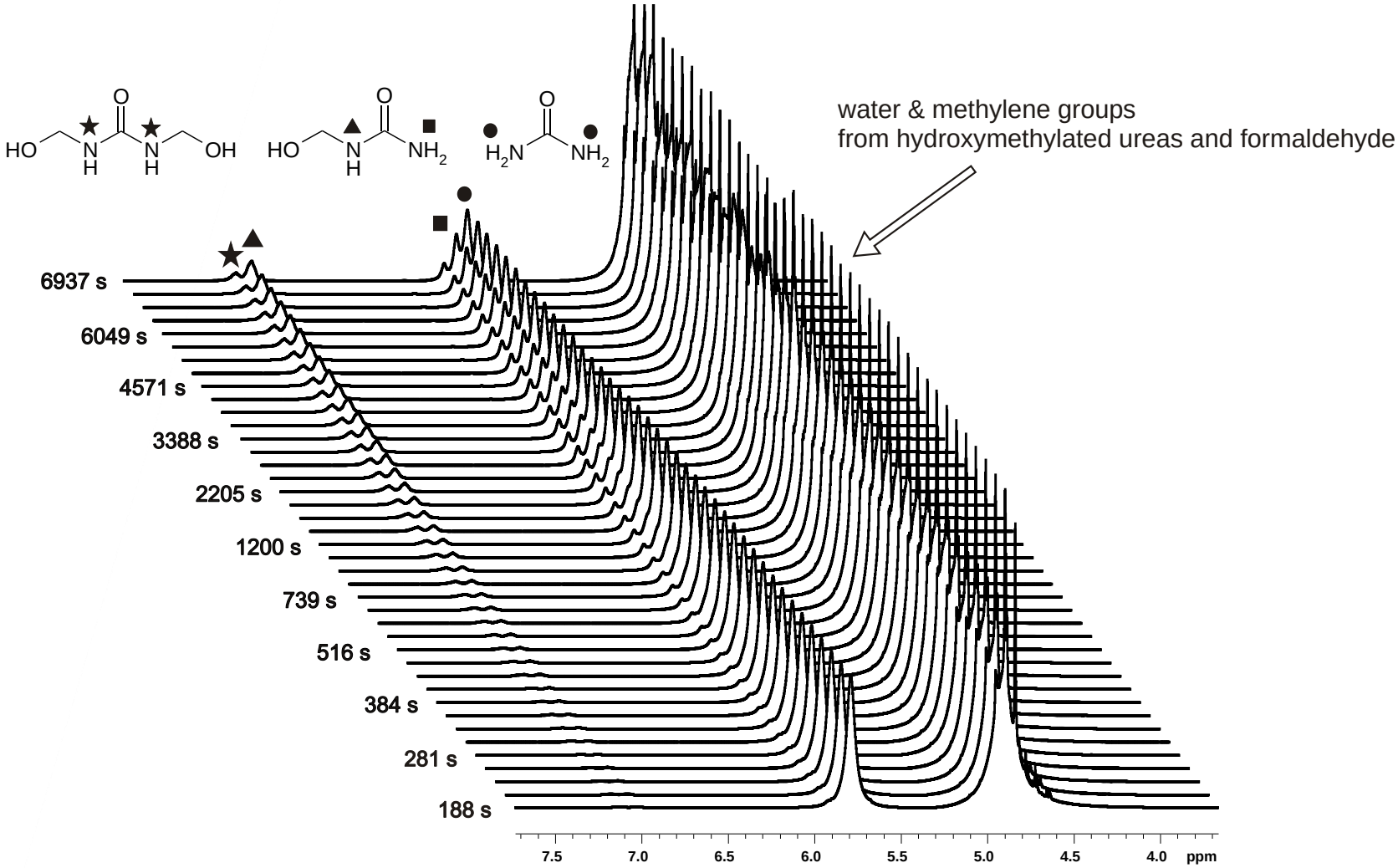
- Similar reations with Methanol yield Hemiformals

Urea-Formaldehyde Resins

- Most common binder for wood products
- Used in very large amounts in wood industry
- Production for ~ 80 years, yet still not fully understood

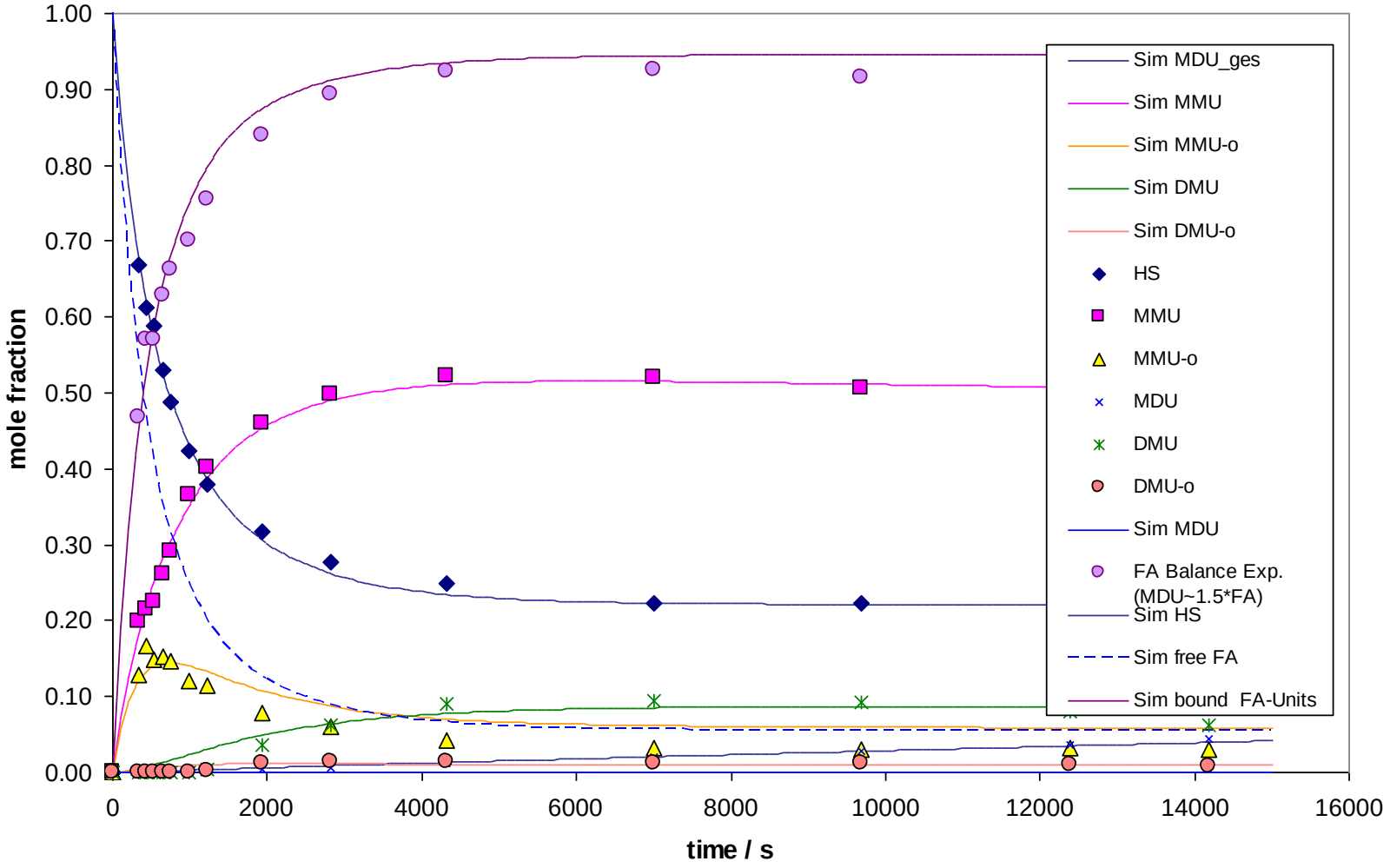


Reaction Monitoring - Hydroxymethylation of Urea



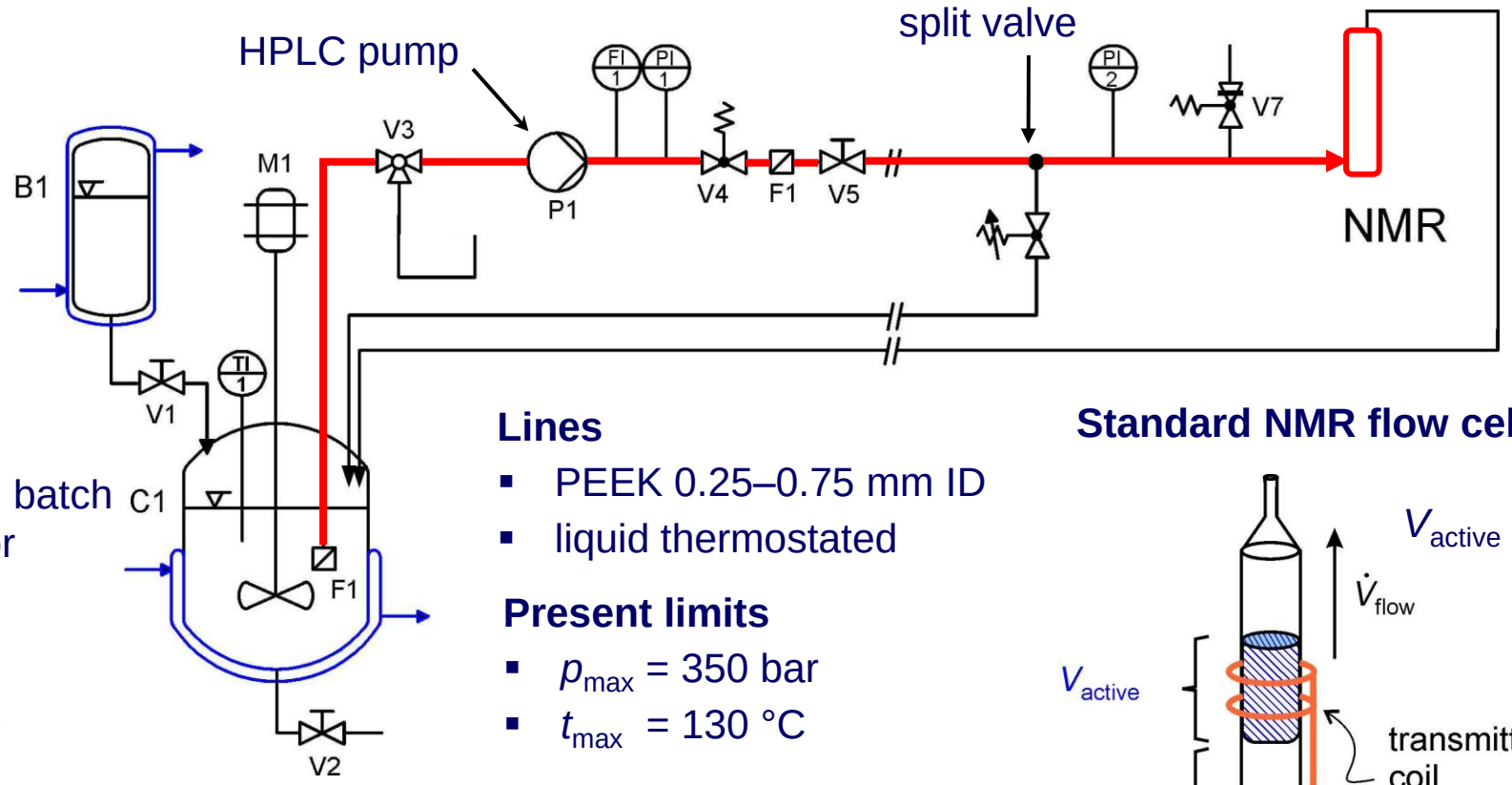
Modeling Urea Hydroxymethylation Kinetics

Comparison of experiment and simulation



Hyphenation of Reactors with NMR Spectrometer

Typical set-up



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Present limits

- p_{max} = 350 bar
- t_{max} = 130 °C

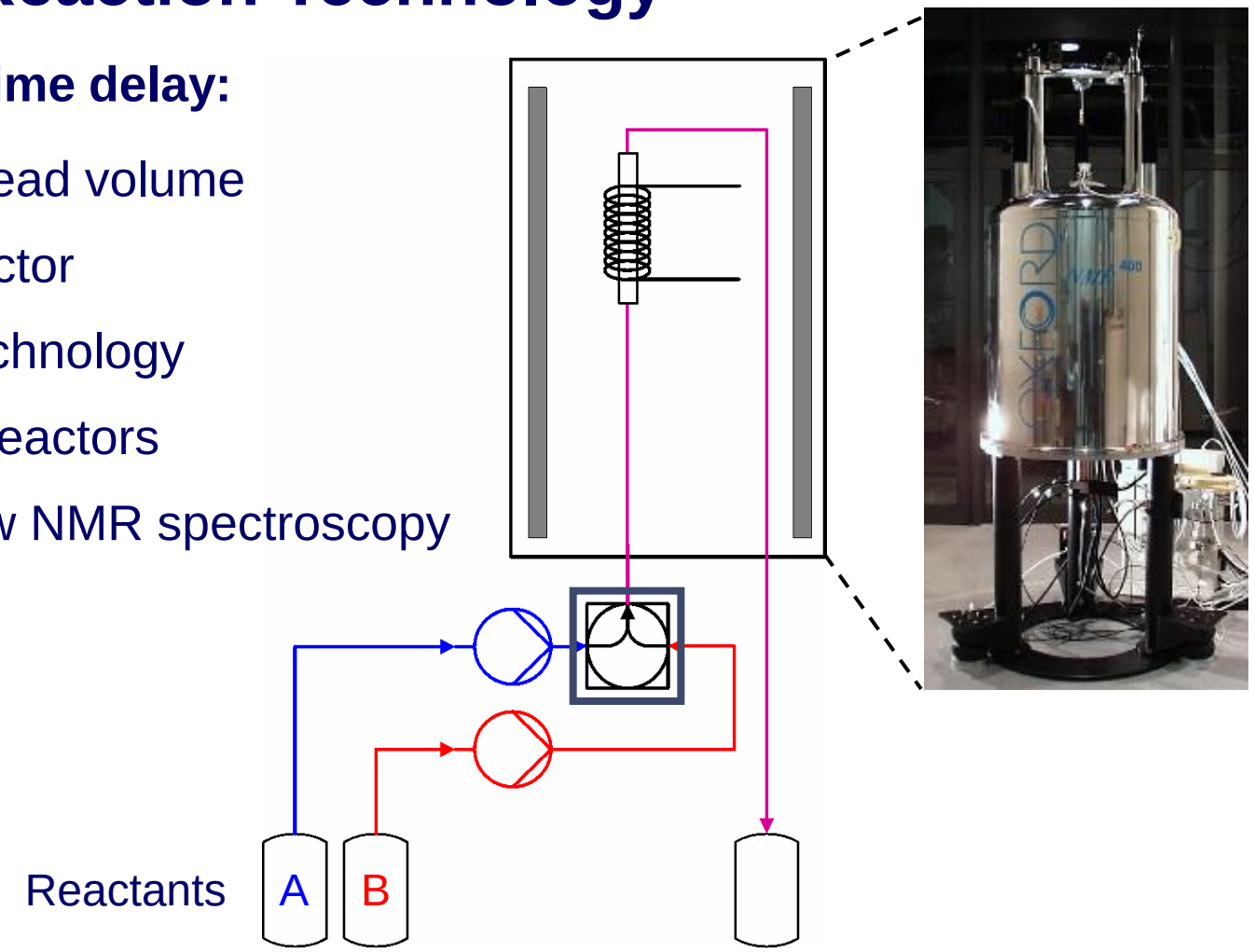
Standard NMR flow cell

➢ Set-up for reactions with τ > 10 min

Monitoring Fast Reactions with NMR Spectroscopy Using Micro-Reaction Technology

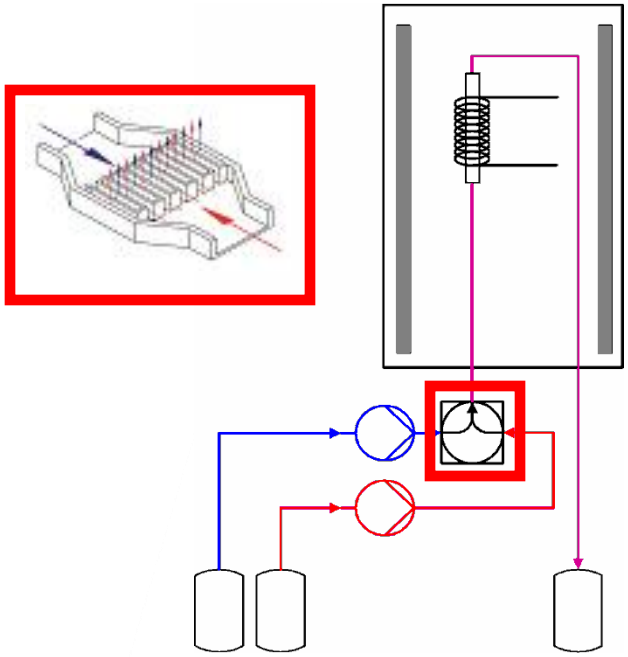
Need for reduced time delay:

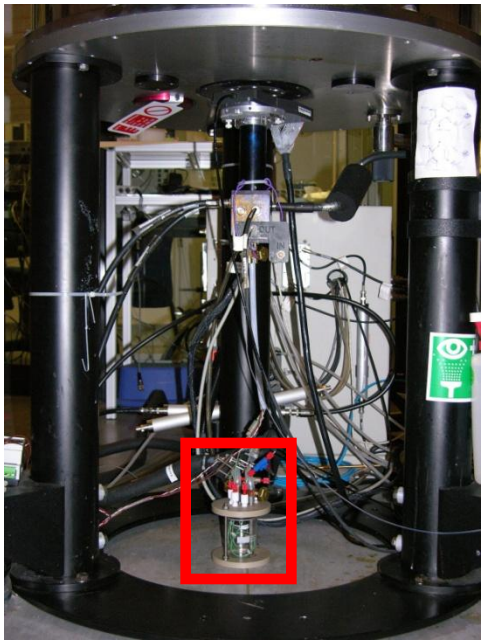
- Minimization of dead volume
- Relocation of reactor
- Micro-reaction technology
- Micro-mixers as reactors
- Coupling with flow NMR spectroscopy



Coupling Micro-Mixer with Online NMR

Thermostated mixer below NMR magnet





- Hastelloy mixer (max. 20 bar, 0.1 – 200 ml/min)
- Syringe pumps (max. 500 bar, 0.1 –100 ml/min)

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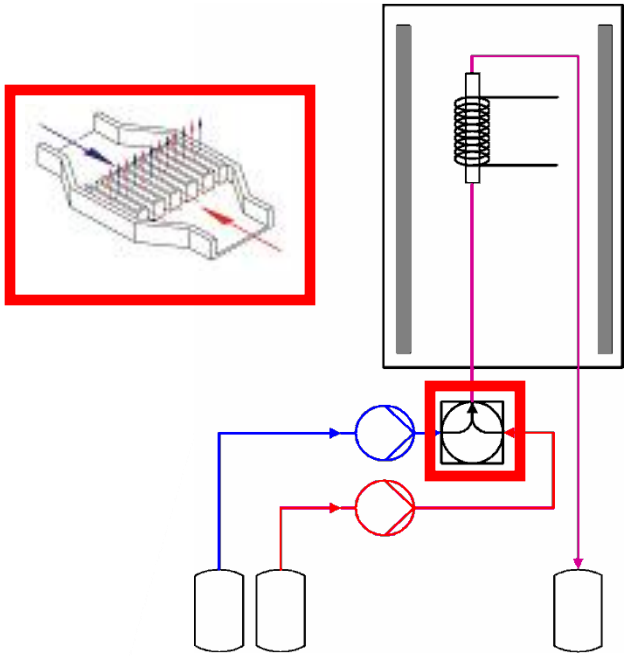
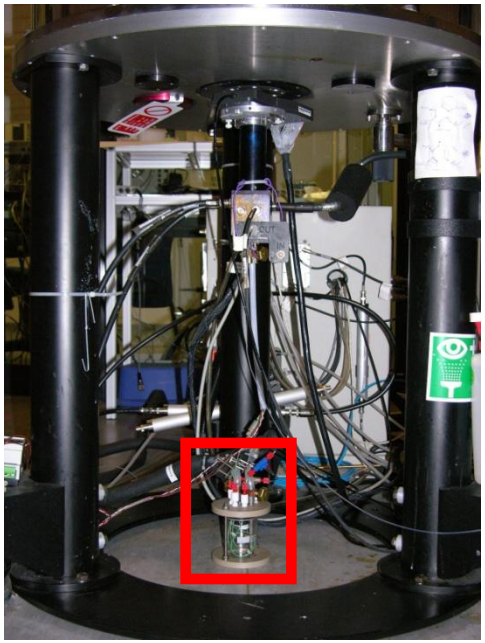
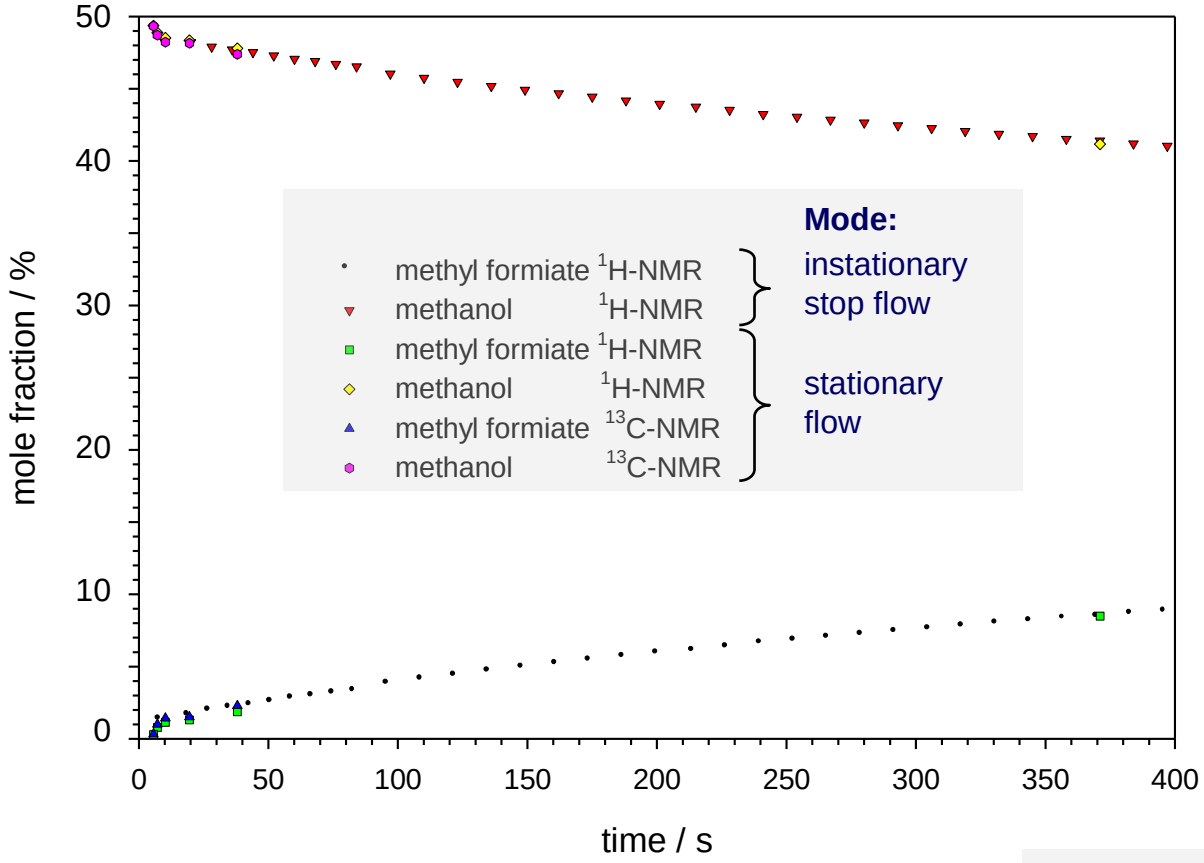




- Hastelloy mixer (max. 20 bar, 0.1 – 200 ml/min)
- Syringe pumps (max. 500 bar, 0.1 –100 ml/min)
- **Operation modes:**
  - stationary flow mode (^{1}H and ^{13}C NMR)
  - instationary stop-flow mode (^{1}H NMR)

Comparison of Results of Different Methods



Test System:

$$CH_3OH + HCOOH \rightleftarrows CH_3COOH + H_2O$$

- All methods give consistent results
- Set-up for reactions with $\tau > 1$ min

Coupling Micro-Mixer with Online Capillary NMR

Preliminary set-up

- Installation of micro-mixer in NMR probe head, next to active volume
- Need for very small mixer

  NanoMixer (Upchurch Scientific)

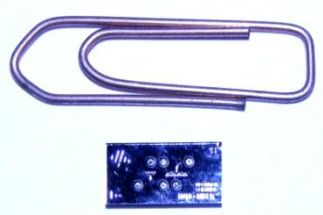
  flow:10 nl/min - 500 µl/min
- Solenoidal capillary ^{1}H NMR probe

  V_{active} = 5 µl

  t_{max} = 150 °C

  p_{max} = 120 bar

  flow = 0.1 – 200 µl/min
- Set-up for reactions with τ > 0.1 min



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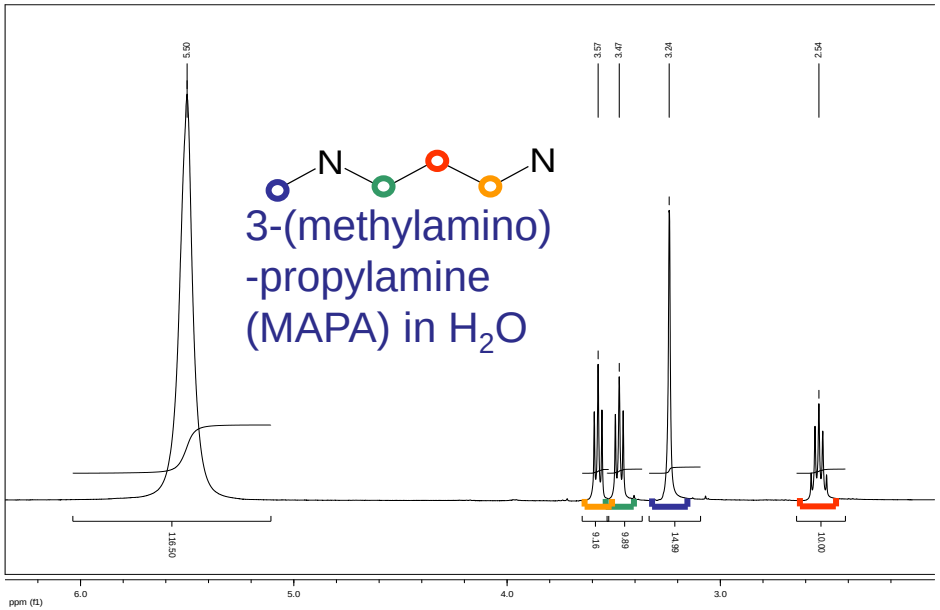

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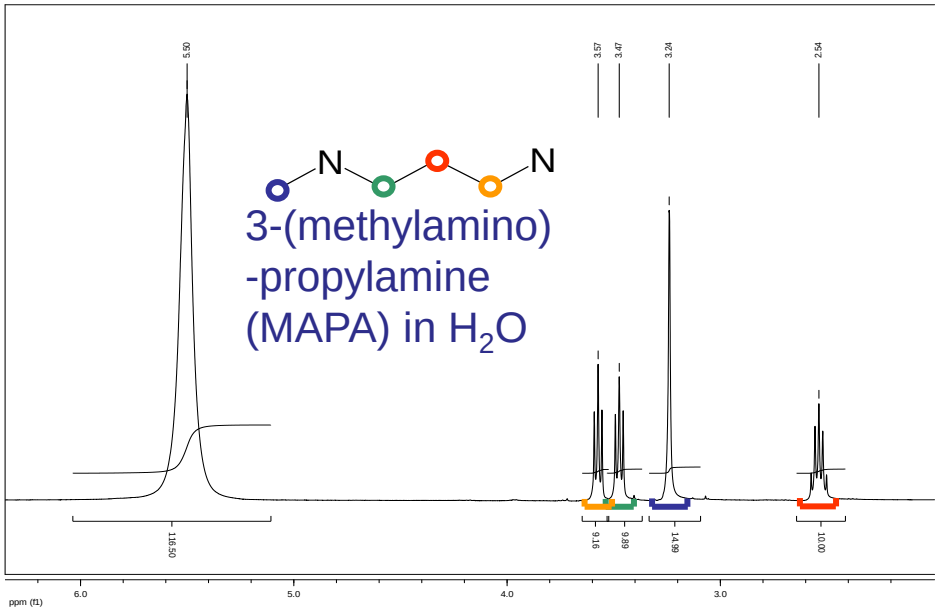
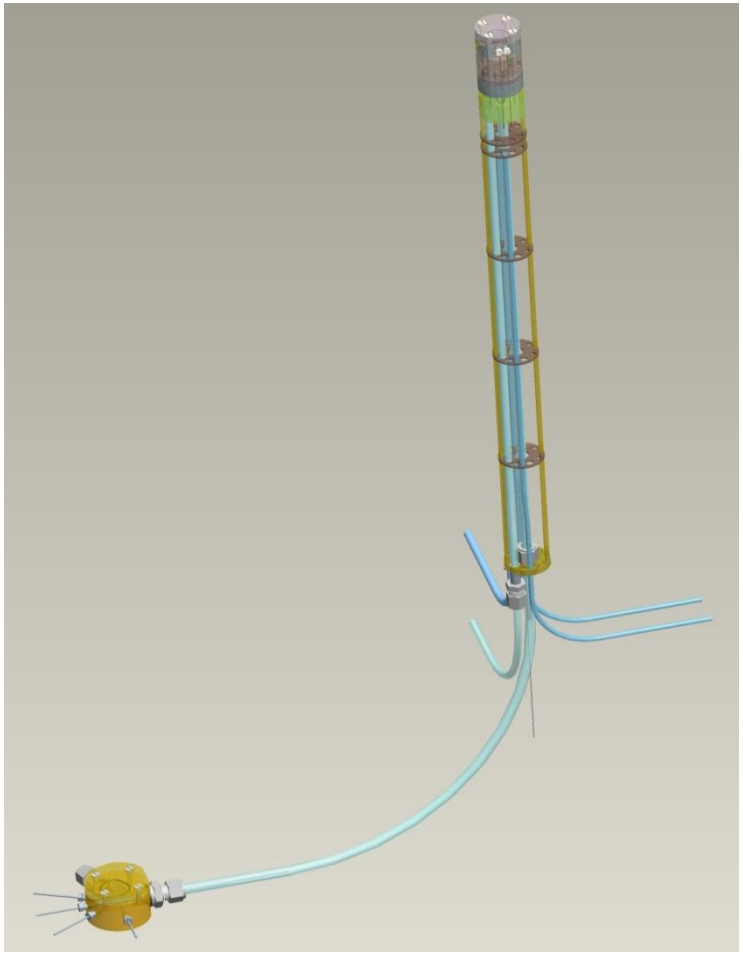
- **Problem: efficient thermostatization**



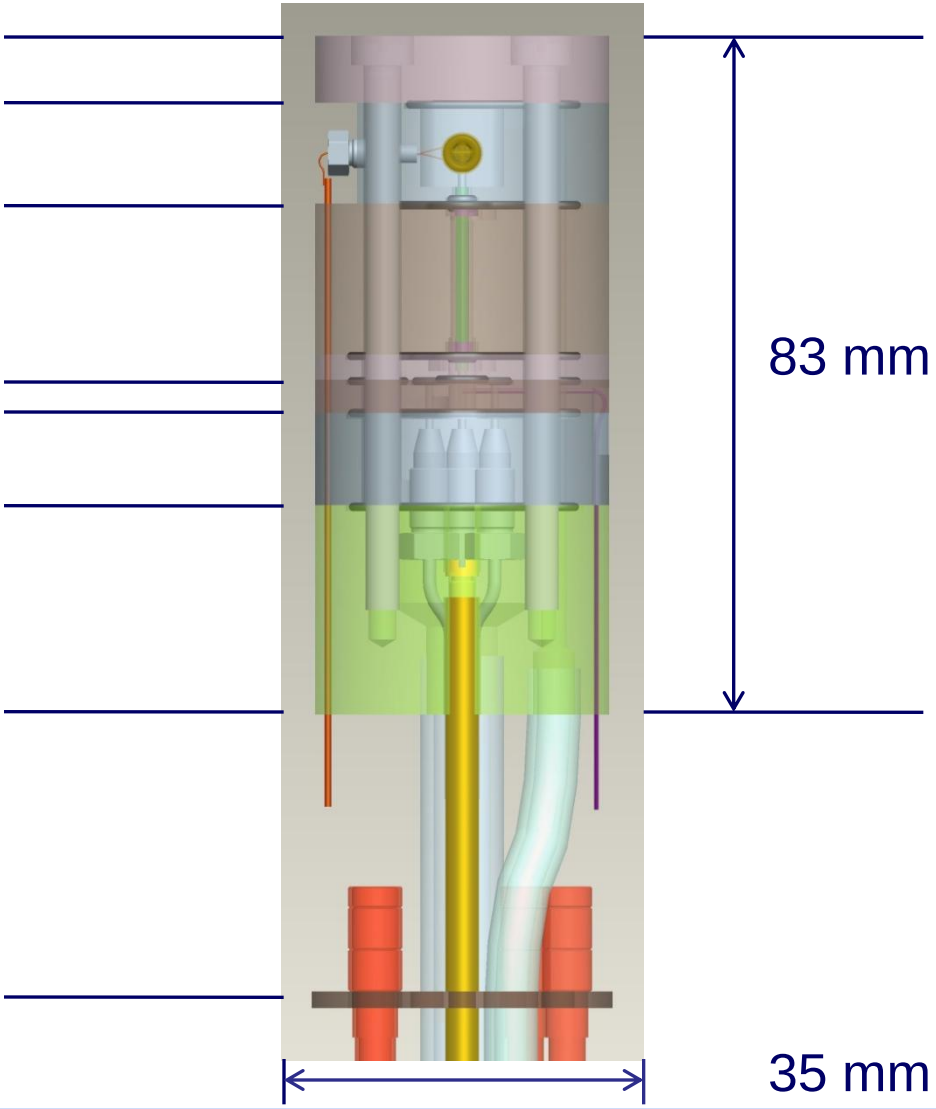
Thermostated Micro-Mixer NMR Probe Head

Prototype

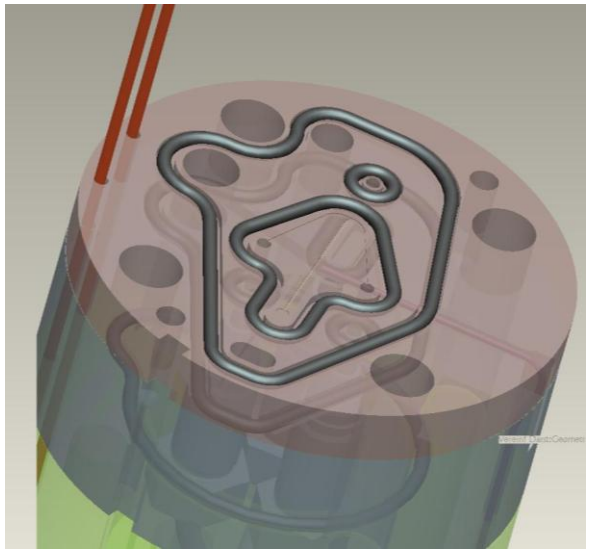
- Co-operation:
  - ✓ TU Kaiserslautern
  - ✓ Universität Tübingen
  - ✓ Institut für Mikromechanik Mainz (IMM)
- Capillary NMR probe + micro-mixer
- Completely liquid-thermostated
  - ✓ medium: FC 43 (Perfluorotributylamine)
  - ✓ educt- and product lines
  - ✓ micro-mixer
  - ✓ NMR probe
- Air cooling: electronics, body
- t_{max} = 120 C, p_{max} = 150 bar
- Reactions with τ > 0.1 min



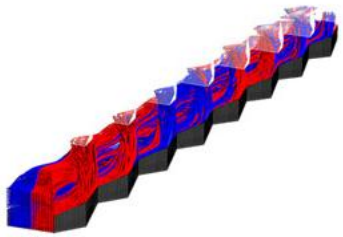
Overview New Probe Head



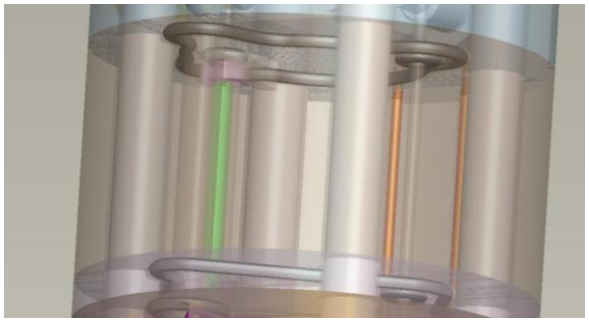
Probe Head Details: Mix & Dwell



Micro-mixer (IMM)



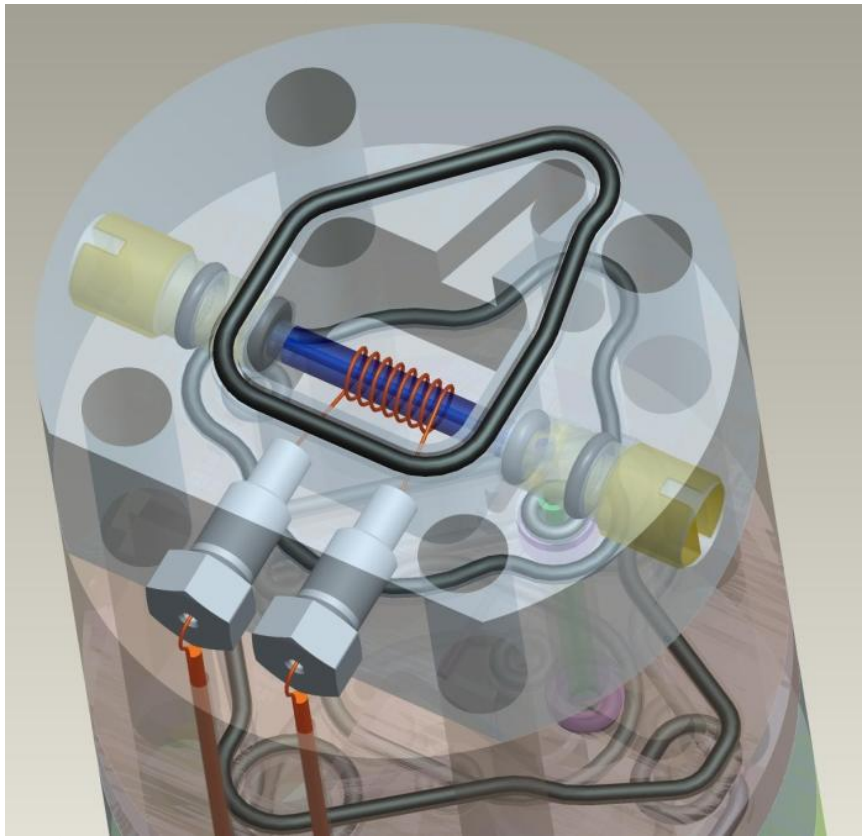
- Material: PEEK
- Split & mix „crawler“ type
- Flow rate: 0.5 - 500 µl/min



Dwell unit

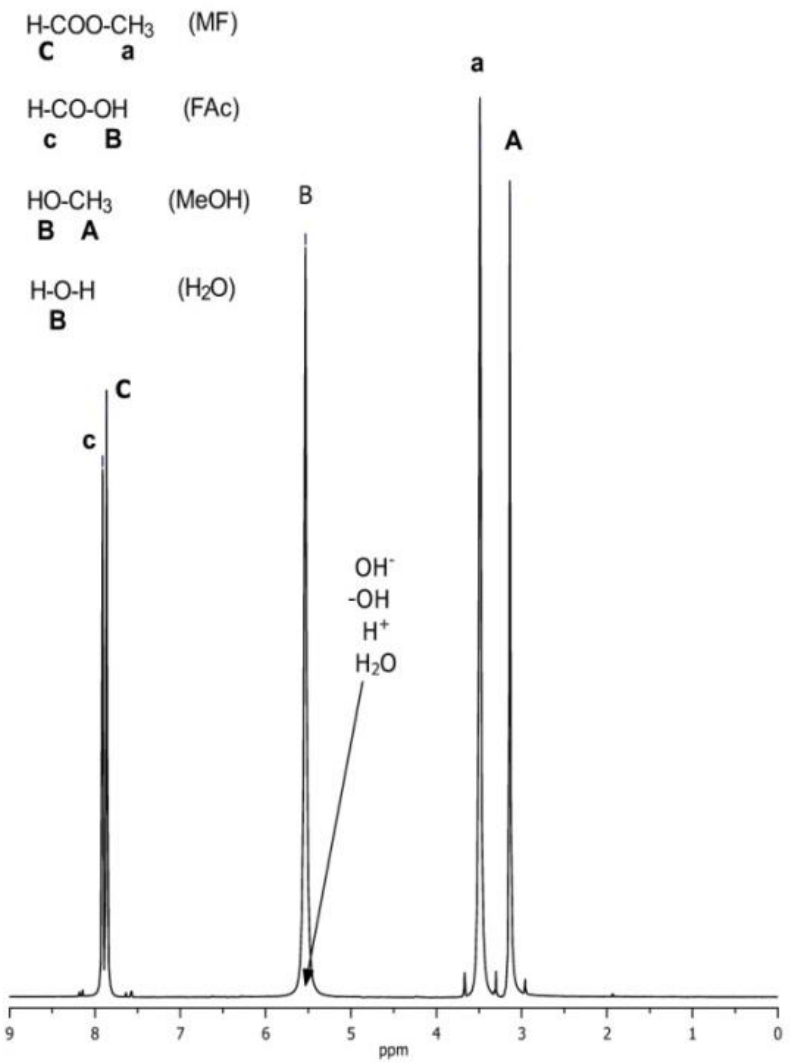
- Material: PEEK
- Various line diameters available
- Adjustable residence time

Probe Head Details: NMR Flow Cell



- Material flow cell: silica glass
- Solenoidal coil
- V_{active}: 4 µl
- Thermostating liquid FC 43 flows around coil & cell
- Temperature measurement (in FC 43)

New Probe Head: Typical ^{1}H NMR Spectrum



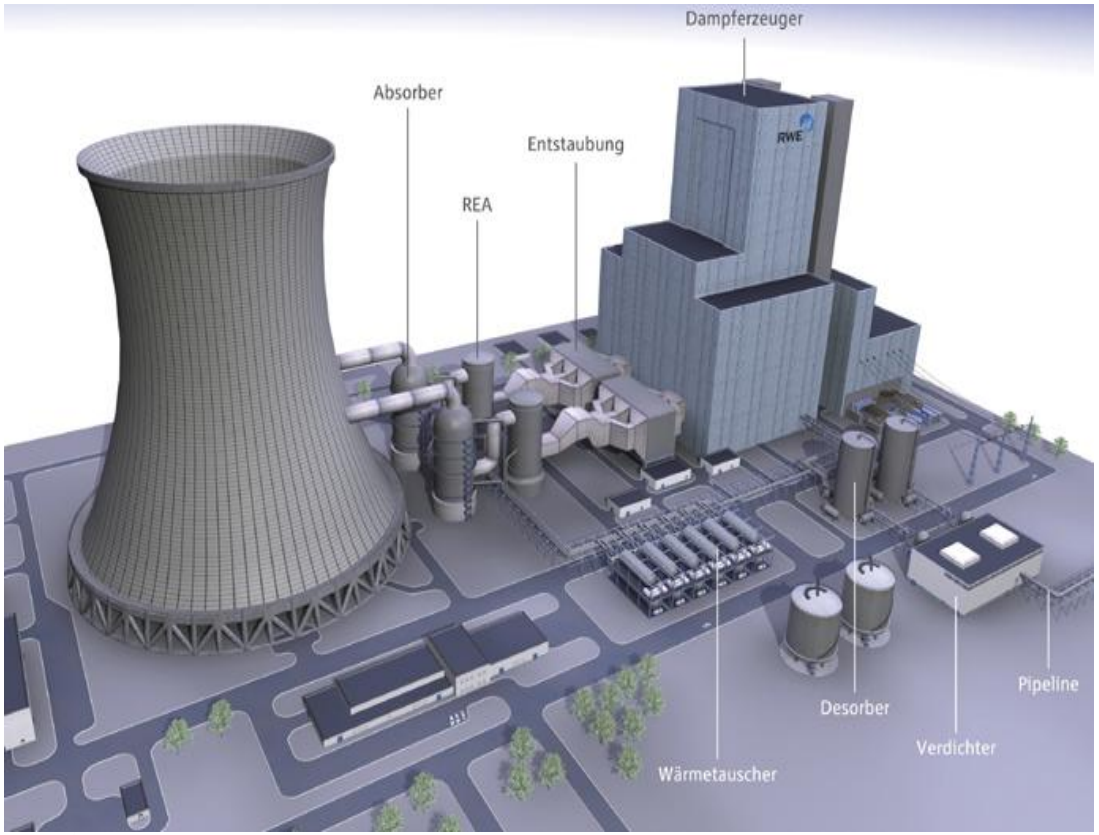
t = 25 C

x_{MeOH} = 0.5 mol mol^{-1}

x_{FAc} = 0.5 mol mol^{-1}

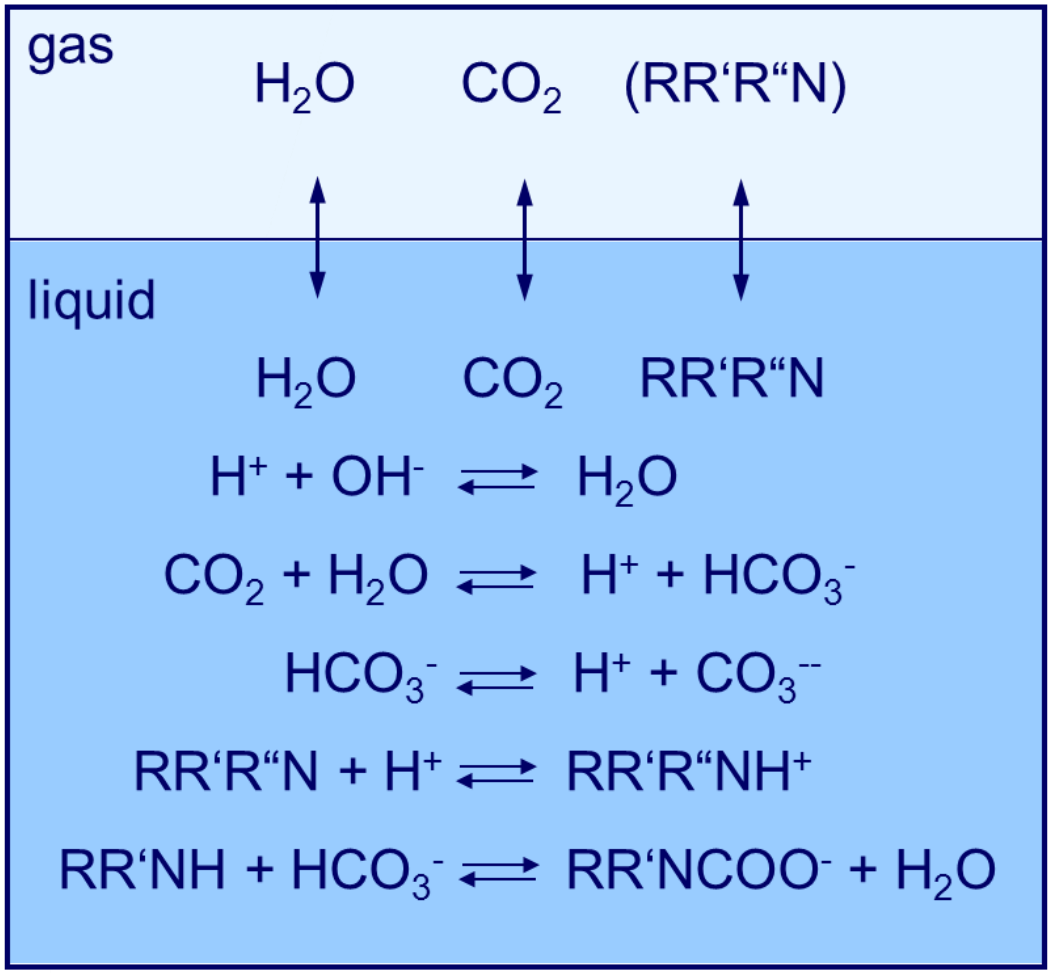
Post Combustion Carbon Capture (PCC)

First Application of New NMR Probe Head



- Reactive absorption with aqueous amine solutions

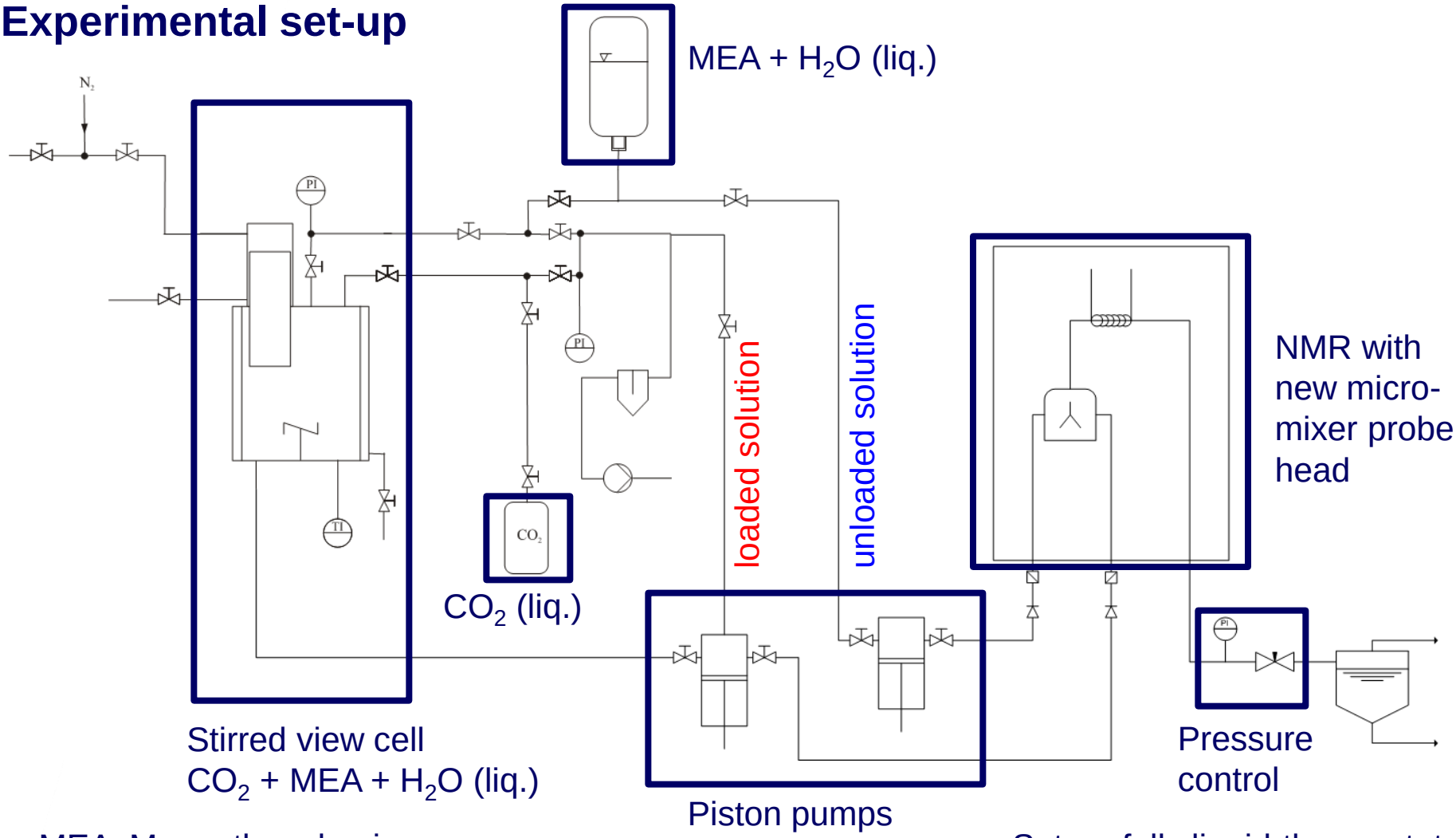
CO_2 Absorption in Aqueous Amine Solutions: Complex Reacting Systems



- NMR spectrocopy for studying liquid phase reactions

NMR Monitoring CO_2 + MEA + Water Dilution

Experimental set-up

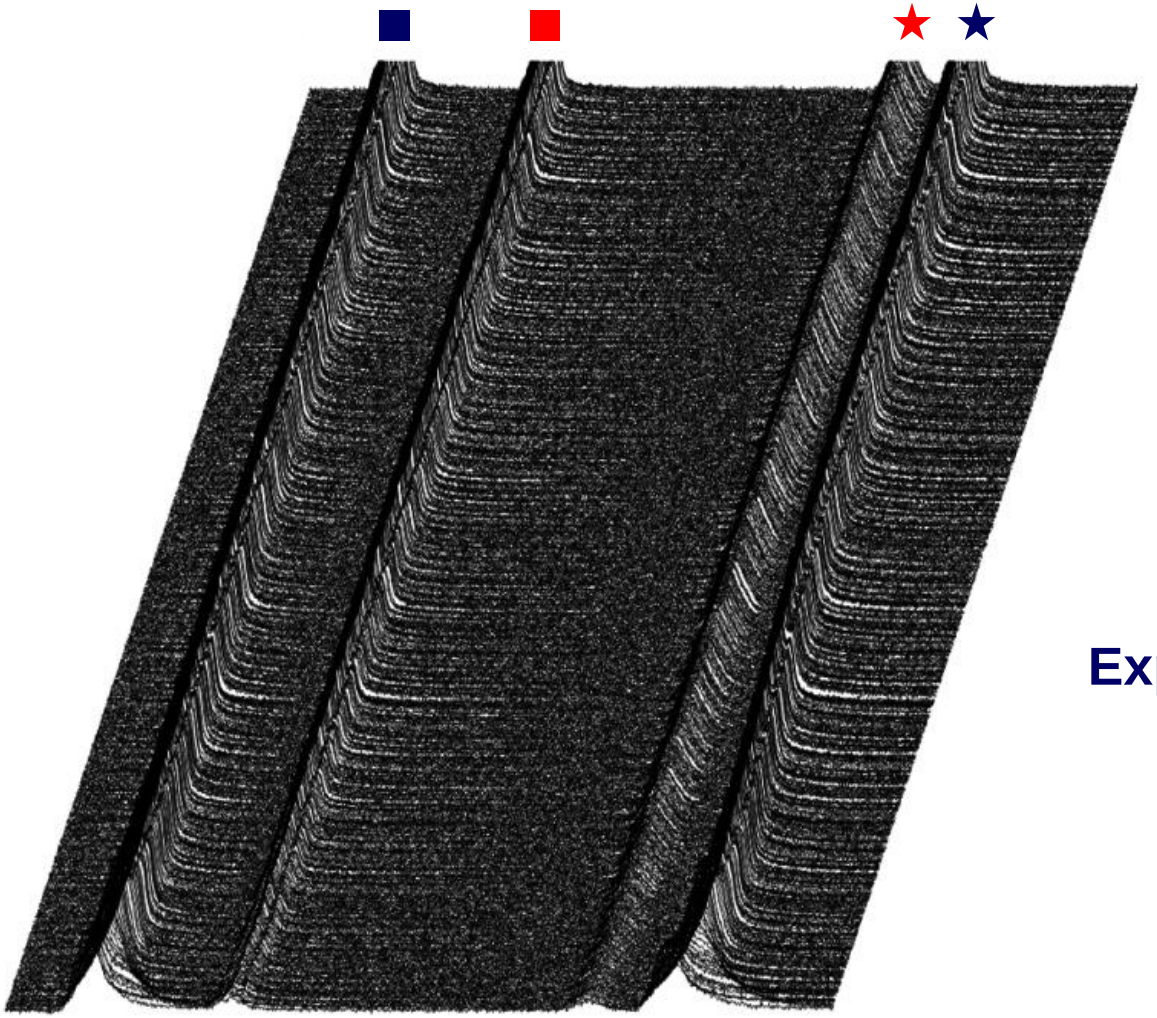


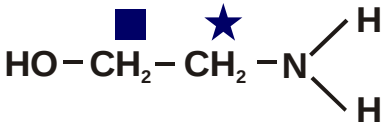
MEA Monoethanolamine

Set-up fully liquid-thermostated

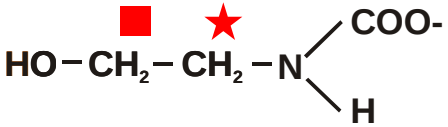
NMR Monitoring CO_2 + MEA + Water Dilution

Stacked ^1H NMR Spectra





MEA/$MEAH^+$



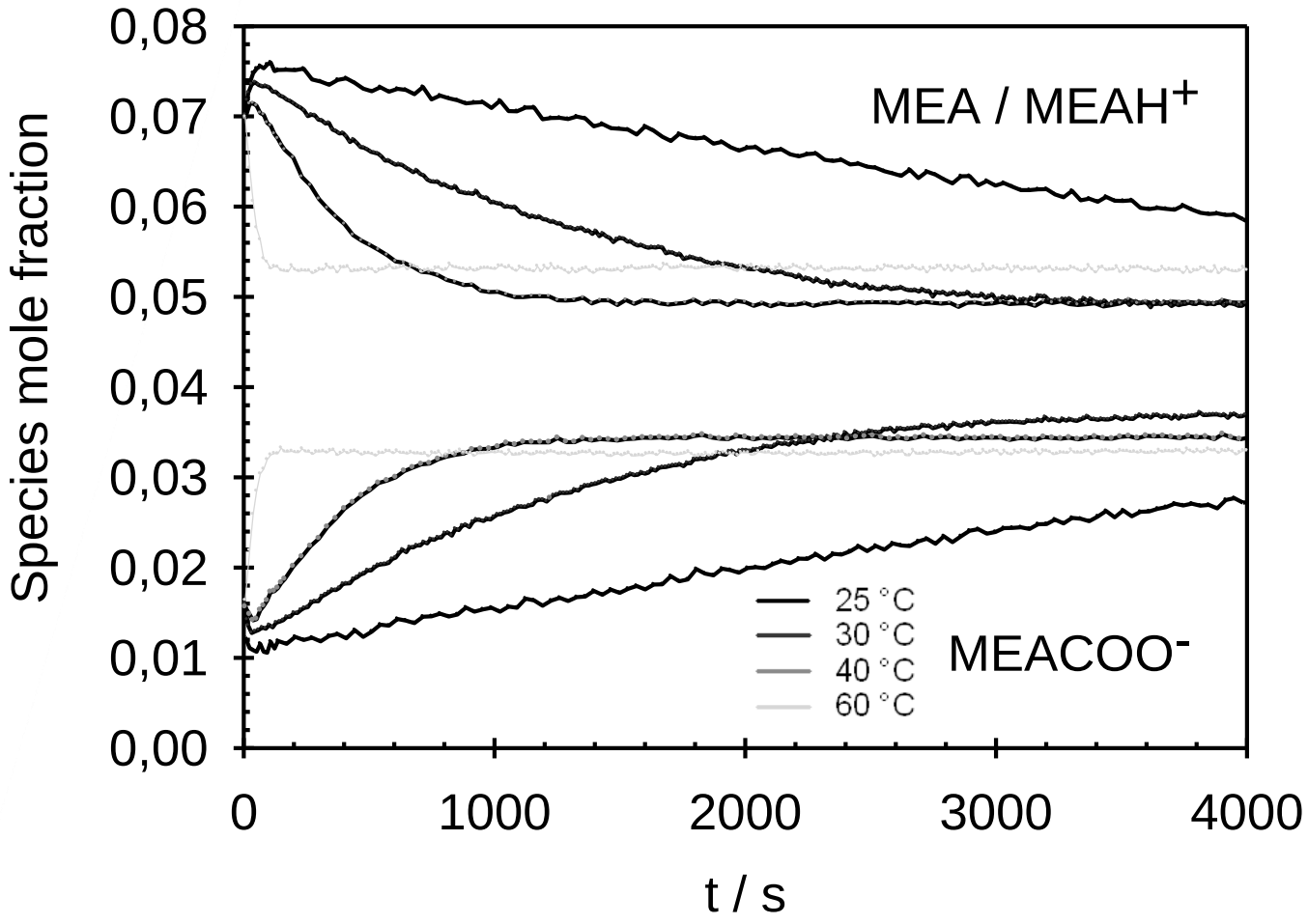
$MEACOO^-$

Experiments:

- t = 25, 30, 40, 60 °C
- Stop flow (τ_0 = 1.7 s)
- Equilibrium @ 60 °C after τ < 200 s

NMR Monitoring CO_2+MEA+Water Dilution

Experimental concentration profiles



Summary

- Quantitative online NMR spectroscopy in chemical engineering
- Reaction and process monitoring and elucidation
- Relaible quantification of speciation of complex mixtures
- Coupling of NMR flow probes with:
  - conventional external reactors → $\tau_{min} \approx 10$ min
  - external micro-mixer → $\tau_{min} \approx 1$ min
- Coupling of capillary NMR flow probes with:
  - internal micro-mixers → $\tau_{min} \approx 0.1$ min
- New thermostated micro-mixer NMR flow probe head
- Valuable method for chemical and pharmaceutical R&D

Thanks

- Michael Maiwald (BAM)
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Deutsche Forschungsgemeinschaft DFG

NanoKat

BASF The Chemical Company

Lonza