Karlsruher Institut für Technologie

Production and conversion of liquid fuels and hydrogen from biomass and natural gas using micro-reactor technology

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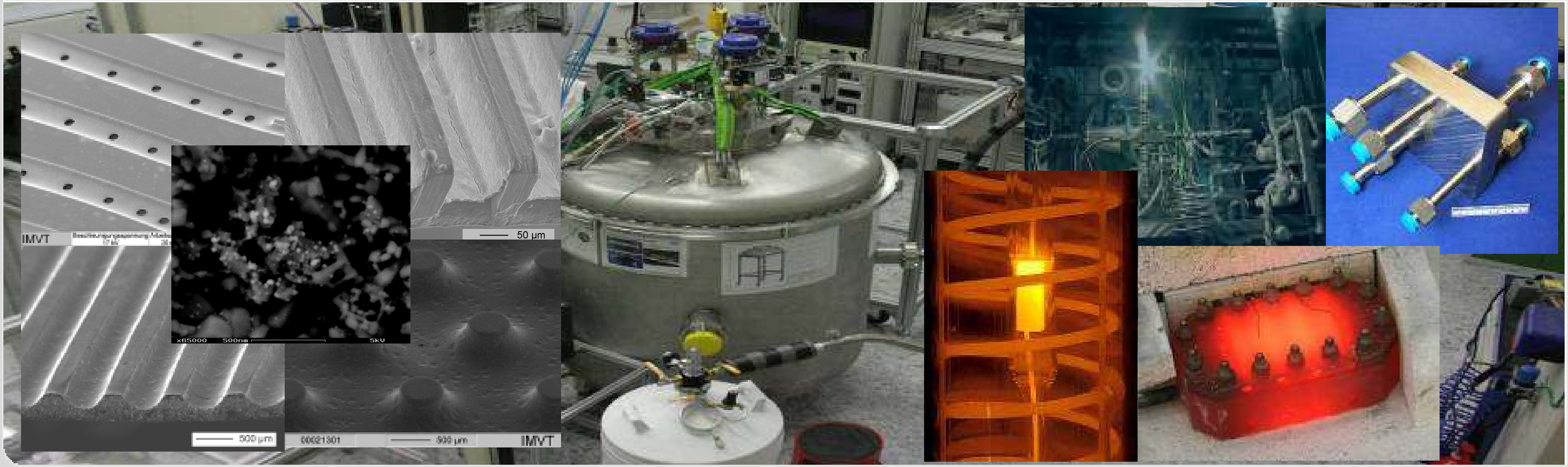
Institute for Micro Process Engineering / Group Chemical Micro Process Engineering 1

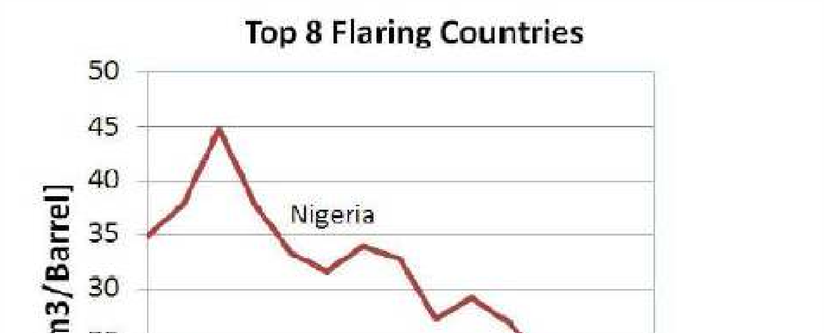


Contents

- Motivation
- Methods of catalyst application
- Fuel routes and current projects
- Reactor design for lab-scale testing
- **Applications and results from laboratory**
- Scale-up / feasibility
- Conclusion

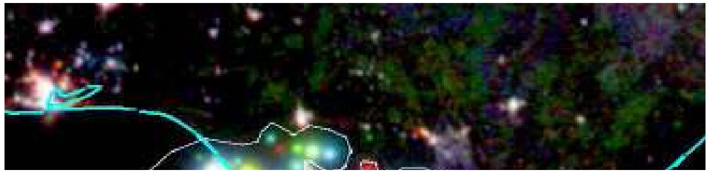
Motivation

- Flexible and compact systems for fuel production are needed worldwide for application to



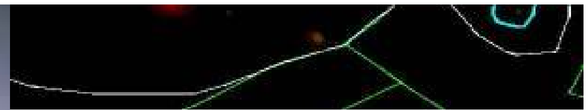
off-shore stranded (flared) natural gas

~ 0,04 m^3(gas)/l(oil)



A own tentative LC analysis shows 3% increase in net energy and a possible reduction of CO_2 on-site of about 40% with a micro-GTL system

C. D. Elvidge, Energies 2, 595 (2009).



Satellite photo of Nigeria showing gas flaring

Flaring on a oil platform

Motivation

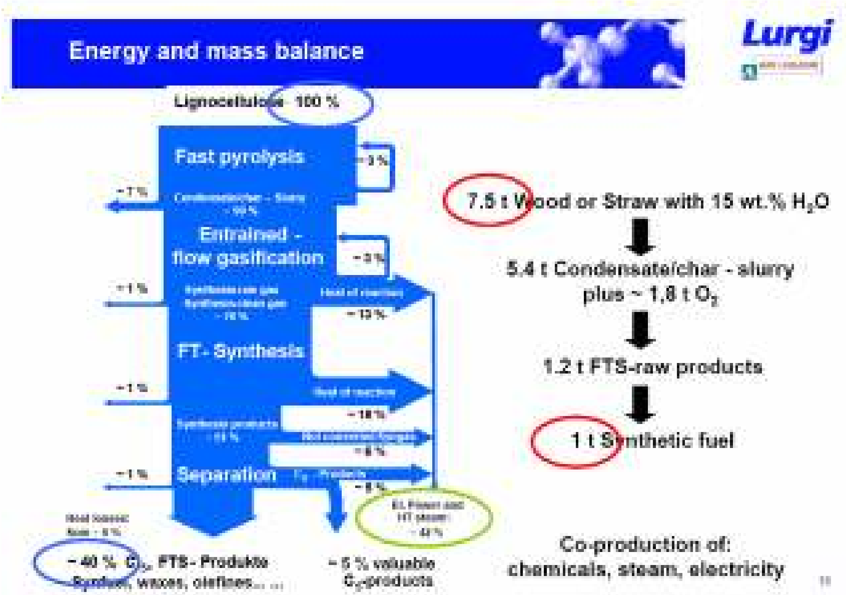
- Flexible and compact systems for fuel production are needed worldwide for application to

Virginia farmland

Straw as source

small scale biomass gasifiers

- minimize space (nicely fit into environment)
- cope with different feed (waste, straw etc.)
- competitive with large scale synthesis



http://www.greencarcongress.com/2008/12/air-liquide-mov.html

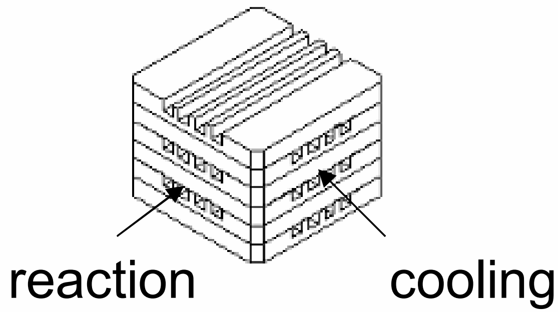
Motivation

- Microreactors allow the control of fast, highly energetic reactions
  - due to good heat transfer

    in the wall: λ/s is not limiting

    in the fluid: laminar => *Nu* = const.

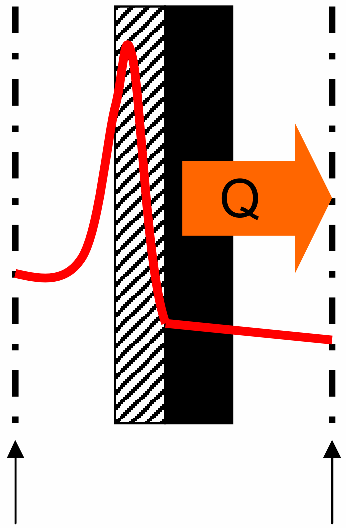
    $\Rightarrow \alpha \sim d^{-1}$



  - due to absence of

    mass transfer limitations

    (diffusion length is small)



- BUT: A low specific loading with catalyst

  => High reaction rates are necessary

  to avoid manufacture costs consequences

  => chance for preventing new and highly active

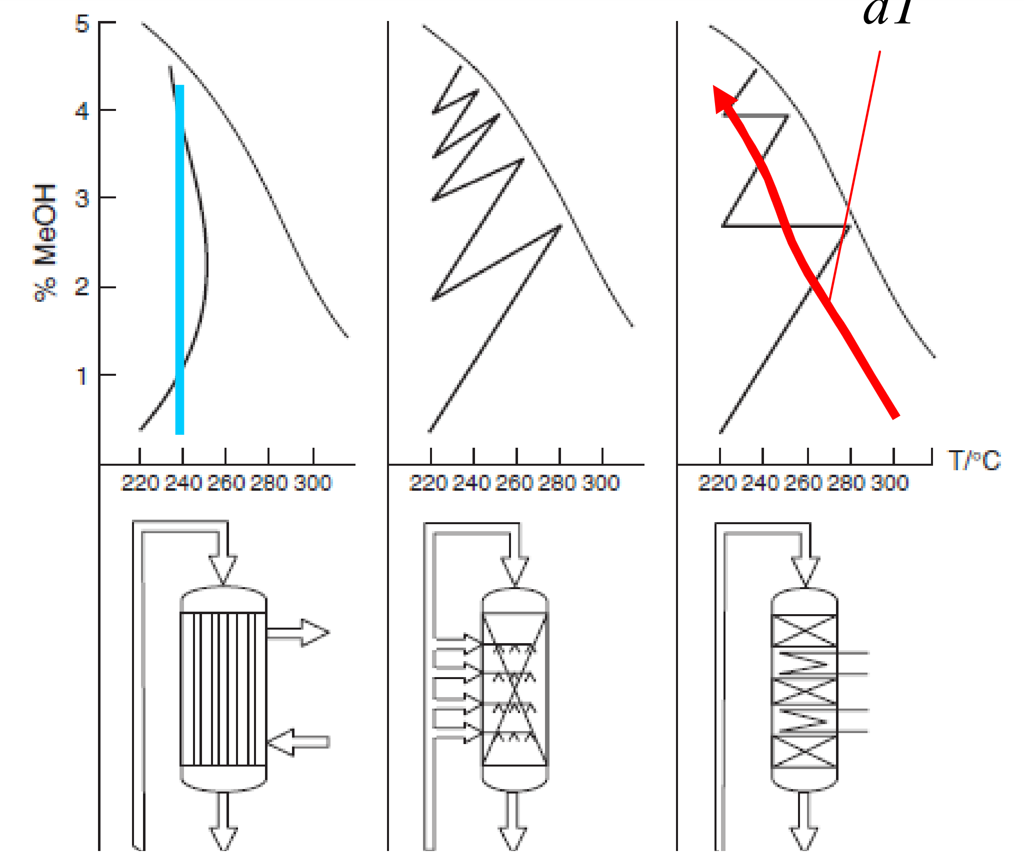
  catalysts of deactivation
- Easy control of performance / conversion at changing feed

Motivation

- A optimized falling temperature profile can be established for exothermic fuel synthesis

Isothermal **Optimum trajectory:** $\frac{dr(X)}{dT} = 0$

$$r = k_o e^{\left(\frac{-E_A}{RT}\right)} \left(x_a x_b - \frac{x_c x_d}{K(T)} \right)$$



Hansen, J.B. and P.E. Højlund Nielsen, Methanol Synthesis, in Handbook of Heterogeneous Catalysis. 2008: Wiley-VCH

- Less heat loss due to smaller reactors

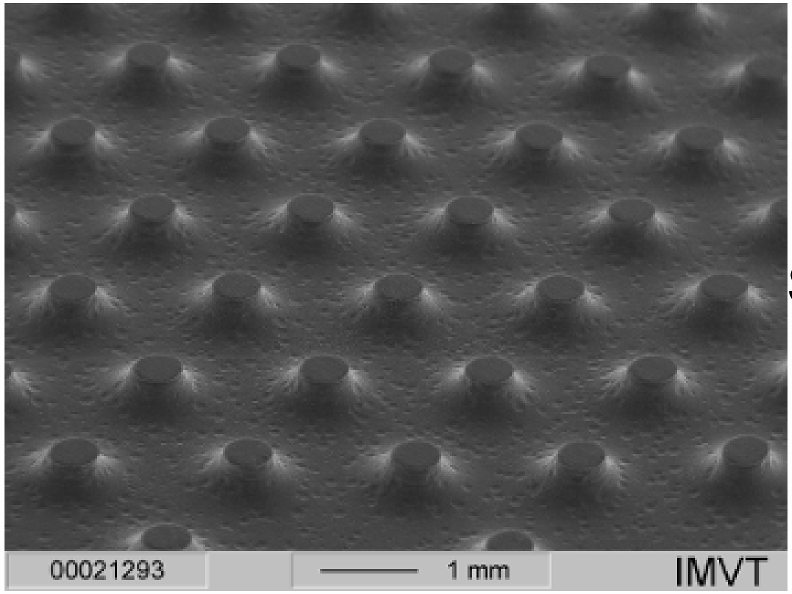
- Cooling fluid leaves the system with high temperature

$\Rightarrow$ efficient scale-down for "small scale" utilization of resources

Methods of catalyst incorporation

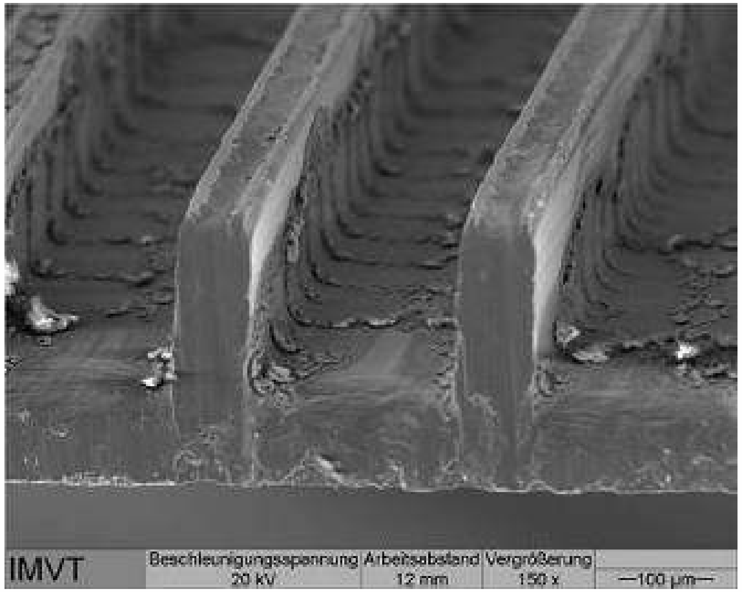
- Two different concepts

Catalyst packing („micro fixed bed“)



Comparable STY possible

Coated channel walls



Catalyst packing:

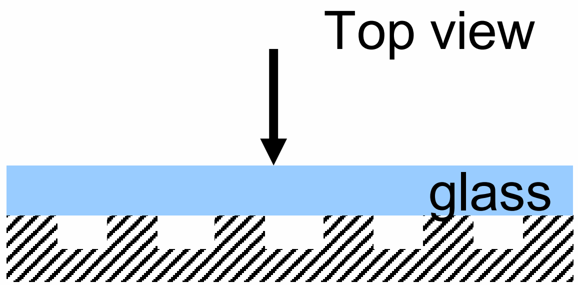
- *High catalyst amount per volume (V_{cat} / V_R up to 50 %)*
- *Conventional catalysts applicable (powder)*
- *Catalyst easy to be replaced*

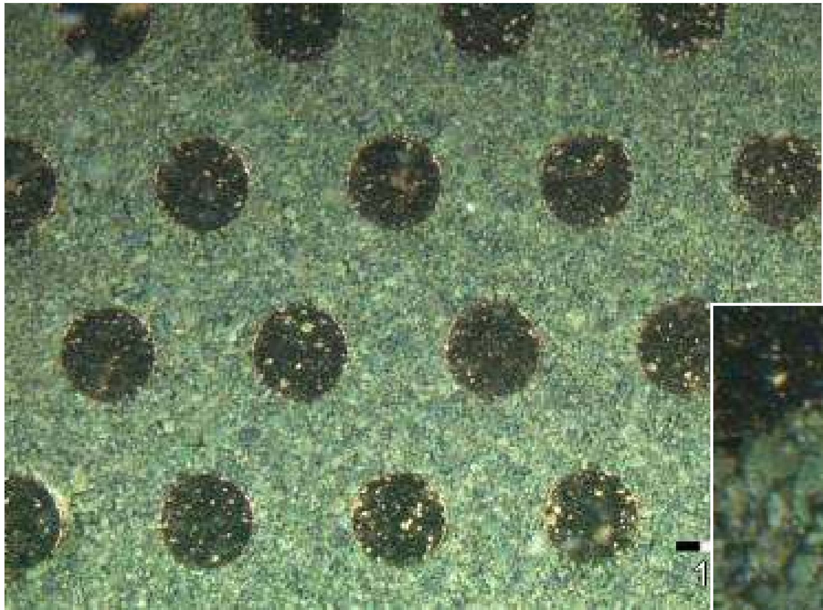
Coated channel walls:

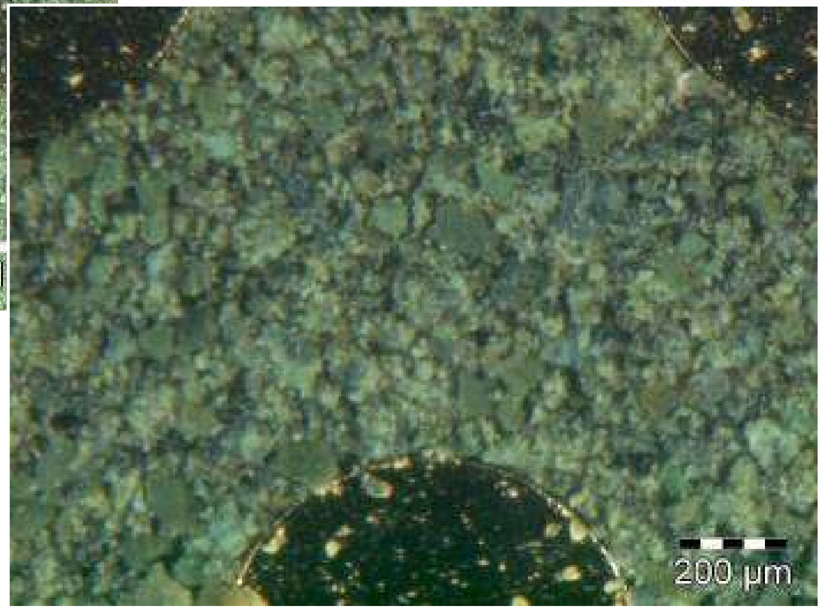
- *Excellent temperature control*
- *Suitable for highly active catalysts (>20 $kg_{Prod.}$/kg_{cat}h)*
- *Coating process to be developed (adhesion, etc.)*

Methods of catalyst incorporation

- Packed structure with catalyst mixture (Cu/Zn/Al + H-ZSM5)

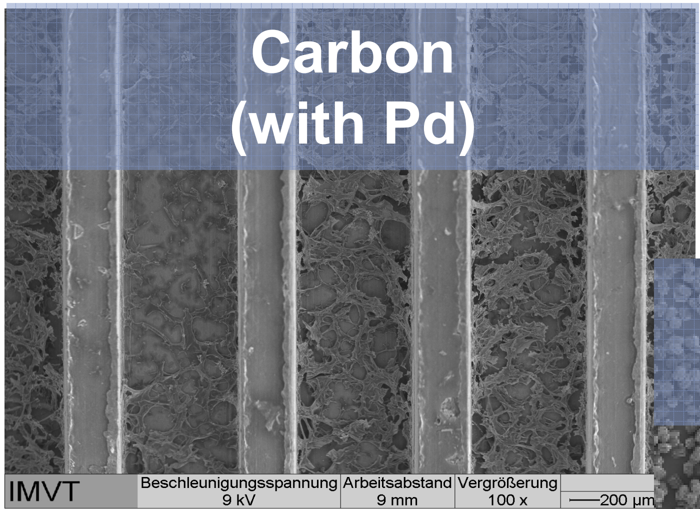


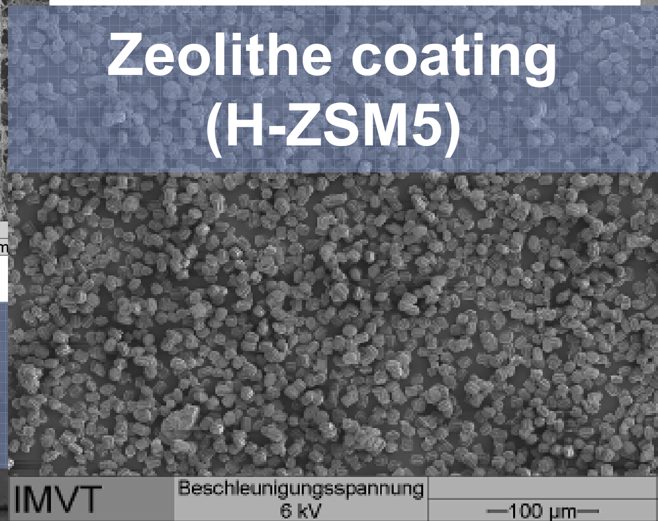


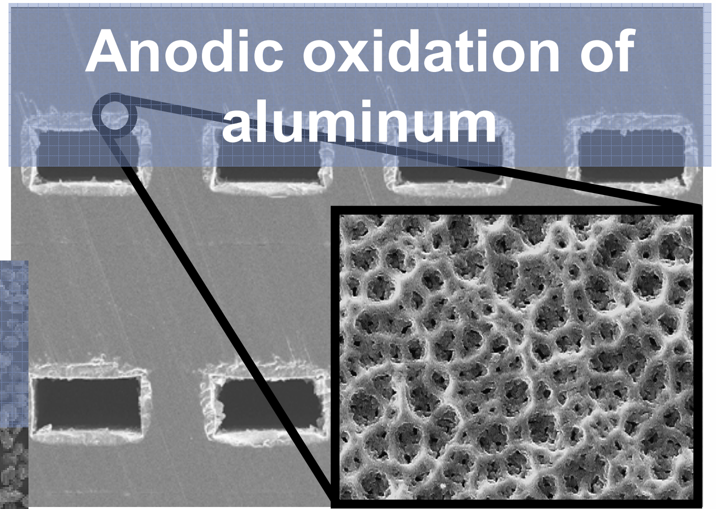


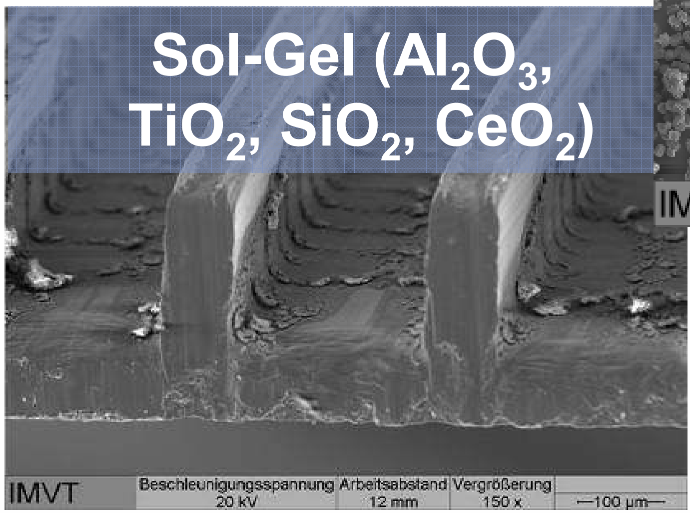
Methods of catalyst incorporation

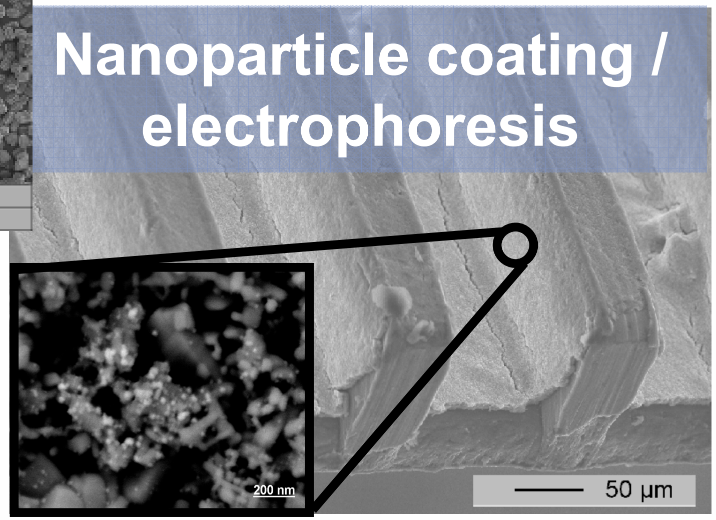
- Coatings



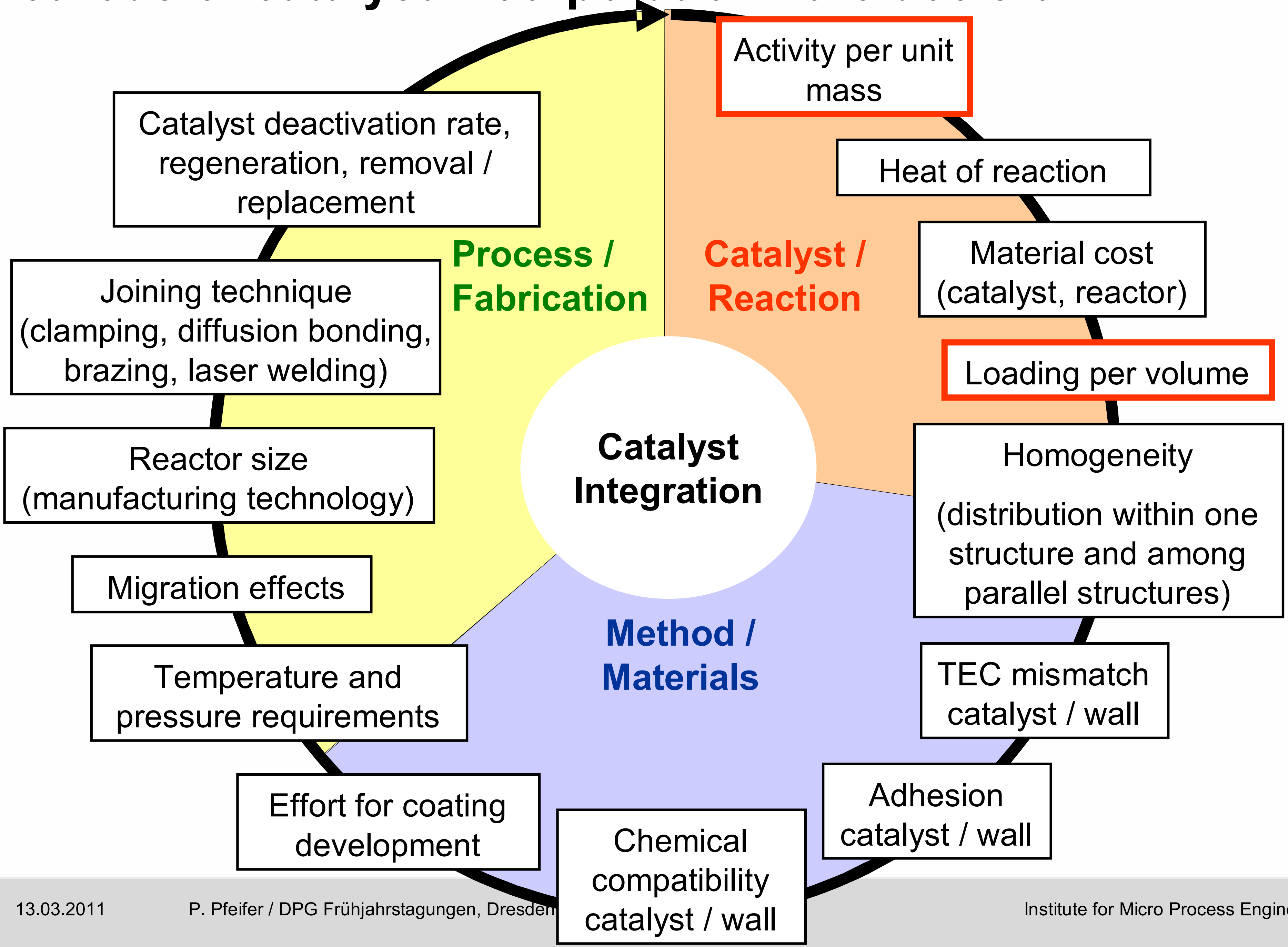




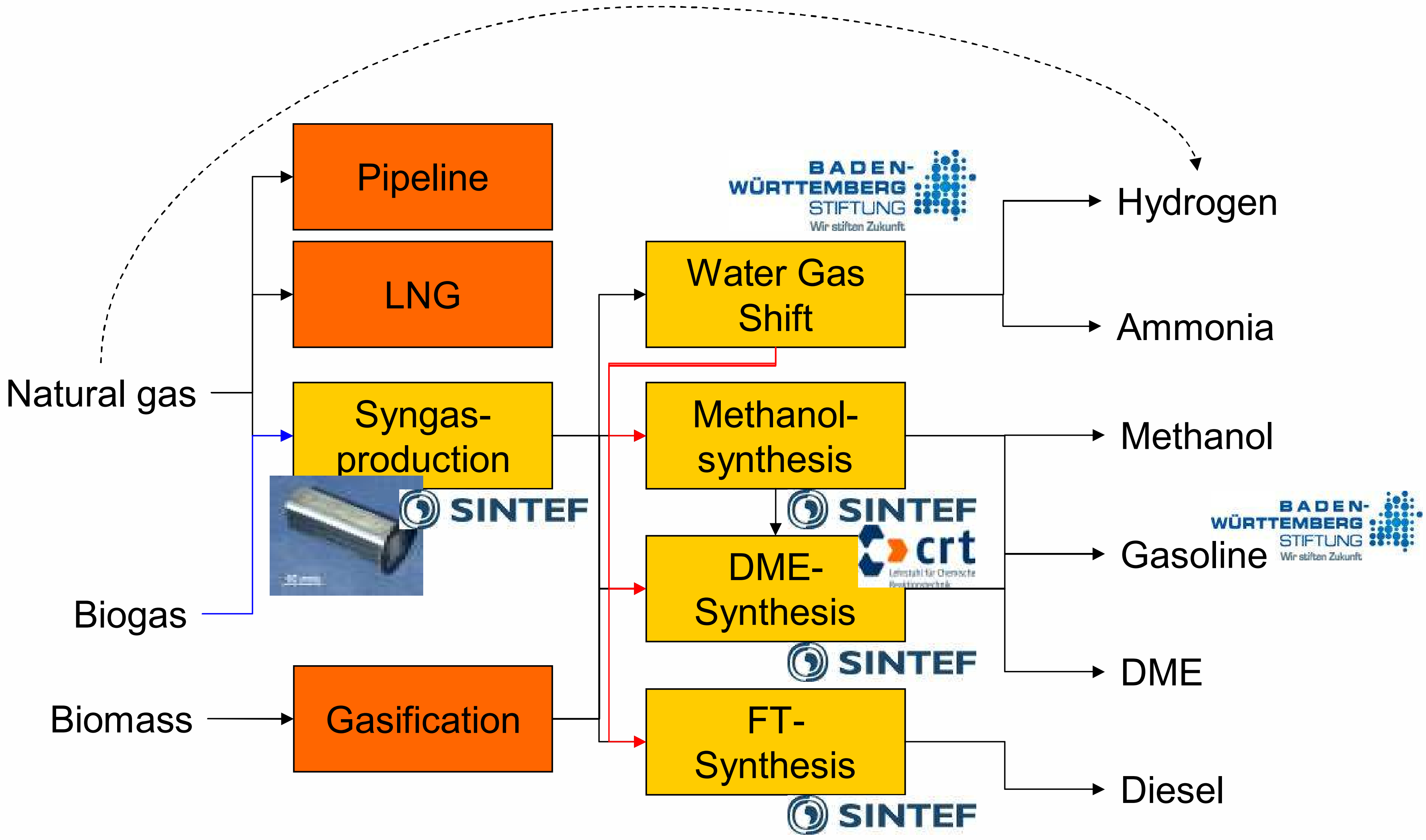




Methods of catalyst incorporation - the decision?



Fuel routes and current projects

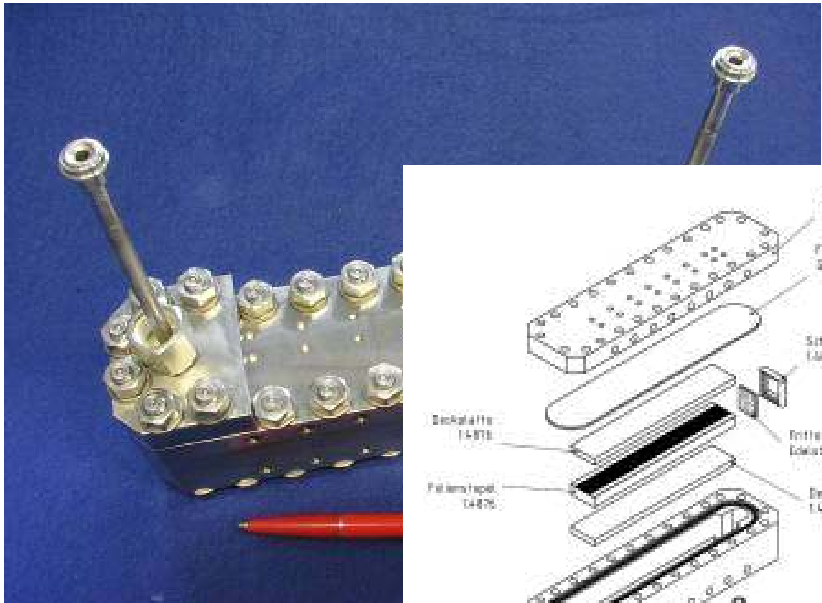


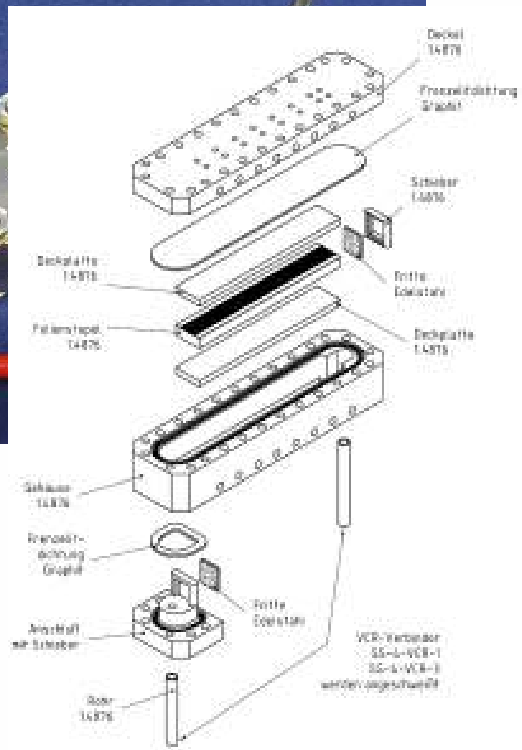
Reactor design for lab-scale testing

- Two different concepts

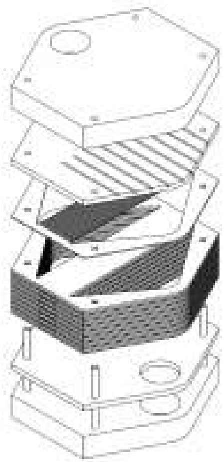
Variable structure (coating+packing)
Electrically heated

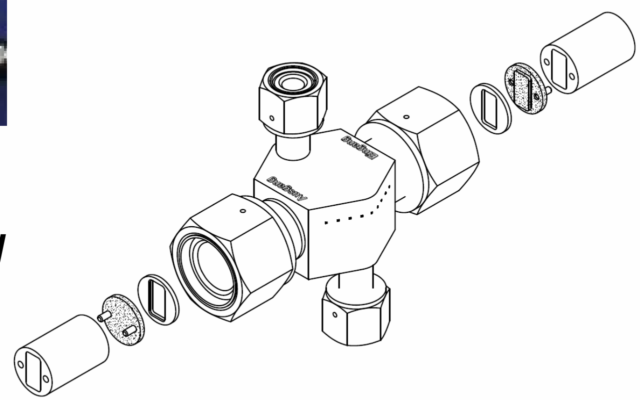
Catalyst packing
Fluidic heating/cooling





Enabling
T-gradients



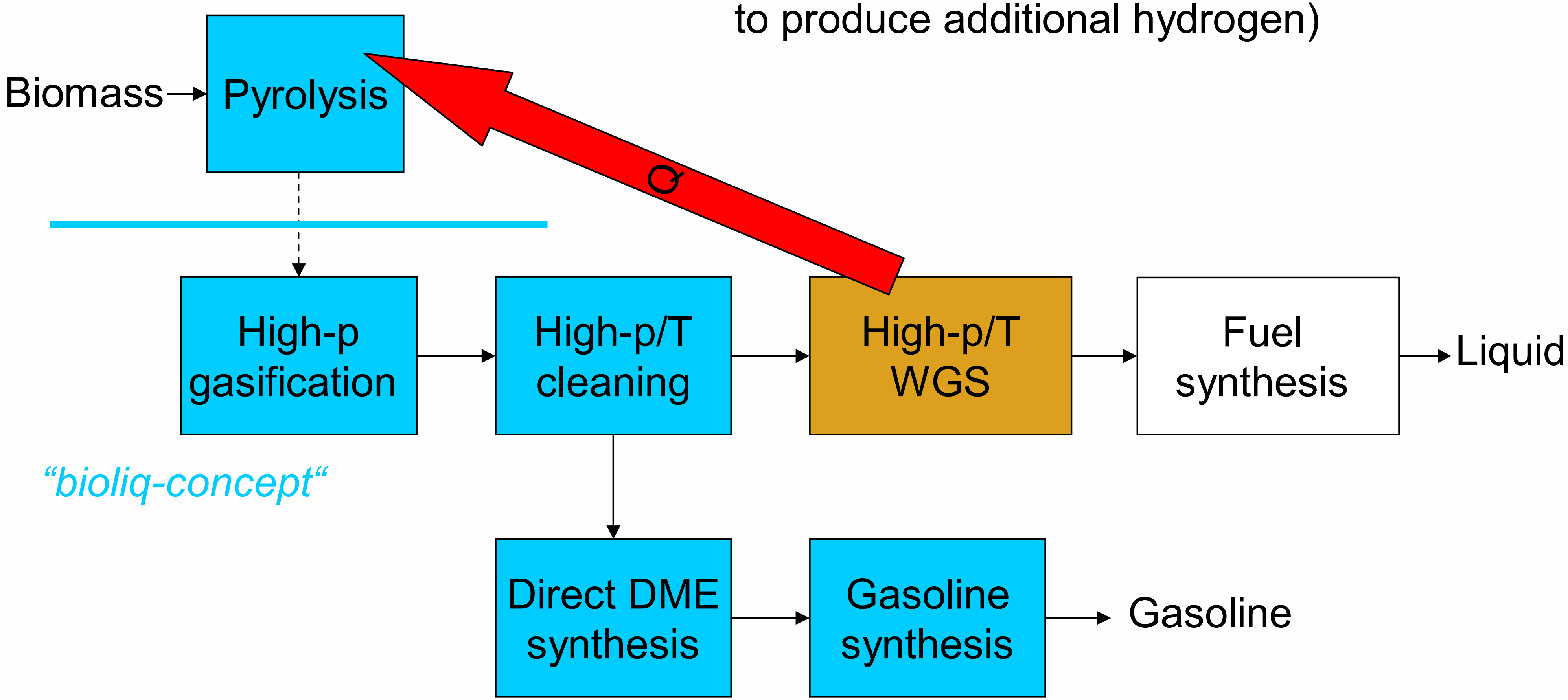


Strictly
isothermal

High-p high-T water gas shift

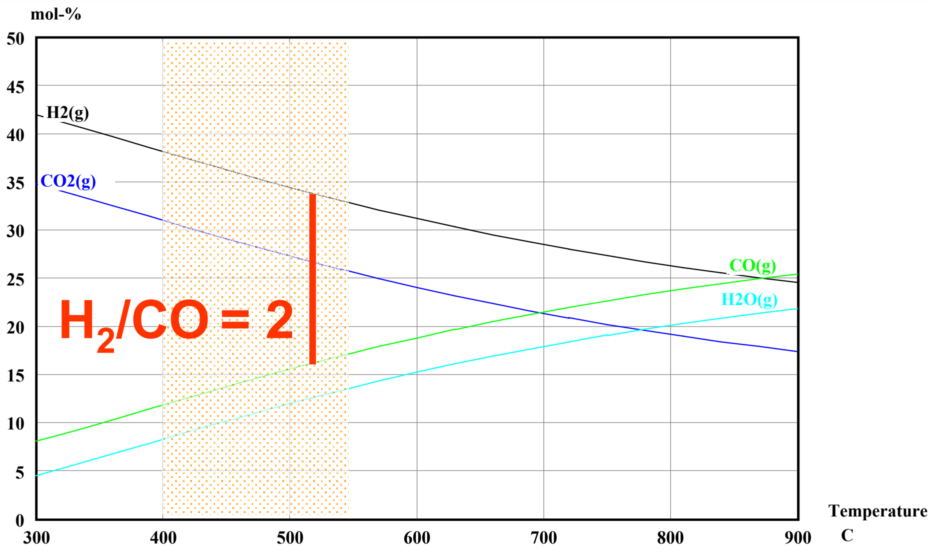
$CO + H_2O = CO_2 + H_2 + 49$ kJ/mol

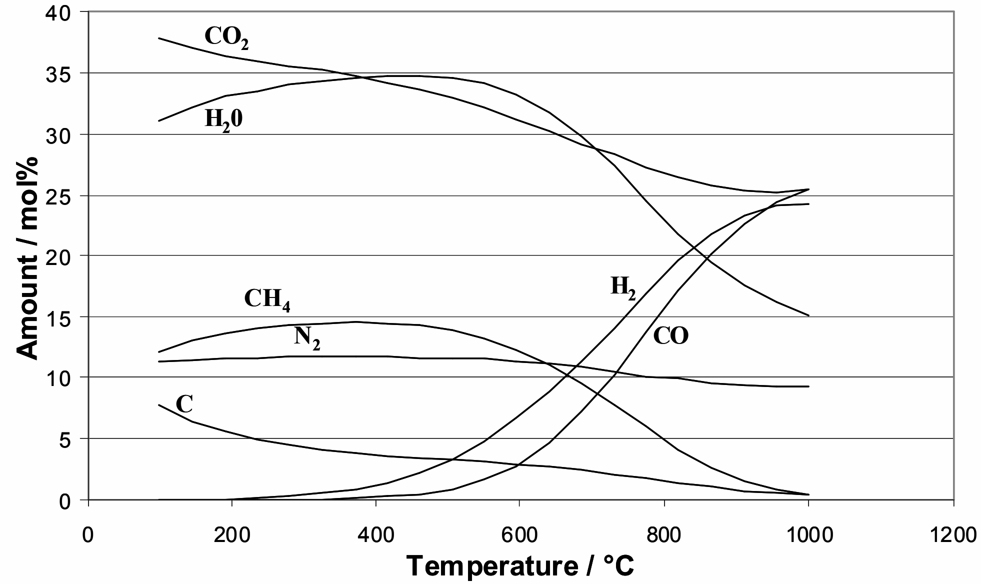
(use excess CO in the gas
to produce additional hydrogen)



High-p high-T water gas shift

Temperature region and importance of byproduct formation (thermodynamics)



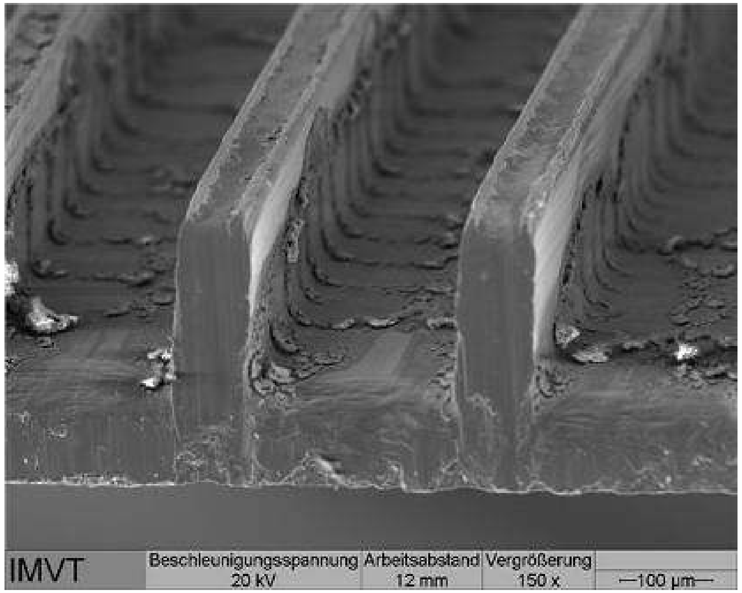


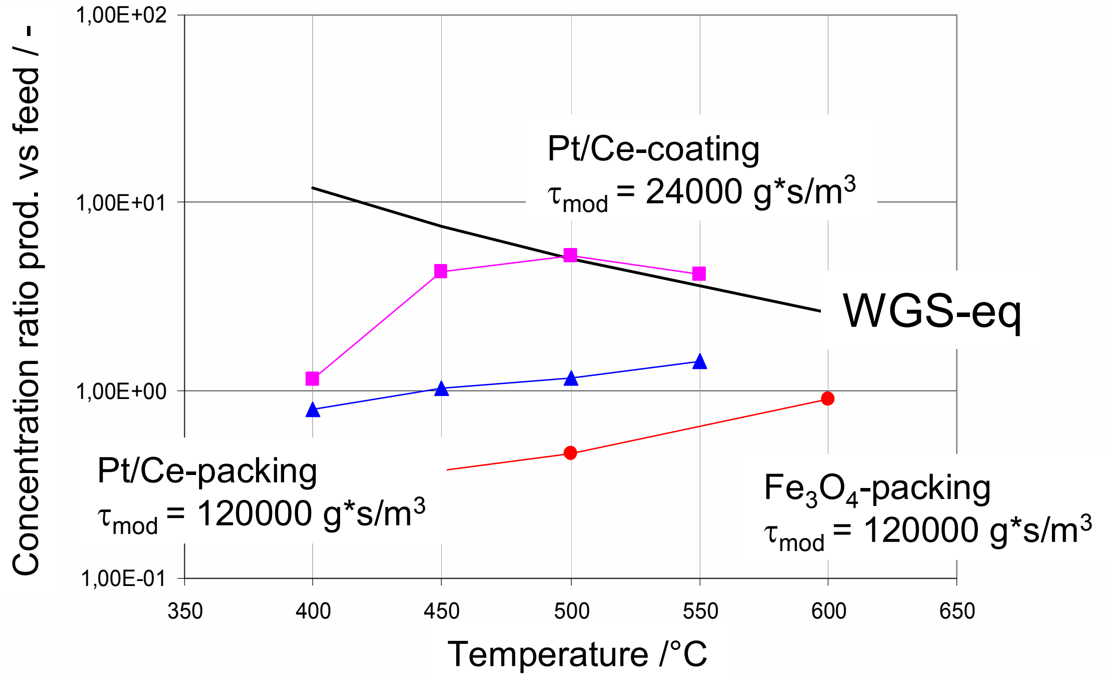
<u>Feed:</u> 32 % CO
18 % H_2
11 % CO
11 % N_2
28 % H_2O

<u>Press.:</u> 50 bar

High-p high-T water gas shift

- highly active wall coatings – 5% Pt/CeO_2 : up to 80 g_{CO}/gh

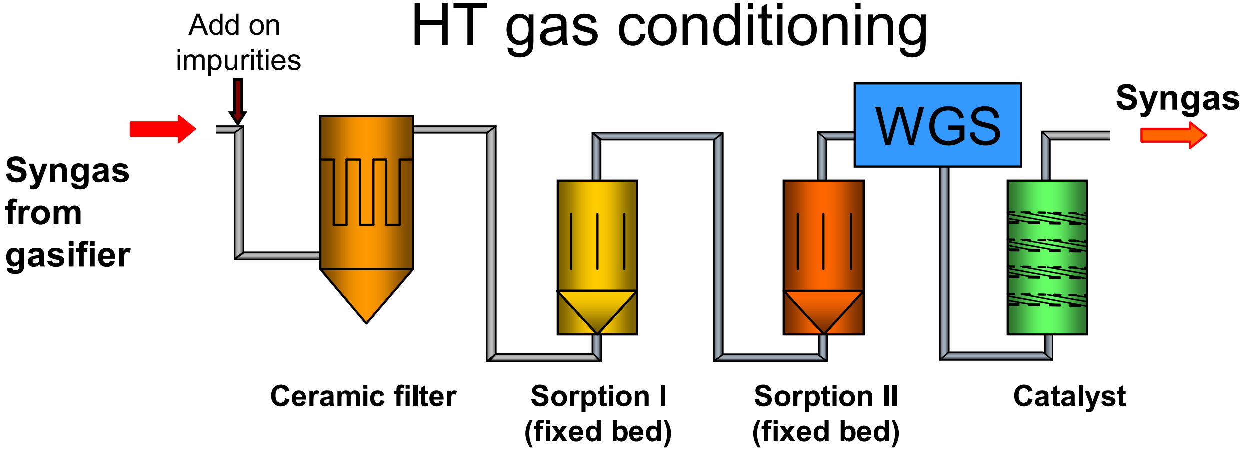




		CH_4 / Vol.%	ΣC_2+ / Vol.%
Pt/Ce/Al:	1 bar	-	-
	45 bar	2,82	0,91
Pt/Ce:	1 bar	-	-
	45 bar	2,39	0,63

High-p high-T water gas shift

HT gas conditioning



REGA Gasifier

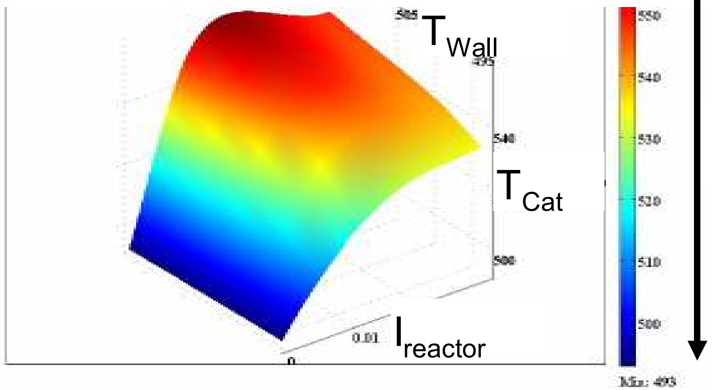
Filter Sorption I Sorption II Catalyst

WGS

Fischer-Tropsch synthesis

Simulated temperature distribution in a fixed bed reactor

assuming undiluted catalyst (d = 3 cm)



Reactor	Diluted fixed bed				Micro packed bed					
Catalyst	A	A	A	B	A	A	B	B	B	B
Temperature [°C]	210	210	210	210	215	215	210	215	225	240
Pressure [bar]	20	20	20	20	20	20	20	20	20	20
GHSV [ml g^{-1} h^{-1}]	11000	10600	5600	11700	13900	8750	12300	14400	14400	20548
Contact time [s]	0,33	0,34	0,64	0,31	0,25	0,41	0,29	0,25	0,25	0,18
CO-conv [%]	47	47	74	47	47	72	47	51	72	83
selC5+ [%]	84	84	85	85	83	86	84	83	84	82
selCH4 [%]	9	8	7	8	9	8	9	9	9	12
HCrate [g g^{-1} h^{-1}]	1,0	1,0	0,8	1,1	1,3	1,3	1,1	1,5	2,1	3,4

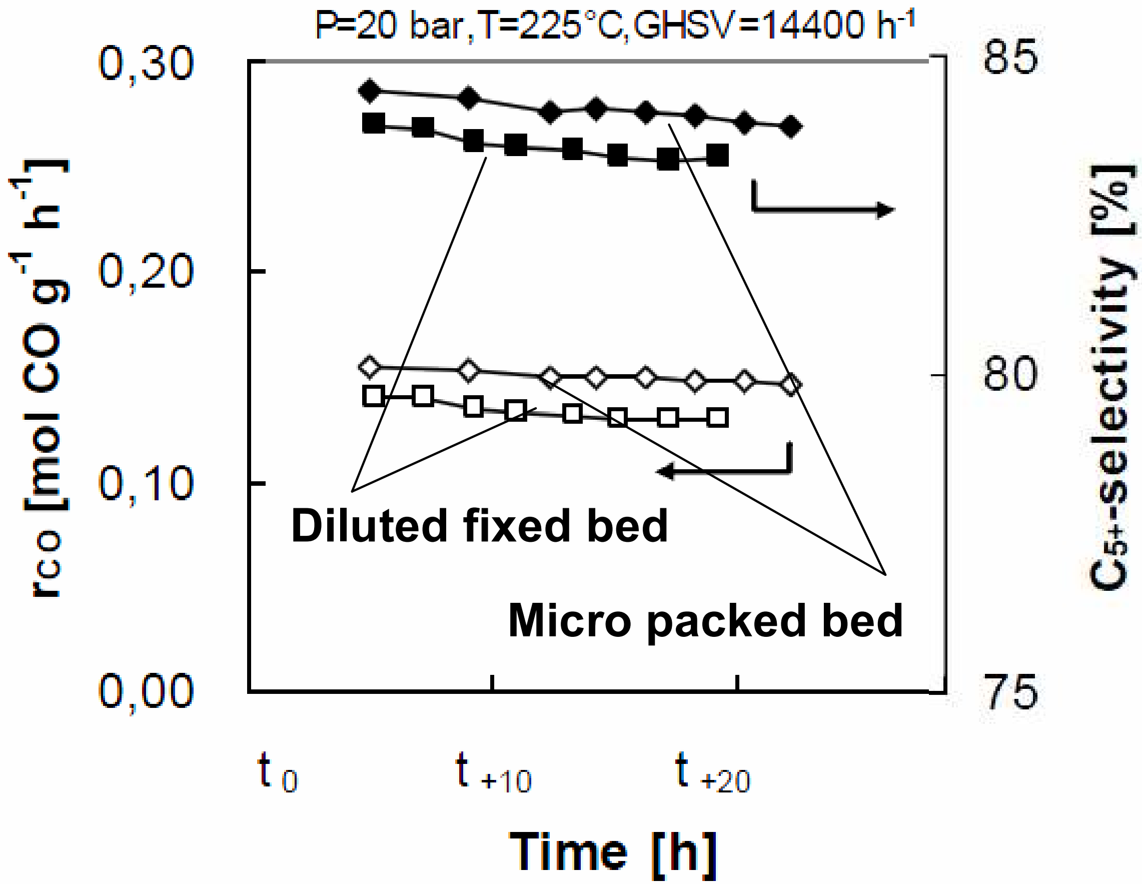
A: 20Co0.5Re on Al_2O_3

B: 20Co0.5Re5Ni on Al_2O_3

up to 50 % increase in space time yield possible (catalyst mass basis)
or <u>at least</u> **reactor size reduction by 90 %**

Fischer-Tropsch synthesis

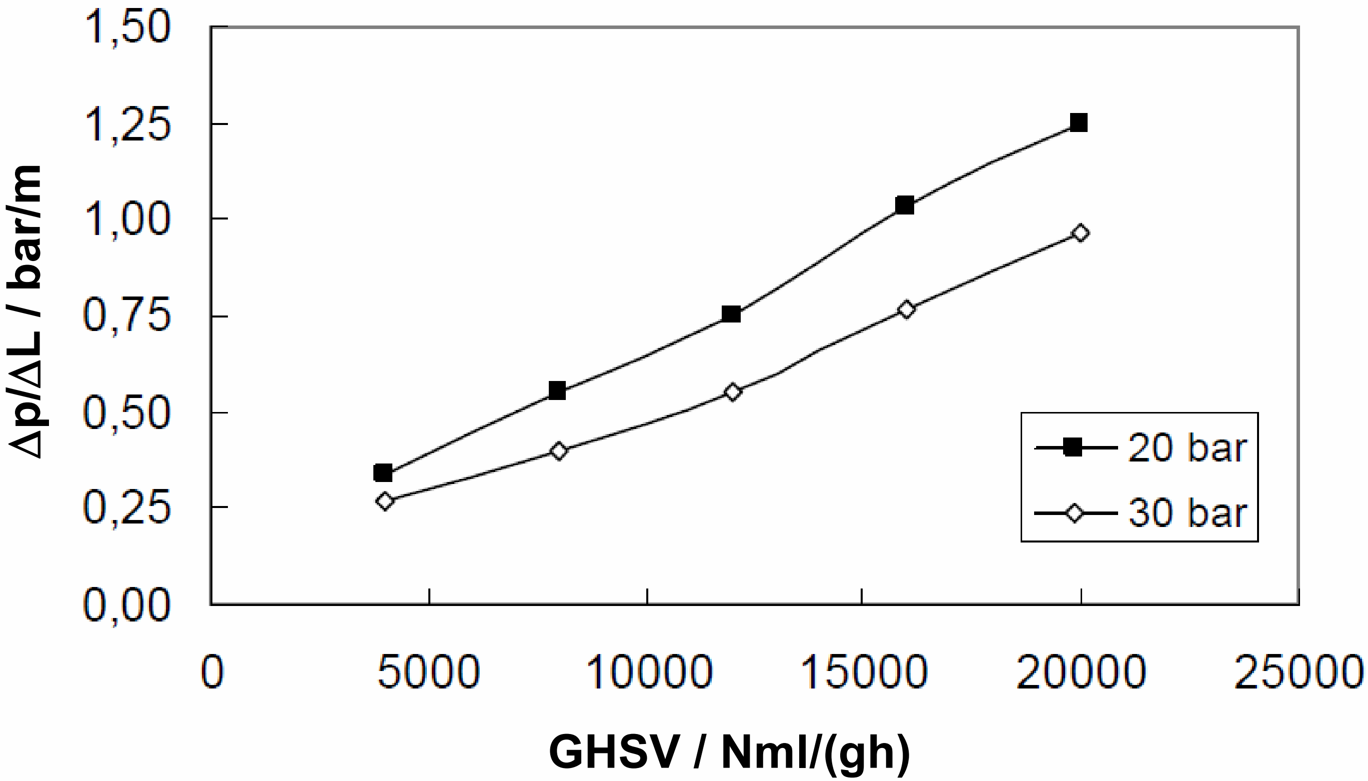
- Deactivation performance compared to conventional technology



=> No deactivation due to hot spots or wall effects !

Fischer-Tropsch synthesis

- Pressure drop at small particle size?



=> Negligible even at high bed length!

Myrstad et al., Catalysis Today 147S (2009) 301–S304

New catalysts for direct DME synthesis

$CO + 2H_2 \rightleftarrows CH_3OH$ $\Delta H_R^{298} = -90{,}4$ kJ/mol

$2CH_3OH \rightleftarrows CH_3OCH_3 + H_2O$ $\Delta H_R^{298} = -23{,}0$ kJ/mol

$CO + H_2O \rightleftarrows CO_2 + H_2$ $\Delta H_R^{298} = -41$ kJ/mol

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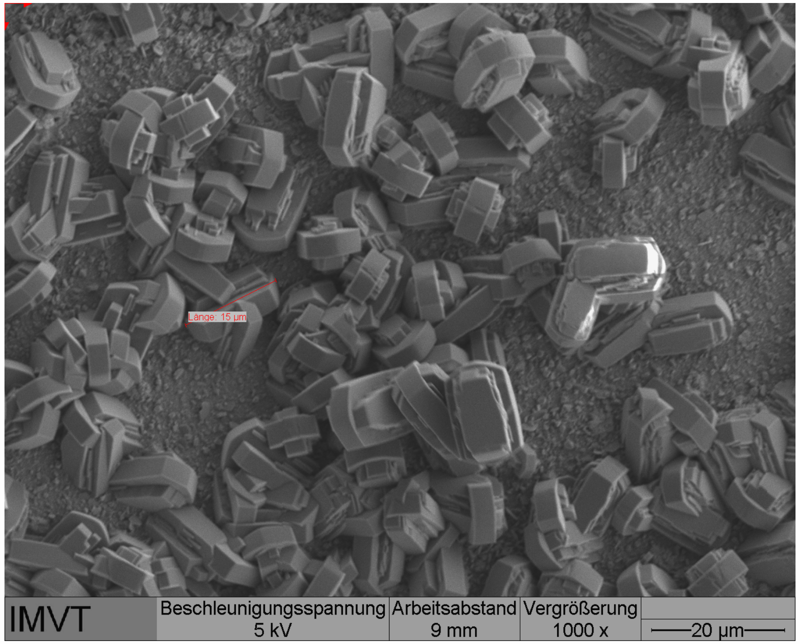
$3CO + 3H_2 \rightleftarrows CH_3OCH_3 + CO_2$ $\Delta H_R^{298} = -244{,}8$ kJ/mol

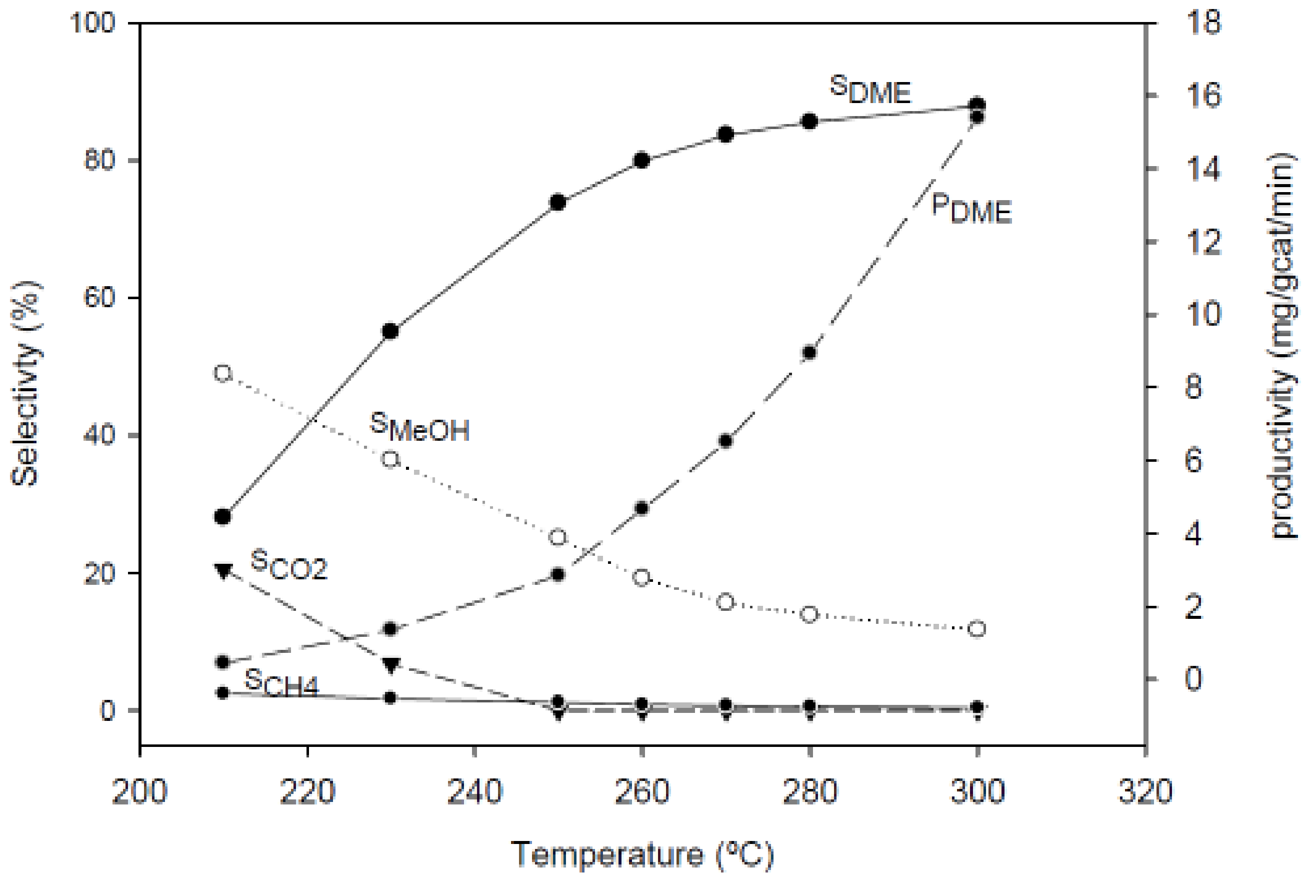


Coating with H-ZSM5 (dehydration)

New: Core-shell and double layer catalysts

DME direct synthesis

- Results from Cu/Zn/Al + γ-Al_2O_3



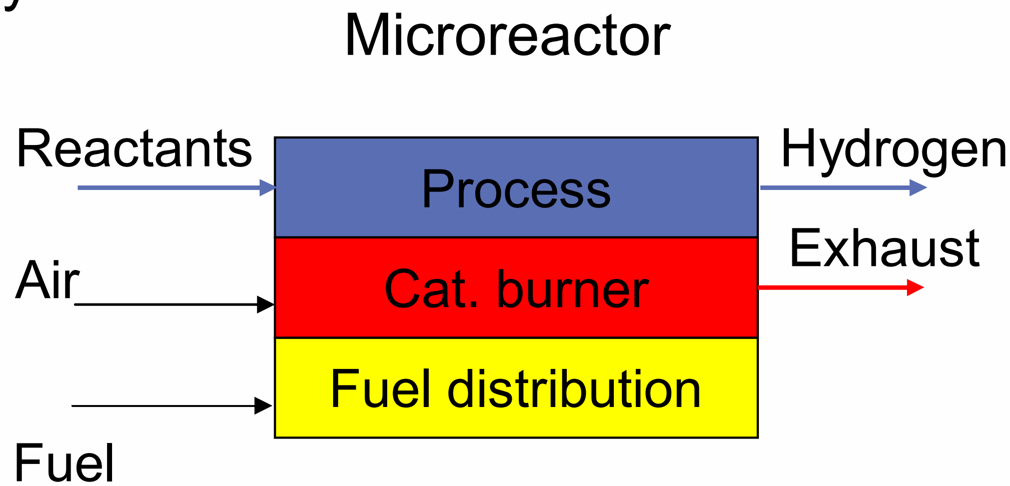
Feed: 42 % H_2
42 % CO
5 % CO_2
Rest N_2

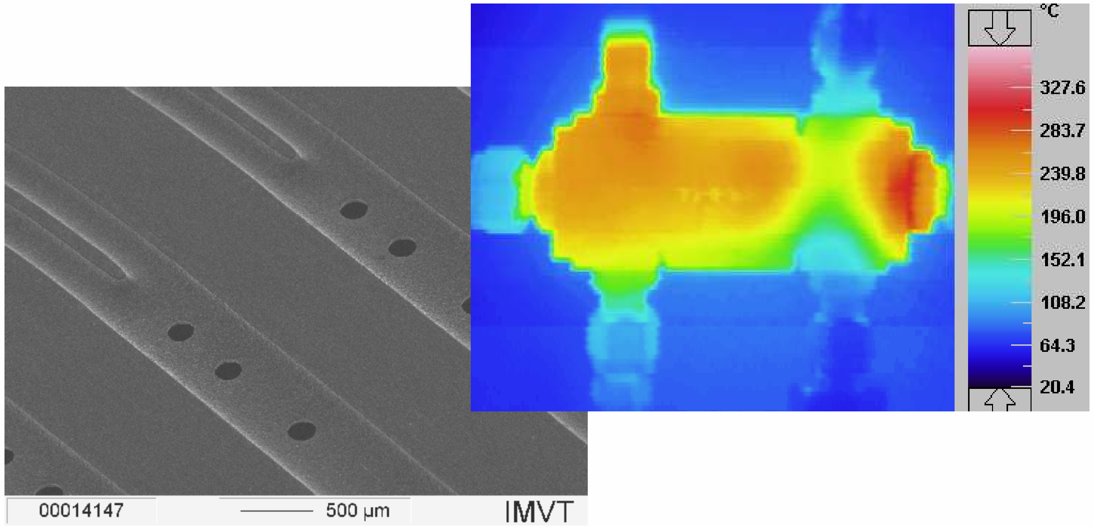
50 bar
H_2:CO = 1
SV = 15000 Nml/g_{cat}h

Hayer et al., Chem. Eng. J. (2010 online)

Hydrogen Production Processes

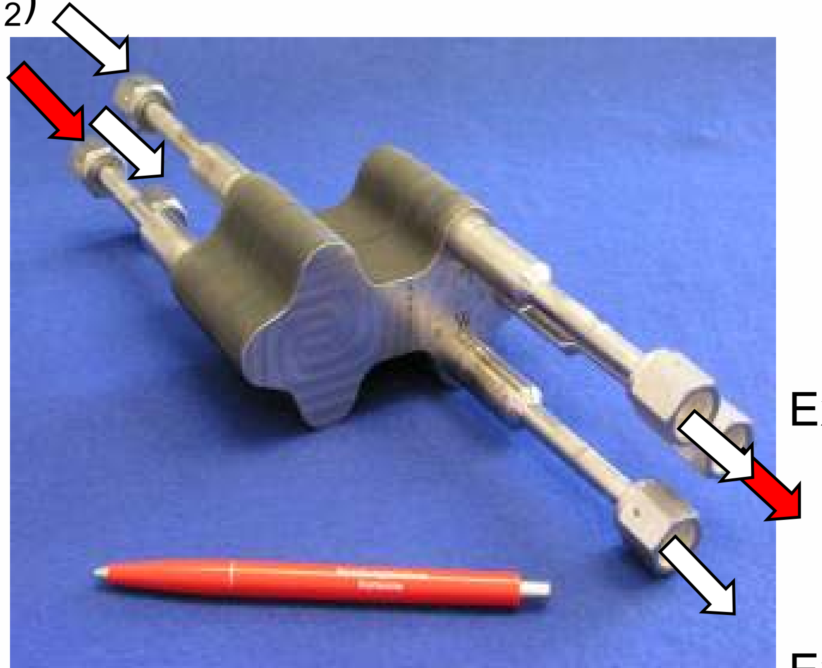
- Effectively coupling endo- und exothermic processes for increasing efficiency





Hydrogen Production Processes

- Example for a reactor with integrated combustion



- Future step: Microreactors with integrated membrane for in-situ hydrogen separation of H_2 => synergies through

  1) Increase eq-conversion / increase of kinetics

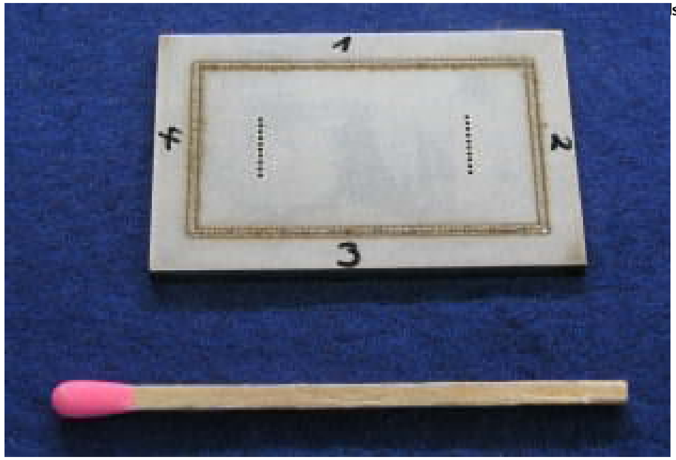
  2) Stabilization of the membrane

Membrane integration

- Foil concept < 400°C

10 micro channels
(500 µm x 300 µm x 20 mm)

Foil obtained from CETH, Paris

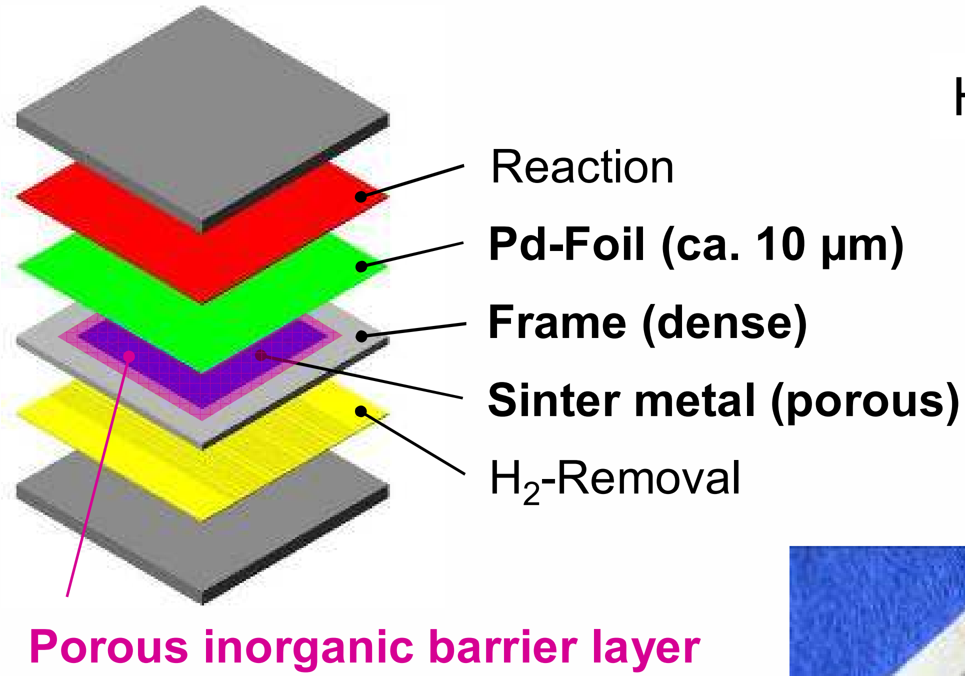


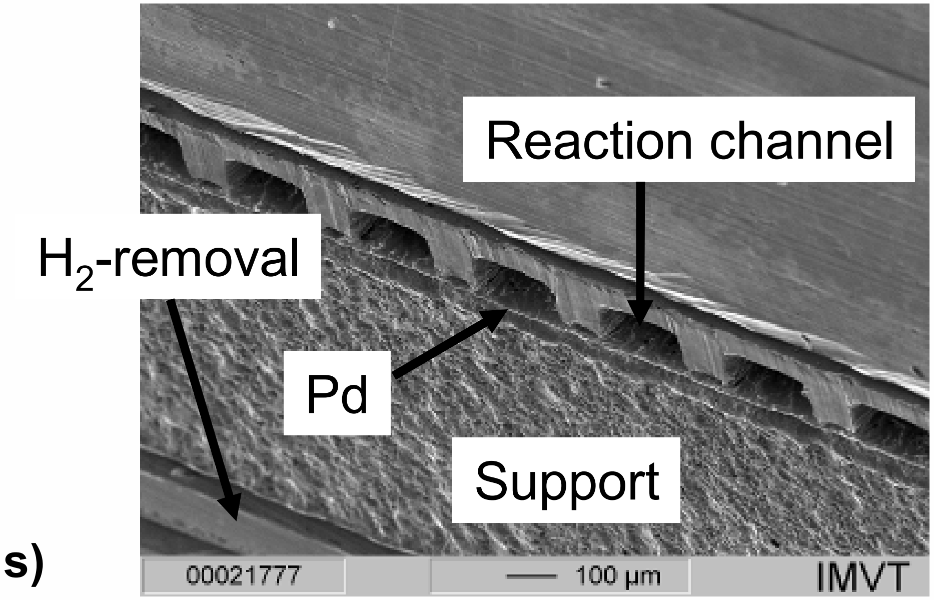
Laser welded unit
(Pd foil size: 40 x 27 mm²)

Test arrangement (elec. heated)

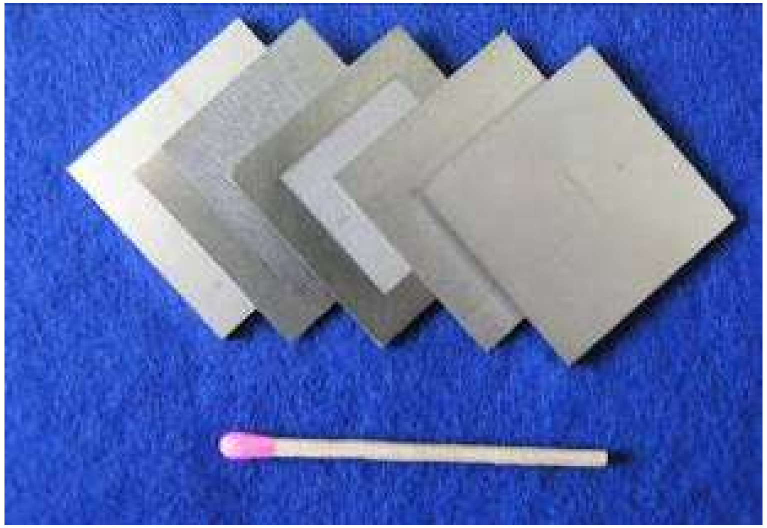
Membrane Integration

- Foil concept > 400°C



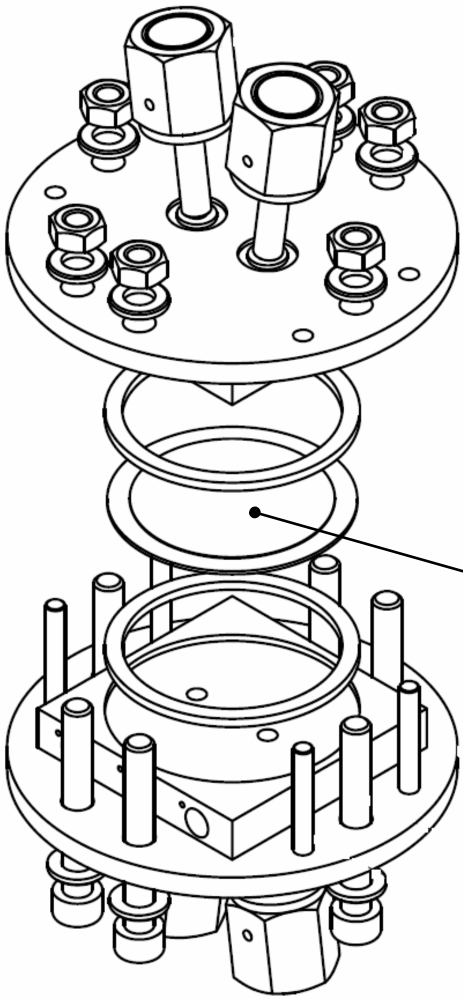


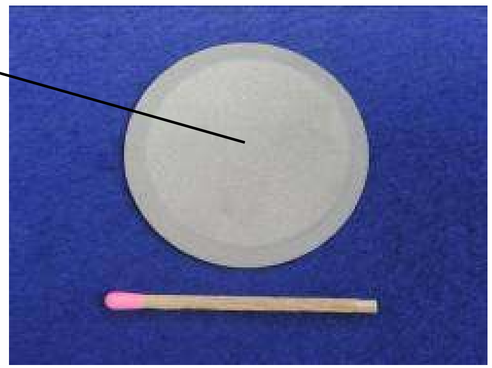
Diffusion bonded foils



Membrane Integration

- Coating concept > 400°C

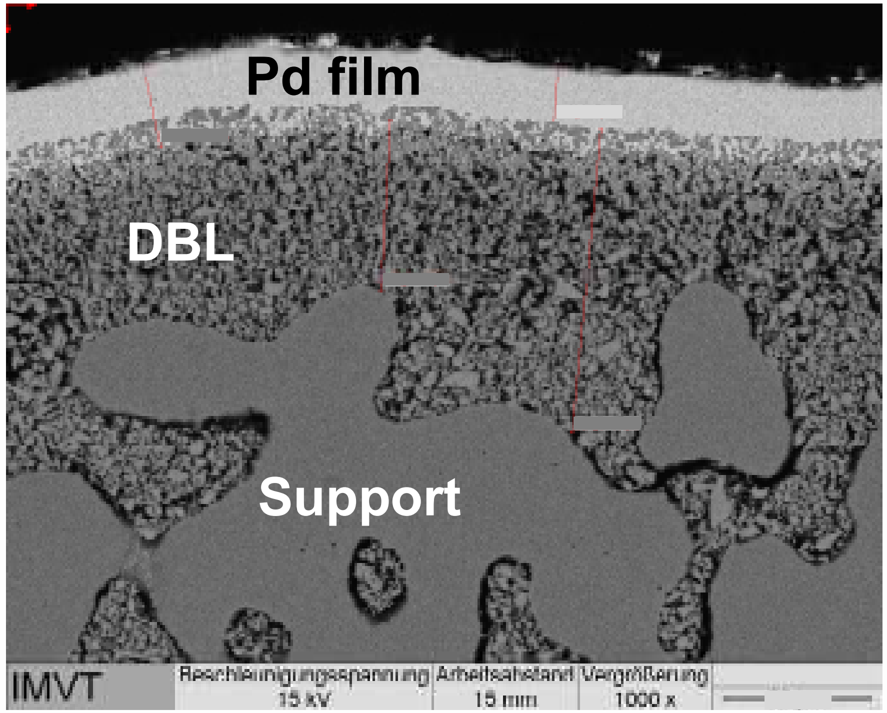




Test arrangement (electrically heated)

Pd thickness 5-15 µm

Pd penetrates few microns into DBL



Example: Pd by electroless plating

Scale-up / feasibility

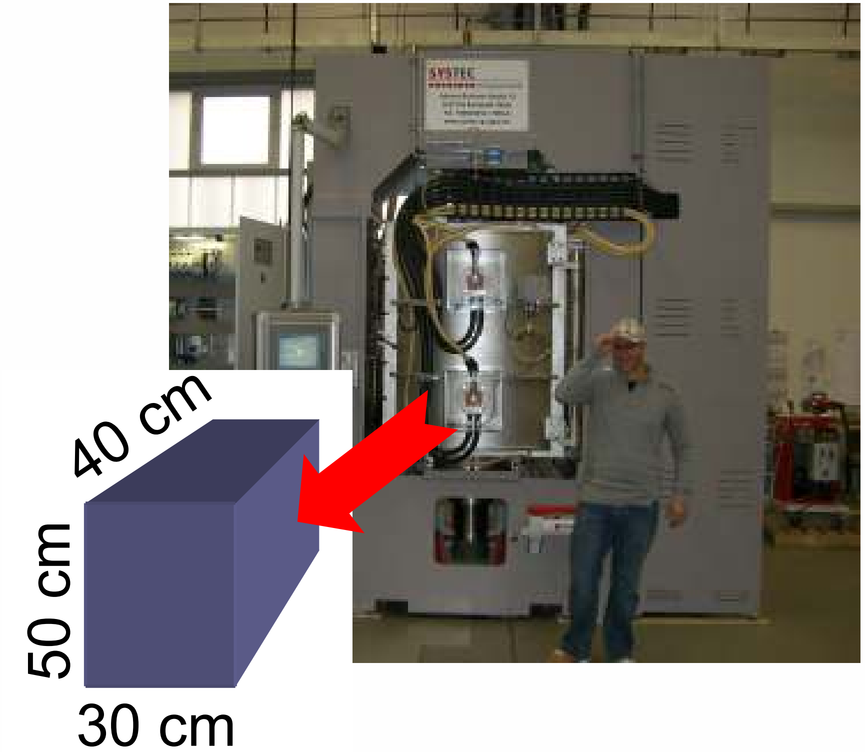
Scale-Up

Scale today

2 g catalyst / lab

200 g catalyst / tech

Scale in 2011



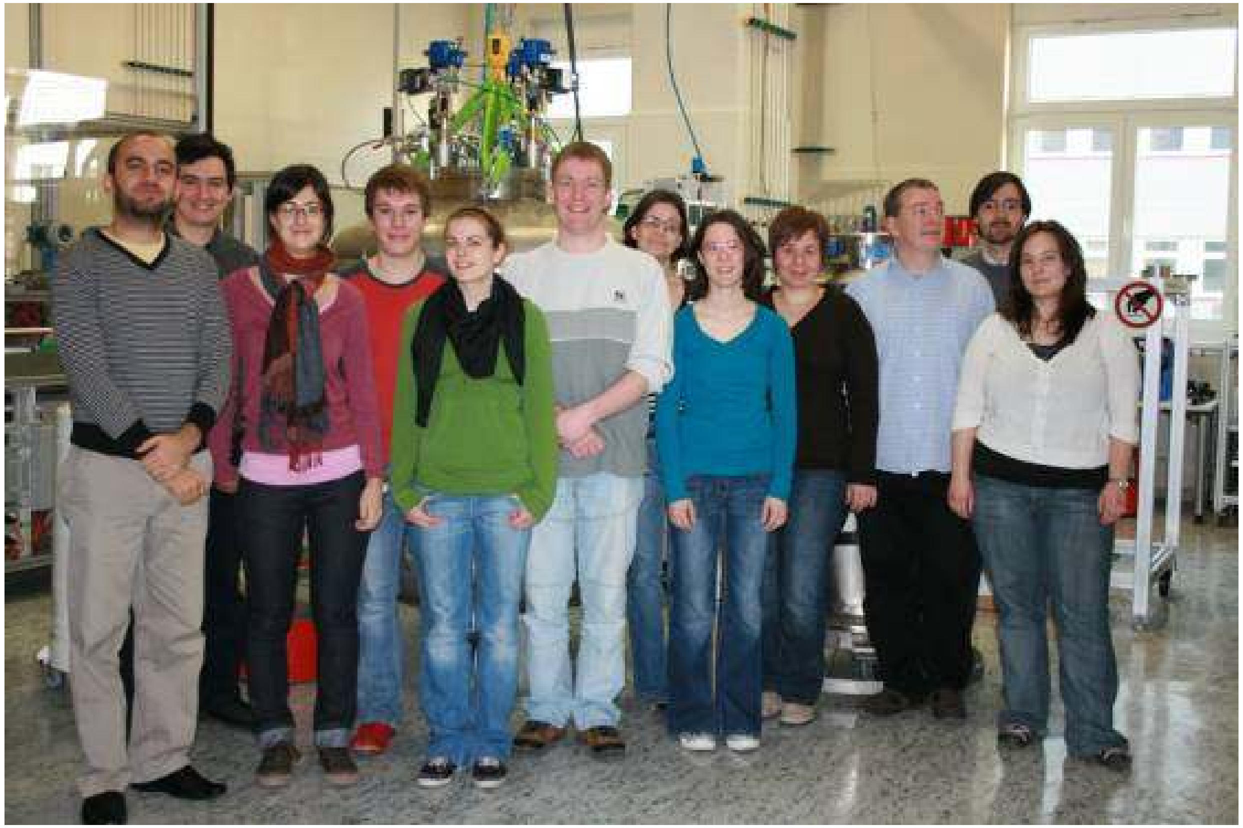
~ 7-30 kg catalyst
for pilot scale FT-synthesis

Conclusions

- Advantages like temperature profiles for fuel synthesis
- Reactor designs, catalysts and possible applications
- New approaches with highly active catalysts
- Compact systems feasible
- Scale-up feasibilities – current state is promising

Pearl GTL project
www.arabianoilandgas.com

Thank you for your attention



and thanks to my team….