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Gas Technology Conference
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Fischer-Tropsch synthesis in a microstructured reactor

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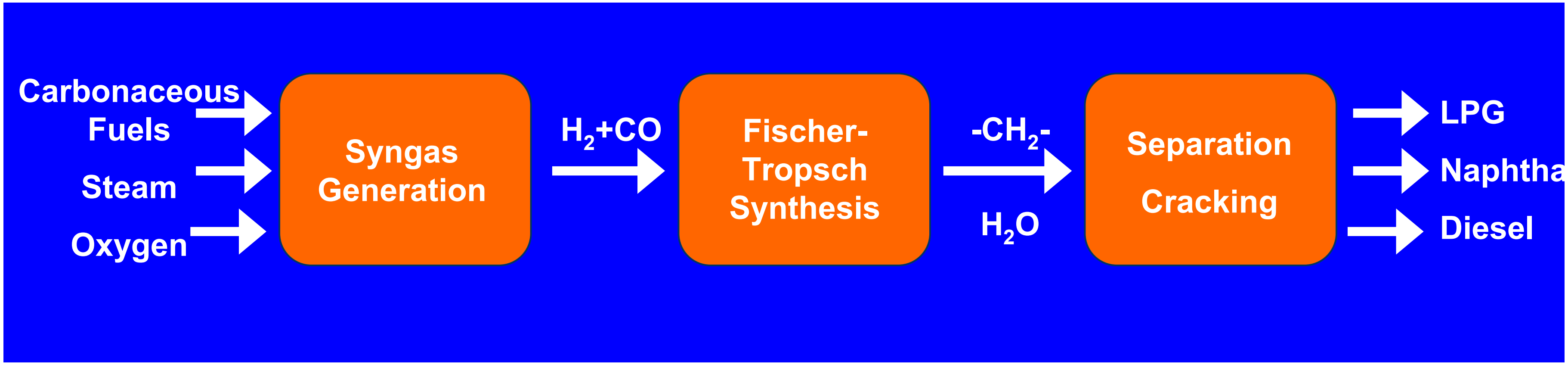
Fischer Tropsch Process



Oryx GTL, Qatar/Sasol: 34.000 bpd

Pearl GTL, Qatar/Shell (2011): 140.000 bpd

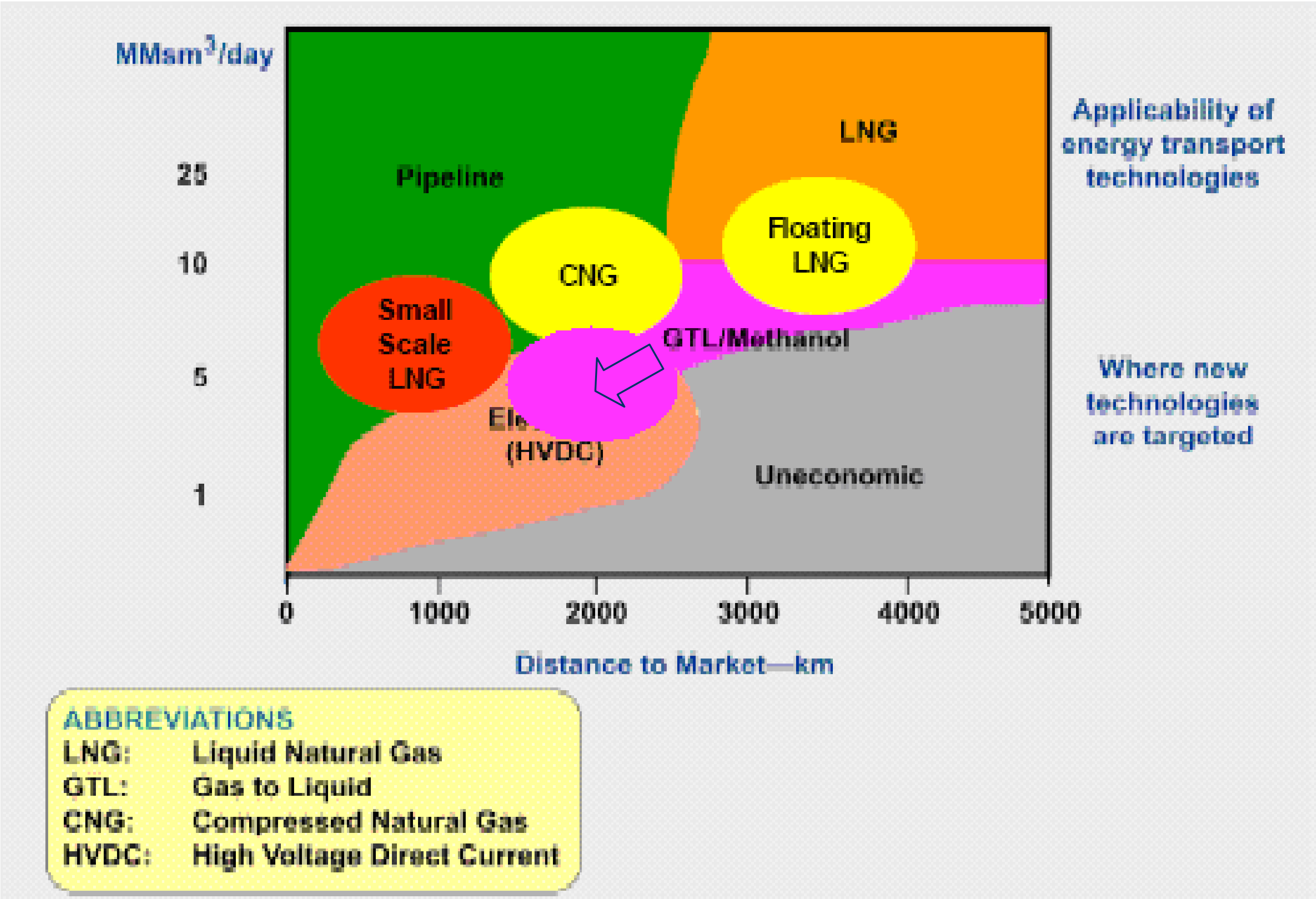
World Stranded Gas Resources

* Stranded gas: Discovered but not developed reserves because too remote or too small to be economic viable

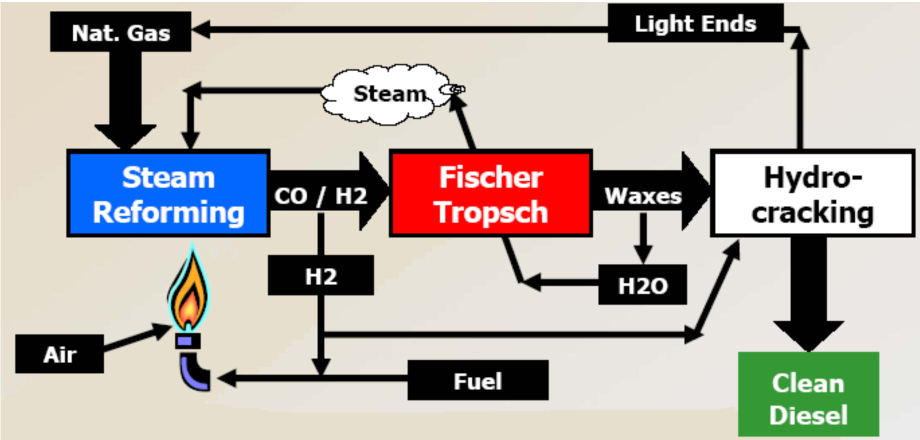
- World natural gas resources >6000 tcf.
  - North Sea 170 tcf
  - Norway 75 tcf

- Methane from biomass
  "stranded gas"

Utilization Options for Natural Gas



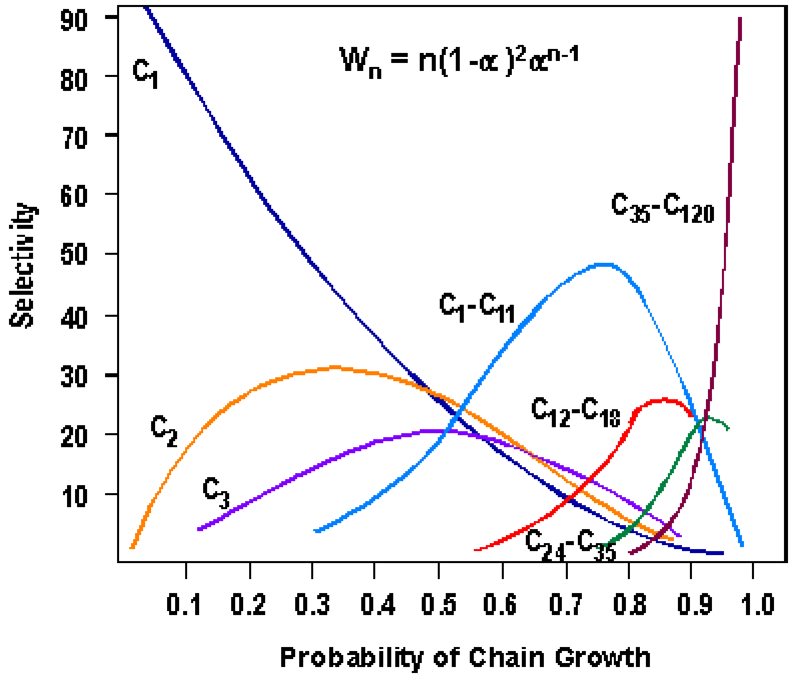
E. Brendeng, J. Hetland, Proceedings of NATO ARW "Security of Natural Gas Supply through Transit Countries", Tbilisi, 2003


Nat. Gas
Light Ends
Steam
Steam Reforming
CO / H2
Fischer Tropsch
Waxes
Hydro-cracking
H2
H2O
Air
Fuel
Clean Diesel

Fischer-Tropsch Synthesis

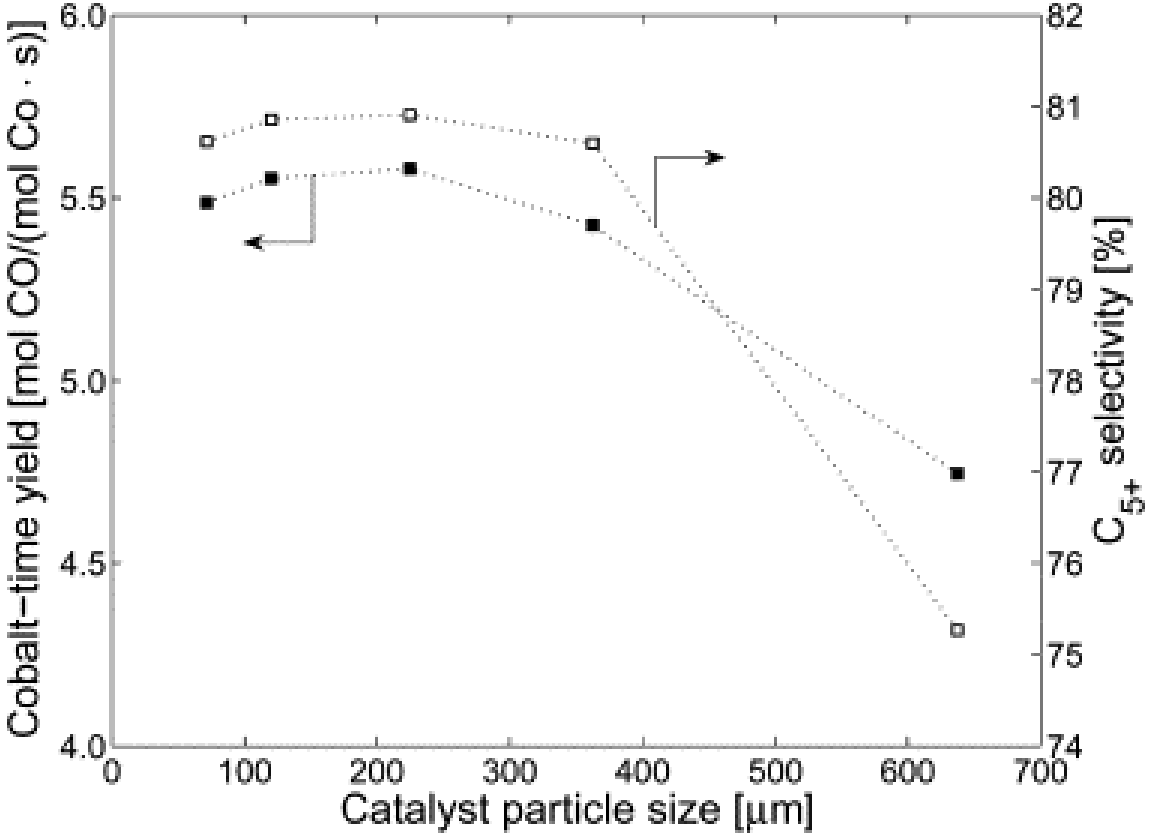
- Heat control
  1. Reaction, very exothermic

     $CO + 2H_2 \rightarrow -CH_2- + H_2O \quad \Delta H \approx -165$ kJ/mol
  2. Product distribution



Fischer-Tropsch Synthesis

- Mass transfer



Ø. Borg. et al, J. Catal 248 (2007)

Microstructured reactors

- Large number of small, parallel channels in µm range
  - Short distance to wall
  - High surface/volume ratio
- Advantages
  - Enhanced heat and mass transfer properties
  - Use of more active catalyst and/or operating at more severe conditions
    - Increased throughput
    - Smaller, more productive reactors → **FTS**
    - Improved productivity
  - Scale-up risk minimized. ”Scaling-out” /Parallelization

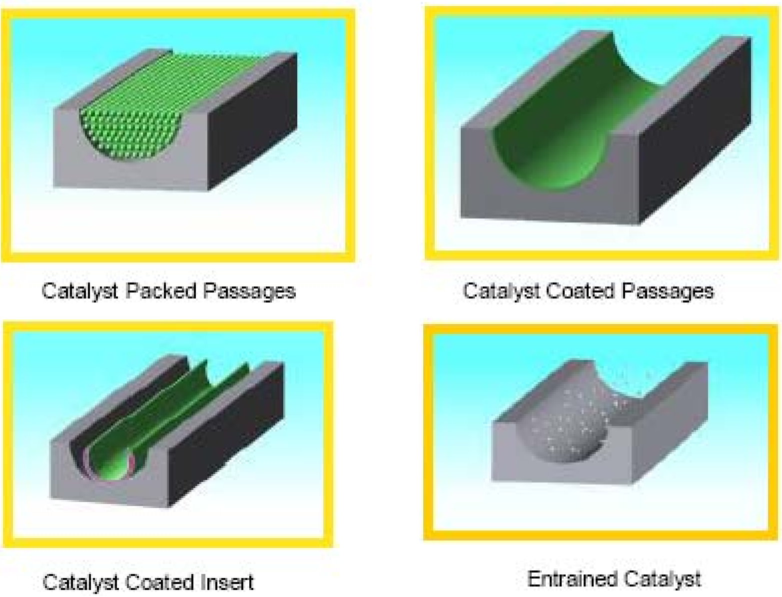
Microstructured reactors

- Disadvantages?
  - Catalyst deactivation and frequent reactor repacking, reactivation or reactor replacement
  - Fouling and clogging of channels
  - Malfunctioning

Catalyst loading in MSR's

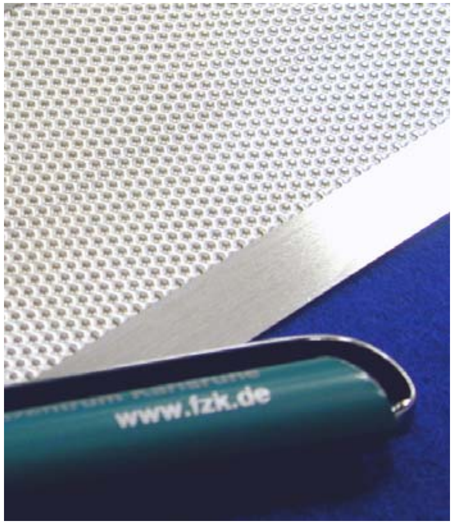
1. Catalyst packed passages
2. Catalyst coated passages
3. Catalyst coated inserts
4. Entrained catalyst

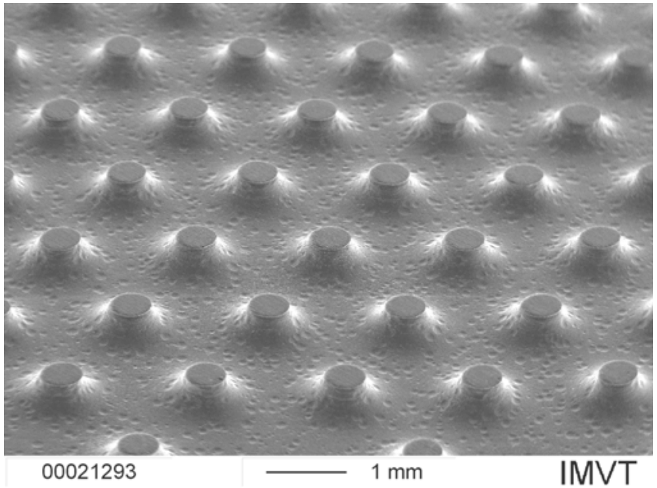
- Advantages
  - Easier catalyst replacements
  - Reactor efficiency
- Main challenge
  - Pressure drop?
  - Maldistribution?

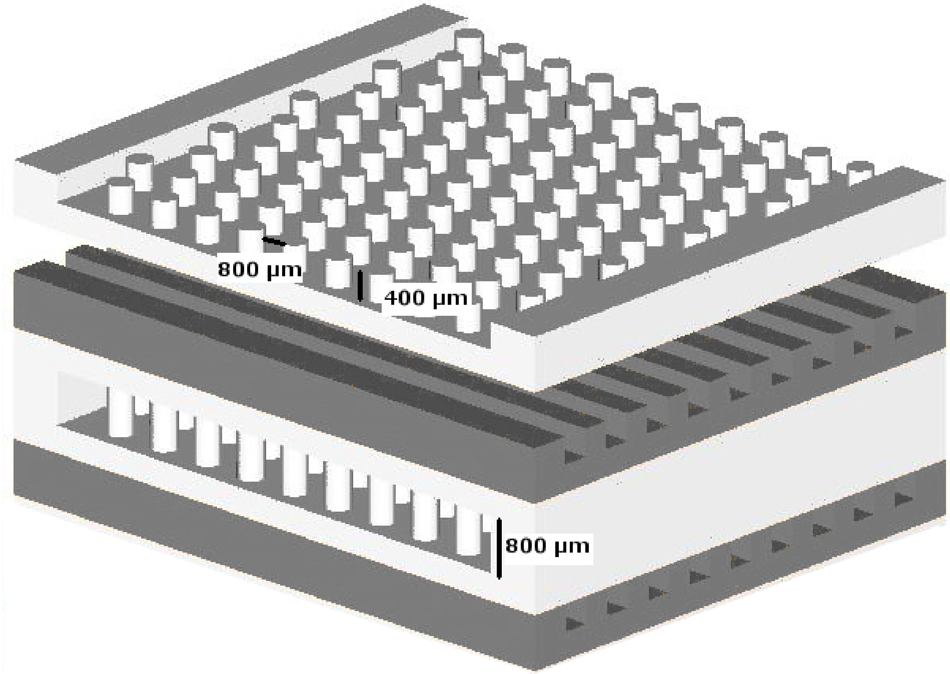


In-Passage Catalyst Options
(www.heatric.com)

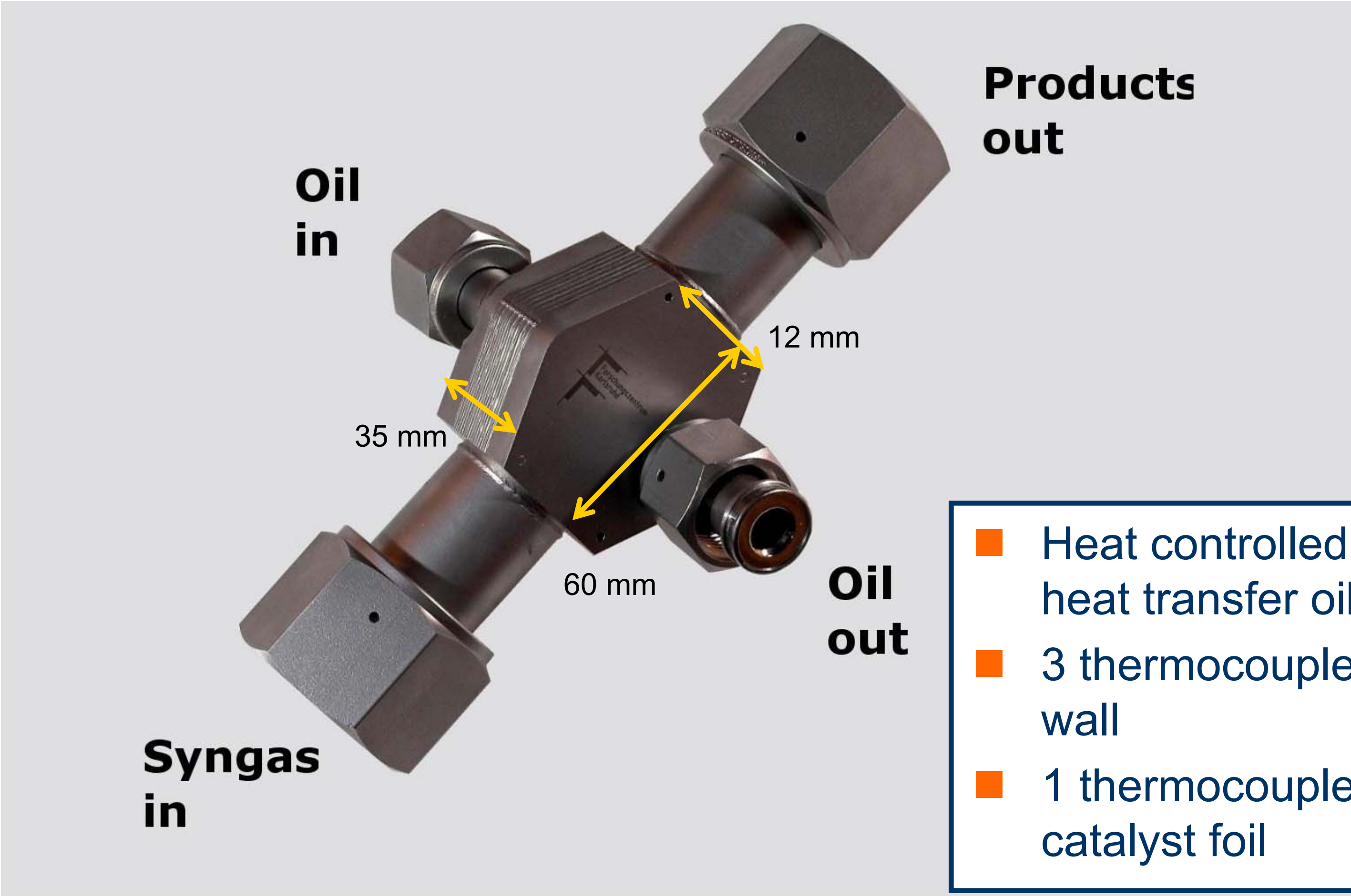
Microstructured reactor
2 cm^3 stainless steel







Microstructured reactor



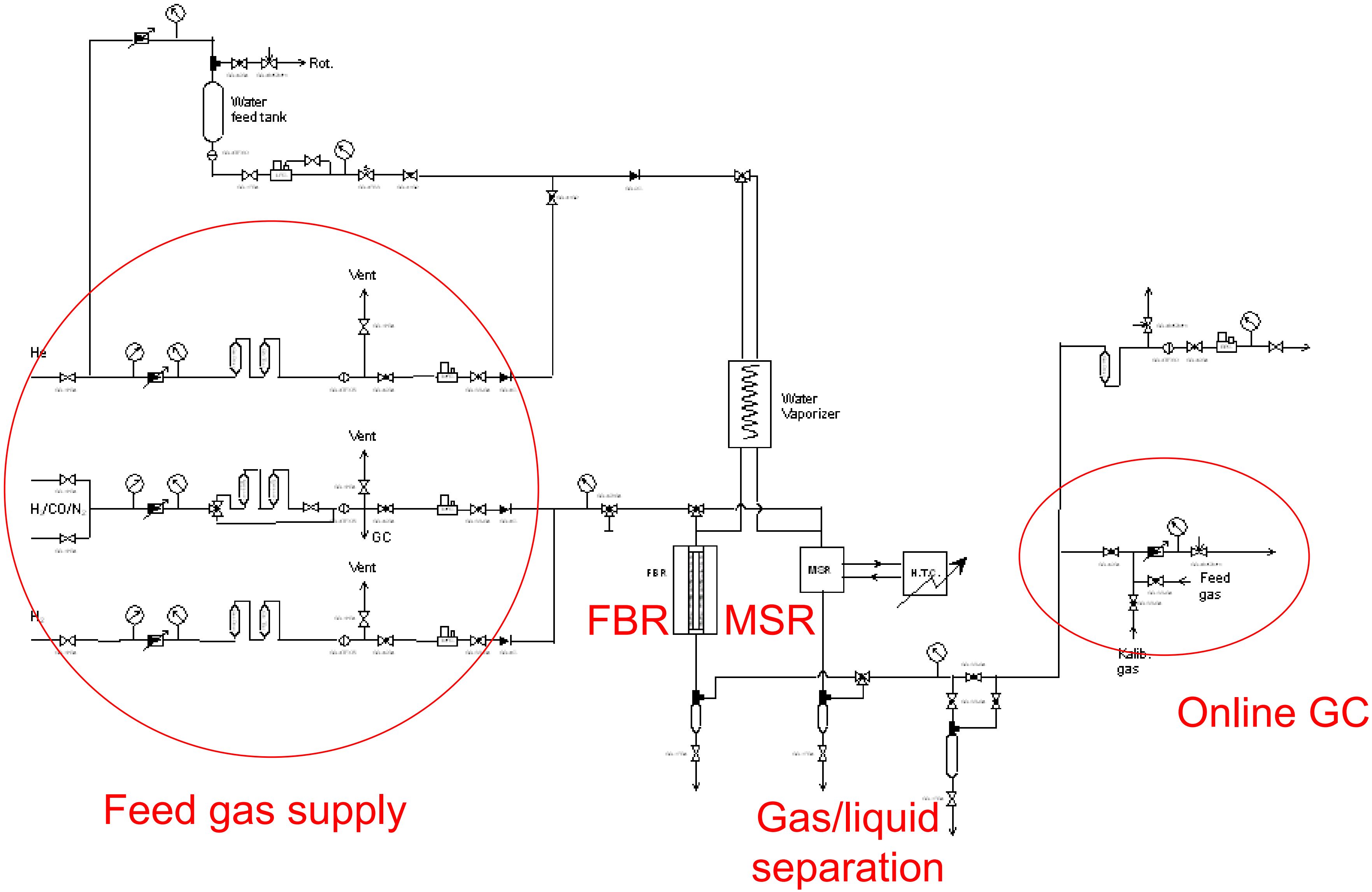
- Heat controlled by circulating heat transfer oil.
- 3 thermocouples in reactor wall
- 1 thermocouple in centre catalyst foil

Fixed-bed reactor

- Conventional ½” stainless steel tube with 10 mm i.d.
- Clamped inside an aluminum block and heated by a Kanthal oven.
- 3 temperature measurements inside the reactor
- Regulated against the temperature in the aluminum block.

FTS studied in MSR and FBR at identical conditions
(incl. catalyst particle size and catalyst weight)

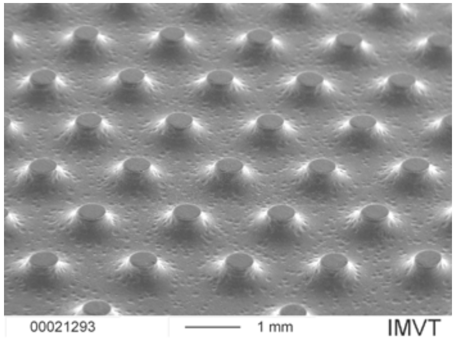
Experimental setup

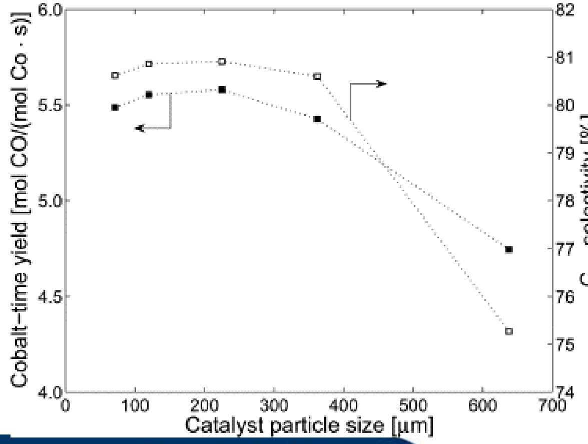


Catalysts

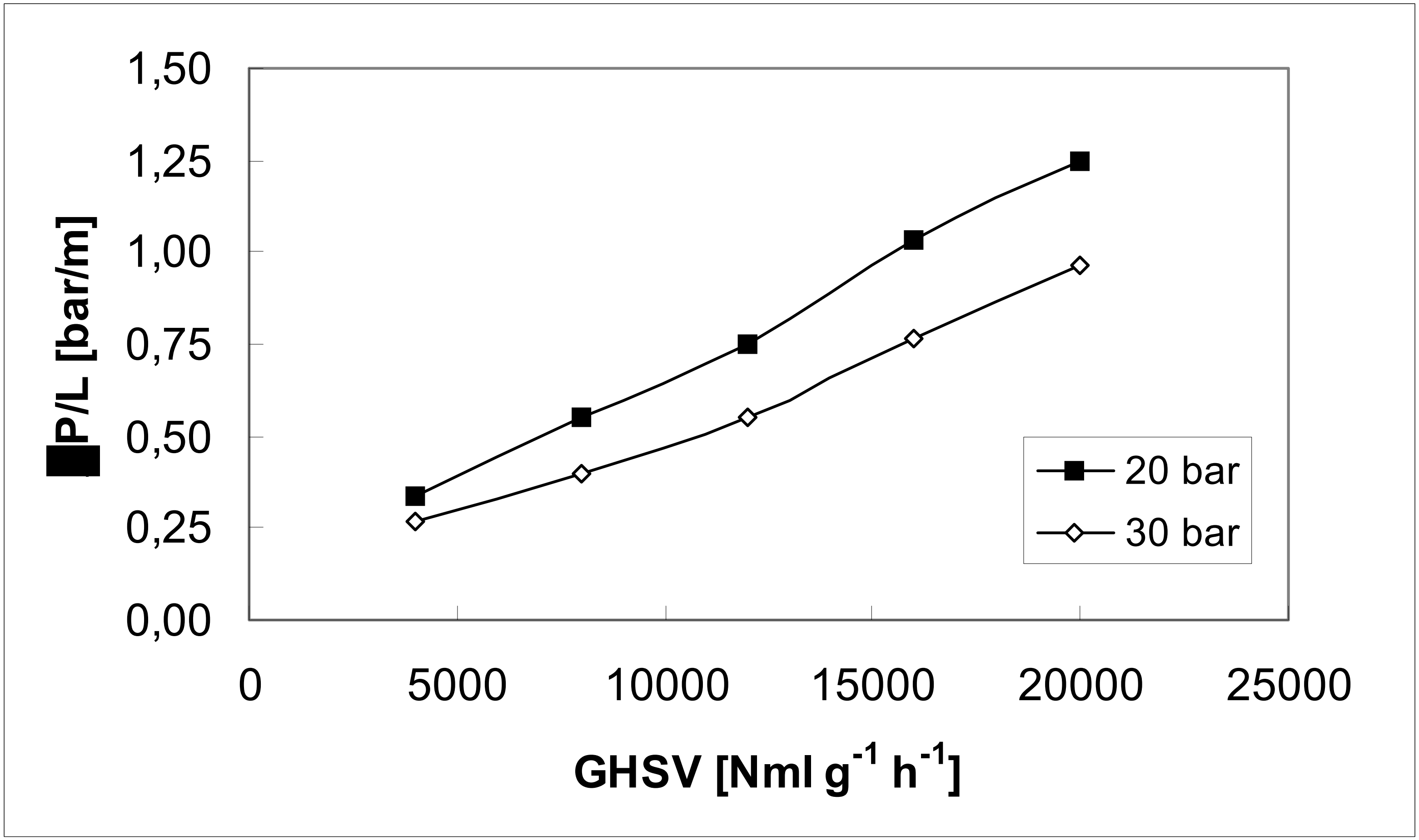
- Promoted 20 and 40 wt.% Co on γ-Al_2O_3
- Reactors loaded with powdered catalyst
  - MSR, undiluted catalyst
  - FBR, diluted 20:1 with SiC

Cat	Sieve fraction (µm)	Co (wt%)	Re (wt%)	Ni (wt%)	Dispersion (%)	Cobalt surface area (m^2 g^{-1})
A	53-90	20	0.5	5	10.3	13.9
B	53-75	40	1.0	0	3.6	9.8

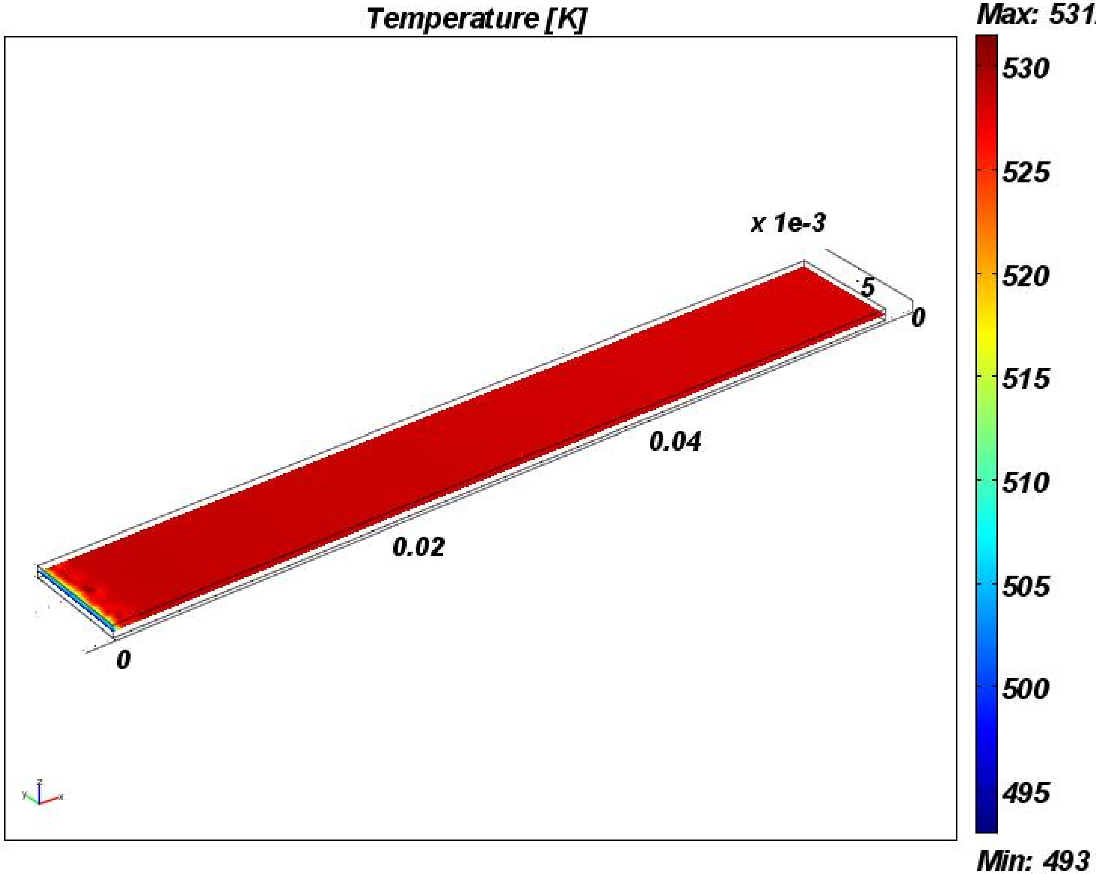




Pressure drop in MSR
(53–75 µm particle size, syngas 225°C)



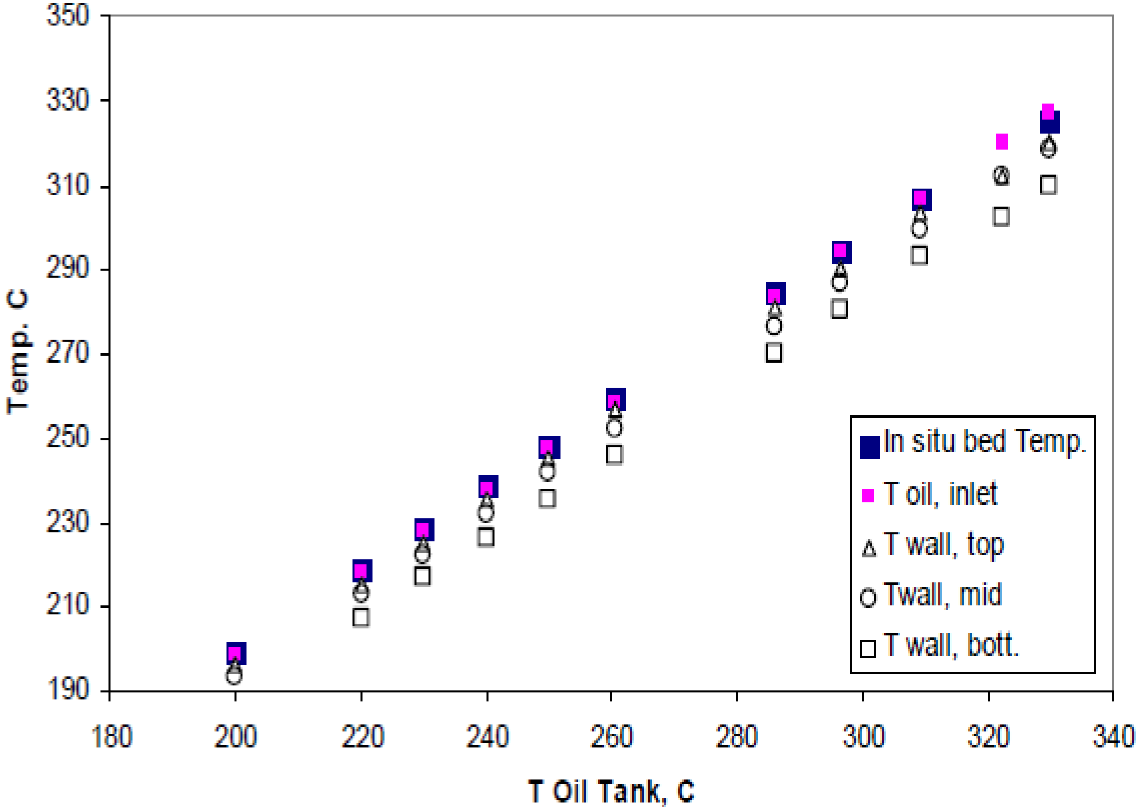
Temperature profile in MSR
(Methanol synthesis[1] simulated in COMSOL)



More than 97% of channel length is fully isothermal

(1) H. Bakhtiary D. et al, in: Lecture 21st NAM Conference, San Francisco June 2009 (2009)

Temperature profile in MSR
(Methanol synthesis[1])



Temperature measurements shows channel temperature identical to oil inlet temperature

(1) H. Bakhtiary D. et al, in: Lecture 21st NAM Conference, San Francisco June 2009 (2009)

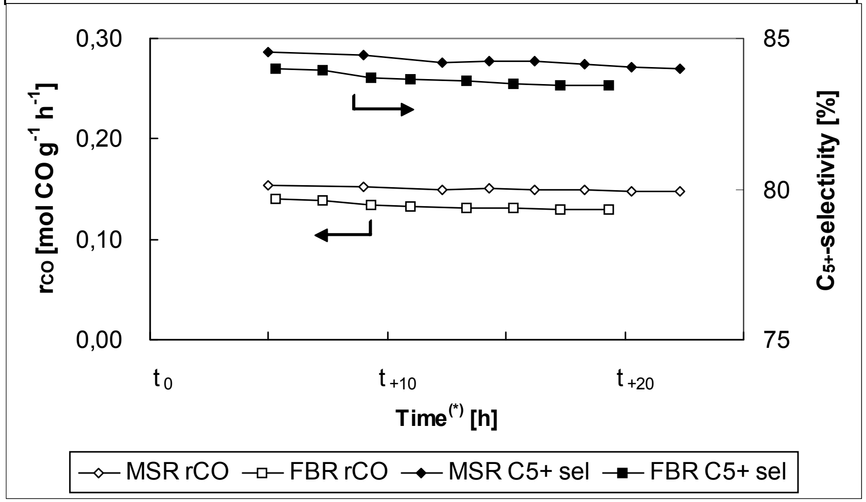
Productivities and selectivities, Catalyst A

Reactor	MSR *non-diluted catalyst*			FBR *diluted catalyst*		
Temperature (°C)	215	225	240	215	225	240
Pressure (bar)	20	20	20	20	20	20
GHSV (mln g^{-1} h^{-1}	14400	14400	20500	12300	14400	20500
CO-conv.(%)	51	72	83	48	69	80
CH_4 –sel. *(%)*	9	9	12	9	9	12
rCO (mol g^{-1} h^{-1})	0.10	0.15	0.24	0.08	0.14	0.23
C_{5+} -sel. (%)	83	84	80	83	84	81
C_{5+} -prod. (g g^{-1} h^{-1})	1.2	1.7	2.6	1.0	1.6	2.6
Rel. deact. rate[(1)] ($x10^{-3}$)	1.2	2.9	4.9	1.0	6.4	8.7
TOS (h)	40	120	140	115	130	150

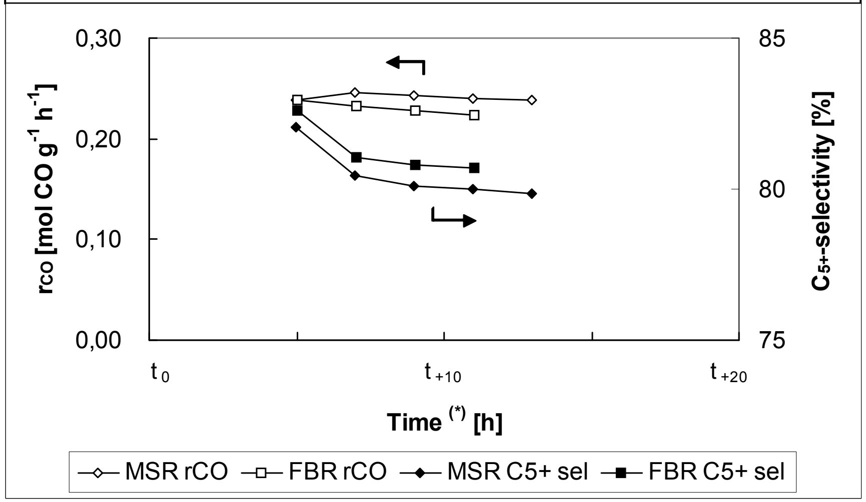
[(1)]Relative deactivation rate at this time on stream, $\Delta r_{CO}/(r_{CO} \times \Delta t)$

MSR vs. FBR, 20Co0.5Re5Ni/Al_2O_3

P=20 bar,T=225°C,GHSV=14400 h^{-1}
(≈ 70% CO-conv.)



P=20 bar,T=240°C,GHSV=20500 h^{-1}
(≈ 80% CO-conv.)



(*) Time at constant conditions

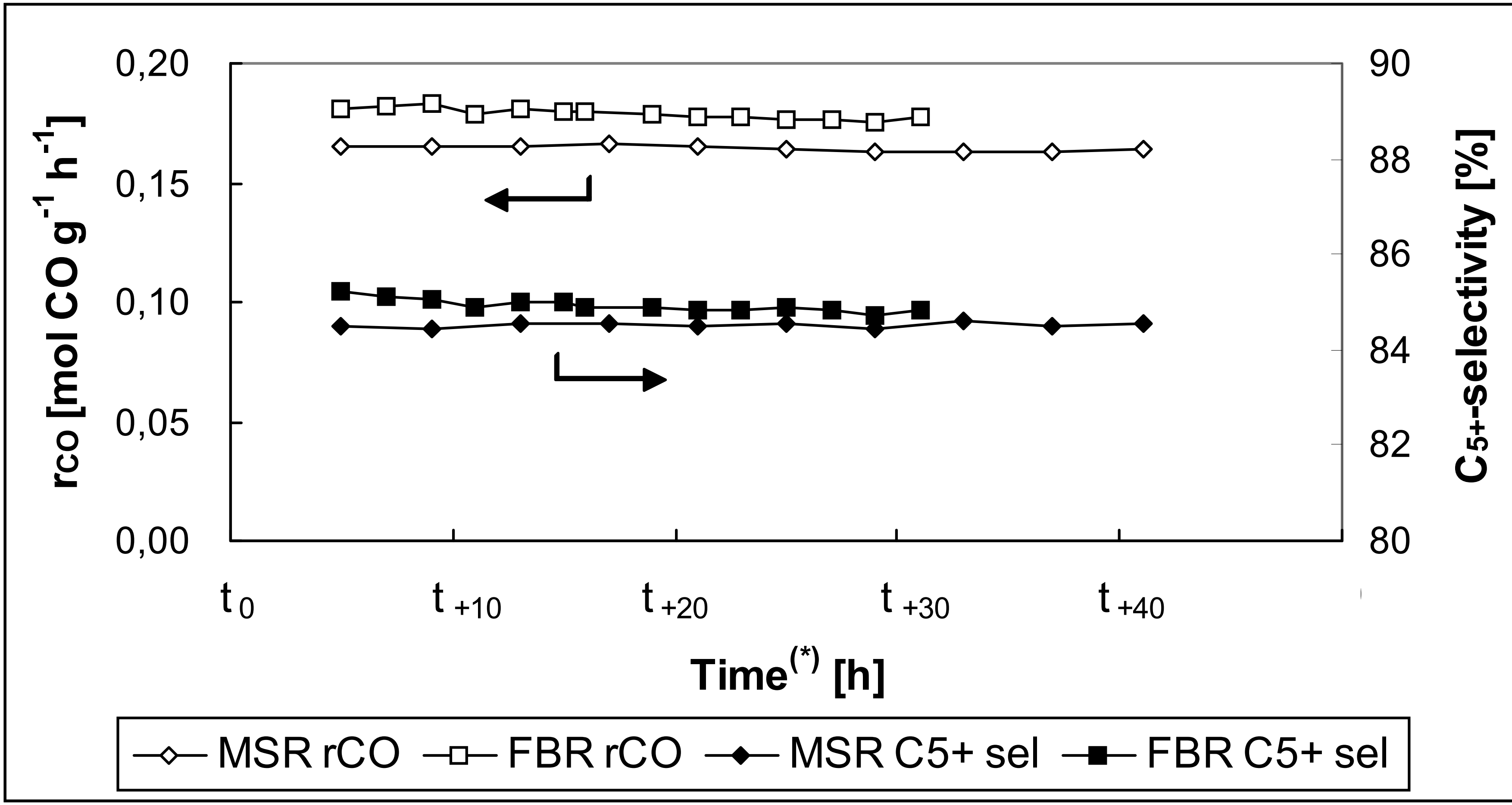
Productivities and selectivities, Catalyst B

Reactor	MSR *non-diluted catalyst*					FBR *diluted cat.*	
Temperature (°C)	215	225	215	225	225	218	228
Pressure (bar)	20	20	30	30	30	20	20
GHSV (mln g^{-1} h^{-1}	16200	16200	16200	16200	12500	16200	16200
CO-conv.(%)	46	72	49	80	91	48	77
CH_4 –sel. *(%)*	9	9	9	9	8	9	9
rCO (mol g^{-1} h^{-1})	0.10	0.16	0.11	0.18	0.16	0.11	0.18
C_{5+} -sel. (%)	84	84	84	86	87	85	85
C_{5+} -prod. (g g^{-1} h^{-1})	1.2	1.9	1.3	2.1	1.9	1.3	2.1
Rel. deact. rate[(1)] ($x10^{-3}$)	2.7	0.8	1.1	0.5	0.2	2.4	1.3
TOS (h)	65	115	165	210	270	70	100

[(1)]Relative deactivation rate at this time on stream, $\Delta r_{CO}/(r_{CO} \times \Delta t)$

MSR vs. FBR, 40Co1.0Re/Al_2O_3

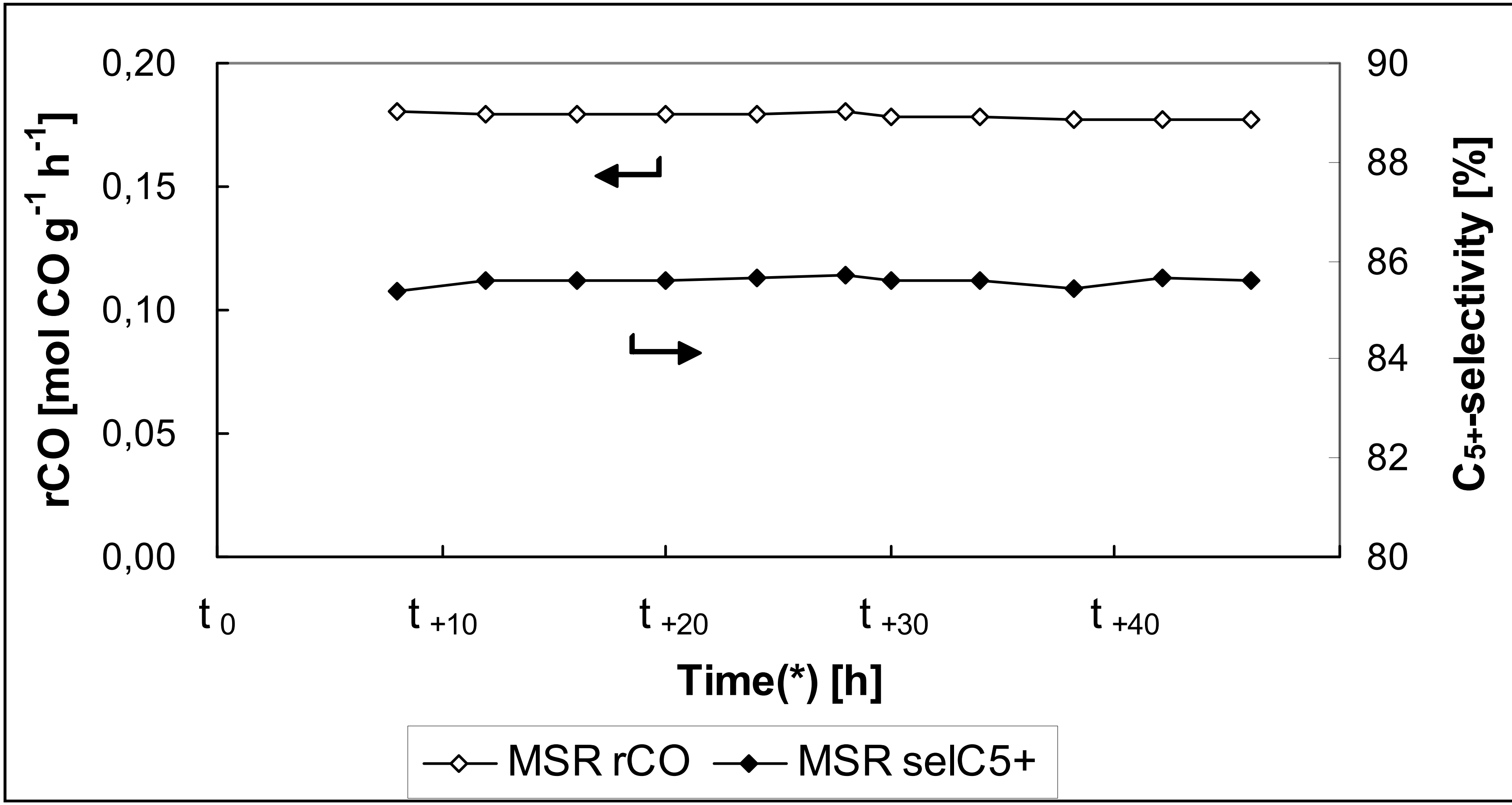
P=20 bar,T=225°C,GHSV=16200 h^{-1} (≈ 75% CO-conv.)



(*) Time at constant conditions

MSR, $40Co1.0Re/Al_2O_3$

P=30 bar,T=225°C,GHSV=16200 h^{-1} (≈ 80% CO-conv.)



(*) Time at constant conditions

Conclusions

- A multichannel microstructured packed bed reactor with excellent heat and mass transfer properties and low pressure drop is manufactured.
- FTS is performed with high activity Co/Al_2O_3 catalysts and the performance of the microstructured reactor fits well with results obtained with diluted catalysts in a lab-scale fixed-bed reactor.
- Due to the heat and mass transfer properties of the microstructured reactor, the microstructured reactor can be operated at severe conditions (high temperature, pressure, CO-conversion) without large temperature gradients and increased catalyst deactivation.

Acknowledgements

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Thank you for your attention!