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Transfer in Research and Development
Division Energy

Ammonia as a Hydrogen Source for Fuel Cell Propulsion Systems and as an Energy Carrier for Combustion Engines

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Business Division Energy at Fraunhofer IMM

Portfolio

Areas of activity:

- Fuel Processors (Reformers) for Hydrogen generation from all kind of hydrogen carriers
  - ➢ Methanol
  - ➢ Ethanol
  - ➢ Diesel, LPG, (synthetic) Natural Gas
- Ammonia Decomposition
- Catalytic Combustion
- Sustainable Fuel Synthesis
  - ➢ Catalytic Methanation of Biogas

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Portfolio

- Modelling and Life Cycle Analysis
- Catalyst Technology
- Reactor Technology
  - Catalytic Combustion

- Process Development and Control
  - Fuel Processors
  - System Automation
- Reformer Technology

  Public information

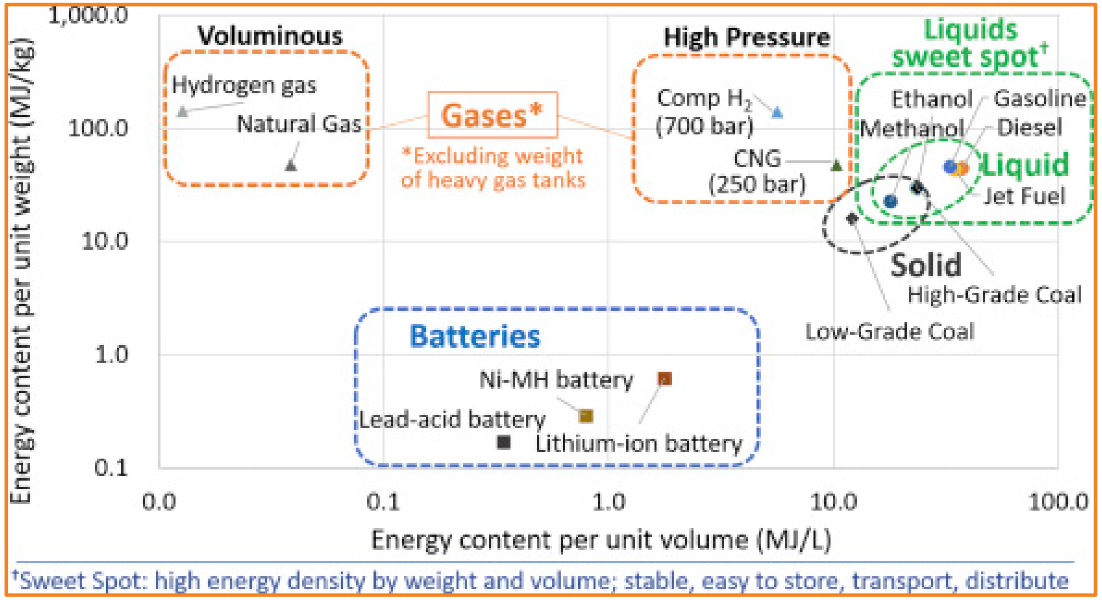
Introduction – Batteries vs. Fuel Cells

Derived from theory, batteries show intrinsic low volumetric and gravimetric energy density

They are therefore little suited for a variety of applications such as:

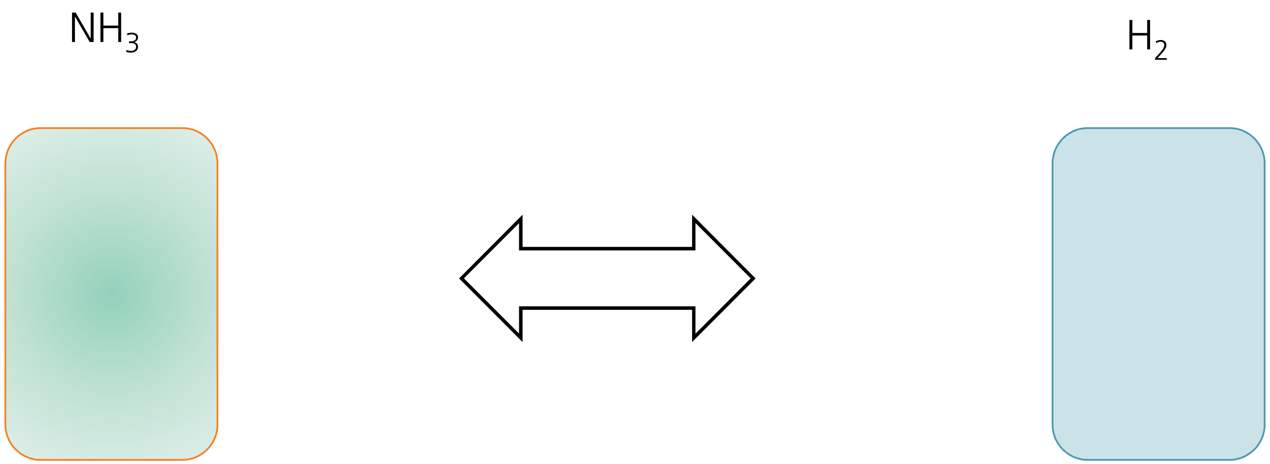
- Long-distance road transport of passengers and goods
- Aviation
- Maritime applications

Fuel cells offer numerous advantages compared to combustion engines:
- **Higher efficiency**
- **Less emissions (catalytic processes)**



Source: Cell Press

Comparison of hydrogen storage options – ammonia vs. hydrogen



→ Liquid storage at 25°C / 10 bar

→ Liquid storage at 25°C / 10 bar
→ Density: 512,43 kg/m³
→ Energy density: 2,665 kWh/l

→ Storage as gas at 25°C / 700 bar

→ Density: 41,289 kg/m³
→ Energy density: 1,376 kWh/l gross
→ Energy density[1]: 1,211 kWh/l net

[1] About 12% of the heating value of hydrogen is consumed for the compression to 700 bar

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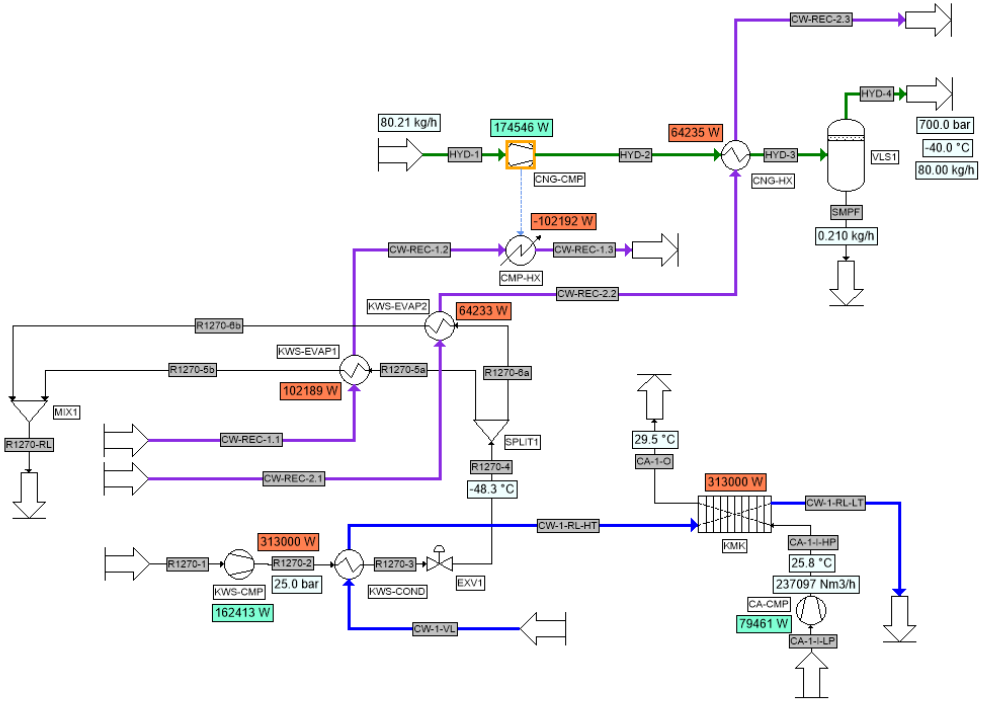
Energy losses by hydrogen compression to 700 bar

- Energy content of H_2 (LHV 241,826 J/mol):
  - 2.666 MW
- **Power for compression and cooling:**
  - **416.4 kW from 25 bar to 700 bar**

Energy loss of 15.6%



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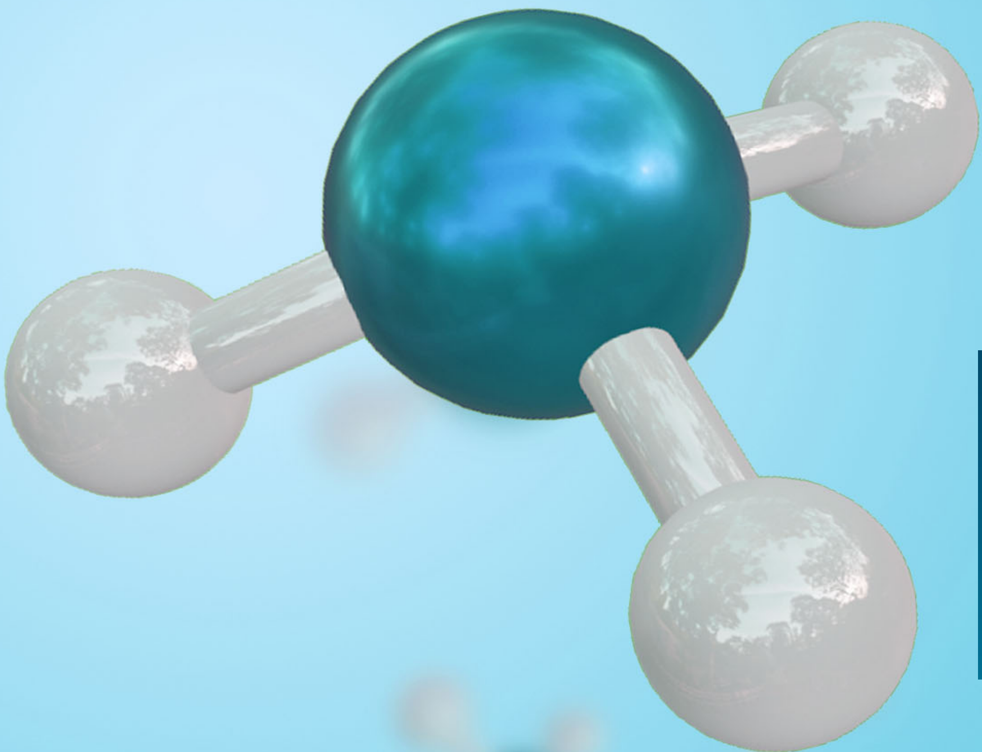
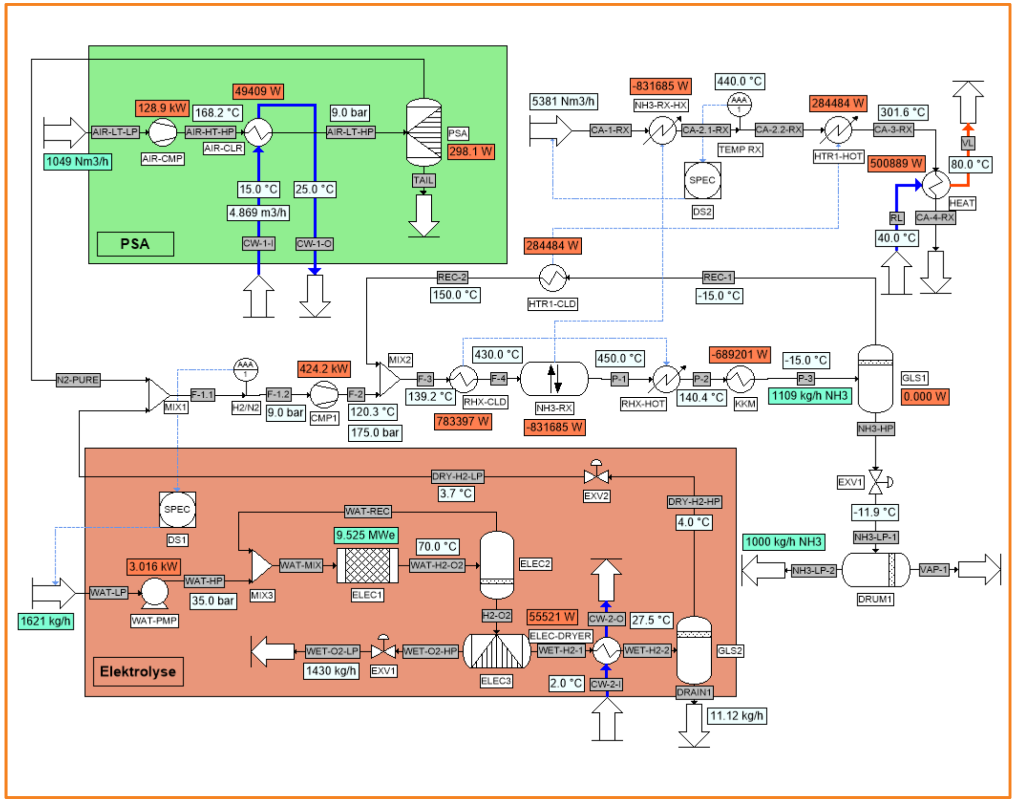


Ammonia as hydrogen carrier

Energy efficiency of ammonia production

- Energy Input of the process chain from H_2 to NH_3:
  - Pressure Swing Adsorption: 128 kW
  - NH_3 synthesis: 562 kW
  - **Electrolysis: 9,525 kW**

- Energy required for ammonia production:
  - 0.691 kWh/kg without electrolysis
  - 10.22 kWh/kg with electrolysis



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Energy efficiency of ammonia production

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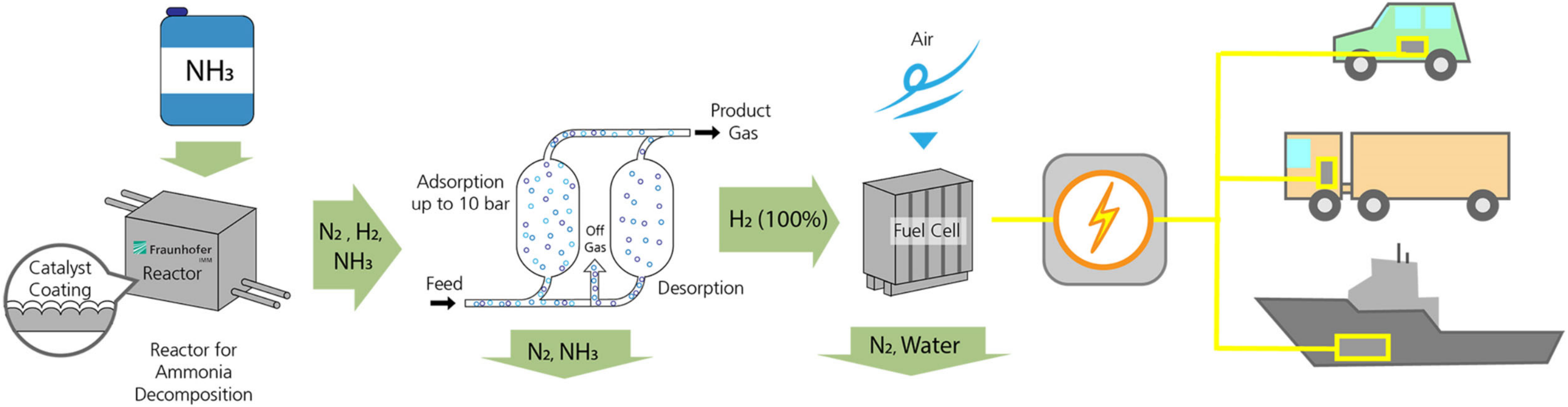
- **Efficiency without electrolysis: 85.3%**
- Efficiency with electrolysis: 55.5%

- The origin of electricity for hydrogen generation
  - wind power or
  - solar power

  does not affect the efficiency but the carbon footprint of the ammonia produced.

AMMONPAKTOR: 50 kW hydrogen supply from ammonia for fuelling Stations, smaller scale maritime



Efficiency of Ammonia decomposition: 88% (without heat utilization)

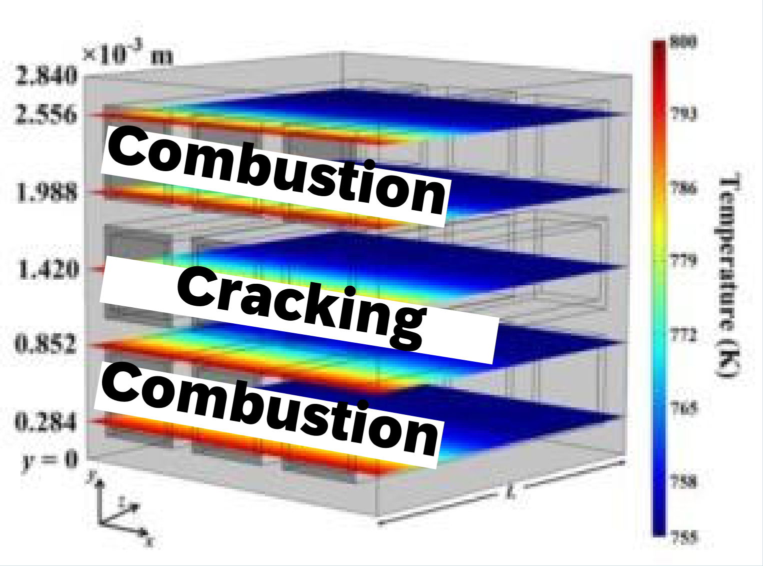
Overall process efficiency: 50%

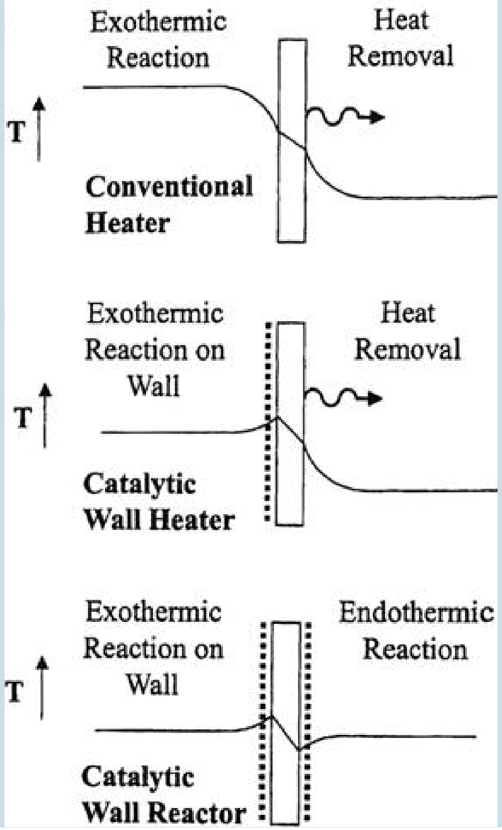
„Nutzung von Ammoniak als kohlendioxidfreien Wasserstoff-speicher für die dezentrale Bereitstellung von Wasserstoff – Entwicklung eines innovativen kompakten Reaktorkonzeptes", AMMONPAKTOR, funded by the Ministry of Science, Education and Culture of Rhineland-Palatinate;

Introducing Catalyst into a Heat-Exchanger: The Catalytic Wall Reactor

Simplification of the heat management and design

- Heat transfer frequently takes place from the fluid to the wall at the reactor inlet almost completely
- Coupling of heat formation and consumption through the lateral heat conduction of the wall is advantageous
- The lateral heat transfer conductivity of the wall is high
- The unit cells shown right are repeated in a pile up to 200 times as shown right





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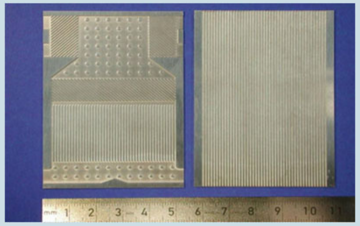
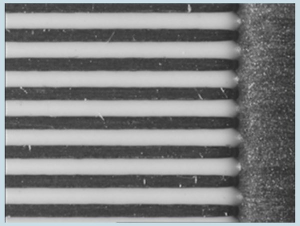
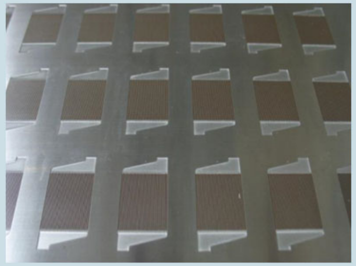
Production Steps of the Reactors

How to make 1.000 - 10.000 reactors per year?

- Process of formation of microchannels in the metal foils, wet chemical etching / embossing
- Catalyst coating, Screen printing
- Sealing, Laser welding
- Attachment of connections / tubing, Orbital welding




Development of ammonia decomposition catalysts at IMM

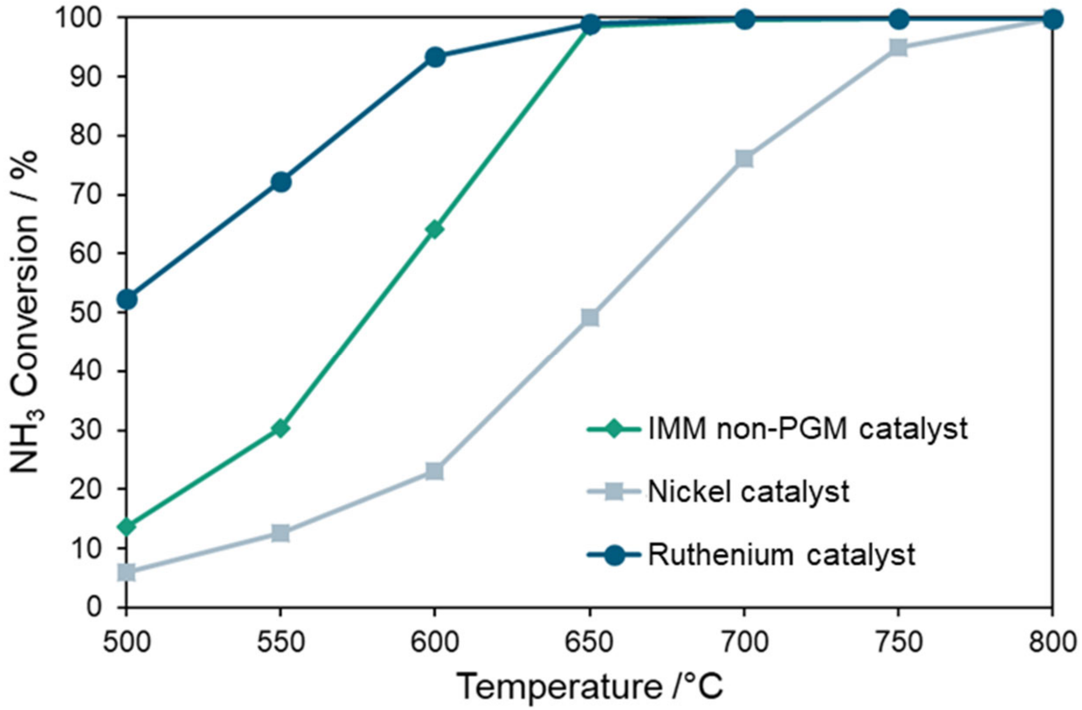
Catalytic activity of different supported catalysts

Catalytic activity at elevated pressure

- allows the operation of a pressure swing adsorption (PSA) unit down stream of the reactor.
- applied gas hourly space velocity (GHSV) of 180 $L_{NH3}/g_{cat}/h$ is very high compared to the literature.

New Non-PGM catalyst developed at IMM

- Enhanced activity compared to Ni/Al_2O_3 catalyst
- High ammonia conversions at ≥650°C comparable to the ruthenium-based catalyst
  - X_{NH3} = 97.7% at 650°C, 98.7% at 700°C
- High hydrogen production rate of 198 $mmol_{H2}$ /g /min at 650°C



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Comparison

Catalytic performance of different materials

Comparison to literature values of highly active NH_3 decomposition catalysts

Catalyst	Temperature °C	Conversion %	H_2 production $mmol_{H2}$ /g /min
Cs-Ru/MgO [1]	500	88.2	59.1
K-Ru/CNTs [2]	450	97.3	32.6
Ru/Fe-C [3]	600	97.5	21.7
Ru/graphitic C [4]	550	95.0	29.1
Ni/Mica [5]	650	97.2	32.5
$Ni_{0.6}$ $(Mg_{0.29}Al_{0.57}O_n)$ [6]	600	99.3	33.3
Ni/MRM [7]	700	95.5	32.0
Ni_1/C-LDH_s-ST [8]	600	98.8	11.0
Ni/ZSM [9]	650	97.6	32.7
IMM non PGM catalyst	**650**	**97.7**	**198.1**

[1] N. Shimoda, R. Yoshimura, T. Nukui and S. Satokawa, J. Chem. Eng. Japan, 52, 10 (2019).

[2] S.-F. Yin, B.-Q. Xu, C.-F. Ng and C.-T. Au, Appl. Catal. B, 48, 237 (2004).

[3] L. Li, F. Chen, Y. Dai, J. Wu, J. L. Shao and H.Y. Li, RSC Adv., 6, 102336 (2016).

[4] Li, Z.H. Zhu, Z.F. Yan, G.Q. Lu and L. Rintoul, Appl. Catal. A, 320, 166 (2007).

[5] Z.-P. Hu, C.-C. Weng, G.-G. Yuan, X.-W. Lv and Z.-Y. Yuan, Int. J. Hydrogen Energy, 43, 9663 (2018).

[6] Q. Su, L. Gu, Y. Yao, J. Zhao, W. Ji, W. Ding and C.-T. Au, Appl. Catal. B, 201, 451 (2017).

[7] J.-L. Cao, Z.-L. Yan, Q.-F. Deng, Y. Wang, Z.-Y. Yuan, G. Sun, T.-K. Jia, X.-D. Wang, H. Bala and Z.-Y. Zhang, Int. J. Hydrogen Energy, 39, 5747 (2014).

[8] J. Zhao, L. Deng, W. Zheng, S. Xu, Q. Yu and X. Qiu, Int. J. Hydrogen Energy, 45, 12244 (2020).

[9] Z.-P. Hu, C.-C. Weng, C. Chen and Z.-Y. Yuan, Appl. Catal. A, 562, 49 (2018).

Development of ammonia decomposition catalysts at IMM

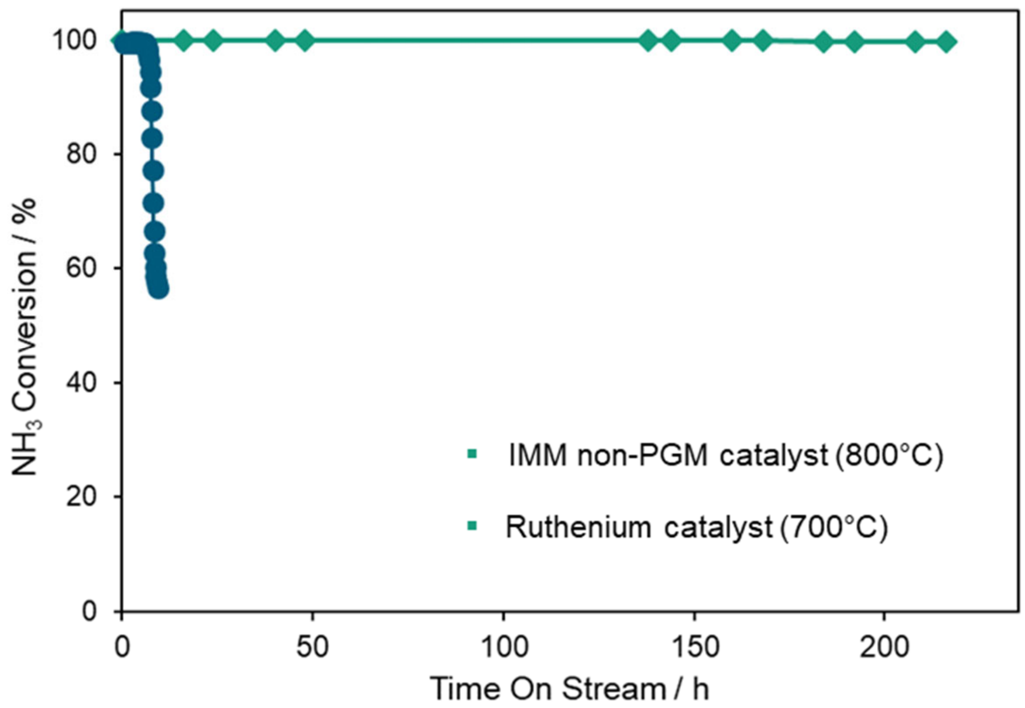
Catalyst stability of different supported catalysts

Stability tests at elevated pressure and 700/800°C

Experiments were carried out at elevated pressure and gas hourly space velocity (GHSV) of 180 $L_{NH3}/g_{cat}/h$ at 700°C and 800°C for the ruthenium catalyst and the IMM non-PGM catalyst, respectively.

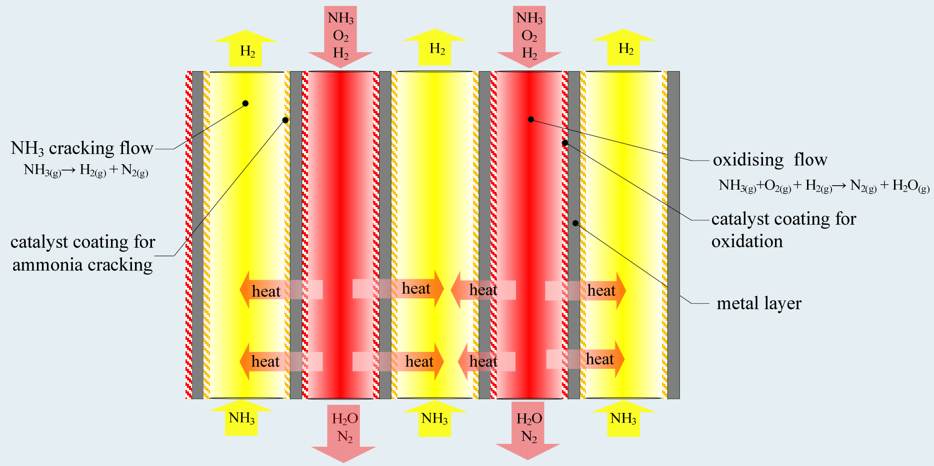
New non-PGM catalyst developed at IMM

- At high reaction temperatures the IMM non-PGM catalyst is much more stable than the ruthenium-based catalyst
- No significant catalyst deactivation was observed after 220 hours time on stream even at 800°C



Why IMM Compact Ammonia Cracker Technology?

- **90% efficiency** of the process compared to 70% for conventional technology due to integrated PSA off-gas combustion
- **Lower carbon dioxide footprint** compared to electrically heated reactor concepts
- **90% size reduction** of the cracking reactor – important especially for mobile / space limited applications



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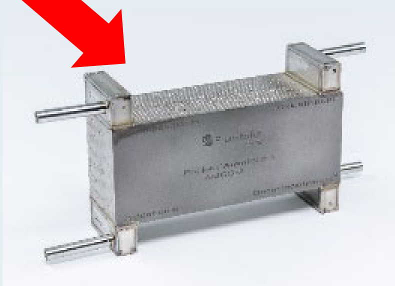
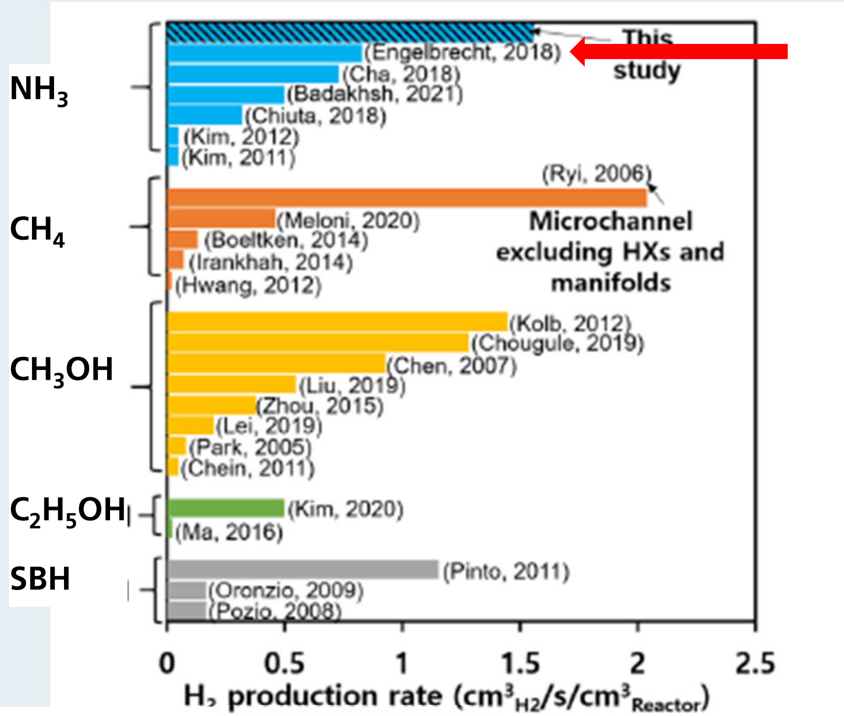
Why IMM Compact Ammonia Cracker Technology?

- Second highest specific hydrogen production rate ever reported was already achieved in 1st gen reactor



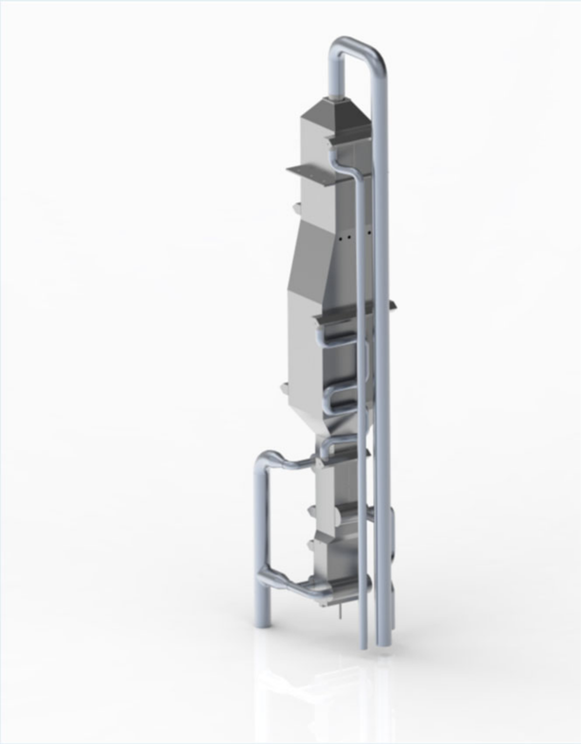


A. Badakhsh et al.

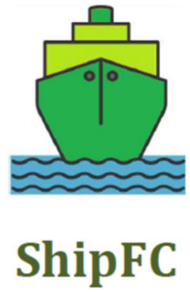
Chemical Engineering Journal 426 (2021) 130802

Why IMM Compact Ammonia Cracker Technology?

- Cracking reactor for **25 kg/h ammonia feed** currently in manufacturing process
- Test results will be disseminated soon!



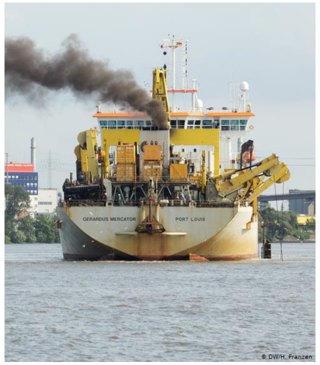
Multi MW Ammonia Ship Fuel Cells

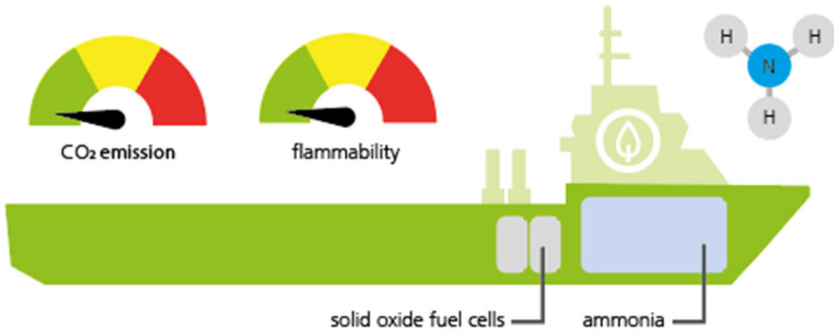


Maritime transport is a major contributor to greenhouse gas emissions.

Maritime transport on the world's oceans is currently responsible for approximately 2.6 percent of global CO_2 emissions (German Environment Agency (UBA).

Clearly, countermeasures are urgently needed.





In 2015, about 932 million tonnes of CO_2 were emitted, and that figure increases every year.

EU Project ShipFC - Project Targets

ShipFC

1. Prove the case for scalable, large-scale zero-emission fuel infrastructure

2. 4 time 500 kW ammonia SOFC system with novel heat/air distribution

3. Ammonia's potential has also been recognized at a political level, with the European Union providing 10 million euros in financial support for the ShipFC project (Grant agreement ID: 875156)

Key Performance Data

1. Viking Energy, supply vessel with maximum power demand of 21 MW, 2 MW nominal auxiliary load
2. Operation of a 2 MW ship for 12+ months close to zero emission
3. Potential for 70% electric efficiency, 90% overall efficiency
4. Projected cost of ammonia 500 $/t (compressed H2: 1,250 €/t, liquid H_2: 2,500 €/t)

Project Movie (2 min duration)

ShipFC

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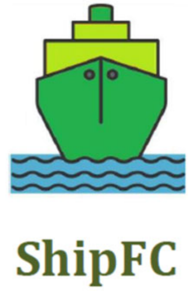
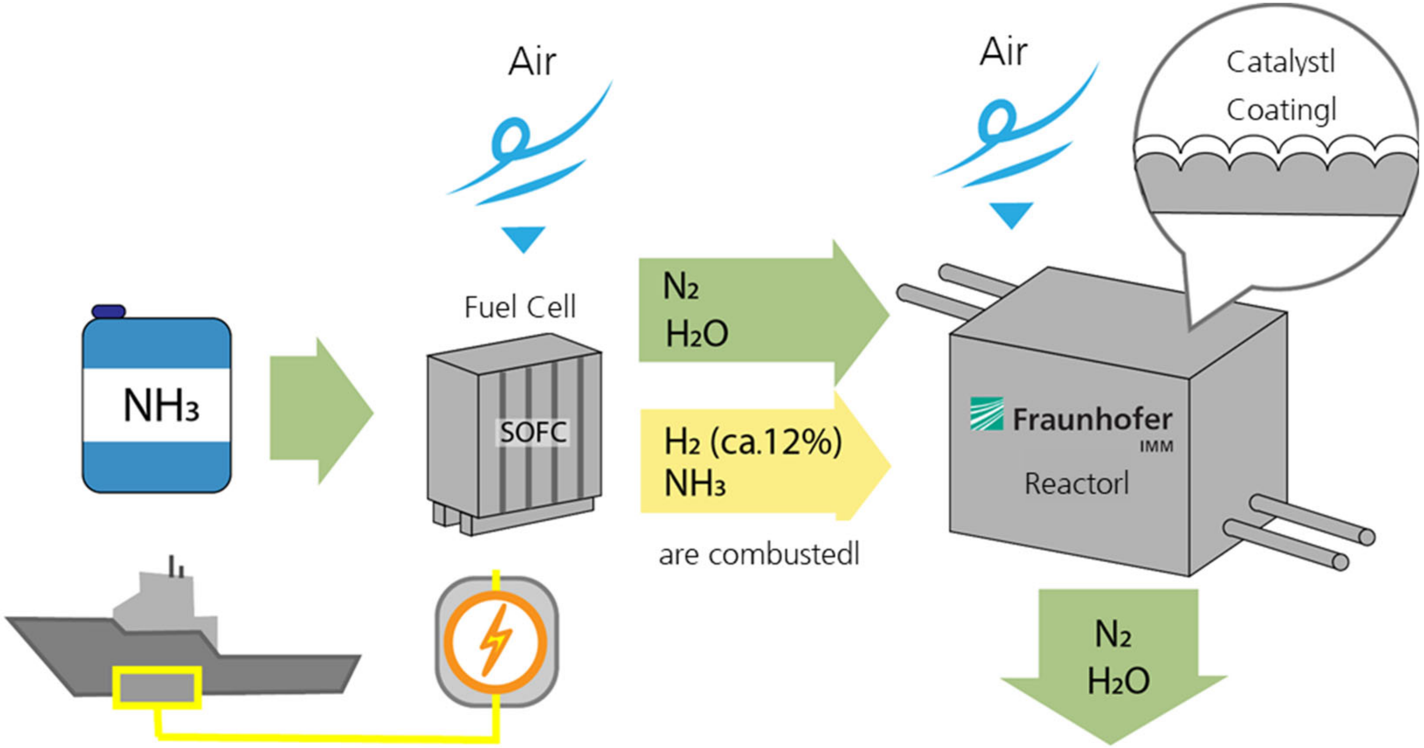
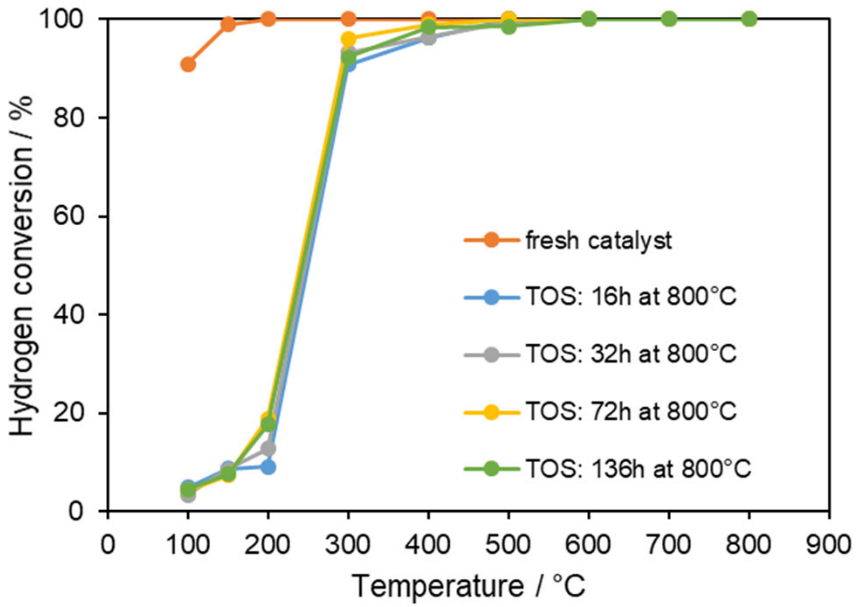
Overall System Scheme

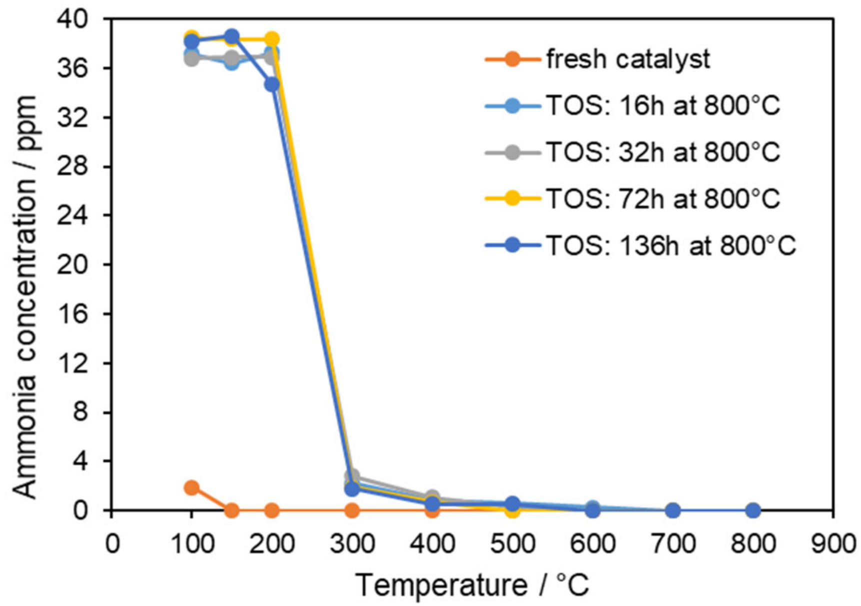




Development of hydrogen / ammonia combustion catalysts at IMM

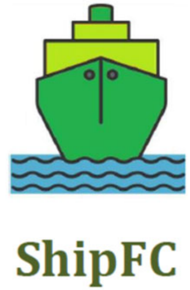
Catalyst stability tests at 800°C

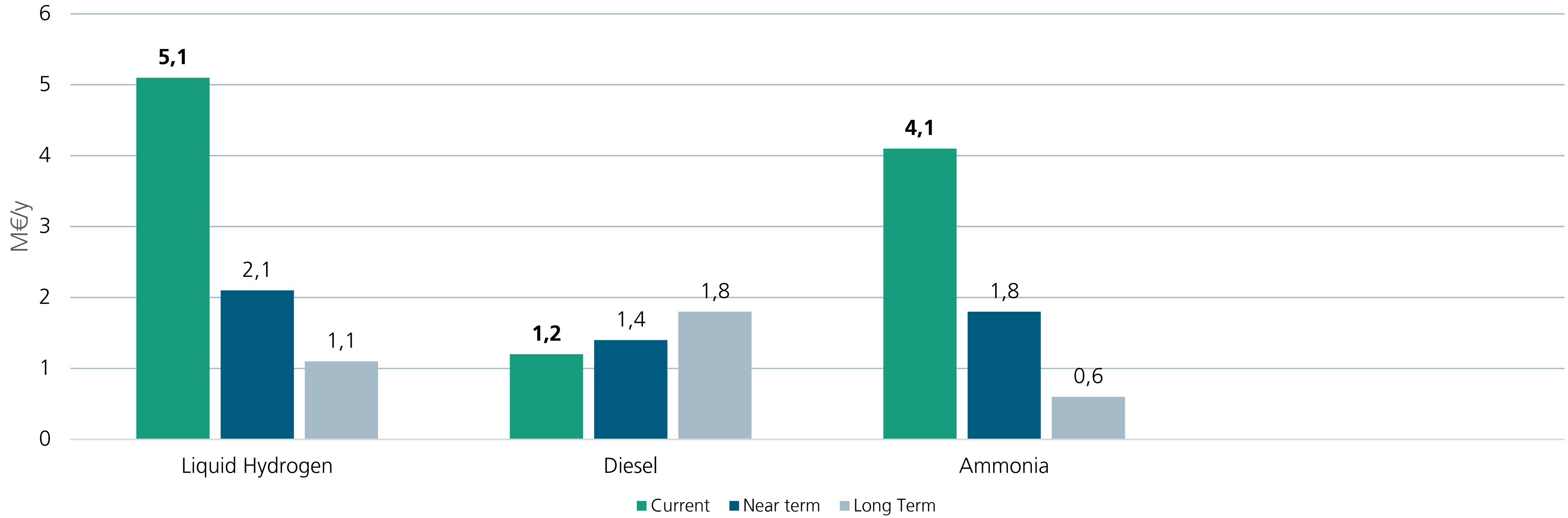




- T.Weißenberger et al., Catalysts 12 (2022) 1186

Future system and fuel cost of hydrogen and hydrogen carriers for 20 MW maritime application





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Projects

Ammonia as hydrogen carrier: Utilization in combustion engines

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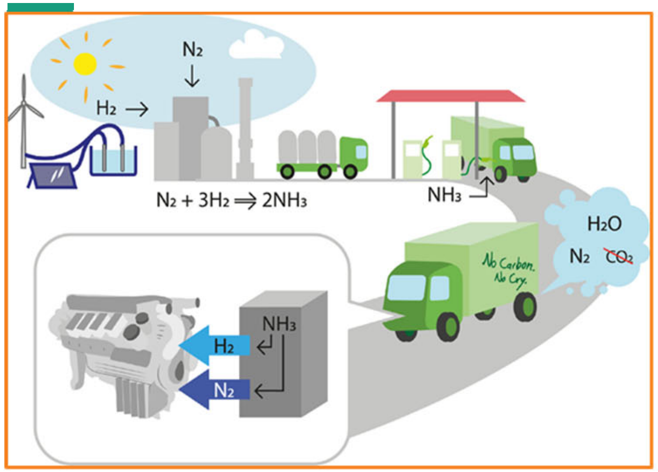
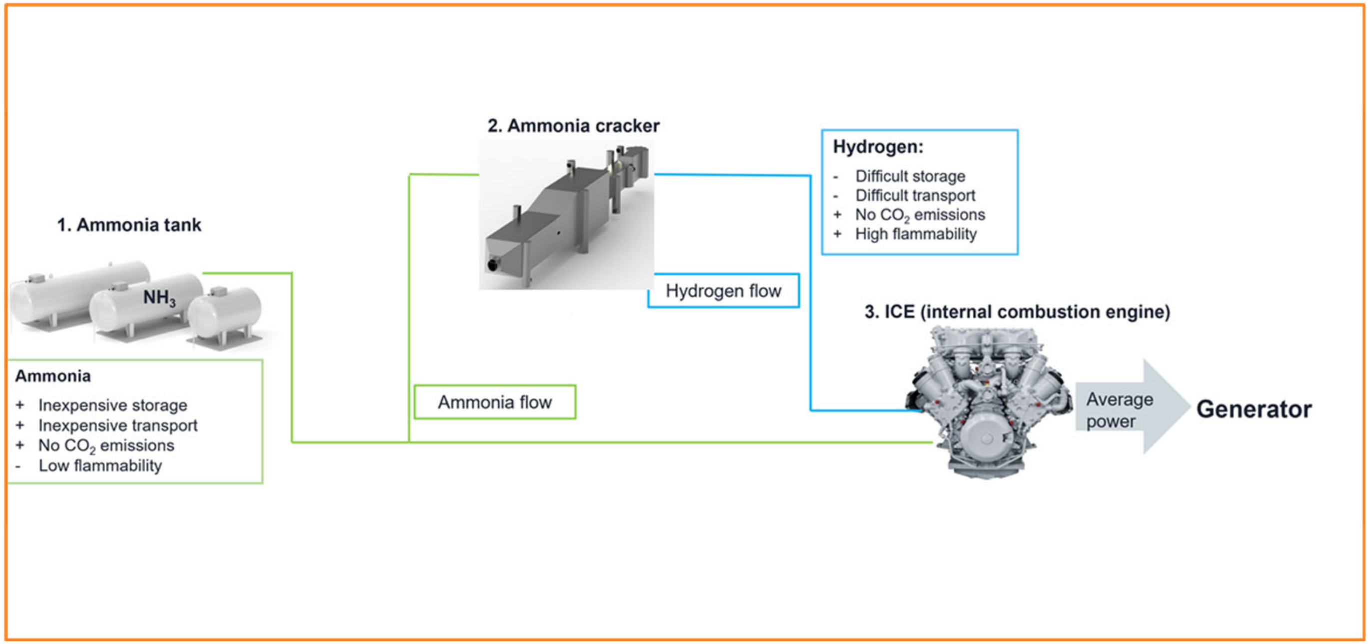
Outlook

Use of NH3 as a substitute for diesel in converted combustion engines





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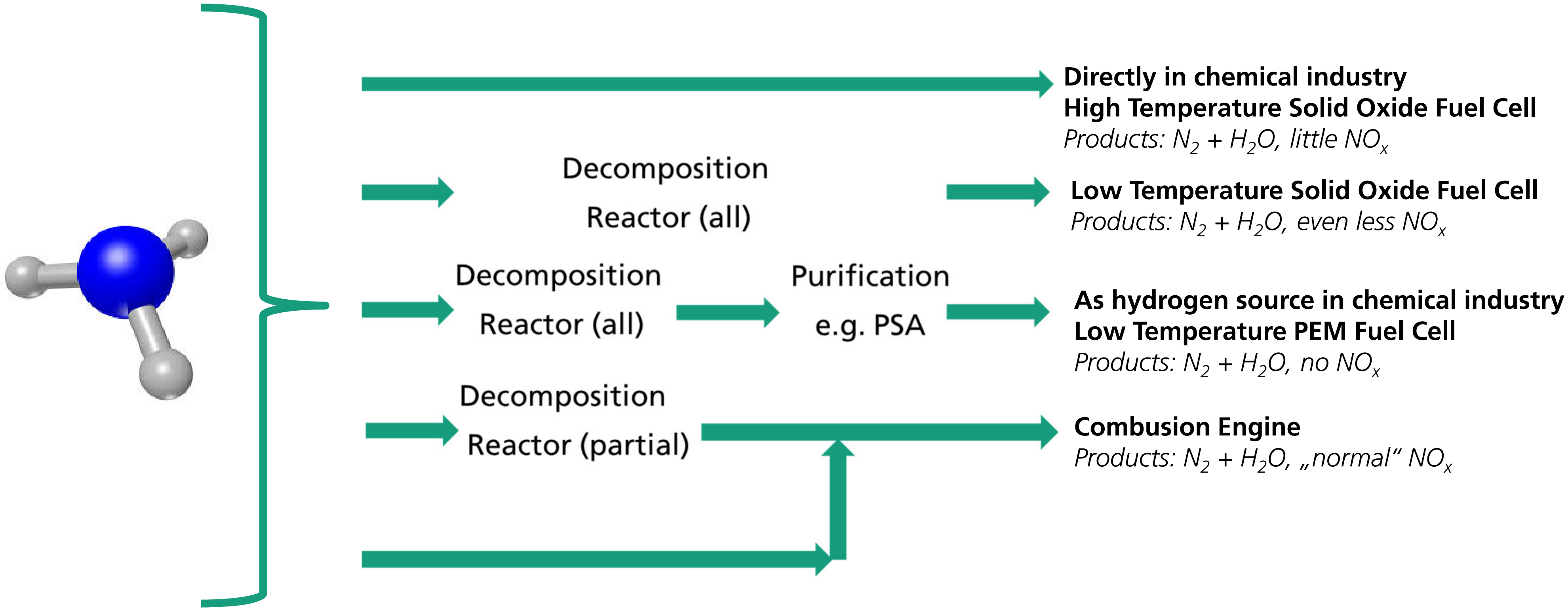
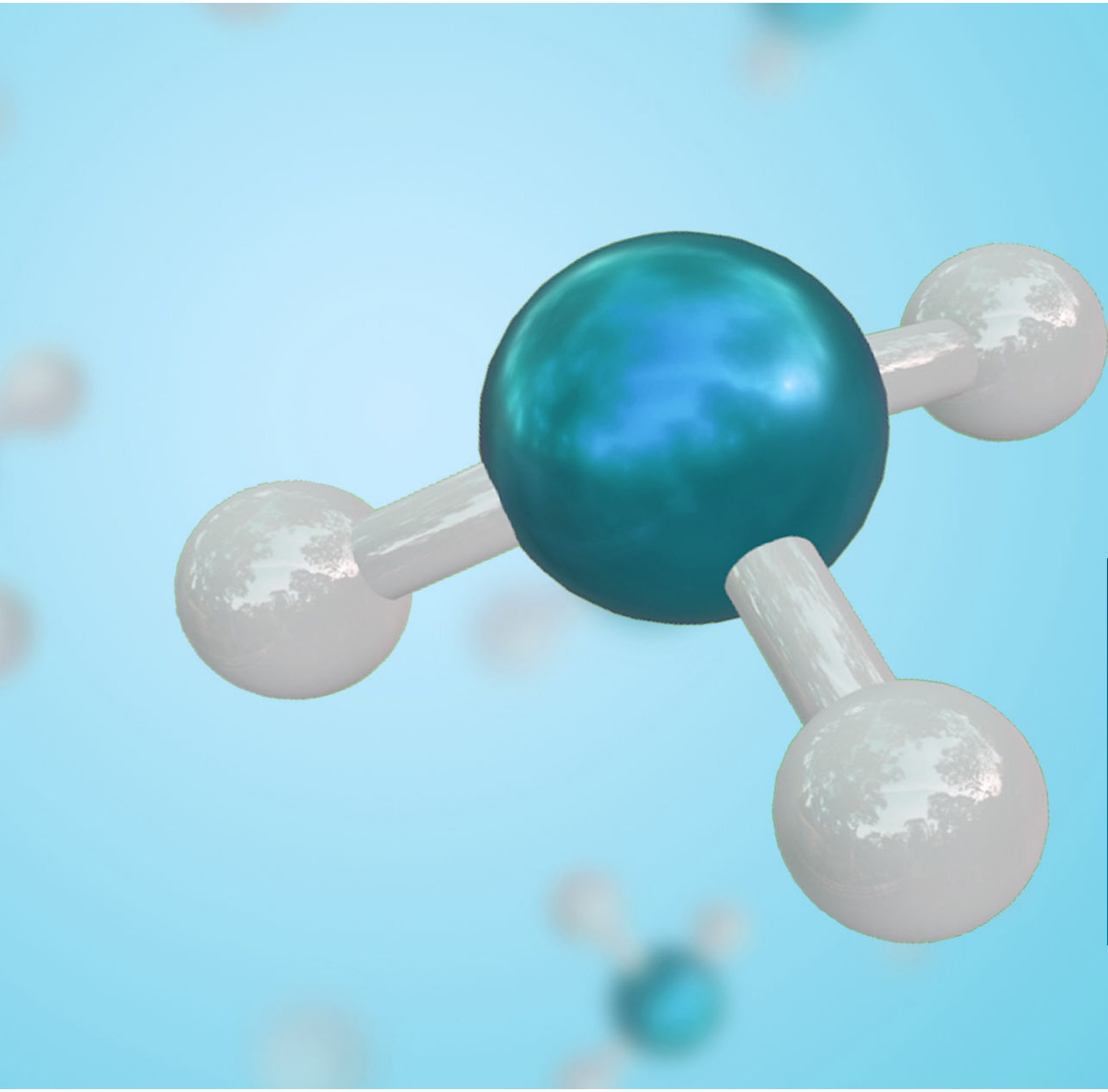
Possible routes of ammonia utilization in fuel cells and combustion engines





03

Safety Aspects

Safety Issues

Released ammonia is washed by a water veil successfully in most cases by fire brigades

Ammonia has, different to methanol, no mutagenic impact

Since 1980 72 accidents happened with ammonia in Germany, 3 persons died

Many cases of release from refrigeration systems, 10% of accidents in ice stadiums !

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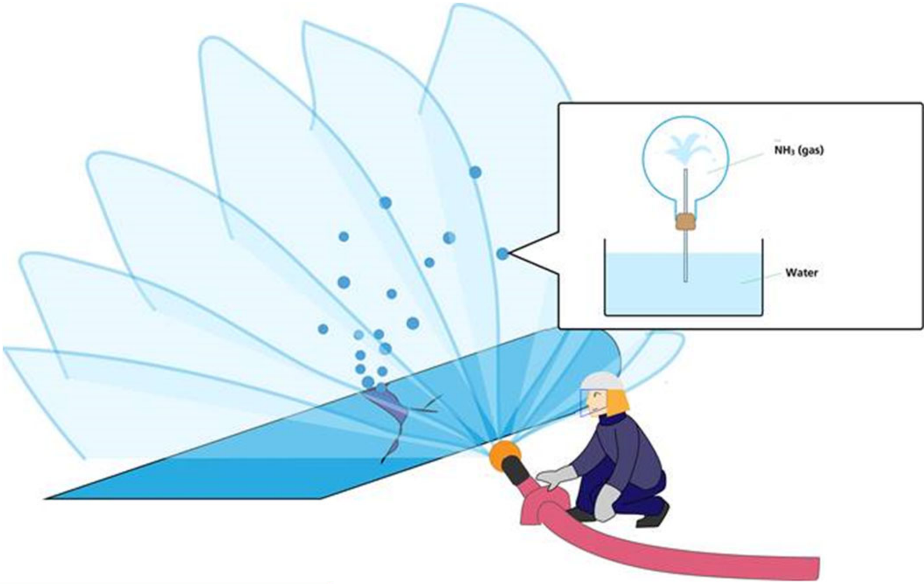
Emergency scrubber



Explosion Limit [Vol.%]	Lower	Upper
H_2	4	77
NH_3	15	33.6

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Summary

Methanol as hydrogen carrier

- Ammonia is a viable option for hydrogen transportation and storage
- Technology exists already for ammonia transportation
- Ammonia can be used as hydrogen source
  - in industrial applications
  - in (existing) combustion engines
  - directly in high temperature fuel cells
  - as hydrogen source
    - for low temperature (PEM) fuel cells
    - Industrial applications

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Make use of our new capabilities in our brand new extension building

- Extensively equipped labs for catalyst testing
- Extensively equipped technical hall for system testing

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Thank you for your attention