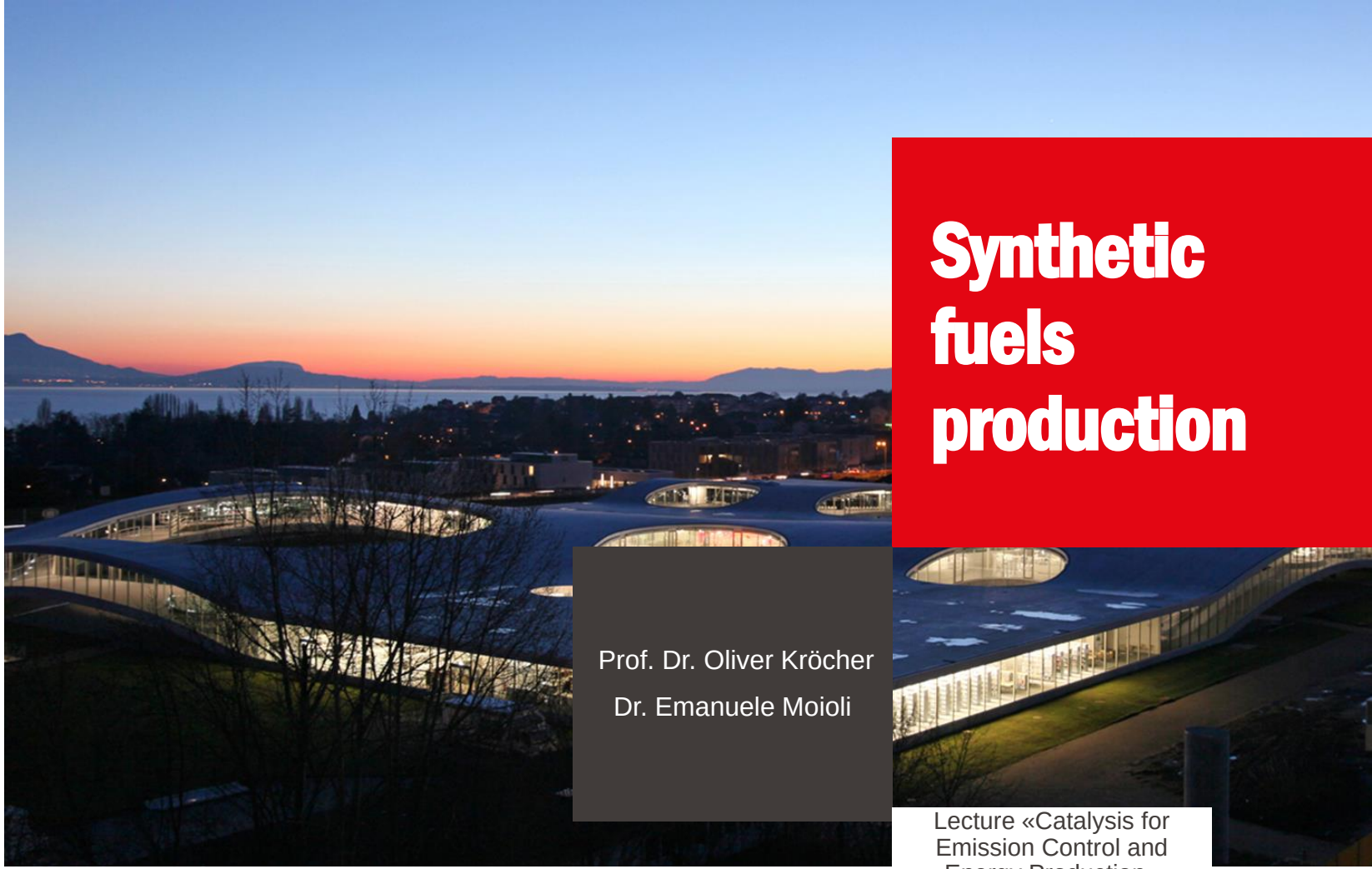
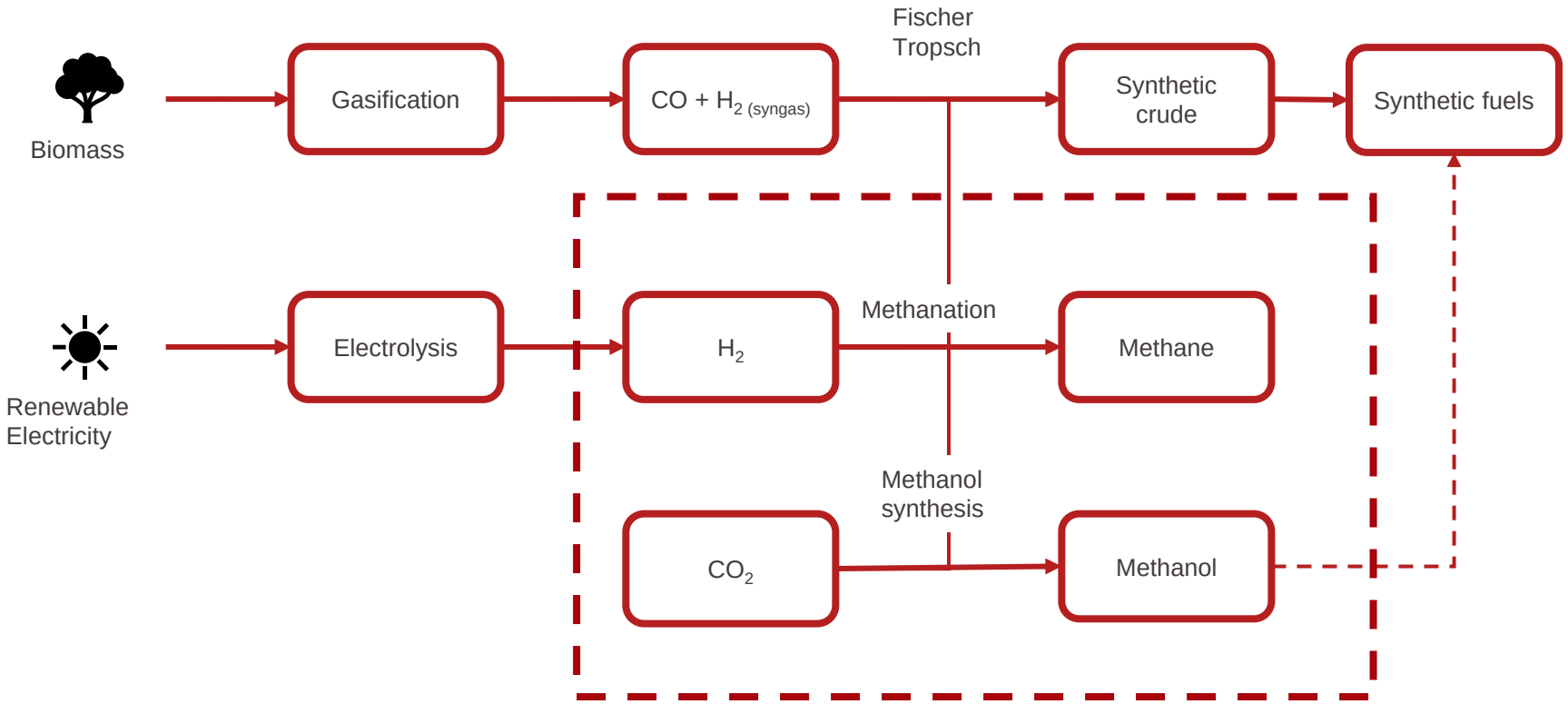


Synthetic fuels production

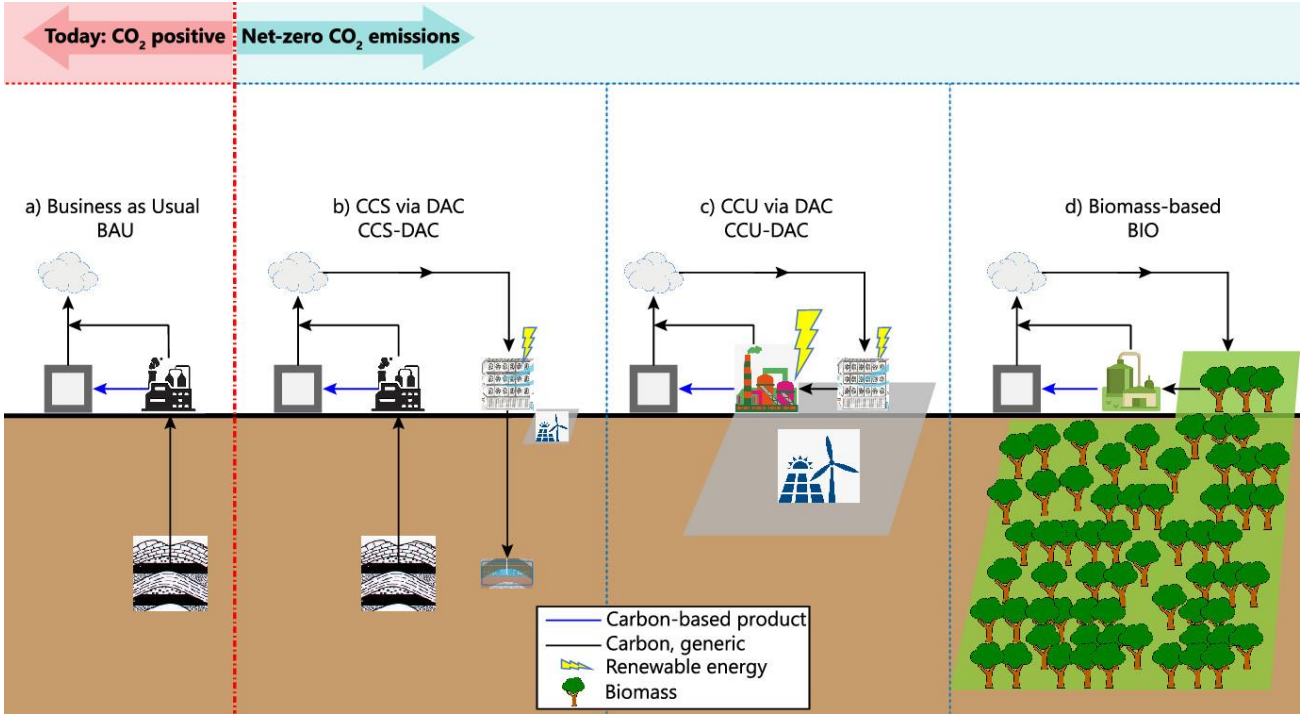
Prof. Dr. Oliver Kröcher
Dr. Emanuele Moioli

Lecture «Catalysis for Emission Control and Energy Production»

Processes for renewable fuels production



Role of synthetic fuels in carbon emissions reduction



Catalysis is essential to ensure fuel production from new resources (bio-based or electricity based)

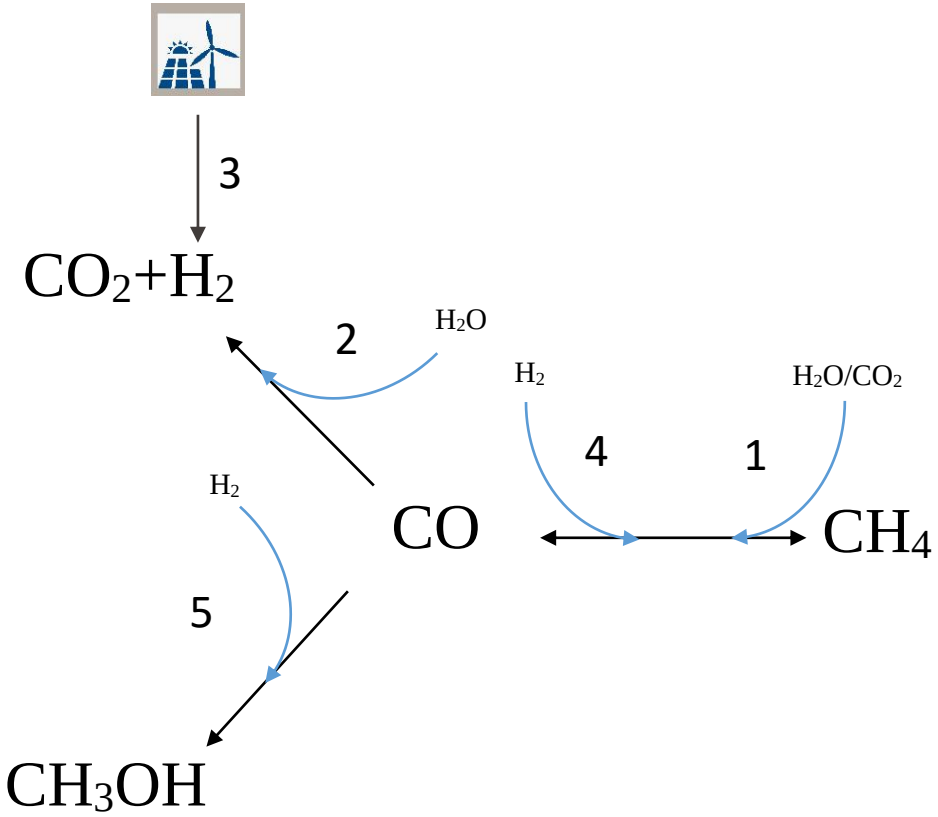
DAC = Direct Air Capture
CCS = Carbon Capture and Storage
CCU = Carbon Capture and Utilisation

DAC : 5-10 GJ/t CO_2

Source: Gabrielli et al IE&CR (2019) DOI: (10.1021/acs.iecr.9b06579)

Contents

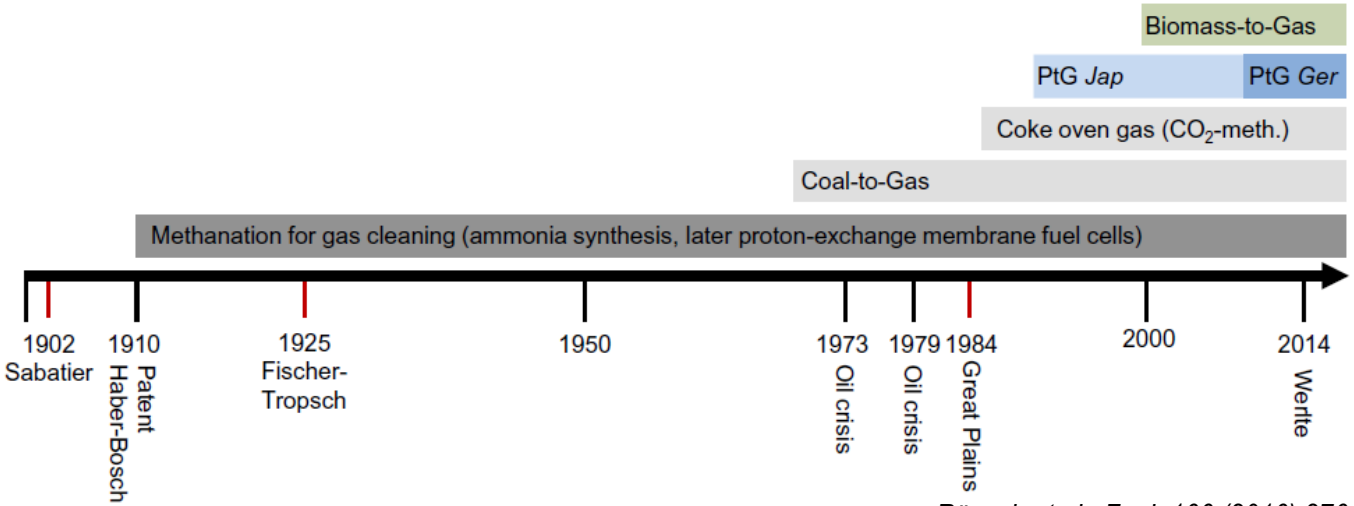
1. Reforming (steam, dry)
2. Water Gas Shift (WGS)
3. Electrolysis
4. Methanation
5. Methanol Synthesis



Methanation

$CO + 3H_2 \leftrightarrow CH_4 + H_2O$ $\Delta H = -206\ kJ\ mol^{-1}$

$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O$ $\Delta H = -164\ kJ\ mol^{-1}$



Rönsch et al., Fuel, 166 (2016) 276-296

Methanation for SNG production

biomass

coal

Gasification

Gas cleaning & conditioning

S, Cl, dust, etc.

Gas Composition		
H_2	%	35-45
CO	%	22-25
CH_4	%	~10
CO_2	%	20-25
C_2H_4	%	2-3
C_2H_6	%	~0.5
C_2H_2	%	~0.4
C_6H_6	g/m^3	~8
Tars	mg/m^3	20-30

Methanation

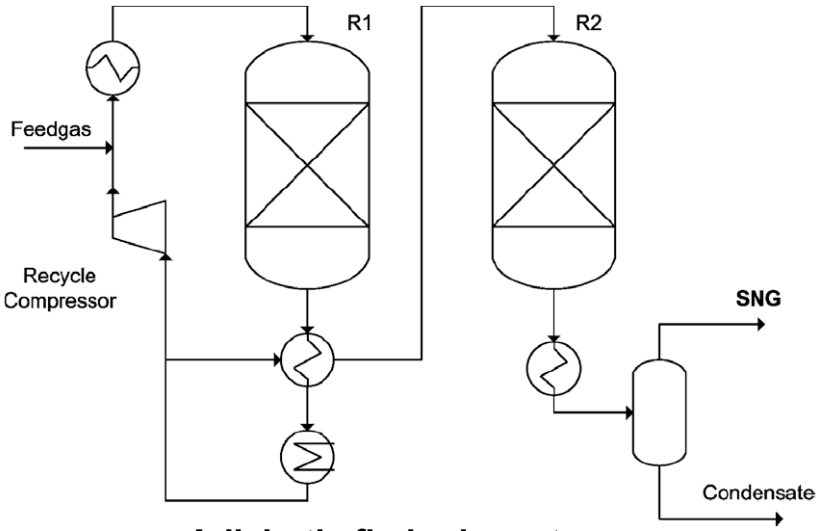
Gas upgrading

CO_2, H_2O, H_2, etc.

BioSNG (CH_4)

J. Kopyscinski et al., Fuel, 89 (2010) 1763

SNG from Naptha – Lurgi Process



Adiabatic fix-bed reactors

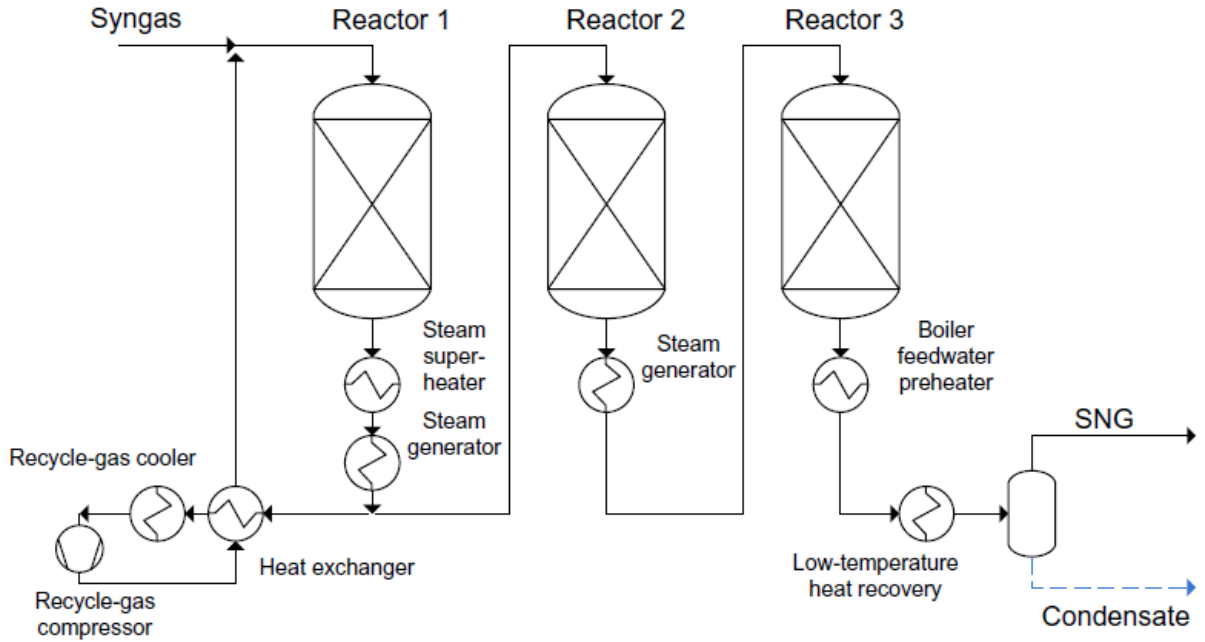
	Feedgas	R1		R2	
	%	Inlet	outlet	inlet	outlet
Temp. (°C)	270	300	450	260	315
H_2	60.1	21.3	7.7	7.7	0.7
CO	15.5	4.3	0.4	0.4	0.05
CH_4	10.3	53.3	68.4	68.4	75.9
CO_2	13.0	19.3	21.5	21.5	21.3
C_2+	0.2	0.1	0.05	0.05	0.05
N_2	0.9	1.7	2.0	2.0	2.0

Two catalysts

- 20 wt%Ni/Al_2O_3 (fast deactivation)
- higher Ni content (BASF)

J. Kopyscinski et al., Fuel, 89 (2010) 1763

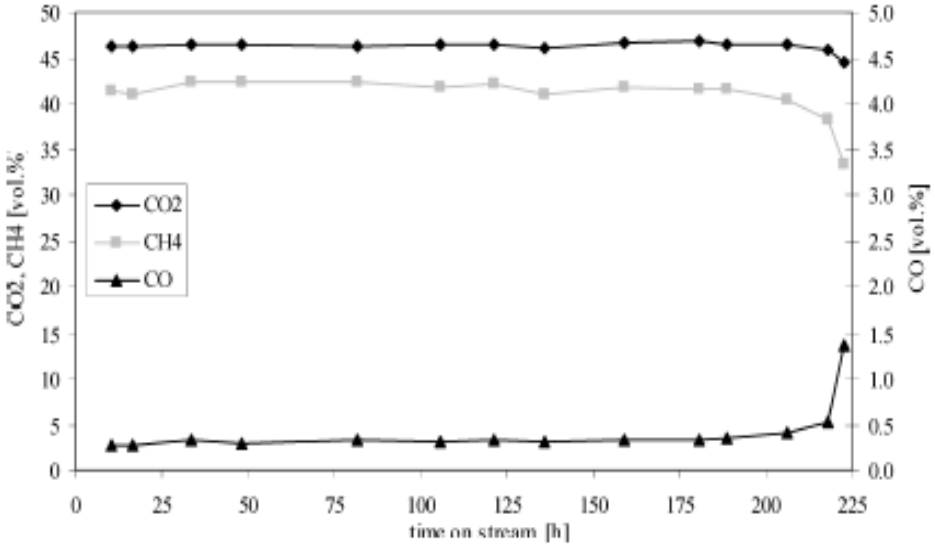
SNG from Naptha – TREMP Process



TREMP process: Haldor Topsøe, High temperature methanation process
Catalyst: MCR-2X, MCR-4

Rönch et al., Fuel, 166 (2016) 276-296

SNG from biomass



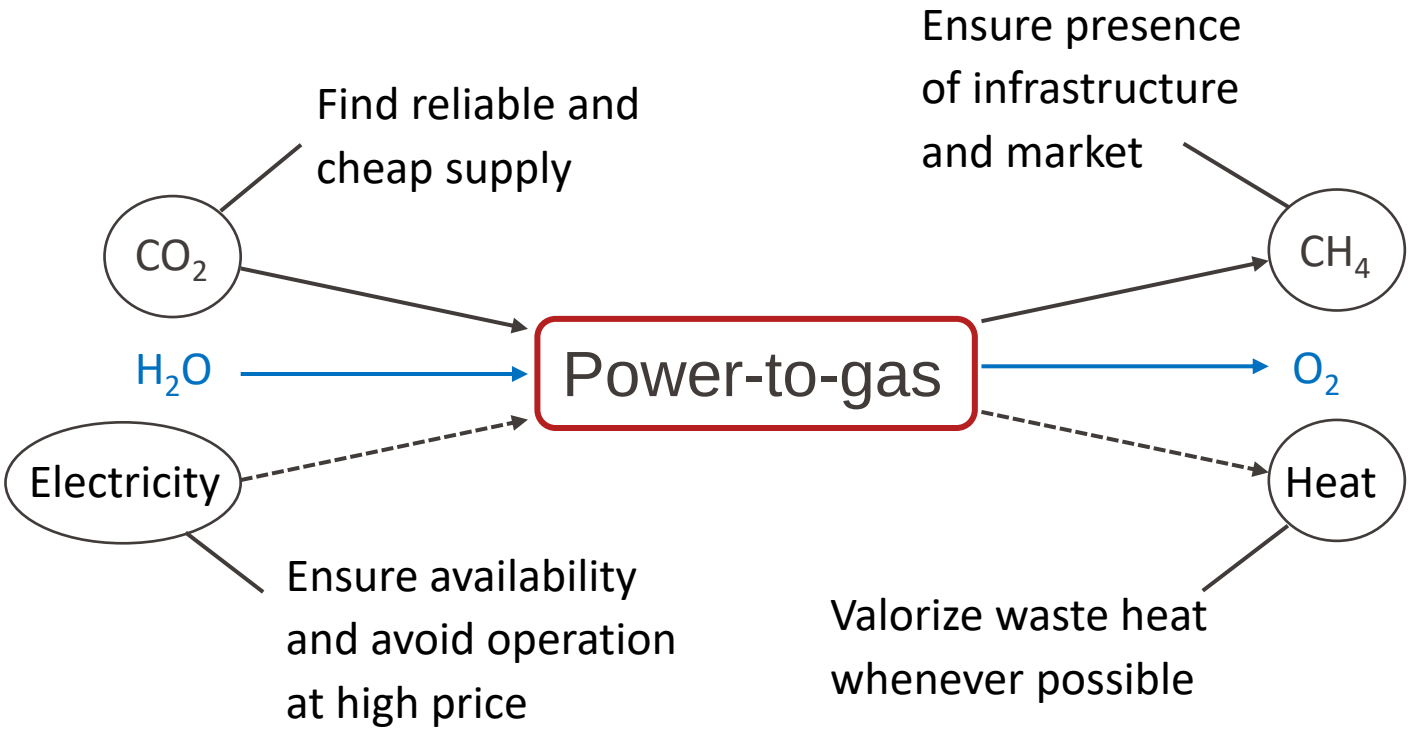
Fluidized-bed methanation reactor

Ni/Al_2O_3 catalyst with high Ni content

Güssing, Austria, PSI Technology

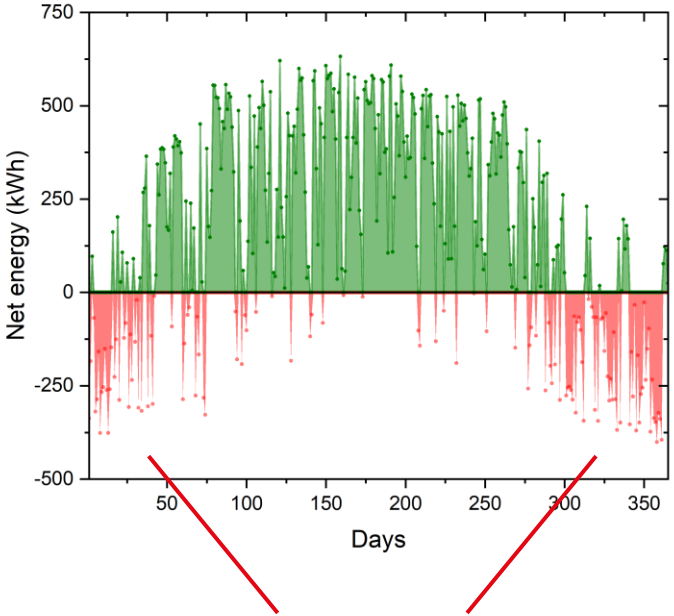
J. Kopyscinski et al., Fuel, 89 (2010) 1763

Power – to –gas basics



Power – to – gas

Electricity produced from PV – electricity demand



- Renewable electricity is intrinsically subject to seasonality
- Need to store electricity seasonally
- Batteries only suitable on short time spans
  - Limited space
  - Too high cost
- Possible storage in chemical bonds → power – to – X

CO_2 methanation

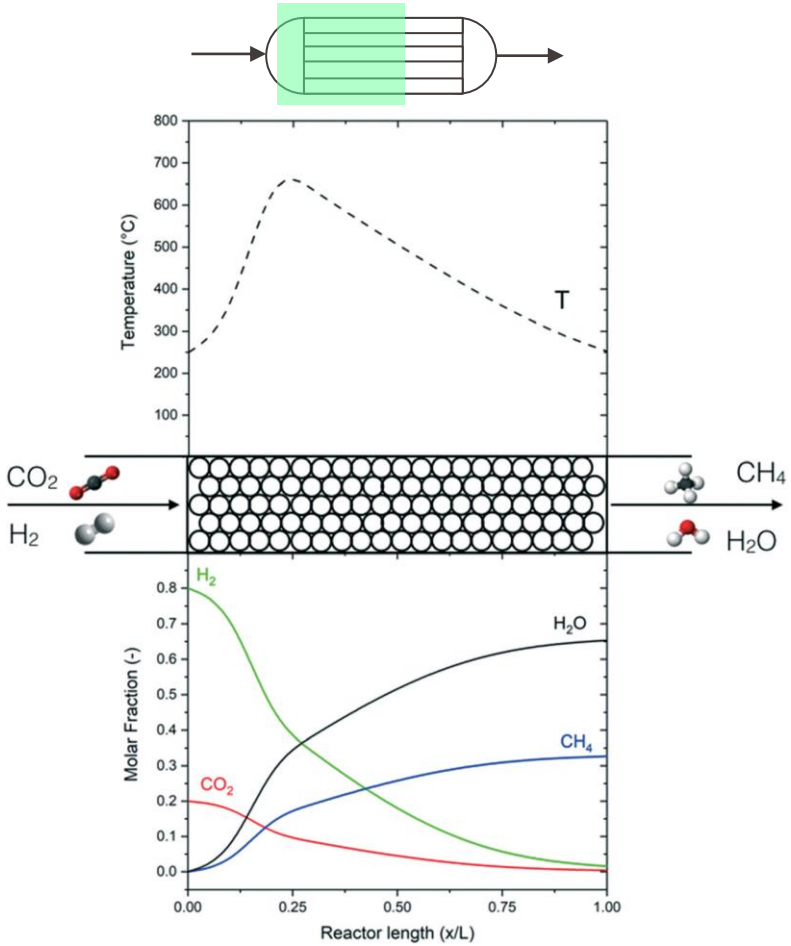
- H_2 storage is challenging: no liquefaction, no specific infrastructure, large volume required in gas phase
- CH_4 is better in terms of storage and utilisation: wide infrastructure, higher volumetric calorific value

- CO_2 methanation converts H_2 in CH_4
  - $CO_2 + 4H_2 \leftrightarrow CH_4 + H_2O$
  - $\Delta H_R = -165 \frac{kJ}{mol}$

- Strongly exothermic reaction
- Thermodynamic equilibrium limited
- Avoid excessive temperature for catalyst lifetime and productivity

Considerations for reactor design

- When using a standard fixed-bed reactor:
  - Temperature hotspot difficult to avoid
  - Influence of RWGS to consider
  - Different reaction when CO is formed (CO methanation)
  - Further problems to consider (e.g. catalyst poisoning by CO)
  - Trade-off between hotspot extension and reactor activation → either safe activation or low hotspot

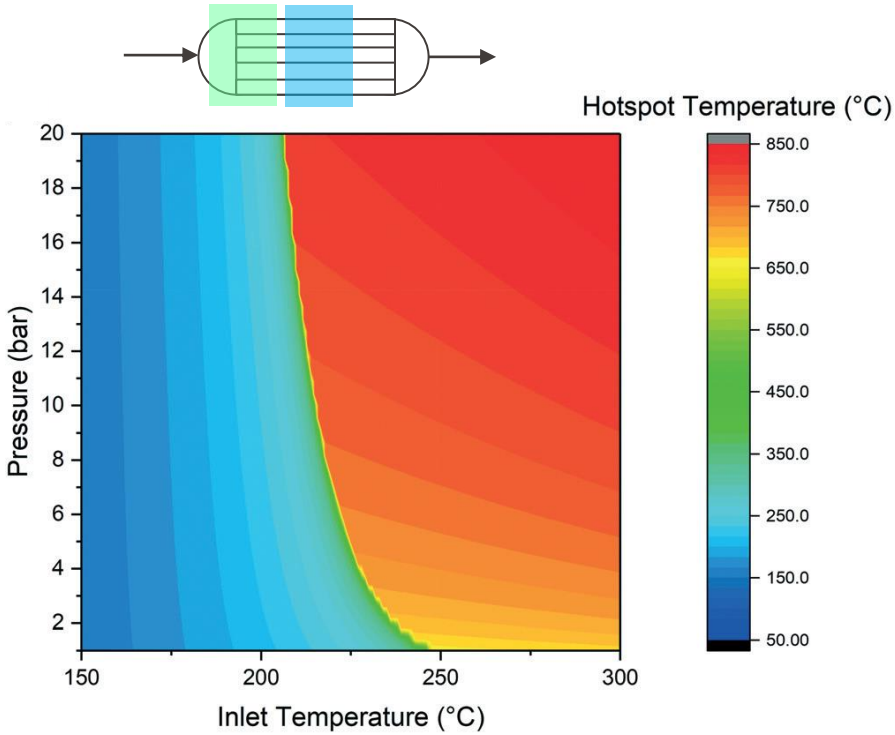


Reaction activation challenges

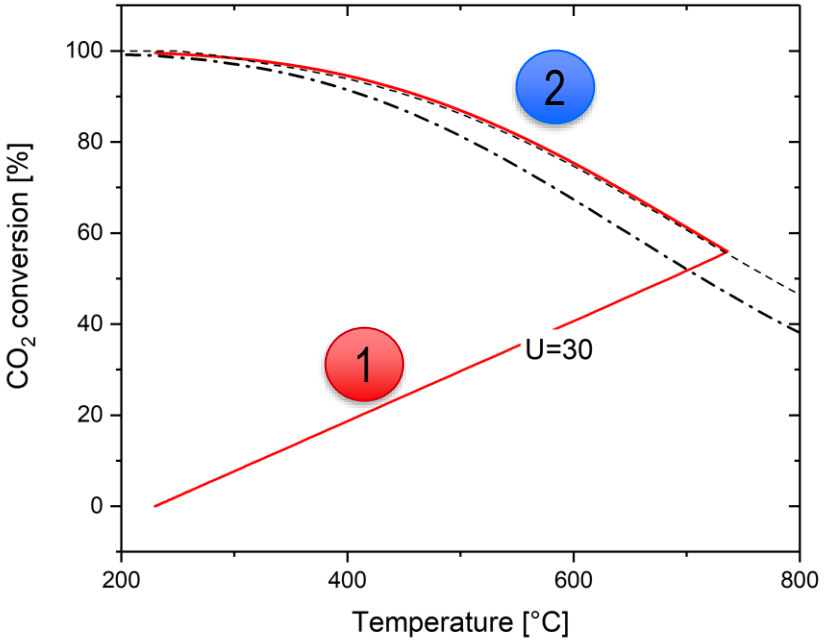
- There is a critical temperature (dependent on catalyst, pressure, space velocity and cooling) where the reactor activates

- The temperature increase is large across this threshold

Caution due to possible catalyst deactivation (sintering)



Effect of cooling



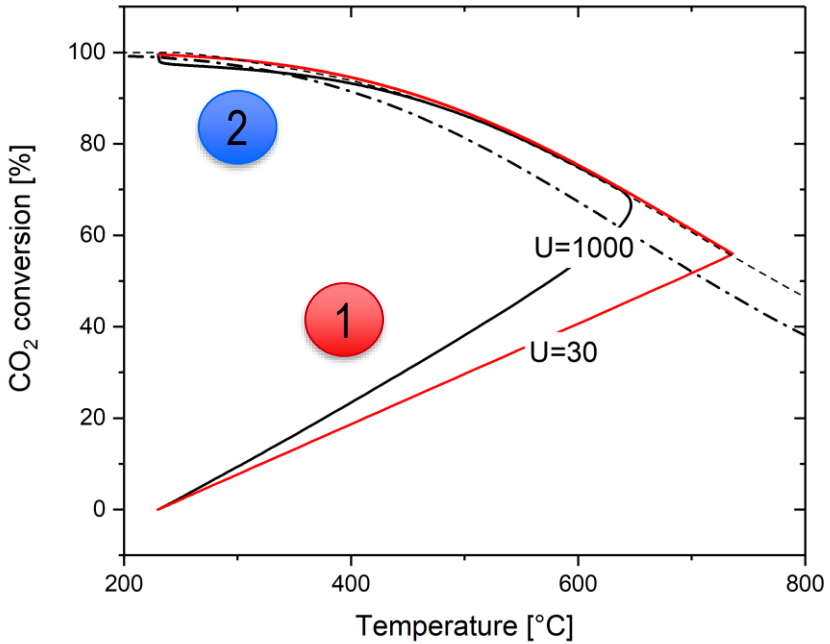
Low cooling rate

1. Initial adiabatic operation
2. Slow decrease of temperature and slow reaction

$$\frac{dT}{dt} = \boldsymbol{U}A(T - T_C) - r\Delta H^R$$

E. Moioli et al., *Chem. Eng. J.*, **2019**, 375, 121954
E. Moioli et al., *Reac. Chem. Eng.*, **2019**, 4, 100-111

Effect of cooling



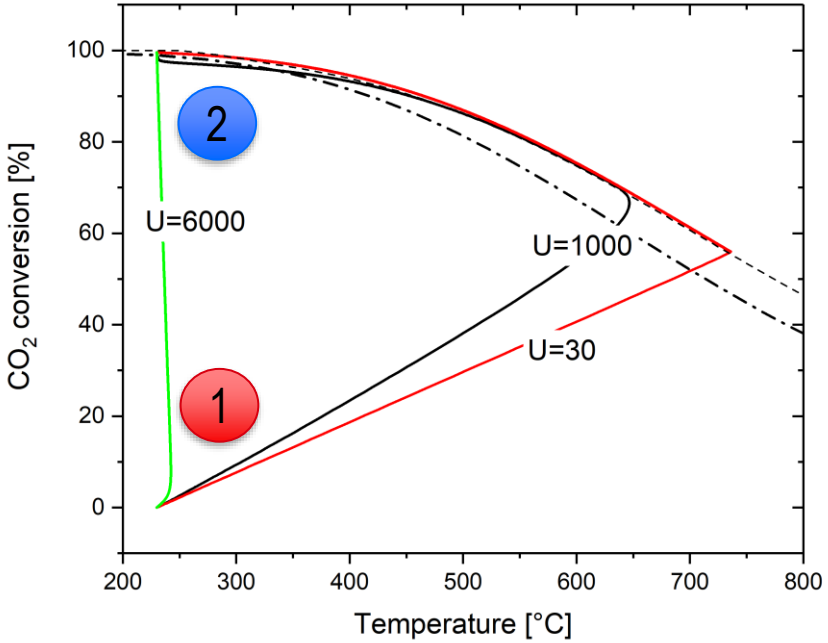
Higher cooling rate

- Temperature increase to hotspot (not adiabatic)
- Excess cooling in the low temperature range

$$\frac{dT}{dt} = \boldsymbol{U}A(T - T_C) - r\Delta H^R$$

E. Moioli et al., *Chem. Eng. J.*, **2019**, 375, 121954
E. Moioli et al., *Reac. Chem. Eng.*, **2019**, 4, 100-111

Effect of cooling



Extremely high cooling rate

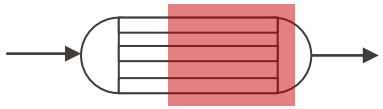
- No evident temperature increase – no pronounced hotspot
- Isothermal operation until final reach of thermodynamic limitation

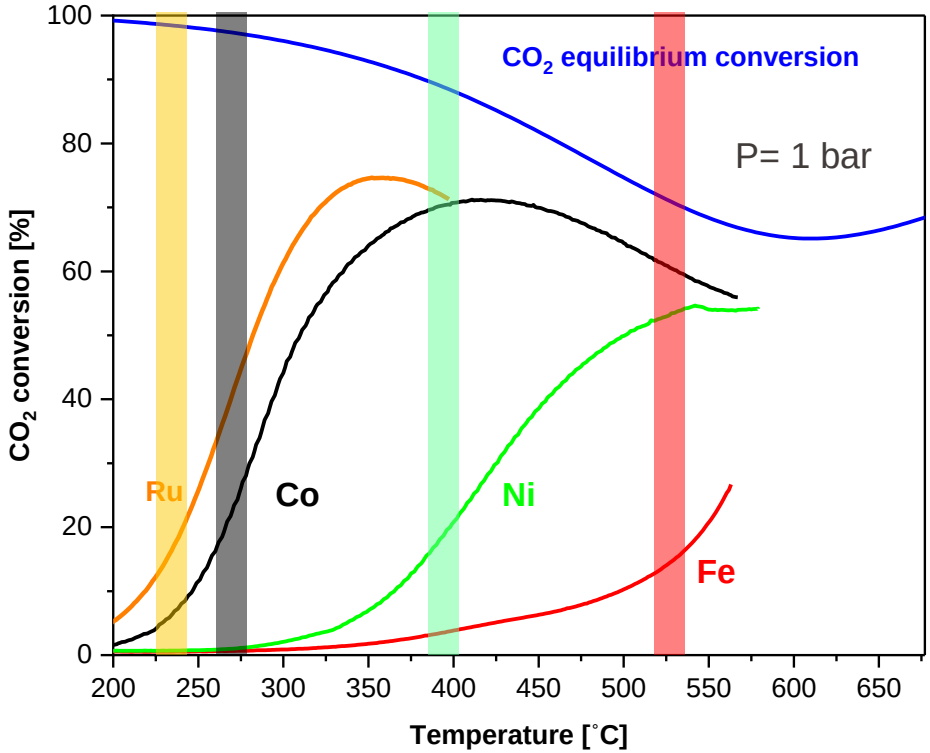
$$\frac{dT}{dt} = \boldsymbol{U}A(T - T_C) - r\Delta H^R$$

E. Moioli et al., *Chem. Eng. J.*, **2019**, 375, 121954
E. Moioli et al., *Reac. Chem. Eng.*, **2019**, 4, 100-111

Catalysts available for methanation

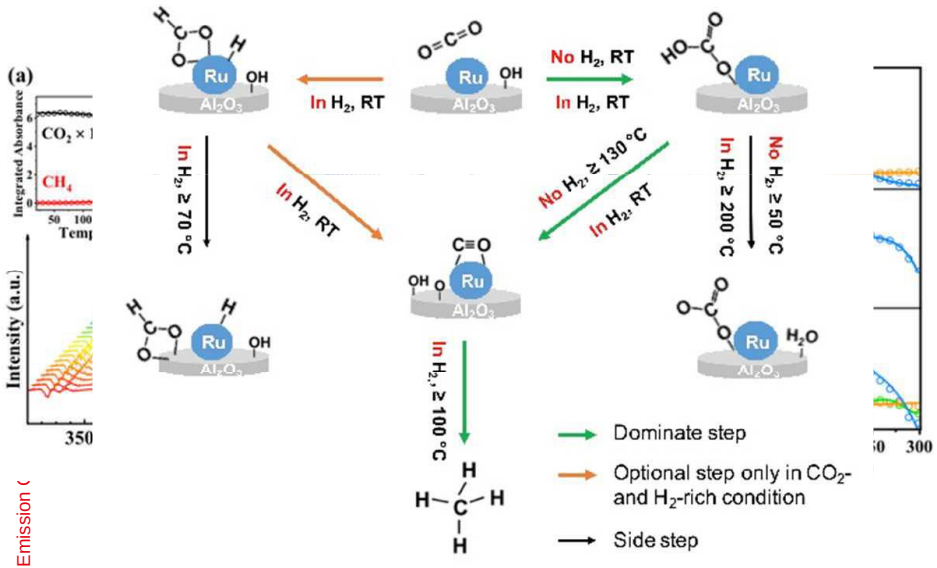
- Ru: active at 230 ˚C, expensive
- Co: active at 270 ˚C, less expensive
- Ni: active above 350 ˚C, cheap
- Fe: not active in CO_2 methanation, very cheap





R. Mutschler, E. Moioli et al., J. Cat., 2019, **375**, 193-201

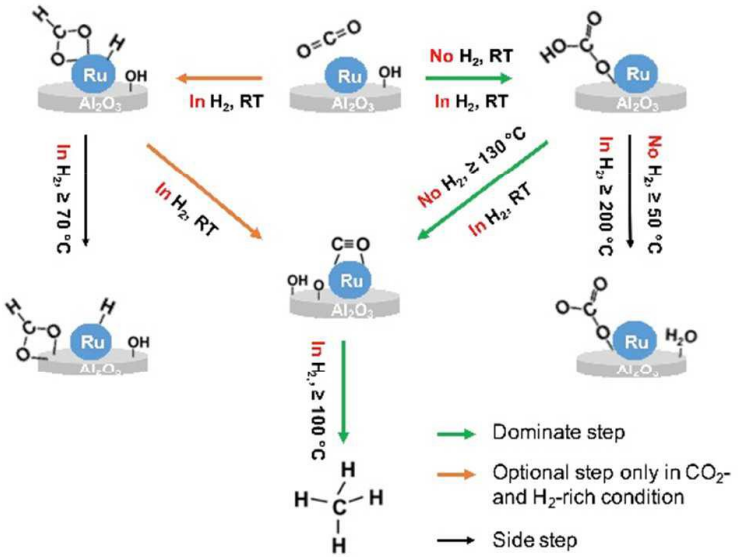
Mechanism on Ru-based catalyst/1



- We obtained the response to IR excitation: what is on the catalyst surface?
- We observed the presence of several surface species:
  - Active species: CO*, HCO_3*, HCO_2*
  - Spectator species: HCO_2* on Al_2O_3, HCO_2* on Metal-Support-Interface
- The local concentration determines the formation of species:
  - Presence of H_2 causes the formation of adsorbed species on the metal
  - Limited H_2 availability calls for reactive properties of Metal Support Interface

K. Zhao, E. Moioli et al., J. Phys. Chem. C, 2018, **122**, 20888-20893

Mechanism on Ru-based catalyst/2



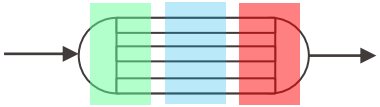
- Independently from the conditions, Rate Determining Step is the CO hydrogenation to CH
- This can happen only by producing CO* at the MSI, while keeping the Ru surface reduced
- An adaptation of the local concentration of species and of the amount of MSI would generate

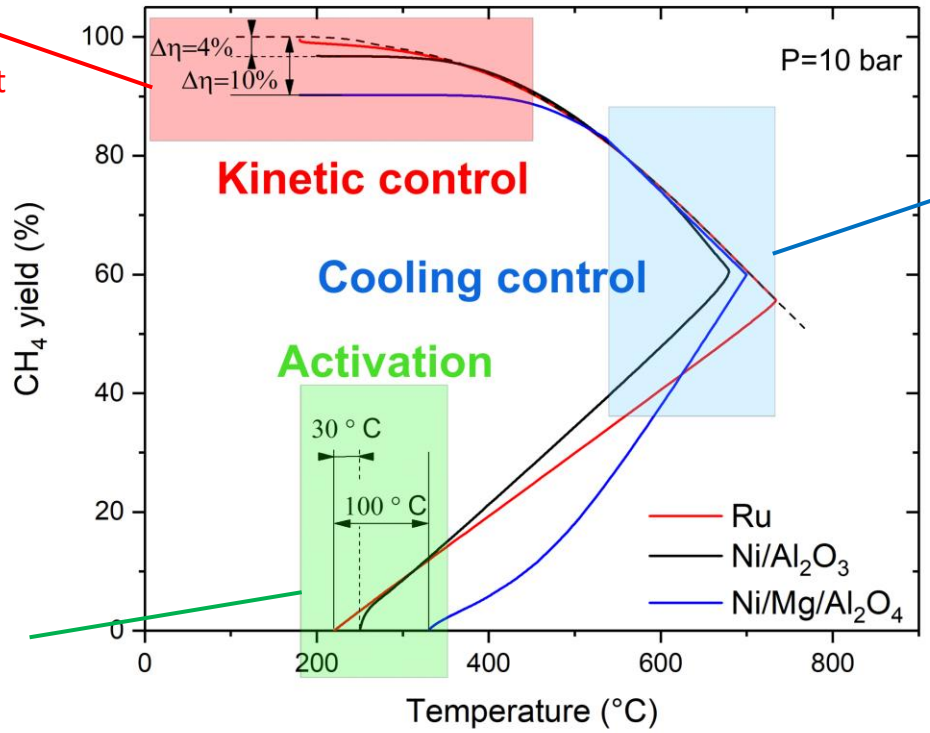
Key information for the synthesis of improved catalysts

K. Zhao, E. Moioli et al., J. Phys. Chem. C, 2018, **122**, 20888-20893

Multi-stage reactor?

Kinetic control:
Need of high-
Performance catalyst



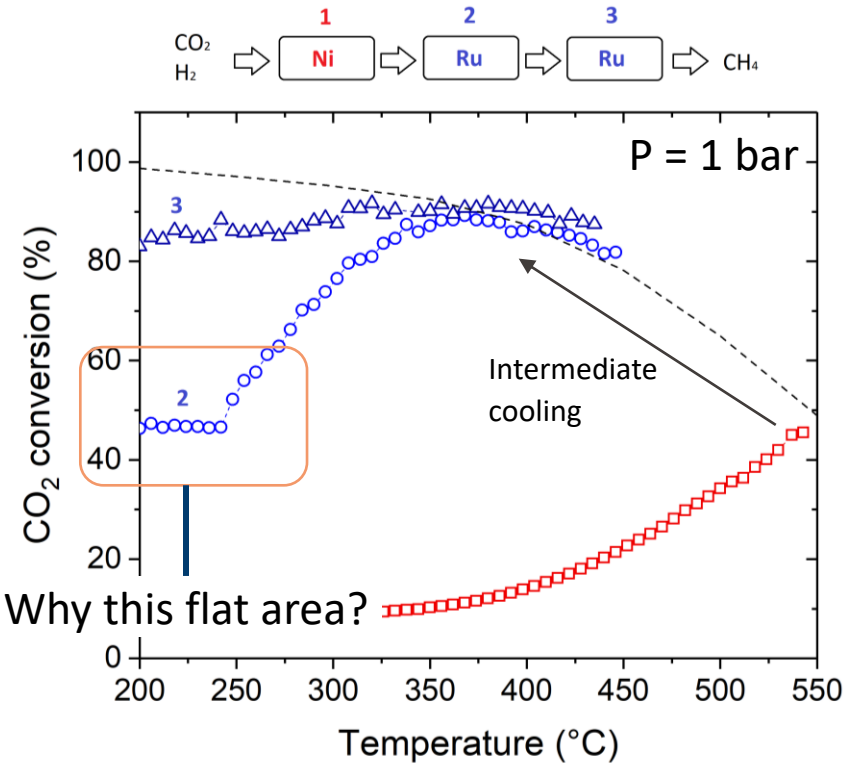


Cooling control section:
Possible to use Ni-catalyst
AVOID SINTERING
From steam reforming

Reaction activation:
possible with standard
Ni-catalyst, appropriate
Reactor design required

Hybrid Ni/Ru reactor/1

- Motivation: reduce the Ru content, but keep high activity where needed
- We use Ni (pristine) at the inlet and then Ru/Al_2O_3
- Over pristine Ni, TD equilibrium is reached at 550 ˚C -> significant CO production
- Ru can handle the products from first stage and reach target conversion

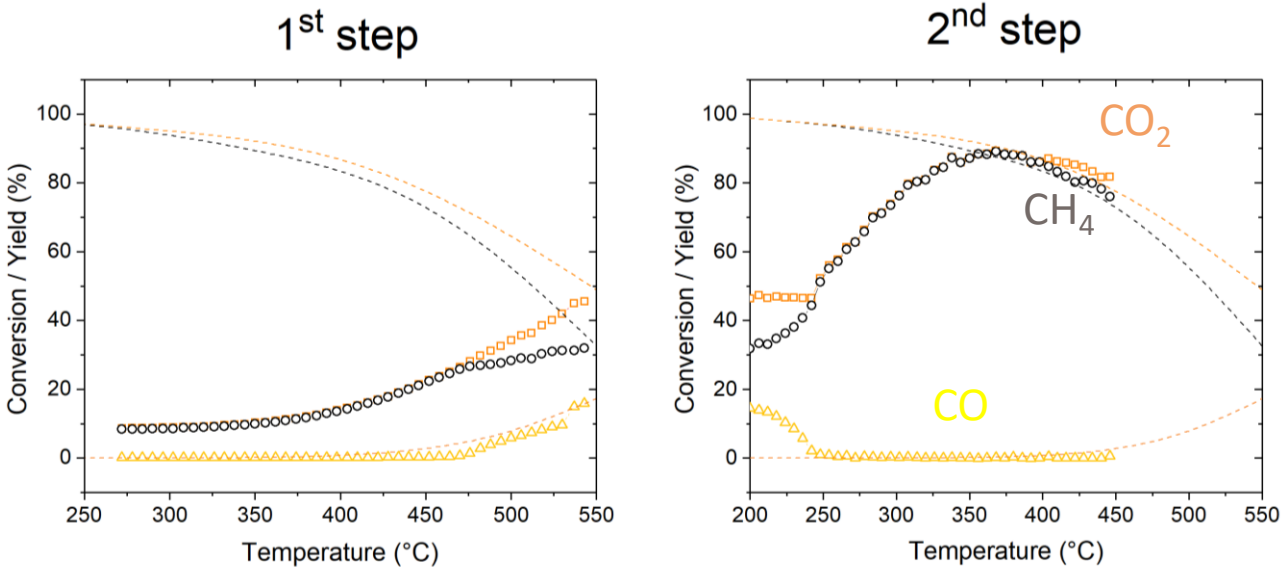


E. Moioli et al., CES:X, 2020, **8**, 100078

Hybrid Ni/Ru reactor/2

- CO_2 conversion does not increase until CO is completely consumed

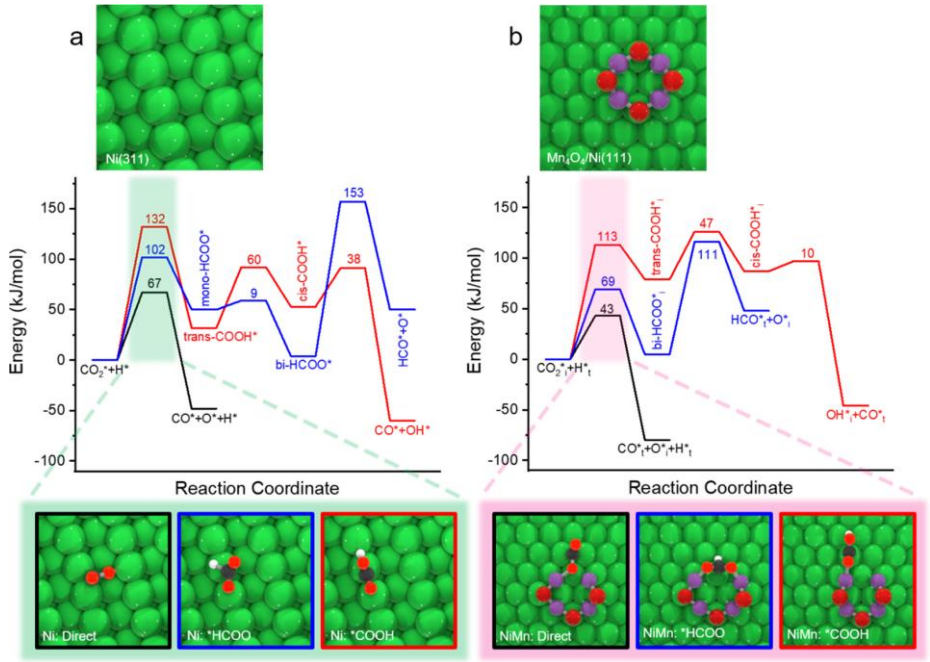
  ➔ Competitive adsorption of CO and CO_2



E. Moioli et al., CES:X, 2020, **8**, 100078

Improving the Ni-catalyst

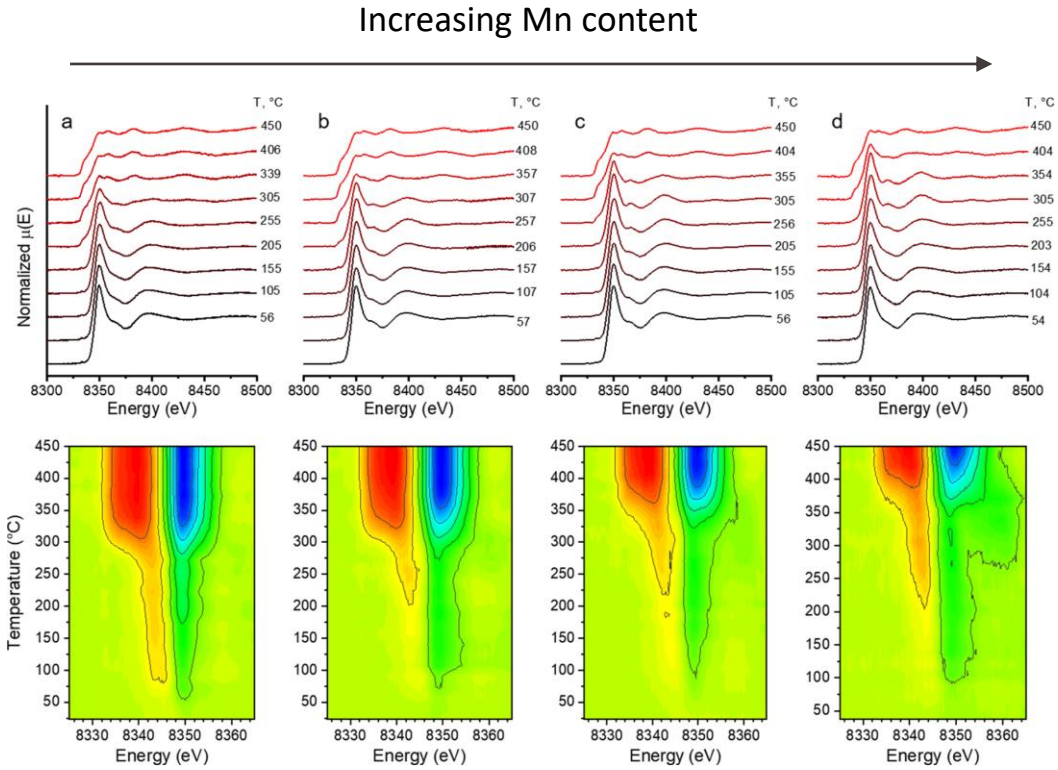
- What does Ni need to perform better?
  - Formation of interfaces to better interact with CO_2
  - This can be achieved with an appropriate promoter
- DFT calculations showed that Mn may be an appropriate promoter, as it decreases the energy barrier of CO_2 adsorption



DFT = density functional theory

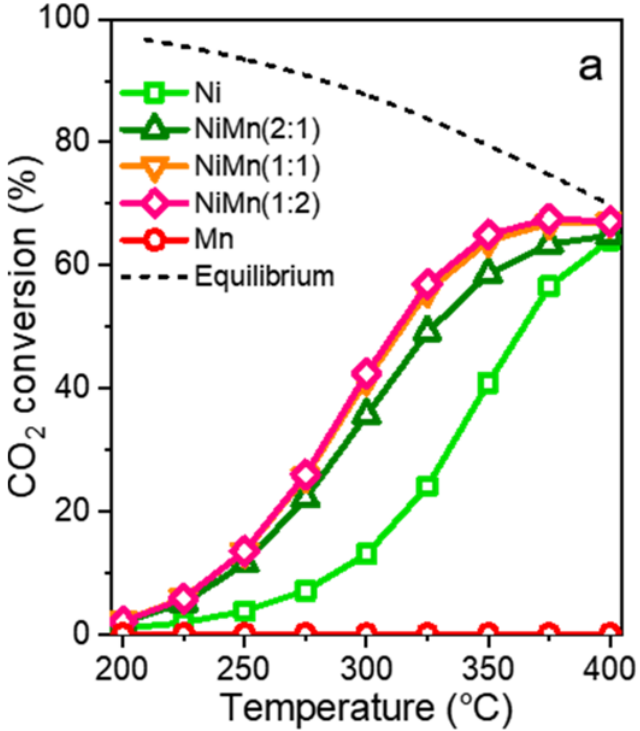
Effect on Mn on Ni reduction

- Presence of Mn increases the reduction temperature of Ni (observed by Ni K-edge XANES)
- We can hence form the optimal mixture of Ni^0/ Ni^{2+} to perform the CO_2 methanation reaction



W. Vrijburg et al., ACS Catal., **2019**, 9, 7823−7839

Catalyst performance



- Catalyst synthesized via wet-impregnation
- Important affinity between Ni and Mn
- High performance of the 1:2 Ni:Mn catalyst → ideal for CO_2 methanation

W. Vrijburg et al., ACS Catal., **2019**, 9, 7823−7839

Optimisation of reactor AND catalyst

? *Stabilize the temperature*

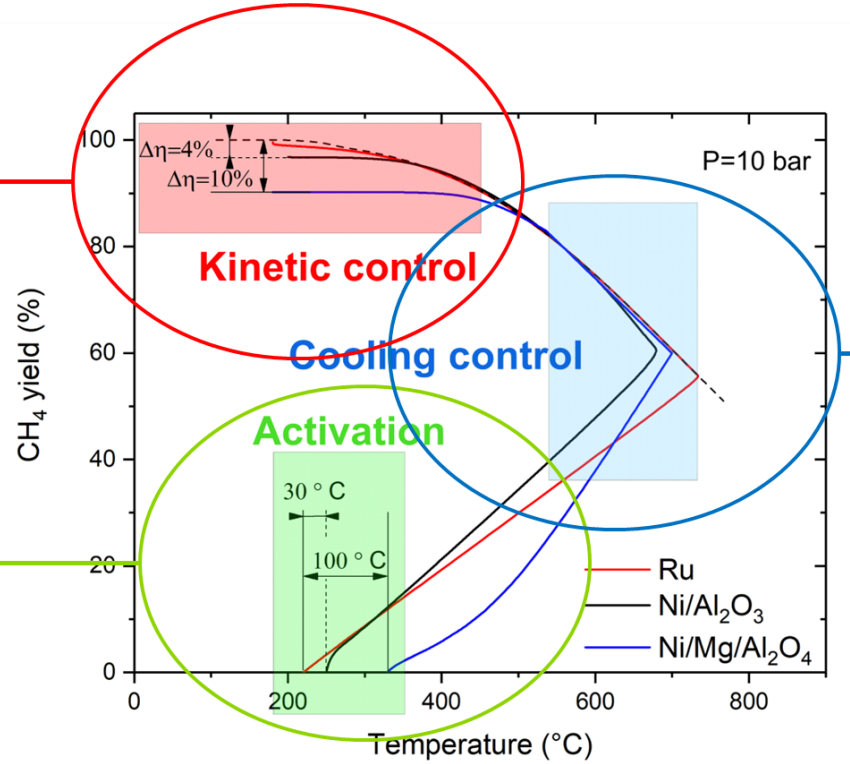
Precise control of the coolant

Activity at low temperature (< 250 ° C)

? *Reach activation temperature*

Use approriate economizer

Activate at (sufficiently) low temperature



Maximize cooling ?

Large exchange area + high heat transfer

Resist high temperature

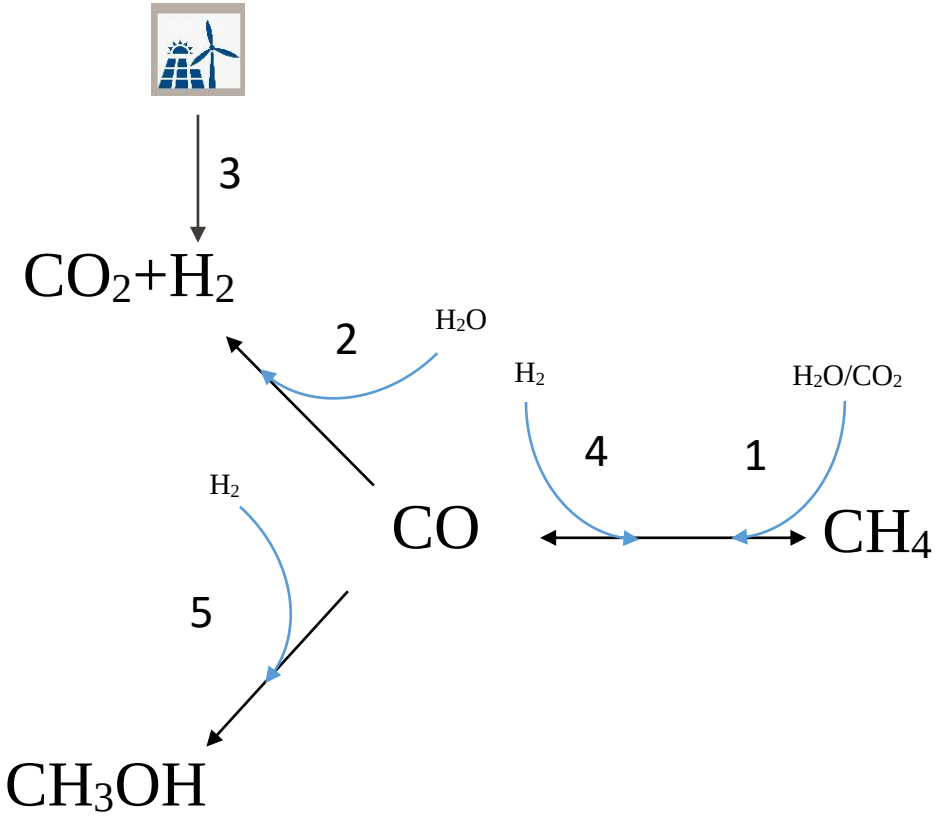
? *Requirements*

Reactor

Catalyst

Contents

1. Reforming (steam, dry)
2. Water Gas Shift (WGS)
3. Electrolysis
4. Methanation
5. Methanol Synthesis



Methanol Synthesis - Reactions

$CO + 2H_2 \leftrightarrow CH_3OH$ $\Delta H = -90.7\ kJ\ mol^{-1}$

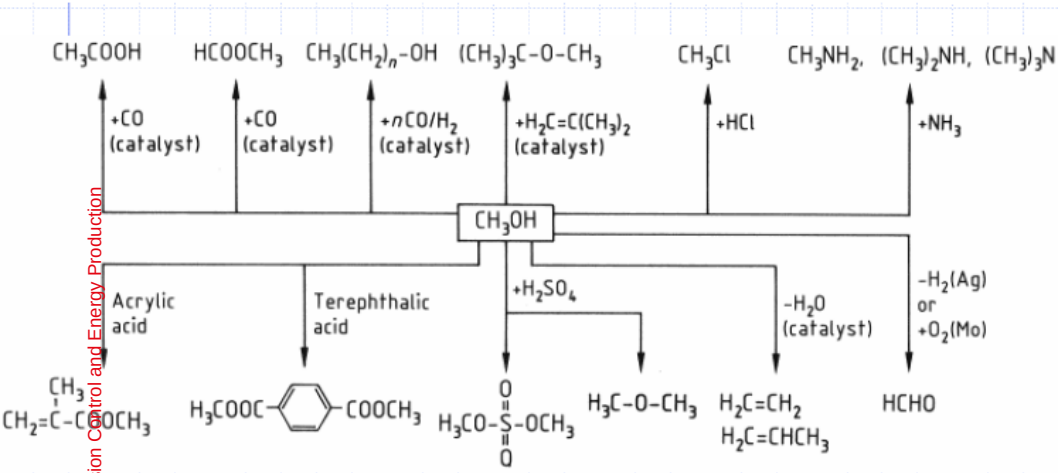
$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O$ $\Delta H = -40.9\ kJ\ mol^{-1}$

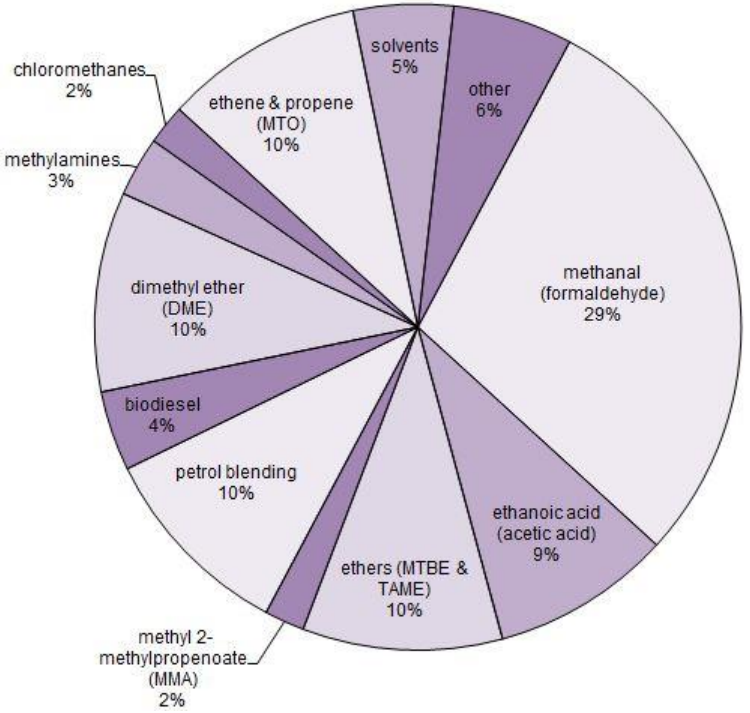
$CO + H_2O \leftrightarrow CO_2 + H_2$ $\Delta H = -49.8\ kJ\ mol^{-1}$

- **Why methanol?**

- Liquid at ambient temperature (can be barreled and transported).
- One of the most important intermediaries in the synthesis of clean fuels.
- Production of other chemicals (formaldehyde, olefins, etc.)
- Blend directly with gasoline to improve its octane rating and combustion.

What is methanol used for?



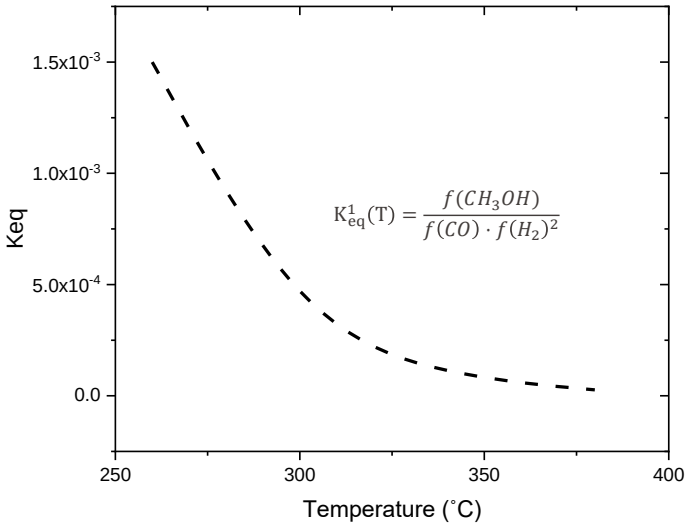


Data for 2015, from IHS Markit, 2015

Thermodynamic equilibrium!

1 $CO + 2H_2 \overset{\lambda_1}{\leftrightarrow} CH_3OH$

2 $CO + H_2O \overset{\lambda_2}{\leftrightarrow} CO_2 + H_2$



λ_i = extent of reaction

Species	In	Out
CO	CO^{in}	$CO^{in} - \lambda_1 - \lambda_2$
CO_2	CO_2^{in}	$CO_2^{in} + \lambda_2$
H_2	H_2^{in}	$H_2^{in} - 2\lambda_1 + \lambda_2$
CH_3OH	-	$+\lambda_1$
H_2O	H_2O^{in}	$H_2O^{in} + \lambda_2$
Total	n_{tot}^{in}	$n_{tot}^{in} - 2\lambda_1$

Decrease in the number of moles

Thermodynamic equilibrium!

Effect of pressure on TD eq.

$$K_{eq}^{1}(T) = \exp\left(\frac{\Delta G^{1}(T)}{RT}\right) = \frac{f(CH_3OH)}{f(CO)\cdot f(H_2)^2} = \frac{P\cdot\phi(CH_3OH)}{P\cdot\phi(CO)P^2\cdot\phi(H_2)^2} = \frac{\phi(CH_3OH)}{\phi(CO)\cdot\phi(H_2)^2}\cdot\frac{1}{P^2}$$

$$K_{eq}^{2}(T) = \exp\left(\frac{\Delta G^{2}(T)}{RT}\right) = \frac{f(CO_2)\cdot f(H_2O)}{f(CO)\cdot f(H_2)} = \frac{P\cdot\phi(CO_2)\cdot P\cdot\phi(H_2O)}{P\cdot\phi(CO)\cdot P\cdot\phi(H_2)} = \frac{\phi(CO_2)\cdot\phi(H_2O)}{\phi(CO)\cdot\phi(H_2)}$$

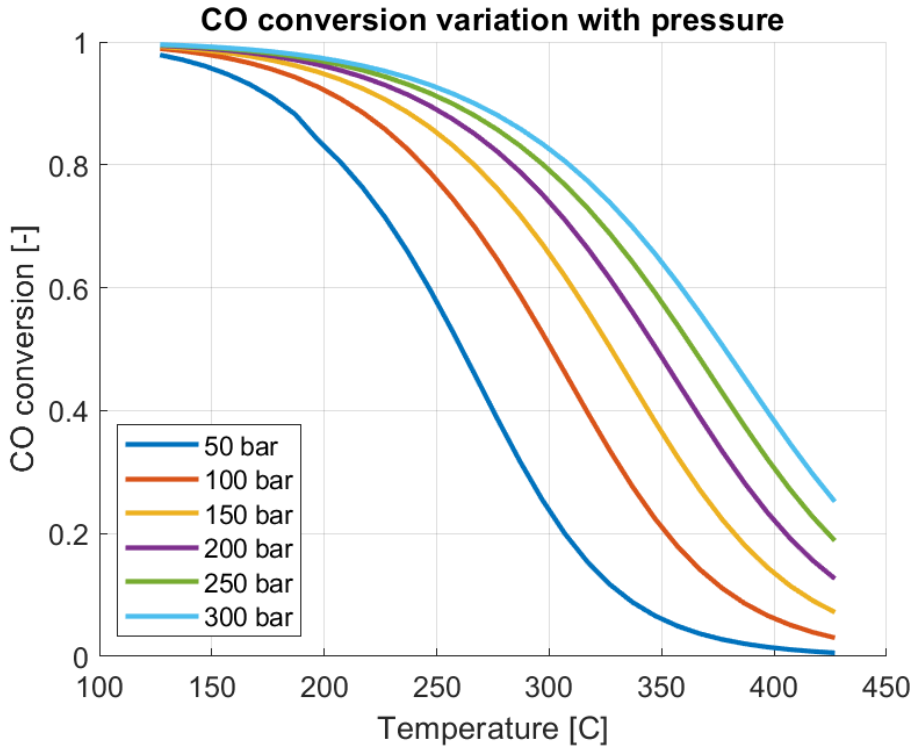
Species	In	Out
CO	CO^{in}	$CO^{in} - \lambda_1 - \lambda_2$
CO_2	CO_2^{in}	$CO_2^{in} + \lambda_2$
H_2	H_2^{in}	$H_2^{in} - 2\lambda_1 + \lambda_2$
CH_3OH	-	$+\lambda_1$
H_2O	H_2O^{in}	$H_2O^{in} + \lambda_2$
Total	n_{tot}^{in}	$n_{tot}^{in} - 2\lambda_1$

Decrease in the number of moles

$f(i)$= fugacity of component i
$\phi(i)$= fugacity coefficient component i

Higher pressure
=
Higher eq. conversion

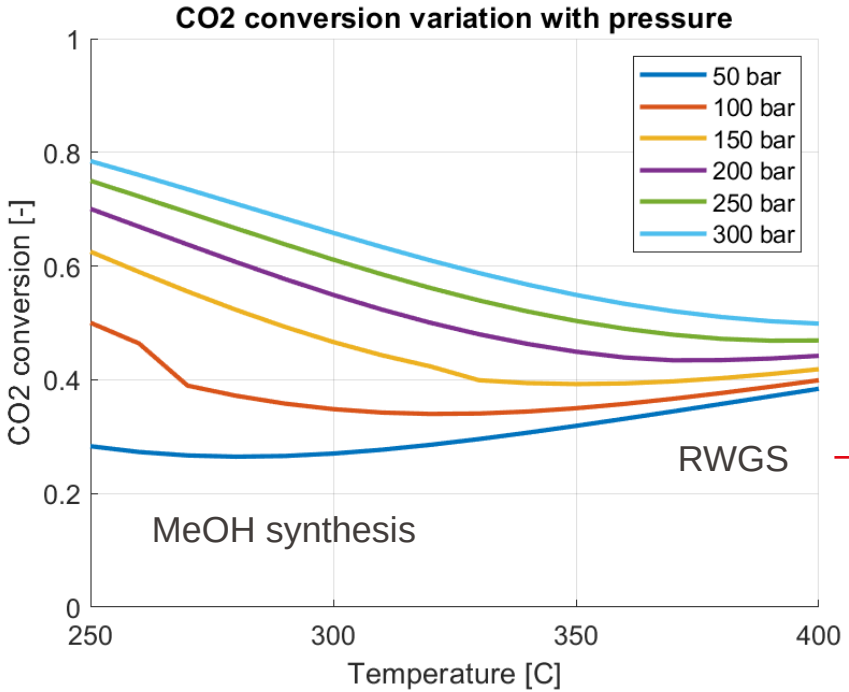
Results equilibrium calculations



Inlet: 1 CO / 2 H_2

High conversion only below 300 ˚C

Results equilibrium calculations



1 CO_2 / 3 H_2

conversion only below 300 ˚C

→ CO_2 conversion to CO

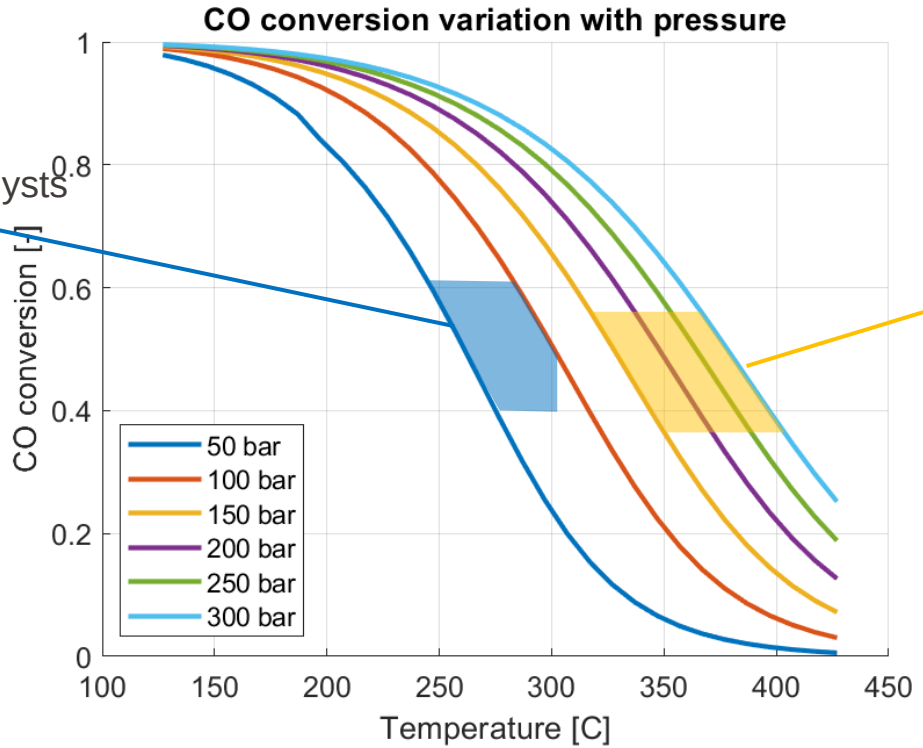
Catalysts for the synthesis

- Historically, the first catalysts were based on ZnO/Cr_2O_3, operating the so-called BASF process (1923)
  - Active above 400 ˚C -> high pressure needed
  - Problem: side methanation reaction ($CO + 3H_2 \leftrightarrow CH_4 + H_2O$)

- Modern catalysts are based on $Cu/ZnO/Al_2O_3$, are active at lower temperature (ICI process, late 1960s)
  - Active at 250 ˚C -> possible to operate at lower pressure

We need appropriate catalysts

Second generation catalysts (ICI) – $Cu/ZnO/Al_2O_3$



First generation catalysts (BASF) – ZnO/Cr_2O_3

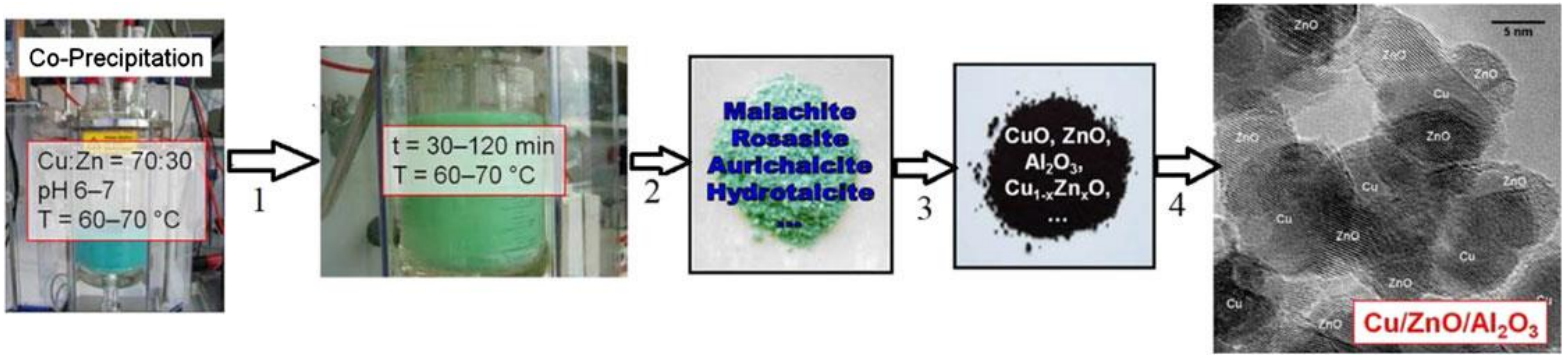
Properties of the commercial catalyst

$CuO/ZnO/Al_2O_3$

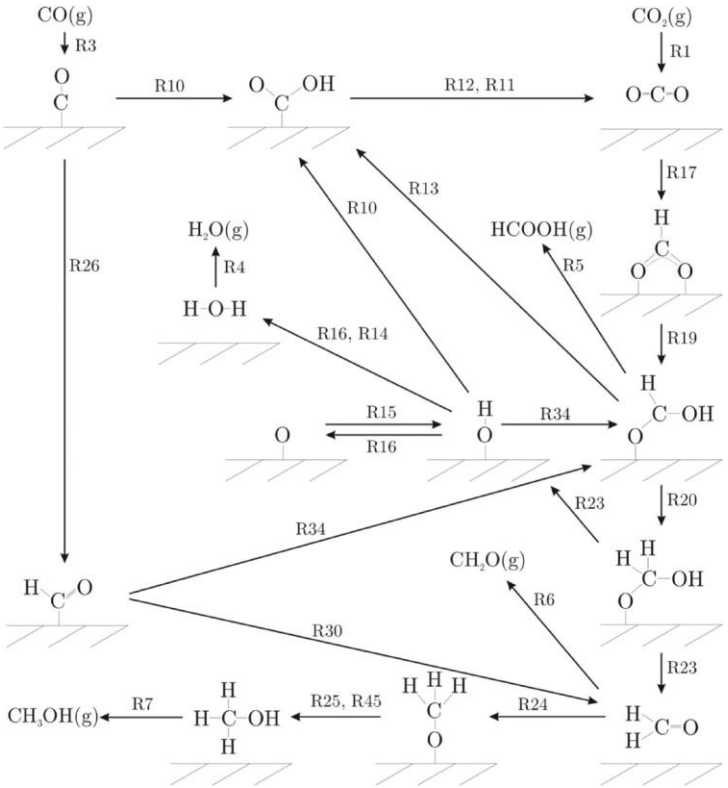
Desirable properties
- -Large surface area
- -Cu particles defect
- -Cu-ZnO interface

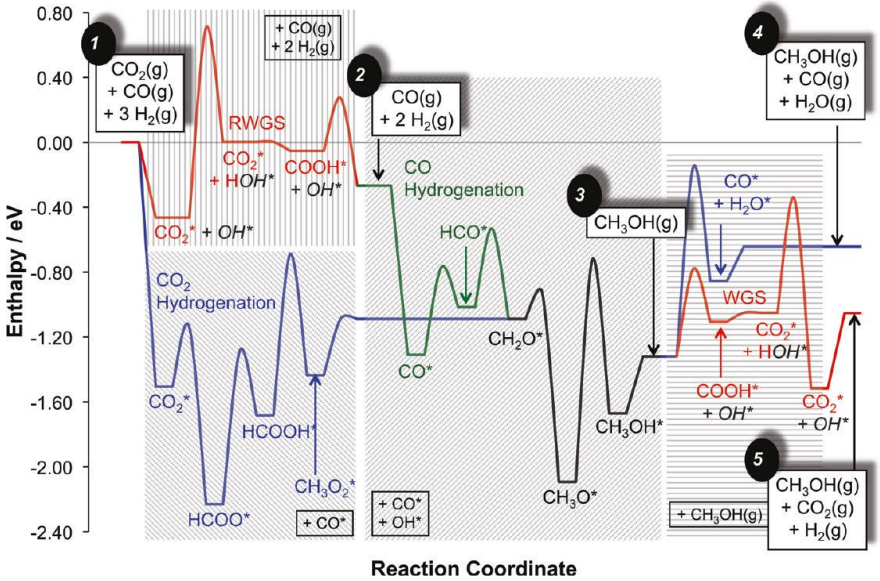
Challenges
- -Easily deactivated by sintering and water poisoning
- -Low equilibrium conversion (10%)
- -Low methanol selectivity

Solutions
- -Use of hydrophobic materials as catalyst components
- -Stabilization of Cu nanoparticles in porous materials
- -Use of binder in catalyst composition
- -Development of new catalysts



Proposed mechanism over Cu/ZnO





L. C. Grabow and M. Mavrikakis, ACS Catal. 2011

Reactor design

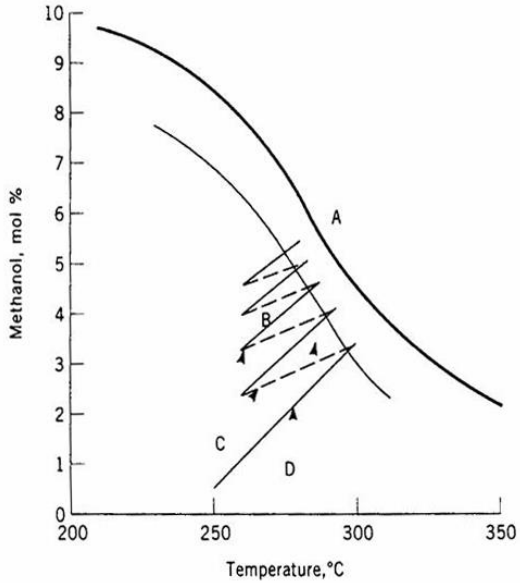


Fig. 8. Quench converter temperature profile. A, equilibrium line; B, maximum rate line; C, quench line; and D, intrabed line.

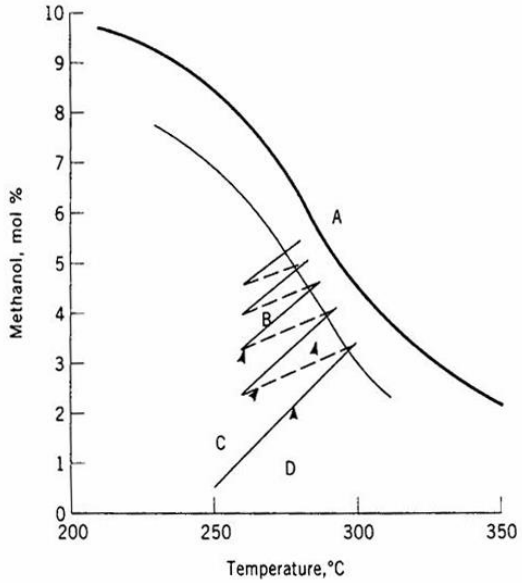
- Due to thermodynamic equilibrium, the maximum in the reaction rate function is found at lower temperature with increasing conversion

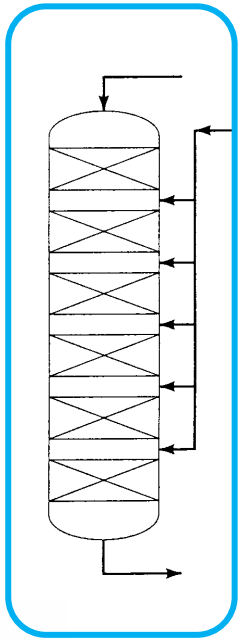
- The reactor design must consider this phenomenon

Easiest solution for this reactor:

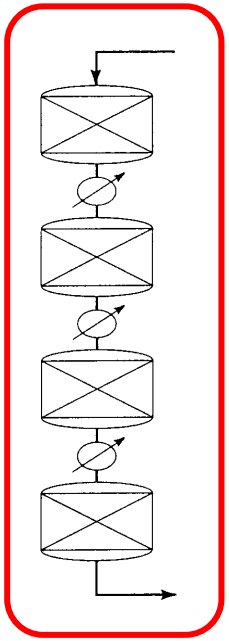
Adiabatic reactor with intermediate cooling

Adiabatic reactor with intermediate cooling



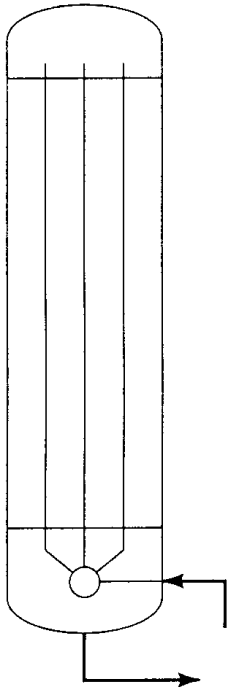


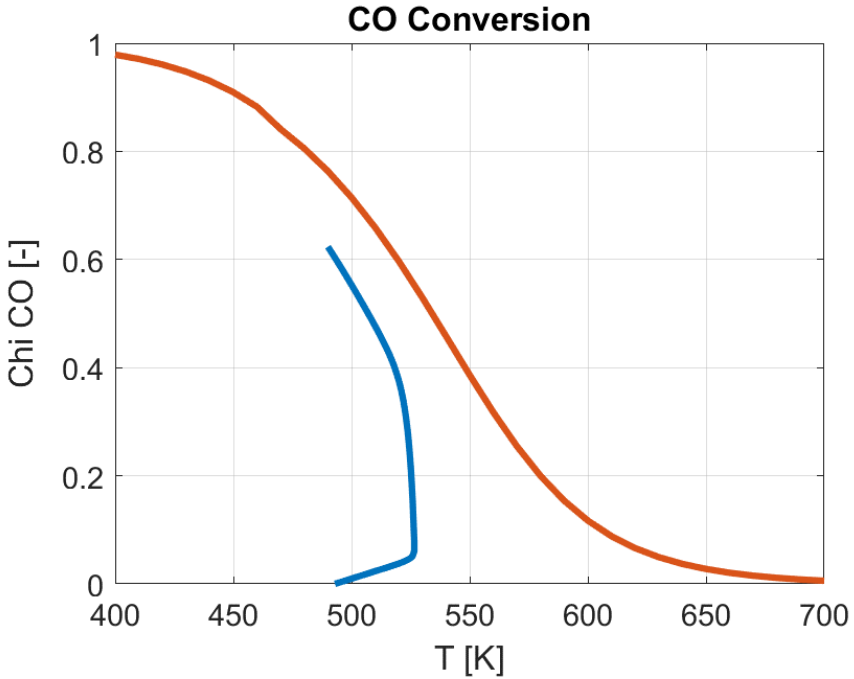
Intermediate cooling with quench



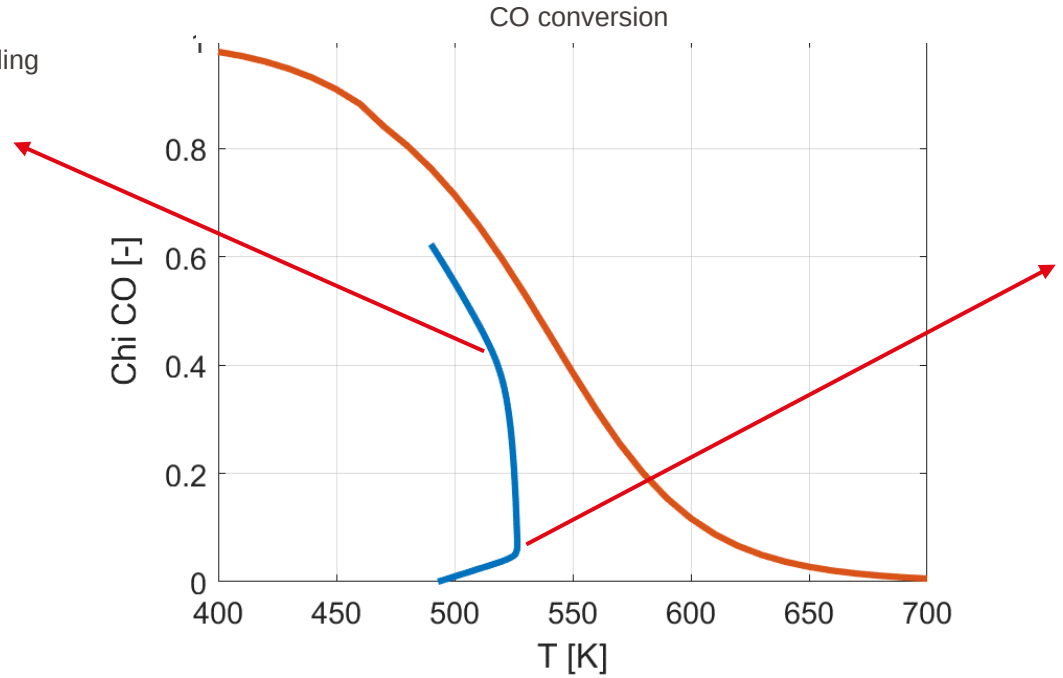
Intermediate indirect cooling

Cooled reactor





Temperature profiles



Reaction proceeding while cooling

Reaction hotspot (can be avoided with larger heat exchange)

Better performing reactor (less volume needed) but more complex

Methanol synthesis: new perspectives

- Possible new technologies:
  - Multistage reactors
  - Sorption- enhanced synthesis
  - In situ separation of products