

Microstructured reactors in compact conversion of natural gas and biomass to liquid fuels and hydrogen

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StatoilHydro





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OUTLINE

- Motivation and background
- Results from
 - Synthesis gas (hydrogen) production in metallic microchannel monoliths
 - Methanol synthesis in a Integrated Micro Packed Bed Reactor-Heat Exchanger
 - Compact synthesis of *dimethyl ether (DME)*
 - *Fischer-Tropsch* synthesis in a microstructured reactor
- Summary and outlook





Motivation and background







BP Statistical Review of World Energy 2009

Proved reserves at end 2008

Trillion cubic metres

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"Global proved reserves of natural gas in 2008 is 185.02 TCM "

7.31	1.87	14.65	15.30	62.89	75.91
S. & Cent. America	North America	Africa	Asia Pacific	Europe & Eurasia	Middle East



25% (?) is stranded natural gas

- Long distance to market
- Volume too low for pipeline
- Complicated/costly production
- Examples
 - Associated gas
 - Arctic gas
 - Off-shore





Natural gas to market







Natural gas processing/conversion



StatoilHydro Tjeldbergodden methanol plant 900.000 tons/year of methanol 25 % of production capacity, 13 % of consumption in Europe





Natural gas processing/conversion



Shell Pearl GTL, Quatar. 140,000 barrels/day of GTL products 120,000 barrels/day of associated condensate and LPG





...economy of scale.







Autothermal reformer for synthesis gas production with partial combustion zone





...requirements to operation:

Safety Stability

. . .

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COMPACT GAS TO PRODUCTS TECHNOLOGY

Offshore conversion of remote gas to liquids

Challenges:

- Footprint
- Weight
- Robustness
- Safety
- Tilting



Future Solution for Stranded Gas Fields?





... and then there is BTL



Distributed, compact and efficient conversion of biomass to fuels.





Natural gas to market



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Results from different projects on microstructured reactors





Microstructured reactors

- Good heat and mass transfer
- Up-scaling by parallellization Overcome "economy of scale"?

Inherent safety
On ships, platforms and farms?





Natural gas to market







Syngas (hydrogen) production from alkanes in metallic microchannel monoliths





Metallic microchannel reactors (Rh/Al₂O₃/Fecralloy) with 100 µm wide channels



Reactor no.	1	2	3	4
Material	Fecralloy	Rh	Fecralloy	Fecralloy
H×W [mm ²]	5.5×5.6	5.5×5.6	5.5×5.6	5.5×5.6
Length [mm]	20	20	20	20
No. of channels	676	676	676	572
Channel dimension [µm ²]	120×130	120×130	100×120	100×120
Thermocouple channel dimension [µm ²]	-	-	-	600×600
Geom. surface of channels [cm ²]	67.5	67.5	59.5	50.8
Porosity	0.34	0.34	0.26	0.22
Flow at 12.7 ms residence time [Nml/min]	1000	1000	769	614
Impregnated with	Rh	-	-	- / Rh



Reactors are produced at Institute for Micro Process Engineering (IMVT), Forschungszentrum Karlsruhe*.

* Now Karlsruhe Institute of Technology



Temperature profile, propane partial oxidation in Rh/Al₂O₃/Fecralloy (100µm)





I. Aartun, H. J. Venvik, A. Holmen, P. Pfeifer, O. Görke, K. Schubert, Catalysis Today 110 (2005) p.98.





Conversion and products,

propane partial oxidation in Rh/Al₂O₃/Fecralloy (100µm)



I. Aartun, H. J. Venvik, A. Holmen, P. Pfeifer, O. Görke, K. Schubert, Catalysis Today 110 (2005) p.98.

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Partial oxidation and oxidative steam reforming in metallic microchannel reactors, additional results:

Good results also with CH_4 in Rh/Al_2O_3 /Fecralloy *

✓ Rh/Al₂O₃/Nicrofer not so good *

- Addition of steam to reactant mixture increases hydrogen production
- ✓ Microchannels suppress gas phase reactions leading to C₂₊ by-products

* B. C. Enger, J. Walmsley, E. Bjørgum, R. Lødeng, P. Pfeifer, K. Schubert, A. Holmen, H. J. Venvik Chemical Engineering Journal,144(2008) p. 489





Natural gas to market







Methanol synthesis in a Integrated Micro Packed Bed Reactor-Heat Exchanger (IMPBRHE)



800 µm channels with pillars, packed with particles of Cu-based catalyst



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Microchannel reactor made by Karlsruhe Institute of Technology, Germany







Conversion comparison between IMPBRHE (---MSR) and laboratory fixed bed reactor (--- FBR)

- Equal conditions, commercial Cu based catalyst



H. Bakhtiary D., F. Hayer, X. K. Phan, R. Myrstad, H. J. Venvik, P. Pfeifer, A. Holmen, in preparation

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Compact synthesis of DME

Also with IMPBRHE





Natural gas to market



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Direct synthesis of DME in IMPBHE



Reaction conditions: Temp.: 250 °C Pressure: 50 bar GHSV: 9000 ml gcat⁻¹ h⁻¹ Premixed synthesis gas mixture $(H_2/CO/CO_2/CH_4/N_2)$

F. Hayer, H. Bakhtiary D., R. Myrstad, P. Pfeifer, A. Holmen, H. J. Venvik, in preparation





Effect of dehydration catalyst



Reaction conditions: Temp.: 250 °C Pressure: 50 bar GHSV: 9000 ml gcat⁻¹ h⁻¹ Premixed synthesis gas mixture $(H_2/CO/CO_2/CH_4/N_2)$

F. Hayer, H. Bakhtiary D., R. Myrstad, P. Pfeifer, A. Holmen, H. J. Venvik, in preparation II





Temperature profiles methanol and DME synthesis



Simulation of fixed bed temperature peak

Simulation of single channel of IMPBRHE - practically isothermal

Simulations supported by temperature measurements

H. Bakhtiary D., F. Hayer, X. K. Phan, R. Myrstad, H. J. Venvik, P. Pfeifer, A. Holmen, in preparation





Summary: Methanol and DME synthesis in the IMPBRHE

 Promising in terms of Methanol/DME production Catalyst integration Operation at high pressure ✓ Compactness Thermal behaviour (isothermal) Negligible pressure drop and diffusion limitations

+ room for development and optimization



Fischer-Tropsch synthesis in a microstructured reactor





Natural gas to market







...works as well!

See presentation by Rune Myrstad, SINTEF at 10:00 Thursday (tomorrow)

and

R. Myrstad, S. Eri, P. Pfeifer, E. Rytter, A. Holmen Catalysis Today 147 (2009) p. S301





Microstructured reactors need new/different catalyst innovations

- Structure
- Ratio of components
- Reaction conditions



Synthesis of macroporous structured AI_2O_3 support from a polystyrene- AI_2O_3 core-shell composite

Xuyen K. Phan, J. Yang, H. Bakhtiary D., R. Myrstad, H. Venvik, A. Holmen, in preparation





Conclusion

- Microstructured reactors show promising performance for GTL.
 - ✓ Syngas production step included
 - ✓<u>Methanol</u> production for fuel or petrochemical application
 - <u>Dimethyl ether</u> (DME) by direct synthesis, as a fuel or LPG alternative
 - Synthetic diesel via the Fischer-Tropsch synthesis





Thank you for your attention!

Questions?



