

Methane pyrolysis

(Thermocatalytic decomposition of methane)

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29.3.2023



Sustainable Chemistry Research Unit



FACTS (2020):

Staff: 47

3 Full professor, 3 docents, 17 post docs

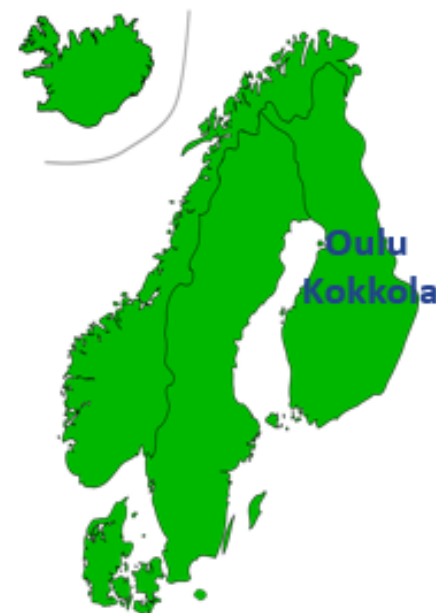
Degrees: 15 M.Sc., 3 Ph.D.

14 research projects (BF, AF, EU funded)

32 international publications, 2 pending patents

Close company collaboration

Several disciplines in chemistry



RESEARCH FOCUS AREAS IN APPLIED CHEMISTRY

- I. Lithium-ion battery chemicals
Metals recovery, leaching, and precipitation
- II. **New water treatment chemicals and solutions**
- III. **Catalysis in biomass conversion**
- IV. **Technical carbons and applications**

(Scientific results during past years)

(3 PhD, 6 PhD students, 20 M.Sc., publ.,)

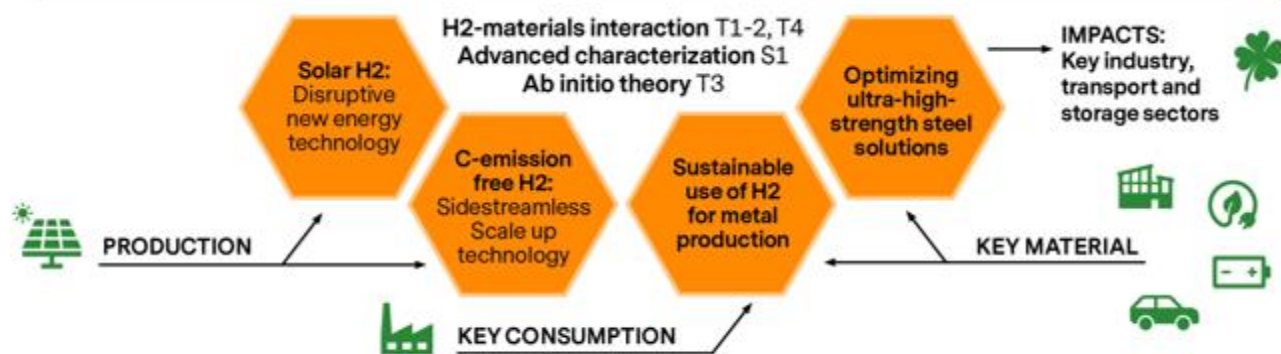
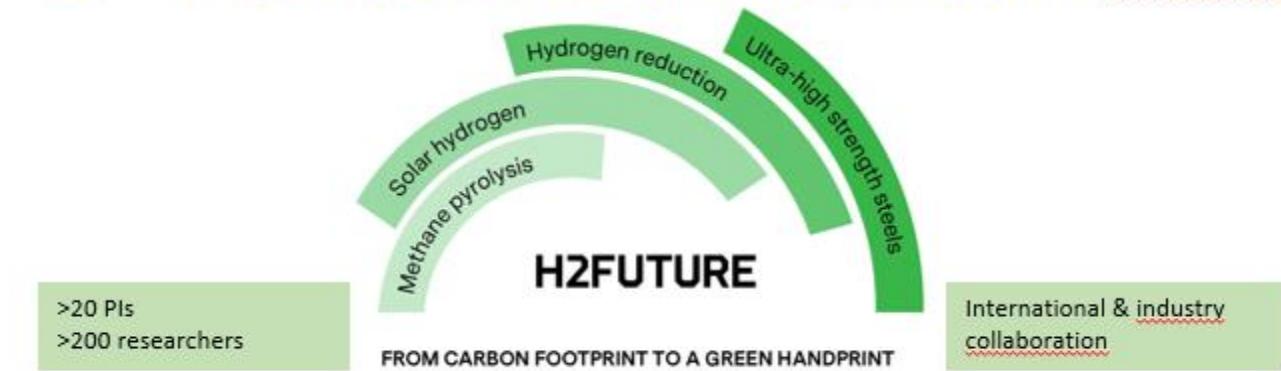
(6 PhD, 6 PhD students, 10 M.Sc., 30 publ)

(5 PhD, 4 PhD students, 6 M.Sc., 15 publ.)

(3 PhD, 3 M.Sc., 20 publ.)



H2FUTURE - Multidisciplinary Research and Education as a Foundation of the Green Transition



STATE-OF-THE-ART RESEARCH INFRASTRUCTURES (TRL 1-8)

CENTRE FOR MATERIALS ANALYSIS



(PHOTO)CATALYST SYNTHESIS, TEST & VALIDATION



FABRICATION, SCALE-UP AND COMMERCIALIZATION



- National profilation project **H2FUTURE** 2023-2028
- CO₂ free and energy efficient H₂ production methods: solar H₂ and (bio)methane pyrolysis
- Energy materials research: electroceramics
- Solar panels and nanocoatings
- Coordination of Hydrogen Research Forum Finland (9 research organization members): Research based view on hydrogen transition
- National graduate school on H₂ transition under construction
- I4WORLD EU-Horizon MSCA docotoral program focusing on UN SDG themes
- Offering courses on energy technology and systems, minor on sustainable development
- Open university and continuous learning, education on H₂ transition (FiTech) and UNIC collaboration



BUSINESS FINLAND

SUOMEN AKATEMIA



Hydrogen roadmap – Sustainable chemistry

2008-2015

FT synthesis
Catalytic conversion of biomass-derived synthesis gas to olefins/FT diesel



Collaboration with LTU & NTNU

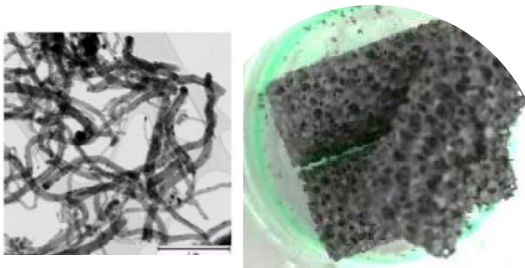
PhD thesis Romar 2015
PhD thesis Tuomikoski 2014

2015-2021

Methane pyrolysis to hydrogen and carbon

Carbon applications (activated carbon, carbon foams, carbon catalysis)
Carbon use in batteries

Hydrogen reduction (with MET)

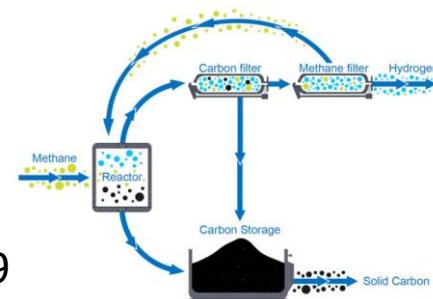


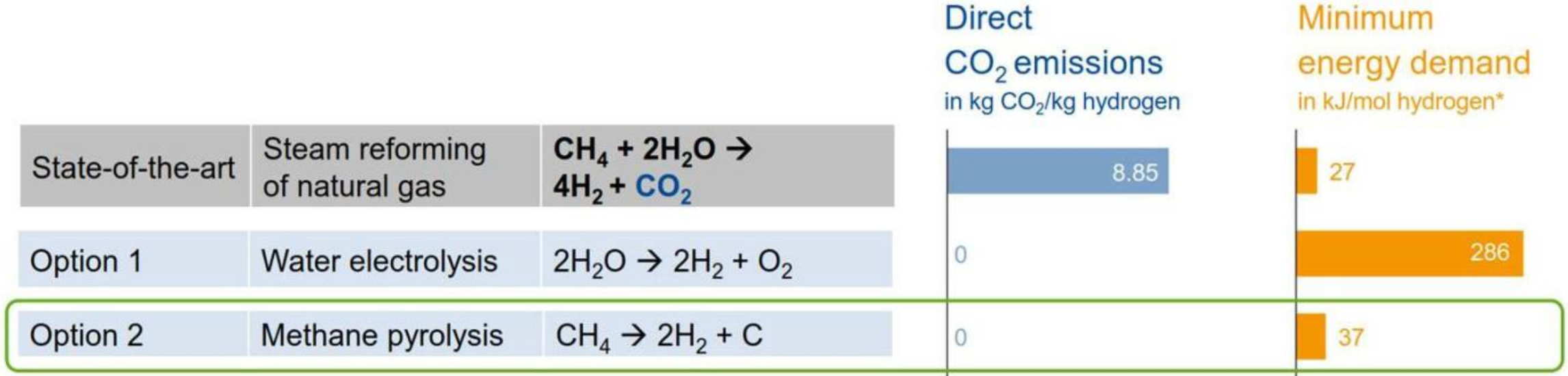
PhD thesis Bergna 2019
PhD thesis Kupila 2021
PhD thesis Varila 2020

2022-

Improved material efficiency for **methane pyrolysis** (use of secondary materials)

Hydrogen reduction in metallurgical industry (with MET)



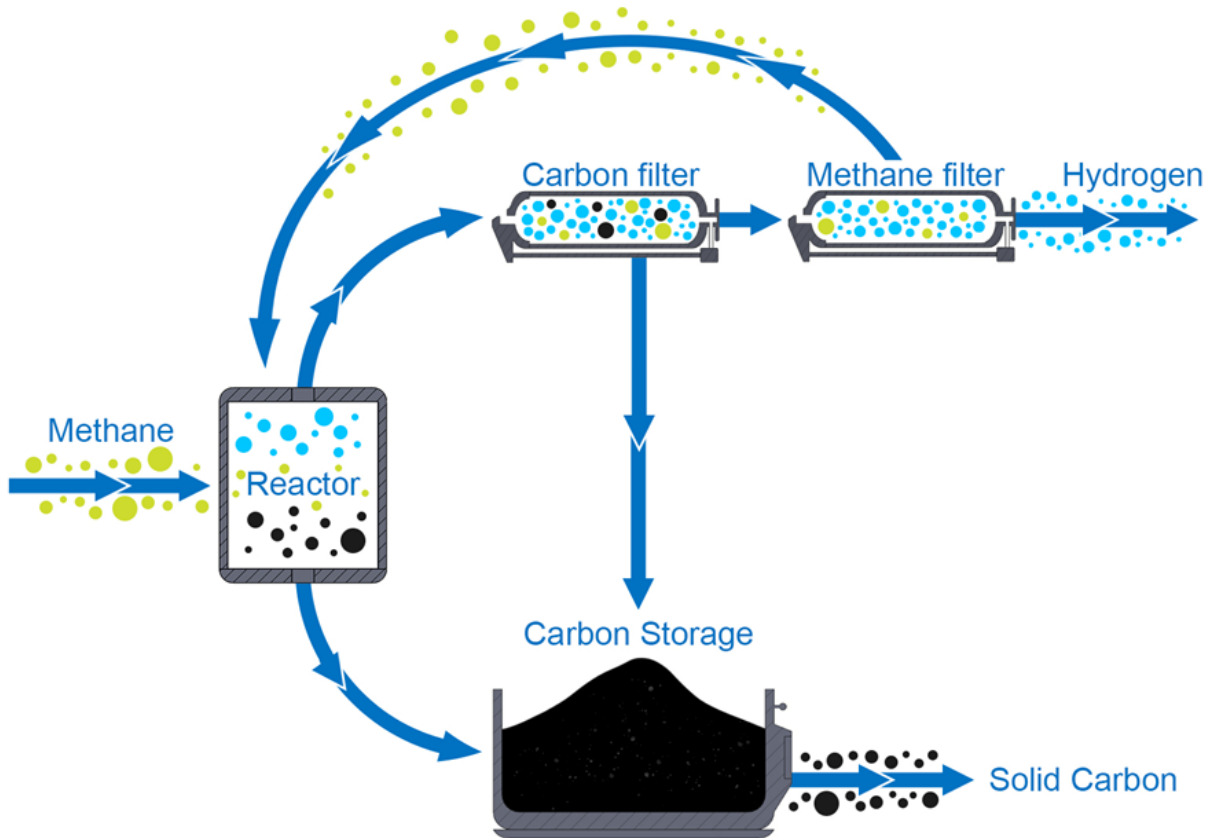


Production of hydrogen (options)

- Daloz, W., Frederik Scheiff, Kai Ehrhardt, Dieter Flick and Andreas Bode, The quest for CO₂-free hydrogen – methane pyrolysis at scale, ARPA-E Methane Cohort Kickoff, Houston (US), Dec 10, 2019.



Methane pyrolysis



TRL3 -> TRL7

Several innovations behind this:

- 1) Use of CO₂/CO free technology
- 2) Catalyst
- 3) Reactor set-up
- 4) Solid carbon for energy storage applications



TCD of (bio)methane

Table 1. Chemical reactions for hydrogen production from methane and corresponding reaction enthalpies. In the first three reactions (SMR, DRM, and PO), carbon is emitted as CO₂ or CO, whereas in TDM and TCD, solid deposits of carbon are formed.

Production Method	Chemical Equation	Reaction Enthalpies	Equation Number
Steam methane reforming (SMR)	$\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$	$\Delta H_{298\text{K}} = 206 \text{ kJ/mol}$	(1)
Water gas shift reaction (WGS)	$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$	$\Delta H_{298\text{K}} = -41 \text{ kJ/mol}$	(2)
Dry reforming of methane (DRM)	$\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2$	$\Delta H_{298\text{K}} = 247 \text{ kJ/mol}$	(3)
Partial oxidation (PO)	$\text{CH}_4 + 0.5\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2$	$\Delta H_{298\text{K}} = -23 \text{ kJ/mol}$	(4)
Thermal decomposition of methane (TDM)	$\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$	$\Delta H_{298\text{K}} = 75 \text{ kJ/mol}$	(5)
Thermocatalytic decomposition of methane (TCD)			

Välimäki, Emmi; Yli-Varo, Lasse; Romar, Henrik; Lassi, Ulla (2021) Carbons Formed in Methane Thermal and Thermocatalytic Decomposition Processes: Properties and Applications., C. 7 (3), 50 .
<http://dx.doi.org/10.3390/c7030050>



Catalysts

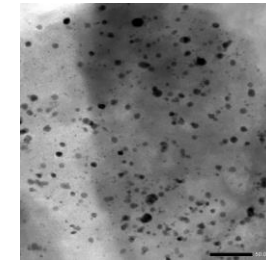
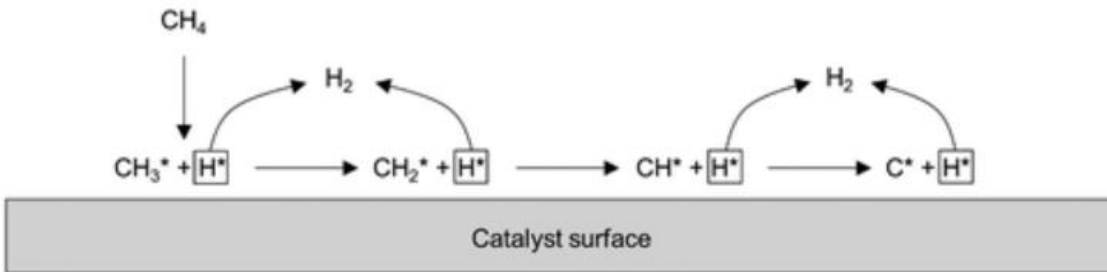
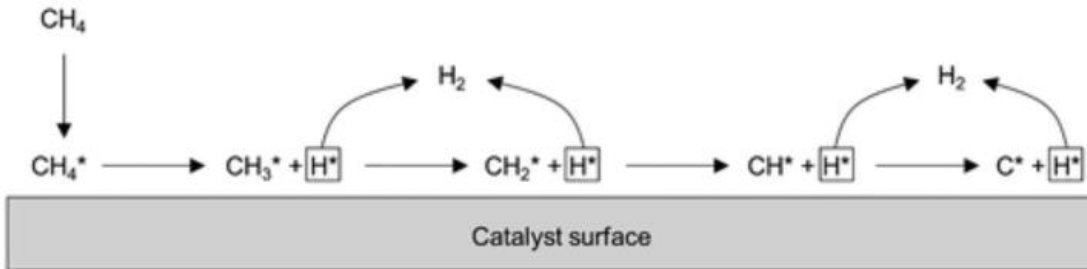


Table 2. Initial Activity of Nickel, Iron, and Cobalt Catalysts in the Decomposition of Methane for Hydrogen Production

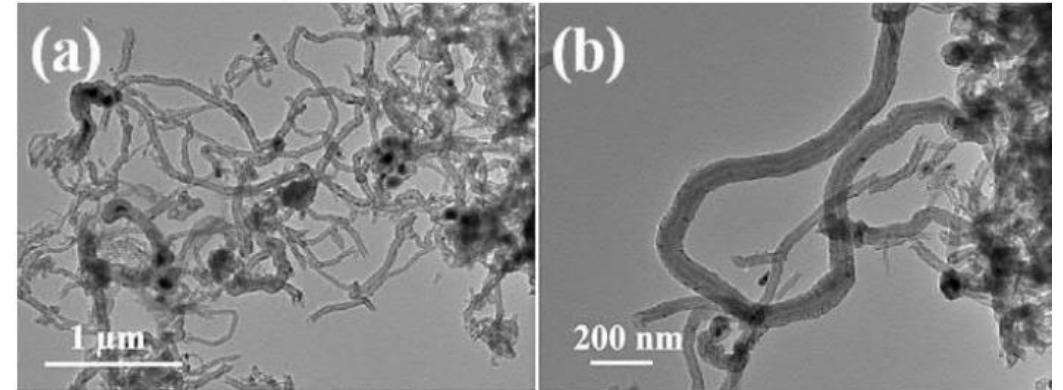
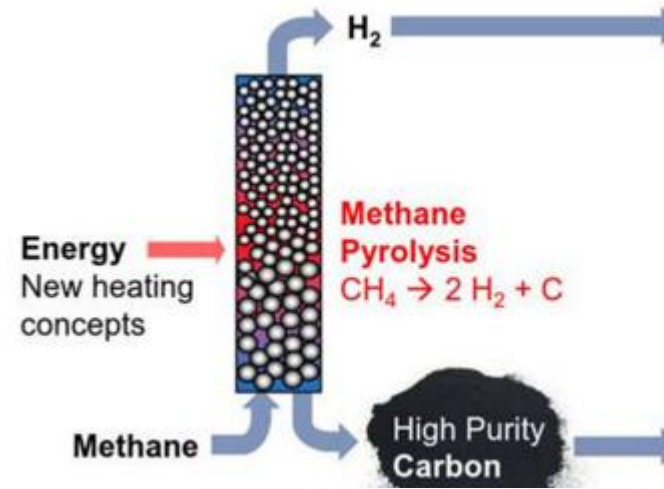
catalyst	T [°C]	P [atm]	CH_4/N_2 [vol vol ⁻¹]	flow rate [mL min ⁻¹]	space velocity [mL h ⁻¹ g _{cat} ⁻¹]	H ₂ yield [%]	ref
Ni/CeO ₂	700	1	1/0	150	4500	53	139
Ni/La ₂ O ₃	700	1	1/0	150	4500	60	139
Ni/SiO ₂	700	1	1/0	60	7200	73	140
Fe/CeO ₂	700	1	1/0	150	4500	51	141
Fe/La ₂ O ₃	700	1	1/0	150	4500	40	141
Fe/SiO ₂	700	1	3/7	70	42000	20	94
Ni/SiO ₂	800	1	1/0	250	5000	74	134
Fe/SiO ₂	800	1	1/0	250	5000	39	134
Co/SiO ₂	800	1	1/0	250	5000	48	134



Catalysts



B



Ind. Eng. Chem. Res. 2021, 60, 32, 11855–11881

Välimäki, Emmi; Yli-Varo, Lasse; Romar, Henrik; Lassi, Ulla (2021) Carbons Formed in Methane Thermal and Thermocatalytic Decomposition Processes: Properties and Applications., C. 7 (3), 50 .

<http://dx.doi.org/10.3390/c7030050>

Sustainable Carbon as a secondary product supplementing the sales

PRODUCTS

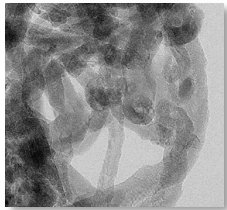
Carbon nanotubes (CNT)

Carbon nanofibers (CNF)

Amorphous carbon → activated carbon

Graphite

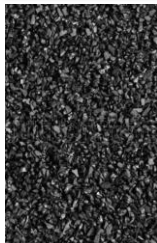
Graphite



- ▶ Battery industry
- ▶ Lightweight materials for automotive and aerospace industry

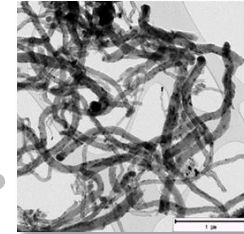


Activated carbon



- ▶ Water treatment
- ▶ Pharmaceutical purification
- ▶ Industrial applications

CNT, CNF



- ▶ Battery industry
- ▶ Electric vehicles (supercapacitors)
- ▶ Catalysts





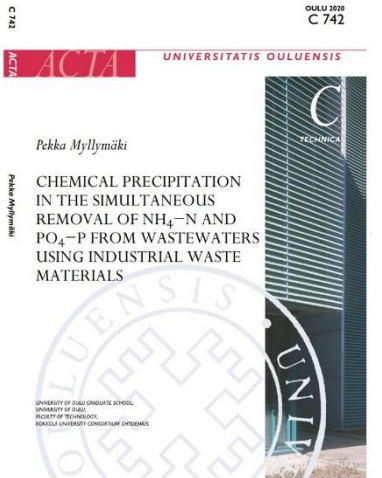
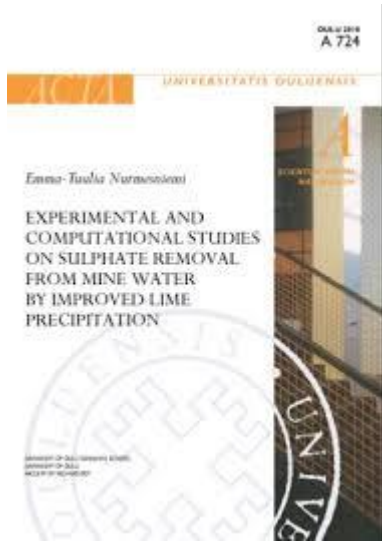
Conclusions

- Methane pyrolysis feasible technology for (bio)methane conversion to hydrogen and solid carbon
- Currently under pre-commercialization stage
- CO/CO₂ free technology
- Added-value from the utilization of carbon



Thanks for your attention!

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Battery
chemistry
research
since 2007