Process Chemistry Center

GSCE

Methyl chloride synthesis in a microreactor

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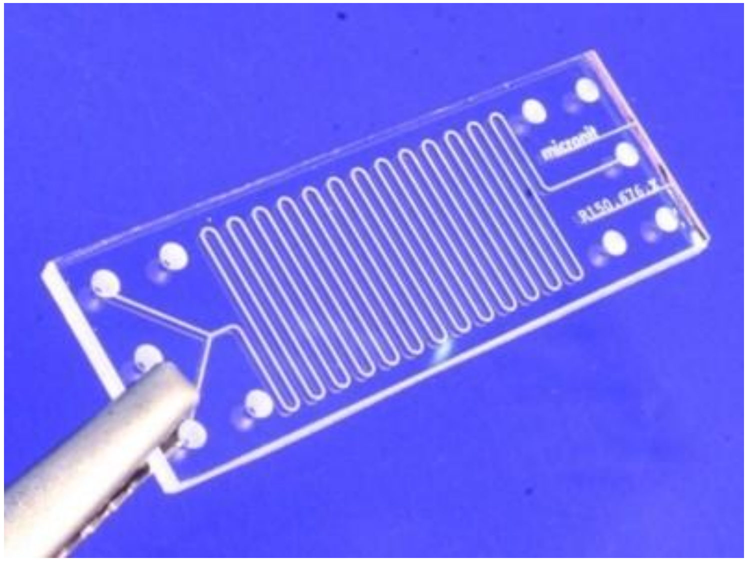
Outline

- Introduction
  - Microreactor technology
  - Methyl chloride
- The work
  - Key points
  - Kinetics of MeCl synthesis in the microreactor
- Summary

Microreactors

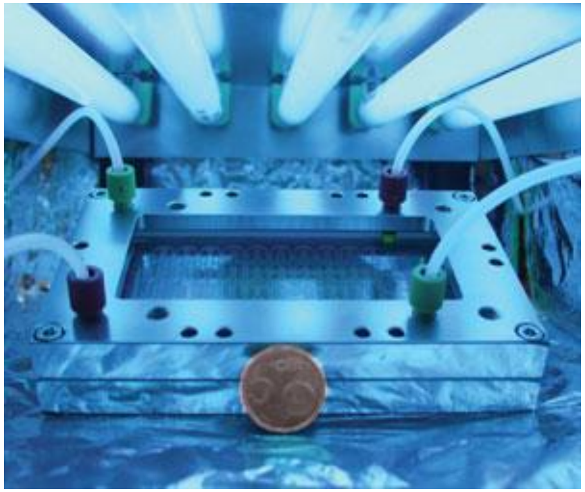
- Microstructured reactor:

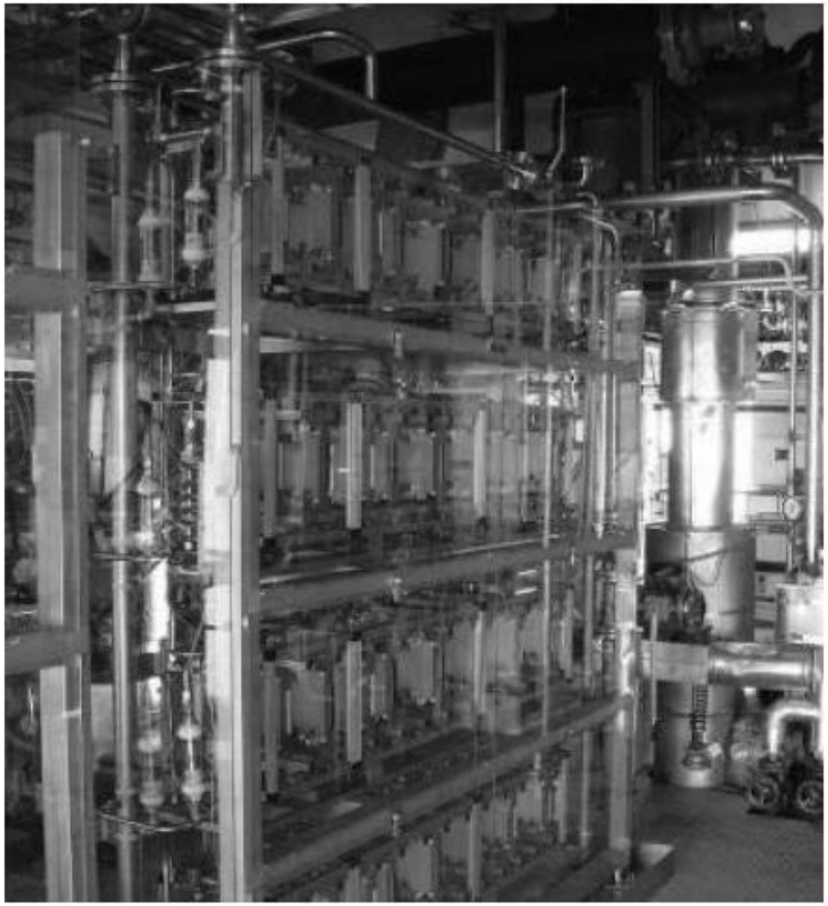
  - A device with a three dimensional inner structure with at least one dimension smaller than 1 mm



Microreactors

- Variable functions, shapes, material and sizes



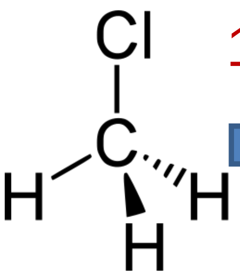


Benefits of microreactors

- ✓High surface/volume ratio:
  - High heat transfer rates
  - Increased safety
- ✓Short diffusion distances
- ✓Fast mixing

- ➢ Perspective in production of poisonous intermediates
- ➢ Useful to study fast reactions; low in- and output of chemicals

Methyl chloride



10^6 tons/year to everyday products

- Solvent in synthesis of butylrubber

- Reactant in:
  - Methyl cellulose (food thickener / glue) production
  - Silikone production

Methyl chloride and Safety

- Highly flamable and toxic gas

- Transportation and Storage = ☹ / a risk and a cost
- Failure (e.g. runaway) of a big unit is dangerous

- Idea: produce methyl chloride on-site in a microreactor in the amounts needed

Reactions in methyl chloride synthesis

$$CH_3OH + HCl \leftrightarrow CH_3Cl + H_2O$$

$$2CH_3OH \leftrightarrow CH_3OCH_3$$

$$CH_3OCH_3 + HCl \leftrightarrow CH_3OH + CH_3Cl$$

- Industrial Catalyst: Alumina (pure or modified with $ZnCl_2$)
- Fast reaction, full conversion in ≤1s (200-300 C)
- Feasible for a microreactor

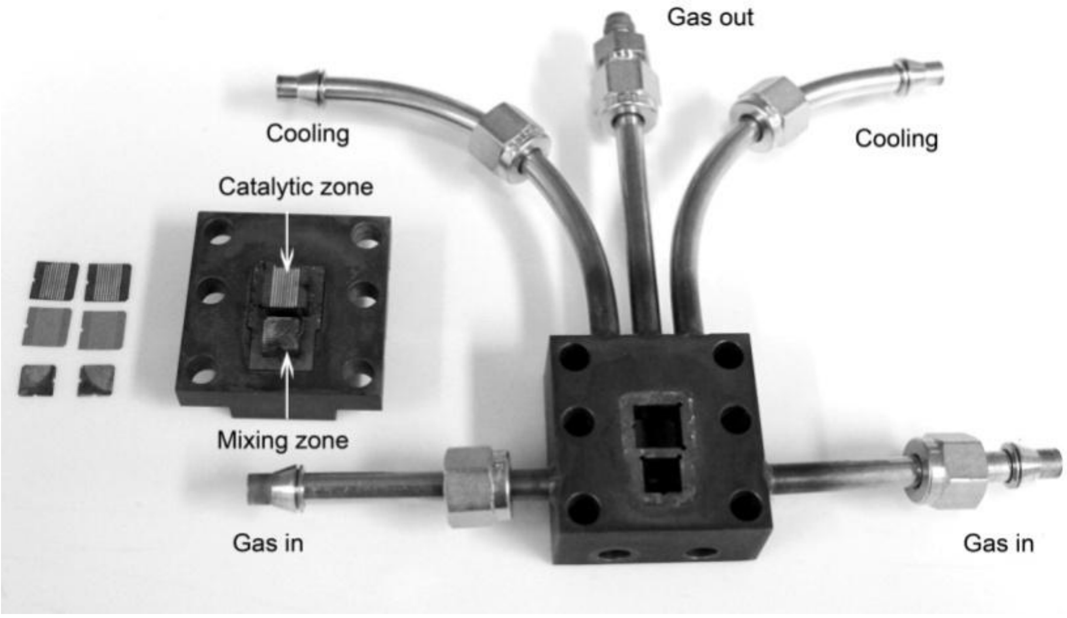
ICIS Chemical Business Americas; 3/19/2007, Vol. 271 Issue 11, p50-50, 1p

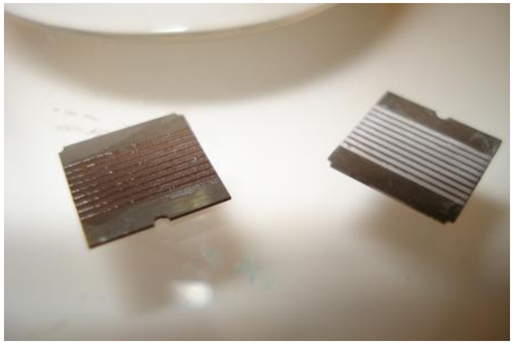
Keypoints

- Catalyst Coating
- Determination of reaction kinetics
- Catalyst development
- ”Numbering up” and product separation

Microreactor

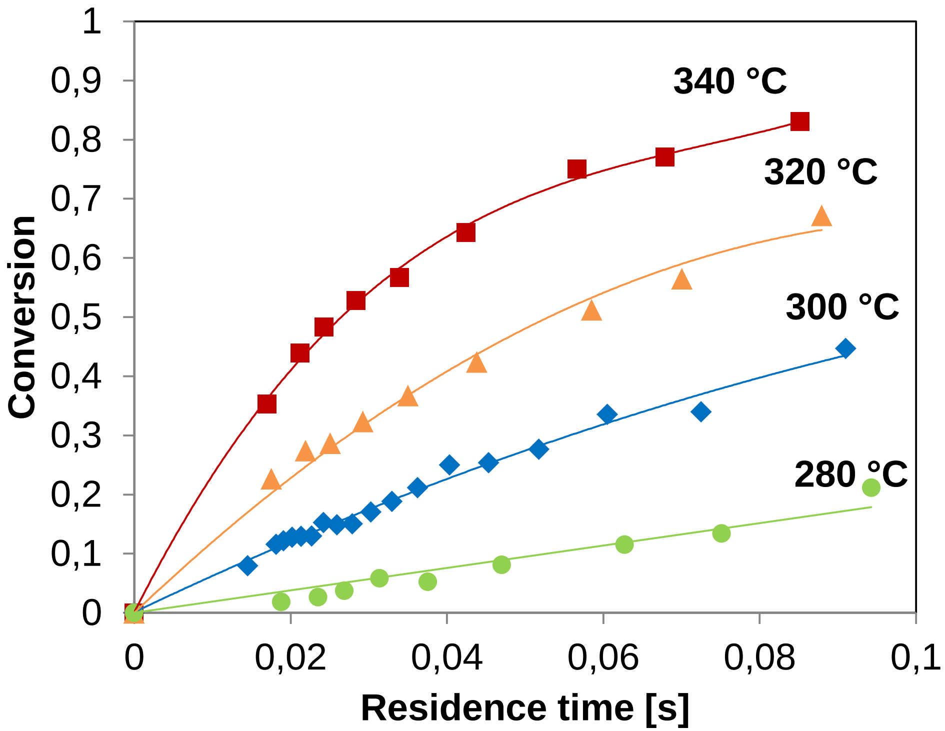
- IMM stainless steel gas-phase microreactor

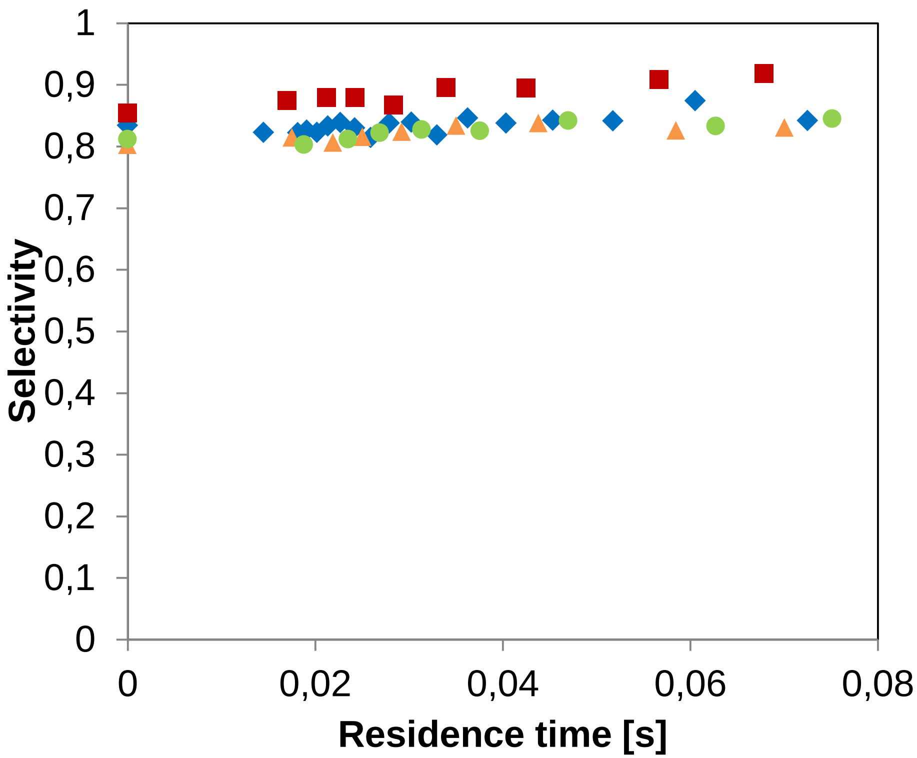




Catalyst: μ- alumina

Conversion and Selectivity





- Conversions up to 83 %
- Selectivities up to 91 %
- Selectivity increases with conversion and is rather independent of temperature

Proposed model

- Langmuir-Hinshelwood Mechanism

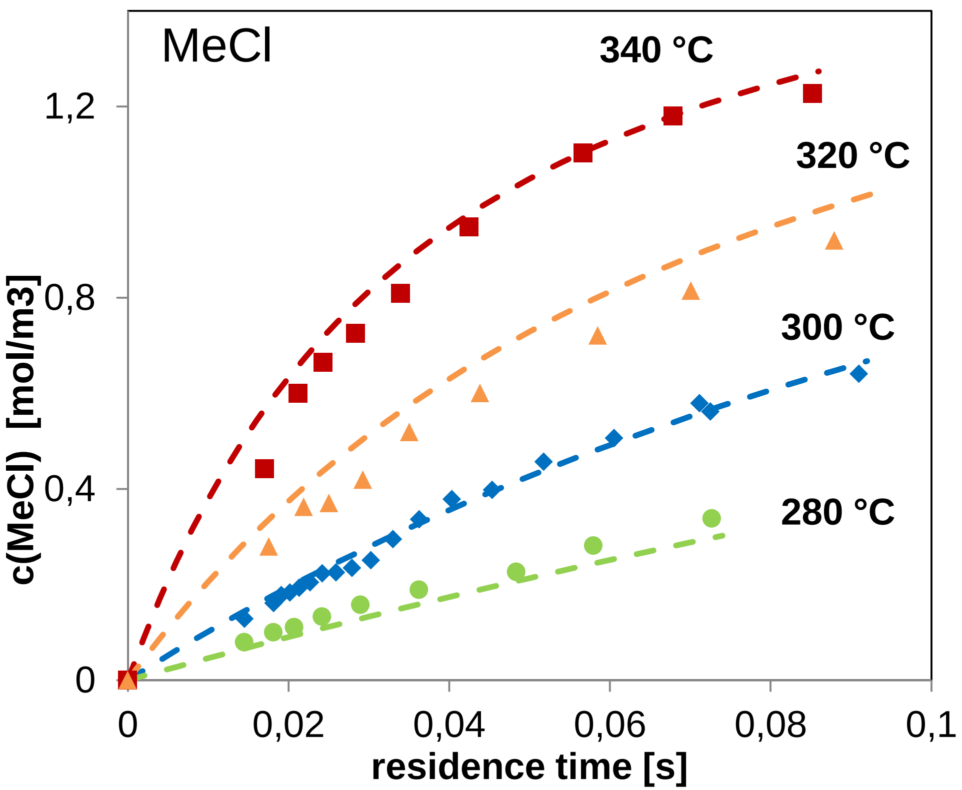
$$r_1 = k_1 \frac{(c_{CH3OH} c_{HCL} - \frac{c_{CH3Cl} c_{H2O}}{K_1})}{D^2}$$

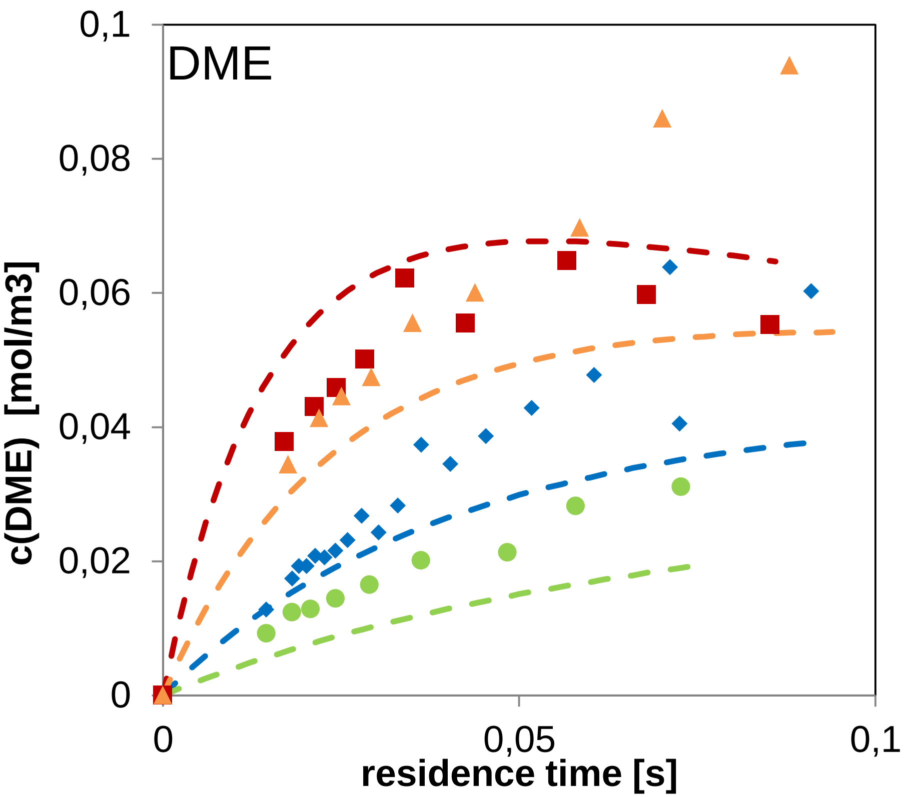
$$r_2 = k_2 \frac{(c_{MeOH}{}^2 - \frac{c_{DME} c_{H2O}}{K_2})}{D^2}$$

$$r_3 = k_3 \frac{(c_{DME} c_{HCL} - \frac{c_{MeOH} c_{MeCl}}{K_3})}{D^2}$$

$$D = K_{HCl} c_{HCl} + 1$$

Kinetic studies





- Detailed description of MeCl formation
- DME formation shows deviation
    - Significantly lower concentration

Mass transfer limitations

! Obtained activation energy of reaction 1 is about the double of the previously reported

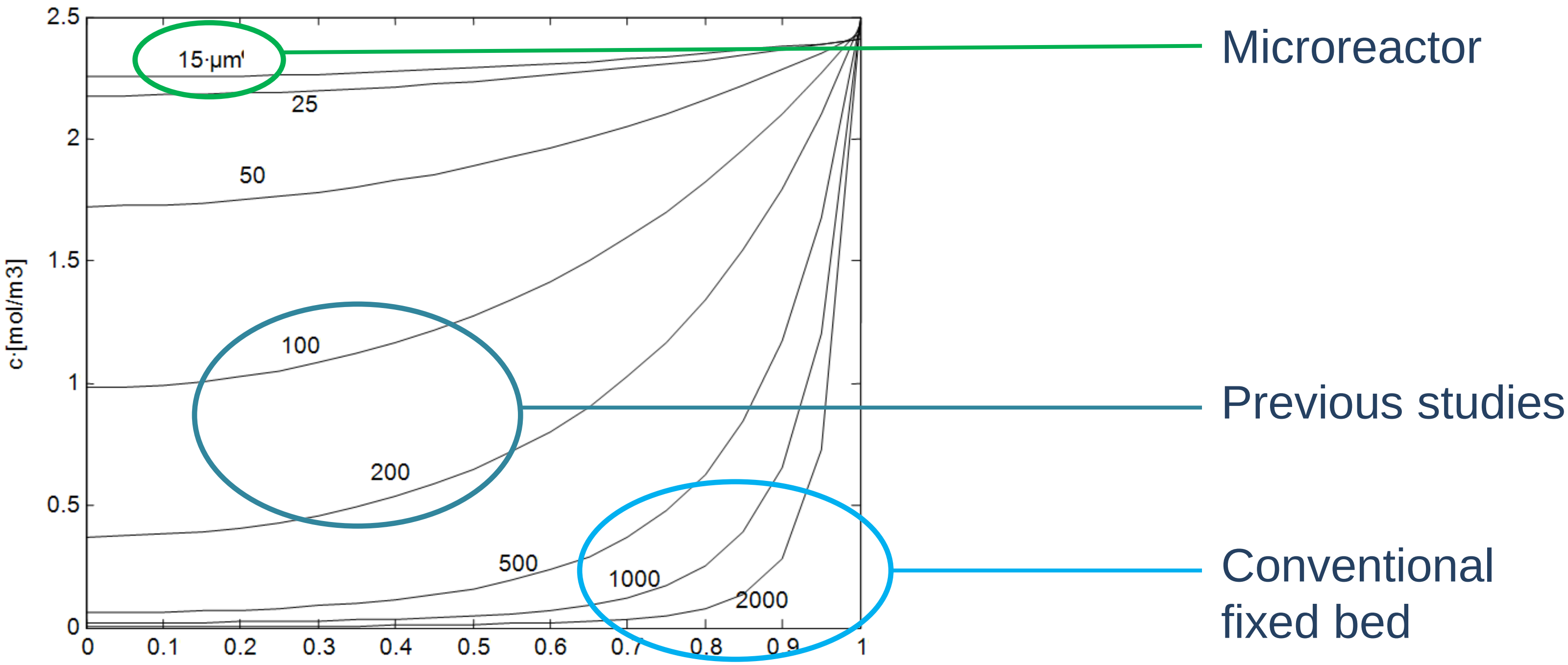
➢ Possible mass transfer limitations → modeling of diffusion in catalyst layer

Parameter	Value	Error /%
A_1 [$m^3 \cdot mol^{-1} \cdot s^{-1}$]	$3.33*10^{10}$	4.5
A_2 [$m^3 \cdot mol^{-1} \cdot s^{-1}$]	$2.73*10^{10}$	3.3
A_3 [$m^3 \cdot mol^{-1} \cdot s^{-1}$]	33500	n.d
E_{a1} [kJ/mol]	108	1.5
E_{a2} [kJ/mol]	118	2.6
E_{a3} [kJ/mol]	36	n.d
K_{HCl}	0.116	13.6

Author	E_{a1} [kJ/mol]
Schlosser et al. (1970)	41.8
Svetlanov et al. (1966)	53.09
Becerra et al. (1992)	54.4
Thyagarajan et al. (1966)	80.16

Modeling of internal diffusion

- Methanol concentration profile inside the catalyst layer



- Diffusion limitations are prominent already at coating thicknesses of 50 µm
- Explains deviation from previously published activation energies

”Numbering up”

- Two microreactors are installed in series

- T = 340 °C
- Residence time: 0.17 s
- Conversion 97.3 % and Selectivity of 98.8 %
  - Close to the thermodynamic equilibrium

- This setup corresponds to a production of ca 4 kg /year

Summary

- Motivation: On site production of MeCl to minimize risks due to transportation and storage and increase process safety.
- Reasonable MeOH conversion and selectivity are reached in one microreactor
- Kinetic model for reaction system was developed with data collected in the microreactor
  - Mathematical modeling showed that significant diffusion limitations occur starting from catalyst layer thicknesses of 50 µm
- Thermodynamic equilibrium conversion can be reaced using two microreactors

Thank you for your attention!