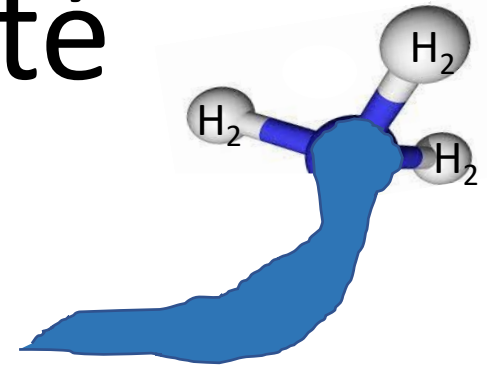


L'ammoniac, ce vecteur d'hydrogène pour décarboner la mobilité



Christine MOUNAIM-ROUSSELLE

Laboratoire PRISME

Fédération de Recherche pour l'Innovation et la Transition énergétique

TRANSPORTS
De PERSONNES



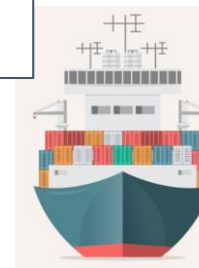
MOBILITE à FAIBLE IMPACT CARBONE

=

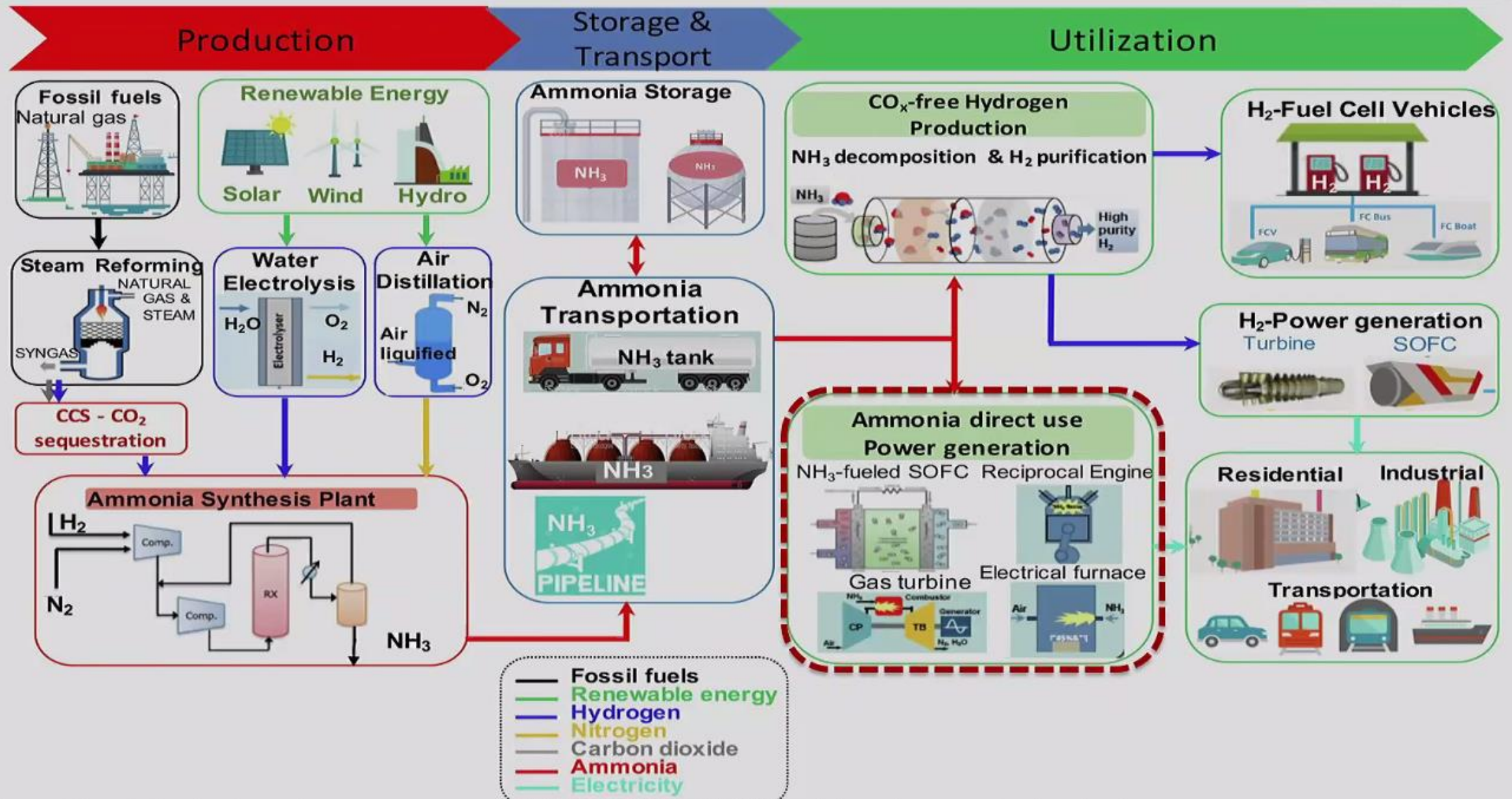
TRANSPORT à FAIBLE IMPACT
CARBONE

= ENSEMBLE DE SOLUTIONS

ISES



Role of Ammonia in the Energy System



Yesterday...



EQUIPMENT

WinGD engines to run on methanol and ammonia by 2025

13 days ago



COLLABORATION

Wärtsilä, SHI partner up on ammonia-fuelled engines

2 months ago



COLLABORATION

Jurong Port joins ammonia-fuelled tanker initiative

4 days ago



VESSELS

Japanese trio to develop large ammonia-powered ammonia carrier

about 1 month ago

Why Ammonia for transport ?

9X

Ammonia holds **9X THE ENERGY** of Lithium-Ion Batteries

Ammonia is **LESS FLAMMABLE, EASIER TO TRANSPORT**, and more **COST EFFECTIVE**.

1.8X

Ammonia has **1.8X THE ENERGY DENSITY** of Hydrogen

stored at -33C

Ammonia is **STORED AT-33C** compared to **-253C** required for Hydrogen

Ammonia can become the CO2-free fuel of the future

2/21/2019



Ammonia has the potential of playing a central role in a more sustainable future. It can be used as a CO2 free fuel instead of gasoline, diesel and fuel oil. Moreover, the highly energy-consuming production of ammonia for fertilizer and other purposes can be based on green power instead of natural gas. That will save large amounts of CO2 – and at the same time efficiently “store” excess power from wind turbines and solar cells.



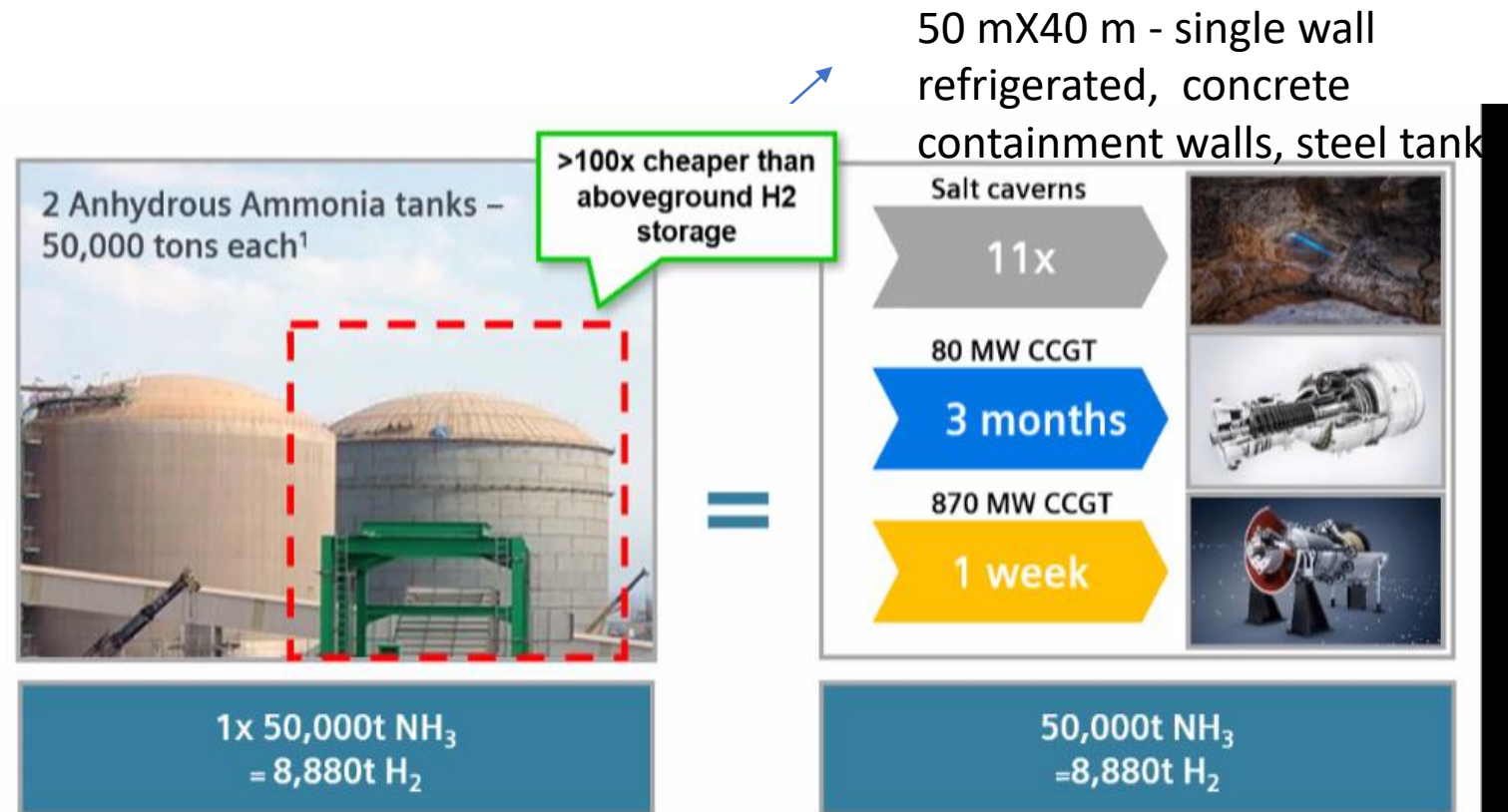
Project Leader, Senior Principal Scientist John Bagild Hansen, Topsoe, at the research facility in Frederik, Denmark.

A new research project, SOCANH3 (Solid Oxide Cell based production and use of ammonia) with a number of strong partners will over the next years develop and demonstrate the technology and thereby bring it a big step closer a commercial breakthrough.

“We expect that ammonia can be used for transportation and efficient storage of energy. The greatest advantage of ammonia is that it has a high energy density which makes it an effective fuel and energy storage option – and it can thereby solve some of the most important challenges of creating a sustainable energy system of the future,” says project leader, Senior Principal Scientist John Bagild Hansen, Haldor Topsoe A/S.

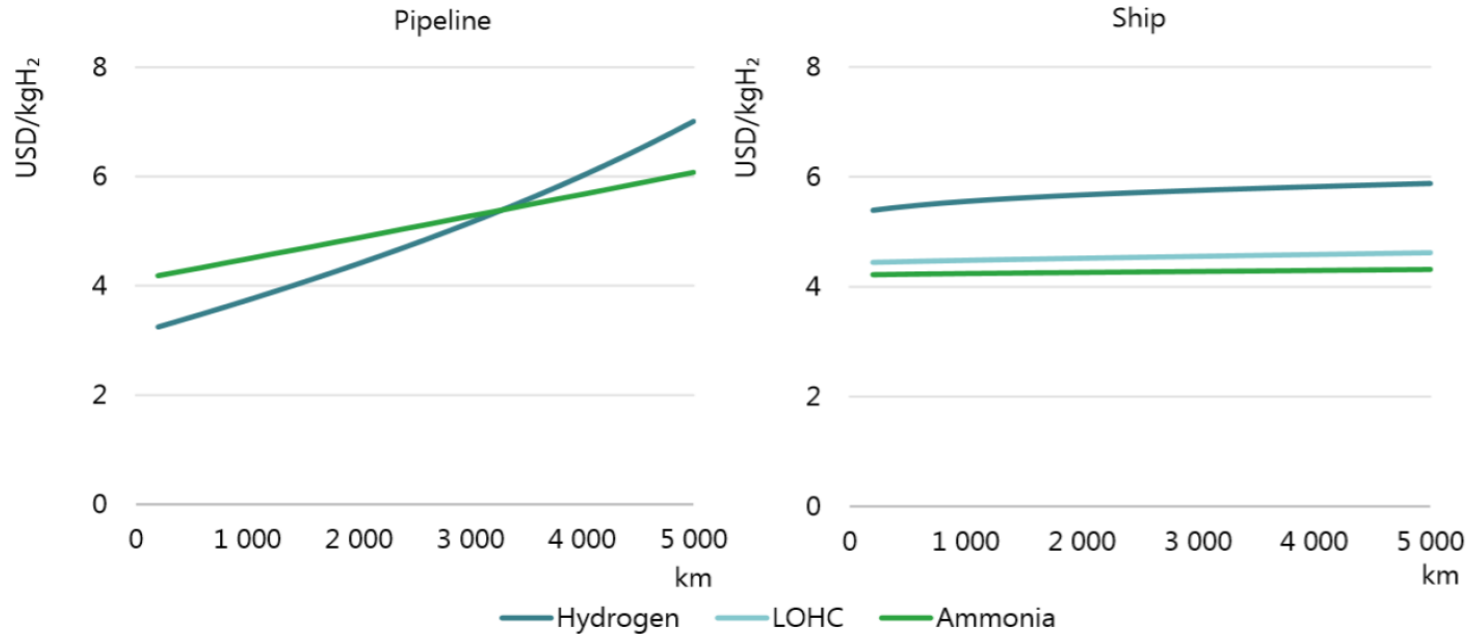
Ammonia storage

- high pressure or high refrigeration to store it in a liquid phase
 - 1) storage vessels = 300 tons
 - nearly 17 bars of pressure to maintain liquid phase and meet minimum safety requirements for storage and transportation.
 - 2) refrigerated vessels = high storage capacity (as high as 66.2 million liters)
 - temperature requirement for low pressure storage : -33°C at 1 atm.



Cesar Z, UK-India Ammonia meeting, 2020

Storage cost and transport



Full cost of hydrogen delivery to the industrial market by pipeline or by ship in 2030 for different transmission distances

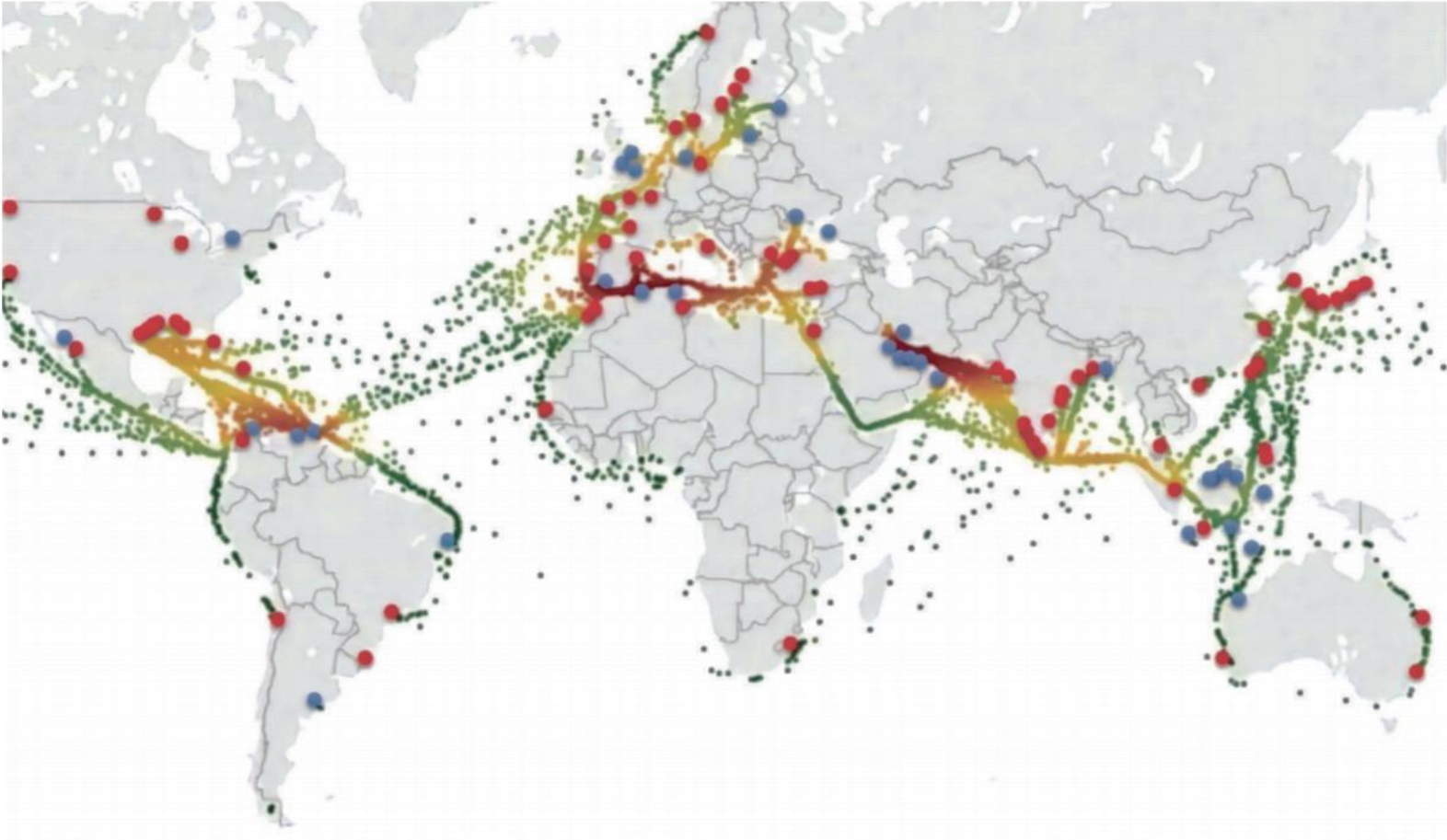


Comparison of Hydrogen and Ammonia As an Energy Vector, in 2019 USD¹⁶³

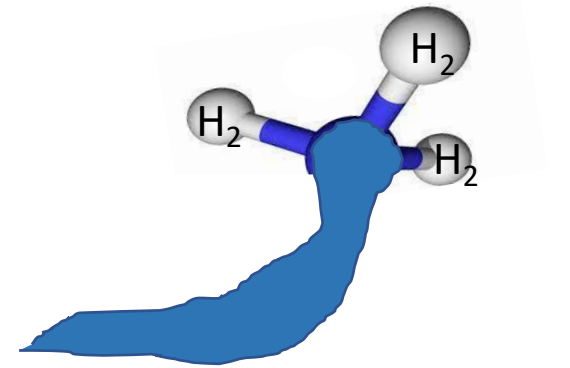
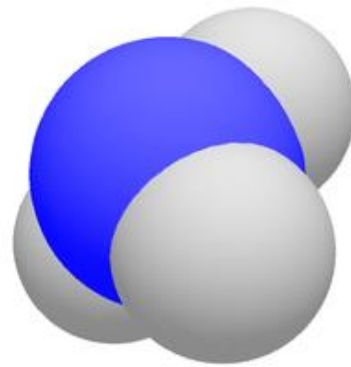
		hydrogen (\$ kg·H ₂ ⁻¹)	ammonia (\$ kg·H ₂ ⁻¹)
production pipeline		3.7	4.7
transport		2.3	0.24
storage	182 day	18.5	0.67
	15 day	2.4	0.08

Worldwide network

● Ammonia loading facilities ● Ammonia unloading port facilities



Production



Classical way : Haber-Bosch Process

Synthèse : $\text{N}_2 (\text{g}) + 3 \text{H}_2 (\text{g}) \rightleftharpoons 2 \text{NH}_3 (\text{g})$

Exothermique $\Delta H^\circ = -46 \text{ kJ/mol}$

Mise au point du premier réacteur : **1913**

Réaction Cinétique : **impossible à Tambiante**

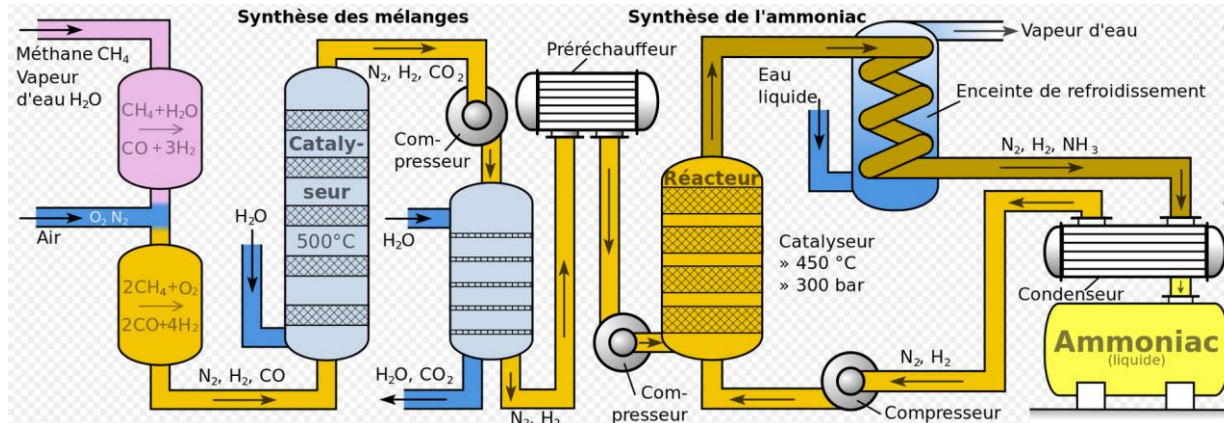


catalyseur nécessaire : à base de fer (Fe) et nickel (Ni)



haute T pour bonne réproductivité (**>670 K**) + haute P (**~100-300 Bars**)

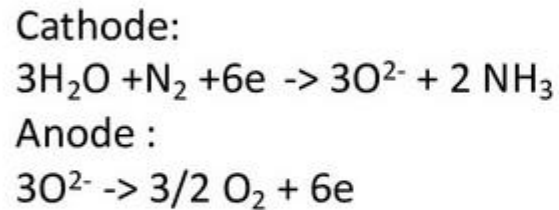
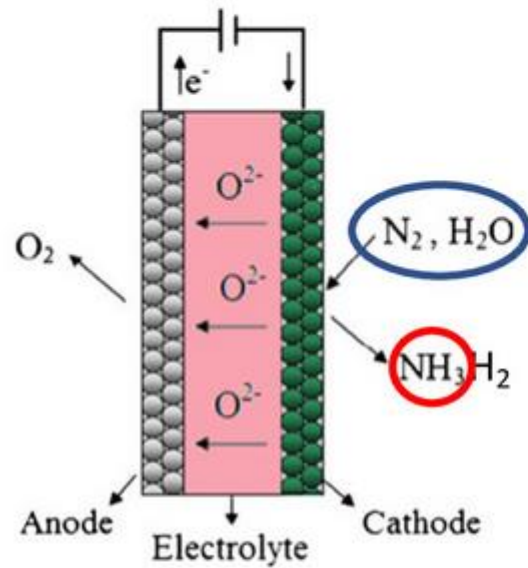
Procédé en réacteur-tube



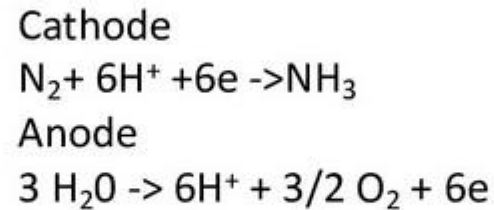
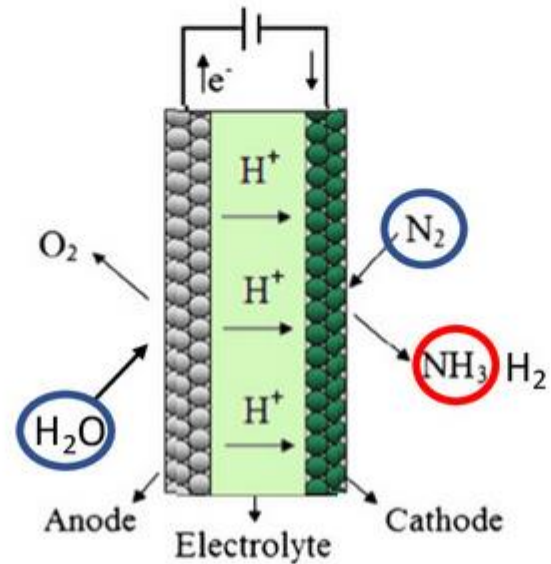
Problème majoritaire :

- soit à partir du CH₄
- Soit à partir du H₂ (lui-même produit à partir du CH₄ Hydrogène jaune/bleu et non VERT)

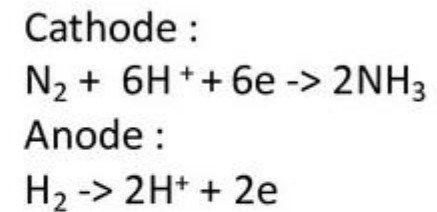
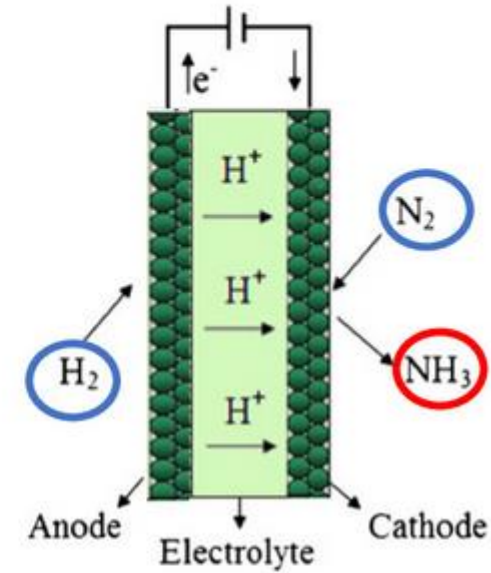
New Process Electrochemical reactor at High T



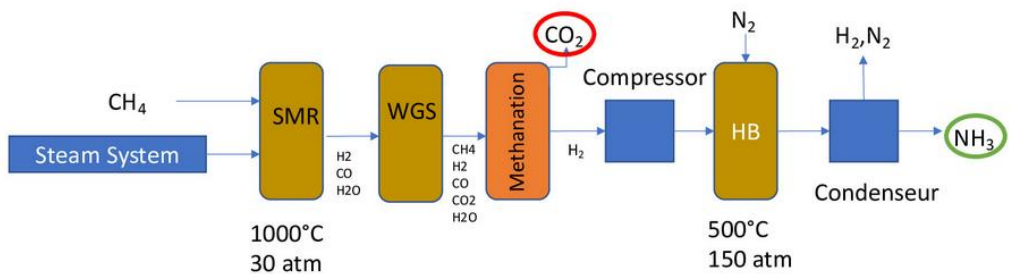
« SOEC »



« PEEC »



« PH »



VP-HB

FORCES

- Eprouvé
- Fiable
- Répond aux besoins

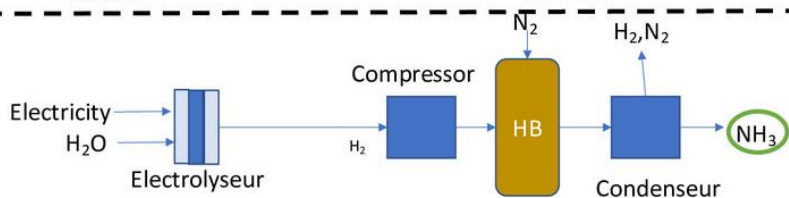
FAIBLESSES

- Energivore
- Empreinte C
- Centralisé
- Purification N₂ et H₂

OPPORTUNITES

MENACES/RISQUES

- Réglementation C



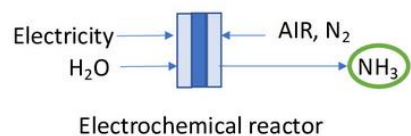
E-HB

- Technologie Mature
- Empreinte C

- Energivore
- Centralisé

Décarboner l'industrie

- Investissement
- Coût



E

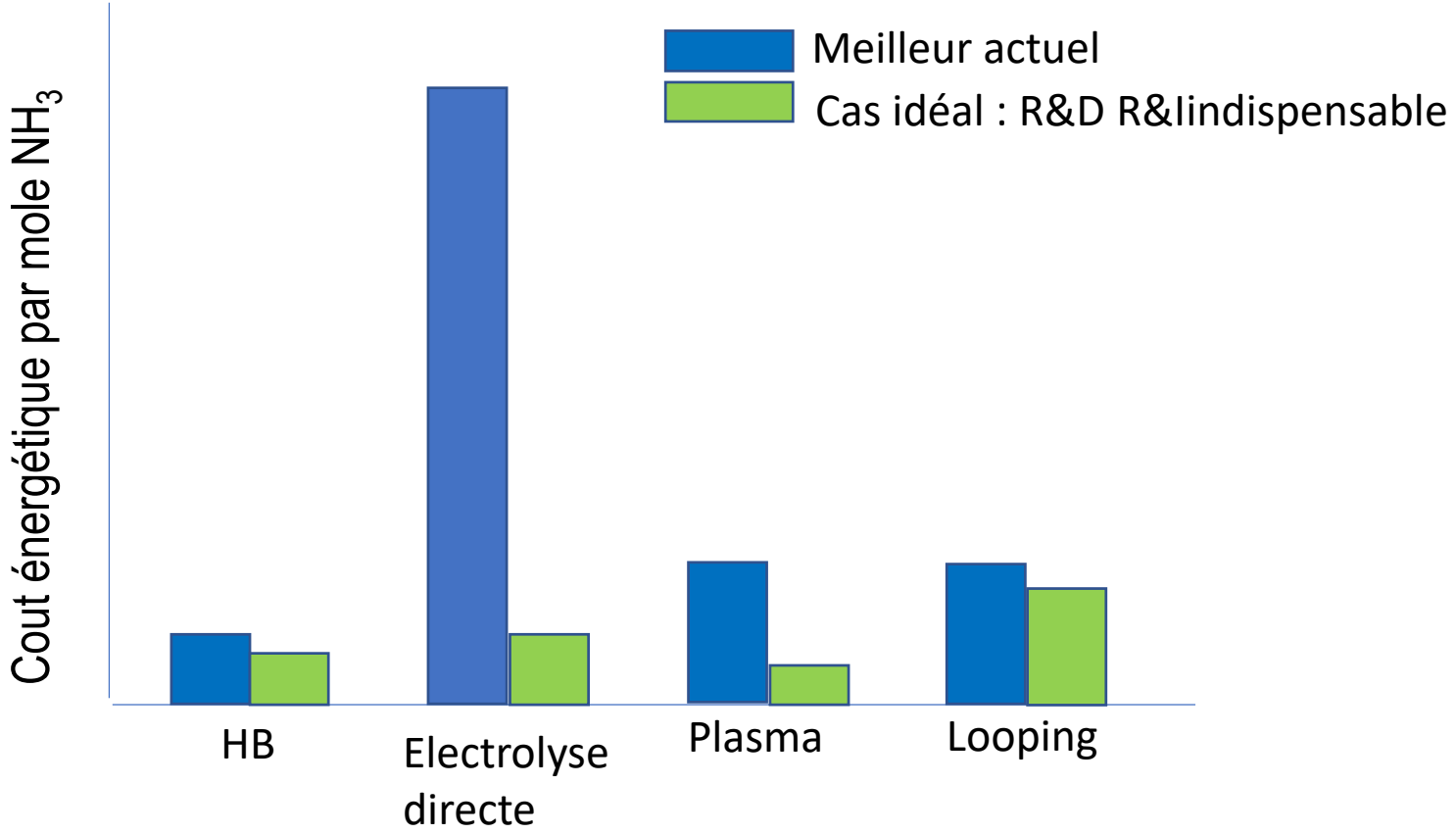
- Electrification totale
- Empreinte C

- TRL 2-3

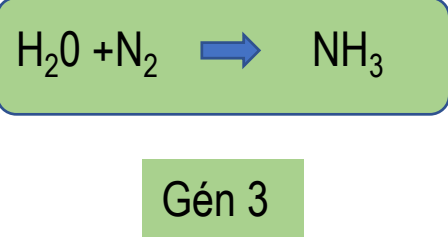
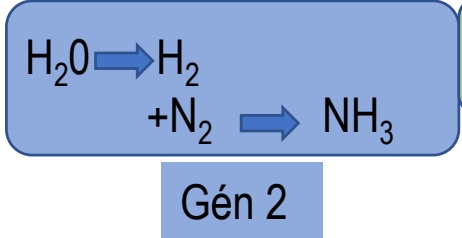
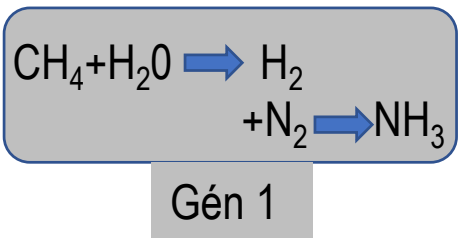
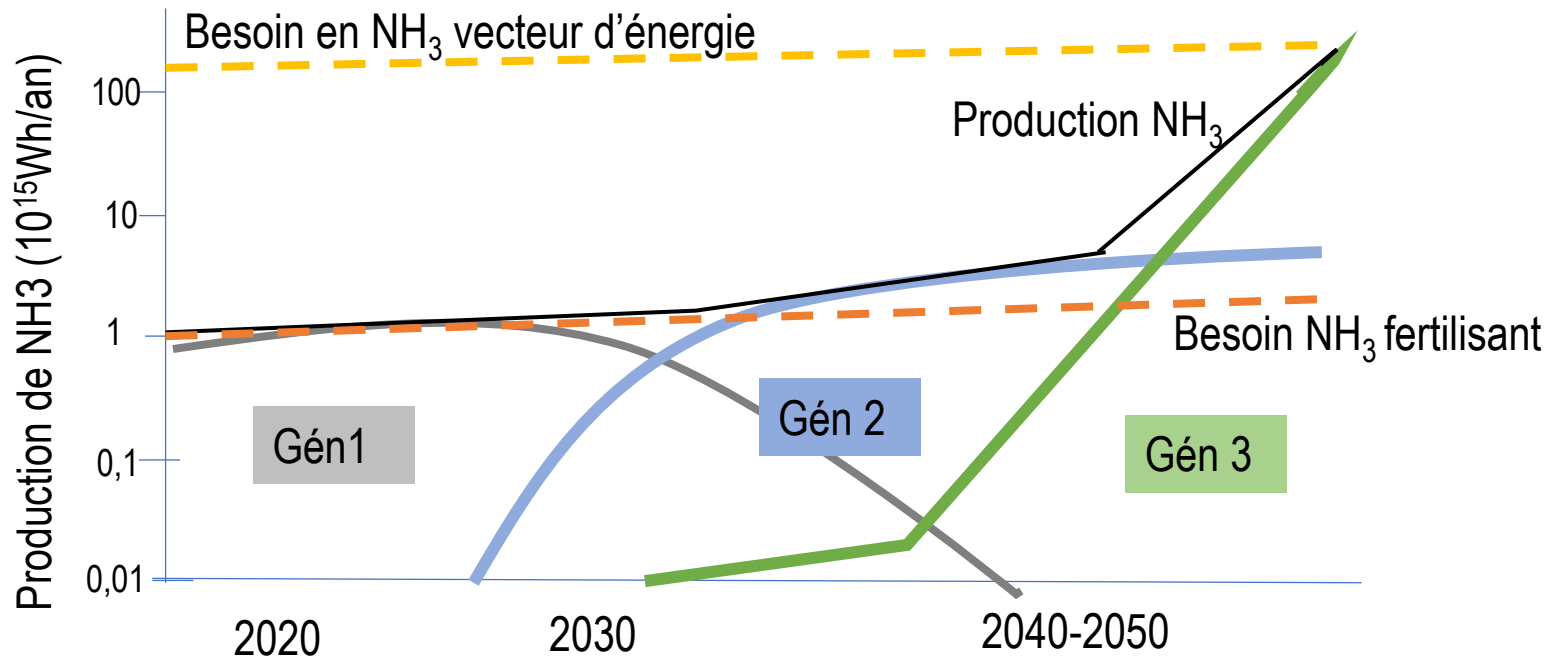
H₂O, AIR
Décentraliser la production de NH₃

- Innovation
- Performances

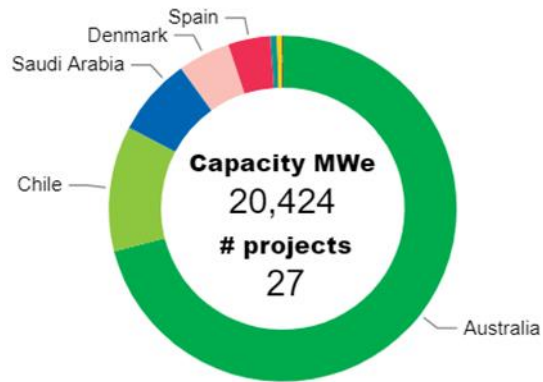
Différentes techniques de production de NH₃



Répondre à la future demande !



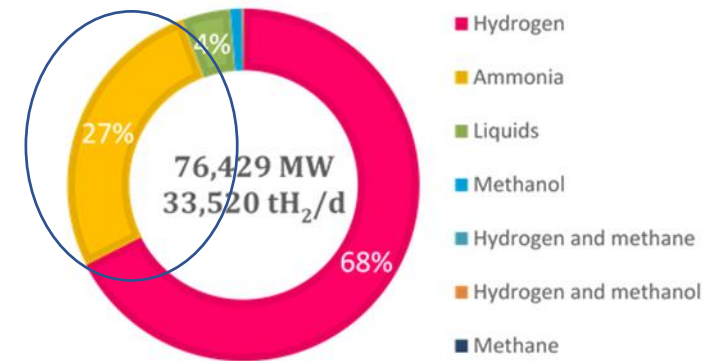
Ammonia production today



Announced global electrolysis capacity for power-to-ammonia projects (2021)



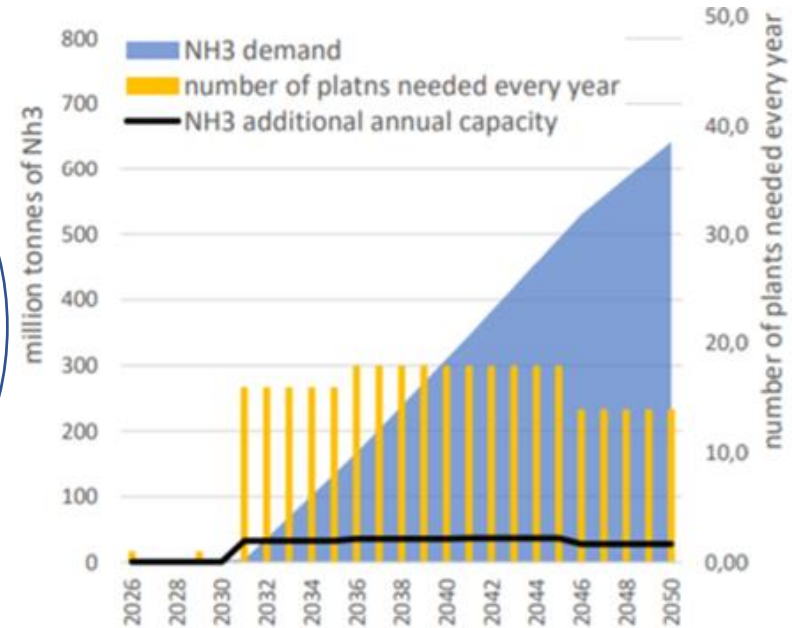
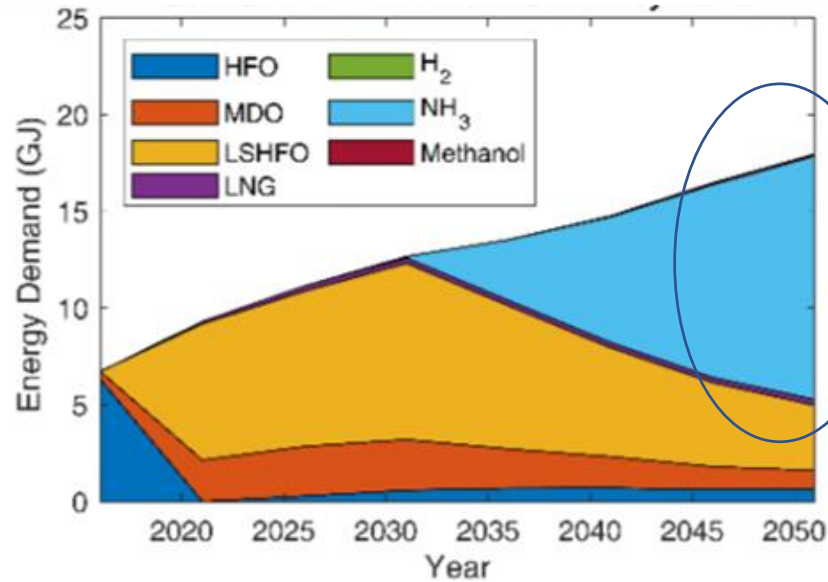
Electrolysis by end-product (2021)



A total of 27 ongoing or announced Power-to-Ammonia projects mostly concentrated in Asia (70% Australia), most dated between 2020 and 2030 = RECENT INTEREST for Power-to-Ammonia

Energy demand for maritime sector

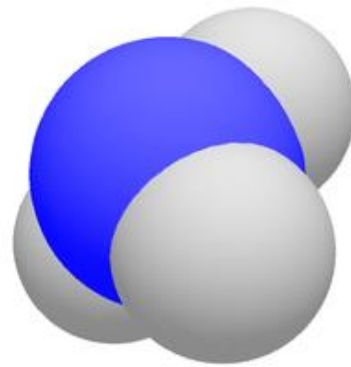
- Decarbonize for 2050



Needed ammonia plants to meet IMO target (plant capacity of 7000 MTPD)

LSHFO = light sulfur heavy oil

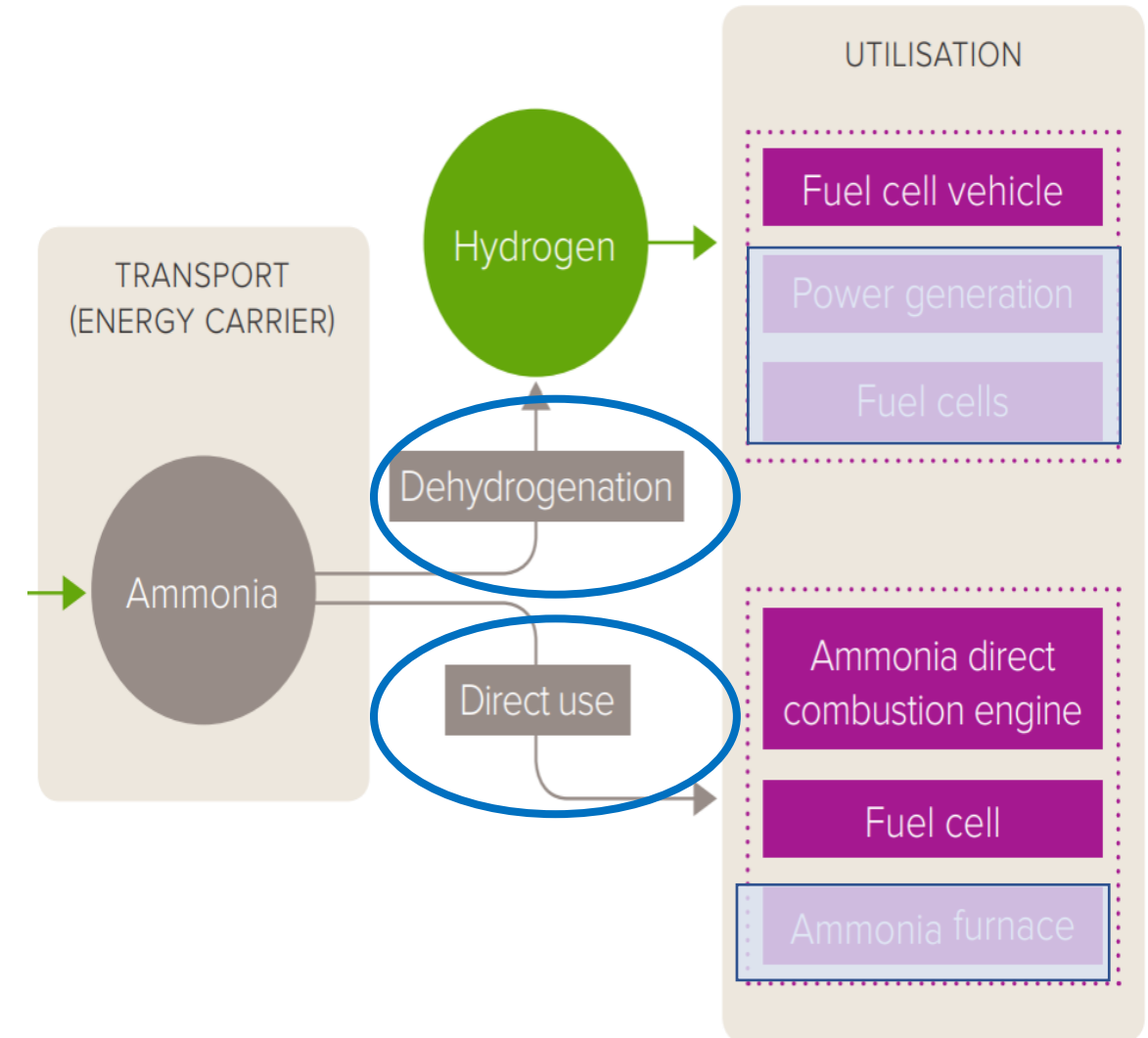
Energy carrier



How to extract this energy content ?

3 solutions

- ❑ To decompose ammonia by means of new optimized reactors in order to provide hydrogen
- ❑ To use ammonia directly
 - ❑ in fuel cells
 - ❑ To employ the chemical in combustion systems such as turbines or internal combustion engines.



How to extract this energy content ?

3 solutions

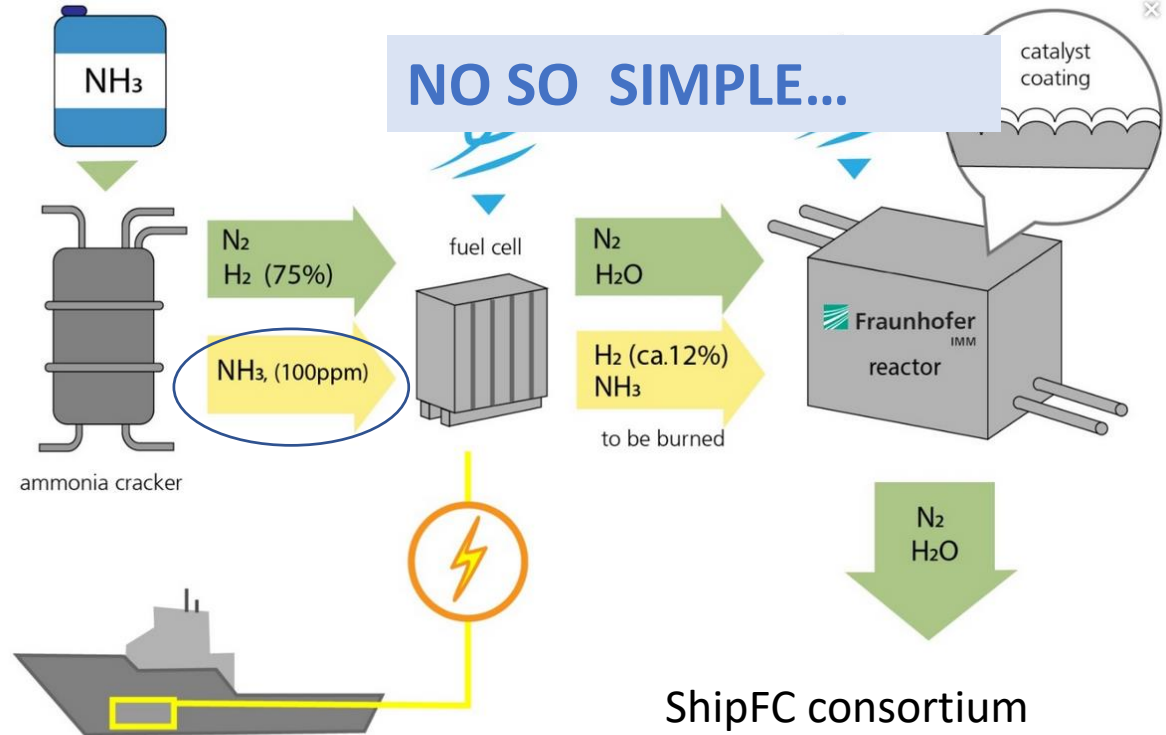
- ❑ To decompose ammonia by means of new optimized reactors in order to provide hydrogen
- ❑ To use ammonia directly in fuel cells
- ❑ To employ the chemical in combustion systems such as turbines or internal combustion engines.

ULTRA-PURE HYDROGEN PRODUCTION VIA AMMONIA DECOMPOSITION IN A CATALYTIC MEMBRANE REACTOR ,

Cechetto, Di Felice, Gutierrez-Martinez, Arratibel-Plazaola, Gallucci



areNH₃a

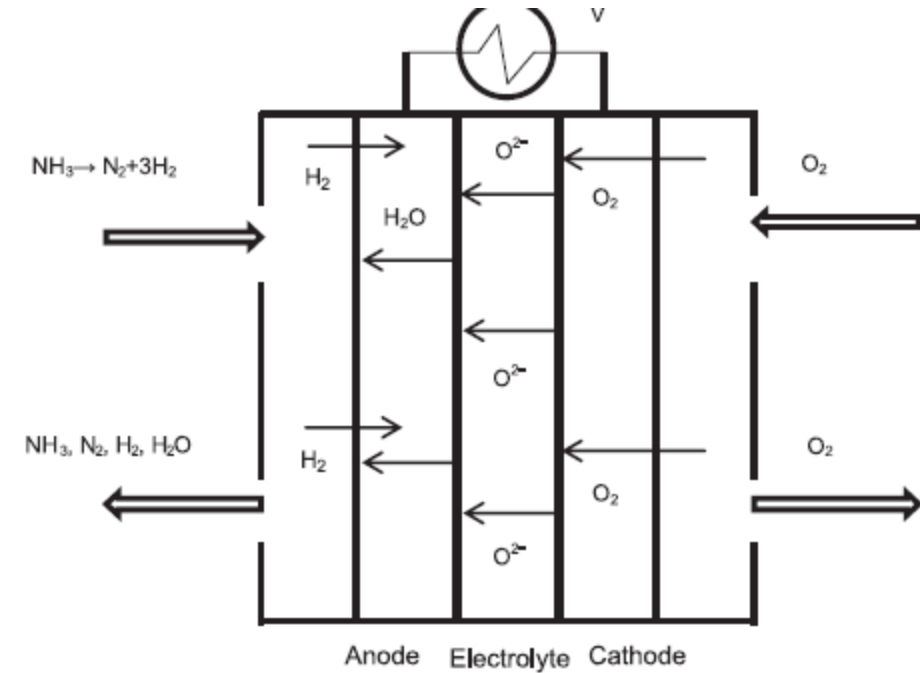


© Fraunhofer
Ammonia is split into nitrogen and hydrogen in the ammonia cracker. The latter is then burned in the fuel cell to generate electricity. The catalytic converter ensures that no harmful nitrogen oxides are produced. The only end products are water and nitrogen.

How to extract this energy content ?

3 solutions

- ❑ To decompose ammonia by means of new optimized reactors in order to provide hydrogen
- ❑ **To use ammonia directly in fuel cells**
- ❑ To employ the chemical in combustion systems such as turbines or internal combustion engines.

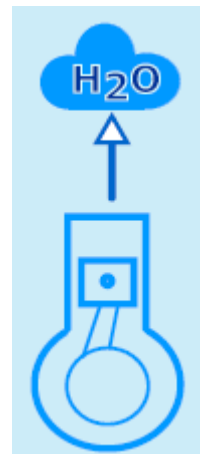


- Direct ammonia solid oxide fuel cell : HT !
- Other fuel cells LT
- Still in progress

How to extract this energy content ?

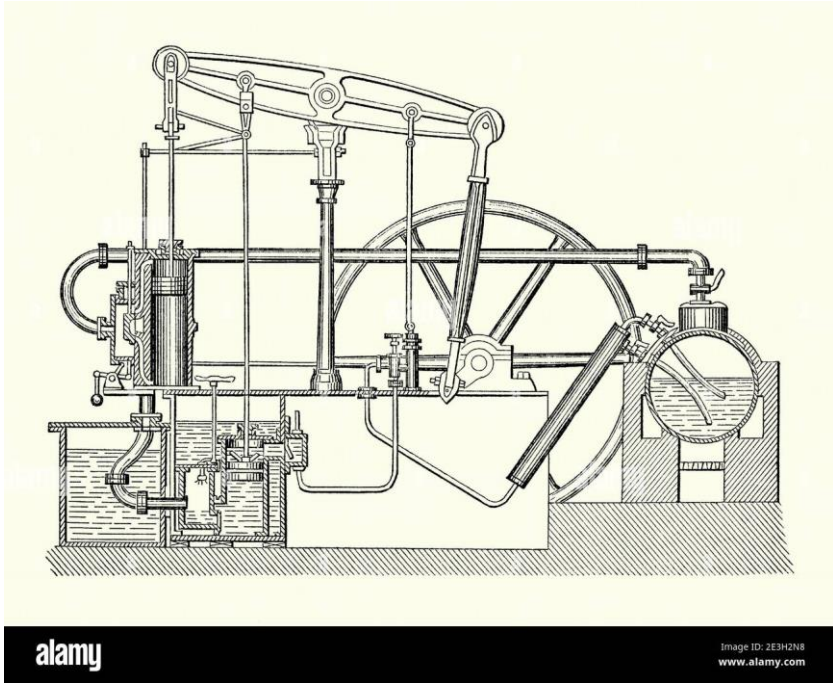
3 solutions

- ❑ To decompose ammonia by means of new optimized reactors in order to provide hydrogen
- ❑ To use ammonia directly in fuel cells
- ❑ **To employ the chemical in combustion systems such as turbines or internal combustion engines.**



researchers from the UK announced that ammonia is a clean and secure hydrogen-containing energy source, proposing the idea to use it directly in engines. As it was underlined in another recent analysis based on the opportunity for NH_3 to be one of best environmentally benign energy carriers for China, other advantages of direct ammonia injection were highlighted, raising that *'ammonia is an ideal fuel since it is not a greenhouse gas and its complete combustion forms only N_2 and H_2O '*

The use of NH₃ as fuel for vehicles = an old story



**Une ancienne gravure du moteur à ammoniac de Delaporte de 1870
'chaudière à ammoniac'**

Vehicles in the past

- From second War



NH3 Fuel Bus, Belgium



Fig. 4 – Norsk Hydro power company first converted truck to run on ammonia [79].

- To recent experiences



Univ Michigan, 2013



Kier/Hyundai, 2014



Marangoni Toyota GT-86 Eco-Explorer, 2013



Università di Pisa Italy, 2013



Activate norwegian project,
Silesian University project 2022 ? 2023 ?



C-Free Run project,
HydrogenEngine Center (Iowa), 2018

> But ...only Toyota considered NH₃ without gasoline or diesel blend

RELEVANCE OF NH₃

	H ₂	NH ₃	Methanol	gasoline	Diesel fuel
Boiling Point (°C) at Patm	-253	-33	65	27-225	
Density (20°C, 1 bar) (kg/m ³)	0,08	0,71 (G)	790	740	
Storage	Gas, Liquid	gas ou Liquid	liquid	liquid	liquid
Liquid pressure at 20°C	700	8.6	1	1	3
Density at storage conditions(kg/m ³)	39.7	610	790	740	800
Energy density at storage conditions (MJ/l)	4.76	11.47	15.72	32	34,9

More>H₂, similar « classical » fuel

3 * > LPG ! > methanol

Fuel Consumption for transport applications

- $\text{NH}_3 = 11.5 \text{ MJ/liter !}$
- 1 single storage tank of $40,000\text{m}^3$ of $\text{NH}_3 =$ annual electricity demand of 30,000 households !



70 l Gasoline



770 L / 530 kg



315 L - 172 kg



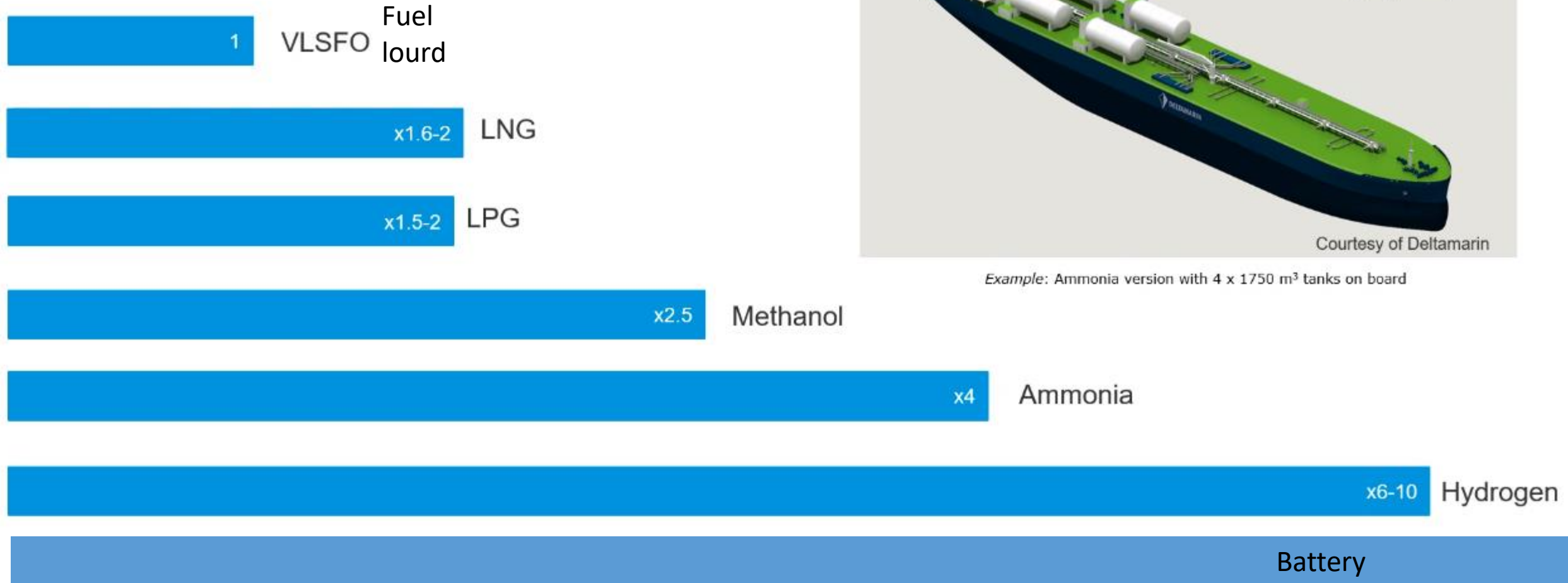
400 l Diesel fuel

5000 L / 3,4 t

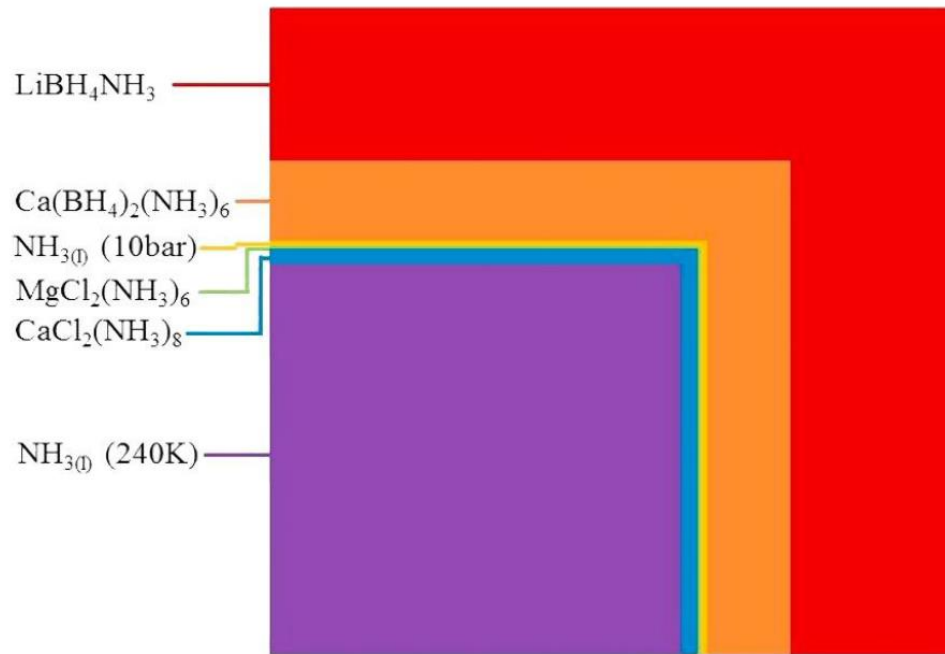
2030 L / 1,1 t

Alternative fuels will require more fuel volume (approximate values)

Fuel tank volume



Other storage solutions...

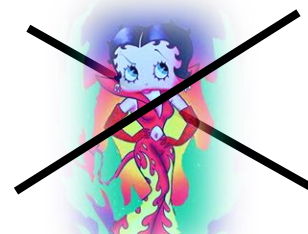


- Current carbon steel ammonia storage vessels = low-cost + satisfactory corrosion resistant
- New materials for ammonia storage and distribution
 - novel metal halide amines (solid salts) (limiting NH₃ release at atmospheric conditions (consequence of the vapour pressure of ammonia under those conditions)).
- Hexa-ammine-magnesium chloride
- Ammonia boranes, materials well known to store ammonia
- Another method for ammonia storage : gelation using silica gel (Metal Ionic Liquid Silica Gel composites)
- Urea and other aqueous nitrogen-based fuels = recovered from animal waste streams

identification of an effective carrier with similarly attractive energy density and overall conversion efficiency while providing a safer and more convenient energy storage media.

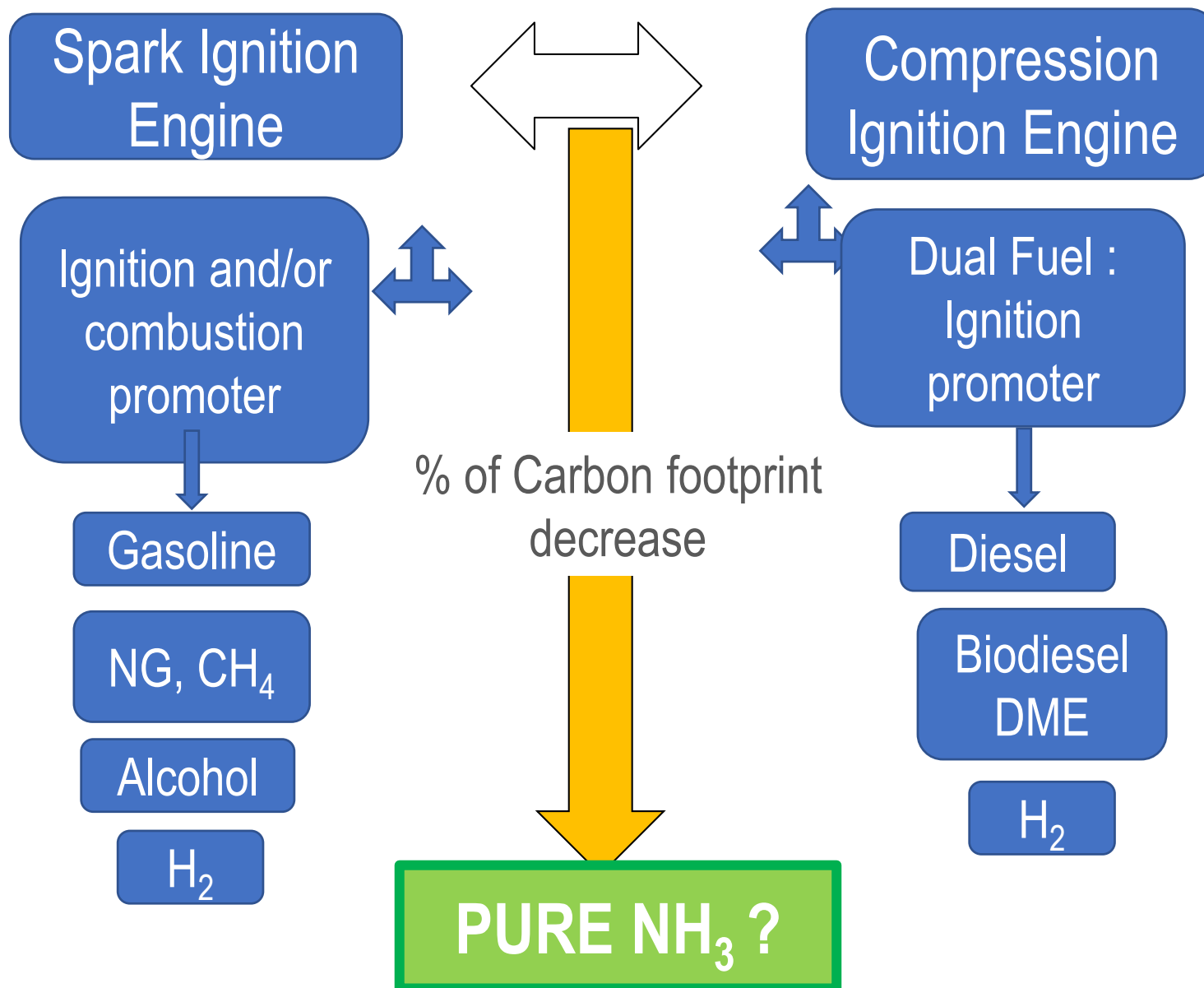
Global ammonia combustion characteristics

	Hydrogen	Methane	Methanol	Gasoline	Diesel Fuel	Ammonia	consequences
Low Heating Value (MJ/kg)	120	49	19.9	44	45	43,2	Similar
Air/Fuel ratio at stoichiometry (kg/kg)	34.2	17.65	6.46	14.6	14.6	6.06	High fuel consumption
Flammability limit in air (vol.%)	4.5-75	5-15	6.7-36	1.3-7.6	1-6	15-30	Low risk
Laminar flame speed (cm/s)	210	38	40	~40	52	7	Difficult propagation
Auto-ignition Temperature(°C)	537	595	465	275	225	651	Difficult ignition
Octane Number (-)	>120	120	109	88-98	20-30	>120	Low knock occurency ?
Adiabatic flame temperature (°C)	2519	2326	2228	2392		2107	Colder flame
Quenching distance (mm)	0.64	2		3	7	7	Lower heat wall loss
Latent heat of vaporization(kJ/kg)	461	510	1168	180-350	1370	400	High



Challenges for Ammonia fuel in ICE

CHALLENGES	Technical Impact	Fundamental needs
High latent heat of vaporization + different saturated vapor curve	Injection sytem	Flash boilling ? Supercritical ? Atomization process
Difficult Auto-Ignition	Ignition range, cold starts Compression ratio, boosted conditions ? Ignition system : reactive fuel pilot injection ? Igniter ?	Auto-ignition delay (T,P, lambda, reactive fuel addition ?) Accurate full kinetics mechanism Reduced kinetics mechanism for CFD use
Narrow flammability range	Combustion stability Operating conditions range (lambda)	flame/stretch, extinction, Neat NH3 + other fuels
Low reactivity/ low flame propagation speed	Efficiency ? Thermodynamics conditions	Flame speed database (T, P, Phi, pilot fuel ..) Kinetic mechanism (neat ammonia+ more reactive fuel ? ...) Flame-turbulence interaction, stretch, wall heat transfer
Fuel nitrogen	Exhaut pollutant : NO, NO2? N2O ? Unburnt NH3, Exhaust post-treatment	Reduced Kinetic mechanism for CFD ?



Best Possibilities to use ammonia only in ICE

- Difficulties to auto-ignite NH₃
 - Spark igniter or ignition by pilot fuel

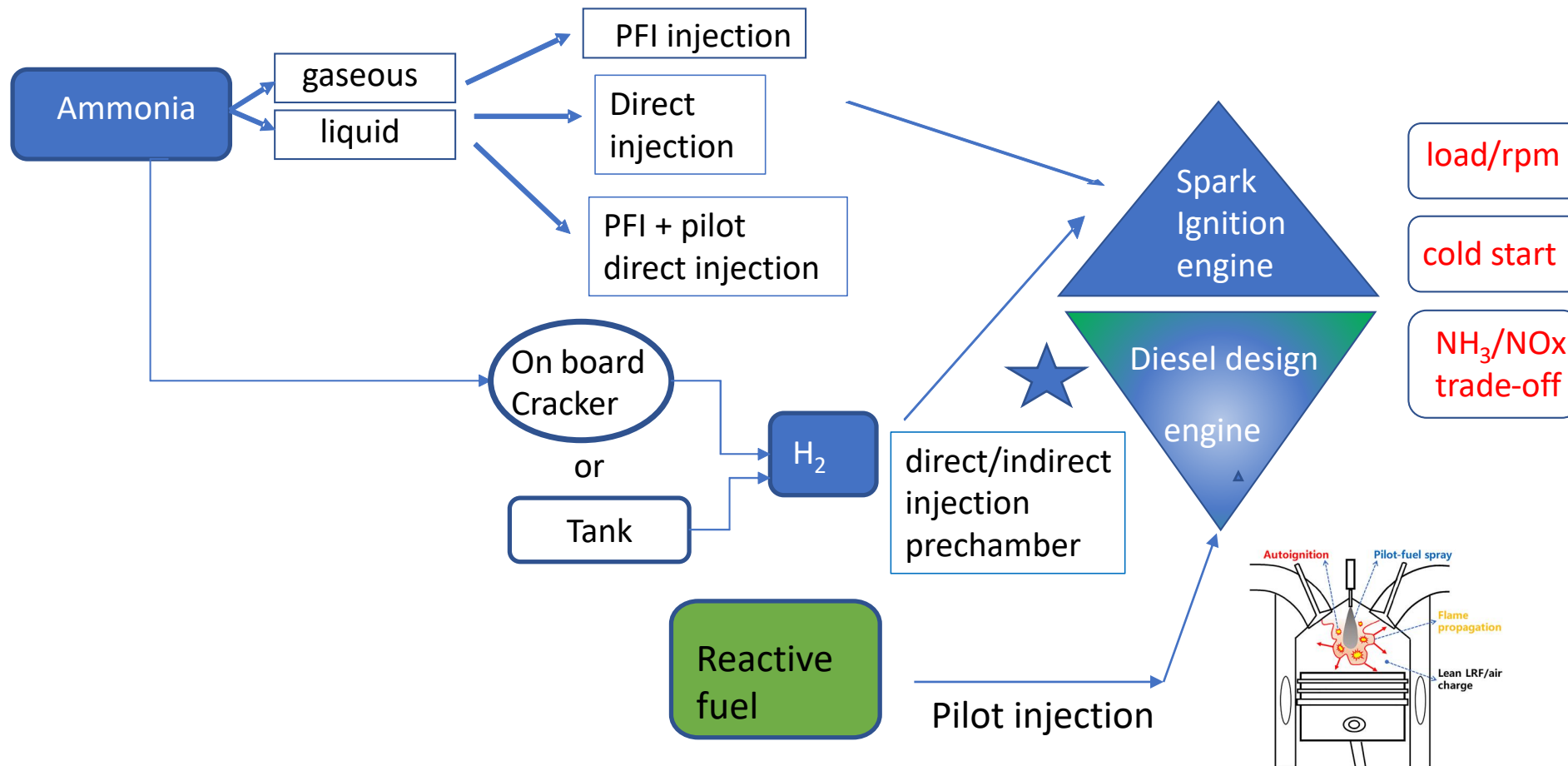


Fig. 1. Multiple combustion modes and transition in typical DF engines.

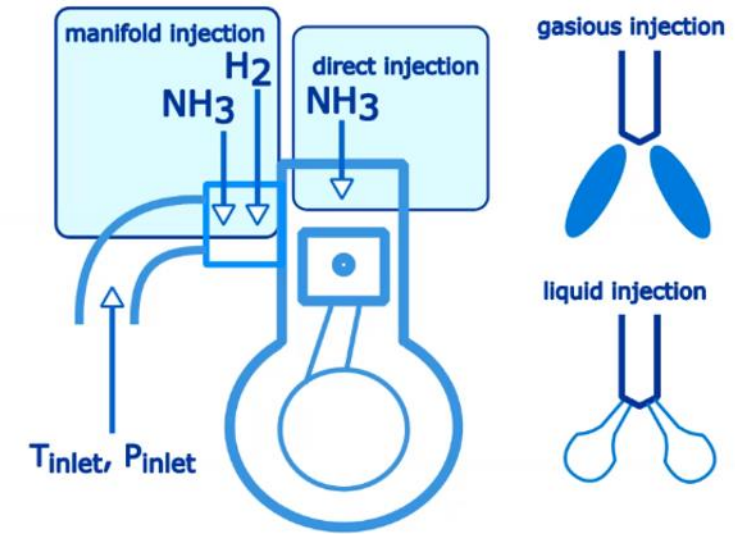
Main results in engine tests with H₂

Combustion and Performances in SI engines				
Minimum H₂ for combustion stability		Efficiency		Output energy
Between 5-10% in vol		Higher for ER ≥ 1		Less than gasoline at low and partial load
Amount needed decreases with load increase (full load. 0%)		Higher than gasoline		Increase with CR or boosted pressure
slight effect of engine speed		Decrease with H ₂ increase		
Pollutant Emissions before any attertreatment device				
	ER decrease (lean)	ER increase (rich)	H₂ increase	Load
NO_x (ppm)	++ maximum > gasoline	--	+	slight increase but no universal trend
Unburnt NH₃	--	++	-- But H ₂ at exhaust	no universal trend

But only from 2000 to 4000 rpm in small engine

Ammonia as fuel for ICE engines

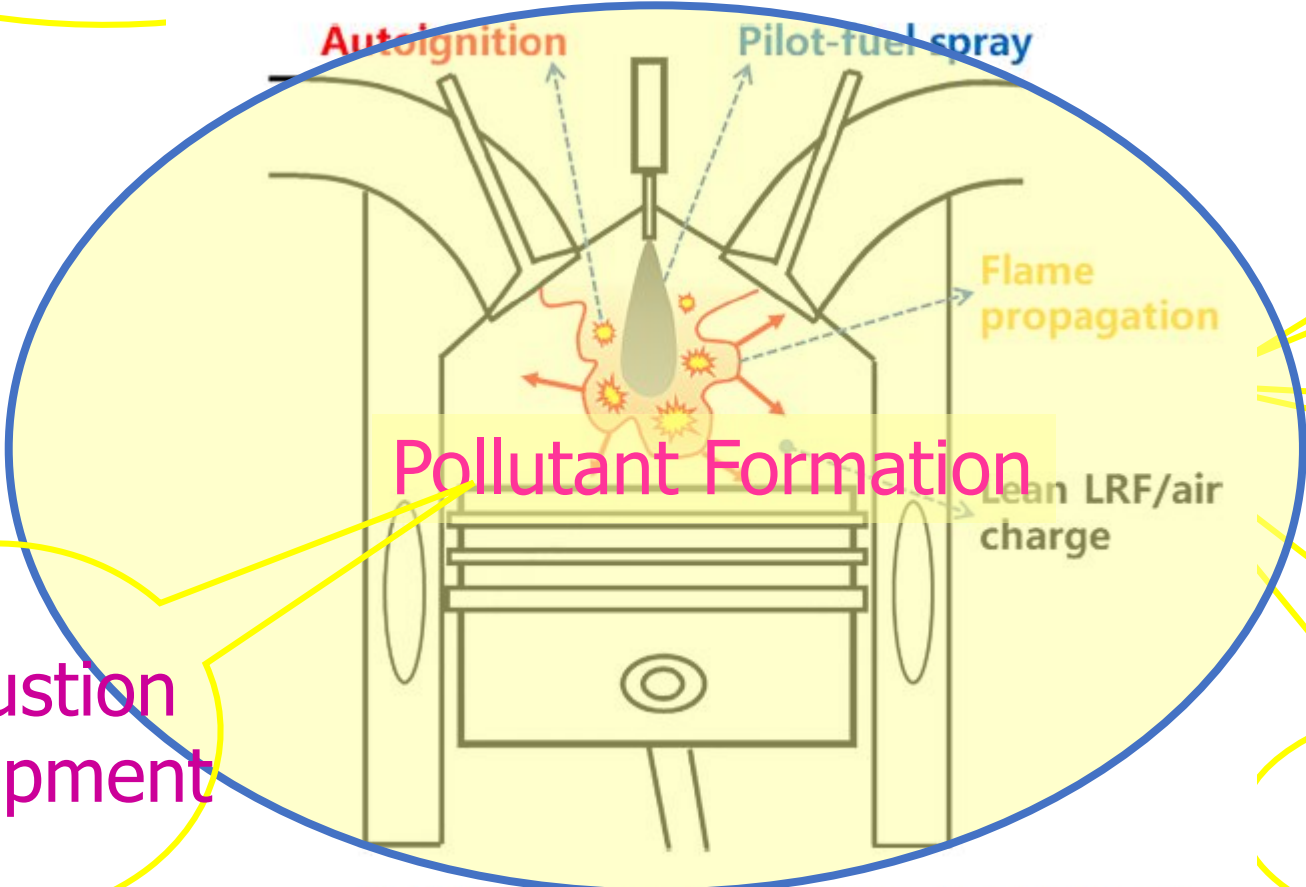
- Port-vapor fuel injection :
 - Displacement of the air supplied to the combustion chamber
 - Reduction of volumetric efficiency of the engine.
- Direct-vapour fuel injection
 - Reduction of in-cylinder temperature (ammonia's high latent of heat)
- liquid ammonia injection
 - better volumetric efficiency (no air displacement and intake mixture cooling).
- One possible way to enhance mixing and thereby facilitate combustion of ammonia :
 - to increase turbulence in the combustion chamber.
- Ammonia more suitable for lower engine speeds due to its low flame speed
- Limited by narrow flammability limits and low flame speed
 - Incomplete combustion ?
 - Real Misfire : ignition process ? .



Main Phenomena description

« Reactive »
fuel pilot injection

Ignition site



Flow fields

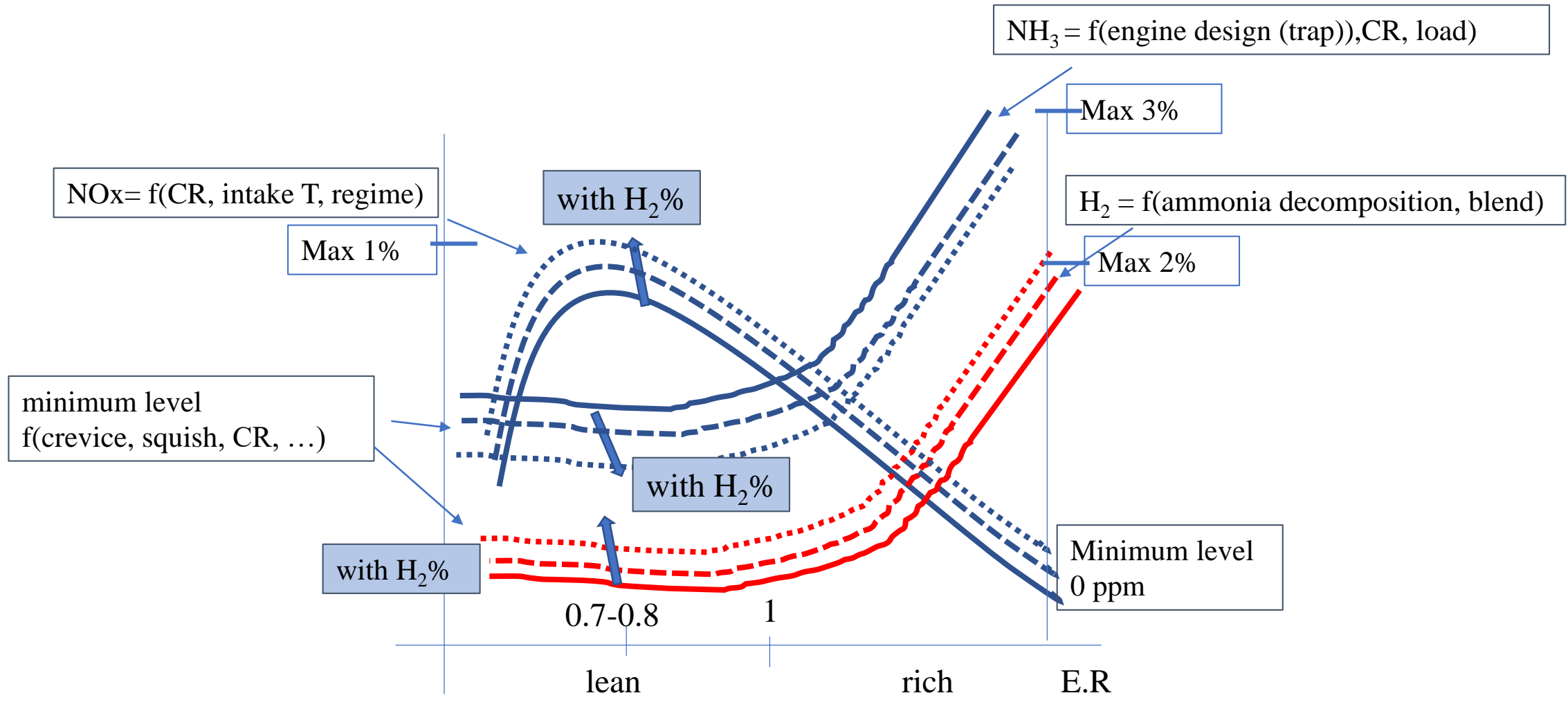
Local Air/fuel
Mixture

Combustion
Development

Wall-heat
Transfer

Multiple combustion modes and transition in typical DF engines.

POLLUTANT EMISSIONS : TENDENCIES



Vehicles applications What best solutions ?

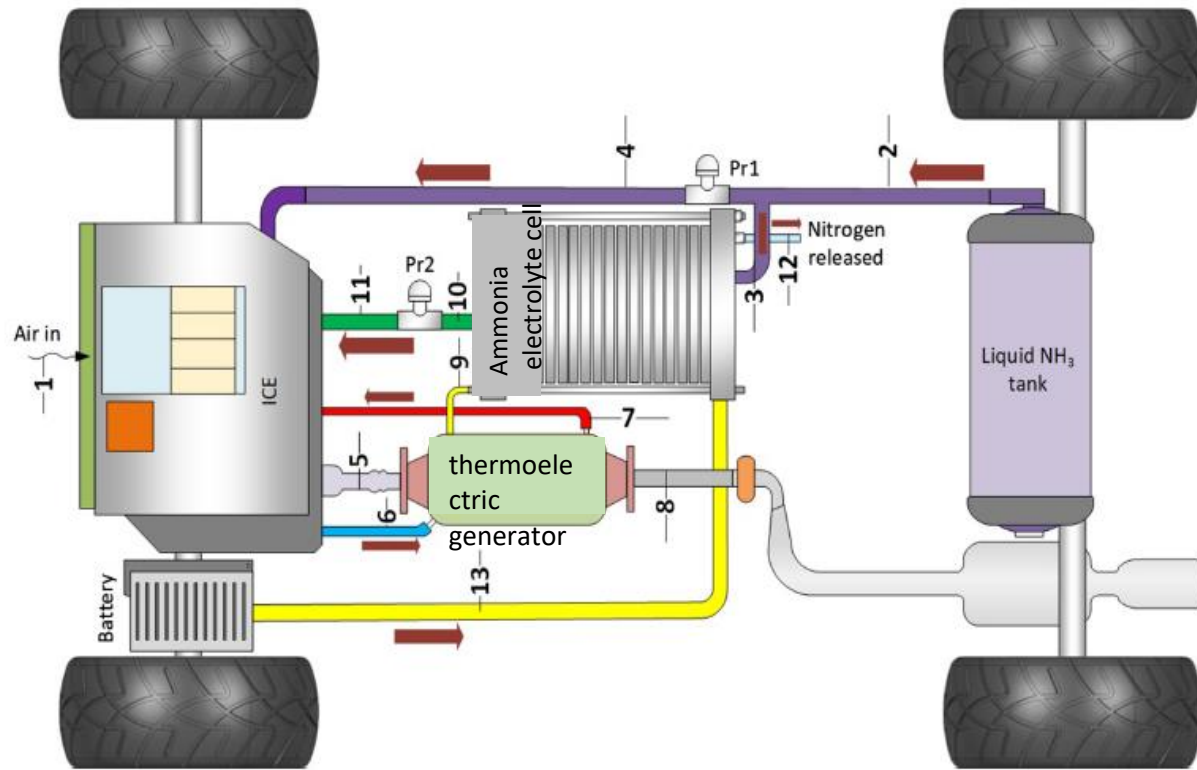
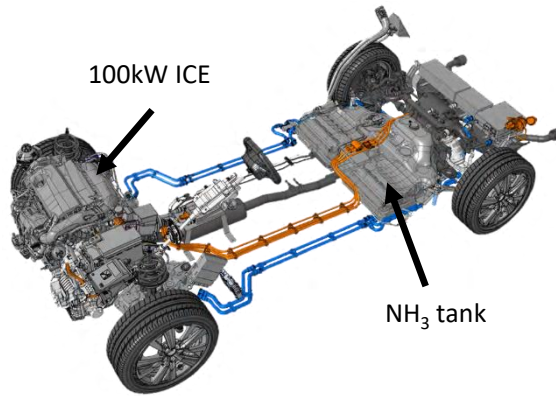


Fig. 1. Schematic of the proposed integrated system comprising ICE, TEG and AEC unit.

what best vehicle architectures ?



Assessment of three vehicle architectures using NH₃ energy storage



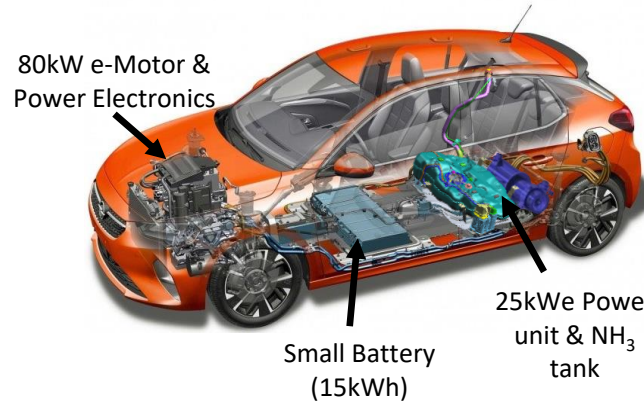
Conventional ICE powertrain

Advantage

- Powertrain cost
- Compactness

Consequence :

- Wide engine operating conditions
- Aftertreatment



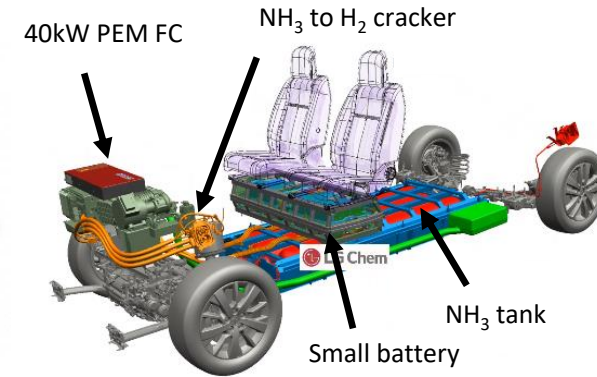
Series-hybrid powertrain with NH₃ power unit (ICE)

Advantage

- Engine single operating condition
- Zero emissions mode

Consequence :

- Powertrain cost and complexity
- Aftertreatment



Series-hybrid powertrain with NH₃ energy storage & H₂ PEM Fuel Cell

Advantage

- Zero emissions

Consequence :

- Powertrain cost and complexity
- Cracker maturity and compactness