AMMONIA AS A REMARKABLE WORKING FLUID AND FUEL FOR ENERGY SYSTEMS

by

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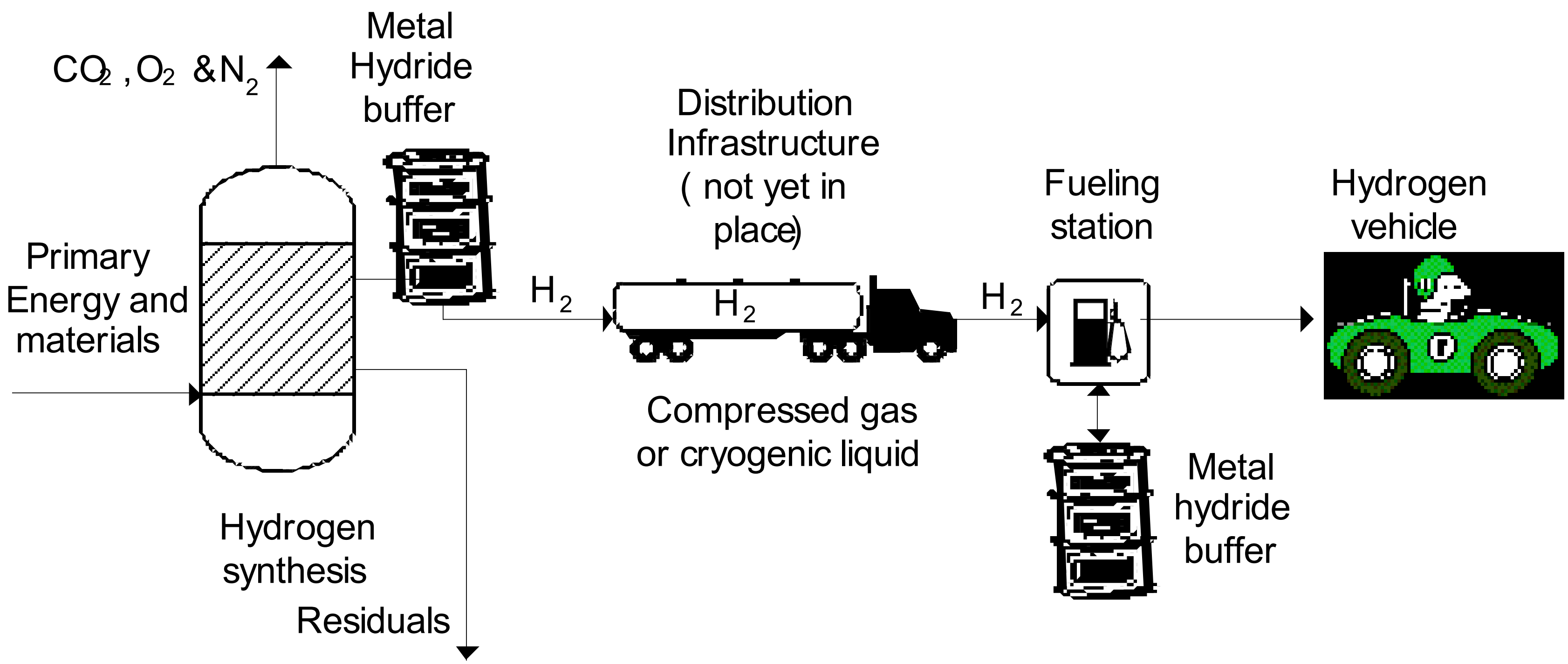
Outline of the presentation

1. Introduction, objective of the study
2. Analysis of the life cycle segments
   - Thermo-catalytic ammonia synthesis
   - Ammonia storage and distribution
   - Ammonia decomposition and separation
3. Results and discussions
   - Lifecycle CO_2 emissions per produced shaft work
   - Energy balance at ammonia bio-synthesis
   - Heat and work recovery potential during power generation
   - Energy balance of an engine fuelled with hydrogen from ammonia
   - Life cycle efficiency and cost
4. Conclusions

Introduction, objective of the study

- Synthetic fuels: a drive towards a sustainable economy
- Europe: 20% synfuels share by 2020 (Larivé et al., 2004)
- Ammonia – NH_3: nitrogen AND hydrogen source
- Ammonia: synfuel AND biofuel
- **OBJECTIVE**: analysis of the life cycle (in terms of costs, efficiency and GHG emissions) of ammonia as hydrogen source (synfuel) – synthesis, distribution and storage, hydrogen generation, power generation.

The common approach to hydrogen economy



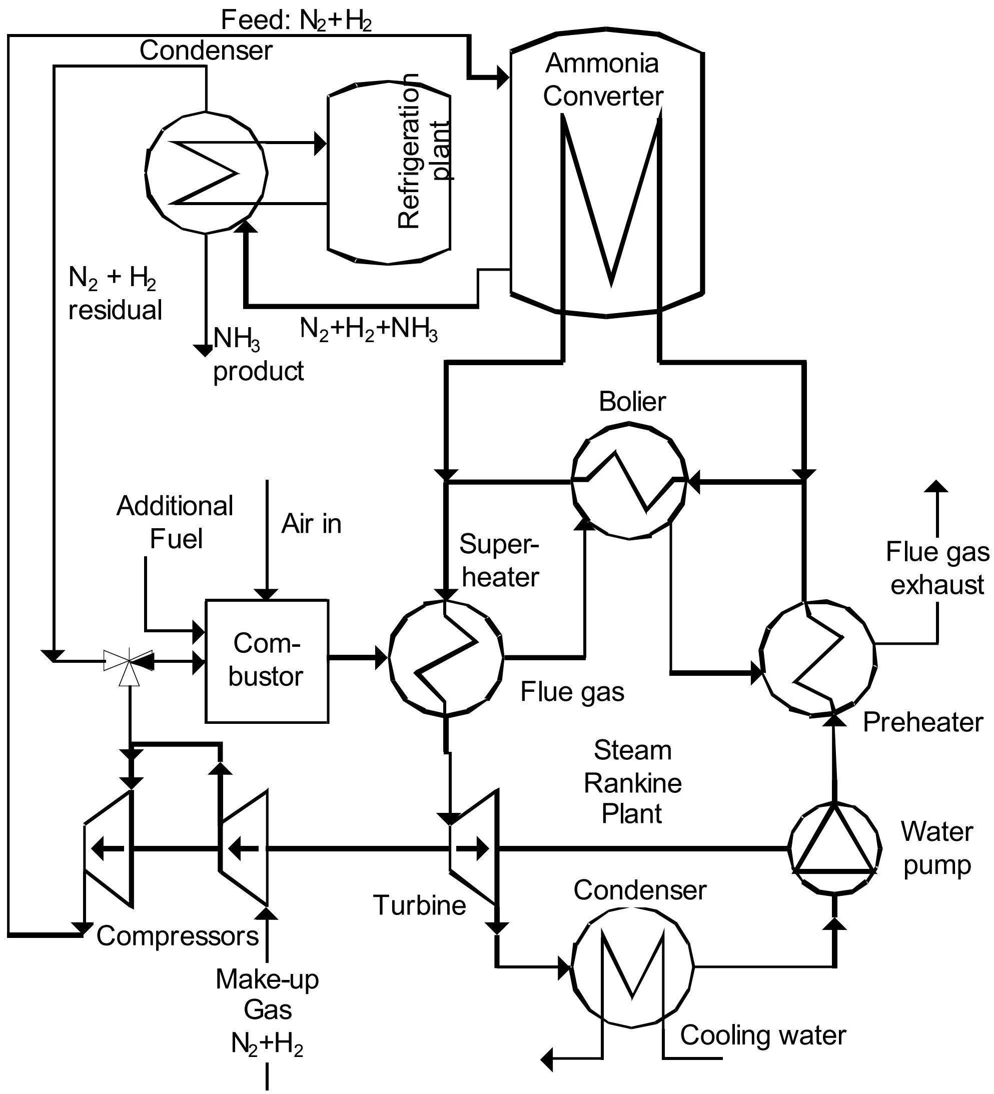
$H_2O(l) \rightarrow H_2 + 1/2\,O_2 + 286\text{MJ}$

It is believed by many that hydrogen is an ideal synthetic fuel. However, implementing a global hydrogen-based economy, at present, appears to be non-feasible unless suitable production, distribution and storage technologies are found

Thermo-catalytic ammonia synthesis

- Haber-Bosh process invented in the beginning of the 20^{th} century
- increasing the temperature such that the nitrogen molecule receives enough energy to be cracked
- If the temperature is not high enough, nitrogen atoms remain strongly bound at the surface and “poison” the catalyst which is therefore not able to perform a new catalytic cycle.
- the forward reaction is facilitated by low temperatures and high pressures
- Typically the operating temperature and pressure are $600^{o}C$ and 100-250 bar, respectively for 25-35% conversion

Haber-Bosch ammonia synthesis unit coupled to a Rankine cycle for heat recovery and work conversion



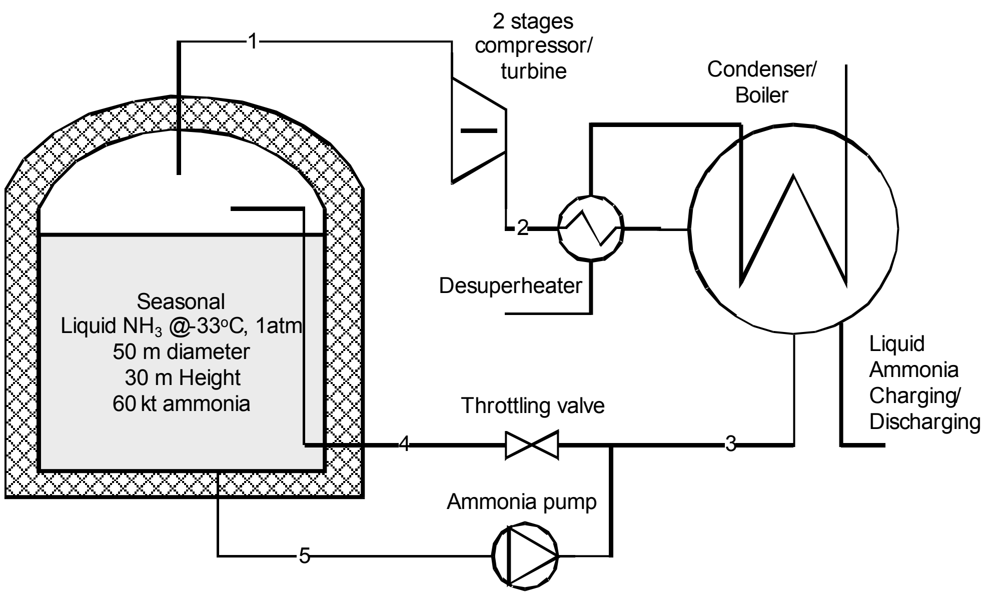
200 bar → 15% conversion
400 bar → 25% conversion
2.7 GJ heat generated per t NH_3
1.5 t steam @125 bar / tNH_3
90% recovery of NH_3 formation heat

0.4 tCO_2/tNH_3 to produce electricity needed to run the plant

2.2 tCO_2/tNH_3 from natural gas

16.2 tCO_2/tNH_3 from coal

Storage and distribution



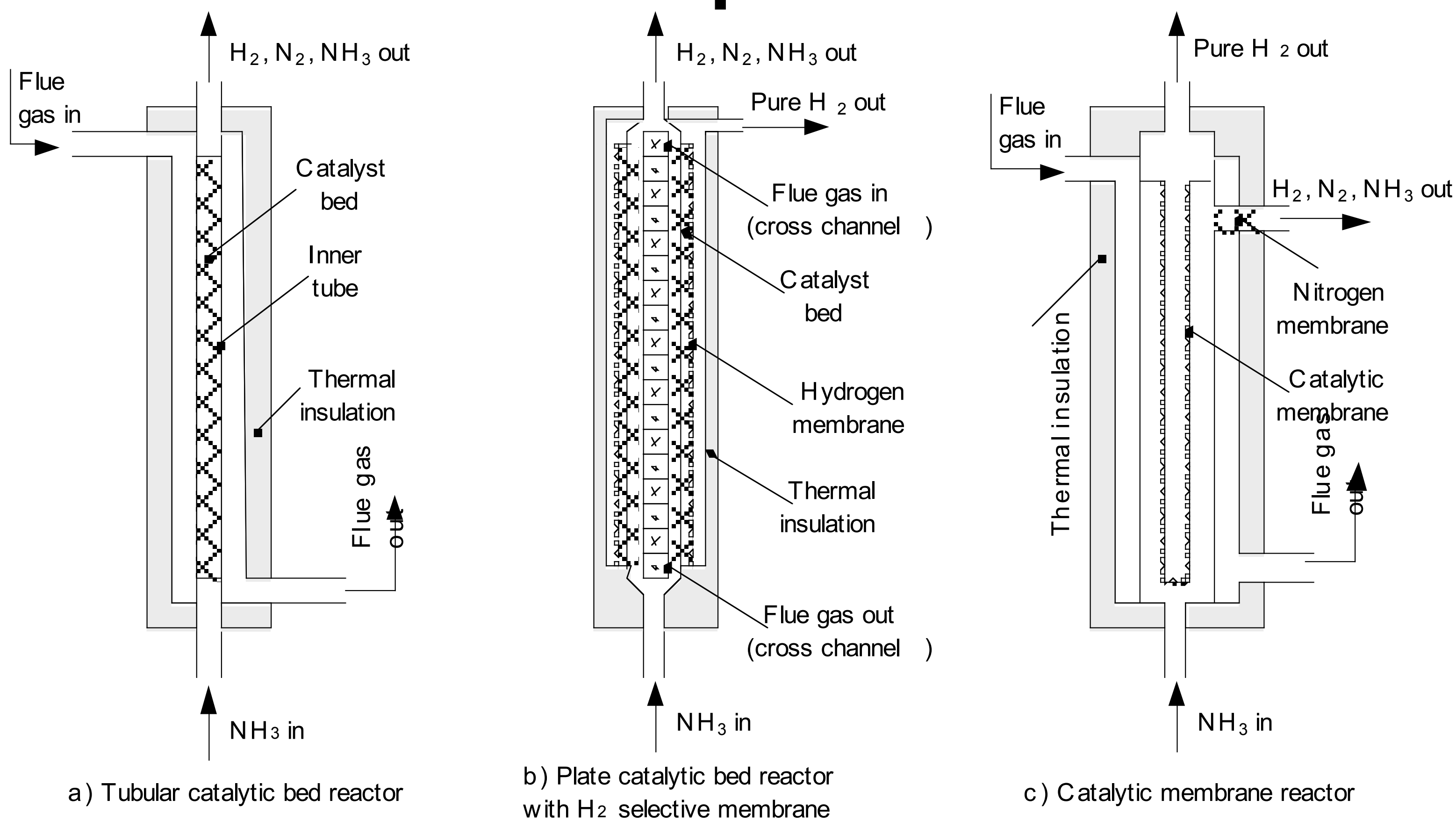
- regular carbon steel, designed for ~20 bar operating pressure
- 3 t of ammonia can be stored per tone of steel
- tank weight is about ¼ from the ammonia mass
- 45klitres road cisterns
- 130klitres rail cisterns
- 50kt ship cisterns
- Pipeline: 93% HHV efficiency @14GJ/m^3

$$ex = (h - h_0) - T_0(s - s_0)$$

specific exergy is 19kJ/kg or 1.1GJ per 60kt

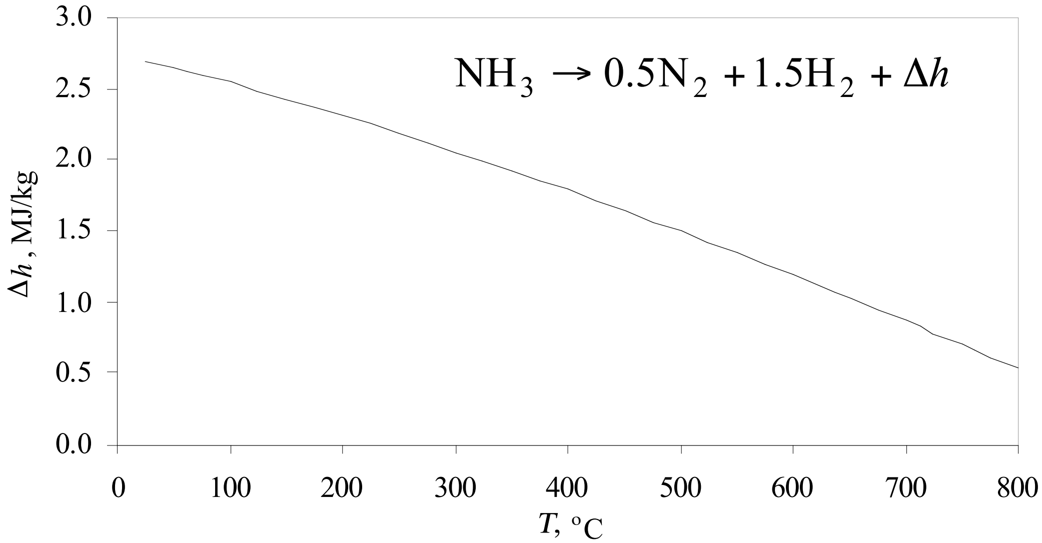
recovered exergy represents ~5% from the energy spent to fill the tank and keep it refrigerated for whole season

Possible options for thermo-catalytic ammonia decomposition reactors



- required enthalpy represents 10.6% HHV or 12.5% LHV of the produced hydrogen
- at 400^{o}C the equilibrium conversion of NH_3 is very high 99.1% (Yin et al., 2004)
- Fe, Ni, Pt, Ir, Pd, Rh, but Ru appears to be the best, >60 kW H_2 power per kg of catalyst
- rate limiting: <~300^{o}C N2 recombination, >550^{o}C cleavage of N-H bond
- Activation energy: 180 kJ/mol at low T and 21 kJ/mol at high T

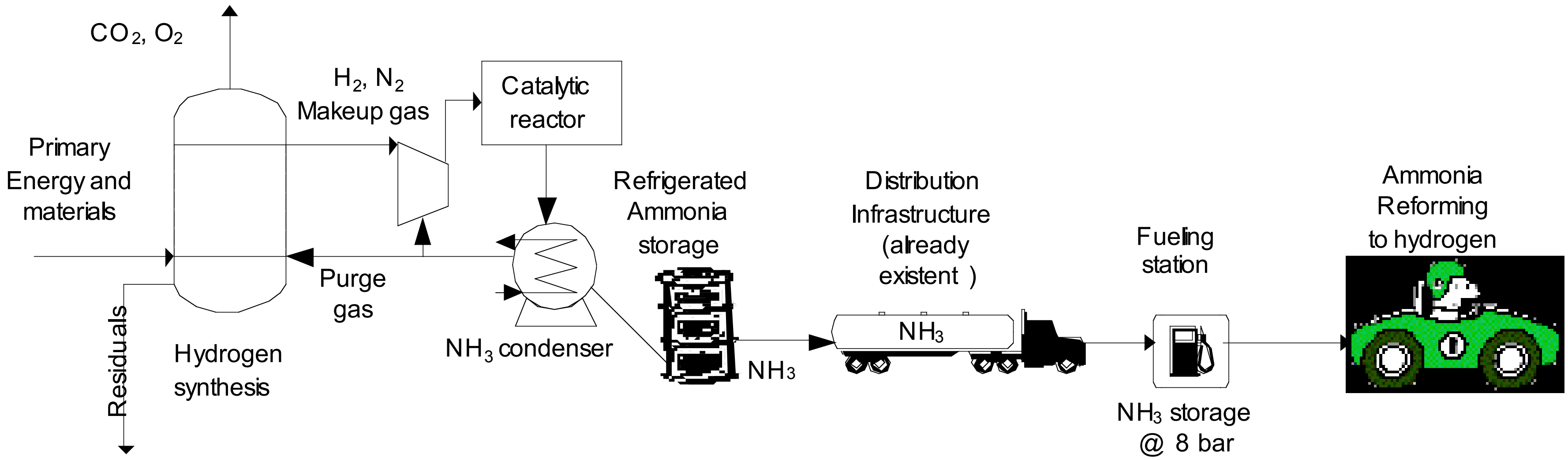
State of the art on ammonia thermo-catalytic cracking



Practical temperature range: 300 to 700°C, where the reaction heat drops below 2.5 MJ/kg which represents 12% from HHV.

Cracking reactor compactness:
50 kW/liter @ 365°C➔Sorensen et al.
170kW/liter @ 600°C➔Ganley et al.
Ammonia electrolysis is a feasible alternative to thermal cracking

The layout of hydrogen from ammonia economy for transportation



From the stoichiometry one has that 1 kg of ammonia contains $3/17 = 0.175$ kg of hydrogen

$$\begin{cases} H_2O \rightarrow H_2 + 1/2\,O_2 + 286\text{MJ} \\ H_2 + 1/3\,N_2 \rightarrow 2/3\,NH_3 - 30.7\text{MJ} \end{cases}$$

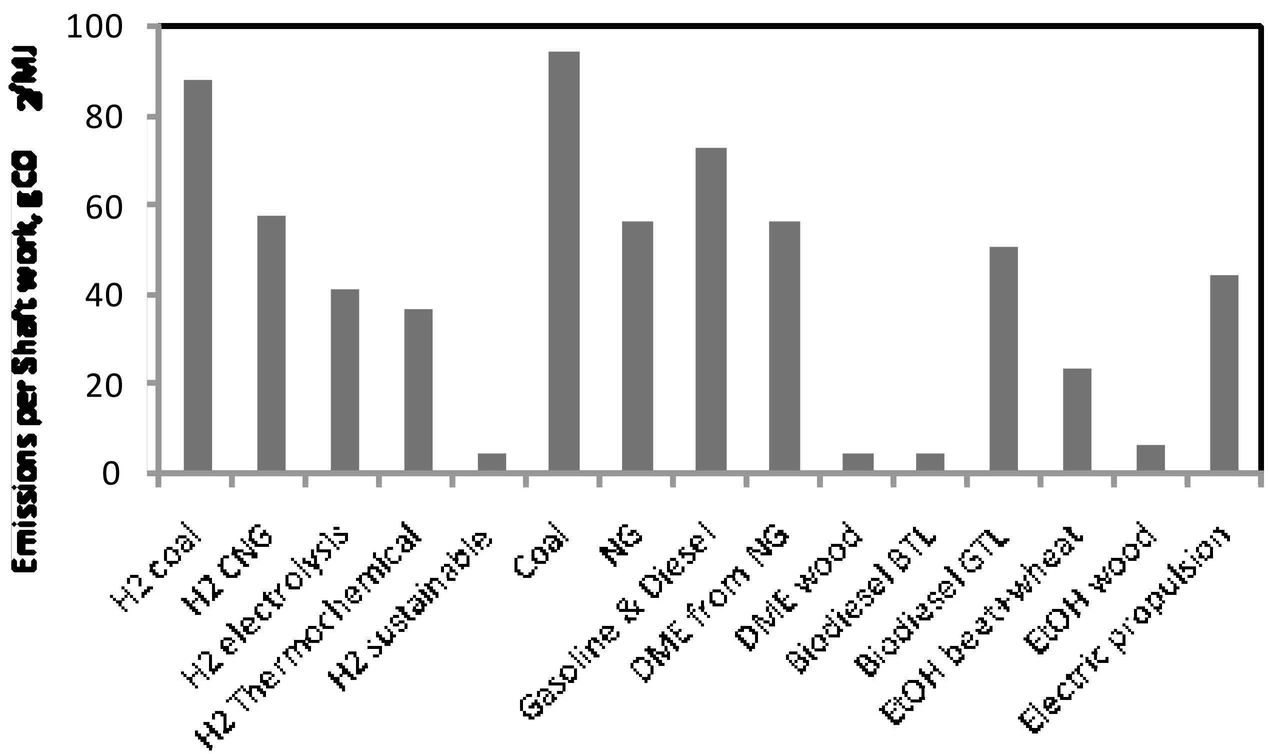
$$\Delta H_{NH_3} = 255.3\,\text{MJ/kmol.H}_2$$

$$\frac{c_{NH_3}}{c_{H_2}} = \frac{3}{\mu_{NH_3}} \frac{\Delta H_{NH3}}{\Delta H_{H2O}} = 0.157$$

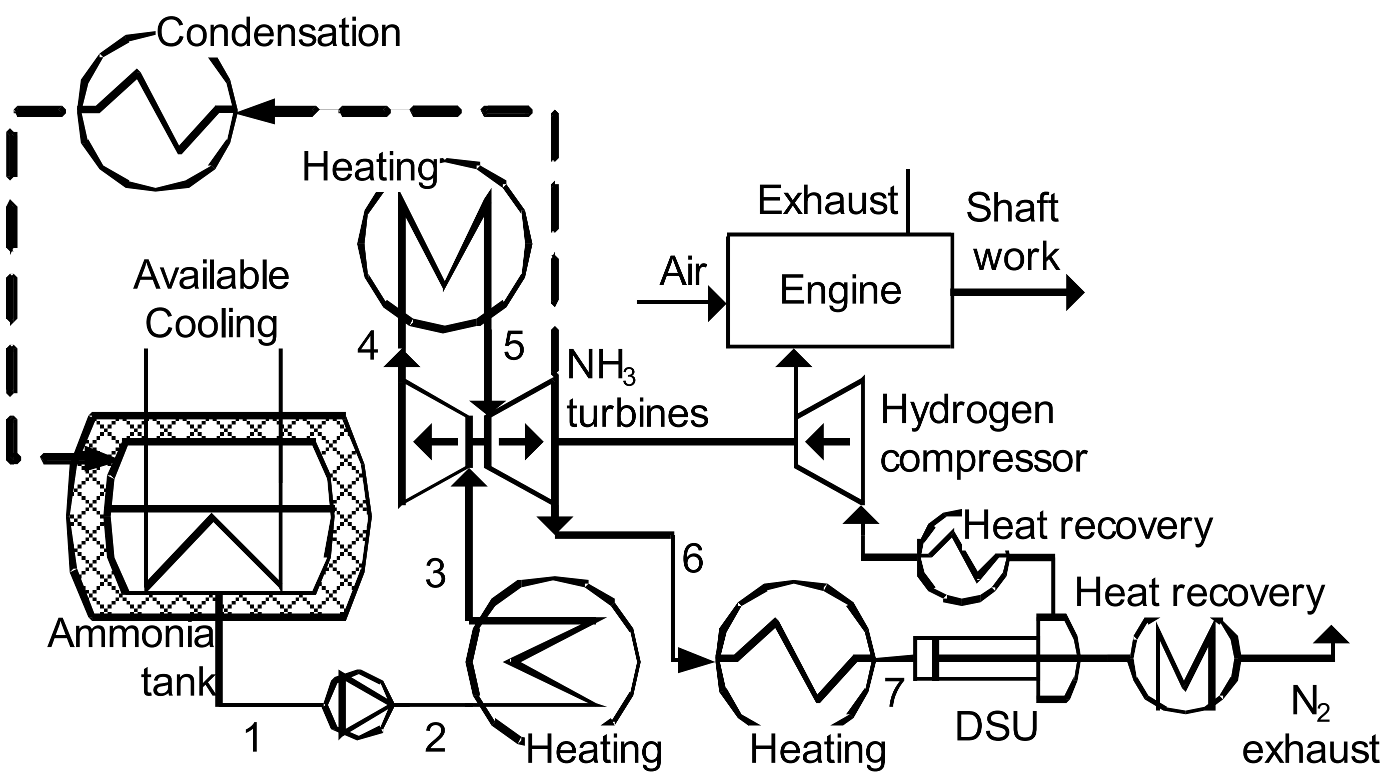
$$\frac{c_{NH_3}}{c_{H_2}} < 0.175$$

Results

•life-cycle: ammonia synthesis, distribution and storage, hydrogen generation from ammonia and its use for power production.
•efficiency, cost and CO_2 mitigation potential of hydrogen-from-ammonia approach

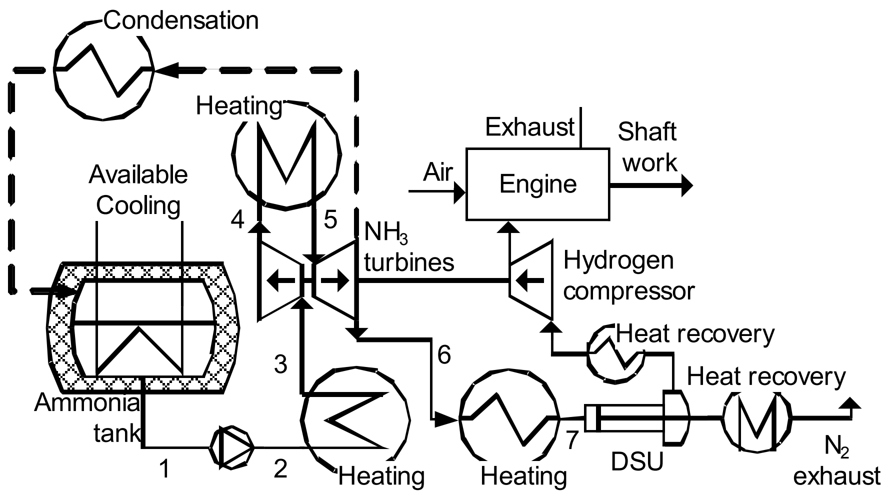


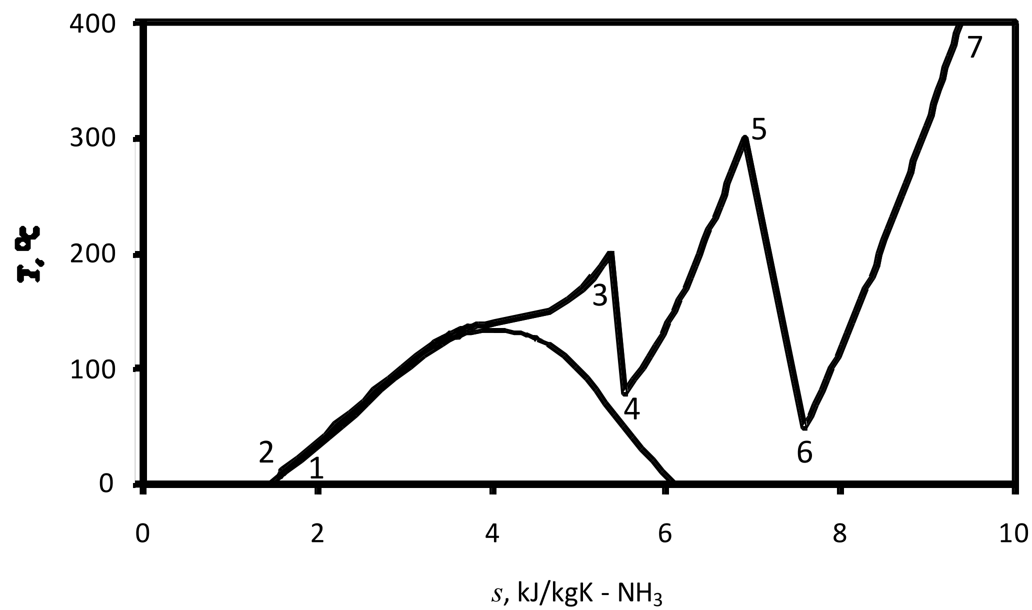
Proposed power generation system using hydrogen from ammonia



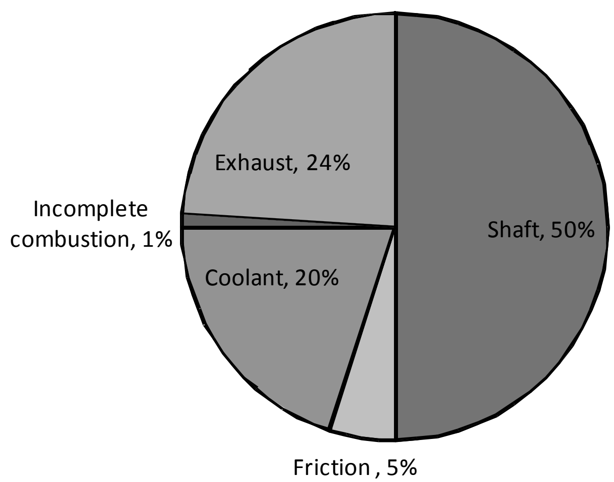
There is a filed patented by Dincer and Zamfirescu (2008) that includes 9 schemes of using ammonia as hydrogen source, working fluid and NOx reduction agent

Heating process and work recovery from the ammonia fuel stream

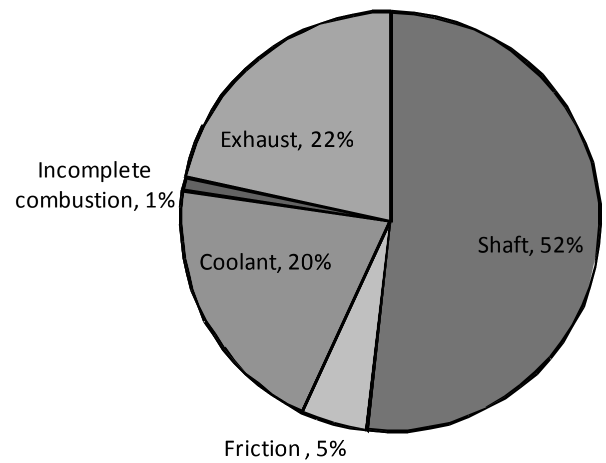




Energy balance on two types of hydrogen fuelled engines

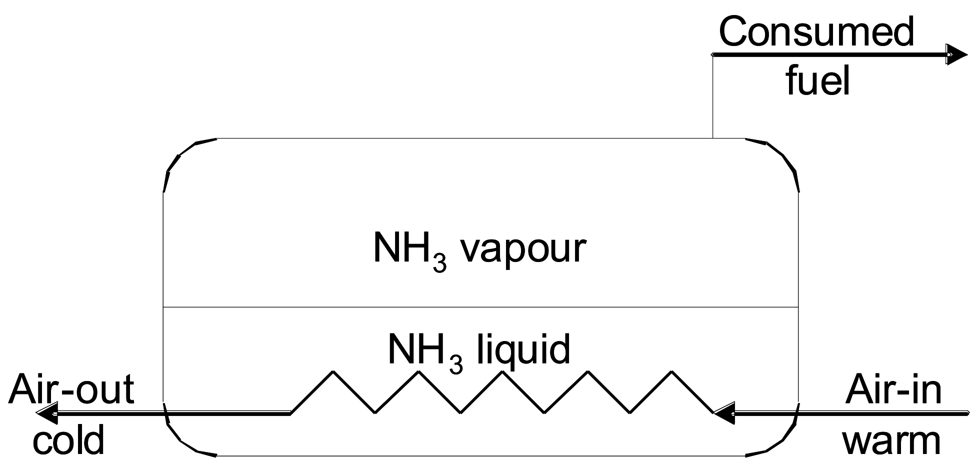


a) Hydrogen fuelled engine



b) Engine fuelled with H_2 sourced from NH_3

On-board cooling with ammonia



$$h''(T)\dot{m}_{\mathrm{NH3}} = \dot{m}_{\mathrm{air}}\left(h_{\mathrm{in}} - h_{\mathrm{out}}\right)$$

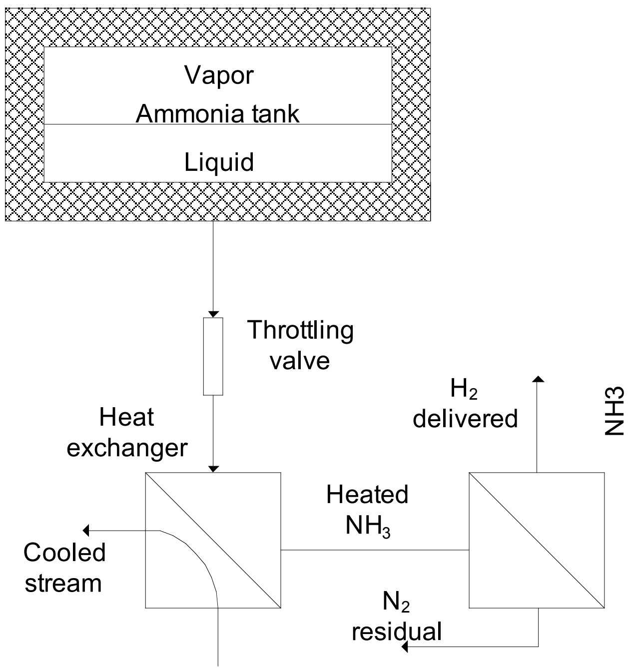
The effectiveness of the cooling effect can be quantified as a fraction of the HHV of ammonia

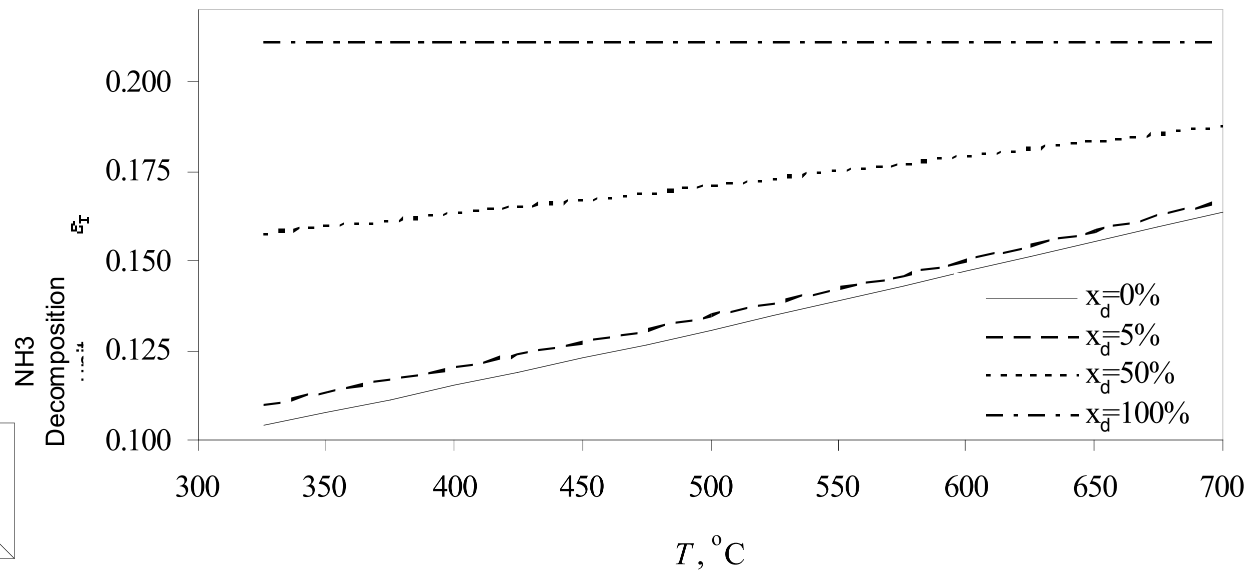
$$\varepsilon_{\mathrm{c}} = h''(T)/\mathrm{HHV}$$

T=15°C ➔ the specific vapor enthalpy is 1.62 MJ/kg which represents 7.2% from the HHV

On-board cooling with ammonia

$\Delta h_{c,NH_3}(T) = h(T) - h'(T_0) + x_d \eta_d \Delta h_d(T)$ cooling effectiveness $\varepsilon_{c,NH_3}(T) = \Delta h_{c,NH_3}(T) / \mathrm{LHV}$





gain in work at the engine shaft $w_{NH_3} = \Delta h_{c,NH_3} / \mathrm{COP}$ $\varepsilon_{r,NH_3} = \frac{w_{NH_3}}{\mathrm{LHV}} = \frac{\varepsilon_{c,NH_3}}{\mathrm{COP}}$ $\varepsilon_r = \eta + \varepsilon_{r,NH_3}$

Total effectiveness

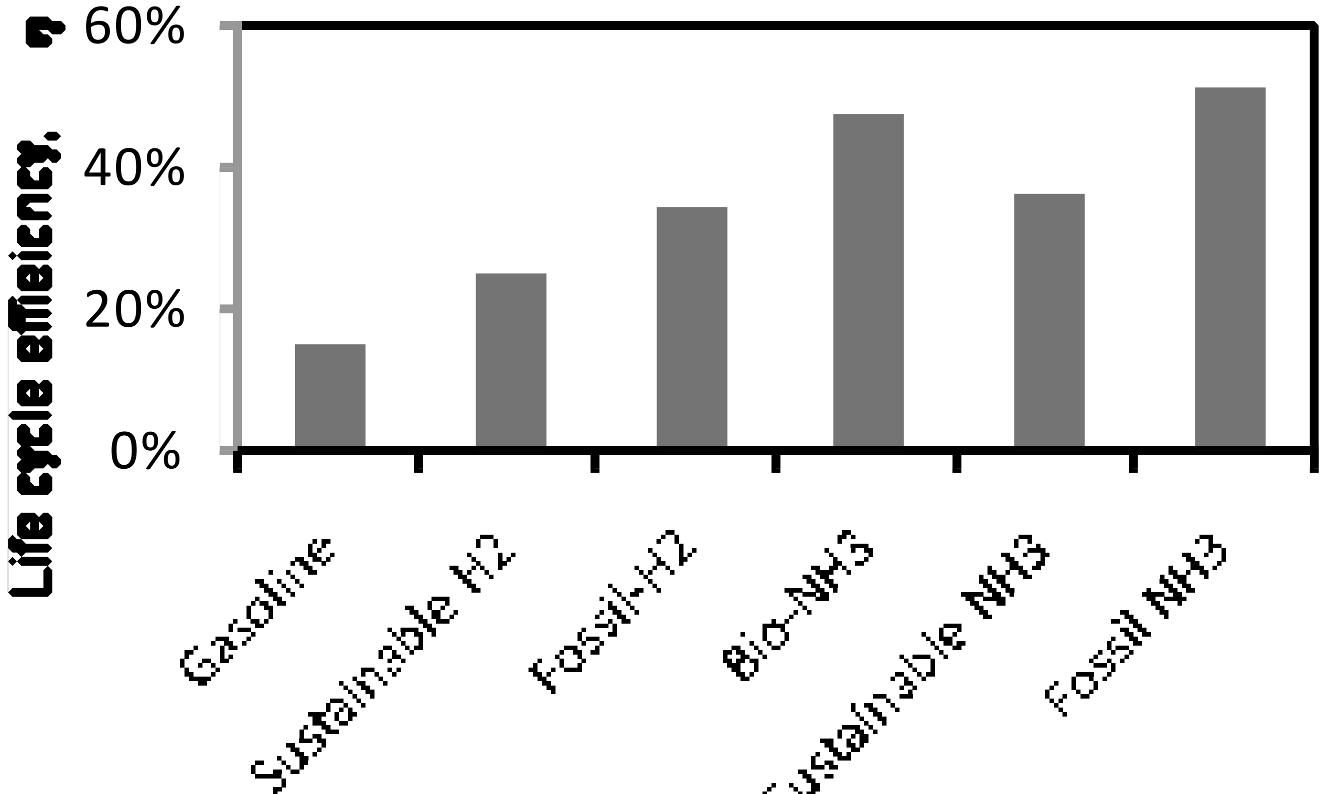
Here we define some effectiveness associated to the cooling effect

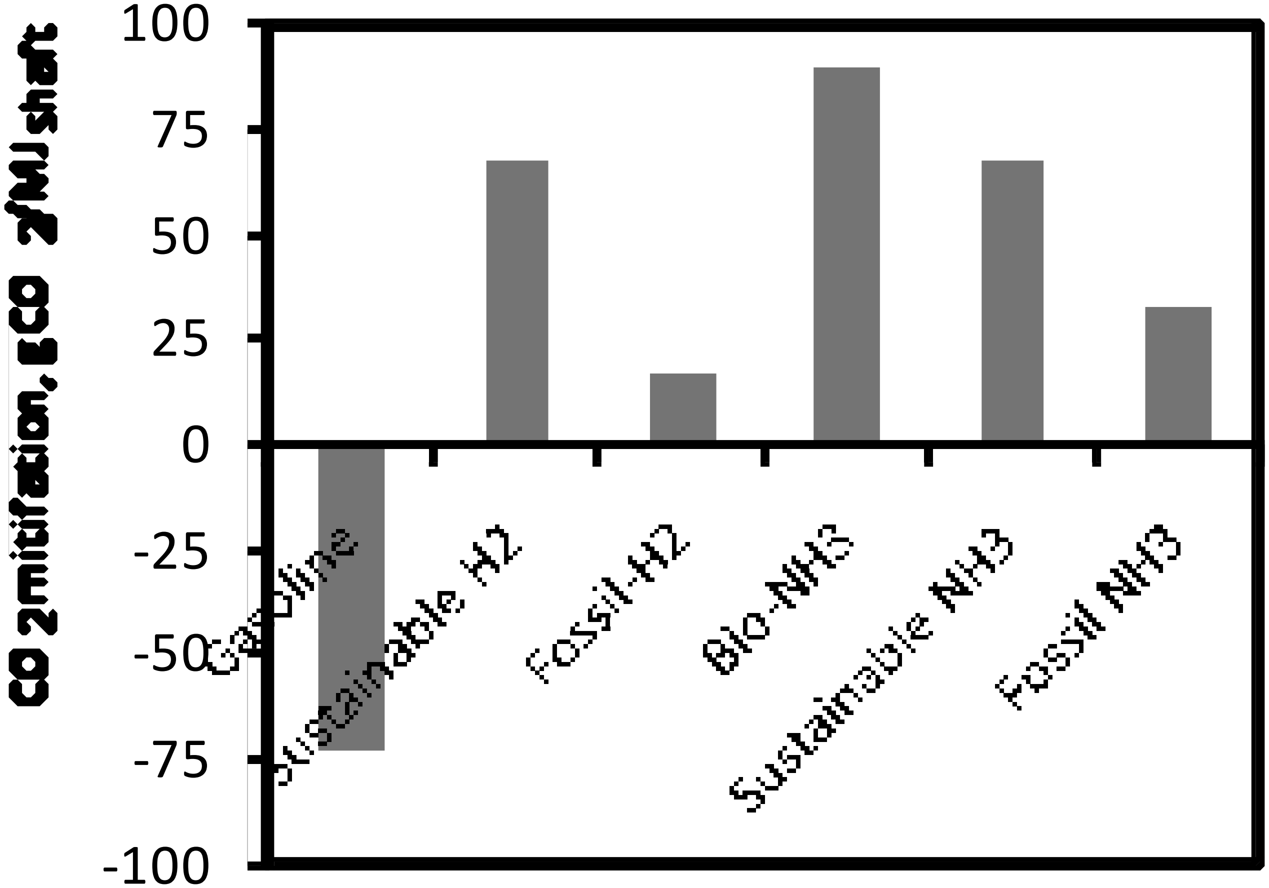
Cooling while extracting ammonia vapor from tank: $\varepsilon_{\mathrm{c}} = h''(T)/\mathrm{HHV}$

Total effectiveness = Engine efficiency +
cooling efficiency +
turnine work efficiency

$$\varepsilon_{\mathrm{r}} = \eta + \frac{\varepsilon_{\mathrm{c}}}{COP} + \varepsilon_{\mathrm{w}}$$

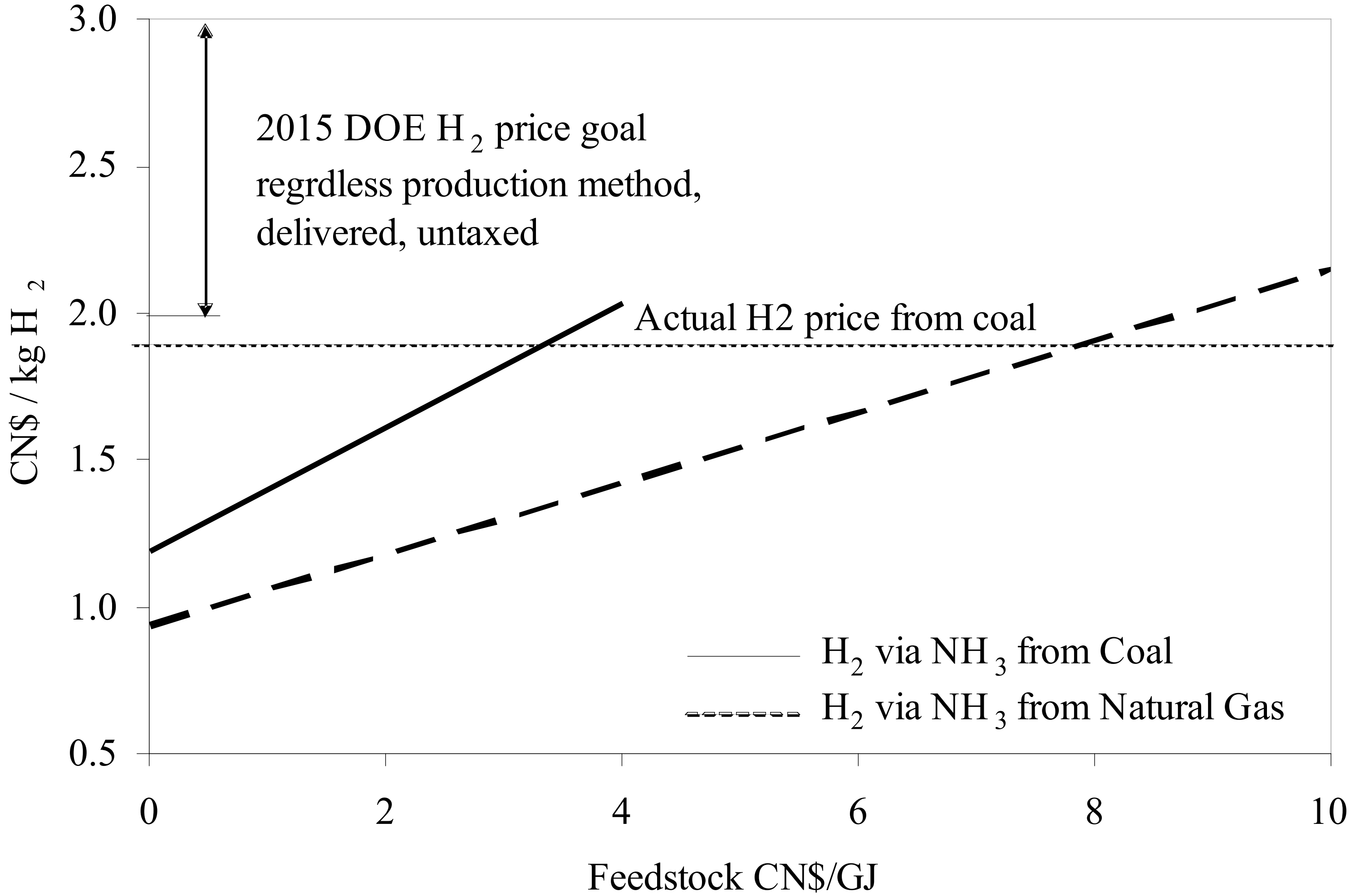
Life cycle efficiency





100
75
50
25
0
-25
-50
-75
-100
Gasoline
Sustainable H2
Fossil-H2
Bio-NH3
Sustainable NH3
Fossil NH3

Cost correlation for hydrogen obtained from ammonia at distribution points



Comparison of ammonia as hydrogen source with other options

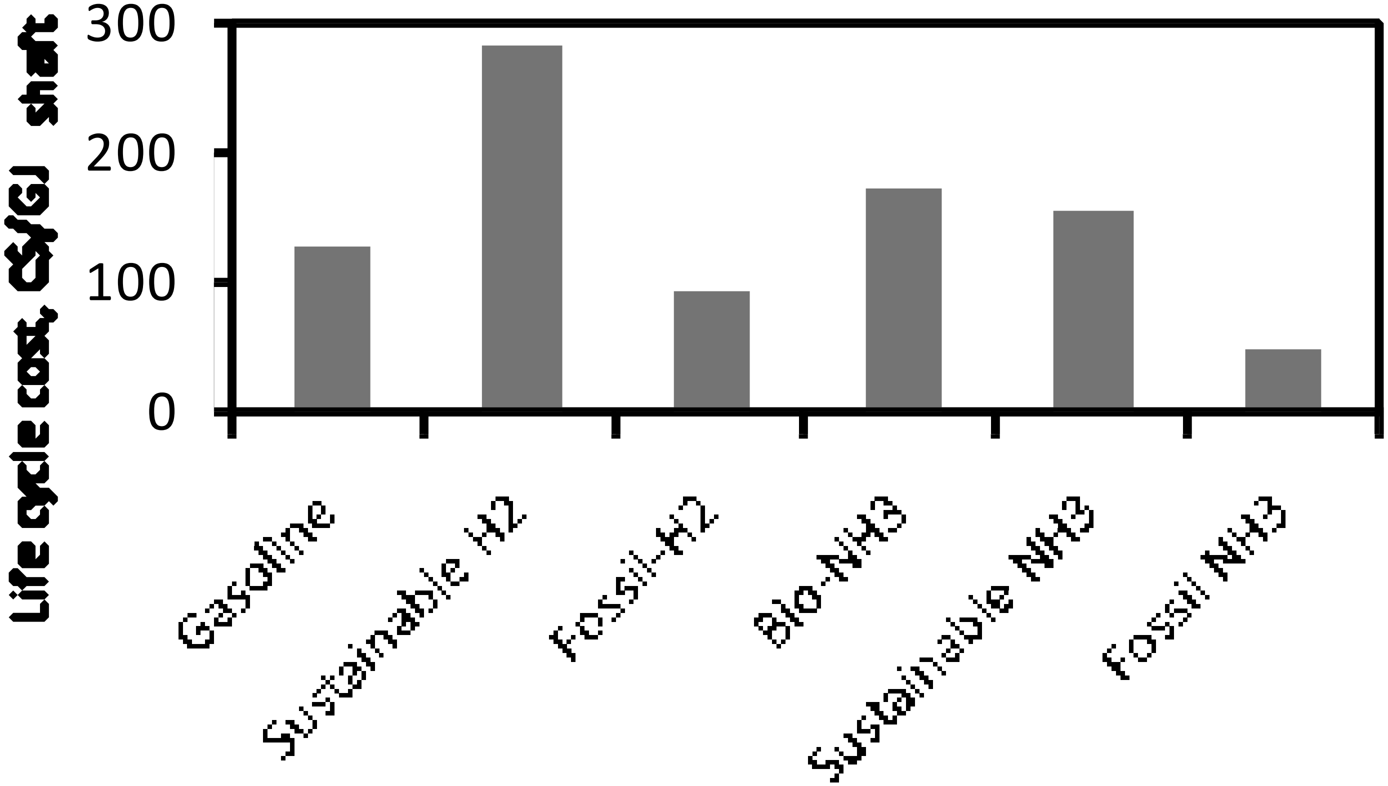
Fuel/Storage	[bar]	[kg/m ^{3}]	HHV [MJ/kg]	[GJ/m ^{3}]	[CN$/kg]	[CN$/m ^{3}]	[CN$/GJ]
Gasoline/Liquid	1	736	46.7	34.4	1.36	1000	29.1
Hydrogen/CH_4 pressurized t ank	250	188	35.5	6.6	1.20	226	33.8
Hydrogen /Metal hydrides	14	25	142	3.6	4.00	100	28.2
Hydrogen /NH_3 pressurized tank	10	603	25.0	15.1	0.30	181	12.0

Ammonia vs Methane:

Methane cracking: $1/2\,CH_4 \rightarrow 1/2\,C + H_2 + 75MJ$

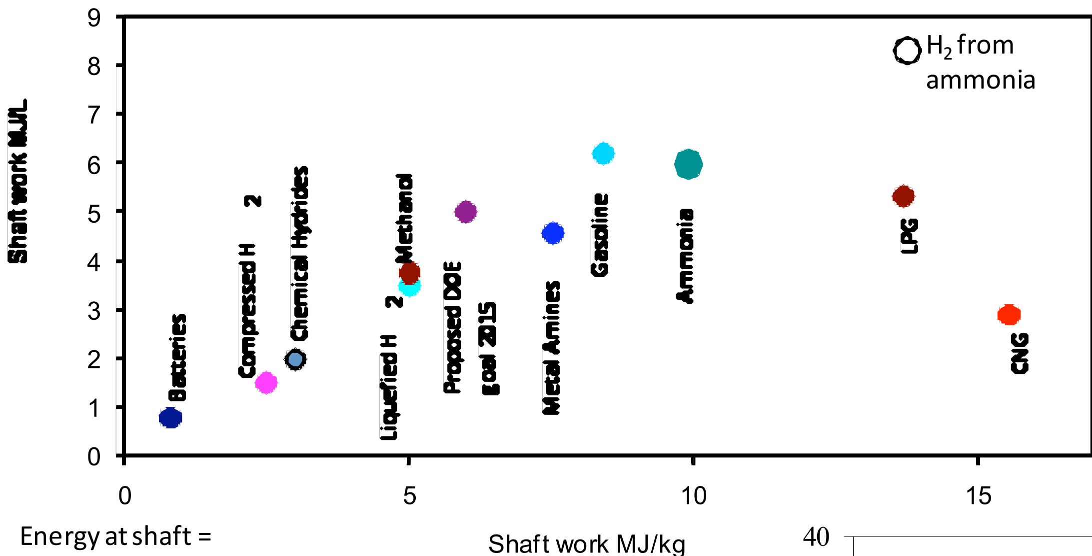
$$\begin{cases} H_2O \rightarrow H_2 + 1/2O_2 + 286MJ \\ 1/2\,C + H_2 \rightarrow 1/2\,CH_4 - 75MJ \end{cases}$$ 211 MJ for one kmol of H_2 equivalent

- methane cost is 0.185 from the cost of hydrogen for equivalent energy content
- 16 kg of CH_4 contain 4 kg of H_2
- CH_4 decomposition needs about 22% from its HHV vs. 12% for NH_3
- CH_4 is toxic with long term health effects, flammable, has explosion danger and greenhouse gas effect
- Cost in Ontario ~CN$0.45 per uncompressed natural gas
- compression work is significant and this raises the CNG price about 3 times
- Because of its gaseous phase the energy density in the CNG tank is low (i.e., 6.6 GJ/m^3) and this fact leads to an expensive specific energy (i.e., 33.8 $/GJ)
- Ammonia vs CH_4: stores more hydrogen energy per tank volume, energy cost is about 3 times less, despite of its toxicity it has short term and completely recoverable health effects, it presents less danger because ammonia is not flammable and does not present explosion risk .

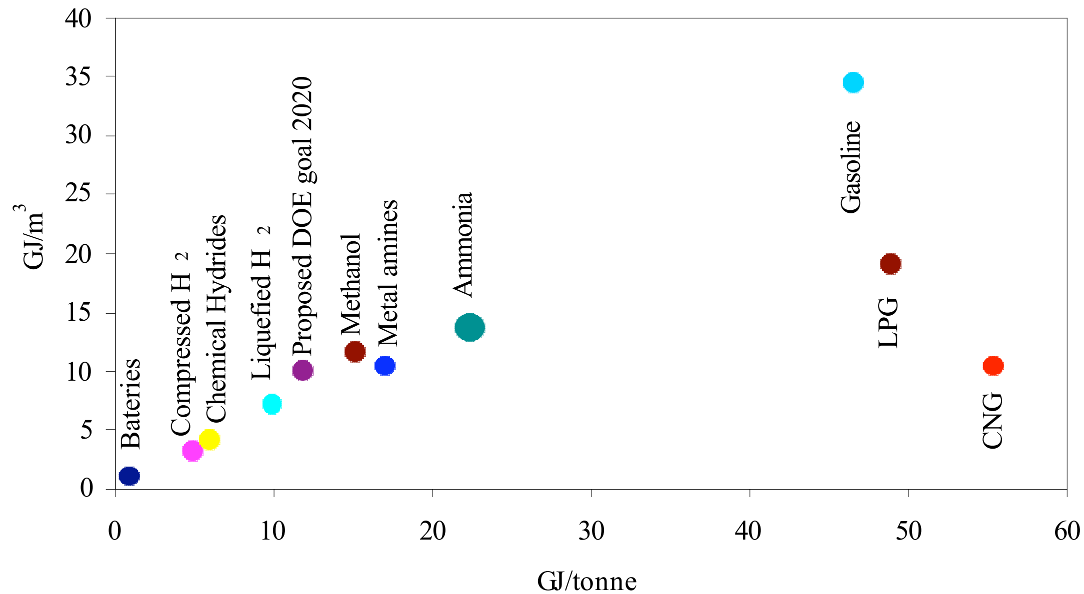


Life cycle cost, C$/GJ shaft
300
200
100
0
Gasoline
Sustainable H2
Fossil-H2
Bio-NH3
Sustainable NH3
Fossil NH3

Energy at shaft with respect to the energy stored in fuel tank



Energy at shaft =
Energy in tank _ Engine Efficiency



Ford Focus on ammonia vs hydrogen

Parameter	Unit	H_2 fuel	NH_3 fuel
Storage tank volume	liter	217	76
Storage pressure	bar	345	10
Energy on -board	MJ	710	1025
Cost of full tank	$	25	14…28
Driving range	km	298	430
Driving cost	$/100km	8.4	3.2…6.4
Tank Compactness	Liter/100km	73	18

- power-train performance is characterized by 1.19 MJ/km.
- the cost of ammonia is assumed in the range $0.30…0.6/kg

CONCLUDING REMARKS

- Ammonia: hydrogen source, working fluid and Nox reduction agent on-board
- GHG mitigation if hydrogen used to synthesize ammonia is 68 gCO_2 per MJ.
- Thermo-catalytic membrane reactors are the most promising devices for hydrogen generation from NH_3.
- If ammonia is used simultaneously as working fluid and fuel, the efficiency increases with at least 2%.
- NH_3 can be stored seasonally as opposing to H_2 which must be consumed in few days after production.
- It is suggested a method to recover at least 5% from the energy consumed at cold NH_3 storage.
- Due to high distribution cost hydrogen is the most expensive fuel with ~282 C$/MJ.
- Ammonia delivered and converted into shaft energy is cheaper than hydrogen even if at the production phase ammonia could be with up to ~25% more expensive than the hydrogen from which is synthesised.
- The energy generated at shaft is 25% higher in hydrogen-from-ammonia case with respect to gasoline, per unit of fuel volume, and per unit of mass it is 30% higher.

Acknowledgements

The authors acknowledge the support provided by the Natural Sciences and Engineering Research Council.

Thank You!