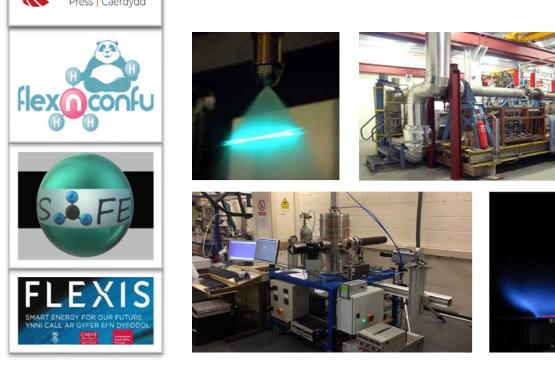


Cardiff Gwasg

Use of ammonia blends for zero carbon power

Prof. Agustin Valera-Medina











- INTRODUCTION
- CHALLENGES
- CENTRE OF EXCELLENCE ON AMMONIA TECHNOLOGIES (CEAT)
- DEVELOPMENTS
- CONCLUSIONS



Professor at Cardiff School of Engineering. He has participated as PI/Co-I on 31 industrial projects with multi-nationals including PEMEX, Rolls-Royce, Siemens, Ricardo, Airbus and FloGas (>£35M). He has published 225 papers (h-index 39), 94 of these specifically concerning ammonia power. Prof. Valera-Medina led Cardiff's contribution to the Innovate-UK 'Decoupled Green Energy' Project (2015-2018) led by Siemens and in partnership with STFC and the University of Oxford, which aims to demonstrate the use of green ammonia produced from wind energy. He is currently PI of various projects (Endeavr Green Propulsion, SAFE-AGT (EP/T009314/1), FLEXnCONFU (884157), OceanREFuel, etc.) to demonstrate ammonia power in turbine engines, Internal Combustion Engines and furnaces. He has been part of various scientific boards, chairing sessions in international conferences and moderating large industrial panels on the topic of "Ammonia for Direct Use". He has supported two Royal Society Policy Briefings related to the use of ammonia as energy vector, and he is principal authors of the book "Techno-economic challenges of ammonia as energy vector". He is Co-Director of the Institute of Net Zero Innovation, Cardiff University and Director of the Centre of Excellence on Ammonia Technologies (CEAT). He is a Fellow of the Learned Society of Wales.

ESPN





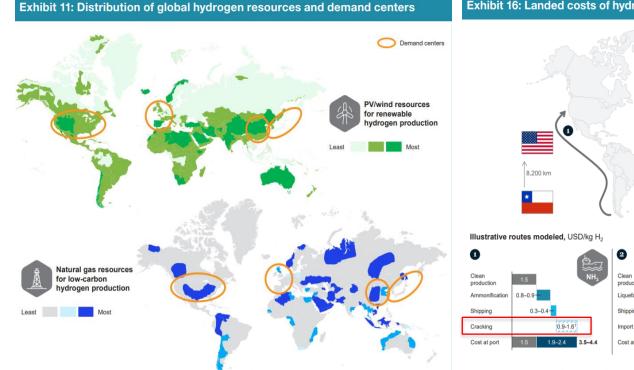
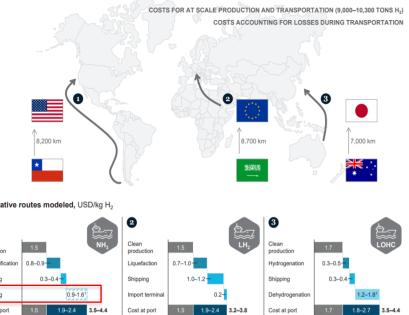


Exhibit 16: Landed costs of hydrogen at port for selected global transport routes



1. Dependent on whether hydrogen feedstock or heat from grid is used for dehydrogenation heating requirement

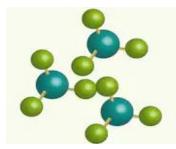
Hydrogen Distribution and comparison between vectors [Hydrogen Council 2021]

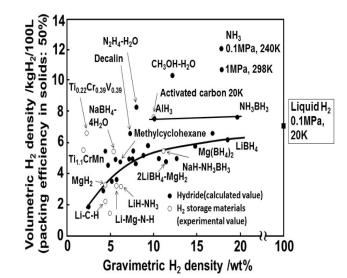


Ammonia can

- be obtained from renewable sources,
- allow the rescue of stranded resources,
- enables the use of waste streams,
- allow storage of vast amounts of energy 30 times cheaper than H2,
- be used to produce energy in Islands or isolated regions,
- be used as a fuel, but also as a fertilizer,
- High hydrogen content (higher than liquid H2),
- have a great economical potential, with a market size up to 184 Billion Euros per year.

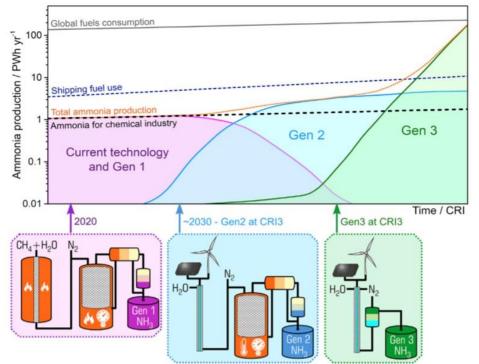






Hydrogen densities in hydrogen carriers. Courtesy of Prof. Yoshitsugu Kojima, Hiroshima University.





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Generation developments needed for an "Ammonia Economy" [McFarlane et al. Joule, 2020]

- However, it has been conceived that for the progression of an "Ammoniabased Economy" there is a need for 3 Generation of technologies.
- Generation 3 does not require the split of water into hydrogen and oxygen.







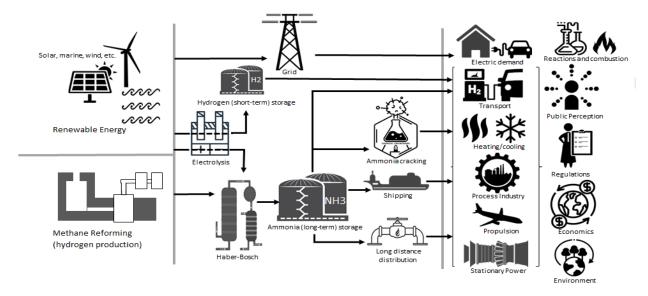
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- A new potential method for the production of ammonia is taking place for research and development, aiming at large scale demonstration in the next 5 years.
- Pink ammonia via Thorium reactors is currently being developed across Europe, US, Japan and China.
- The technology promises to reduce the cost of ammonia to half of its current price.
- <u>https://www.youtube.com/watch?v=HUu</u> <u>e5-QjT_o</u>



 Although ammonia combustion is still seen as the lowest end of the use of ammonia for energy, cheaper distribution, higher hydrogen content and easier operation will change the position of NH3 in the energy arena.

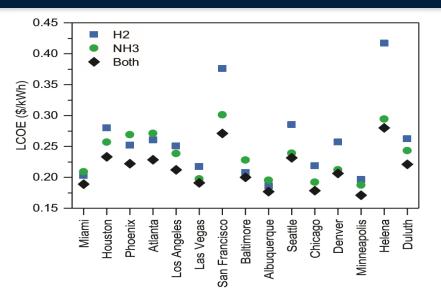


Green Ammonia/Hydrogen Economy [Valera-Medina and Banares-Alcantara, 2020]

 Ammonia is not intended to substitute Hydrogen, but to support the use of the latter;

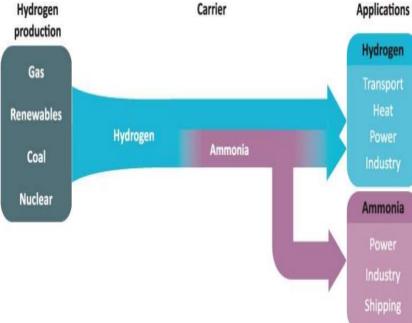
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- Recent studies show that ammonia can be combined with the use of hydrogen to optimise energy generation systems;
- Ammonia offers the flexibility to store hydrogen over long periods at relatively much lower costs;
- Ammonia can be used to store seasonal stranded energy (ie. Summer) for its later use (ie. Winter).
- Thus ammonia **COMPLEMENTS** the hydrogen transition.



Using hydrogen and ammonia for renewable energy storage: A geographically comprehensive technoeconomic study [Palys MJ et al. 2020. Computers and Chemical Engineering]







International program working on ammonia

SSI

Cross-ministerial Strategic Innovation Promotion Program (SIP)

Energy Carriers

Hydrogen: Accelerating and Expanding Deployment, IEA [Birol F, 2018]



Challenges

However, the technology faces the following obstacles,

- 1.Ammonia Carbon-free synthesis (cost reduction, efficiency improvement)
- 2.Power generation at utility-scale from ammonia production (stable, low emissions)
- **3.**Public acceptance through safe regulations and appropriate community engagement.
- 4.Economics profitable scenarios (cannot be applied everywhere)

Key barriers for ammonia-based energy systems

Carbon-free synthesis of ammonia



This is critical because ammonia production methods are heavily reliant on fossil fuels and burning fossil fuels for this purpose severely releases carbon dioxide emissions into the Earth's atmosphere, which is extremely detrimental to the environment.

Power generation at utility-scale

This is important as most developments have focused on improving small-to-medium scale devices for transportation purposes. More importantly, pure ammonia combustion has several technical challenges include high auto-ignition temperature, low flame speed, narrow flammability limits, high heat of vaporization and high NOx emissions.



.......................



Public policy and safety regulations

They are essential to be implemented throughout health and safety impact analyses and the review of currently associated legalisation and end-user perceptions and acceptability.

Competitive economics

It is needed to undergo thorough economic studies in order to determine the potential of ammonia and its viability for use as energy systems.





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Current outcomes

- 1st International Demonstrator on Green Ammonia Energy
- Director of the Green Ammonia Working Group (UK)
- 2 Royal Society Policy Briefings
- Publication of 92 (+5 under 2nd review) papers, two books and 3 book chapters
- Editors in Chief of the new Journal on Ammonia Energy
- Lead of the 1st Symposium on Ammonia Energy
- Chair of the Combustion Section of the Ammonia Energy Association

Current funding profile

 Current projects (for Cardiff) are £12.3m



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Vision

- Establish a physical facility for the Net Zero Innovation Institute with labs for CEAT/LCB/etc.
- CEAT, under the umbrella of NZII, will
 - Develop bespoke ammonia technologies for
 - Heat (boilers, furnaces)
 - Power (gas turbines, ICEs)
 - Transport (aerospace, terrestrial, heavy load)
 - Social sciences and Geopolitics
 - Biotechnology and physics
- Demonstrate NZ technologies at commercial scale at Aberthaw Green Park





Developments - ICEs



Internal combustion engine running on H2/NH3

Ammonia Demonstrator at RAL, Oxford. Cardiff developed the ammonia engine and container for the production of power and its transmission back to the grid.

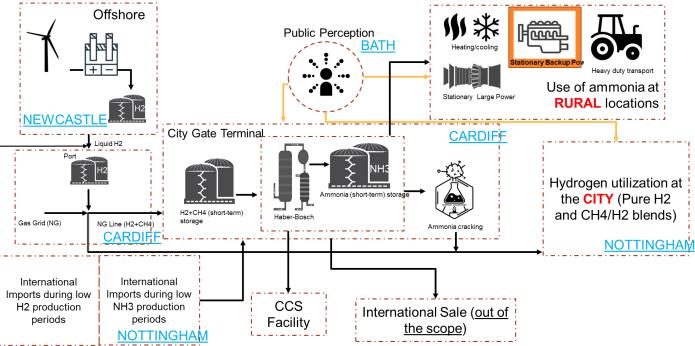


Emissions (CO2 and NOx) using ICE-H2/NH3



Developments - ICEs





OceanREFuel Program to develop ammonia-based capabilities in the UK.

GE and IHI Sign Agreement to Develop Ammonia Fuels Roadmap across Asia

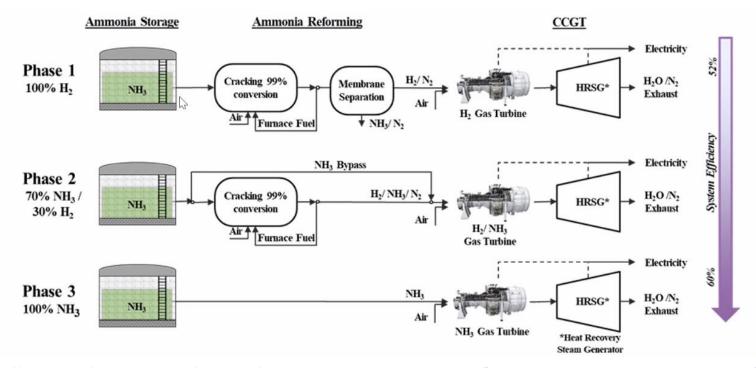
June 22, 2021

First Ammonia Gas Turbine Engine, MHI (H25), 40 MW Power [https://power.mhi.c om/news/20210301. html]





IHI Ammonia Gas Turbine- 100% NH3 [https://www.ihi.co.jp/en/all_news/2022 /resources_energy_environment/119793 8_3488.html



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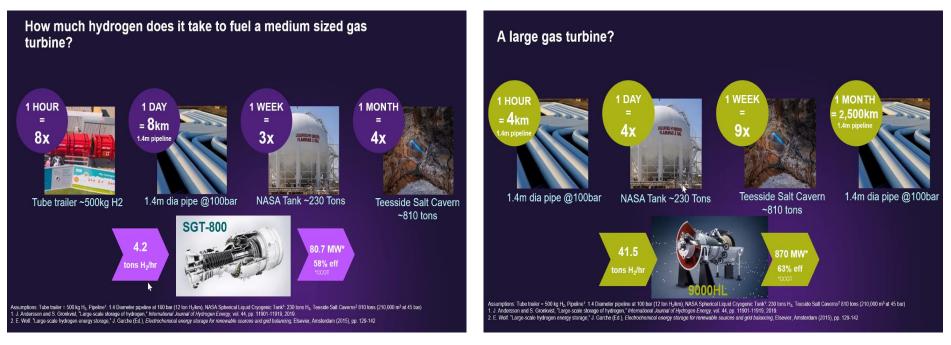
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Efficiency of conversion of energy from ammonia in gas turbines [Cesaro Z, et al. Applied Energy, 2020]

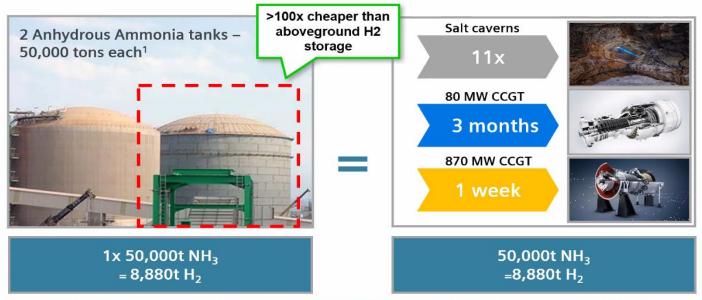




Hydrogen requirements for two different sized gas turbines [Cesar Z, UK-India Ammonia meeting, 2020]



Bulk hydrogen stored as ammonia



1. https://www.mcdermott.com/What-We-Do/Project-Profiles/QAFCO-Ammonia-Storage-Tanks - tanks are approximately 50 meters in diameter and 40.5 meters high, single-wall refrigerated, concrete containment walls.

Hydrogen requirements for two different sized gas turbines [Cesar Z, UK-India Ammonia meeting, 2020]



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The Whitegate gas-fired power plant in southwest Ireland, where Centrica wants to develop ammonia-fired facilities.



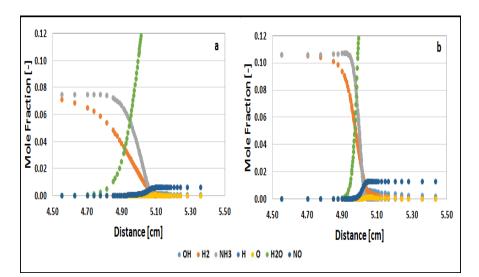
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50%_{vol} NH3 - 50%_{vol} H2

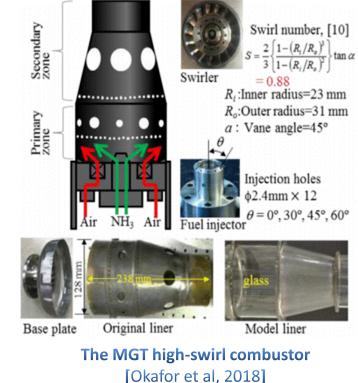
Developments – Micro Gas Turbines



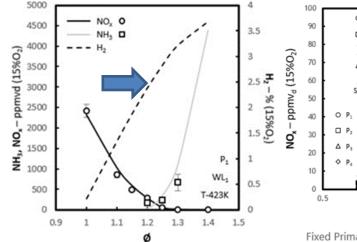
1-D Model for 50:50 ammonia/hydrogen reaction at a) Ø=0.52; b) Ø=0.80.



Developments – Micro Gas Turbines



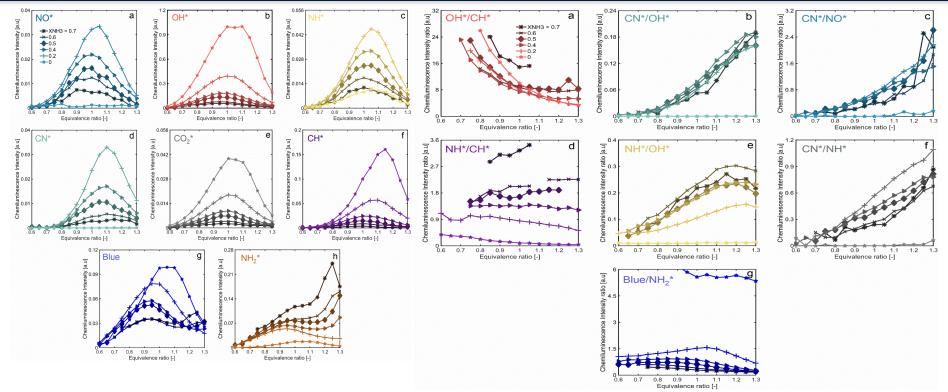
70%_{vol} NH3 30%_{vol} H2. Cardiff University.



Ø=1.25 WL2 ONO, ONH 500 HΝ ppmv_d (15%O₂) SA 300 SA. SA: 200 100 ò. Δ 0.7 0.9 1.1 1.3 **Global Equivalence Ratio** Fixed Primary Equivalence Ratio and Water Loading

Clear reduction of NOx at high E.R. and high concentration of hydrogen Secondary Air (SA) addition with steam injection. Cardiff University [Pugh et al, 2018]

Developments – Micro Gas Turbines



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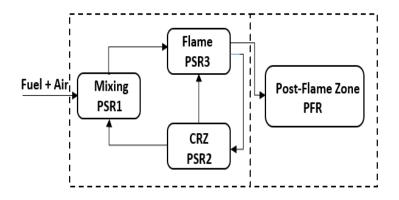
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Spectral signals of various radicals and their correlation between each other [Mashruk S et al. 2022].





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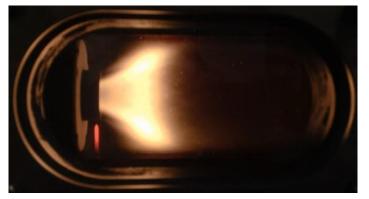
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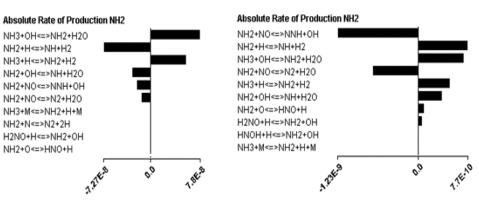
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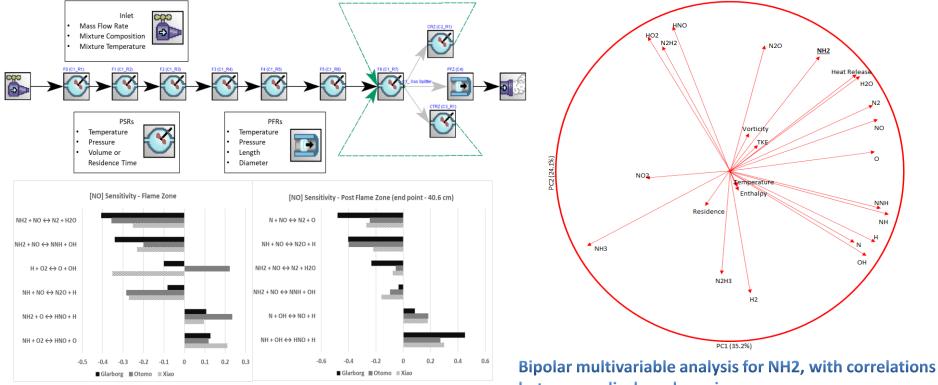


Reactions	A	п	Ea	Ref.
N+NO=N ₂ +O	2.10E+13	0	0	[26]
NO+H+M=HNO+M	1.50E+15	-0.4	0	[27]
HNO+H=NO+H ₂	4.40E+11	0.7	650	[27]
N2O+H=NH+NO	6.70E+22	-2.16	37155	[28]
N2O+H=N2+OH	5.00E+13	0.00E+00	1.52E+04	[29]



Correlation between experiments and numerical modelling adequate but not perfect.

Developments – Micro Gas Turbines



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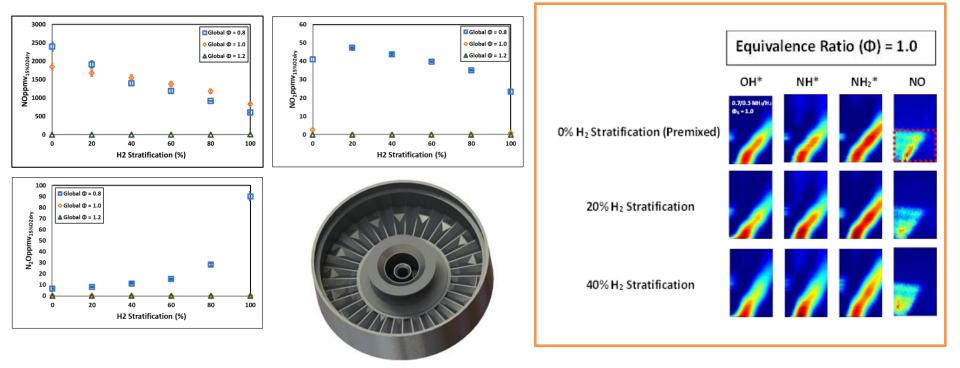
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between radicals and species.





Stratification appears as a good potential for NOx mitigation whilst enabling good flame stability.

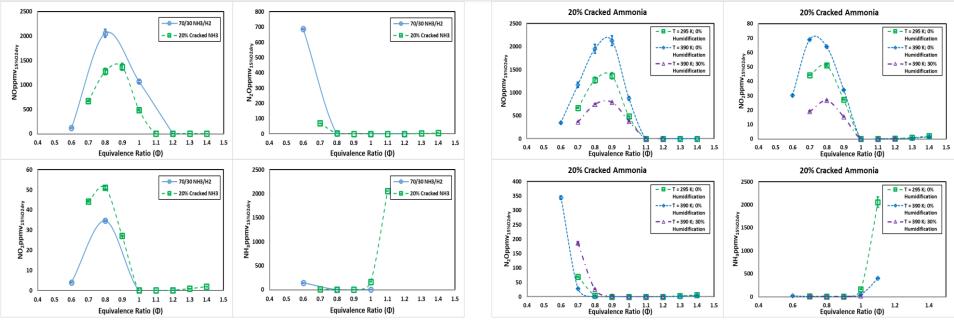
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Developments – Micro Gas Turbines



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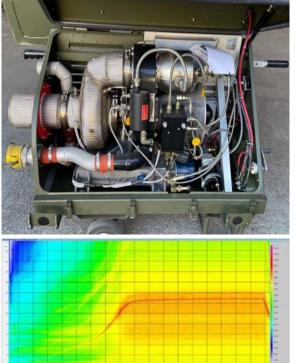
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Ammonia/Hydrogen vs Cracked Ammonia (20%) under atmospheric and higher temperature inlet conditions, with/without humidification.

Developments – Micro Gas Turbines

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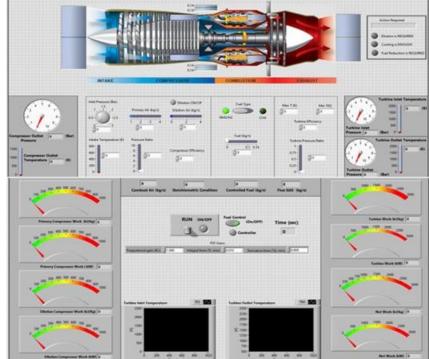
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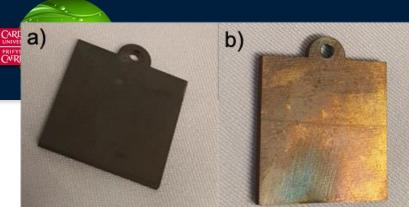
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HELICOPTER AIR START UNIT (HASU)

- Combustor will be replaced by new combustor
- Acoustic signature of the unit has been obtained
 - A bespoke controlling systems is under development to enable stratified/humidified combustion



Ammonia/H as received

200

– Ammonia/H surface removed

0.005

0.005

0.003

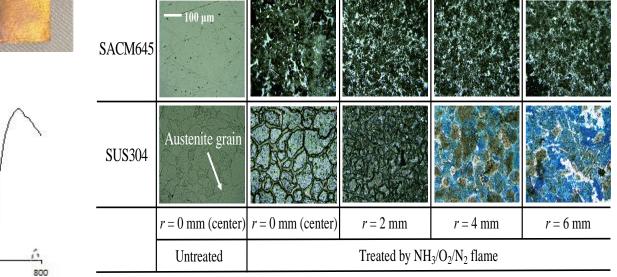
0.001

n

-cim bpm 0.004

H desor ption 0.002

Developments – Micro Gas Turbines



Samples exposed to ammonia/hydrogen and methane, respectively. Also, the peak at ~400oC denotes hydrogen permeation [Kovaleva M et al. 2022].

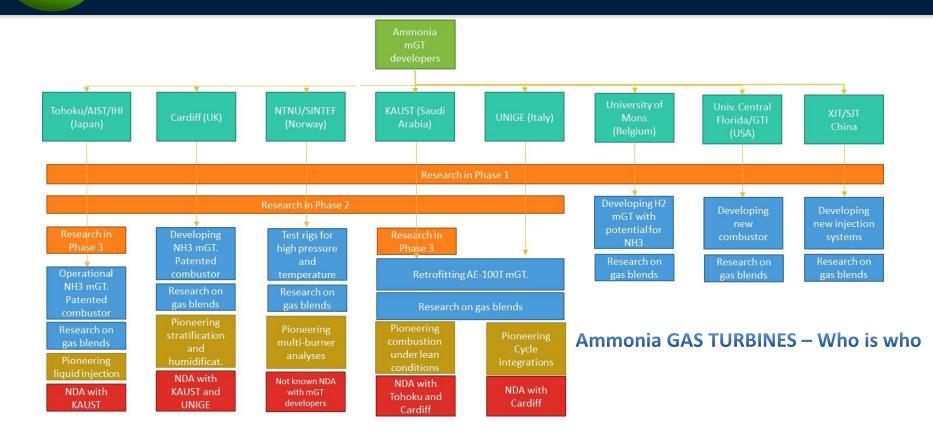
400

Temperature / °C

600

Optical micrographs of the SACM645 and SUS304 test plate surfaces after being exposed to the NH3/O2/N2 flame at 550 °C for 5hr [Wang et al. 2023].

Developments – Micro Gas Turbines



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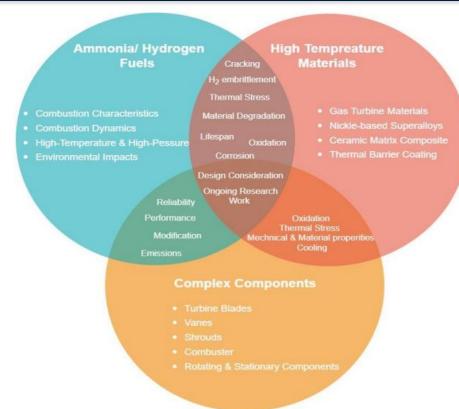
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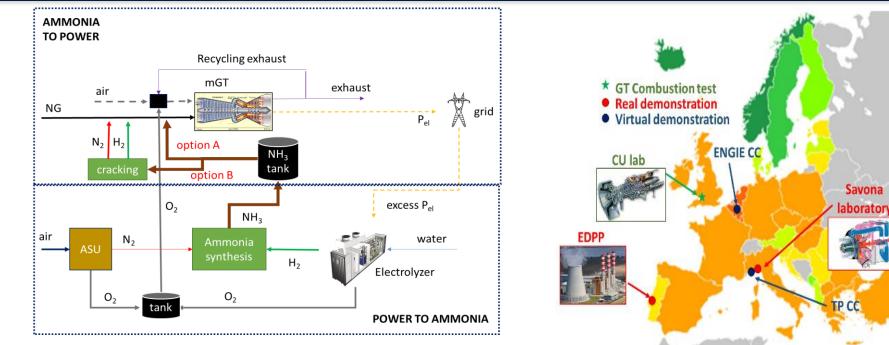




Complex Interactions with Gas Turbine materials

- Hydrogen Embrittlement
- Ammonia Nitration
- Acids
- Basic atmospheres
- Third Body reactions
- Heat Losses
- Radiation





FLEXnCONFU – First large GT ammonia/hydrogen/NG demonstrator



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Developments – Gas Turbines

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Initial Results

High NOx at low

Equivalence Ratios

Hydrodynamic and

Thermodiffusive

impact on flame

Up to 20% NG/H2

replacement can be

feasible without major

morphology

retrofitting.

Rich conditions boost

the production of NH2*

instabilities have a high

Equivalence Ratio (Φ) = 1.2

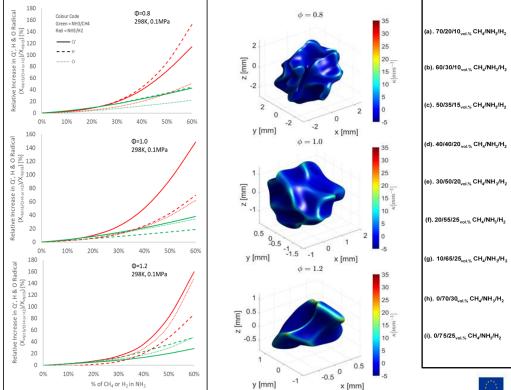
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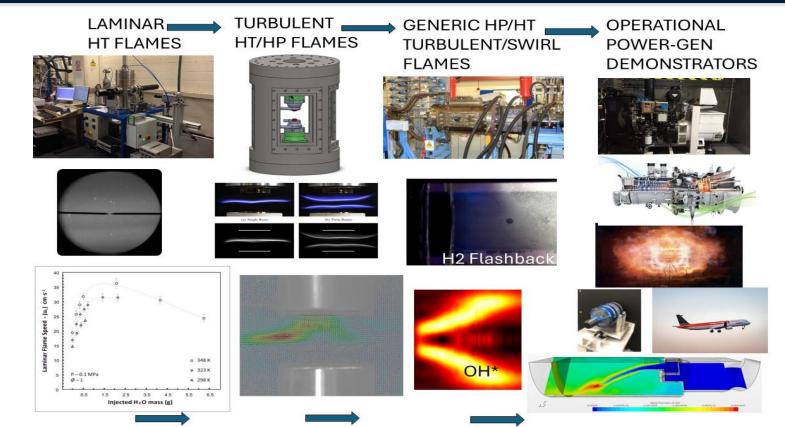
0

NH,

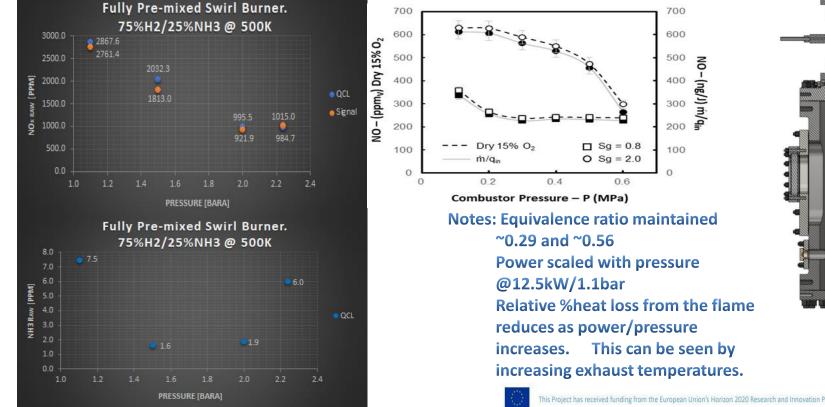


(mm) ⁴⁵ 0 1







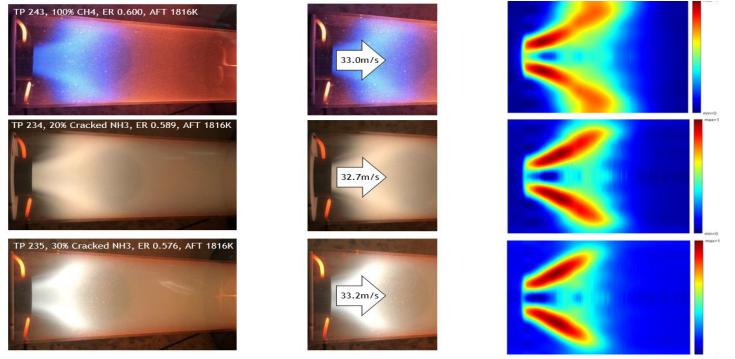


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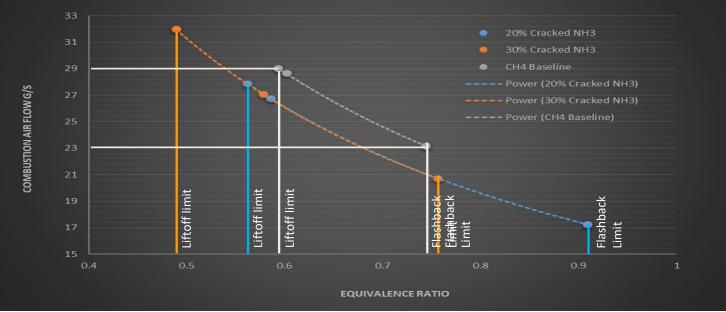


Photographs and OH*Chemi. 50kW,1.1bara, 538K



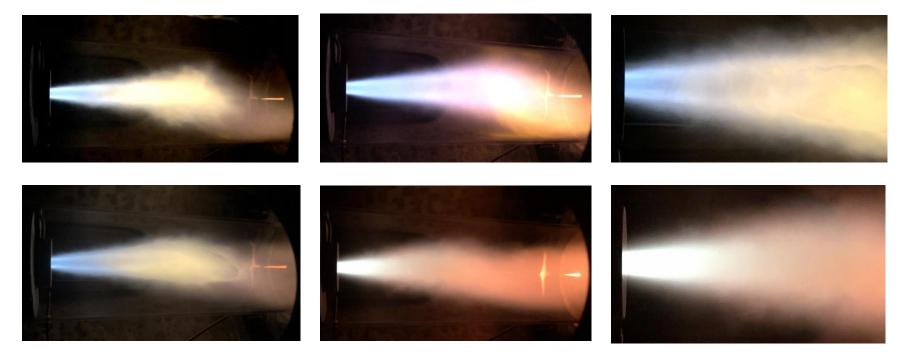


GSB 50kW, 1.1bara, GSN0.8, Stability Map



Operability limits using cracked ammonia compared to methane.





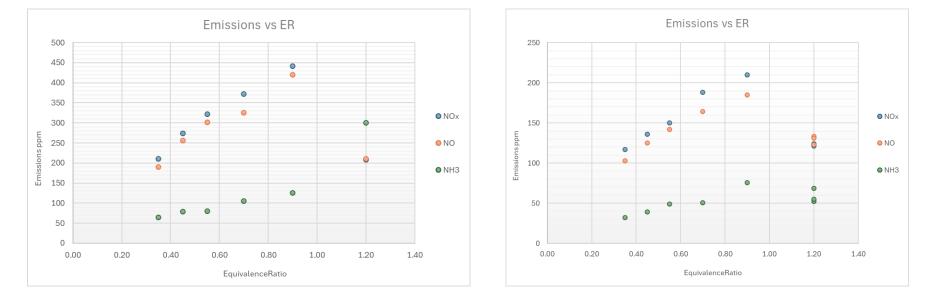
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Photographs. 50kW,1.1bara, 538K. Heavily cracked conditions.





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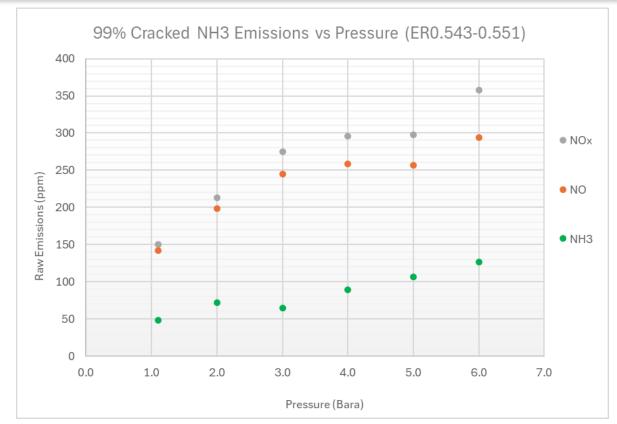
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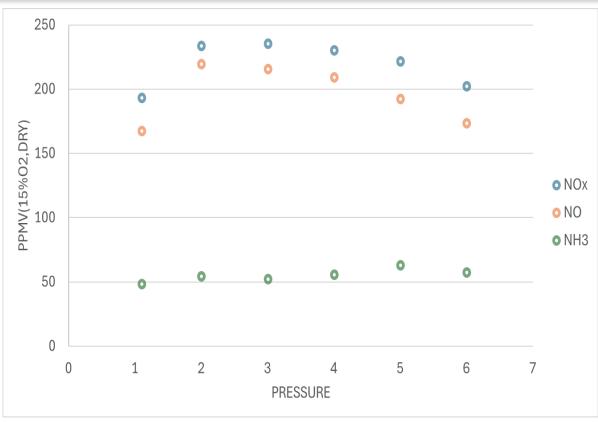
Emissions. 50kW,1.1bara, 538K. 92 and 99% cracked conditions.





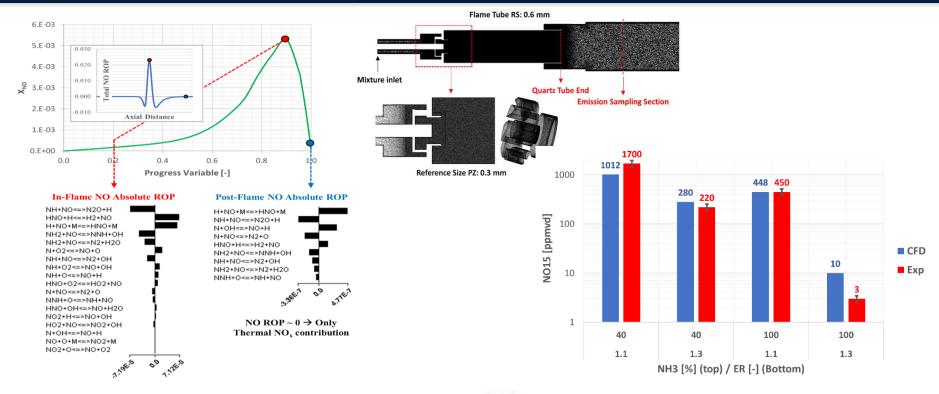
Emissions. Up to 75kW,1.1-6 bara, 538K. 99% cracked conditions.



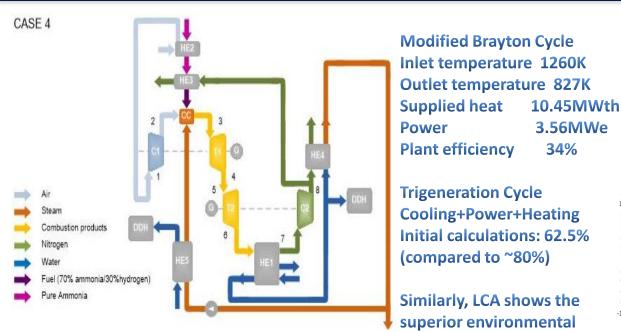


Emissions. Up to 75kW,1.1-6 bara, 538K. 92% cracked conditions. Corrected to 15%O2.

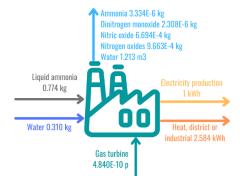


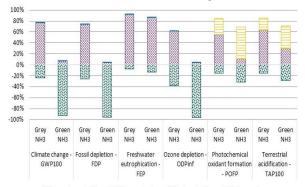






advantages of green NH3

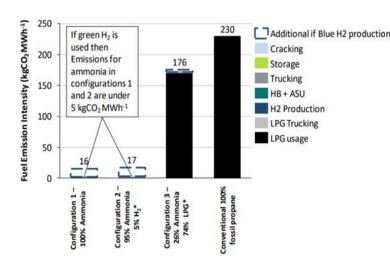




S Ammonia production ■ Water production D Heat production Plant operation

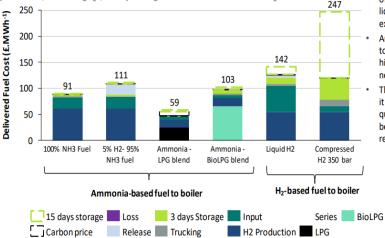


Developments – Boilers/Furn.



 $\label{eq:scenario} Scenario 1: Delivered cost of fuel to an industrial end users comparing low-carbon ammonia and H_2 fuels with increased end user storage at boiler site, 15 days (£.MWh^1, Lower Heating Value)$

12 MW distillery, 200 km distribution distance, large scale 200MW NH₃ synthesis, Blue H₂ production, at £1.80.kgH₂⁻¹, 15 days storage at boiler – Carbon tax £50 tCO₂⁻¹

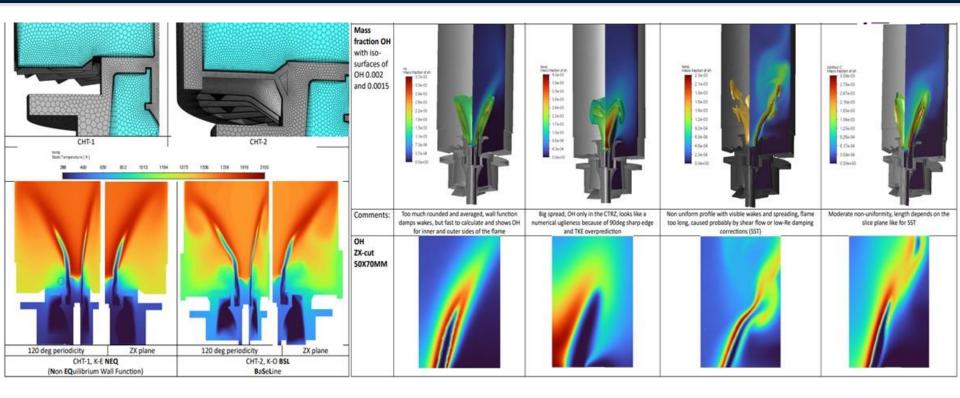


- Existing off-gas grid boiler sites have between 10 and 15 days of storage.
- If this higher storage is needed Ammonia offers a comparative cost improvement over liquid and compressed hydrogen which are expensive to store.
- Ammonia can be stored at similar conditions to LPG whilst compressed hydrogen needs high pressures (350 bar), or liquid hydrogen needs extremely low temperatures (-253 °C).
- Though this gives an advantage to ammonia, it may be that for new technologies lower quantities of storage are used due to storage being more expensive and possible regulatory/safety constraints.

Emissions and Delivery Fuel Cost of various options (report 2023, 145 pages)



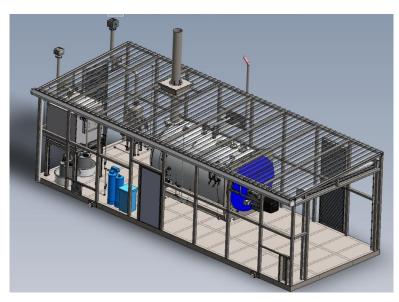
Developments – Boilers/Furn.





Developments – Boilers/Furn.

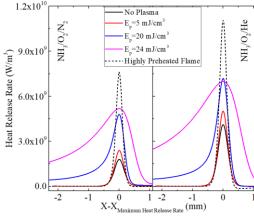
• The unit will be used for demonstration in a Poultry farm. Further developments are expected for the deployment of ammonia to isolated regions.

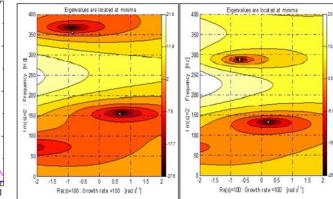






Developments – Other areas





Experimental Additions

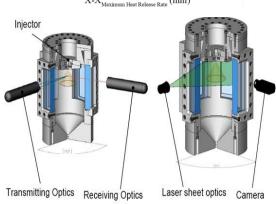
Plasmas Combustion (Nox reduction)

Thermoacoustics (flames stability)

Multi-phase injection (fuel replacement)

Direct ammonia injection (liquid spray)

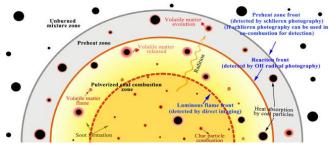
Pulse detonation (explosions)



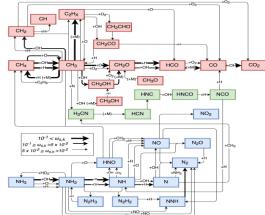




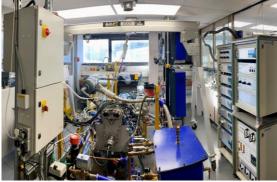
Developments – Other areas



Assumption of co-combustion flame structures [Xia et al. 2021]







Experimental Additions

Jet Injection (in collaboration with Nottingham)

Materials Analyses

Multi-phase Injection

Coal-ammonia co-firing

Additional molecules (ie. cyanide) in reaction pathways

Radiation studies

Health and Safety

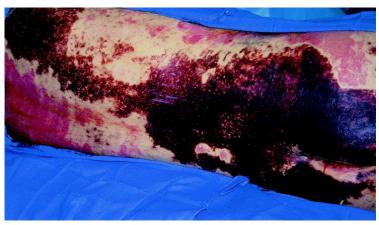


Developments – H&S/Envirn.



Ammonia gas cloud in Seward, Illinois. Cause: ruptured hose





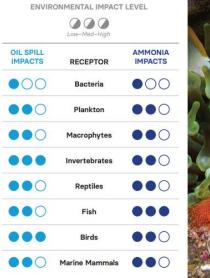
Exposure of skin to anhydrous ammonia [Amshel et al 2000].

Explosions and cylinder damage



Developments – H&S/Envirn.







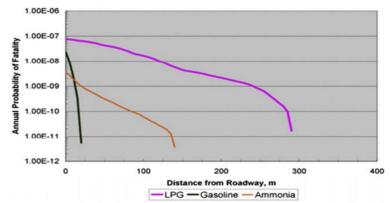
Environmental Defence Fund, 2022. [Online]. Available in: https://cdn.ricardo.com/ee/media/assets/ammonia-at-seareport-summary.pdf

TABLE 10.6

Reported Accidents With Transporting Anhydrous Ammonia and Ammonia Solutions, United States, 1971 –2019 (Reports Only for Anhydrous Ammonia).

	Total reported	Total fatalities	Total hospitalized injuries	Total nonhospitalized injuries
Highways	3209 (797)	25 (23)	36 (29)	744 (602)
Rail	2460 (2301)	11 (11)	23 (21)	321 (290)
Water	21 (14)	0 (0)	0 (0)	4 (4)

Appl Energy 2017. https://doi.org/10.1016/j.apenergy.2016.10.088.

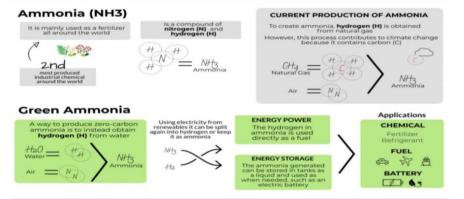


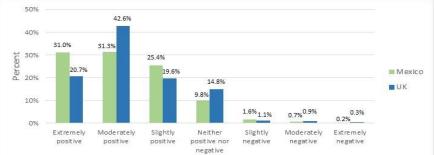
Quest Consultants Inc. Comparative Quantitative Risk Analysis of Motor Gasoline, LPG and Anhydrous Ammonia as an Automotive Fuel. Iowa, USA: 2009. Courtesy of Quest.)



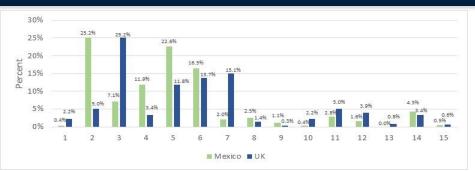
Developments – H&S/Envirn.

From ammonia to green ammonia

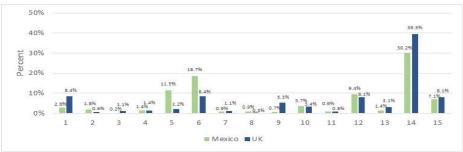




Percent of responses for opinion of green ammonia technology (920 individuals – 357 UK, 563 Mexico).



Percentages for most common answers by country of <u>first associations of ammonia</u>. (1) Nothing/Don't know (2) Poison/toxic (3) Smell (4) Safety (5) Chemical (6) Cleaning products (7) Urine/manure (8) Pollutant (9) Death/killing (10) Fuel (11) Fertilizer/refrigerant (12) Other products (13) Negative (14) Substance (15) Confusion with other chemicals.



Percentages for most common answers by country of <u>perception of green ammonia</u>. (1) Nothing/Don't know (2) Poison/toxic (3) Smell (4) Safety (5) Solution/alternative (6) Novel concept (7) Cost (8) Pollutant (9) Complex/confusing (10) Need more information (11) Water (12) Positive for the environment (13) Negative (14) Generic positive (15) Sceptical.



Conclusions

- Ammonia blends can be used efficiently, with low NOx, and production of species that can be used for combined processes.
- However, ammonia will be only useful for some niche applications.
- Reaction mechanisms need to be accurate and include a variety of complex processes still requiring vast research.
- There are still many points in the combustion of ammonia that require further research, with a lot of input from Public Perception.





Techno-Economic Challenges of Green Ammonia as Energy Vector

AGUSTIN VALERA-MEDINA RENE BANARES-ALCANTARA



Cardiff Gwasg University Prifysgol Press Caerdydd

Issue 1 Spring 2022

Ammonia Energy





THANKS FOR YOUR ATTENTION

FURTHER INFORMATION: VALERAMEDINAA1@CARDIFF.AC.UK



