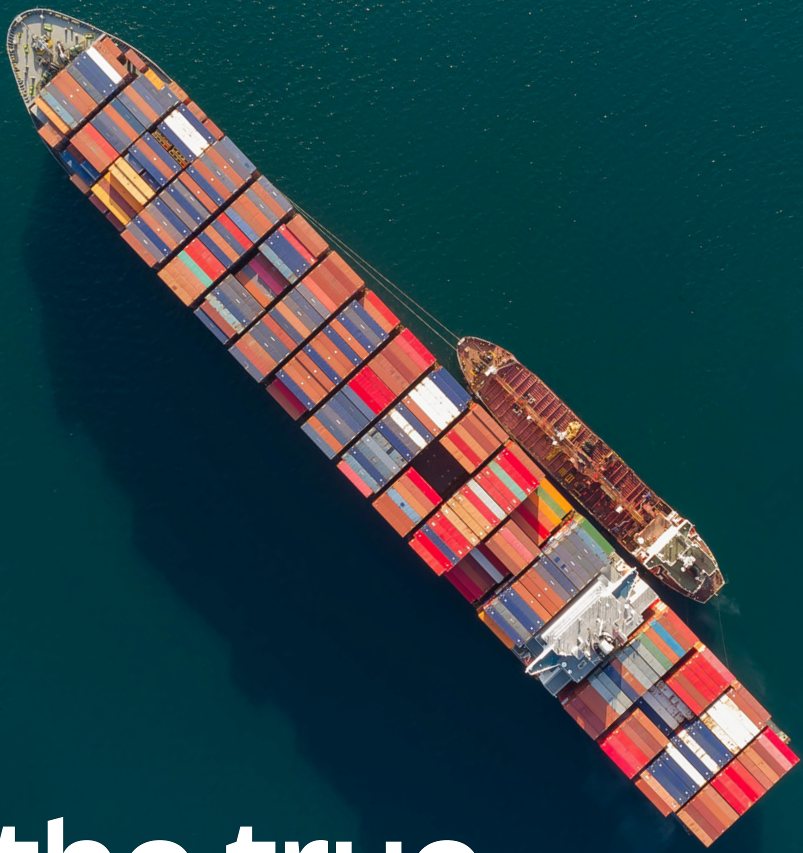


Tracing the true carbon intensity of sustainable marine fuels

Innovative technologies for end-to-end assurance of the new fuel supply chain

January 2023

The Lloyd’s Register Maritime Decarbonisation Hub in partnership with

Safetytech Accelerator

Executive Summary

Shipping's decarbonisation is currently focused on delivering alternative fuels that significantly reduce Greenhouse Gas (GHG) emissions. But to be sure that these fuels achieve the emissions reductions needed, GHG emissions across the entire fuel supply chain should be measured and traced. In shipping, this Well-to-Wake (WtW) measurement is critical due to the different production routes of sustainable marine fuels, with grey, blue and green variations entering the market, each with different GHG emissions, but nearly identical end product.

In principle, ship operators lack clear visibility of the entire fuel supply chain responsible for producing, delivering and bunkering a fuel used on ships. This creates uncertainty because fuel supply chains are subject to a wide range of factors that can lead to considerations over the nature of the fuel in a ship's tank, such as the following:

- Each different production method will have a different carbon intensity and cost, with the greenest molecules being associated with the most intense effort to decarbonise the supply chain, and most likely with the highest cost.
- Distinguishing a high emissions fuel from a low or zero emissions fuel could be difficult, as even identical production methods, such as electrolysis of water to make hydrogen, could be performed with electricity produced by sources of varying carbon intensity.
- Fuel mislabelling could occur when molecularly identical fuels enter the markets at different price points, creating a commercial incentive to pass off a fuel as a higher priced but nearly identical end product, concealing the production method.
- Fuels are often blended during transportation and distribution before they reach the bunkering station in a port. There is thus no guarantee that the fuel loaded on board a ship is the same as the fuel that left the production facility.
- Early utilisation of these fuels may take the grey or blue production routes (albeit with efficiency measures or carbon capture to lower their environmental impact), so the likelihood of having different environmental performance grades of a fuel simultaneously in the market is present.
- At present there is no regulation in place to directly address these issues. Even as LCA methodologies and regulations are being discussed, the scope for widespread non-compliance would still remain a challenge, without a method to assure the carbon intensity of the fuel.

In addition, legitimate producers will seek assurance that investments in production of green fuels will provide a guaranteed return in a fair and governed marketplace. We need a mechanism to demonstrate the quality, carbon intensity and origin of these fuels as evidence of the real contribution to decarbonisation and for compliance with regulations. This will be critically important to validate the environmental and commercial impacts from using green fuels.

Current marine fossil fuel certification methods rely predominantly on a paper trail, with the ability to sample and test fuels once bunkered to determine their quality. Carbon intensity is thus not measured or captured, with little or no attention paid to where or how the fuel is produced.

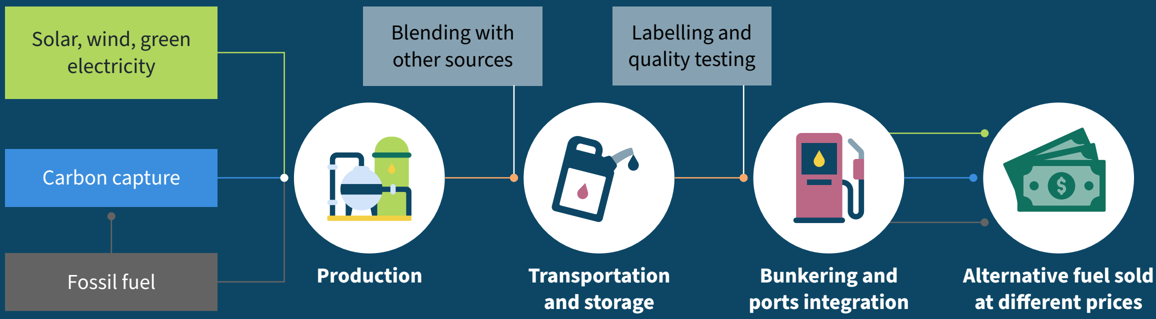
So how can the crew operating a ship, as well as the wider stakeholder community, be sure that the fuel they have purchased and are using was produced, transported, stored and handled in a way that ensures it will deliver the emissions performance expectations?

For successful introduction of zero carbon shipping fuels, the development of specific mechanisms to authenticate and trace the origin of green fuels will be essential. Such a mechanism would provide transparency to consumers while fostering market demand, avoiding at the same time the double counting of renewable energy attributes.

A study investigating fuel assurance options

This report considers the feasibility of using innovative technologies to track the carbon intensity of hydrogen and ammonia. Initiated by the Lloyd's Register Maritime Decarbonisation Hub, Safetytech Accelerator followed a rigorous selection process to select two technology vendors who have complementary approaches that have the potential for providing sustainable fuel assurance across the fuel supply chain.

In collaboration with the selected technology vendors TYMLEZ and Authentix, this study examines methods to capture and verify information on how a fuel has been produced, from the source of the electricity to the delivery of an un-altered final product. In essence, it assesses a guarantee of origin (GO) scheme combined with verifiable blockchain, and a method of physical authentication of carbon in the end-product by the method of marking.



The **TYMLEZ** solution proposes a guarantee of origin (GO) certificate for each unit of hydrogen (or ammonia) produced. In order to produce the certificate, the platform ingests data during the production of the fuel such as water and fuel usage and grid electricity emissions. A necessary component for this solution is to have live facility data available as well as certain offline parameters pre-programmed. Installing the sensors or smart meters to capture this data can be done retrospectively for existing facilities or could potentially be included during the construction of the facility.

Capturing this data and the associated calculations on a publicly verifiable ledger can ensure the level of transparency needed to validate the information, including the carbon intensity of the fuel, once this is produced.

Given that hydrogen can also be the basis for different synthetic fuels such as methanol and methane, many of the considerations in this report could also be applied to these fuels.

A key challenge to pilot this solution globally is to deliver a proposal for harmonised international standards and regulations to fairly set the boundaries and the required methodologies for the calculations.

Once the fuel is produced and supplied with a GO certificate, downstream assurance that can account for any blending or mis-labelling is hereby proposed through a combined fingerprinting and marking approach.

An evaluation by **Authentix** of the various production and purification methods for hydrogen and ammonia can determine if there is a ‘fingerprint’ that might exist to distinguish green from blue, grey or other categories of hydrogen and ammonia. It was found that while this may be possible between production methods, the distinguishing differences may also be intentionally erased, through purification processes. This presents a risk that fingerprinting may not be suitable if the cost of purification is less than the price premium that could be achieved by selling green variants of ammonia or hydrogen.

Alternatively, adding a unique synthetic marker to the fuel is evaluated, to chemically detect the origin of the fuel as well as any occurred dilution. The development of a marker system for any new product requires the careful consideration of several factors including stability, launderability, and detectability of the marker along with potential dosing techniques for the addition of a unique ‘marker’. For ammonia, similarities in storage requirements to Liquid Petroleum Gas (LPG) can be an advantage, as developed markers are already in use and can be assessed for their direct feasibility in ammonia.

Noting the combustion challenges such as low lubricity associated with ammonia and hydrogen, potential markers could be designed and incorporated in conjunction with performance and combustion additives.

Recommendations

- There are no significant limitations or barriers discovered at this stage for the technology solutions assessed in this report.
- The solutions proposed by TYMLEZ and Authentix require validation and testing in parallel with the development of the fuel technology and infrastructure to adequately mitigate the risks described above and which relate to regulatory compliance and falsification when green fuels will become commercially available. It is important to expedite trials to further assess feasibility, whist ensuring that viable solutions as well as a competitive market will indeed be available, at the time shipping will switch to green fuels.
- Moreover, policymakers considering the implementation of Lifecycle assessment regulations should invest sufficient resource and capability into ensuring that the technology solutions are available to enable robust and enforceable policy actions. This could materialise through the development of harmonised standards that would provide a level playing field for fuel assurance, whilst allowing international trials to take place.

Contents

List of figures

Abbreviations

ATR	Autothermal Reforming
CCS	Carbon Capture and Storage
CO_2	Carbon Dioxide
DLT	Distributed Ledger Technology
ESG	Environmental, Social and Governance
FC	Fuel Cells
GA	Green Ammonia
GC	Gas Chromatograph
GH	Green Hydrogen
GHG	Greenhouse Gas
GO	Guarantee of Origin
HFO	Heavy Fuel Oil
ICE	Internal Combustion Engines
IMO	International Maritime Organization
IoT	Internet of Things
LCA	Life-Cycle Assessment
LNG	Liquefied Natural Gas
LPG	Liquid Petroleum Gas
MS	Mass Spectrometry
MRV	Measurement, Reporting, Verification
PEM	Proton Exchange Membrane
ppb	part per billion
ppm	part per million
PSA	Pressure Swing Adsorption
SOECs	Solid Oxide Electrolysis Cell
SOFC	Solid Oxide Fuel Cell
PEMFC	Proton Exchange Membrane Fuel Cell
SMR	Steam Methane Reformation
UOM	Unit of Measure
WtW	Well-to-Wake

1. Introduction

Talking about the prospects of alternative fuels, two of the most promising long-term candidates are hydrogen and ammonia. While neither will emit carbon dioxide during combustion, their associated production methods may generate significant quantities of greenhouse gases (GHG).

For this reason, various color ratings are available to classify the types of hydrogen and ammonia based on the carbon footprint of their production process. Typically, grey is used to designate a process that has uncontrolled release of CO_2 and this production is often based on fossil fuels as raw materials. Blue fuels may also be produced from fossil sources, but by utilizing carbon capture and storage (CCS), the overall CO_2 emissions are greatly reduced. When sustainable electricity is utilized in the production, the fuel can be rated as green, emitting the lowest possible CO_2. A variety of other color ratings exist to describe alternate methods of production between grey and green, but the long-term goal is the transition to Green Hydrogen (GH) or Green Ammonia (GA) to minimize the impact of maritime emissions to the environment.

Indeed, the deployment of hydrogen and ammonia as alternative fuels in the maritime sector will drive shipping's decarbonization only if these fuels are produced using carbon-neutral energy resources. However, it is still not clear how the buyers of marine fuels could be assured that the purchased fuel was produced, transported, stored and handled in a truly green way. In addition, legitimate producers will also seek assurance that investments made to produce green fuels will provide a guaranteed return in a fair and governed marketplace.

To this end, the development of specific mechanisms to label and track the origin of green fuels will be essential. Such a mechanism would provide transparency to consumers while fostering the market demand, avoiding at the same time the double counting of renewable energy attributes.

The scope of this study is twofold with each part comprising the holistic context for sustainable fuel assurance:

Section 3 of this report assesses the feasibility of Guarantee of Origin (GO) solutions for the sustainable marine fuels, by deploying blockchain technology for green hydrogen and ammonia tracking systems. Given that hydrogen can also be the basis for the production of different synthetic fuels such as methanol and methane, many of the considerations in this section could also be applied to these fuels.

Section 4 examines the various production and purification methods for hydrogen and ammonia to determine if there is a 'fingerprint' that might exist to distinguish green from blue, grey or other categories of hydrogen and ammonia during the downstream transportation and supply to the vessel. In addition, if fingerprinting is not viable, the chemistry of marking those products is evaluated along with potential methods and locations for addition of a unique 'marker'.

Recommendations for policy and potential trial aspects of these technologies are further presented in **section 6**.

2. Alternative bunker fuels

2.1. Hydrogen derived fuels

Hydrogen

Hydrogen will be a critical element in decarbonizing the shipping sector. However, the carbon emissions related to the production and purification of hydrogen vary widely. As shown in Figure 1 below[1], the carbon emissions of hydrogen vary widely depending on starting resources used in production and the methods of powering the process. For this reason, the maritime industry, along with several stakeholders of the circular economies globally, pursue the vision of a green driven global economy through their effort to minimise their overall carbon footprint that stems from their activities.

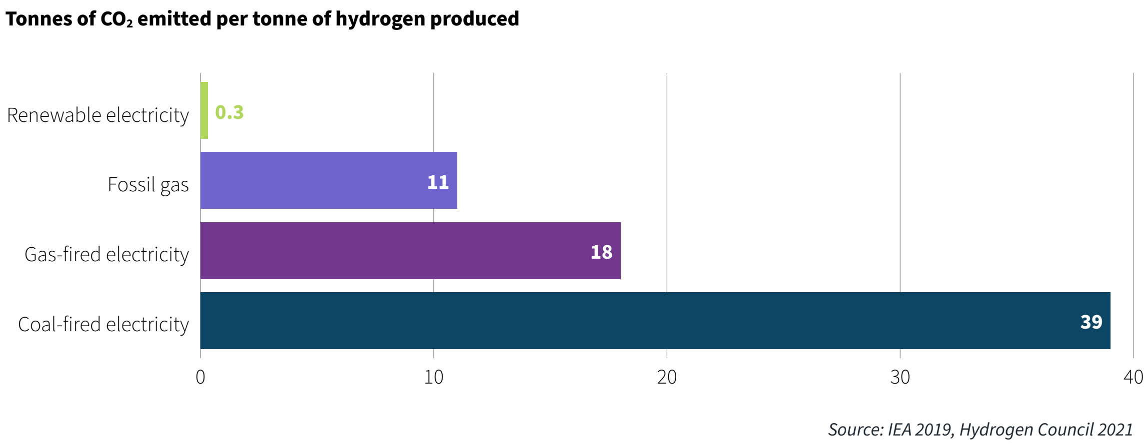


Figure 1: Carbon emissions from different methods of producing hydrogen

1 Global Witness. 1 September 2022. The Trouble with Hydrogen. Retrieved online: The problem with hydrogen | Global Witness

Hydrogen for ship propulsion

Both fuel cells (FCs) and internal combustion engines (ICEs) can be fueled by hydrogen. FC engines can perform well in large, heavy vehicles where an extended range is required. However, the fuel cell has high thermal management requirements, is less robust and durable and requires hydrogen purity levels of >99.9% as opposed to hydrogen-fuel ICEs, which have fewer weaknesses and are more versatile[2]. Currently, companies such as MAN Energy Solutions are developing a variety of dual fuel and spark-ignition four stroke engines for the shipping industry, beginning with demonstrations in a number of small-scale pilot projects within this decade[3]. While safety and storage requirements for hydrogen remain undoubtedly the biggest challenge for an accelerated uptake it's use in shipping is currently negligible, as the infrastructure and bunkering facilities are not sufficiently developed, space onboard ships is demanding and costs exaggerated. However, hydrogen is an important element of potential pathways to the decarbonization of the global shipping industry[4]. Technological development and associated policy support are accelerating the use of hydrogen as the alternative fuel in the maritime sector. Several projects are under development focusing on hydrogen-derived fuel production, with a clear trend towards green hydrogen electrolysis[5,6].

Ammonia

In the commonly used Haber-Bosch process, hydrogen and nitrogen react together at high temperature and pressure to produce ammonia. As with hydrogen, ammonia provides a path to zero-carbon emissions but it's production may lead to a significant quantity of GHGs being released. Relative to hydrogen, ammonia has the key advantage of higher energy density and significant reduction in storage requirements.

Leaving aside the limited experience in combustion engines and the low energy utilization rate, the major drawback of ammonia as a marine fuel relates to its safe utilization both onshore and onboard ships. Ammonia's prospective corrosion and toxicity levels cannot remain unnoticed and should be addressed through quantitative risk assessment (QRA) studies in an effort to safeguard the health of crews and passengers at all times during operations[7].

Also, since ammonia is largely used as fertilizer, the infrastructure for its transport and handling is well developed. However, the development of bunkering infrastructure remains a barrier for its use as a fuel for marine propulsion.

2 Stepień, Z.A.. A Comprehensive Overview of Hydrogen-Fueled Internal Combustion Engines: Achievements and Future Challenges. Energies 2021, 14, 6504. https://doi.org/10.3390/en14206504
3 Nakamura, T. *Expectations from a shipowner on using ammonia as maritime fuel for zero-emission ships*. Special presentation for the International Maritime Organization (IMO) Symposium on Alternative Low-Carbon and Zero-Carbon Fuels. NYK Group. 9th February 2021. https:///www.cdni.imo.org/localresources/en/OurWork/Environment/Documents/Symposium2021/Presentations
4 Lloyd's Register, "Low carbon pathways 2050", 2016.
5 Heidi Kilemo, Robert Montgomery, Project Advisor, and Ana Madalena Leitão, "Mapping of Zero Emission Pilots and Demonstration Projects," Global Maritime Froum, 2022.
6 IEA, "International Shipping," IEA, Paris, 2022.
7 Lloyd's Register and UMAS, "Techno-economic assessment of Zero-carbon fuels," 2020.

Ammonia for ship propulsion

From a technical perspective, ammonia can be used in both FCs and ICEs for ship propulsion. Ammonia can be used directly in high temperature FCs such as solid oxide fuel cells (SOFC) or after being cracked and purified of trace ammonia in low temperature FCs such as proton exchange membrane fuel cells (PEMFC).

Currently, there are no commercially available ICE designs available, but the development of 2-stroke and 4-stroke engine technologies are on parallel paths to enable introduction into deep-sea and regional short-sea shipping in the next few years.

Ammonia is emerging in recent years as the preferred solution for large vessel ship technology projects due to its storage requirements in comparison to hydrogen. It has been reported that in the first half of 2022, 66 new build orders were for ammonia-ready vessels[8].

2.2. Methods of production

Hydrogen production and purification methods

Hydrogen for use in FCs or ICEs can be produced by a variety of processes from a range of starting materials. As of 2020, 76% of the global hydrogen supply was produced from natural gas through steam methane reformation (SMR), 22% through coal gasification (primarily in China) and only 2% using electrolysis13. Thus, 98% of all hydrogen production is based on fossil fuels and has the potential to emit significant quantities of greenhouse gases.

At large scale, SMR is the most widespread technology for hydrogen production from natural gas. Natural gas in SMR is both a fuel and a feedstock (together with water). SMR is likely to remain the dominant technology for large-scale hydrogen production in the near future because of its favorable economics and the large number of SMR units in operation today[9].

The untethered SMR process emits significant CO_2. However, various methods of CCS can lead to a reduction in carbon emissions of up to 90%. These are processes, which can provide blue hydrogen, where CO_2 destined to be emitted into the environment is held in a containment system.

Another cost-effective method for hydrogen production is autothermal reforming (ATR). As for SMR, a hydrocarbon feedstock is utilized and when combined with oxygen and steam, hydrogen, carbon monoxide and carbon dioxide are produced. Again, ATR can be combined with CCS to reduce CO_2 emissions to create blue hydrogen.

8 J. Snyder, “Green wave: 61% of newbuilds ordered will burn alternative fuels,” 6 July 2022. [Online]. Available: https://www.rivieramm.com/news-content-hub. [Accessed 2022].

9 Office of Fossil Energy. *Hydrogen Strategy: Enabling a Low-Carbon Economy*. U.S. Department of Energy. July 2020. https://www.energy.gov/sites/prod/files/2020/07/f76/USDOE_FE_Hydrogen_Strategy_July2020.pdf

For hydrogen to be classified as green, the starting material must be water, the production process must be electrolysis and the entire production and purification processes must be powered by renewable energy. Water electrolysis is an electrochemical process that splits water into hydrogen and oxygen. Three main electrolyser technologies are currently in use. These are alkaline electrolysis, proton exchange membrane (PEM) electrolysis, and solid oxide electrolysis cells (SOECs). However, less than 0.1% of production facilities globally are dedicated to water electrolysis today and the hydrogen produced by this means is mostly used in markets where high-purity hydrogen is necessary (for example, electronics and polysilicon)[10].

After production, hydrogen may be passed through a variety of purification processes, depending on final application. The process of purification can be broken down into 3 steps.

1. **Pretreatment of the 'crude' hydrogen**
   Based on how the hydrogen was generated, specific impurities are targeted for removal by chemical reactions or conventional or physical adsorption.

2. **Removal of impurities**
   Pressure swing adsorption (PSA), a technique used to separate gases under pressure using the affinity for an adsorbent material is the dominant technology.

3. **Final purification**
   Cryogenic adsorption, which is usually carried out at extremely low temperatures with catalytic membranes.

All these processes would be critical to hydrogen use in FCs. For use in ICEs, the final purification steps may not be required, thus potentially leaving specific, identifiable impurities in the final product.

When hydrogen is used directly as a fuel, it appears that SMR with CCS will be an important first step in helping to decarbonise shipping fleets. However, the ultimate goal in the long term would be the use of green hydrogen for ship propulsion, by direct water electrolysis.

Through the various methods of production, purification, storage and transport of hydrogen, certain impurities may be introduced into the product. The question arises, when looking to identify green hydrogen versus any other type of hydrogen used as fuel for ship engines, is there an inherent fingerprint left behind from non-green production methods?

10 International Energy Agency (IEA). *The Future of Hydrogen: Seizing today's opportunities*. Report prepared by the IEA for the G20, Japan. June 2019. The Future of Hydrogen (windows.net)

Ammonia production and purification methods

As with hydrogen, there are a range of methods used to produce ammonia, each having variable GHG by-products.

Grey ammonia is produced using the conventional synthesis methods that have remained essentially the same for over 100 years. This involves the Haber-Bosch process, diagrammed in Figure 2, below[11]. This process, which is responsible for nearly all of the world's ammonia production, reacts hydrogen and atmospheric nitrogen, with the hydrogen often being harvested from the steam reformation of methane. This is a process that emits significant quantities of CO_2.

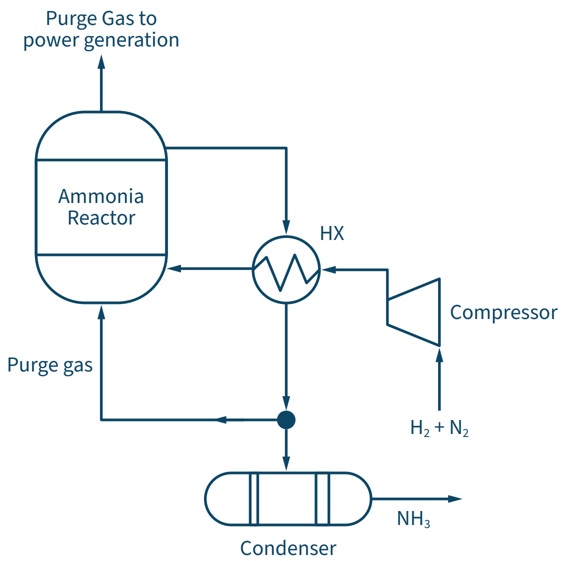


Figure 2: Basic flow diagram of the Haber-Bosch process

Blue ammonia is produced by the same process, in which the CO_2 by-product has been captured and stored, thus reducing the carbon-footprint.

Green ammonia utilizes hydrogen from water electrolysis as a raw material. This hydrogen is of high purity, thus eliminating the need for CO or CO_2 removal, which is necessary for SMR. Nitrogen is acquired from air separation and these raw materials are then fed into the Haber-Bosch process.

11 Darmawan, A., Aziz, M. 2021. *Abstract in Innovative Energy Conversion from Biomass Waste*, 1st Edition, August 21, 2021. Elsevier Ltd. Retrieved online: Haber-Bosch Process – an overview | ScienceDirect Topics

When all processes are powered by sustainable energy, green ammonia is produced, as illustrated below in Figure 3. There are other less common methods for green ammonia production, but this remains the primary process used today.

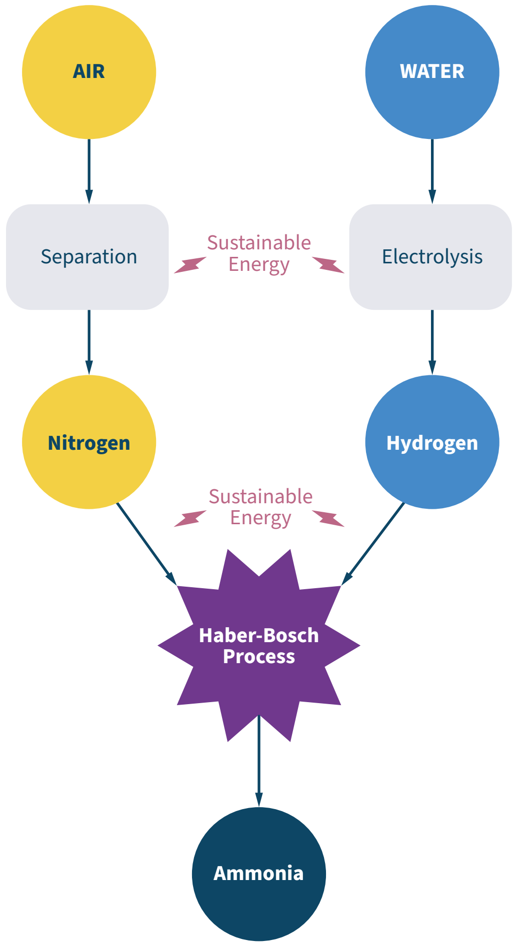


Figure 3: Green ammonia production via sustainable energy sources

As with hydrogen, there may be an inherent fingerprint left behind from non-green production methods of ammonia that could be used to assure the identification of green ammonia.

2.3. Assurance mechanisms for hydrogen and ammonia

Assurance of alternative fuels requires a robust method for tracing and verifying the fuel, as well as clear standards against which the fuel shall be measured. Specifications for hydrogen and ammonia exist, but do not include carbon intensity. In today's practise, with virtually no green fuels being commercially available for use by the maritime ecosystem, this remains an undocumented variable, with most standards focussing on quality issues alone.

Specifications for hydrogen as fuel

When gaseous hydrogen is used for on-road fuel cell electric vehicles, it must meet stringent quality standards such as ISO 14687:2019, EN 17124 and SAE J2719. These standards stipulate limits on several impurities, which could damage the fuel cells or the infrastructure. In accordance with these standards, Figure 4 below[12] lists the allowable contaminants for hydrogen.

Compounds	Limits		
	Min. (%)	Max. (μol.mol-1)	Max. (m/kg)
Hydrogen (H_2)	99.97		
Total non hydrogen gases		300	
Water (H_2O)		5	
Hydrocarbon compounds (excluding CH_4) (CH_1 equivalent)		2	
Methane (CH_4)		100	
Oxygen (O_2)		5	
Helium (He)		300	
Nitrogen (N_2)		300	
Argon (Ar)		300	
Carbon Dioxide (CO_2)		2	
Carbon Monoxide (CO)		0.2	
Formaldehyde (HCHO)		0.2	
Fomic acid (HCOOH)		0.2	
Total content of CO_2, HCHO and HCOOH		0.2	
Total sulfur compounds		0.004	
Total halogenated compounds (Halogen ion equivalent)		0.05	
Ammonia (NH_3)		0.1	
Particulates			1

Figure 4: Hydrogen quality requirements specified in ISO 14687:2019, EN 17124 and SAE J2719 standards (ISO/TC 197 2019) (CEN/TC 268 2018) (SAE Fuel Cell Standards Committee, 2020)

12 Beurey, C. et al. *Review and Survey of Methods for Analysis of Impurities in Hydrogen for Fuel Cell Vehicles According to ISO 14687:2019*. Frontiers in Energy Research, Volume 8, 24 February 2021. https://www.frontiersin.org/articles/10.3389/fenrg.2020.615149

As seen, a minimum purity of 99.97% hydrogen is required. The impurities helium, neon, nitrogen, argon and methane dilute the hydrogen and carbon monoxide and carbon dioxide decrease the lifetime of the fuel cell[13].

Currently, there are no specifications for hydrogen as a fuel when powering FCs for the maritime industry. However, due to the requirements of various types of fuel cells, it is likely that future specifications will closely mirror those seen in road fuels.

For ICEs, however, the purity requirements are not as critical. At this time, there do not appear to be specifications for the use of hydrogen in ICEs for either road or maritime use. For this reason, hydrogen bound for ICE use will likely allow higher levels of impurities with no impact on engine performance. Therefore, hydrogen will be less expensive to produce, and will be more readily available. With the variable methods of producing hydrogen, these impurities may serve as an important 'fingerprint' for the type of hydrogen used in ship propulsion.

Specifications for ammonia as fuel

Ammonia is a common commodity that is used across a variety of industries. Depending upon the production process and methods to purify the final product, ammonia can have a range of impurities. These include water, oil and particulates, among other lower-level contaminants. There are currently three grades of anhydrous ammonia:

- Premium grade, "Metallurgical" at 99.995% purity
- Refrigeration grade, "R-Grade" at 99.98% purity
- Commercial grade, "C-Grade" or "Ag Grade" at 99.5% purity

The majority of ammonia used in the world is C-Grade.

Today there is no standard for utilizing ammonia as a fuel in either ICEs or FCs. This is likely to change, as some industry stakeholders, such as MAN Energy Solutions have proposed standards and the International Maritime Organisation (IMO), and International Standards Organisation (ISO) are likely to begin formulation of standards prior to broadscale adoption[14].

During a panel session in the 2020 Ammonia Energy Conference, Dorthe Jacobsen of MAN Energy Solutions outlined a preliminary marine standard for the use of ammonia. Notably, this standard is based on the use of the common, less expensive C-grade ammonia. While higher purity products are available, it appears that for some FC and all ICE applications, C-grade ammonia would be of sufficient purity[15].

13 Office of Fossil Energy. *Hydrogen Strategy: Enabling a Low-Carbon Economy*. U.S. Department of Energy. July 2020. https://www.energy.gov/sites/prod/files/2020/07/f76/USDOE_FE_Hydrogen_Strategy_July2020.pdf

14 Atchison, J. 15 December 2020. *A Fuel Standard for Ammonia: panel wrap-up from the Ammonia Energy Conference 2020*. Ammonia Energy Association. Retrieved online: A Fuel Standard for Ammonia: panel wrap-up from the Ammonia Energy Conference 2020 – Ammonia Energy Association

15 Jacobsen, D. *A marine fuel standard for Ammonia – an engine designer's perspective*. Special presentation for the Ammonia Energy Conference. MAN Energy Solutions. 17 November 2020. IMO GHG (ammoniaenergy.org)

To utilise a higher grade of ammonia would simply increase cost with minimal benefit and, in some cases, increase risk. Ammonia absorbs water easily and this impurity is expensive and energy-intensive to remove. In addition, ammonia with a water content of 0.5% or less is known to cause corrosion stress cracking in tanks and pipes. Thus, the benefit of using C-grade purity not only improves the economies of ammonia as a marine fuel, but also increases safety in storage and transport.

An example specification for ammonia as a fuel is shown below:

Designation	Unit	Value	Test method reference
Ammonia	% (w/w)	≥ 99.5	TBD
Water	% (w/w)	0.1 – 0.5	ISO 7105
Oil	% (w/w)	≤0.4	ISO 7106
Oxygen	% (w/w)	TBD	TBD
Nitrogen	% (w/w)	≤ 0.3	TBD
Sulfur	% (w/w)	TBD	TBD
Particles	-	TBD	TBD

Source: Guiding fuel spec for Ammonia at the engine inlet, D. Jacobsen, Man Energy Solutions: ME-LGIA, November 17, 2020.

Figure 5: Specification for ammonia as fuel

Incorporating GHG emissions into fuel standards and assurance

As discussed, depending on the production pathway of hydrogen and ammonia, yielded GHG emissions would vary.

The general methods to transfer, monitor, and control related specific information to the supply chain of a product[16] are:

Book and claim model: This system is currently being employed for renewable electricity. In this system, renewable electricity is disconnected from certification meaning that the claim of consuming renewable electricity is separate from the physical flow. Using these certificates for green fuels will require temporal and geographical correlation between renewable energy generation and green fuel production to ensure the renewable nature of electricity consumption.

Mass balancing: This model is mainly used for biofuels. It requires a physical link between the production and consumption of green fuels and consignments must be in contact to prove physical traceability. It involves balancing volume reconciliation to ensure the exact account of volumes of in and out of scope sources is maintained along the supply chain.

16 IRENA Coalition for Action, "Decarbonising end-use sectors: Green hydrogen certification," International Renewable Energy Agency, Abu Dhabi, 2022.

On the demand side, consumers are showing interest in utilizing green fuels to reduce their carbon footprint and are willing to pay a premium for these low-emission fuels. The uptake of green hydrogen and ammonia will rely on the widespread acceptance of tracking instruments to certify their origin, ensuring that their production relies on renewable energy sources. An assurance mechanism is thus needed to provide customers with transparent, traceable, and complete information about the origin and carbon footprint of the fuel. The drivers associated with the need for an assurance mechanism[17] are summarized as follows:

a. customers are willing to pay premium prices for green fuels for which they need to have transparent information in relation to their carbon origin,

b. green fuel suppliers and consumers need the verifiable data to make informed decisions to transform this data into actions on their decarbonization route.

17 Lloyd's Register, "First movers in shipping's decarbonisation," LR, 2021.

3. Upstream: fuel assurance at production

3.1. Guarantee of origin (GO) certification

A guarantee of origin (GO) certification scheme for hydrogen and ammonia provides a consistent and accurate approach to track the key attributes associated with their production, in particular their carbon footprint. A GO certificate is an electronic document, which provides proof that a given quantity of hydrogen or ammonia is produced by a registered production device meeting specific quality criteria and method of production. It is suggested that this certificate relates to a tonne of hydrogen and includes information about emissions, production facility and location, production technology and primary fuel source[18].

A GO scheme would provide transparency to maritime stakeholders on the environmental impact of the fuels being purchased and used onboard ships. A certification approach is considered the easiest way to verify and track the attributes of a unit of hydrogen or ammonia, as it requires only the hydrogen producer's data to be reviewed. Certification schemes are generally efficient, leading to more open market trading, which allows for more transparency and efficiency. GO certificates also help avoid double counting by enabling consumers to claim a certain volume of energy generated.

Certification can also foster environmental sustainability initiatives among ocean-going vessels through programmes such as 'Green Port Programme'[19], which reduces port dues for low carbon fuel users. They would also foster new investments in zero/low emission fuels. Certification schemes for hydrogen and ammonia are in the nascent state as the use of these fuels as an energy commodity to support decarbonization is still in its infancy. Nonetheless, GOs have been in place for green electricity, and many lessons can be drawn from their use in this sector before application on the green hydrogen production path.

A key benefit of GO certification is that it incentivizes vessel owners and operators to invest in the procurement of green fuels to reflect their actions towards meeting their sustainability goals. GO certificates increase transparency and liquidity by providing a reliable and transparent instrument that gives the consumer trust in the product's quality and origin. The certification scheme for hydrogen and ammonia provides a unique opportunity to develop new business models, which unlock new value for fuel suppliers and end users. It also provides investment signals for the efficient deployment of green fuels according to consumers' needs.

18 DISER, "A Hydrogen Guarantee of Origin scheme for Australia," Australian Government Department of Industry, Science, Energy and Resources, 2021.
19 GAC Green Port Programme, [Online]. Available: https://www.gac.com/hot-port-news/enhancement-of-the-maritime-singapore-green-initiative-green-port-programme. [Accessed 2022].

Some countries have already started developing GO schemes for green hydrogen. The most well-known scheme, currently in development, is CertifHy, a pilot for hydrogen GO scheme in the European Union[20]. The scheme classifies hydrogen as green or low carbon based on the GHG emission and the source of energy and issues certificates for green hydrogen that are deployable in all of Europe. Other countries, such as Australia, US, UK and China are working on developing tracking systems for green hydrogen to help end-users track and quantify the impact of their consumption of green fuels[21,22].

In preparation for a successful GO scheme, design elements include but are not limited to timeline, system boundary, accounting methodologies, governance, labelling, thresholds, carbon offsets, handing of electricity use, and interaction with other schemes. There are also some features that should be avoided in the design, such as significant compliance cost, complexity, and self-certification (see Figure 6). Choosing the system boundary is a challenging task as it involves a trade-off between completeness and complexity. The system boundary can be as broad as lifecycle emissions associated with a unit of hydrogen or ammonia (well-to-wake) or it can be considered only a gate-to-gate boundary which would just cover the emissions occurring at the hydrogen or ammonia production facility. The broader the system boundary, the more information on the emissions associated with a product are provided. However, it makes the implementation more complex.

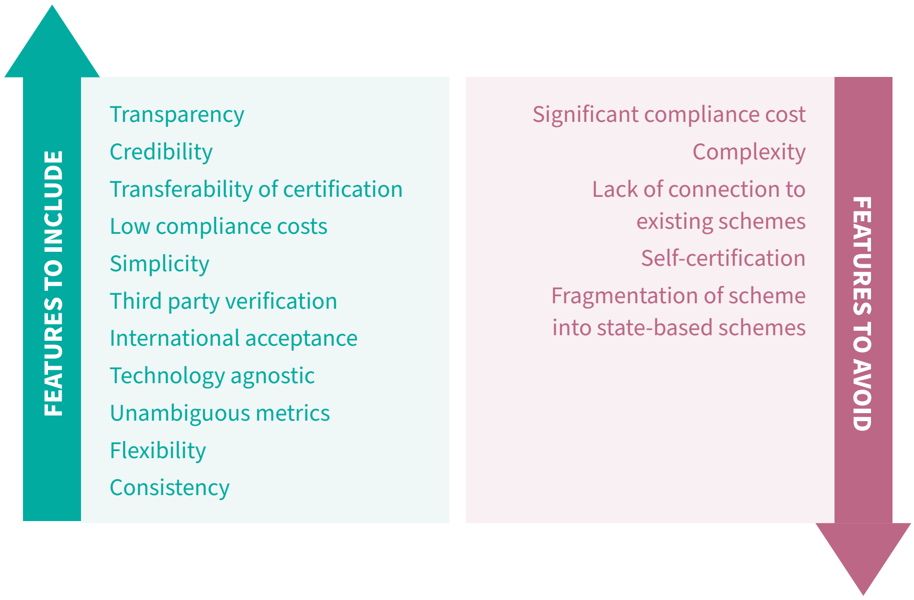


Figure 6: Features to include/avoid in designing a GO scheme

20 Certifhy certification scheme," Certifhy", [Online]. Available: https://www.certifhy.eu/. [Accessed 2022].
21 DISER, "A Hydrogen Guarantee of Origin scheme for Australia," Australian Government Department of Industry, Science, Energy and Resources, 2021.
22 World Energy Council, DENA, "Global Harmonisation of Hydrogen Certification", Berlin, 2022.

In order to apply GO schemes for the maritime industry, we have considered a well-to-tank boundary covering the emissions from fuel production to the ship's fuel storage tanks. Figure 7 shows the well-to-tank boundary, which includes all upstream emissions associated with the supply of feedstocks (including extraction, processing and transportation of fossil fuels) as well as emissions incurred during hydrogen or ammonia production. It excludes emissions associated with capital goods and downstream emissions (hydrogen handling, consumption and end-of-life). By considering emissions related to the entire production cycle of fuels, policymakers can have a more complete picture of the environmental profile of future marine fuels and, in doing so they will be in a position to determine a more accurate path to true net carbon neutrality.

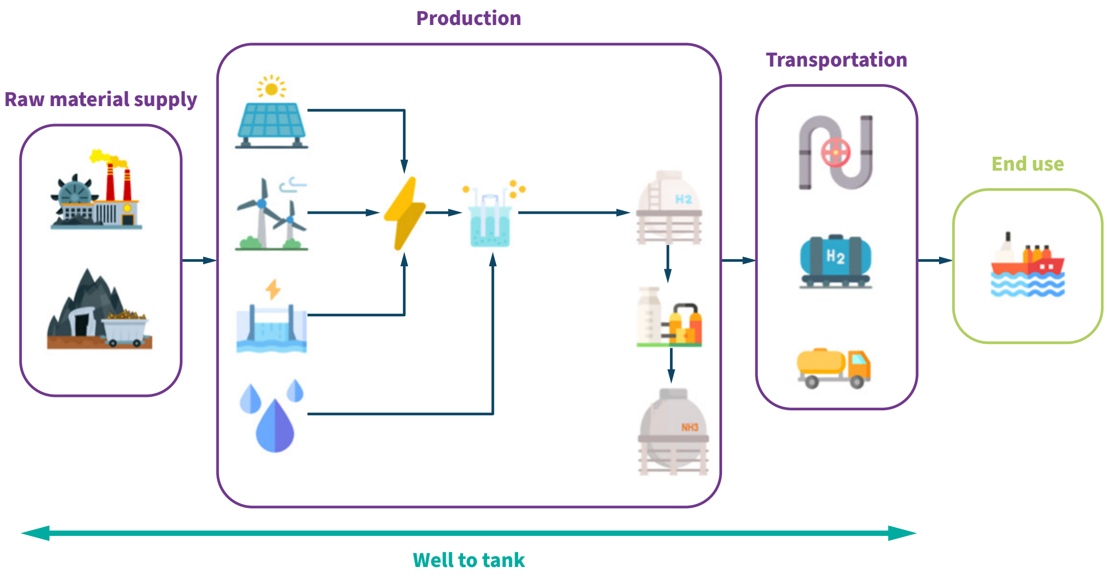


Figure 7: Well to tank boundary for emission reporting of maritime fuels

3.2. Challenges with GO certification

Regulatory compliance

Enforcing clear international regulations is challenging, as it is difficult to create compliance with the same standards and rules internationally. In the absence of a regulatory framework, multiple certification schemes might be developed worldwide and the discrepancies between different tracking systems may lead to misuse. A lack of applicable international regulations, processes and standards could lead to inconsistency in tracking systems to provide standardized information on the origin of fuels such as sustainability criteria (e.g., origin, CO_2 intensity, other emissions) across the full lifecycle.

Information on the production process and transport

GO certification schemes require access to data from the production process and transport of hydrogen and ammonia. Without transparent and reliable information on the production and transportation process the GO certificates cannot serve as fuel assurance mechanism. Without a requirement to provide access to the data on the emissions associated with raw materials as well as information about emissions from the transportation mode and the emissions produced in the event of conversion, the certification may be unreliable.

Link to renewable energy certificates

The deployment of hydrogen and ammonia for the maritime sector should support the energy transition by moving towards renewable energy sources. Hydrogen and ammonia produced using electricity can lead to increased shares of fossil-generated electricity elsewhere in the electricity system. It is therefore important to ensure green fuels' certificates have an additionality requirement attached to them.

3.3. Blockchain technology and fuel assurance

Fuel assurance in the maritime sector requires a technology push to make traceability and transparency of the fuel supply chain feasible. To issue a GO certificate for fuels, a reliable and secure tracking system, which is developed and is based on clear objectives is needed. This will allow the verification of all data by any third party. Blockchain technology could provide the information system for issuing and tracking GO certificates.

Any certification scheme requires sensitive data to be controlled with privacy, transparency, and security between different participants. Blockchain technology has revolutionized the way data is stored and shared. Blockchain provides a decentralized database the so called “digital ledger” of information, using cryptography to keep information secure[23]. Based on a network of computers that must all approve an update before it can be verified and recorded, it also reduces the dependency on and vulnerability of centralized data storage. Apart from its tamper-proof nature, blockchain has the inherent ability to prevent double spending, as assets that do not exist cannot be transferred.

Moreover, blockchain technology provides a digital system of record-keeping that supports highly sensitive data sharing with the improvement of security and privacy using cryptography. It creates complete, transparent, tamperproof history of information flows, inventory flows, and financial flows in transactions, which provide end-to-end visibility over the supply chain. In fact, blockchain can act as a digital notary that tracks the origin of fuels sourced to the ships to verify their origin. When a certificate is issued, the data is digitized, and a digital identity is assigned to each certificate. All certificates are tagged and traceable. The original is safely stored in the network of computers in the blockchain, commonly referred to as nodes.

23 M. Khorasany et al., “Paving the Path for Two-sided Energy Markets: An Overview of Different Approaches,” IEEE Access, vol. 8, pp. 223708-223722, 2020.

3.4. The TYMLEZ solution

TYMLEZ GO certification platform

TYMLEZ has developed a GO solution utilizing blockchain technology. TYMLEZ specifically leverages blockchain as its information validation layer through tokenization without exposing private or confidential data. The decentralization properties of blockchain create an immutable chain of custody, which makes the TYMLEZ solution scalable and unifying, while fostering trust and collaboration across complex supply chain networks.

How does it work?

Core to the TYMLEZ GO solution is the trust-chain that certifies all fuel supply chain actors, ensuring a full audit trail for each datapoint recorded on the platform. The data points are validated by node operators to create a fully verified and immutable database that can be utilized for various GO certification schemes. The Platform is fully self-auditing and features the flexibility to produce customized reporting and display user-friendly dashboards for internal uses, customers, and regulators. It provides access to a real-time digital dashboard in which the green fuels value chain can be verified and visualized. The platform can be integrated, where appropriate, for use with existing systems and is unique in its ability to verify green credentials in hydrogen production.

To credibly certify the origin of green fuels, certificates state the GHG content of each produced kilogram of the fuel that may occur along the value chain, from production to the point of delivery. TYMLEZ platform follows the methodology developed by the International Partnership for Hydrogen and Fuel Cells in the Economy[24] to calculate the GHG emissions for different production pathways. To calculate the GHG emissions associated with the hydrogen and ammonia, the primary sources of emissions should be identified. Key emission sources for hydrogen production using electrolysers, as an example, include:

- **Water supply and treatment:** Electricity for purification and filtration of the water.
- **Hydrogen production:** Electricity for electrolyser units is the main source of emissions. Other sources include steam (where purchased), liquid, solid and/or gaseous fuel combustion for steam generation, and liquid, solid and/or gaseous fuel combustion for electricity generation units.
- **Hydrogen compression, purification, drying and cooling:** The main emission sources include the electricity for relevant units, steam (where purchased), solid, liquid and/or gaseous fuel combustion and/or steam generation.
- **Transportation:** Emissions from diesel, fuel oil or electricity used for motive power to transport hydrogen to the ships. Electricity and/or gaseous fuel combustion for pipeline transport is another source of emissions.

24 IPHE Hydrogen Production Task Force, "Methodology for Determining the Greenhouse Gas Emissions Associated with the Production of Hydrogen," IPHE, 2021.

To calculate the GHG emission and issue a GO certificate, the TYMLEZ platform needs to have access to the following information from the production facility:

Category	Data to be collected
Facility details	Identity, location, capacity
Product specification	Hydrogen weight, pressure, and purity
Electricity	Quantity, and emission factor of the grid electricity
Fuel feedstock	Quantity, and emission factor of the combusted fuels
Water feedstock	Quantity and source of water
Waste and/or co-products	Quantity and emission allocated to oxygen
Particles	TBD

Figure 8: Required information for calculating GHG emissions (Hydrogen with electrolysis)

Figure 9 provides a basic illustration of the data collection process in the TYMLEZ platform. Some of the data, such as facility details, will be ingested offline. For electricity, smart meters and monitoring devices are required to monitor the real-time energy consumption. If there is more than one generation source (e.g., electricity from both grid and solar), the metering device should be installed so that all inputs are monitored separately. For the measurement data, such as the quantity of hydrogen, water and feedstock, digital flowmeters, pressure gauges, and temperature sensors will collect the required data. Then, PLC and Modbus devices will be used to feed data into the platform. It is expected that future hydrogen production facilities will be equipped with digital metering devices. These devices can also be easily retrofitted to the existing facilities.

All information related to metering devices and their installation will be recorded in the platform. The installer qualification data can be directly recorded from public registries (for example Worksafe in Australia or NICEIC in the UK) to the platform. Each metering device usually has a calibration certificate that is part of the yearly maintenance procedures, this is to ensure that the device is measuring within tolerance and is certified for a period in the future (e.g., 1 year). Additionally, there might be certificates to prove functionality in a range of environmental tolerances (e.g., temperature) or that they have been manufactured to particular standards. All these certificates can be taken and uploaded into the platform as required. These certificates can also act as gateways to the data so that should a certificate be out of date, readings can automatically be rejected or placed on hold until the certificates are brought up to date.

The data ingestion to the platform is done by way of a publicly verifiable signature. This signature is either produced at the source via custom device firmware that hashes the data as it leaves the device, or via a publicly verifiable, open-source code mechanism. This data forms a measurement, reporting and verification (MRV) package. These MRVs are then aggregated alongside the unit of measure (UoM), for example, 1 tonne of hydrogen or ammonia, to give the carbon footprint for that UoM. Once the UoM target is hit, a token is created that contains all of the signed MRV's for that particular UoM. This token contains the full traceability of all the information that an auditor would require to validate the readings (including Installer/calibration certificates, the carbon factors used and any other pertinent information). Anyone can take this information and independently verify that the calculations have been performed correctly.

H_2 SHIPPING

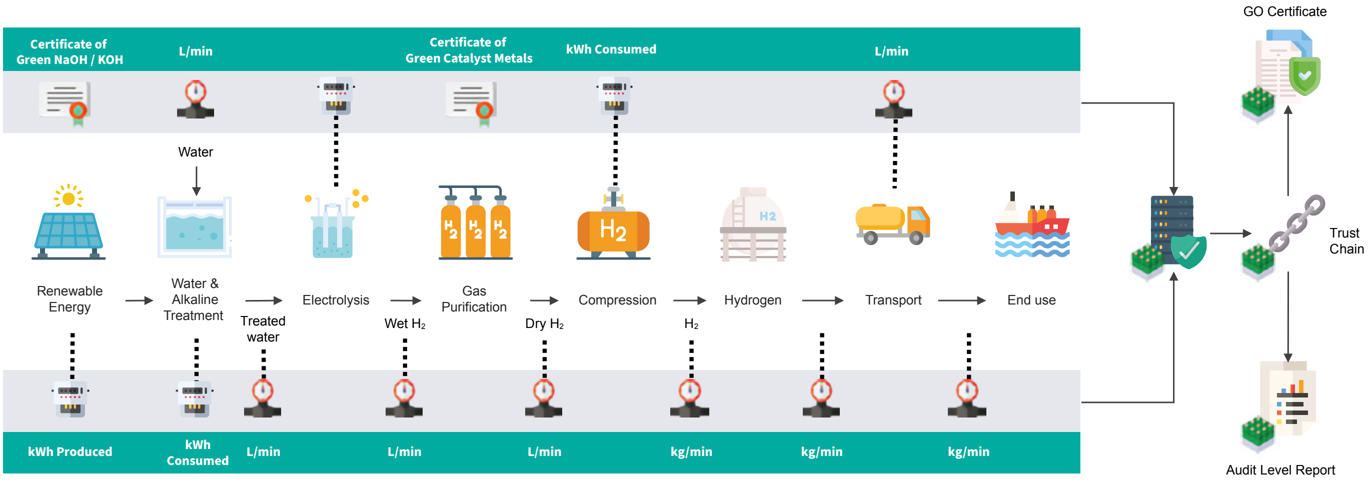


Figure 9: An example implementation of blockchain-enabled GO for green hydrogen plant

The TYMLEZ platform employs the Hedera Guardian to trace events that lead to token event on-chain. Hedera is a fully open source, proof-of-stake, public network and governing body for building and deploying decentralized applications. Hedera is unique in that it is incredibly fast, energy-efficient (carbon negative), and secure. The Guardian is a modular open-source solution that includes best-in-class identity management and distributed ledger technology (DLT) libraries, which allow for full traceability of carbon offsets and credits to be put into practice. As shown below, the issued certificate includes information about emissions, the production facility and the location, the production technology as well as the primary fuel source of the produced fuel.

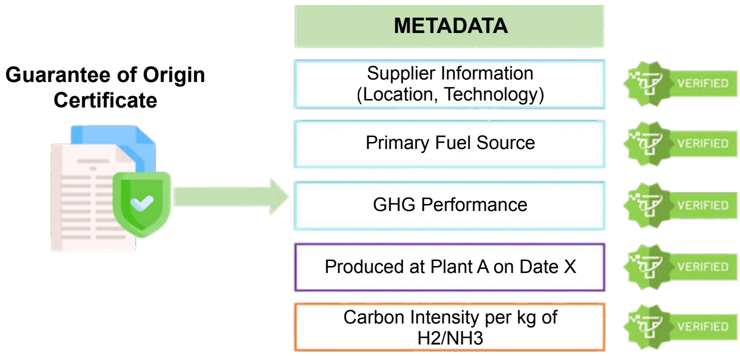


Figure 10: Information included in the GO certificate

Pilot Requirements

Running a GO solution pilot requires the following elements:

- Access to the data collection points from a hydrogen or ammonia production facility.
- Configuration of TYMLEZ Platform.
- Configuration of TYMLEZ Guardian and policies.
- Hedera wallets and ongoing fees.

The TYMLEZ platform runs on cloud infrastructure and its configuration requires the connection to IoT devices. In case the access to real production facility is not possible, APIs of IoT devices can be mocked for pilot programmes or digital twins where mock data is provided.

The Guardian in the TYMLEZ platform is configured through the creation of token and information policies. To create these, the TYMLEZ team works with our partners to determine the data schema fields required to support the GO tokens being tracked.

GO pilots running on the TYMLEZ platform and TYMLEZ Guardian can be deployed using a shared environment or custom environment model. When deployed on a shared platform, costs are heavily associated with the volumes and granularity of data ingested. Data-heavy parts of the GO solution are the ingestion of resource and emissions data.

Transporting this data through the Hedera configuration for a pilot programme change depending on the required blockchain deployment. Testnet deployments can be used where mock data is in use and mock GO tokens will be minted. GO tokens on Testnet deployments are not retained for more than a few months as this network is wiped for development. Mainnet deployment is required when the pilot uses real IoT data and thus real GO tokens will be minted. These tokens will be retained on the Hedera network indefinitely. Blockchain costs, due to predictability and low cost associated with transacting on the Hedera network, are minimal and have a low impact on the overall cost of the solution.

4. Downstream: fuel tracing and verification to point of use

4.1 Fingerprinting hydrogen

Chemical or isotopic fingerprinting has been used for many years to identify the geographic origin of products, such as uranium ore[25] and olive oil[26] in addition to the botanical origins of some products, such as biofuel[27]. A unique, detectable fingerprint based on the source or production method, could be a valuable method of assurance.

In this case, does green hydrogen have a unique fingerprint that could allow clear identification and separation from grey, blue or other types of hydrogen? As discussed earlier, hydrogen can be produced by green methods, where water is directly electrolyzed into hydrogen and oxygen, leaving the purity of the final product quite high and at levels that would be ready for use in FCs. However, if the end use is in ICEs the purity of the hydrogen is less critical and blue or grey hydrogen could be used as effectively as green. Here, the chemical impurities of the higher carbon footprint hydrogen may provide an identifiable fingerprint, not of the green hydrogen, but of the other production methods. Nevertheless. it should be noted that purification of grey or blue hydrogen could mimic the signature of green hydrogen, thus if the financial benefit of having designated the fuel as green is higher than the cost of purification, like a skilled criminal the fingerprints may not be left behind.

A literature search for the use of impurity fingerprints to identify the method of hydrogen production indicates that little, if any, work has been done in this area. As a path forward, further investigation and analysis of various types of hydrogen might indicate that in some situations, hydrogen produced through electrolysis is clearly different to that produced by other, less environmentally friendly processes.

What about an isotopic fingerprint? Hydrogen is a combination of two stable isotopes. Protium (1H), which contains one neutron in the atomic core and Deuterium (2H), which contains two neutrons. The ratio of these two isotopes can be used as a 'fingerprint' for a variety of substances, allowing the source of oil, coal, natural gas and a variety of other materials to be identified. In relation to fuels, the hydrogen isotopic ratios could be used to help determine whether biofuels are truly from a biological source[28].

25 Hamutoko, J.T. et al. *A fingerprinting method for the identification of uranium sources in alluvial aquifers: An example from the Khan and Swakop Rivers, Namibia*. Report: Physics and Chemistry of the Earth, Parts A/B/C, Volumes 72-75, 2014, Pages 34-42. Elsevier Ltd. A fingerprinting method for the identification of uranium sources in alluvial aquifers: An example from the Khan and Swakop Rivers, Namibia – ScienceDirect

26 Stilo, F. et al. *Chromatographic Fingerprinting Enables Effective Discrimination and Identification of High-Quality Italian Extra-Virgin Olive Oils*. Journal of Agricultural and Food Chemistry, 2021, 69,8874-8889. Chromatographic Fingerprinting Enables Effective Discrimination and Identitation of High-Quality Italian Extra-Virgin Olive Oils | Journal of Agricultural and Food Chemistry (acs.org)

27 Vignali, M., Serra, F. *Methodology for Differentiating Source and Provenance of Biofuels Feedstock: a scientific tool in support of Biofuels Certification Schemes*. EUR 25023 EN. Luxembourg (Luxembourg): Publications Office of the European Union; 2011. JRC66527. JRC Publications Repository – Methodology for Differentiating Source and Provenance of Biofuels Feedstock (europa.eu)

28 Kracht, O., Tuthorn, M., Brodie, C. E*A-IRMS: Tracing botanical origin of biofuels with hydrogen isotope fingerprints*. Thermo Fisher Scientific Inc., 2020, AB30729-EN 0520C. AB30729 – EA-IRMS: Hydrogen isotope fingerprints of biofuels from different botanical origin (thermofisher.com)

But could the hydrogen isotope ratios be used to assure that the fuel is from a green source? This is unlikely. The ratios of these two isotopes of hydrogen can be impacted by a wide variety of forces. For example, municipal tap water was assessed in southern Africa for both hydrogen and oxygen isotope ratios seasonally. Even within this limited geographic region, the hydrogen isotope ratios changed throughout the year[29]. Thus, while isotope ratios can be used to identify the source of a wide variety of materials, applying this method to identify green hydrogen is very unlikely to succeed.

4.2 Marking hydrogen

Over the past few decades, industry has developed a wide range of bespoke chemical markers and associated detection technologies to protect virtually every fuel type in use across the planet[30,31,32]. The development of a marker system for any new product requires the careful consideration of several factors including stability, launderability, and detectability of the marker[33]. In addition, considerations as to whether analytical instrumentation that can detect the marker in the field exists, or whether samples need to be transported to a laboratory for analysis.

In the case of a marker system for liquid hydrogen destined for use as a maritime fuel, there are some additional significant challenges that result from extreme storage conditions of the fuel, the need for the marker to stay homogeneously blended with the hydrogen through potential phase changes, as well as purity requirements, should that fuel be used to power the ship by fuel cells. In addition to requirements associated with basic detectability of the marker, the ability to accurately quantify the marker will be vital to a successful marking system for hydrogen as it provides the option to detect any potential dilution or mixing of green hydrogen with hydrogen produced by any other means. This is a likely scenario where fuel is blended as it passes through the distribution system to final delivery, a common occurrence in most currently used maritime fuels.

A marker applicable to hydrogen would need to exist, at standard temperature and pressure, as a gas. Selection of this 'gaseous' class of marker would need to be done carefully to ensure that the required purity of the marked hydrogen remains within acceptable limits. Further study is needed to determine optimal markers, which could be utilized without impacting the hydrogen specifications.

A gaseous marker added to liquid or pressurized hydrogen would have the advantage of being detectable both in the field through recently developed portable gas chromatographic systems as well as in a laboratory-based setting using conventional benchtop chromatographic systems. Additionally, in a laboratory setting, these marker systems are compatible with forensic level gas chromatographic/mass spectrometry (GC/MS) instrumentation and methodology, which has the benefit of being recognized by judicial systems across the globe as the highest level of forensic analysis.

29 de Wet RF, West AG, Harris C. *Seasonal variation in tap water δ2H and δ18O isotopes reveals two tap water worlds*. Scientific Reports. 2020 Aug 11, 10(1):13544. doi: 10.1038/s41598-020-70317-2. PMID: 32782259; PMCID: PMC7421565. Seasonal variation in tap water δ2H and δ18O isotopes reveals two tap water worlds – PubMed (nih.gov)

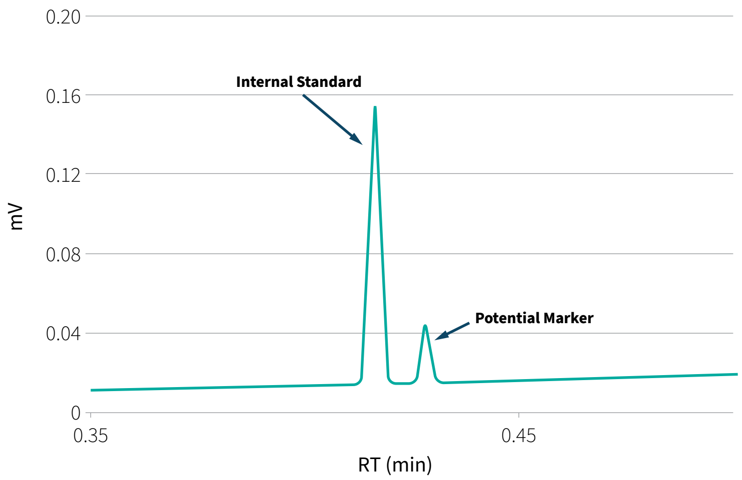
30 Conroy, J.; Forshee, P.; Cronin, P.; Soyemi, O. (2018) Determining the Quantity of a Taggant in a Liquid Sample (U.S. Patent No. 9,995,681). U.S. Patent and Trademark Office. https://tinyurl.com/3eymebt8

31 Forshee, P.; Hundt, G.; Conroy, J. (2015) Dipyrromethenes and Azadpyrromethenes as Markers for Petroleum Products (U.S. Patent No. 9,222,043). U.S. Patent and Trademark Office. https://tinyurl.com/2p95bdx2

32 Conroy, J.; Forshee, P. (2019) Method of improving the accuracy when quantifying fluorescence markers in fuels (U.S. Patent No. 10,351,789). U.S. Patent and Trademark Office. https://tinyurl.com/bdzvwhnt

33 Conroy, J.; Forshee, P.; Boyer, J. (2016) Fuel markers and methods of producing the same (U.S. Patent No. 9,366,661). U.S. Patent and Trademark Office. https://tinyurl.com/45me5vvd

Another potential path for marking hydrogen may be through a performance additive. When used as fuel for ICEs, hydrogen is known to have very low lubricity. Use of low lubricity fuels in ICEs can cause damage to injectors and other components. As with very low sulphur diesel fuels, which also have low lubricity, one chosen path has been to add a lubricity additive. If engine development is not able to adapt to the low lubricity of hydrogen, an additive may be developed to reduce the engine wear and improve lubricity. Should that be the case, a marker that is added only to verifiably green hydrogen, at the source, may be a path to uniquely identifying that product throughout the market.



The marker was dosed in the low part per million range (ppm) in a hydrogen matrix.
Note: Field-based portable instrumentation yields a very fast, sensitive, and accurate analysis for the marker system.

Figure 11: A chromatogram of a potential marker structure (and associated internal standard) acquired on a portable micro gas chromatograph

4.3 Fingerprinting ammonia

As noted, the use of ammonia as a marine fuel does not demand the highest purity available. Whether used in fuel cells or in traditional internal combustion engines, it appears that the most abundant C-grade ammonia can be used for ship propulsion. While this grade of ammonia may be produced by SMR with no carbon capture (grey), by SMR with carbon capture (blue) or through direct hydrolysis of water and the entire process being powered solely by sustainable energy (green), the most expensive of these processes will be the green production of ammonia. For this reason, there are cost drivers that may motivate suppliers to designate an ammonia source as green, when it is in fact blue or grey.

As described earlier in this report, one key ingredient in the production of ammonia, hydrogen, when produced by green methods, comes from direct water electrolysis. Only a few impurities are expected to be produced in comparison to grey and blue methods using SMR, where it is known that oil, water, sulphur compounds and other lower-level impurities will be produced. Since the required purity of ammonia for both FC and ICE use is equivalent to or even below C-grade ammonia, these chemical impurities may be left behind as a fingerprint of the higher carbon footprint processes without negative impact on use as marine fuel. If unpurified, this type of ammonia should have a signature indicative of non-green production methods.

It should be noted, that if non-green ammonia were to have a unique impurity fingerprint, illicit actors could mimic the signature of green ammonia through purification methods. Thus, if the financial benefits of having designated an ammonia fuel as green are higher than the costs of purification, those fingerprint compounds would be removed.

To determine if impurity fingerprints could be used to identify non-green sources of ammonia, further investigation would be required.

Nitrogen, a primary component of ammonia, occurs in nature in two stable isotopic forms. The vast majority (99.6%) is nitrogen-14, named this because it contains 7 protons and 7 neutrons. The remainder is nitrogen-15, where there are 7 protons and 8 neutrons. Is the ratio of these two stable isotopes of nitrogen an indicator of grey, blue or green ammonia production methods?

While some research has been conducted in determining if nitrogen isotope ratios could be used to identify the source of ammonia emissions (agricultural versus vehicle emissions)[34], there is little evidence that these isotopes could be used to identify green ammonia production. Since nitrogen used for the production of ammonia in most cases, is from air, whether the process of production is grey or green, the isotopic ratios are unlikely to be indicative of the carbon footprint of the method. These ratios will be related to the natural air abundances and are unlikely to be affected by green or grey processing methods.

34 Walters, W., Hastings, M.G., Colombi, N.K. *"Fingerprinting" Vehicle Derived Ammonia Utilizing Nitrogen Stable Isotopes. December 2017. Abstract in American Geophysical Union*, Fall Meeting 2017, abstract #A53F-2317. Retrieved online: "Fingerprinting" Vehicle Derived Ammonia Utilizing Nitrogen Stable Isotopes – NASA/ADS (harvard.edu)

4.4 Marking ammonia

Use of a unique marker to identify a pressurized liquid fuel is currently being done with liquid petroleum gas (LPG). This is done through the use of a fluorescent marker, which is advantageous as it is readily detectable at part per billion (ppb) concentrations in the product. The marker is introduced into bulk LPG tanks on filling or when transport containers are being loaded. This marker is homogeneously mixed with the LPG and can then be used to detect the identity of that product as well as signal whether it has been adulterated or exchanged for a lower quality fuel. The analysis is performed in the field using a fluorimeter with a special high-pressure cell, thus detecting the marker in the liquid phase of the LPG. Figure 12 below gives the principle of fluorescence detection and shows an example of a field analyzer.

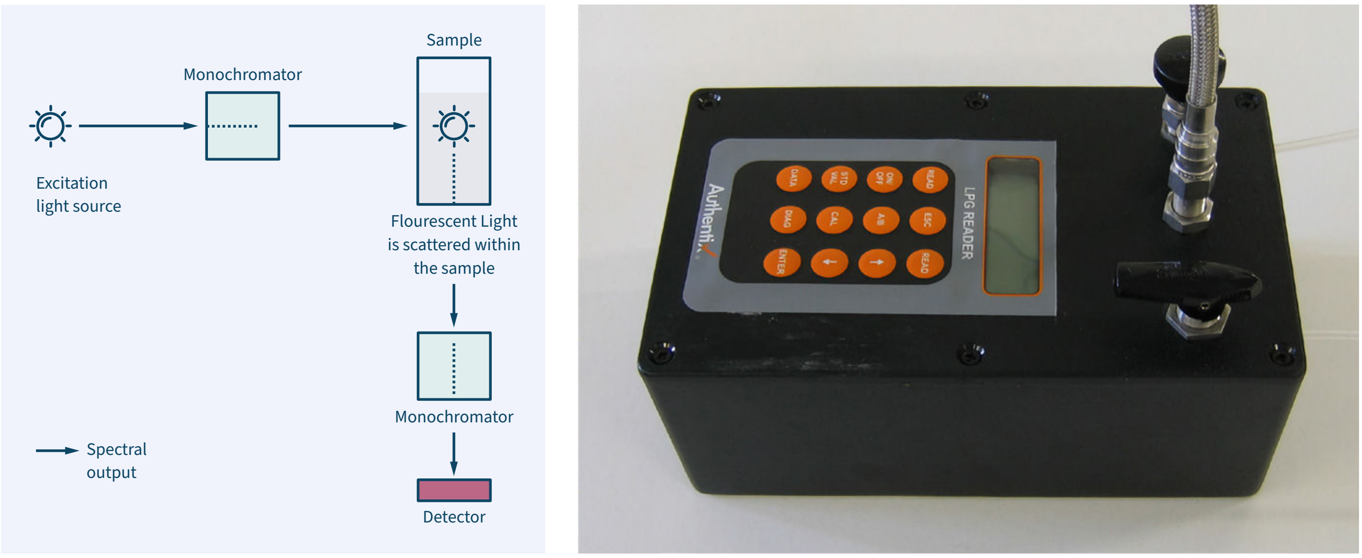


Figure 12: The principle of fluorescence detection (left), a method conducted by the LPX 1000 analyser (right)

The similar physical properties of LPG and ammonia indicate that this fluorescent technology may be extended to mark liquified ammonia. To identify and deter the dilution of green ammonia, a proprietary fluorescent marker would be required to be developed. This marker would need to be soluble in the liquid ammonia and quantifiable, at a maximum, at low part per million (ppm) levels. The chemistry of the marker would have to be tested to ensure that it will not react with the ammonia in any way that would cause degradation and be sufficiently stable so as to be maintained at operative concentration throughout the supply chain.

The marker creates a unique fluorescent fingerprint that would identify legitimate ammonia. Quantitative measurements of the marked ammonia could be taken using a modified device analyzer. To quickly authenticate green ammonia throughout the supply chain by safely detecting the unique covert marker injected into the fuel. The analyzer would need to be coupled directly to a liquid ammonia source through appropriate valving. A portion of the ammonia would be introduced into the instrument and the presence and quantity of the fluorescent marker determined. Readings would be acquired in a short time frame (<5 minutes) using a relatively small amount of ammonia (<5 milliliters). The accuracy of detecting dilution of this marked ammonia, for example with grey ammonia, may be as good as ± 5%, but is not expected to be more accurate than this. Combined errors in marker addition and testing make the ability to detect less than 5% dilution of the green ammonia unlikely.

Another potential type of marking method may be a gas-phase small hydrocarbon or an amine. Laboratory-based analytical methods, using gas chromatography with a range of detectors exist for the detection of these type of compounds in gas streams. The method may be suitable for the determination of low ppm or even part per billion (ppb) levels of hydrocarbon and amine markers in gaseous ammonia. In this analysis, samples are obtained in appropriate sampling bottles and returned to a laboratory. The bottle of gaseous sample is connected to a gas chromatography (GC) and may be detected by mass spectrometer (MS).

When used as a marine fuel for ICEs, similarly to hydrogen, ammonia can have low lubricity and be corrosive. This could damage to injectors and other components. Should an additive be developed to minimise these effects, a marker that is added only to verifiably green ammonia, at the source, may be a path to uniquely identifying that product throughout the supply chain.

4.5 The Authentix solution

Marker addition to hydrogen

Hydrogen may be stored at the producer facility in several ways.

- **Compressed hydrogen:** storage of hydrogen as a gas, which requires high pressure of 350–700 bar.
- **Liquified hydrogen:** storage of hydrogen as a liquid, which requires cryogenic temperatures. At one atmosphere pressure, this temperature must be −253°C.
- **Chemical storage (also called materials-based storage):** a variety of methods currently under development to store hydrogen on the surfaces of solids using adsorption or within solids using absorption.
- **Geological storage:** storage in salt caverns, depleted oil/gas fields, and aquifers.

Today, hydrogen is typically transported from the point of production to the point of use by pipeline and on the road using cryogenic liquid tanker trucks or gaseous tube trailers. The transportation method is largely determined by the original storage method.

Should a marker be used to uniquely identify green hydrogen, addition of the marker could be achieved by one of the three different methodologies currently used in the industry.

- **Continuous dosing**: A constant flow of the marker is dosed based on a fixed setpoint. This is independent of external process conditions. This method could be done during pipeline transport or loading of on-road tankers.
- **Batch dosing:** A single injection of marker is dosed on a per batch basis. This may be done at the storage tank prior to transport.
- **Ratio dosing:** The accurate dosing of the marker based on both the process flow and a predefined dosing ratio. Depending on process flow conditions, this could in principle replicate batch or continuous dosing operations.

Many factors must be taken into consideration in the design and location of the marker injection systems. If properly designed, continuous and ratio dosing would be the most accurate. Batch dosing, if done while filling a tank, can also be accurate if sufficient mixing occurs during filling. If dosed into a filled tank, unless some form of recirculation or mixing exists, there will be risks of creating a non-homogeneous mixture of marker in the hydrogen. These are all considerations that are addressed when designing an injection system for liquid fuels, such as gasoline or diesel as well as compressed liquid fuels such as liquid petroleum gas (LPG). It is expected that a system for marker addition to the various forms of hydrogen could be developed fairly simply from these current systems.

Sampling and Testing

Hydrogen fuel quality analysis has been in existence for many years. To determine the quality of hydrogen, samples must be obtained, stored in cylinders and delivered to the laboratory. ASTM, ISO and companies such as Air Liquide and Linde have methods for accurately sampling hydrogen tanks. These methods should be directly applicable to sampling hydrogen at the producer's facility or from on-board ship tanks. Once a representative sample is captured in a cylinder it may be tested in the field or may require transport to a testing lab for either hydrogen fingerprinting or marker analysis.

As with sampling gases, testing gases from pressurized cylinders is a common practice in analytical chemistry. Using currently available equipment, the hydrogen sample can be transferred from the cylinder into the testing device.

There do not appear to be significant limitations to sampling and testing of hydrogen, whether at the producer's facility, during transport or on-board the ship.

5. Conclusions

Both hydrogen and ammonia enable promising paths to a low carbon future for moving ships around the globe. For green fuel production, the required power must be sustainable, and the purity of the end products is likely to be much higher than fuels produced through grey or blue processes. Compared to blue or grey fuels, green fuels have higher costs and complexity. One indicator of this is the fact that less than 0.1% of the production facilities globally are dedicated to water electrolysis today, which is the source of hydrogen for both green production processes. However, as the demand for green fuels increases, the number of facilities is expected to increase as well and with this growth the amount of high purity product coming from green processes will equally increase.

For those wishing to fraudulently represent their hydrogen or ammonia supply as green, using grey or blue hydrogen would be the most cost-effective option, since the production methods and lack of purification processes would greatly reduce costs. These products may carry an identifiable fingerprint, which could help distinguish them from green sources. And, since the purity requirements of the hydrogen and ammonia does not necessarily have to be high, even for use in some fuel cells, using higher carbon footprint fuels will be even more appealing. However, should the financial incentives be significant, this may drive illicit sellers to purify high-carbon footprint fuels, thus wiping those fingerprints from the fuel.

Upstream assurance

Creating a strong and reliable tracking system is essential for informing the stakeholders in the maritime sector about the origin of the fuels they use. A GO platform can support the rapid deployment of green fuels by providing transparency and incentivizing their use. Adoption of a blockchain-enabled GO platform for fuel assurance would require attention to some key factors:

a. Cost-effective and easy-to-implement fuel assurance systems. Accelerating the uptake of green fuels in the maritime sector requires a cost-effective and easy-to-implement fuel assurance system that moves away from administrative burdens and barriers that make the process complicated. Furthermore, it is crucial to leverage cost-effective technologies to reduce certification costs for the stakeholders.

b. Facilitate the deployment of blockchain technology. There are some barriers for using blockchain technology that need to be considered by the stakeholders and regulatory bodies. On the regulatory front, stakeholders must be educated about blockchain and its value to avoid any misconceptions about its true potential. Since blockchain is an emerging technology, the drafting of specific regulatory requirements for its deployment in the maritime sector should also be considered.

Downstream assurance

Fingerprinting higher carbon footprint fuels or adding a unique marker to either green fuel, hydrogen or ammonia, was evaluated. Further investigation would be required to determine if inherent and detectable fingerprints exist to distinguish between green and other production methods for hydrogen and ammonia. With marking, whether added directly or potentially through a performance additive when that fuel is used in ICEs, there appear to be paths worth further investigation. However, there are some risk factors that need to be considered in marking this 'high-value' fuel.

Where fuel marking is the chosen path, the financial incentives for the various methods of 'cheating' should be evaluated. In a program where known lower-value products are being marked and tracked, as is often the case with subsidized kerosene or low-tax fuels, those products are likely to be used as adulterants or fraudulently represented as higher-value products, like fully taxed road fuels. There, when testing the road fuels, detection of the marker added to kerosene or low-tax fuel indicates fraud. The illicit actors would then wish to remove that marker from the marked products to make them appear like road fuel. Thus, the chemistry and identity of that marker can be publicly known, but more critically it must be resistant to any methods of 'laundering'.

When adding a marker to the high-value fuels, the secrecy and security around marker identity is critical. In the example above, if the highly taxed road fuels are marked, allow the detection of any adulterant, the marker identity must not be open to the public. That identity, should it become known, may allow criminals to synthesise and add the same chemical to low-value products, thus mimicking the high-value signature. Through strict security processes, the marker and its associated identification can be tightly controlled. However, should local or regional regulations require that the identity should become published, this may open the door for weakening the integrity system.

In the cases of hydrogen and ammonia, illicit actors will be motivated to represent high carbon footprint fuels as green, thus attempting to circumvent any controls that may exist. If markers were used to indelibly identify the lower quality, higher carbon-footprint fuels, the secrecy of the chemical identity of the marker would not be critical. It would only be critical that the marker could not be economically removed. However, in this case, all grey, blue or other non-green products cannot be reliably located, identified and marked. Therefore, assuring the integrity of the green fuels would require the marking and tracking of the green fuels themselves. When marking these high-value products, the chemical identity of the marker(s) must be kept secret. If publicly identified, as is required in some situations, illicit actors may be able to synthesise the chemical and add it to the lower-value products, thus making them appear high-value and green. In conclusion, programme security must be an important aspect to determining if marking green fuels would be an effective method for fuel assurance.

6. Recommendations for future work

Further research

This study has identified knowledge gaps across several aspects of potential fuel assurance for hydrogen and ammonia. Further work is needed to explore these gaps.

A trial or partial trial in a sandbox environment

Solutions such as those described in this document require validation and testing in parallel with the development of the fuel technology and infrastructure to adequately mitigate the risks described with regulatory compliance and falsification when green fuels will become commercially available. These solutions can be tested under sandbox environments whereby certain real-world variables can be held constant to enable the validation of the effect of the solution being tested.

In particular the complexities of an extensive supply chain can be removed from test environments if the goal is to validate the technical feasibility of solutions, such as by piloting one element of the proposed solution at a single stage of the process. This could, for example, be the validation of the detectability of the marker in an ammonia cargo parcel before, during and at the end of a single cargo voyage.

Similarly for the upstream solution, dummy data may be injected into the platform to demonstrate the means of using the GO certificate across international regulations, demonstrating a need for harmonized classification system or be used to credibly certify the origin of green fuels, by ensuring access to data on the production and transportation of the fuel.

Streamlined testing of the proposed solutions should be seen as an opportunity in order to build confidence, leading to initial deployment of the end-to-end product, which can be similarly trialled with first mover consortia, such as green shipping corridors.

Other solutions

The solutions discussed in this paper are not intended to demonstrate an exhaustive outlook on the fast-evolving environment, but rather demonstrate the feasibility of an emerging holistic solution being applied to the maritime context. It is in fact expected that with the maturing of technology to deploy hydrogen and ammonia fuelled ships, there will also be a wider emergence of similar or different solutions to provide the necessary assurance.

It is imperative that such solutions are trialled and developed in line with the deployment of fuels. It is also encouraged that such components be combined with other first mover initiatives to ensure the ultimate and timely availability of one or more capable and robust assurance mechanisms.

Appendix A: Project partners

Safetytech Accelerator

Safetytech Accelerator is a non-profit established by Lloyd's Register. It is the first fully dedicated technology accelerator focused on safety and risk in industrial sectors. Their mission is to make the world safer and more sustainable through wider adoption of safetytech.

www.safetytechaccelerator.org

Lloyd's Register Maritime Decarbonisation Hub

The mission of the Lloyd's Register Maritime Decarbonisation Hub is to accelerate the sustainable decarbonisation of the maritime industry. The Hub achieves this by steering the industry, shaping practical solutions and sharing our research insights and knowledge. Our approach is agnostic of technology or fuel and is evidence based. The Hub works in partnership with other forward-looking organisations to deliver credible thought leadership to the entire industry – from ship charterers to fuel producers and from policy leaders to technology developers. The Hub is a partnership between Lloyd's Register and the Lloyd's Register Foundation.

www.maritimedecarbonisationhub.org

Authentix

Authentix was formed in 2003 from the merger of US-based Isotag and UK-based Biocode, combining two of the authentication industry's leading players. Our mission is to safeguard the integrity of global commerce by delivering innovative authentication solutions for governments, central banks and commercial companies. Authentix' services ensure the growth of local economies, provide the highest level of banknote security, and create significant competitive advantages for high value branded products.

www.authentix.com

TYMLEZ

The mission of TYMLEZ is to improve the world's drive towards a more sustainable future where people and organisations work together to meet their sustainability targets. TYMLEZ is a pioneer in the development and delivery of carbon tokenisation and guarantee of origin solutions built using distributed ledger technology. TYMLEZ provides companies across the globe with world-class solutions designed to empower them in their decarbonisation journeys.

www.tymlez.com

Get in touch

www.maritimedecarbonisationhub.org

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