OPEN COMPILATION
Techno-Economics and LCA

1st Symposium on Ammonia Energy

This compilation gathers the basic details of all the works presented during the 1st Symposium on Ammonia Energy at Cardiff, UK, September 2022.

It is not intended as a citable manuscript, but as a guidance to the current research themes taking place on the subject.

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TL01 - Ship Design for Safe Ammonia Integration – EXTENDED ABSTRACT

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Introduction

There are numerous fuels, excluding batteries and nuclear, being proposed for the route to net-zero of the maritime sector, all of which are hydrogen derivatives. The UK Department for Transport view the two main fuels as ammonia and methanol, with over 80% of domestic vessels possibly being fuelled by ammonia in 2050 [1].
The IMO International code of safety for ships using gases or other low-flashpoint fuels (IGF Code) is the main regulation that must be used for low flashpoint fuels, a flashpoint below 60°C [2]. Classification societies have made greater progress for ammonia compared to hydrogen. Bureau Veritas do have tentative rules [3], whilst DNV released a notation for ammonia fuelled ships [4].
With the use of LNG as a transition fuel in the maritime route to net-zero, it may be possible that ammonia is a more likely fuel for at least some ship conversions in the future. This is since ammonia and LNG both require refrigeration for storage, although at quite different temperatures, circa 130°C difference.
Despite the fact ammonia exists as a bunkered commodity at a wide range of locations [5] (due to its widespread use and transportation as a fertiliser), ammonia fuelled ships are still some-way from reality with less than 100 ammonia ready ships being ordered thus far [6]. Since the regulations & standards, as well as the port infrastructure required to refuel a ship is still in the infancy. However, on the assumption that a ship can be refuelled there are still challenges that need to be overcome.
Ammonia has some benefits for usage, namely that it is less flammable compared to hydrogen and methanol [7]. However, the toxic nature of ammonia raises some very different concerns [8]. The mitigation for the toxicity is addressed in the following paragraphs.

Design Considerations

Any location on a ship that is storing or transiting ammonia should be gas tight, this should also be tested during the building of a vessel. This is to ensure that if a leak were to occur that it is contained within the specific location. All entrances and exits to compartments that may contain ammonia should have an air lock, to ensure no ammonia can enter the remaining areas of the ship.

All personnel should also wear gas monitors and carry emergency escape sets, especially in locations where ammonia is present. This is to ensure that crew can safely evacuate an area. This could pose a challenge to ships with passengers present, although any location that is containing ammonia should be out of bounds.

The biggest problem to overcome for ammonia ships is how to safely ventilate any leak. Any ventilation must ensure that ammonia doesn't interact with the people onboard the ship. This is possible by placing duct openings in locations to ensure that prevailing winds will not cause this to occur.

However, this solution only mitigates part of the problem. There is still potential for any leak to interact with a built environment. Especially since many towns and cities have been built around ports. There must be no chance that the toxic cloud can interact with the population of a town when venting from a ship.

One potential solution is the use of ammonia scrubbers to neutralise the gas. However, these would need to be sized such that the accumulation of the toxic cloud internally is minimal. Another solution would be to have a flare stack and burn the ammonia. There is less of a need to ensure complete combustion since the heat produced would then support the diffusion of any remaining toxic cloud. The burning of ammonia should only be used as a last resort, since it will produce significant NOx emissions.

Conclusion

In summary whilst the use of ammonia on board ships is maturing at a record rate, there are still significant areas of development in the ship integration and safety side that need to be considered.

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TL02 - QUANTIFYING THE IMPORTANCE OF CAREFUL WEATHER DATA SELECTION FOR TECHNO-ECONOMIC ANALYSIS OF GREEN PRODUCTION PROCESSES

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TL03 - LIFE CYCLE ANALYSIS OF AMMONIA BASED PRIVATE ROAD TRANSPORT

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Introduction

Ammonia has been fully recognized as an energy carrier with the potential to deliver green hydrogen over long distances and for heavy loads. Life cycle assessments (LCA) have been used extensively for private road transport, and a few have been developed over the years to use ammonia as a fuelling vector. The results of these studies denoted a considerable decrease in greenhouse gas emissions with an acute impact on global warming potential. However, the results also demonstrated that with the reduction of carbon footprint, the increase in nitrogen-based species (i.e. NOx and N_2O) could be considerably high, shadowing the overall balance in greenhouse gas mitigation.

To the authors' knowledge, no previous LCA study has included an operation emissions profile to evaluate the environmental impact of vehicles operating on ammonia only. Therefore, this work aims to assess the environmental profile of ammonia as an alternative fuel for internal combustion engine vehicles from a life cycle perspective, considering the effect of the different vehicle emissions control strategies.

Conclusions

The environmental sustainability of ammonia as an alternative fuel for private passenger transportation was evaluated from a life cycle perspective. This study shows that ammonia-based passenger transportation seems more favourable than fossil-based E. Therefore, ammonia-based ICEV could have an important role in the range of options to contribute to the decarbonization of the transport sector.

TL04 - Technoeconomic Evaluation of Offshore Green Ammonia Production using Tidal and Wind Energy in the Pentland Firth – EXTENDED ABSTRACT

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TL05 - EVALUATING THE SUSTAINABILITY OF AMMONIA FUELLED MINI-TRACTOR FOR ORCHARD OPERATIONS

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Introduction

The search for a fuel that would be renewable, sustainable, carbon-free, and at the same time would replace conventional fossil fuels continues. In this context, ammonia could be perceived as a great candidate for this substitution. It could be considered a hydrogen vector that could be coming from renewable sources whereas it is easier to store and transport than pure hydrogen. Following these motivations, the partners from ACTIVATE project decided to develop a technology for using ammonia as a replacement for fossil fuel used in the internal combustion engine of a mini-tractor. It is expected that by substituting fossil fuel with carbon-free ammonia, the technology will assure favourable environmental impact indicators. However, to be able to conclude about its true environmental influence, the technology must be assessed cumulatively: in terms of its whole life cycle performance and taking into account variable groups of impact indicators (not only focusing on carbon footprint). Typically in the case of vehicles, it is the operation phase that dominates the environmental impact, as shown in the literature. However, when utilizing ammonia as a fuel, the production phase requires careful consideration – so that environmental benefits in terms of the whole life cycle of the vehicle are indeed verified. This abstract presents the methodology applied for the evaluation of sustainability aspects of the proposed technology together with the first results for a technology that is currently under development.

Materials and Methods

A methodology applied for the analysis is the widely-recognized and globally standardized Life Cycle Assessment. LCA is a structured and comprehensive method that quantifies all relevant emissions and resources consumed and the related environmental and health impacts and resource depletion issues that are associated with any goods or services [1]. Life Cycle Assessment takes into account a product's full life cycle: from the extraction of resources, through production, use, and recycling, up to the disposal of remaining waste. The Life Cycle Inventory (LCI) and Life Cycle Assessment (LCA) of the ACTIVATEngine technology are performed in compliance with ISO 14040 and 14044:2006 standards. The models are built in GaBi software environment. The analysis includes:

- Goal and Scope definition - together with Functional Unit definition, reference flows, boundaries, modelling framework,
- Life Cycle Inventory (LCI) - aggregation of inputs and outputs related to the system boundaries,
- Life Cycle Impact Assessment (LCIA) – defining the environmental effects,
- Interpretation of results.

Additionally, for the sake of potential commercialization of the technology, the economic profitability indicators are evaluated, however out of the scope of this manuscript. The complete research planned for the judgment of ACTIVATE technology is aimed at quantifying indicators that will allow for its impartial, independent assessment in terms of environmental sustainability and economic profitability. This abstract, however, focuses on the environmental impact analyses.
Before the LCA modelling started, a comprehensive literature review was performed to establish the state-of-the-art in terms of sustainability assessment of ammonia-based technologies as well as alternative fuel relying engines. The papers have been categorized in terms of the LCA of fuel production cycles (e.g. [2], [5]), assessment regarding the vehicles ([3], [4]) and costs along the life cycle of vehicles, e.g. [5], [6], [7]. If alternative fuel-based engines are analyzed, typically an emphasis is put on the electric vehicles (battery or fuel cell engines) are investigated and put aside with ICE vehicles. Sustainability assessment of ACTIVATE technology covers the

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whole spectrum: LCA takes into account all phases with a special focus on ammonia production paths and in the end, the indicators will be compared to that of a reference diesel engine.

Results and Discussions

The first step towards the evaluation of sustainability aspects defined by LCA analysis is the definition of Goal and Scope. The object of analysis is a tractor to be equipped with an ammonia-driven engine, being a small-scale agricultural vehicle (540 kg) and as such, it is assumed that it will be used for fruit harvesting in the orchard. It was agreed that the function of a tractor will be mirrored by the area covered by its operation. Therefore the Functional Unit defined at this stage is the number of hectares covered in one harvesting season and the input and outputs will be referred to as 1 ha. The core for the analysis is the ammonia fuelled engine component. It is, however, installed in an agricultural vehicle that performs the practical function. Therefore, the production phase covers the fuel preparation together with tractor and engine production merged schematically in one production line. The inventory will focus on engine production and tractor production. The operational phase covers the use of fuel and the use of the tractor itself. The boundaries are graphically presented in Fig. 1.

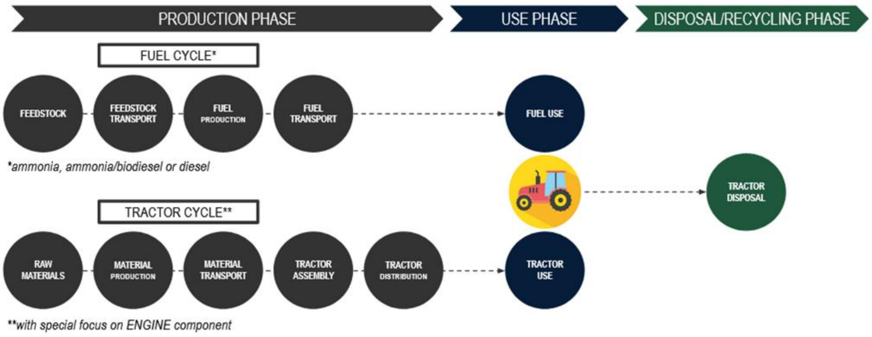

Fig. 1. Life cycle boundaries for ACTIVATE mini tractor

The technology is now being developed and lab works are in progress. At this stage, LCA focused on theoretical assumptions with special attention paid to the fuel production phase. It was assumed that if ammonia is considered, variable scenarios approach realising the consequential modelling will be performed assuming a different kind of ammonia (and the same: hydrogen in ammonia) origin, that is: conventional (steam methane reforming process), green production (electrolysis based on electricity from renewable sources), blue production (conventional steam methane reforming process with carbon capture storage technology). The first results of LCA of the production phase showed that the green ammonia pathway achieves the best performance in terms of climate change and fossil depletion, however, due to its requirement for water, freshwater consumption achieves a value twice as high as grey ammonia [9]. One should, however, remember that the operational phase is expected to be critical in terms of environmental impact.

Conclusions

The methodology for the sustainability assessment of ammonia fuelled mini-tractor for orchard operations is already defined. However, at this stage of this novel technology development, the LCA relies on a secondary data-based Life Cycle Inventory and focuses especially on the fuel production paths phase. It is expected that the operational phase together with emission data will be decisive in terms of ecological competitiveness, but all life phases must be analyzed to judge it reliably. The first results covering the ammonia production scenarios showed that renewable-based ammonia can achieve higher GHG emissions than the production of diesel per MJ (LHV) of fuel. It is clear that for ammonia fuelled vehicle, the emissions avoided during the use phase of the tractor need to compensate for the emissions caused by the production phase.

Acknowledgments

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TL06 - Integrated Process of Solar Pyrolysis of Natural Gas to Produce Turquoise Hydrogen, Ammonia, and Urea for Fuel Cell Power Production

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Introduction

Currently, the leading technologies for hydrogen production from fossil fuels are steam reforming of natural gas, partial oxidation of hydrocarbons, and coal gasification [1]. However, the main drawback of hydrogen production using these techniques is the associated greenhouse gas (GHG) emissions. In the context of this study, hydrogen produced from natural gas via thermochemical cracking at conditions above 1000ºC may be the solution to maximizing the potential of natural gas as a transition energy source and reducing high emissions from fossil fuel-based ammonia synthesis [2-5]. Literature has shown the use of solar energy for the heat requirements of this cracking process [6-8]. The aim of this study is to propose an integrated system for the production of turquoise hydrogen, turquoise ammonia, and urea from natural gas with solid carbon by-product in contrary to gaseous carbon dioxide. This integrated process uses a zero-emission thermochemical cracking process utilizing solar power as the main heat source. This study also aims to analyze and assess the boil-off gas (BOG) emissions during storing and transporting the produced fuels overseas for fuel cell-based power production.

Materials and Methods

The sources of the integrated system are concentrated solar thermal energy, liquid natural gas (LNG), and air, whereas the main systems employed are; a concentrated solar unit, thermochemical cracking, Rankine cycle, carbon combustion unit, ammonia and urea production plants, as well as fuel cells for power generation after overseas fuels transportation as shown in Fig. 1.

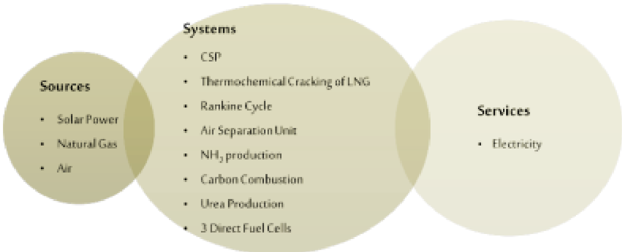

Fig. 1. Sources, systems and services within the proposed integrated turquoise hydrogen, ammonia, and urea production

The thermochemical methane cracking, ammonia synthesis and urea synthesis processes are simulated in Aspen Plus© with NRTL as the fluid package. The simulation is based on the following assumptions:

- The process is a steady state simulation process.
- Pure CO_2 gas is considered and therefore the simulation is carried out in the absence of air.
- Formation of by-products other than the carbon solid produced in thermochemical cracking is neglected.

In this system, feed stream natural gas is fed into the bottom of the fluidized bed reactor and the hydrogen is produced via methane decomposition, which is an endothermic reaction that operates at a high temperature supplied via concentrated solar energy. The integrated system deploys a heat engine (Rankine cycle) using the high temperature waste heat of impurities stream coming from the thermo-cracking unit to enhance its self-dependency on power. The produced hydrogen from the thermochemical cracking catalytically reacts with nitrogen, separated in the air separation unit in the exothermic ammonia synthesis process. Carbon solid is the main by-product of methane cracking with quality varying depending on the reaction temperature and pressure conditions. In the proposed system, a portion of the produced carbon is combusted to yield pure CO_2 and then utilized in the urea production unit. In the scope of this study, three energy carriers; liquid hydrogen, liquid ammonia, and urea, are produced in the natural gas-rich country, Qatar, and transported to other demanding regions considering a 30-day voyage to observe the associated BOG emissions occurring during on-land and on-tanker storage. The parameters used to calculate the BOG values are given in Table 1 along with on-land and on-tanker storage durations. For thermophysical calculations, Engineering Equation Solver (EES) software is utilized.

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Table 1. Storage conditions and reference parameters for BOG calculations

Parameter	Value	Unit
Ambient Temperature	25	°C
Ambient Pressure	101.325	kPa
On-Land Storage Duration	3	Days
Loading and Unloading Time	10	Hours
Voyage Duration	30	Days

Results and Discussions

This section presents a brief description of the obtained results focusing on the efficiencies and BOG emissions. As shown in Table 2, the delivered mass of hydrogen is considerably lower than the initial mass due to a high BOG rate. This is mainly caused by the very low storage temperature of liquid hydrogen. Fig. 2 expresses that if liquid ammonia storage temperature is reduced from -34°C to -73°C, delivered liquid ammonia mass increases to about 113 kton from 108.1 ton. As illustrated in Fig. 3, the BOG emissions are higher when the voyage duration is longer. With 7 days of shipping, the total BOG from liquid hydrogen is about 15.1% whereas it is only 0.42% for ammonia. The delivered mass of liquid hydrogen is reduced to 9.165 kton from 11.38 kton, after 7 days of voyage.

Table 2. Quantities of initial and delivered energy carriers before and after the overseas transport

Total Tanker Capacity, m^3	160,000
Initial Mass of Hydrogen, kton	11.38
Daily Hydrogen BOG during Shipping, %	1.063 %
Delivered Mass of Hydrogen, kton	7.076
Initial Mass of Ammonia, kton	109.2
Daily Ammonia BOG during Shipping, %	0.024 %
Delivered Mass of Ammonia, kton	108.1

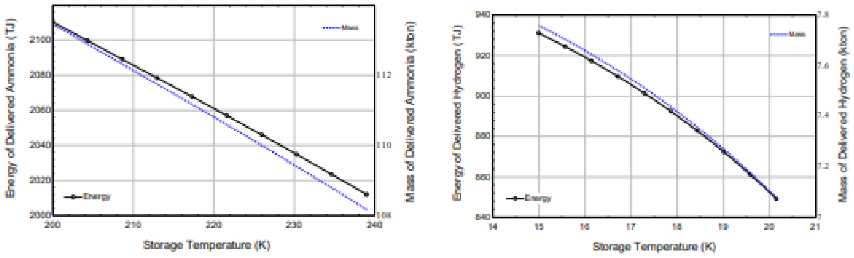

Fig. 2. Effects of storage temperature on the delivered (a) ammonia, (b) hydrogen

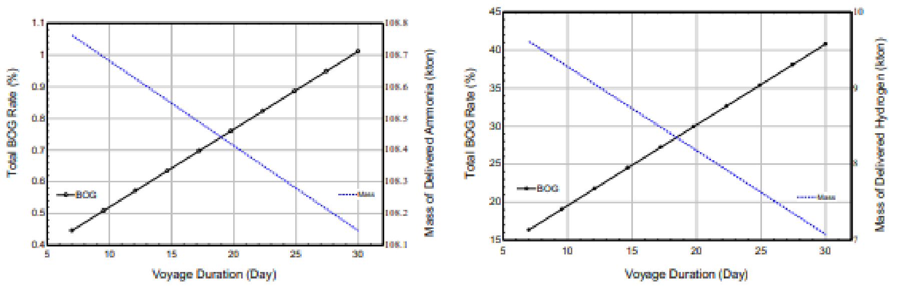

Fig. 3. Effects of voyage duration on BOG emissions and the delivered quantities (a) ammonia and (b) hydrogen

Conclusions

As a transition fuel on the way to decarbonization, natural gas can be converted to turquoise liquid hydrogen, liquid ammonia, and urea, transported to overseas and utilized in fuel cells for cleaner and more efficient power generation. This study assessed the production, overseas transportation, and fuel cell power generation of these energy carriers. For an average medium sized city with 100,000 houses, the transported energy carrier via a single tanker with a volumetric capacity of 160,000 m^3 can deliver electricity needs using hydrogen, ammonia and urea, for about 2, 3.5 and 5 months with a fuel cell energy efficiency of 76%, 55% and 73%, respectively. It is important to minimize BOG emissions and optimize the transported energy carrier based on the voyage duration, emissions, transportation costs and thermophysical properties of the fuels.

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TL07 - The relationship between plant flexibility and optimum cost for green ammonia production

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Introduction

Renewable fuels such as green ammonia create value by enabling the conversion of inherently variable and unpredictable renewable energy into a dispatchable energy source which can be stored for long durations at low costs. Operational flexibility is not difficult for green hydrogen production, which relies on electrolysers which have high ramping rates; however, the Haber-Bosch process which synthesizes ammonia from hydrogen and nitrogen has not historically been operated at variable rates. Since this process is only partially flexible, continuous operation requires back-up storage of both electricity (to power the compressors in the synloop) and hydrogen (as a feedstock), increasing the costs of ammonia production.

There are several constraints on plant flexibility. The Haber-Bosch process occurs at elevated temperatures, which are sustained by excess heat from the exothermic reaction; if production slows excessively, heat loss will exceed heat generation and the reaction will be quenched. Thermal expansion on start-up and shut-down can have damaging impact on plant and catalysts, and therefore frequent cycling between an operating and quenched state is not possible. In order to prevent temperature hot spots inside the adiabatic catalyst bed reactors, rapid ramping of the production rate is also not generally considered practical [1].

To some extent, these limitations on flexibility can be reduced in the long term through sophisticated design of catalysts, reactor beds, and the process as a whole, although these modifications may come at increased costs. However, in the near term, it may not be possible to operate with high degrees of flexibility. In this report, we analyse the extent to which various interventions into plant flexibility enable cost reductions, in order to provide benchmarks for synloop designers to target.

Materials and Methods

The optimisation model used in this study has been extensively described in other articles from these authors [2,3]; it is a Mixed Integer Linear Program which selects the size of each piece of equipment in the green ammonia production process in order to minimize the levelised cost of ammonia (LCOA). It uses hourly wind and solar data over a period of one or more years to confirm the ammonia plant continues to operate above the specified minimum rate, and does not require rapid ramping. In order to assess the extent to which plant flexibility improved costs, an array of HB minimum operating rates and HB ramping rates were tested, which are reported in Table 1.

Table 1. Variation in ramp up and ramp down rates in various sensitivity cases. Between cases, the ramping rates change by a factor (shown in the first row). The actual value of the variables is shown in the bottom two rows; the units are the maximum ramp rate per hour as a fraction of the Haber-Bosch capacity.

Sensitivity Case	Low	Base	High
Factor	**0.1**	**1**	**10**
Ramp down (actual value)	0.02	0.2	2
Ramp up (actual value)	0.002	0.02	0.2

The LCOA depends strongly on the specific weather profile at the nominated location, and for that reason it is not likely that the impact of flexibility will be the same in different places. For that reason, in order to meaningfully assess the impact of flexibility on plant design, a range of sites with different weather profiles need to be considered. This analysis considered 422 locations at varying latitudes and with a range of weather profiles. Similarly, as the cost of equipment falls in the coming decades, the importance of flexibility will also change; these locations were therefore analysed both using current data from IRENA, and forecasts for 2050 obtained from the Oxford Institute of New Economic Thinking (INET),

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Results and Discussions

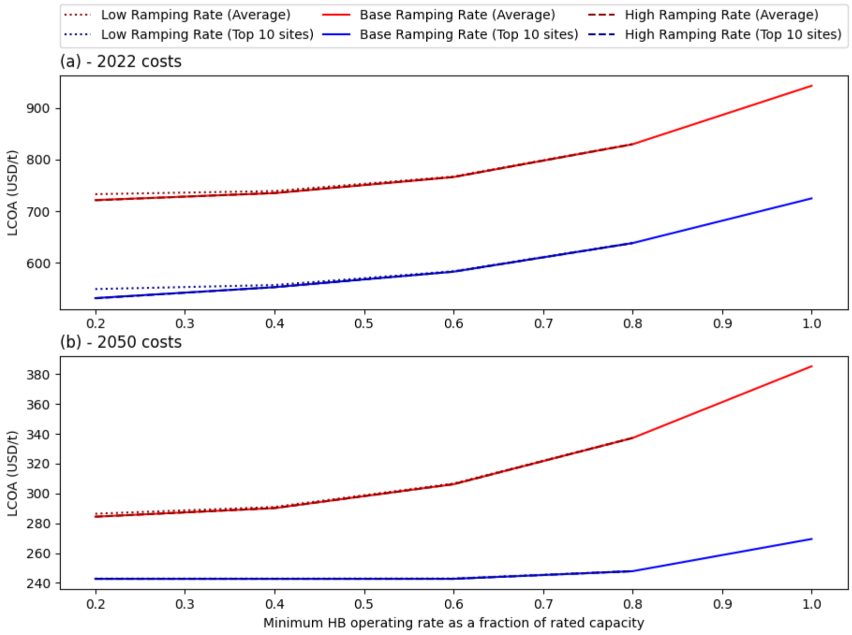

Figure 1 – Levelised cost of ammonia on average (red) and for the top 10 sites (blue).

The most important observation in Figure 1 is that there are diminishing marginal returns on increasing plant flexibility. In both 2022 and 2050, reducing the minimum operating rate from 60% to 20% achieves only one quarter of the cost reduction of reducing the minimum operating rate from 100% to 60% (for the average cases). For the cheapest sites in 2050, the results are even more stark, with almost no benefit gained whatsoever from reducing the minimum operating rate below 60% of rated capacity.

This is predominantly because the ammonia plant represents a significant capital expense, but its power draw is comparatively small. That means that the plant, for most of the year, receives relatively little benefit from turning down the ammonia plant to very low operating rates, since it can sustain operation using the battery and hydrogen storage units (and it is preferable to exploit the capital expense of that equipment to the greatest load factor possible). This causes the stored energy in batteries and hydrogen storage to cycle more (compared to a case in which the HB operating rate was turned down further), but does not significantly increase their size. Therefore the increase in costs is fairly small, as there is no cost imposed by the model for cycling of the batteries or hydrogen storage. The effect is even more pronounced in 2050, because solar electricity and battery storage are expected to fall in price so significantly, whereas the CAPEX of the ammonia plant is likely to remain fairly steady.

While the overall process can operate the HB plant at high rates for most of the year by cycling the battery and hydrogen storage, this only becomes significantly challenging during the longest period of low wind or low solar irradiation. The model can resolve this problem either by (i) turning down the ammonia plant, (ii) increasing the size of energy storage equipment, or (iii) increasing the extent to which the renewable power generation is oversized. The results indicate that the benefits which accrue from using the lever of ammonia plant capacity tail off below 60% of the rated capacity, and that the model can adopt other strategies without significantly increasing cost. These conclusions are reasonably independent of the ramping rate of the ammonia plant (see Figure 1).

Conclusions

The results in this paper report the theoretical minimum cost of green ammonia production, considering over 400 locations with different plant flexibilities. To some extent, improving flexibility reduces ammonia cost, but the opportunity available reduces in magnitude below 60% of ammonia plant rated capacity. However, two key limitations underpin the study: firstly, there are no costs associated with cycling batteries and hydrogen storage, and secondly, the model has perfect forecasting, which may be masking the importance of plant ramp rate. Alongside advances in plant flexibility, research should also focus on enabling rapid cycling of energy storage technologies and incorporating weather forecasting into plant control to mitigate the need for ramping.

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