Release the Crackers

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1. Introduction

In case you are wondering, the title of this paper is a paraphrase of a memorable utterance by Zeus in the 1981 fantasy adventure film *The Clash of the Titans*.

This bit of whim underpins a major development in the UK that will facilitate the future hydrogen economy. Some of the readers of my papers have advocated using ammonia as a hydrogen carrier in responses to my earlier papers on hydrogen. Thus, I started researching this subject and found a document (reference 3 in section 2 below) that described recent ammonia developments.

Ammonia (NH_3) is a potential future hydrogen carrier. However producing ammonia does have a down-side. The most popular industrial process, the Haber-Bosch process, is extremely energy-intensive. This process is shown and described below:

$N_2 + 3\,H_2 \rightarrow 2\,NH_3$ $\Delta H°$ (change in enthalpy) is -91.8 kJ/mol

The Haber–Bosch process is a reaction between hydrogen and nitrogen at an elevated temperature (840 °F) and high pressure (1,500 psi). The reaction happens in a special pressure vessel, but the reaction disrupts the conditions it requires, so it must be continually cycled, making it inefficient and expensive.[1]

Reasons that ammonia is being considered as a hydrogen carrier include:

(1) Ammonia has a higher volumetric efficiency than other carriers (even liquid hydrogen).

(2) Cracking ammonia to liberate the hydrogen does not produce undesirable byproducts like greenhouse gases (GHG).

(3) Renewable energy has become the least expensive energy and its price continues to decrease, allowing cost-effective production of ammonia based on green hydrogen (see next paragraph for hydrogen "colors").

(4) The cyclic nature of the Haber-Bosch process means it can live with renewables' variability.

(5) Under some conditions ammonia can be directly combusted or used in fuel cells, with only water vapor and nitrogen as byproducts.

(6) Ammonia is already widely produced in large quantities, mainly for fertilizer, but also for feedstock for manufacturing other chemicals.

(7) Ammonia can be stored or transported in liquid-form by pressurizing and/or refrigerating it.

(8) Transportation can be via pipelines, tanker ships or tanker trucks.

Since it's an element, other than different isotopes (which we are not considering here), hydrogen is hydrogen is hydrogen. However there are considerations of how it's produced including any undesirable byproducts. A large majority of hydrogen used in

[1] Wikipedia article on Ammonia, https://en.wikipedia.org/wiki/Ammonia

industrial processes (like making most ammonia) is produced by reforming natural gas, but this produces CO_2 (the main GHG). I have heard this called gray hydrogen. Hydrogen produced by electrolysis (no GHG) with 100% renewable (very low GHG) electricity is commonly called green hydrogen. Hydrogen produced by reforming natural gas with CO_2 capture and sequestration is commonly called blue hydrogen.

This paper will investigate why ammonia is probably the best carrier for hydrogen, possibly can be used directly as a fuel, and the latest developments in ammonia technology including crackers.

2. Why Ammonia?

A team of hydrogen technology companies in the UK recently received a grant of over $300,000 to perform *valuable research on the role of ammonia in the delivery of low cost bulk hydrogen for use in the UK energy system.*[2]

Even though we covered the reasons ammonia is a good hydrogen carrier in the intro, we didn't cover all potential alternatives. The paper referenced here does.[3]

Hydrogen can be transported without a carrier compound in gaseous or liquid form. In gaseous form compressed hydrogen is transported in bundles of long cylindrical tanks, installed on trailers. Because of its low density, only 500 to 600 lbs. of hydrogen per trailer can be carried with steel tanks. 1.0 to 1.25 tons of compressed hydrogen can be carried per trailer using advanced composite tanks.

Liquid hydrogen is transported by road in specially constructed and highly insulated cryogenic tanks containing typically 2.5 tons up to 5 tons of hydrogen. Boil-off losses and transfer losses are one of the challenges of handling liquid hydrogen. A recent U.S. study estimates hydrogen loss of up to 25% in the whole service chain from production to dispensing to hydrogen fueled vehicles.[4]

Organic carriers (like methane) can be used to transport hydrogen. Some of these can be produced using biological feedstock (like biomethane), and like ammonia some can be directly combusted or used in a fuel cell. Due to efficiency considerations none of the bio-carriers are truly carbon-neutral (currently). Probably neither is ammonia, but I would guess it can come closer to this metric. Also bio-carriers are not currently made in very large quantities (ammonia is).

Finally bio-carriers are probably more useful as very-low-GHG replacements for geologically-sourced hydrocarbons (for the next decade or two).

Other candidates for a hydrogen carriers include metal hydrides, *however, their use for very large-scale transport of hydrogen (eg., at the TWh scale) is infeasible due to the*

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[2] Trevor Brown, Ammonia Energy Association, "Engie, Siemens, STFC, and Ecuity awarded funding for green ammonia-to-hydrogen in UK", Sep 6, 2019, https://www.ammoniaenergy.org/articles/engie-siemens-stfc-and-ecuity-awarded-funding-for-green-ammonia-to-hydrogen-in-uk/

[3] Companies sponsoring this paper are: Ecuity, Engie, STFC, and Siemens, for the specific authors, see page 2 of the document, "Ammonia to Green Hydrogen Project", April 2020, https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/880826/HS420_-_Ecuity_-_Ammonia_to_Green_Hydrogen.pdf

[4] Guillaume Petitpas, A.J. Simon, Lawrence Livermore National Laboratory. "DOE Hydrogen and Fuel Cells Annual Merit Review – Liquid Hydrogen Infrastructure Analysis", 2017, https://www.hydrogen.energy.gov/pdfs/review17/pd135_petitpas_2017_o.pdf

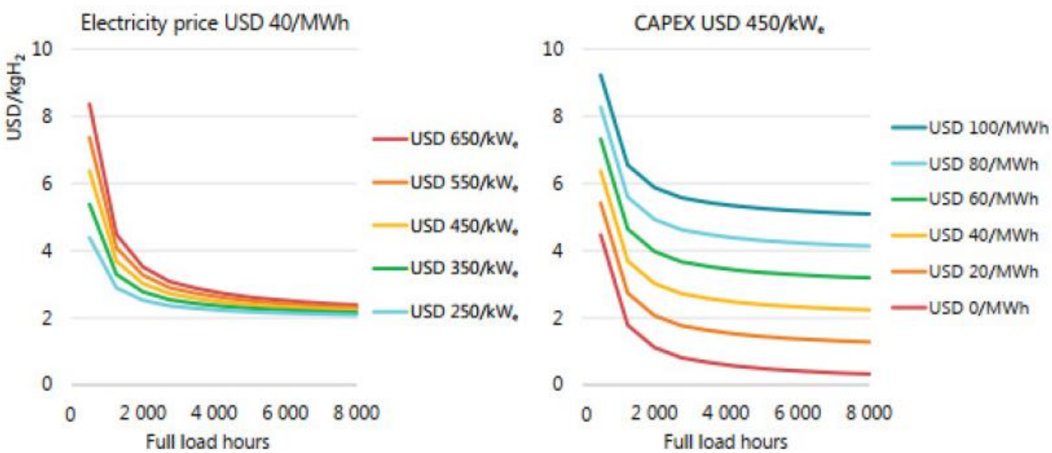
substantial weight and volume of the metal alloy in comparison the quantity of hydrogen it can transport, and a large amount of heat must be provided to di-hydride the metal alloy hydride (to release the hydrogen) and a large amount of cooling must be provided during the re-hydriding process.[3]

3. Financial Considerations

Ammonia production economics are dominated (70-90%) by the feedstock cost, so the potential for ammonia as an international low/zero-carbon hydrogen carrier is highly dependent on the economics of producing the necessary feedstock hydrogen in the locations where the low-cost low/zero-carbon (blue or green) *hydrogen will be available…The lowest low-carbon cost is for the Middle East at just under* $.73 / lbs… *very closely followed by the US.* [3]

The lowest cost of green hydrogen corresponds to the lowest cost for reasonably reliable renewable energy. In the U.S., this is in the West. The latest power purchase agreements for utility scale solar in this region is in the range of $20 per MWh. Although this is typically without storage, there is (at least) one very large project near Los Angeles where this price includes a few hours of storage[5]. Hydroelectric power is also very inexpensive in the Northwest, with wind-power pricing coming down rapidly.

The cost of very low-*carbon hydrogen, produced from renewable electricity will depend upon the economics and scale of production, with the most significant factor being the cost of electricity. This is demonstrated in the chart on the right side of the figure below. Solar electricity generated in the Middle East is expected to be available at less than $32/MWh as indicated by bid process for several recent solar projects. According to IEA, this will result in a zero-carbon hydrogen cost of approximately $2.11/kg H_2… at 4,000+ hours of load per year.*



Future levelized cost of hydrogen production by operating hour for different electrolyzer investment costs (left) and electricity costs (right)

[5] Section 2.2, "2020 Large PV and PV + Storage Update", May 2020, https://energycentral.com/c/cp/2020-large-pv-and-pv-storage-update

4. Developments

Hydrogen and ammonia will probably play important roles in our future evolution to a GHG-free economy. However, there are two potential pathways, and it's probable that we will need to take both.

Pathway one involves cracking green ammonia to create green hydrogen, and then using that hydrogen for future fuel and feedstock.

Pathway two involves using green ammonia directly (without cracking to release hydrogen) as fuel and feedstock.

In the first subsection below we will review recent developments in producing green hydrogen and green ammonia. In the second and third subsections we will individually review the above two paths.

4.1. Green Hydrogen & Green Ammonia

4.1.1. Saudi Arabia

Air products, an American multinational corporation, *in collaboration with ACWA Power and NEOM, announced the signing of an agreement to develop a $5 billion green hydrogen-based ammonia production facility powered by renewable energy.*[6]

According to the release, the worlds' largest green hydrogen project will supply 650 tons of carbon-free hydrogen for transportation globally and will save the world three million tons of carbon dioxide annually.

The project will be equally owned by all the three members and will be located at NEOM in the northwest corner of Saudi Arabia. The project aims to produce green ammonia for export to global markets by 2025.

…The press statement further said that the joint venture project would help in NEOM's strategy to become a global player in the global hydrogen market. The project would include the integration of 4 GW of renewable power from solar, wind, and storage and will produce nearly 650 tons of hydrogen per day by electrolysis using Thyssenkrupp technology. The project will also produce nitrogen by air separation method using Air Products technology, and it will produce 1.2 million tons of green ammonia using Haldor Topsoe technology.

4.1.2. California

My articles tend to focus on California, as this has been my home state for 45 years. I know it well, and can provide background information on various California-related subjects. One subject I have written on in the past is the challenge of recycling materials that are made from petroleum feedstock – like plastic bottles.[7]

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[6] Rakesh Ranjan, Mercom India, "Green Hydrogen Production Facility Worth $5 Billion to Come Up in Saudi Arabia's NEOM", July 9, 2020, https://mercomindia.com/green-hydrogen-production-facility-saudi-arabia-neom/

[7] See section 5 of "Options for Mitigating Climate Change", May, 2020, https://energycentral.com/c/ec/options-mitigating-climate-change

A recent development by has facilitated the construction of the world's largest green hydrogen plant located in Southern California. The input "fuel" for this plant will be waste plastics and newspapers.

Americans have been deluged with news about plastics and how they are littering cities and waterways while consuming space in landfills. There's some good news: an uncommon waste-to-fuel process is planned and one that can convert that material into biogas, which is then used to create green hydrogen.[8]

Hydrogen is a key pillar when it comes to running a decarbonized economy — a fuel that can power both the electricity and transportation sectors. To that end, a proposed plant in Lancaster, California that is just north of Los Angeles, will use plastics and recycled paper as a feedstock — waste that would otherwise go to a landfill. It will be gasified at temperatures of 7,000 degrees Fahrenheit before getting transformed into hydrogen.

…The company doing this is SGH2 Energy Global, which is part of the Solena Group. It says that its technology reduces carbon emissions two-to-three times more than green-hydrogen produced using electrolysis and renewable energy. It also says that its technology is five-to-seven times cheaper. SGH2's green hydrogen is cost-competitive with "grey" hydrogen that is produced from fossil fuels, it says, which is what makes up most of the hydrogen in use now.

…The plant is now in the engineering and design phase — something headed by Fluor Corp. Construction will begin in 2021 and it is expected to be fully operational in the first quarter of 2023. It will be located on five acres and will cost $55 million to build — a project for which it has yet to get financing but will likely include it seeking project financing from lenders active in the U.S. renewables market. Right now, the hydrogen will be used to supply California's 42 hydrogen fueling stations. The goal is to immediately get that to 100 and then eventually to 1,000, which is dependent on the demand for green hydrogen.

For more information on this project go through the link below.

https://www.spglobal.com/platts/en/market-insights/latest-news/electric-power/052020-green-hydrogen-developer-plans-california-startup-of-worlds-largest-facility

4.2. Crackers

Reference 3 provides design details for both a large-scale (industrial) ammonia cracking unit, and a smaller-scale (distributed) cracking unit. For those interested in the former, go through the link in reference 3 (on page 2 above), and go to section 3.1 in the referenced document. However, my interest is in smaller crackers that might be used in transportation application (road vehicles, trains and ships initially, and then possibly long-range aircraft in the future). Thus I am both looking for a smaller cracker and an advanced design. Fortunately reference 3 also provides this.

[8] Ken Silverstein, Forbes, "The World's Biggest Green Hydrogen Plant Is Planned for California. Its Prospects For Electric Power And Transportation?", May 26, 2020, https://www.forbes.com/sites/kensilverstein/2020/05/26/the-worlds-biggest-green-hydrogen-plant-is-underway-in-california-its-prospects-for-electric-power-and-transportation/#57ddb00f2a96

Recently, a new family of catalysts developed by STFC have shown significant promise in this area: metal amides and imides, which are salts consisting of (generally) light metals paired with -amide or -imide ions. These materials have been shown to have cost and performance advantages to existing transition metal catalysts.[9]

Both sodium amide ($NaNH_2$) and lithium amide ($LiNH_2$) were investigated, and the latter was found to have better physical characteristics for this applications.

The lithium amide-imide system showed significantly higher catalytic activity than sodium amide and ruthenium… It has also been shown to behave quite differently to conventional catalysts… all of the nitrogen and hydrogen in the catalyst is able to be exchanged with the reacting gases. This indicates a bulk reaction mechanism as opposed to the surface mechanisms understood for transition metal catalysts. This reduces the need for particle nano-sizing and complex catalyst support architectures such as are often needed to achieve the highest activities in metal-based catalysts, and also improved the stability of the catalyst towards temperature cycling such as may be required with direct coupling to renewable electricity installations. Furthermore, the feedstock elements are far more abundant than ruthenium. Together with the simpler catalyst formulation, this is likely to result in cheaper catalyst formulations using lithium imide.

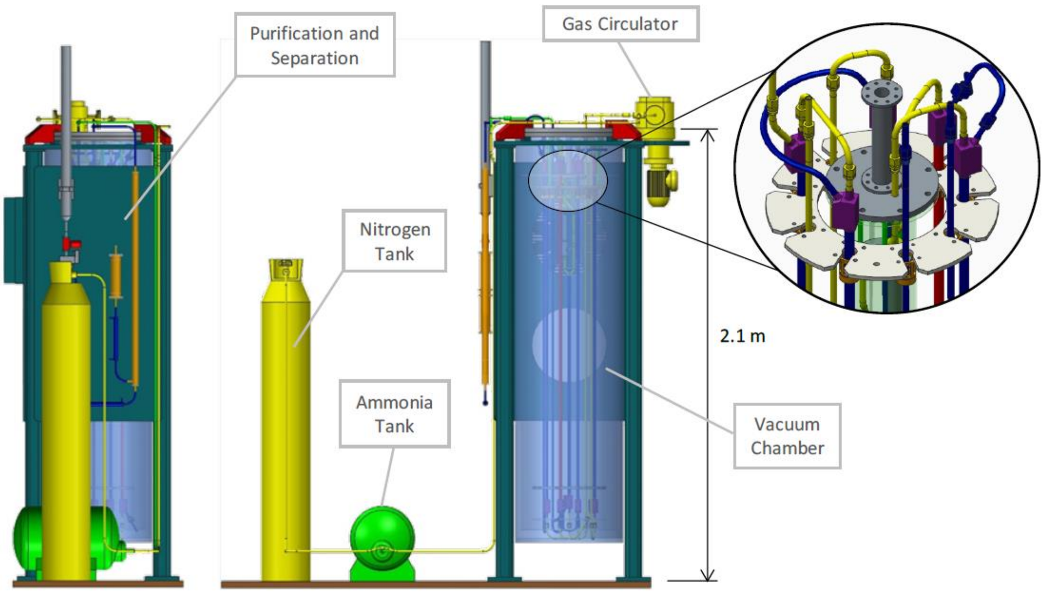
Tests of the catalyst operation over ~60 hours showed no degradation in performance. The promising activity of lithium amide-imide has been developed into a benchtop demonstration unit.

… a number of important steps have been taken in this feasibility study to explore the scale-up potential of this novel catalyst system from the previous system to the 5 kg H^2*/day system proposed in this study:*

- *Scale up of the catalyst synthesis process to an appropriate level for higher-power units, including an appropriate particle morphology for a packed-bed reactor, rather than the flow-over reactor designs which have been used previously*
- *Design of an integrated ammonia decomposition reactor system with fully integrated thermal management system to maximize performance*
- *Ensure system complies with relevant safety standards (EN 60079 Explosive atmospheres, PD5500 Pressure Vessels)*

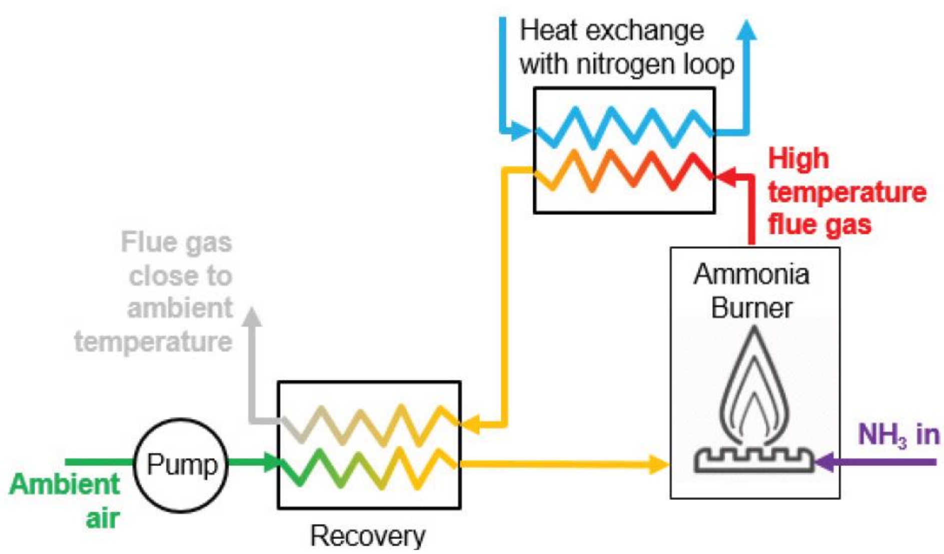
…*A model of the 5 kg/day cracker has been produced* (figure below) based upon the presented system schematic. To minimize thermal losses and increase system safety, the majority of components are to be contained within a vertically mounted cylindrical vacuum vessel. In addition to providing superior thermal performance, the vacuum vessel also allows any leaks to be easily detected and dealt with by the control system. The tubular double-pipe cracker components are mounted to a suspended support structure. Two concentric radiation shields are also fixed to this support to reduce radiation losses. Radiation shielding is extremely effective, reducing the radiative heat loss to 60 W. A controllable 4 kW electric heater is centrally mounted within separate vacuum vessel at the center of the main chamber.

[9] Reference 3, section 4.1.



5kg/day Cracker CAD Model

The engineering design and the thermal management system of the 5 kg/day cracker serves to demonstrate the feasibility of efficiently cracking ammonia with a lithium imide catalyst at any scale. The design is scalable with a larger capacity achievable by adding more reactor and evaporator tubes in parallel and thus still respecting the thermal and safety design constraints determined within this study. While an electric heater was chosen for this small scale demonstrator for convenience, cost and safety, an ammonia burner is the only economical and environmentally viable option for providing the required heat at any commercial scale. The only fundamental difference between this design, and a larger scale cracker, is that flue gas from the ammonia burner would be used to heat the nitrogen via a heat exchanger instead of direct electric heating of the nitrogen. An additional recovery heat exchanger would be used to preheat the flow entering the ammonia burner to maximize efficiency (figure below).



Reference 3 created a computational fluid dynamic model of the 5 kg/day cracker, and analyzed this for performance and economics. I am not going to delve into the details of this analysis. If you would like to, go to section 4.3 in reference 3.

The conclusion of this study is given below.

…Assuming an energy cost per kWh of $0.09, this gives an electricity cost per kg of hydrogen produced of $1.31. The energy consumption cost is equivalent to $33.20/MWh of hydrogen released. We would not necessarily expect this cost to be competitive with large scale crackers because this is primarily a technology demonstrator and because of the use of electricity to provide the required heating.

4.3. No Cracking Needed

If you read the above, and looked at the figure on the bottom of the previous page, you probably noticed an ammonia burner. Yes, you can directly burn ammonia, use it in a fuel cell, or a combustion turbine, but it's not easy. Ammonia has an extremely narrow concentration-range (with respect to air) where it can be combusted. Thus all of the above are very specialized devices. However some projects are taking these on.

On August 6, NYK Line, Japan Marine United Corporation, and Nippon Kaiji Kyokai (ClassNK) signed a joint R&D agreement for the commercialization of an ammonia-fueled ammonia gas carrier that would use ammonia as the main fuel, in addition to an ammonia floating storage and regasification barge. [10]

Since carbon dioxide (CO_2) is not emitted when ammonia is burned, it is viewed to have promise as a next-generation fuel that could mitigate shipping's impact on global warming. In addition, it is said that zero emissions can be realized by utilizing CO_2-free hydrogen as a raw material for ammonia. In particular, a significant reduction in CO_2 emissions is expected to be achieved by replacing coal and natural gas as the main fuels for power generation.*

Parties in Japan have succeeded in generating electricity through the use of a gas turbine with 100% ammonia…

The reduction of GHG emissions is a significant issue in the marine transportation sector. In 2018, the International Maritime Organization (IMO) set the goal of halving GHG emissions from the international maritime sector by 2050 and reaching a target of zero as early as the end of this century.

Ammonia is expected to be used as an alternative fuel for vessels. As demand for ammonia fuel is foreseen to expand, the need for a transportation infrastructure for stable supply is expected to increase…

The following is from a post on "Low Carbon Ships" a couple of months ago.

Solid oxide fuel cell technology company Bloom Energy Corp. (BE: NYSE) and Samsung Heavy Industries Co. Ltd. (010140:KRX) (SHI), a part of Samsung Group, announced that they "have signed a joint development agreement to design and develop fuel cell-powered ships." The two companies reported that they are partnering to work

[10] NYK Line, "Joint R&D Starts for Use of Ammonia in Marine Transportation to Reduce GHG Emissions", Aug 12, 2020, https://www.nyk.com/english/news/2020/20200812_01.html

together toward achieving clean power for ships and creating a more sustainable vessels for the marine shipping industry…

https://www.streetwisereports.com/article/2020/06/30/bloom-energy-shares-charge-higher-on-partnership-with-samsung-for-clean-powered-ships.html

After seeing this, I did a bit of research and found a patent by Bloom, described and linked below.

Patent No.: US 8,916,300 B2

Date of Patent: Dec. 23, 2014

ABSTRACT: Systems and methods are provided in which ammonia is used as a fuel source for solid oxide fuel cell systems. In the various aspects a high temperature fuel cell stack exhaust stream is recycled through one or more separation or conversion devices to create a purified recycled fuel exhaust stream that is recycled back into the fuel inlet stream of the high temperature fuel cell stack. In various aspects a nitrogen separator may remove nitrogen from the recycled fuel cell stack exhaust stream, a water separator may remove water from the recycled fuel cell stack exhaust stream, and/or an ammonia reactor and hydrogen separator may be used to condition the fuel inlet stream of the high temperature fuel cell stack. In a further aspect a molten carbonate fuel cell and/or Sabatier reactor may be used to condition the fuel inlet stream of the high temperature fuel cell stack.

http://www.freepatentsonline.com/8916300.pdf

The above does not mean that Bloom and Samsung are necessarily planning to use a direct-ammonia fuel cell, but this could be the case. Certainly, this should be considered for a future design.