ETH zürich

Carbon Dioxide Hydrogenation

Synthetic Perspectives for Chemical Energy Carriers

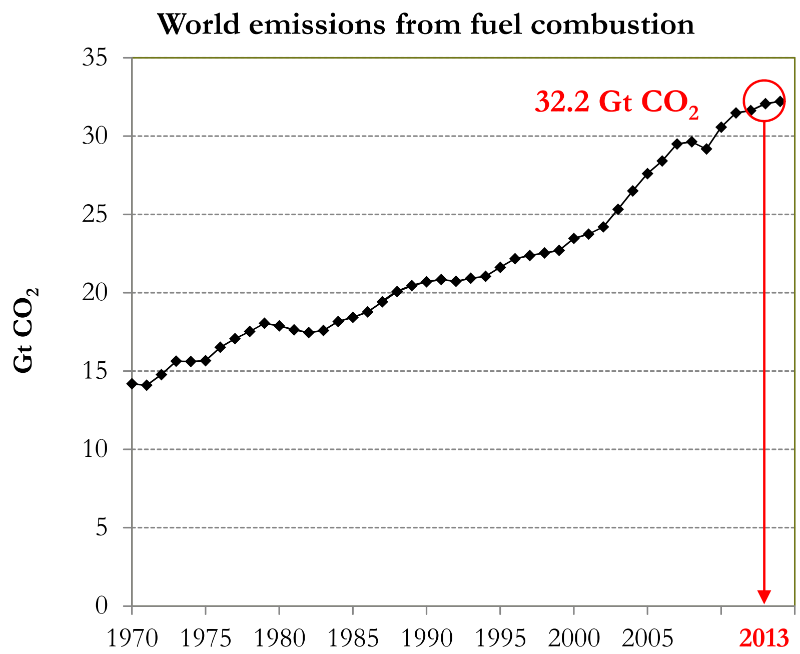
Transport Processes and Reactions Laboratory

Institute of Process Engineering

Helena Reymond

Carbon Dioxide

Economic and Environmental Incentives
Emission Mitigation Strategies



Carbon Capture and Storage

Carbon Dioxide Utilisation

Valuable Chemicals / Fuels

?

PBL Netherlands Environmental Assessment Agency, trends in global CO_2 emissions, 2015 report

Carbon Dioxide

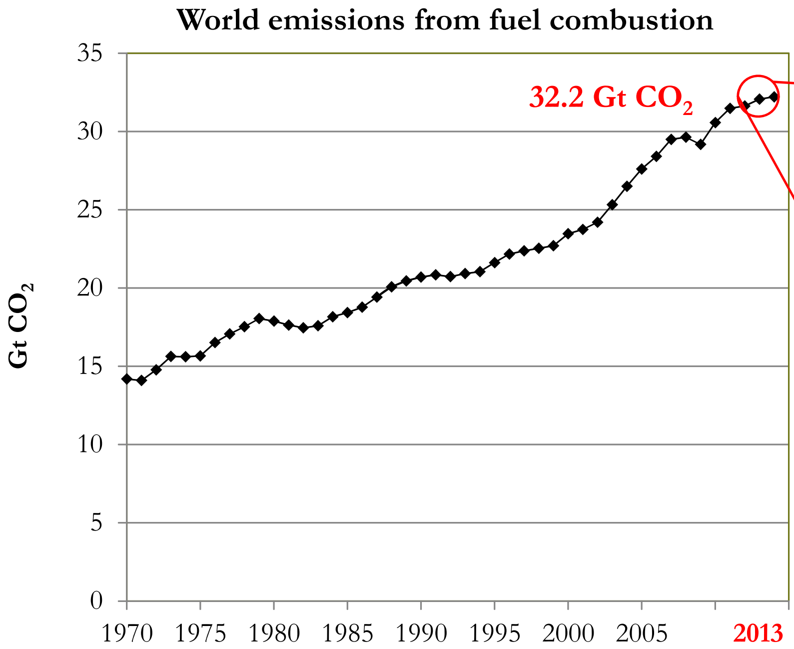
Economic and Environmental Incentives
Emission Mitigation Strategies

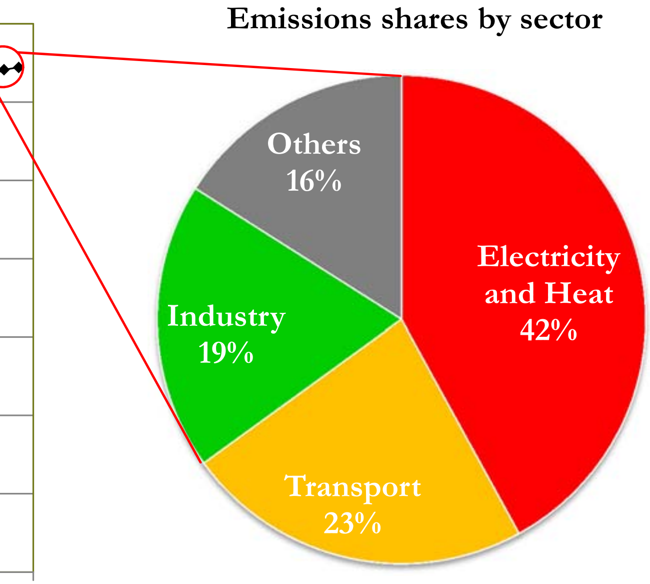
Renewable Energies

Energy Storage

Water splitting

Hydrogen Economy





International Energy Agency (IEA) highlights 2015

Carbon Dioxide

Economic and Environmental Incentives
Emission Mitigation Strategies

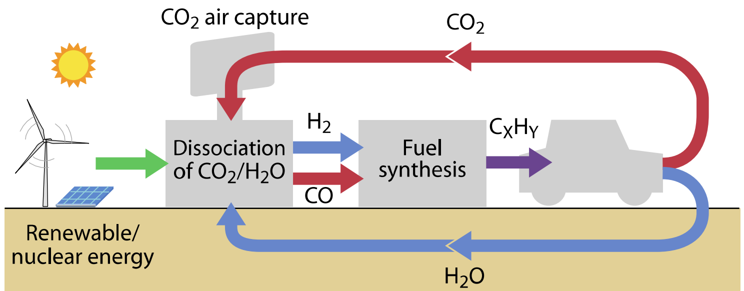
Renewable Energies | Carbon Capture and Storage

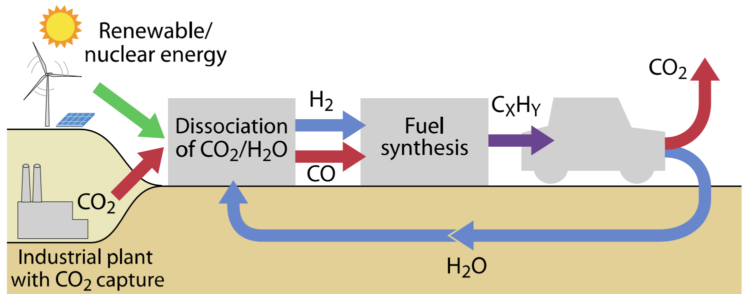
Energy Storage | Carbon Dioxide Utilisation

Water splitting | Valuable Chemicals / Fuels

Hydrogen Economy → **Methanol**

$$3\,H_2 + CO_2 \longleftrightarrow CH_3OH + H_2O$$





Graves *et al.*, Renewable Sustainable Energy Rev 15 (2011) 1-23

Carbon Dioxide

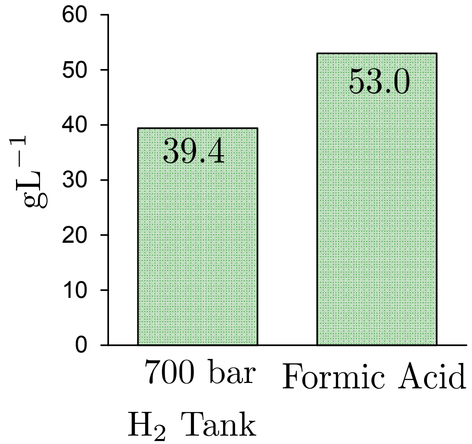
Economic and Environmental Incentives
Emission Mitigation Strategies

Renewable Energies

Energy Storage

Water splitting

Hydrogen Economy

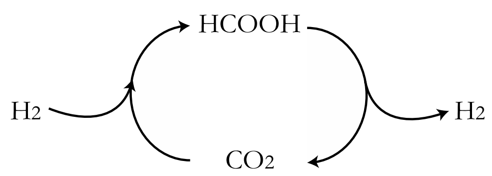


Carbon Capture and Storage

Carbon Dioxide Utilisation

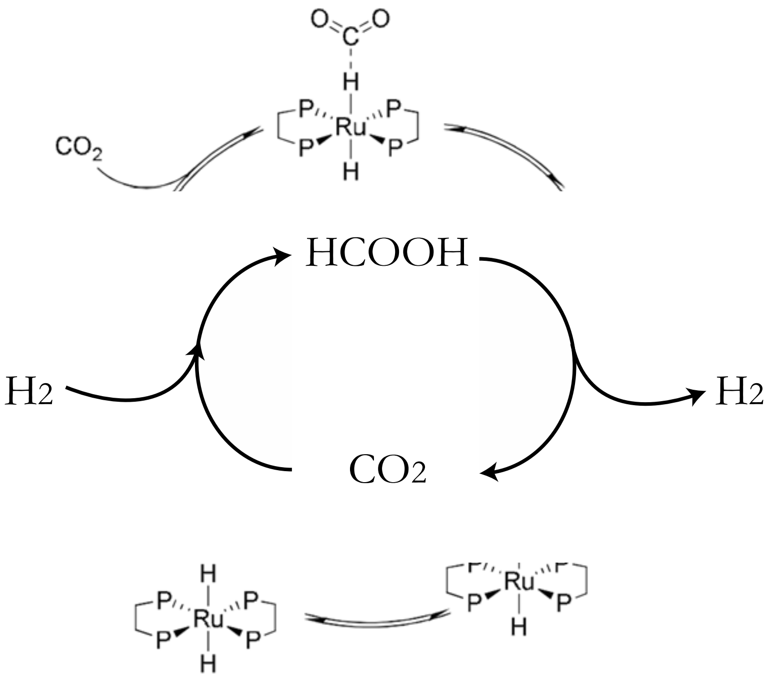
Valuable Chemicals / Fuels

Methanol



Formic Acid

Formic acid synthesis



Noyori *et al.*, Nature 368 (1994) 231.
Noyori *et al.*, Science 269 (1995) 1065.

- Thermodynamically hampered
- Sensitive equilibrium
- Non-spontaneous

$$H_2 + CO_2 \rightleftharpoons HCOOH$$

- Homogeneous catalysis
  - Basic media to stabilise HCOOH
- Heterogeneous catalysis
  - Economically advantageous
  - Unsuccessful: yields methanol

Heterogeneous catalysis

Reactants diffusion

1. External diffusion
2. Internal diffusion

Reaction

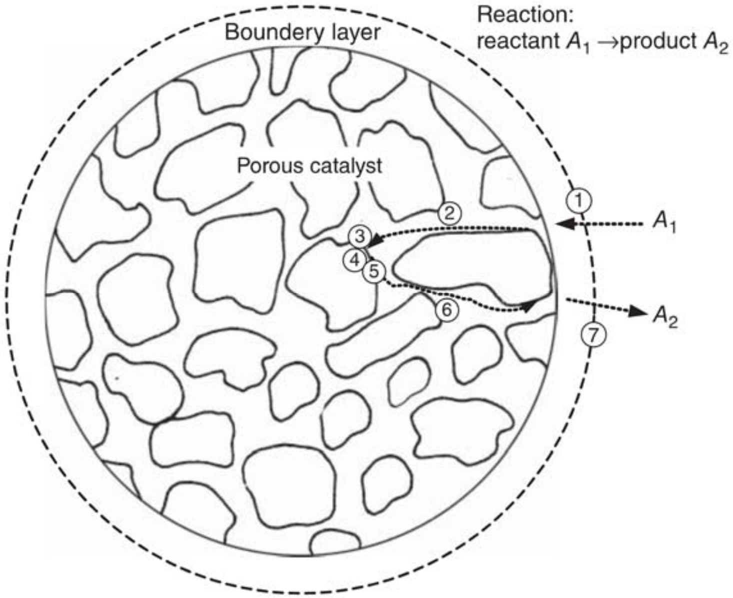
3. Adsorption of reactants on the surface
4. Catalytic reaction on the surface
5. Desorption of the products

Products diffusion

6. Internal diffusion of products
7. External diffusion of products

Rate determining step?

- Kinetically controlled
- Mass transfer limited



Kashid, Renken, Kiwi-Minsker, *Microstructured devices for chemical processing* Wiley Verlag, 2015

Continuous 2-step process

MAJOR PROBLEM

Formic acid decomposition back to H_2 and CO_2

- Conventional heterogeneous catalysts are active in the reverse reaction (metal supported on metal oxides)
- Microscopic reversibility suggests some activity in the foward reaction under appropriate conditions

REACTOR 1

> 100 bar, 200 – 300°C

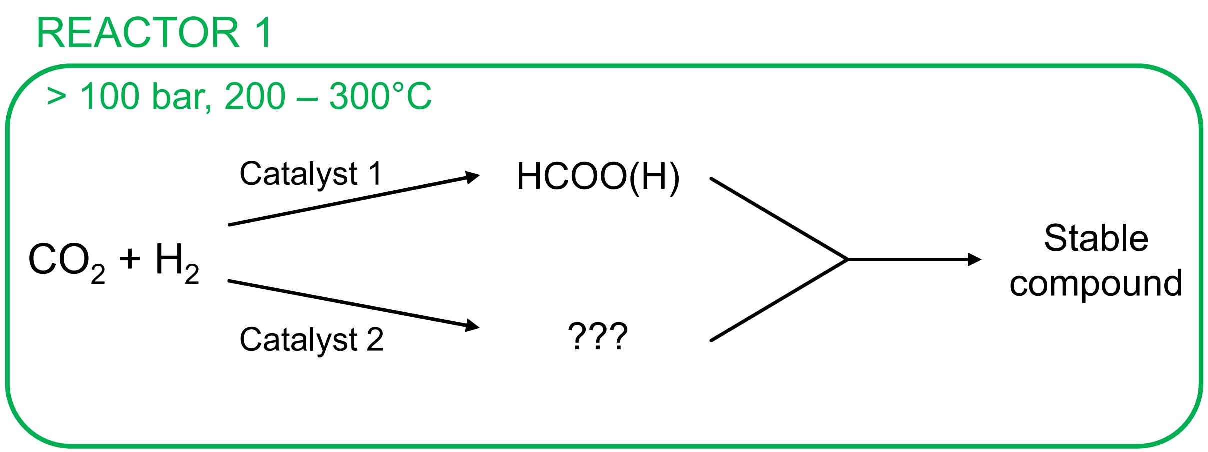
$$CO_2 + H_2 \underset{}{\overset{\text{Catalyst 1}}{\rightleftarrows}} HCOOH$$

Continuous 2-step process

IDEA

Mitigate the thermodynamic barrier

- Shift the reaction equilibrium to the right
- Include a reaction consuming FA faster than its decomposition



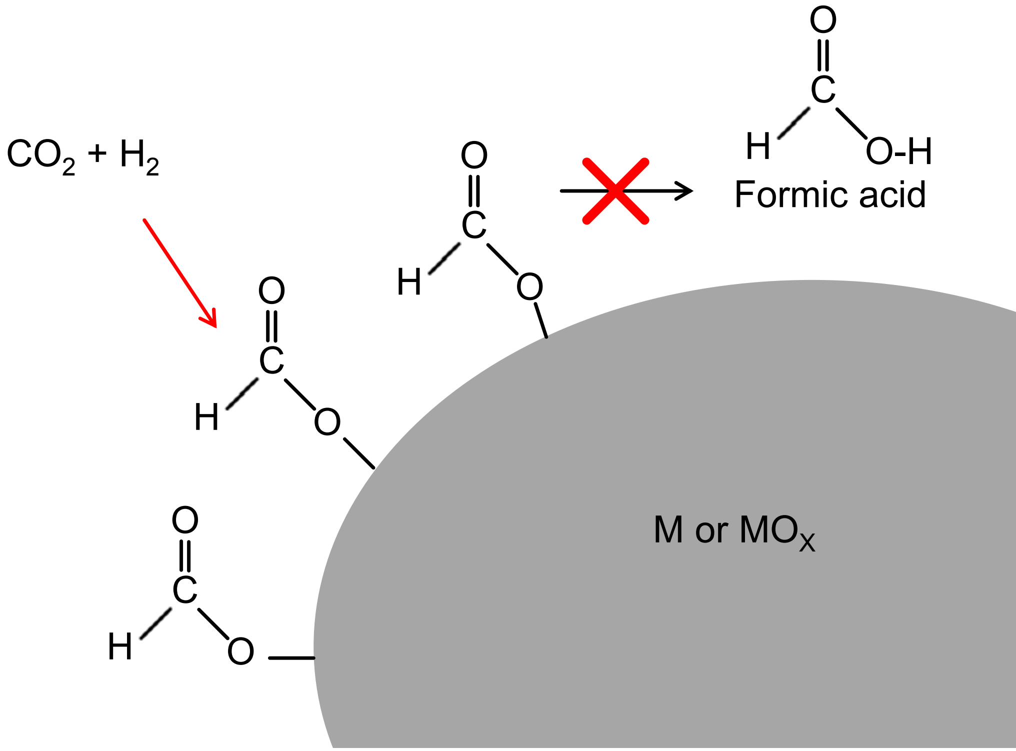
Methyl formate synthesis

IDEA TO MITIGATE THERMODYNAMIC BARRIER

Secondary reaction to transform the FA before decomposition

› Reacting FA with alcohols to yield formate esters

$$\mathrm{HCOOH + ROH \rightarrow RCOOH + H_2O}$$



Methyl formate synthesis

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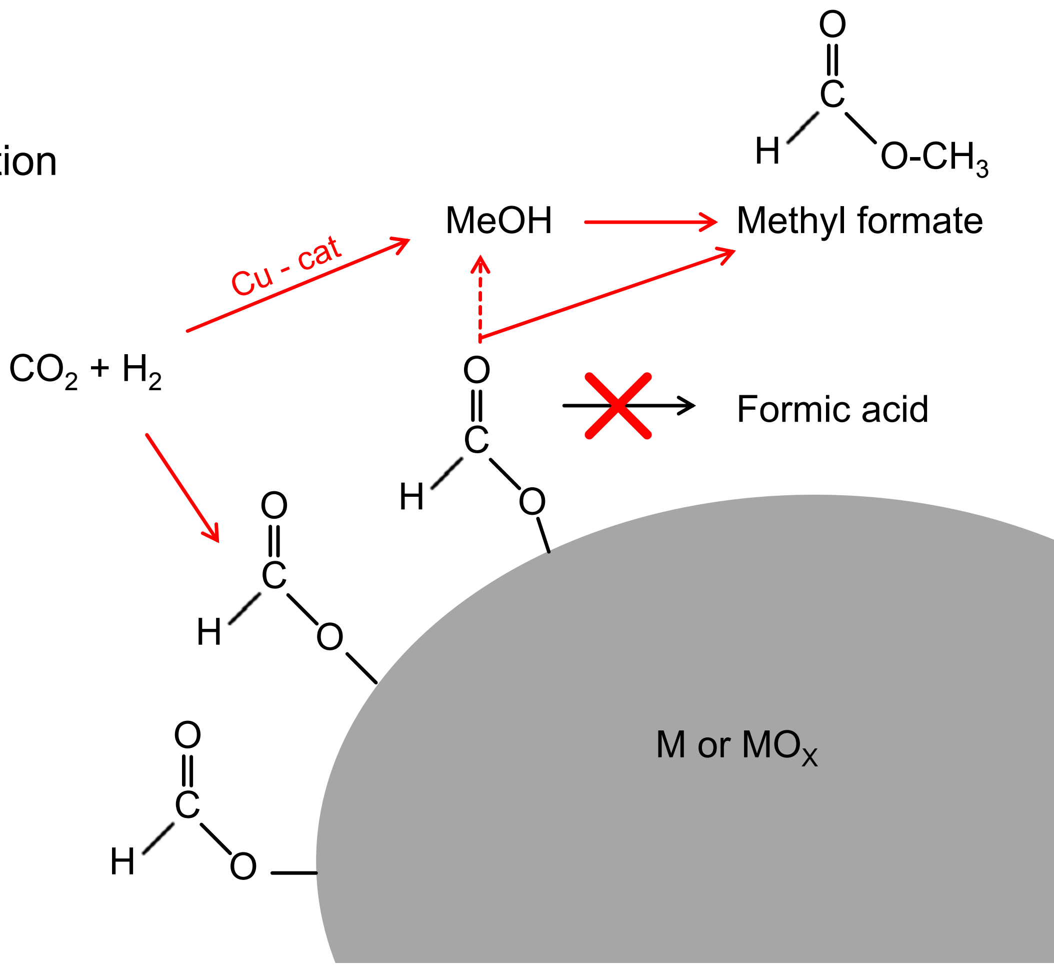
- Reacting FA with alcohols to yield formate esters

$$\mathrm{HCOOH} + \mathrm{ROH} \rightarrow \mathrm{RCOOH} + \mathrm{H_2O}$$
$$\mathrm{HCOOH} + \mathrm{MeOH} \rightarrow \mathrm{MeCOOH} + \mathrm{H_2O}$$

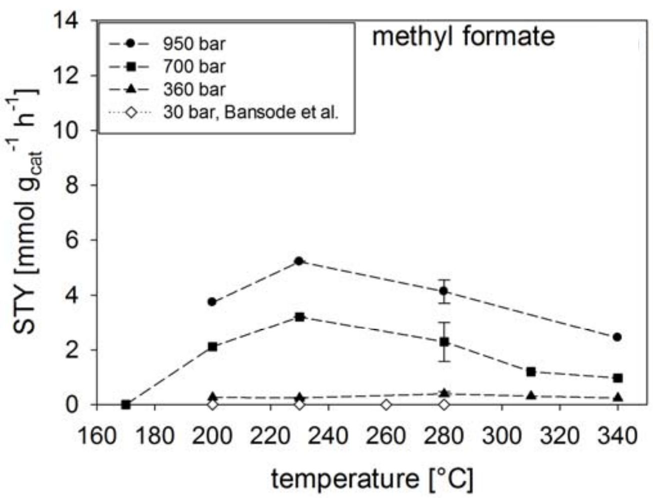


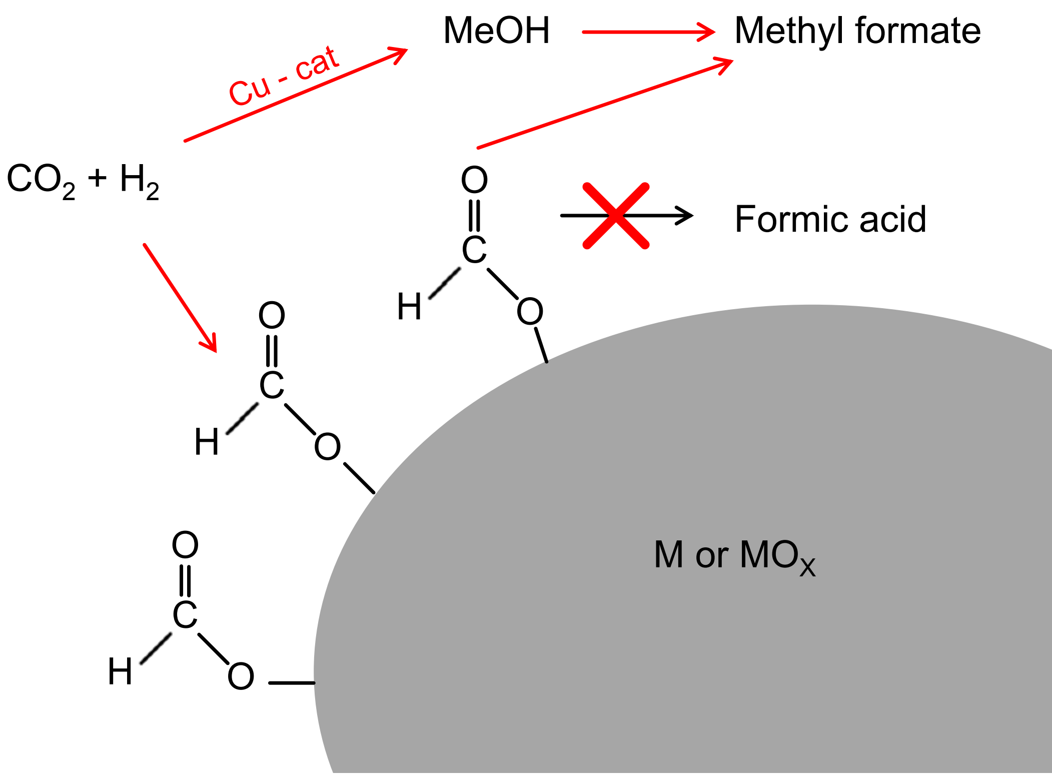
Methyl formate synthesis

IDEA TO MITIGATE THERMODYNAMIC BARRIER

Secondary reaction to transform the FA before decomposition

- Reacting FA with alcohols to yield formate esters
- *In-situ* formed MeOH





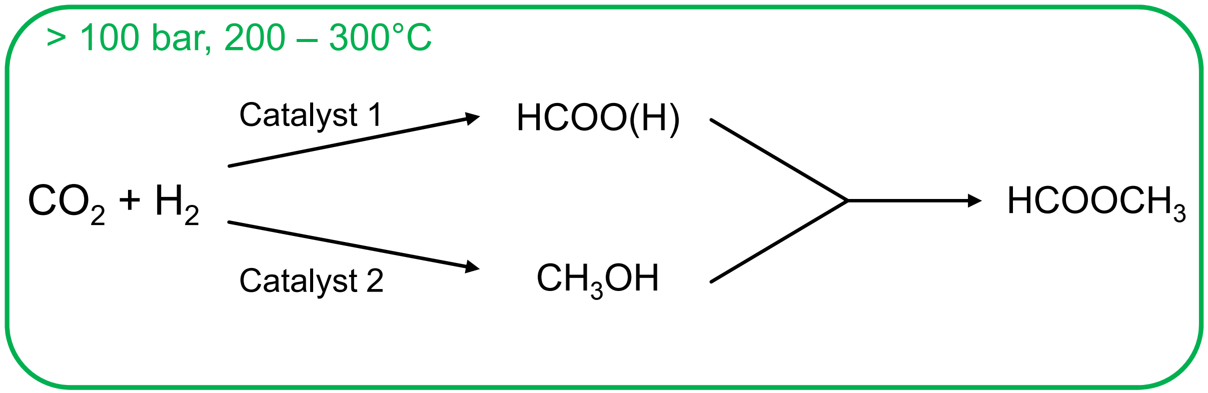
Continuous 2-step process

METHYL FORMATE

- Good chemical properties as fuel
- Not economically viable

⇒ transient intermediate

REACTOR 1



Continuous 2-step process

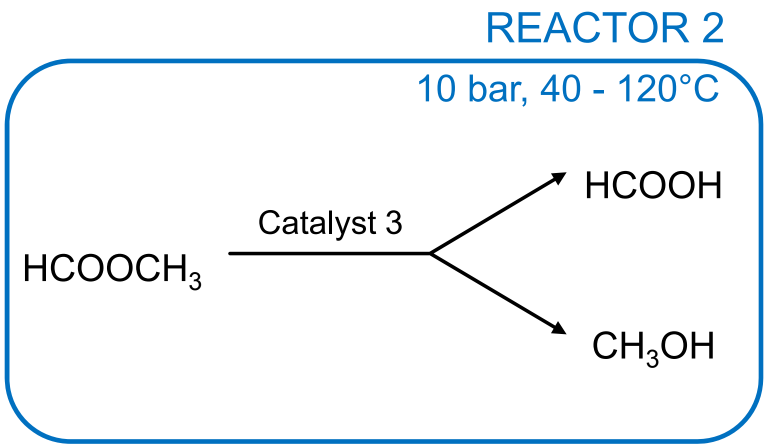
Methyl Formate

- Good chemical properties as fuel
- Not economically viable

⇨ transient intermediate

Formic Acid

- Industrially produced by hydrolysis of MF (BASF)
- MeOH as by-product
- Batch or chromatographic reactors



Continuous 2-step process

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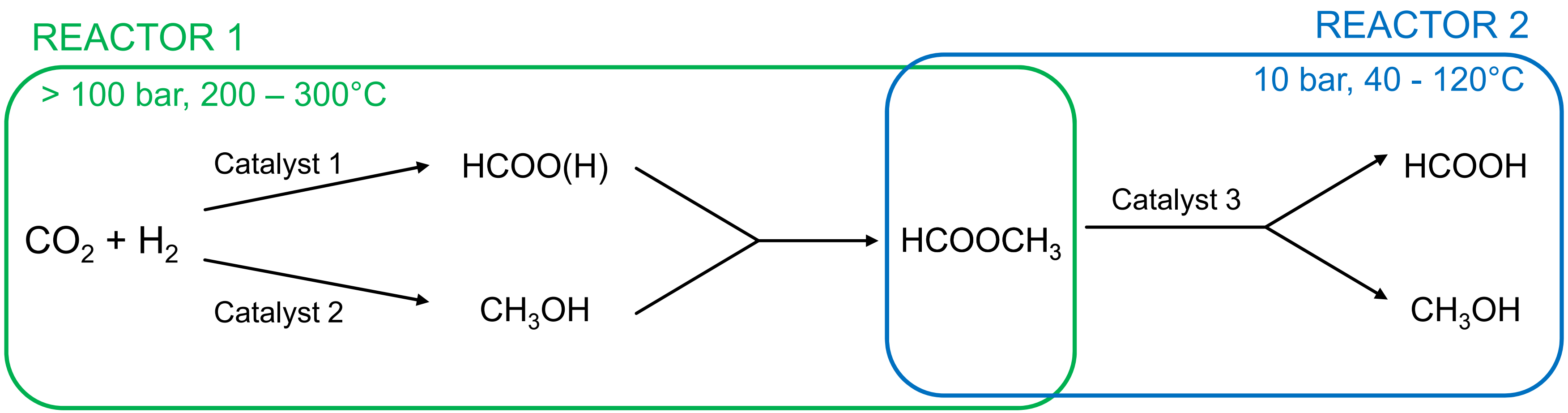
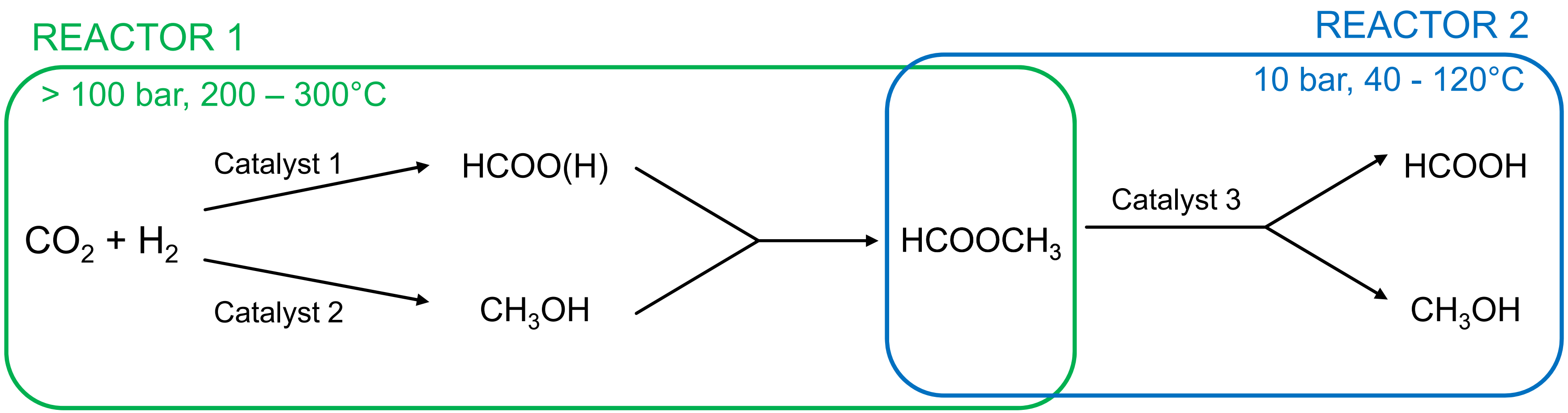


Catalyst and reactor design

The overall process requires the rational design of
a robust heterogeneous CO_2 hydrogenation catalyst selective for formic acid

- Reaction mechanism
- Phase behaviour



Sinergia collaboration

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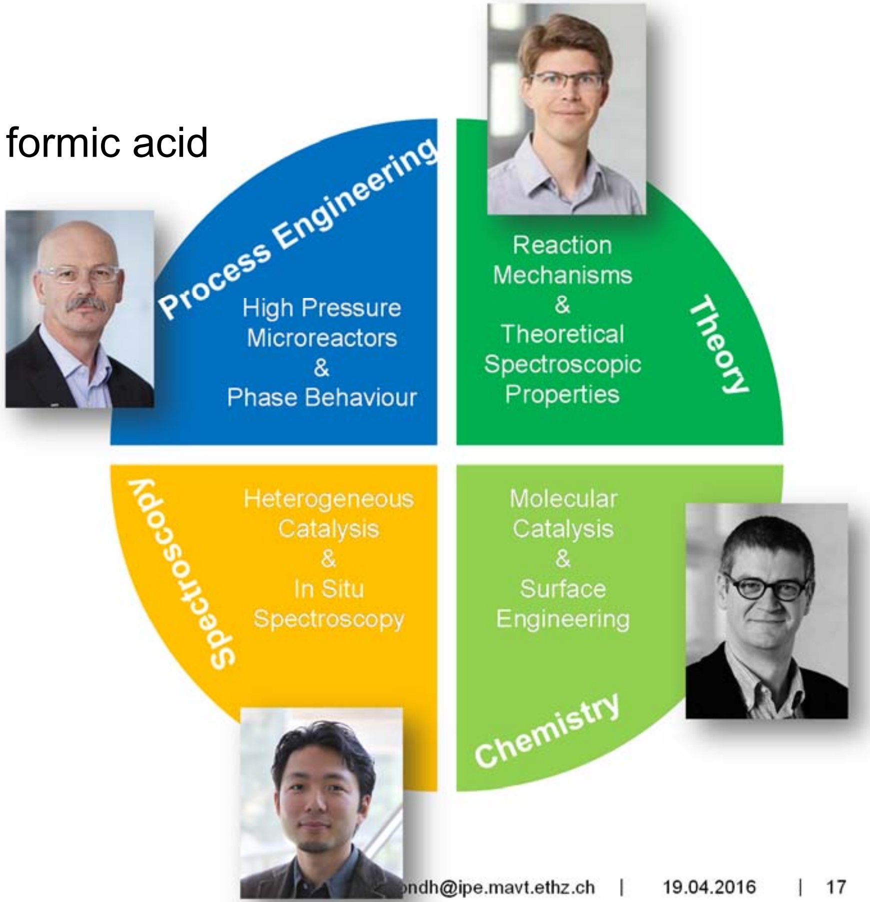
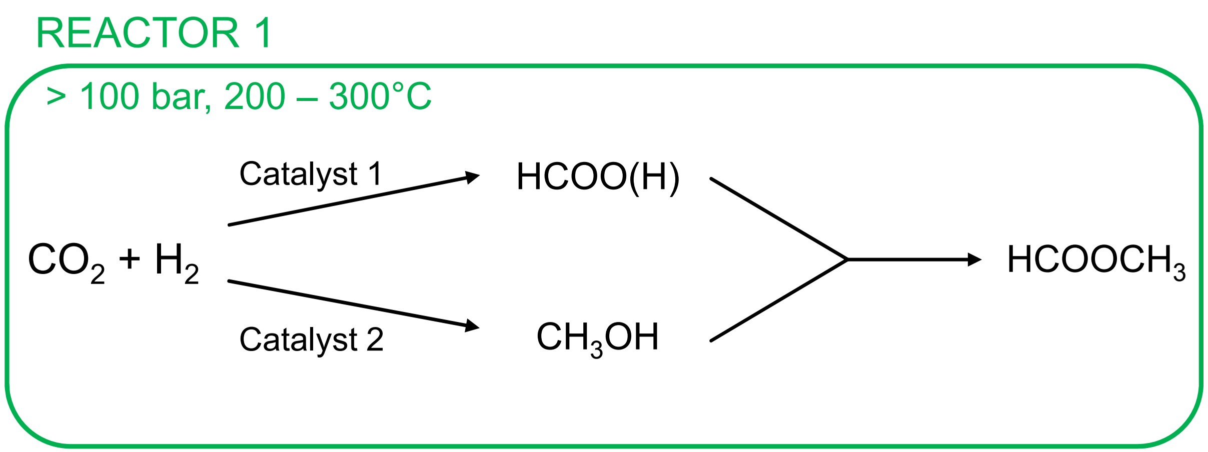
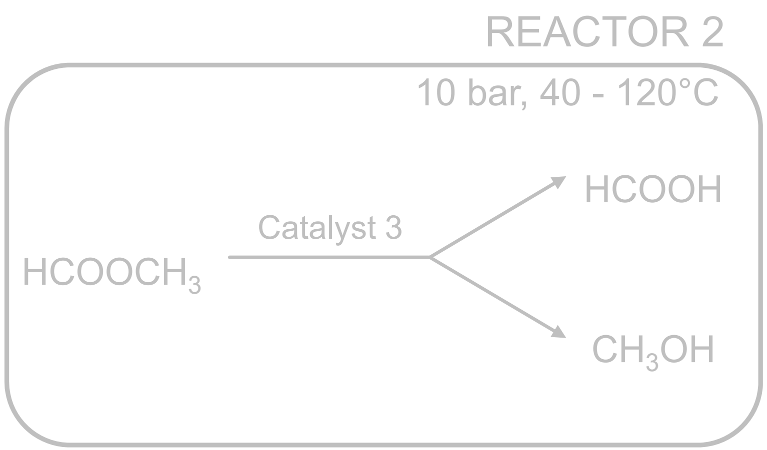
- ⇨ Phase behaviour



Reactor 1: synthesis of methyl formate





High-pressure hydrogenation setup

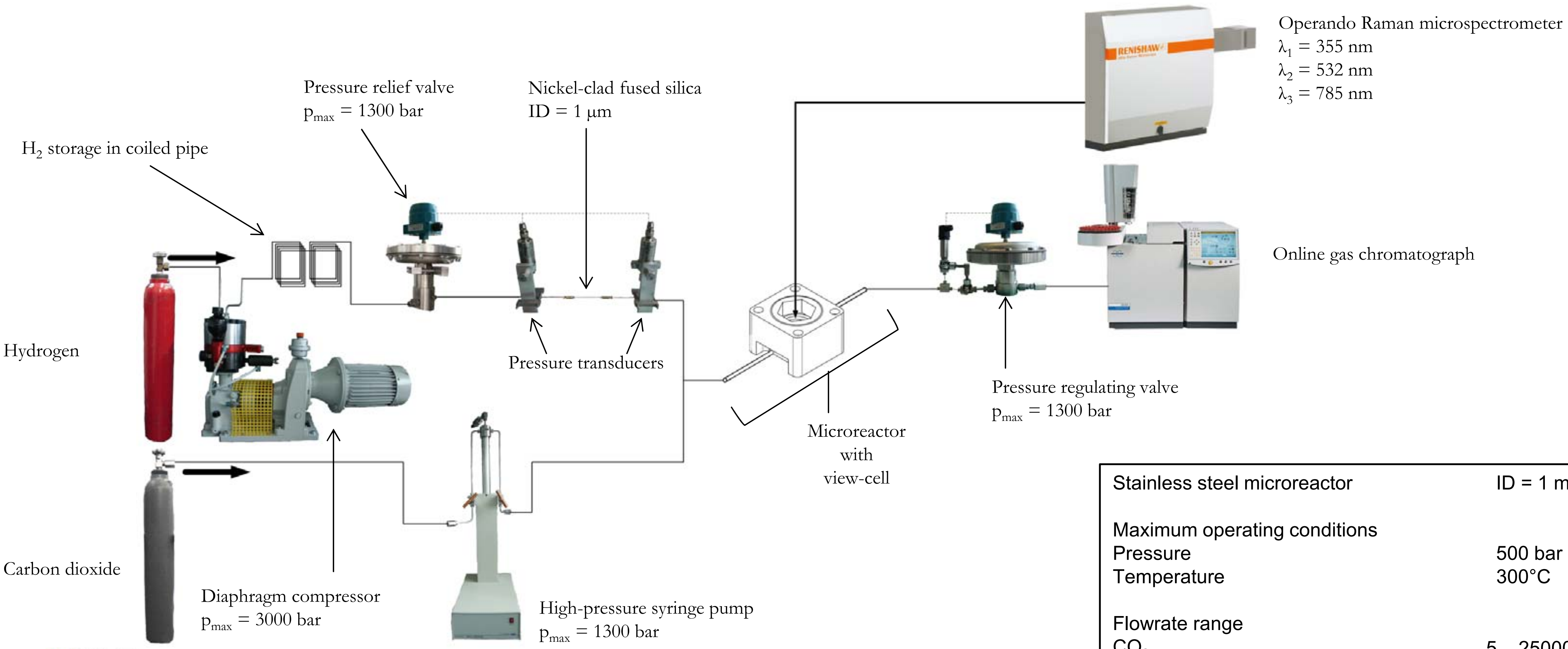
Catalytic activity measurements and simultaneous *in-situ* Raman spectroscopy at reaction conditions

$$3H_2 + CO_2 \longleftrightarrow CH_3OH + H_2O$$
$$H_2 + CO_2 \longleftrightarrow CO + H_2O$$
$$H_2 + CO \longleftrightarrow CH_3OH$$

$$K_{eq,j} = \prod_{i=1}^{N_C} a_i^{\nu_{i,j}} = \prod_{i=1}^{N_C} \left[\frac{f_i(T,p,y_i)}{f_i^\circ(T,p^\circ,y_i^\circ)} \right]^{\nu_{i,j}} \qquad \begin{array}{l} i = 1,\ldots,N_C \\ j = 1,\ldots,N_R \end{array}$$

High-pressure hydrogenation setup

Catalytic activity measurements and simultaneous *in-situ* Raman spectroscopy at reaction conditions

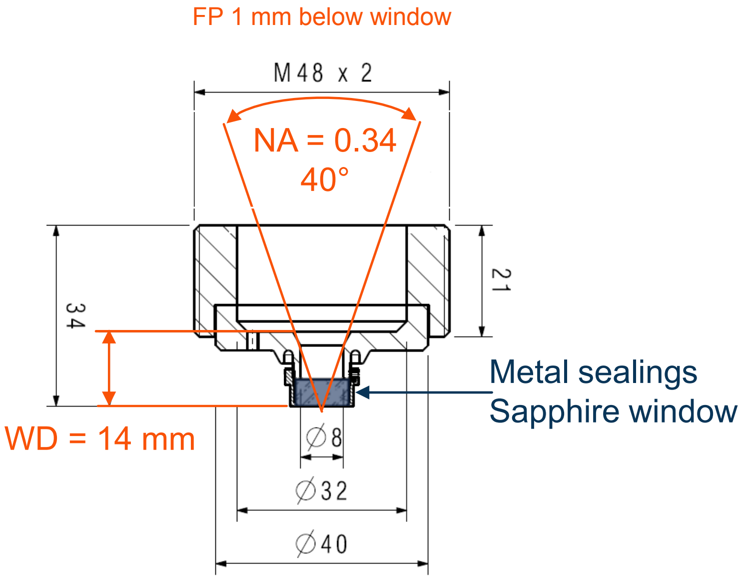


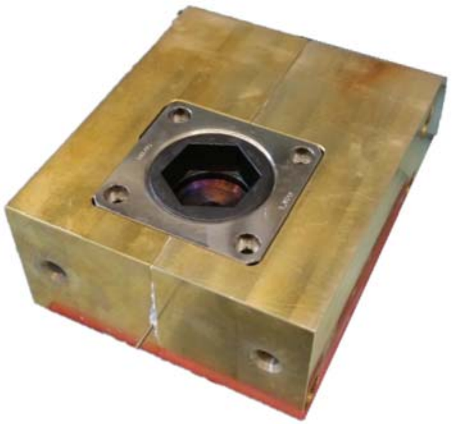
Stainless steel microreactor	ID = 1 mm
Maximum operating conditions	
Pressure	500 bar
Temperature	300°C
Flowrate range	
CO_2	5 – 25000 µL/min
H_2 (via Δp_capillary)	40 – 500 µL/min

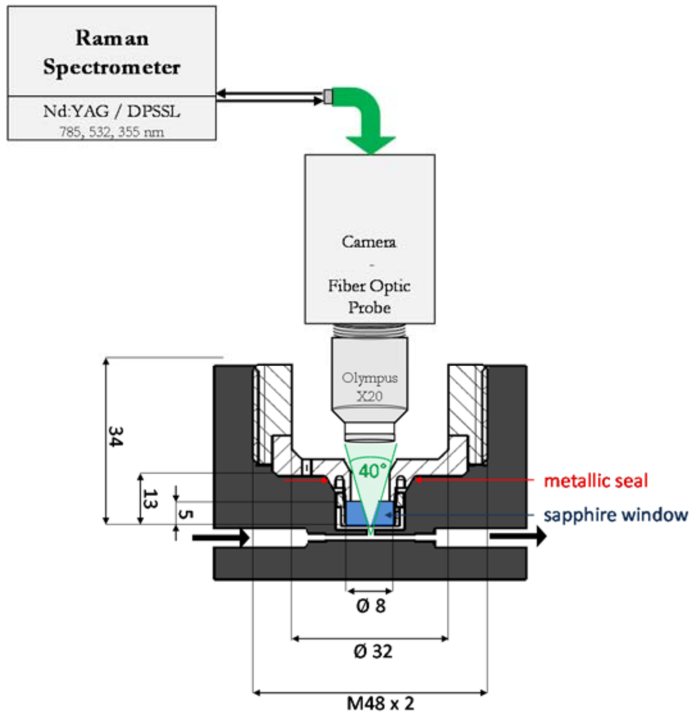
Tidona *et al.*, J. Supercrit. Fluids 78 (2013) 70-77
Tidona *et al.*, Chem. Eng. Process.: Process Intensif. 65 (2013) 53-57

High-pressure micro view-cell

Inner diameter	ID = 1 – 1.5 mm
Length	L = 50 mm
Maximum operating conditions	
Pressure	500 bar
Temperature	300°C
Flow or static conditions	





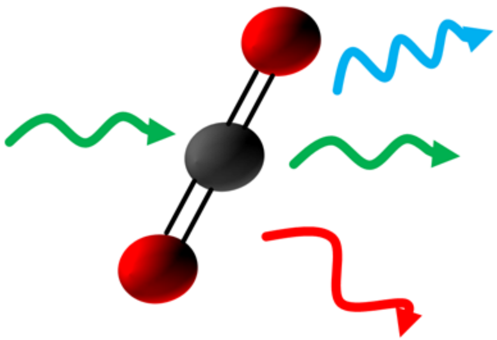


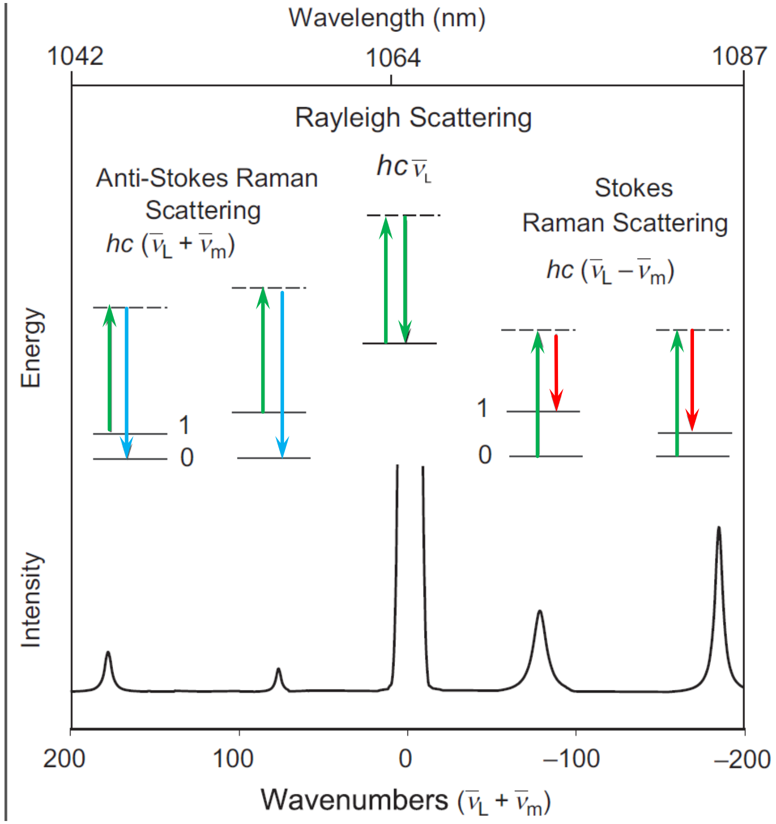
The Raman effect

SPECTROSCOPY = LIGHT – MATTER INTERACTION

- Incident electric field
- Induced dipole moment
- Oscillating molecule

Fingerprint of molecule





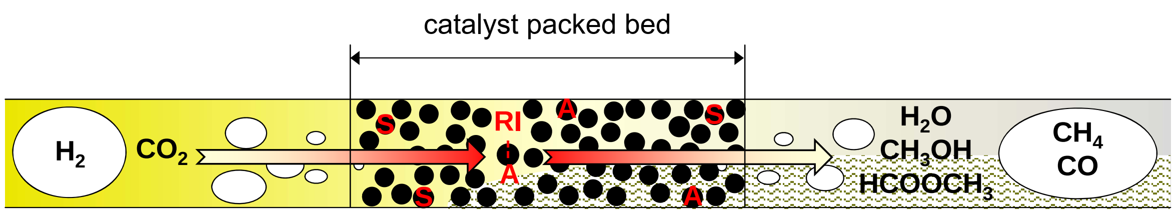
in situ analysis

Surface species analysis by Raman spectroscopy

- Main carbon oxide source ?
- Parallel or consecutive RWGS ?
- Common or different intermediate species ?

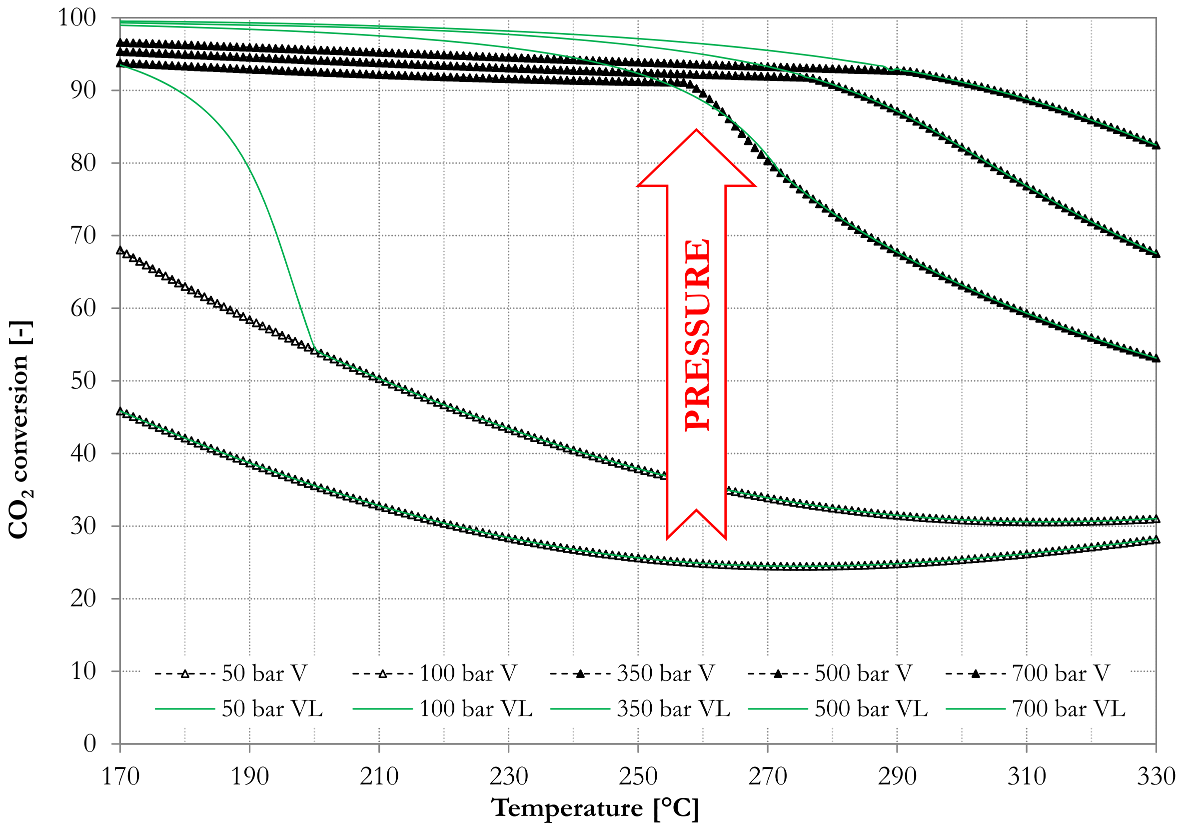
Phase behaviour of reactive mixtures

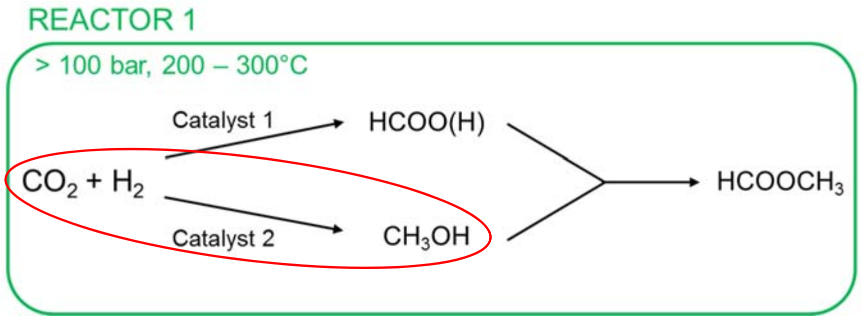
- Number and nature of phases in reactor ?
- Chemical and phase equilibrium ?



$$3H_2 + CO_2 \longleftrightarrow CH_3OH + H_2O$$
$$H_2 + CO_2 \longleftrightarrow CO + H_2O$$
$$H_2 + CO \longleftrightarrow CH_3OH$$

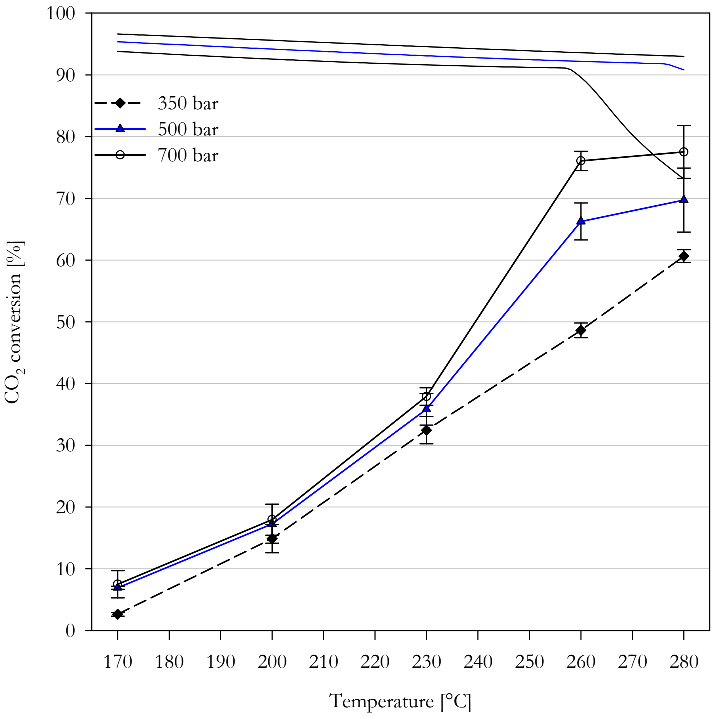
Methanol synthesis: equilibrium conversion

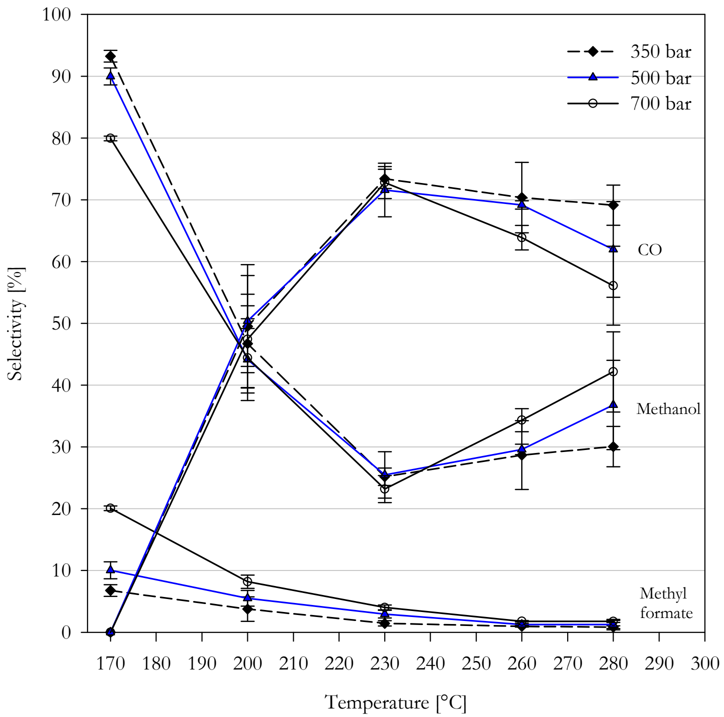


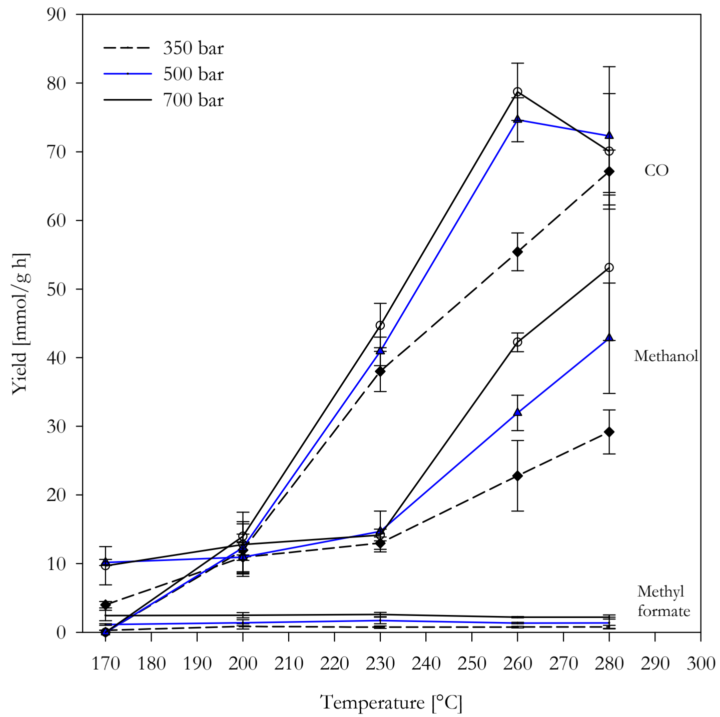


Reaction performance

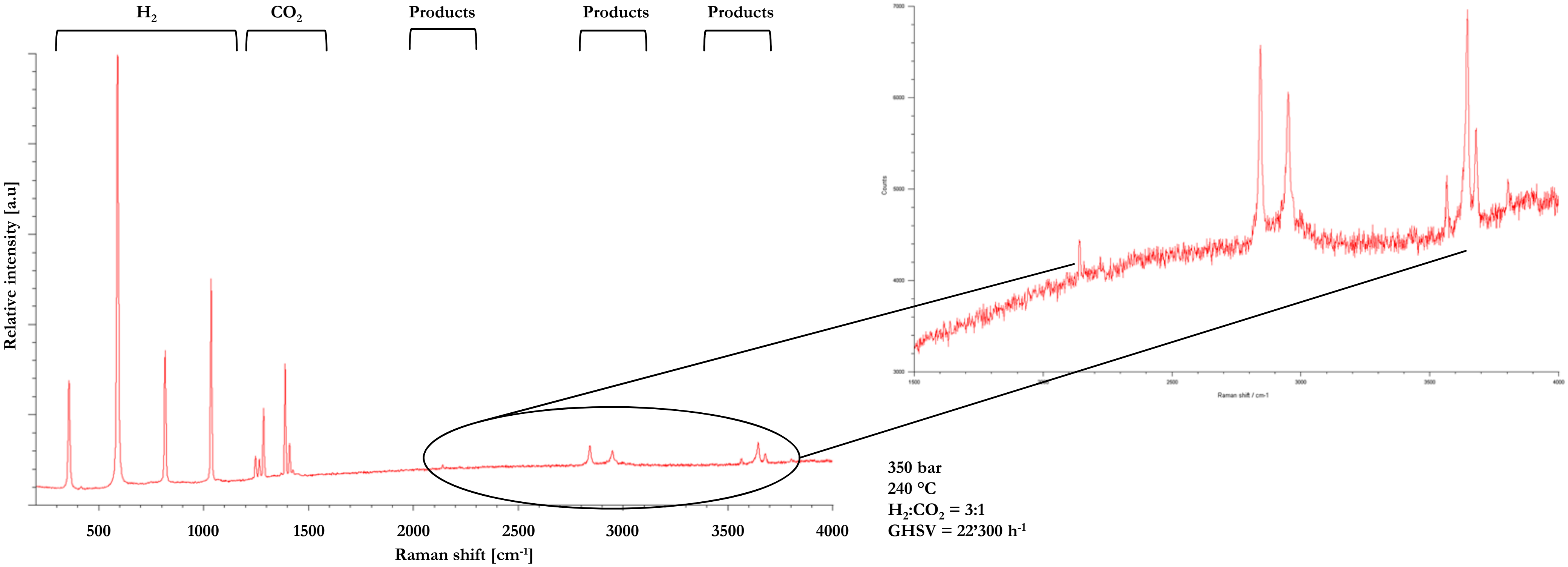
GHSV = 22’300 h^{-1}
H_2:CO_2 = 3:1





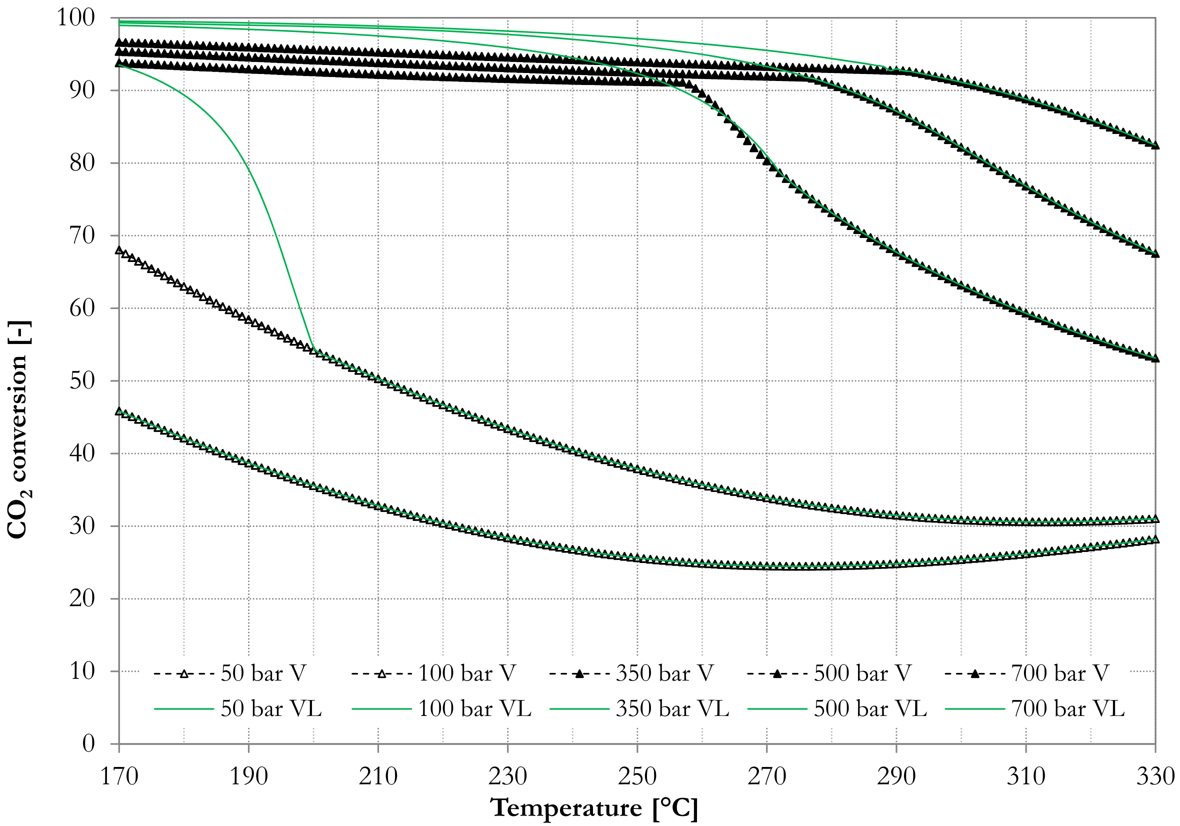


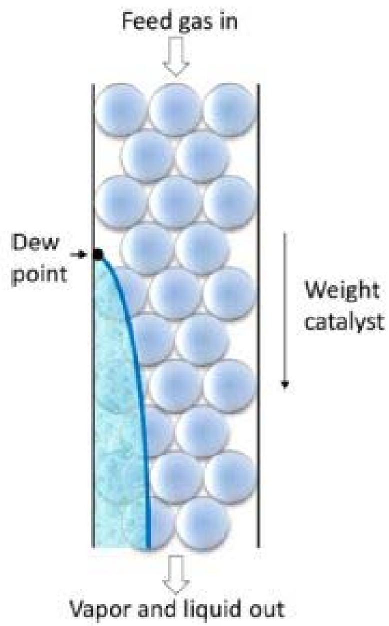
Raman spectrum of reaction effluent



350 bar
240 °C
H_2:CO_2 = 3:1
GHSV = 22'300 h^{-1}

Methanol synthesis: *in situ* condensation

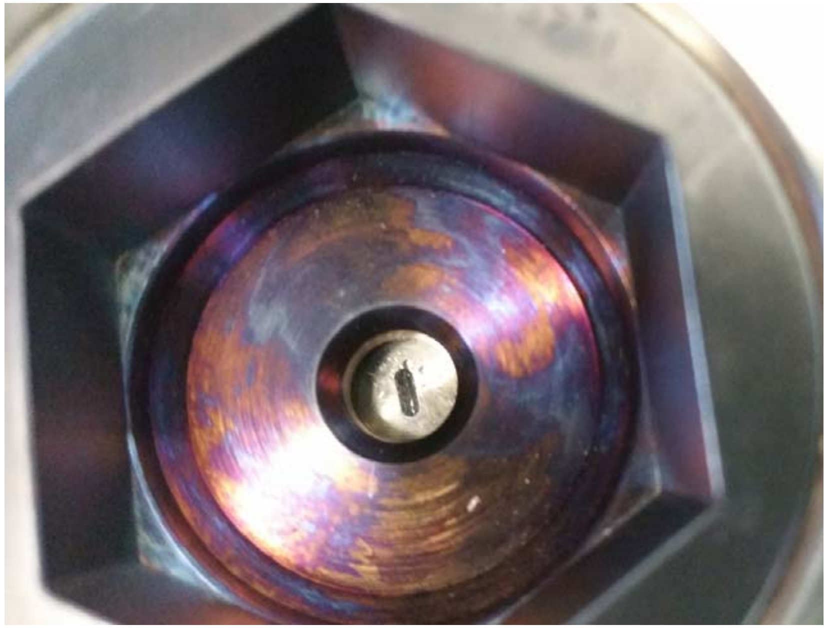


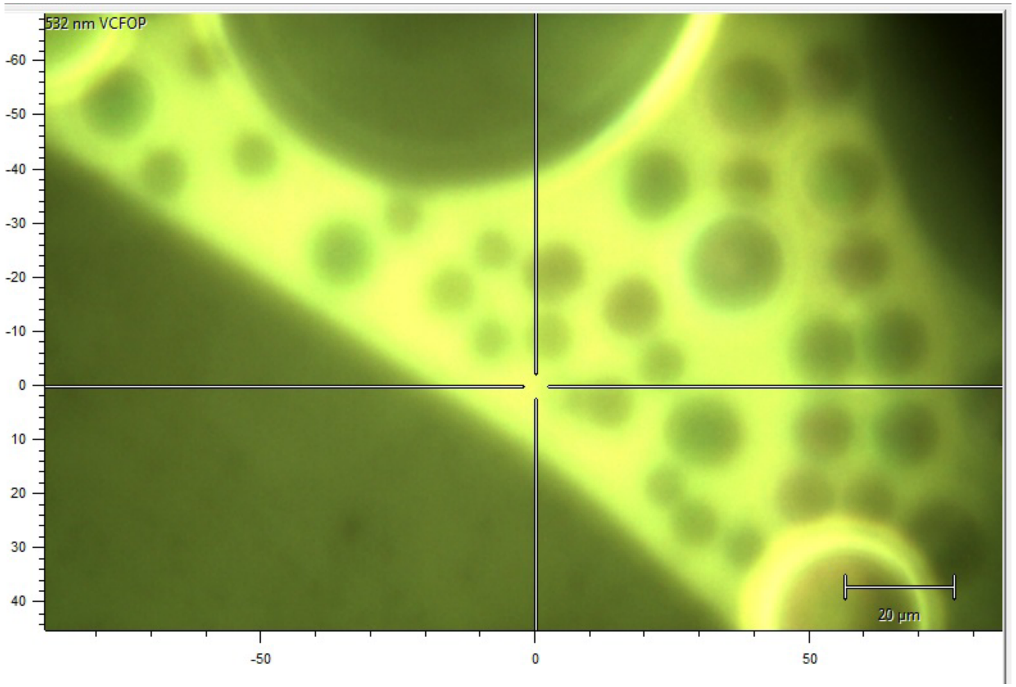


Van Bennekom *et al.*, *Ind. Eng. Chem. Res.*, **51** (2012)

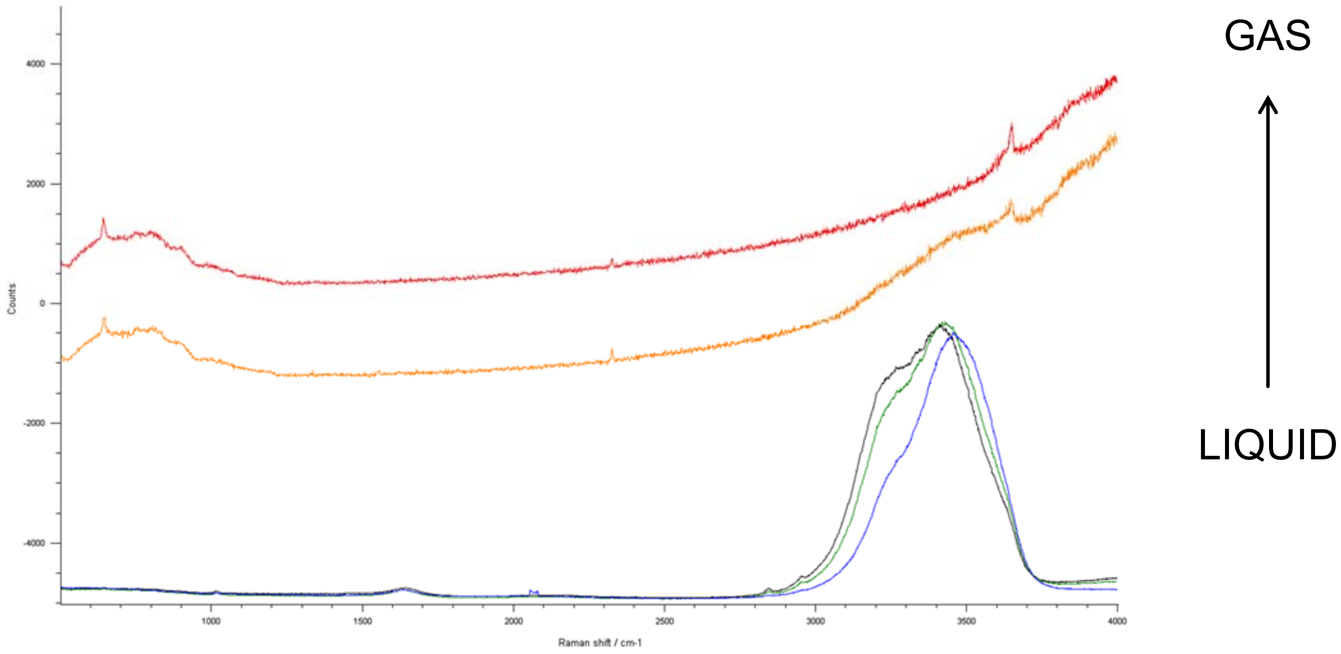
Van Bennekom *et al.*, *Chem. Eng. Sci.*, **87** (2013)

Condensation

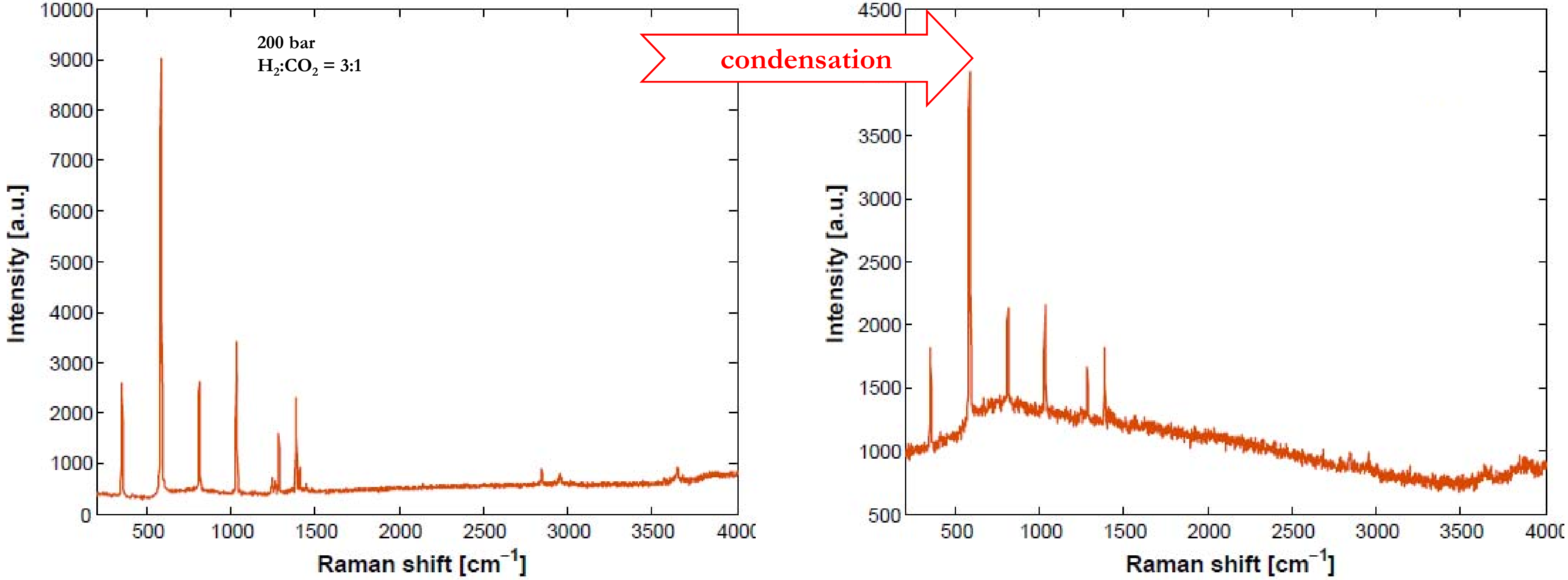




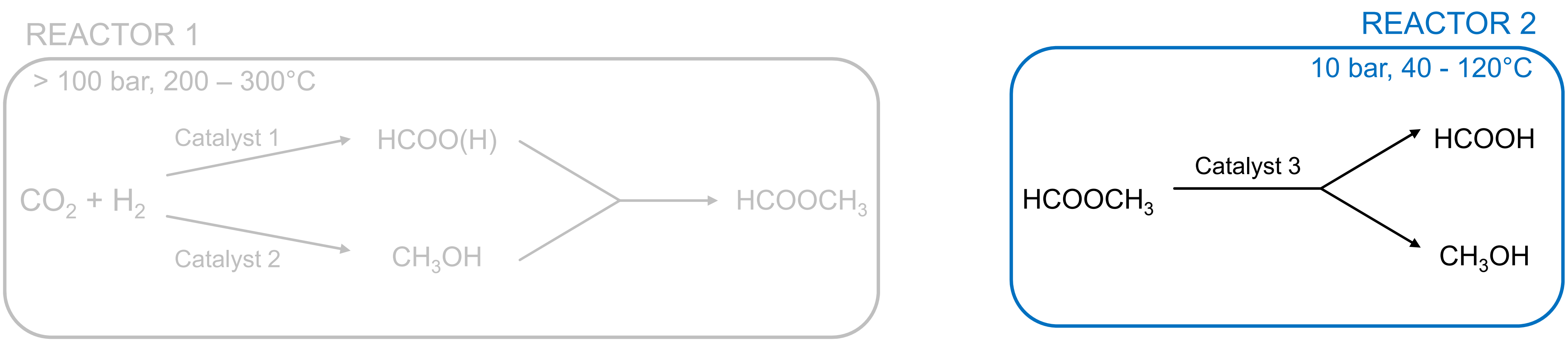
Water structural transformations



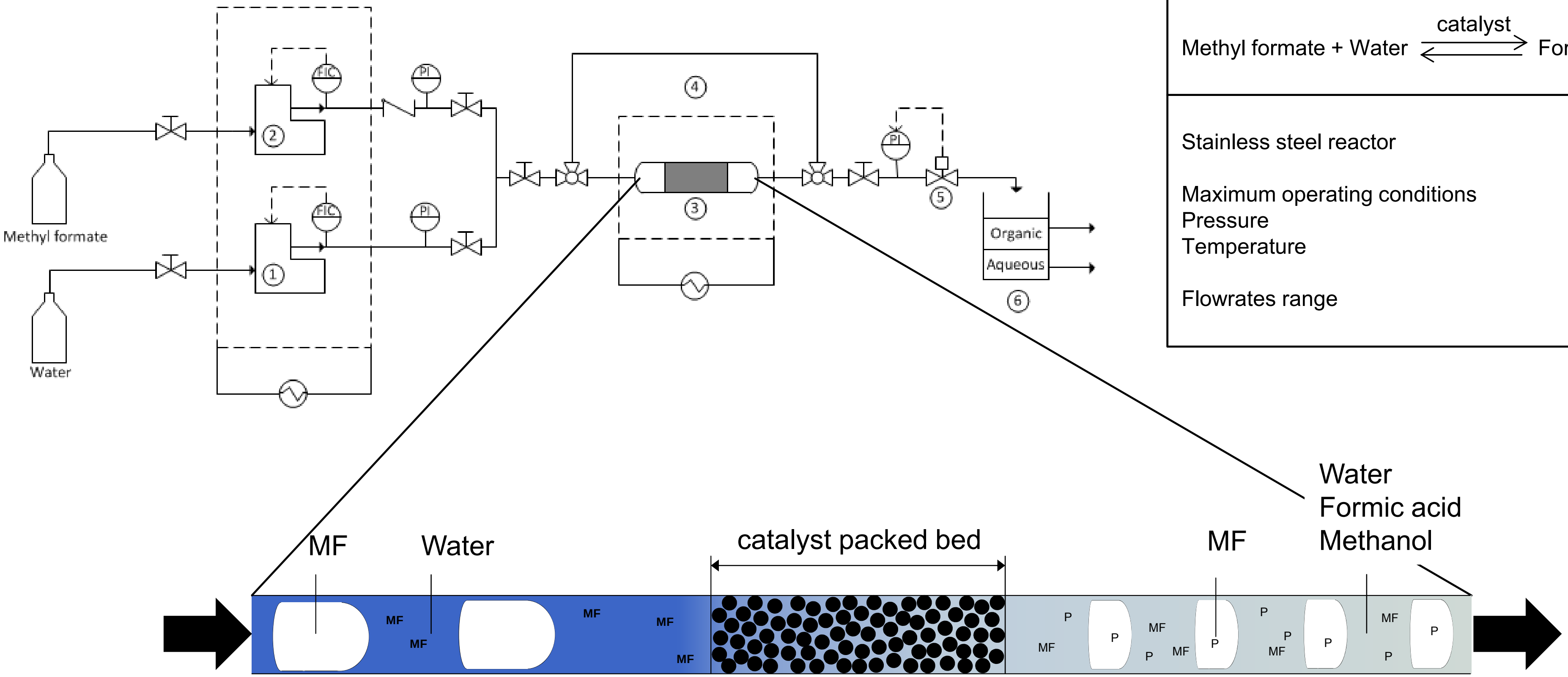
Condensation temperature



Reactor 2: hydrolysis of methyl formate



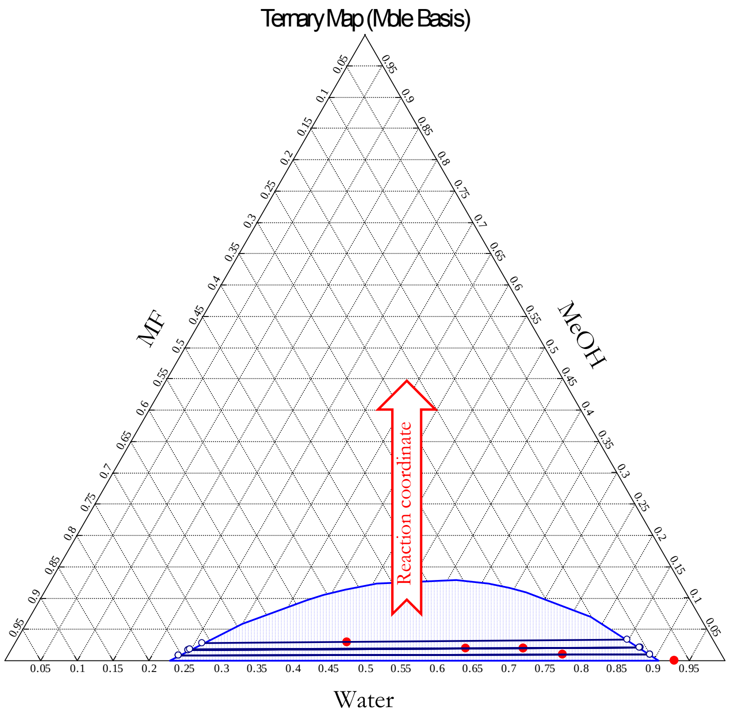
Hydrolysis setup



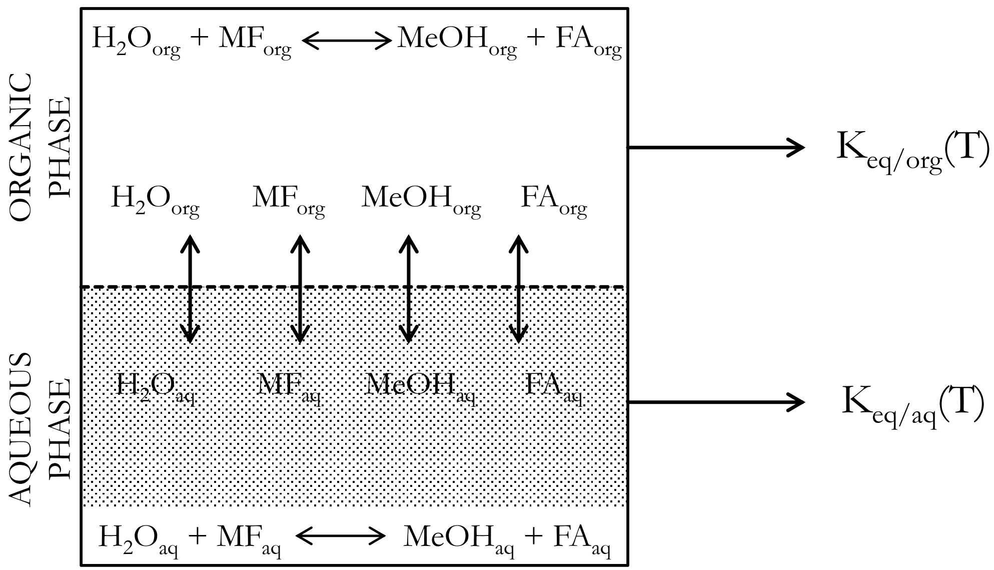
Methyl formate + Water $\underset{}{\overset{\text{catalyst}}{\rightleftharpoons}}$ Formic acid + Methanol

Stainless steel reactor	ID = 2 mm
Maximum operating conditions	
Pressure	100 bar
Temperature	300°C
Flowrates range	0.001 – 100 mL/min

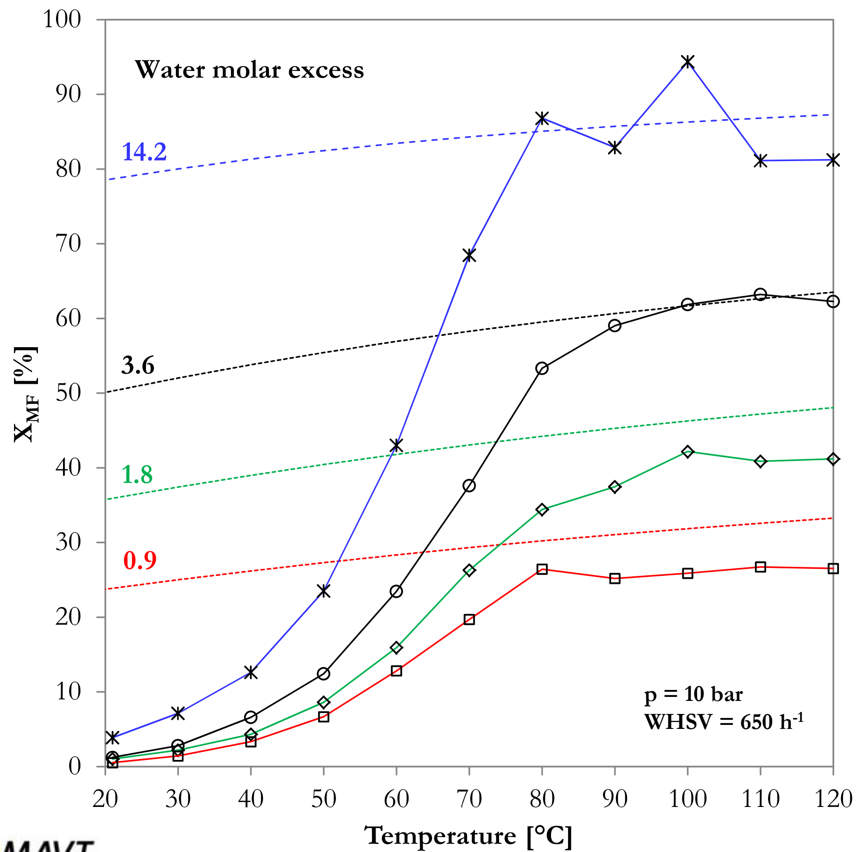
Simultaneous phase and chemical equilibria

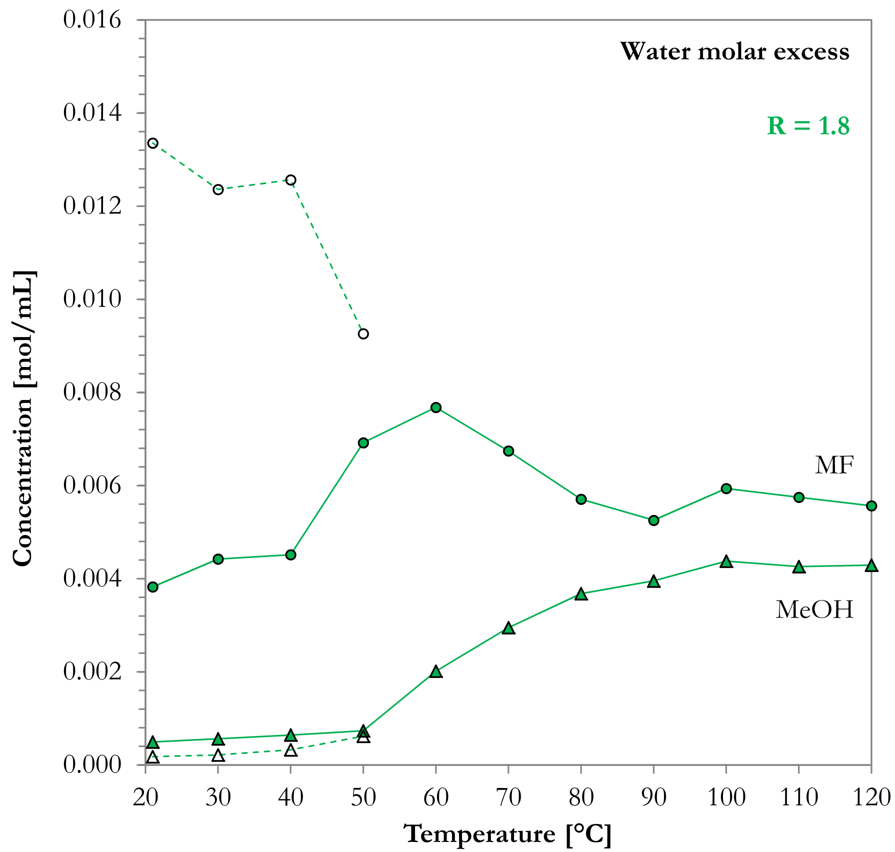


10 bar, 23°C

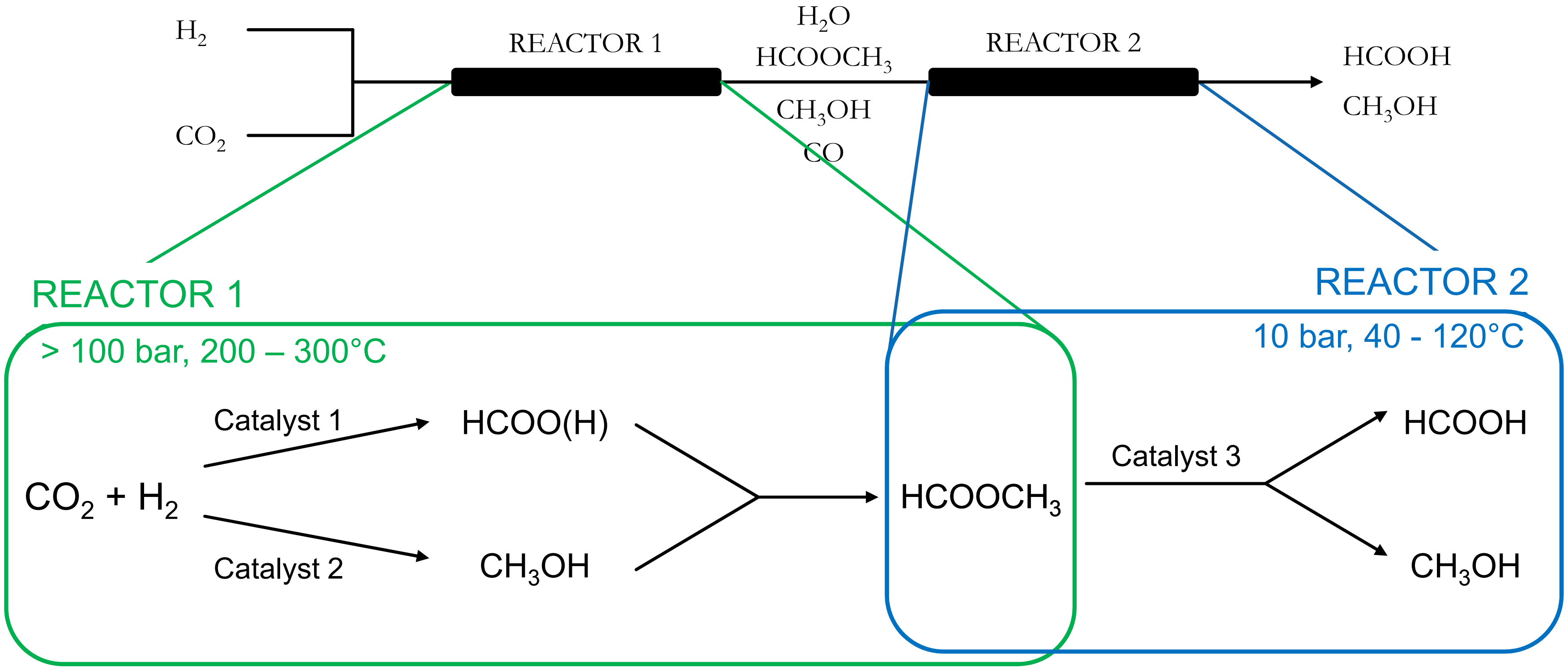


Parametric study





Outlook


H2
CO2
REACTOR 1
H2O
HCOOCH3
CH3OH
CO
REACTOR 2
HCOOH
CH3OH
REACTOR 1
> 100 bar, 200 – 300°C
Catalyst 1
HCOO(H)
CO2 + H2
Catalyst 2
CH3OH
HCOOCH3
REACTOR 2
10 bar, 40 - 120°C
Catalyst 3
HCOOH
CH3OH

Thank you for your attention