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Global trade of hydrogen:

what is the best way to transfer hydrogen over long distances?

GAS

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Abstract

As a manufactured fuel, hydrogen can be produced in a decentralized way in most countries around the world. This means, even in a net zero economy, the global trade of hydrogen could look quite different to the current international trade in fossil fuels, including natural gas. With further declines in the costs of renewable electricity and electrolyzers, regions which have lower cost renewable electricity may develop an economic advantage in the production of low-cost hydrogen, but for hydrogen to become a globally traded commodity, the cost of imports needs to be lower than the cost of domestic production. Unlike oil or natural gas, transporting hydrogen over long distances is not an easy task. Hydrogen liquefaction is an extremely energy-intensive process, while maintaining the low temperature required for long-distance transportation and storage purposes results in additional energy losses and accompanying costs. The upside is that hydrogen can be converted into multiple carriers that have a higher energy density and higher transport capacity and can potentially be cheaper to transport over long distances. Among the substances currently identified as potential hydrogen carriers suitable for marine shipping, liquid ammonia, the so-called 'liquid organic hydrogen carriers' in general (toluene-methylcyclohexane (MCH) in particular), and methanol have received the most attention in recent years. This paper compares the key techno-economic characteristics of these potential carriers with that of liquified hydrogen in order to develop a better understanding of the ways in which hydrogen could be transported overseas in an efficient manner. The paper also discusses other factors, beyond techno-economic features, that may affect the choice of optimum hydrogen carrier for long distance transport, as well as the global trade, of hydrogen.

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I. Introduction

Created in the first few moments after the Big Bang, hydrogen (H_2) is the most abundant element in the universe (US EIA 2022). At the same time, since it rarely exists in its pure form on earth, it has to be manufactured (Energy Observer, 2021). Its ability to store and deliver usable energy, means it could potentially be utilized in numerous applications, such as heat and power generation, transport, and the production of various commodities generally associated with significant emissions (e.g. fertilizers and steel) (Bellona, 2020). Unlike most conventional fuels, the only byproduct of the direct combustion or utilization of H_2 through hydrogen fuel cells is water, and this unique feature is often viewed as an indispensable component in the global decarbonization roadmap (World Economic Forum, 2022).

While hydrogen is often portrayed as a 'more sustainable' alternative to coal, oil, and natural gas, it has some very distinct features that make it quite different not only from these fossil fuels but also from other popular energy sources that are currently in use. In contrast to extracted hydrocarbons, H_2 is a manufactured gas that can be produced using a variety of resources including biomass, hydro, wind, solar, geothermal, nuclear, coal, and natural gas (US Department of Energy, 2016). This variety of feedstocks theoretically removes a great deal of geographical limitation to its production and thus turns hydrogen into a fuel that could potentially be generated in a greater number of locations than fossil fuel hydrocarbons. This, in turn, potentially makes it a lot more decentralized when compared to most of the conventional alternatives currently being used.

On the other hand, given that the conditions for hydrogen production are likely to vary around the globe in the future, hydrogen transportation is likely to play an important role in creating H_2's value chain, as it is this which will bring the fuel from the point of production to the ultimate end-user. While land delivery of hydrogen has already been successfully conducted via road and pipelines (US Department of Energy, 2019), its transportation via maritime shipping is yet to become commonplace. In order for the hydrogen economy to become a truly global phenomenon, H_2 should become a universally traded and, more importantly, a globally transported commodity. Although it is still not clear whether this will ultimately happen, viewing the potential options for hydrogen shipping is a useful exercise, as hydrogen itself may not necessarily be the best transport option.

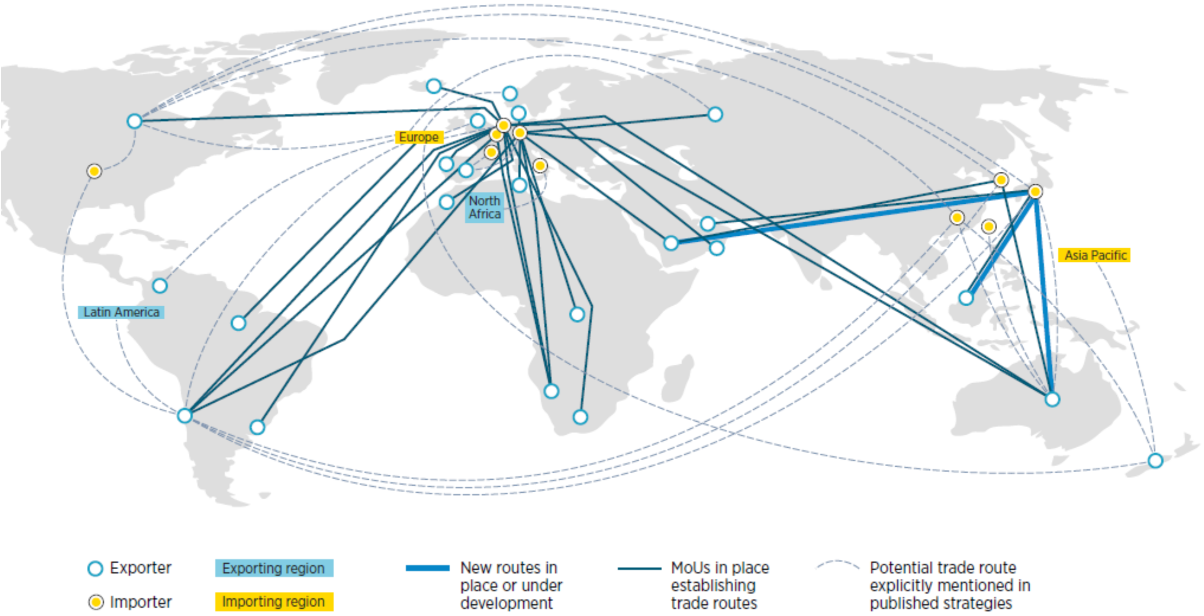
By all accounts, hydrogen appears to be a 'difficult' substance to work with. Its density under ambient conditions is extremely low (see Table 1) and it is easily dispersed because it is considerably lighter than air. In addition, hydrogen is highly flammable and even small amounts of it can be explosive when combined with air (Rhodes, 2011). That is why safe and effective storage and transportation of H_2 normally presupposes either its compression or liquefaction (ibid). While the latter process would allow a substantial increase in hydrogen's volumetric energy density and thus would be more suitable for transoceanic shipping, it requires a cryogenic temperature of -252.87 ^{o}C which necessitates a significant energy input and additional expenses (US EIA, 2022).

Given these challenges, a key question is what is the best alternative to liquid H_2 that could be used for the purposes of delivering hydrogen over extremely long distances? Currently, among the substances identified as potential H_2 carriers suitable for marine shipping, the following three options are arguably the most 'popular': (a) liquid ammonia, (b) the so-called 'liquid organic hydrogen carriers', in general, and toluene-methylcyclohexane (MCH) in particular, and (c) methanol. Since each of these chemicals has its own advantages and drawbacks, it is important to compare their key characteristics in order to develop a better understanding of ways in which hydrogen could be transported across oceans in an efficient manner.

While the delivery of hydrogen is the main focus of this paper, decision makers leaning towards choosing a specific H_2 transportation option should also consider the energy losses and the resulting costs associated with the conversion of hydrogen into its ultimate carrier before the delivery even takes place. In this connection, the high cost of H_2 shipping in addition to the high cost of its production and conversion in many cases will be likely to force the decision makers to question whether hydrogen trade over long distances make sense at all. In these circumstances, in order to bring economic sense to hydrogen delivery over long distances, the costs of its generation and conversion need to be significantly lower in the exporting country than in the importing one so that the transport costs can be compensated for. This cost differential will become larger as the scale of projects increases and technology develops to reduce transport costs (IRENA, 2022b).

Given the lack of geographic homogeneity around the globe (for example, the varying abundance of wind and solar resources), the conditions for hydrogen production in certain parts of the world will be more favourable than in others. This is why some countries will be more likely able to produce cheaper H_2 than others, which will automatically create a precondition for hydrogen trade at least on a regional level (Figure1). At the moment, this feature has already been reflected in the national hydrogen strategies of many countries who expect to play an important role in the to-be-created hydrogen economy.

Figure 1: An expanding network of hydrogen trade routes, plans and agreements[1]



Source*:* IRENA (2022a)

If hydrogen demand rises substantially and an efficient means to deliver this substance by sea appears, the global hydrogen trade may ultimately become a reality. This, however, will also require certain other enabling factors, such as certain geopolitical considerations, and a favourable economic or political environment in the most promising prospective hydrogen producers or consumers. The analysis in this paper aims to better understand the nature of the technical, economic, and regulatory challenges that need to be addressed if H_2 is going to become a truly global commodity.

Through comparing liquid hydrogen, liquid ammonia, MCH, and methanol this paper aims to identify which H_2 carriers appear to be the most suitable ones for enabling future transoceanic hydrogen delivery and thus global hydrogen trade. The outline of this paper is as follows. Section 2 provides a general overview and comparison of the four options, then to identify the most 'effective' carrier in terms of how much H_2 will ultimately be delivered and at what expense, Section 3 compares their thermodynamic and conversion losses as well as approximate minimum levelized costs throughout their value chains. Section 4 considers other factors that would most probably affect the choice of appropriate option to ship hydrogen, and lastly, Section 5 provides concluding remarks.

[1] This figure is based on the information contained in government documents such as hydrogen strategies, concepts, and plans (IRENA, 2022a).

II. Hydrogen and its key derivatives for long-distance shipping

II.1. Hydrogen

Creating a well-functioning economic system for the global use of hydrogen presupposes that it can be utilized in a number of sectors such as industry, transport, and utilities. This requires the ability to store hydrogen in large quantities for extended periods of time as well as (and perhaps even more importantly) delivering hydrogen over extremely long distances, including those of a transoceanic nature (Papadias, Peng, and Ahluwalia, 2018). At the moment, with hydrogen trade being mostly limited to regional markets, only a few pilot projects have been launched to see if transporting H_2 across oceans is technically and economically feasible. In general, with the currently available technological solutions, large volumes of this fuel are normally delivered in either gaseous or liquid forms (Barthelemy, Weber, and Barbier, 2017). Nevertheless, for the development of a mature hydrogen economy in the future, neither option appears to represent the most economically advantageous approach to perform this task.

For instance, on land, apart from hydrogen pipelines (which are unlikely to be applicable for transoceanic delivery routes), tube trailers are often used to transport H_2 in a compressed form at 250-500 bar (Wang et al, 2019). The capacity of these trailers, however, is normally limited in most countries to 280-1000 kg of H_2 due to specific regulations on height, width, and weight imposed by local transport authorities (Papadias, Peng, and Ahluwalia, 2018). Although the compressed hydrogen format could potentially be applied to marine vessels that would deliver gaseous H_2 overseas, shipping hydrogen in liquid form will ultimately result in a significantly greater volume of this fuel being unloaded at the end point.

This is primarily due to the extremely low density of hydrogen, which is only 0.08375 kg/m^3 under ambient conditions[2] (Amos, 1999) (Table 1). In these circumstances, compressing H_2 to 350 bar (35 MPa) will improve this to 23 kg/m^3 (ibid). Liquefying H_2, in turn, will make this number even greater, as it will provide hydrogen density at its maximum level of around 71.1 kg/m^3 [3] (ibid). These figures, however, are far from comparable to those of the most commonly used fuels today: around 830-950 kg/m^3 for diesel[4], 715-780 kg/m^3 for gasoline and 430-470 kg/m^3 for LNG (Viskup, 2020).

In addition, hydrogen liquefaction requires lowering the fuel's temperature to the extreme -252.87 ^oC, which is very close to the absolute zero of -273.15 ^oC (Amos, 1999). As a result, it is not surprising that maintaining this low temperature for any length of time for transportation and storage purposes will result in additional energy losses and accompanying costs. In general, hydrogen liquefaction appears to be an extremely energy intensive process. In fact, cooling gaseous H_2 from ambient temperature down to its boiling point will typically require the use of 30-36 per cent of the energy contained in the hydrogen itself (Garche, 2009).

Another major challenge of liquid H_2 as a hydrogen delivery vector is the significant thermodynamic losses associated with each stage in its value chain (Aziz, Oda, and Kashiwagi, 2019). Although liquid hydrogen does not have to be converted into another fuel before it can be transported and then reconverted back for ultimate consumption (Figure 2), due to the cryogenic temperature of liquid H_2, the heat that leaks into its storage and transportation tanks (vessels) causes boil-off gas (BOG) (Al-Breiki and Bicer, 2020). Since BOG losses significantly reduce the quantity of hydrogen that is ultimately delivered, this has a profound negative impact on its economic value (ibid).

Given this fact, and in an attempt to dramatically reduce costs associated with energy consumption, thermodynamic losses, and other challenges of liquid hydrogen delivery, attention has turned to alternative transportation options which could be less problematic and potentially cheaper. Ammonia, methanol, and liquid organic hydrogen carriers (LOHCs), in general, and toluene/methylcyclohexane (MCH) in particular, have been considered as promising alternatives to liquid H_2 (Papadias, Peng, and Ahluwalia, 2018, Aziz, Oda, and Kashiwagi, 2019, Al-Breiki and Bicer, 2020, BLG, 2021) and are the potential hydrogen carriers which have so far attracted the most attention from analysts (Teichmann, Arlt, and Wasserscheid, 2012, Kamiya, Nishimura, and Harada, 2015, Chapman, Fraser, and Itaoka,

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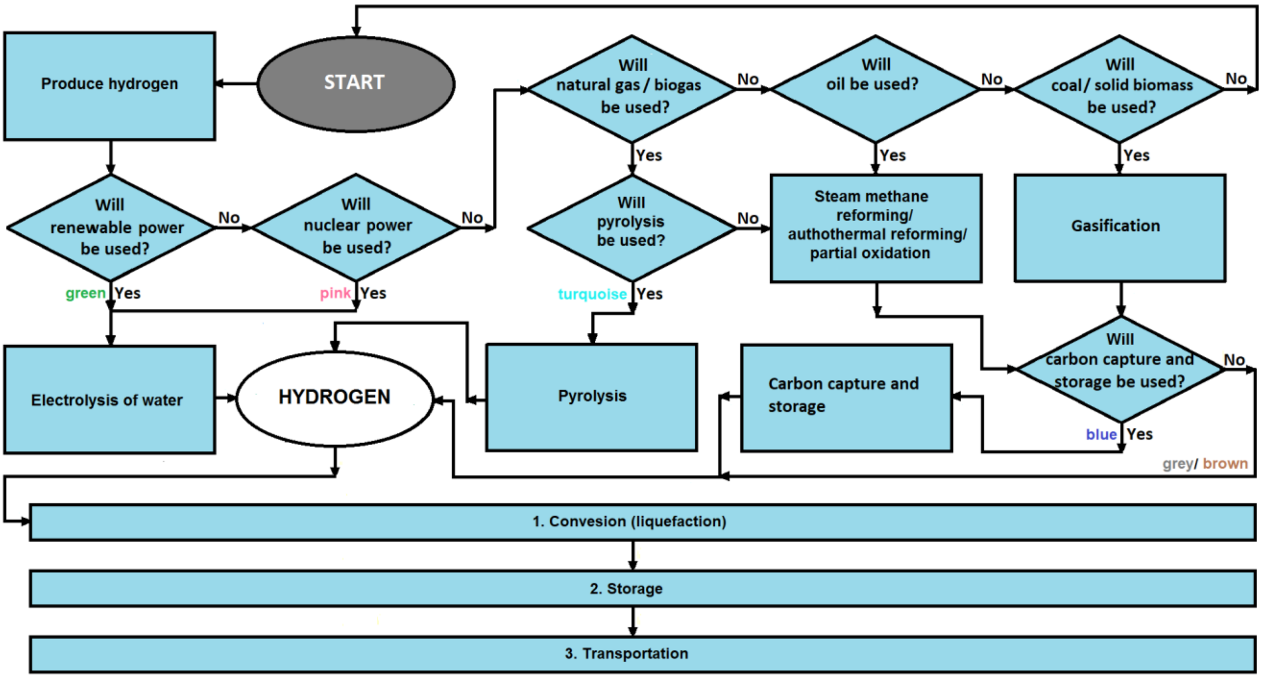
[2] Around 3 kWh/m^3 (IDEALHY, 2022).
[3] About 2,300 kWh/m^3 (ibid).
[4] Over 10,000 kWh/m^3 (H2Data, 2022).

2017, Niermann et al, 2019, Ishimoto et al, 2020, Raab, Maier, and Dietrich, 2021). In addition, they also appear to be the fuels under consideration for most of the current hydrogen delivery projects (ibid).

Figure 2: Simplified decision-making and value chain flow chart for the large-scale production of most common 'colours' of hydrogen



Source: Adapted from US Department of Energy (2020), Air Liquide (2020), Global CCS Institute (2021)

Examples include the shipment in February 2022 by Australia of the world's first commercial shipment of liquid H_2 to Japan with a help of its own specially built liquified hydrogen carrier. This came a year after Saudi Arabia's successful pilot delivery of its 'blue' ammonia to the same destination country (S&P Global, 2020 and Upstream, 2022). More remarkably, half a year prior to the transportation of the Saudi ammonia, Brunei's MCH was first shipped to Japan where it was then separated into hydrogen and toluene with the hydrogen ultimately being supplied to a gas turbine at the Mizue power station (Offshore Energy, 2020a).Methanol shipments have long been conducted over significant distances, with the US importing around 5 million tonnes of this fuel per annum from Trinidad and Tobago and Venezuela a decade ago (Royal Society of Chemistry, 2016).

II.2. Ammonia

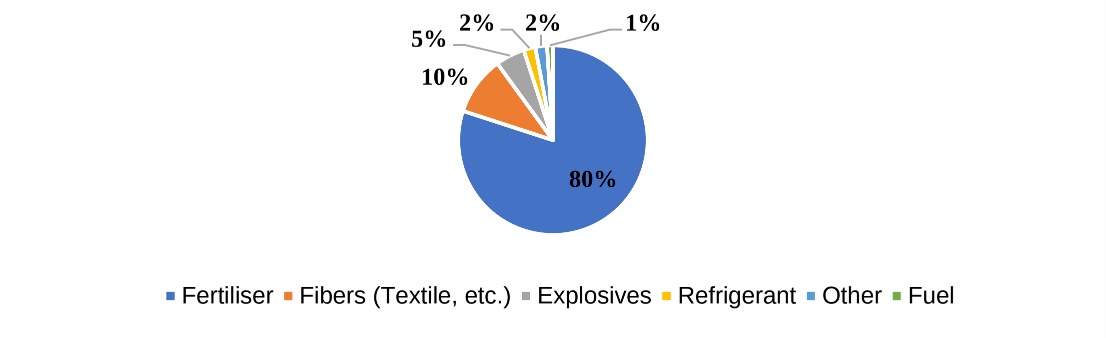
Ammonia (NH_3) has long been a critical commodity for a number of industries (Figure 3), but more recently it has been actively viewed as a potentially promising hydrogen carrier with relatively well-established international trade channels.[5] This is down to a number of factors. Primarily, although like H_2 it is gaseous under ambient conditions and thus needs to be liquefied for optimal delivery over long distances (Figure 4), there is a greater mass of hydrogen in a litre of liquid ammonia than in a litre of liquid H_2 (Kraemer, 2018). This is due to the fact that NH_3 is a 'better molecule at packing together with itself' in comparison to hydrogen (ibid, p. 1).

When liquefied, ammonia has a density almost ten times greater than liquid hydrogen (around 686 kg/m^3 compared to 71.1 kg/m^3) (Table 1). Under these conditions, although its gravimetric H_2 content will only be 17.65 wt% (in comparison to 100 wt% of liquid hydrogen), its volumetric H_2 content will be significantly higher (around 107.7 kg$_{H2}$/m^3 against 70.8 kg$_{H2}$/m^3). In fact, both the gravimetric and volumetric hydrogen contents of liquid ammonia will be higher than those of toluene/MCH (6.1 wt%

[5] At the moment, around 20 million tonnes of ammonia are traded on the world market (IHS Markit, 2022).

and 47.1 kg_{H2}/m^3) and methanol (12-12.5 wt% and 95.04-99 kg_{H2}/m^3), which makes it a more efficient hydrogen carrier compared to these options.

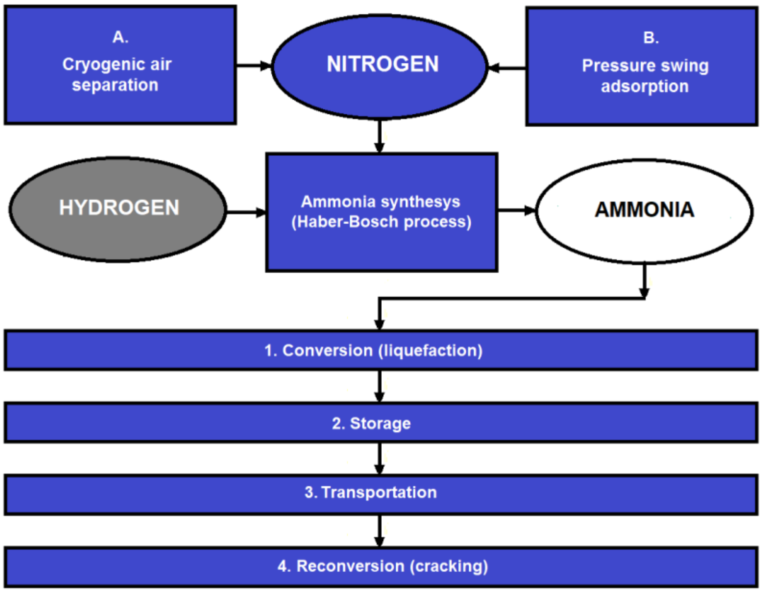
Figure 3: Global application of ammonia



Source: Adapted from Holleman and Wiberg (2001), ASHRAE (2017), Dissanayake (2017), US Geological Survey (2017), Perinelli et al (2019)

In contrast to hydrogen, ammonia's boiling point is much higher (-33.34 ^oC) and thus its conversion and preservation in liquid form requires less energy (Table 1). This higher boiling temperature also means that it will incur lower thermodynamic (BOG) losses when stored and transported, which, in turn, means that a lot more hydrogen can be delivered in the form of ammonia than directly as hydrogen. On the other hand, in contrast to MCH and methanol that are already liquid under ambient conditions, ammonia requires liquefaction which is an additional step in the value chain (see '1. Conversion (liquefaction)' in Figure 4)[6]. This will ultimately result in further energy losses and costs.

Figure 4: Simplified value chain flow chart for ammonia as hydrogen carrier



Source: Adapted from Patonia and Poudineh (2020) and Kim, Huh, and Seo (2022).

Since ammonia consists of nitrogen and hydrogen, another advantage of this fuel is that it could potentially be produced as a CO_2-neutral substance. With the ammonia molecule consisting of three atoms of hydrogen and one atom of nitrogen, H_2 generation constitutes most of the costs associated with NH_3 production. In this sense, through generating renewable hydrogen, the greatest share of the NH_3 synthesis could be made carbon-free. In addition, nitrogen production via either cryogenic air separation or through pressure swing adsorption as well as the ammonia cycle itself (the Haber-

[6] This 'additional' step often appears to be intrinsic in many cases, as ammonia's high boiling point relative to its heavier congeners is indicative of the formation of strong hydrogen bonding, which also results in a high heat of vaporization (23.35 kJ/mol) (Barron, 2020).

Bosch process) are both potentially electrifiable, which means that NH_3 generation can be completely decarbonized (Kyriakou, 2020 and Greenhouse Insights, 2021).

Towards the end of the value chain, ammonia can be used directly as a feedstock (e.g. to produce fertilizers or explosives), but it can also be used as a fuel. The latter usage becomes even more important when one considers that it could theoretically make shipping NH_3 even less challenging if it is used as a propellant for marine vessels carrying the ammonia. The first ship to use an ammonia-powered fuel cell is due to be launched in the second half of 2023, by the Fraunhofer Institute for Microengineering and Microsystems (Fraunhofer, 2021). Similarly, Wärtsilä, a Finnish technology company, is currently coordinating an EU-funded project that aims to develop combustion engines running on pure ammonia that could be used by marine vessels by 2023 (Wärtsilä, 2022). While using ammonia in fuel cells generates neither carbon oxides (COx) or nitrogen oxides (NOx), burning ammonia will most likely be associated with the release of nitrogen oxides without any carbon emissions (as ammonia does not contain carbon) (Lipman and Shah, 2007):

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$$

While emissions associated with NO_x still represent a significant challenge for many ammonia combustion technologies, as they appear to be the product of incomplete oxidation of NH_3 (Mashruk et al, 2021)[7], using ammonia as an H_2 carrier will mean decomposing it at the final stage before the hydrogen can be used by the ultimate consumer. This type of ammonia cracking, in turn, will not result in CO_2 releases for the same reason (NH_3 does not contain carbon):

$$2NH_3 \rightleftharpoons N_2 + 3H_2$$

In this sense, if produced in a carbon-free way, then stored and delivered for ultimate decomposition to extract H_2, ammonia may represent an attractive zero-CO_2 hydrogen carrier.

II.3. MCH

The idea for using liquid organic hydrogen carriers (LOHC) to store and deliver H_2 over long distances is based on the idea that molecules which are typically liquid at ambient conditions could be loaded with hydrogen (i.e. hydrogenated) by the energy supplier and unloaded (i.e. dehydrogenated) by the importer or end user (Papadias, Peng, and Ahluwalia, 2018). Due to the fact that no further conversion (liquefaction) is needed (Figure 5), using LOHCs will result in lower thermodynamic and energy losses and thus reduce ultimate costs incurred by the transporter and the end user (ibid). In addition, apart from a lower risk of leakage, these hydrogen carriers are often already compatible with present transport and refueling infrastructures (Rao and Yoon, 2020). Furthermore, LOHCs in many cases are by-products of oil refining and thus are already available and not specifically produced for hydrogen delivery (Bender, 2013). Here, due to the very nature of LOHCs, they could be re-used as hydrogen carriers many times, which will further reduce hydrogen delivery costs (ibid).

While LOHCs generally encompass quite a wide range of different substances, most of the current research and pilot projects are centred round toluene ($C_6H_5CH_3$), which, when hydrogenated, is transformed into methylcyclohexane (MCH) ($CH_3C_6H_{11}$) that is ultimately used for storing and transporting H_2. Although naphthalene-decalin, benzene-cyclohexane, dibenzyltoluene (DBT)-perhydro-dibenzyltoluene (PDBT), among others, have also been viewed as candidates for performing the role of hydrogen carrier enabling H_2 storage and trade, toluene-MCH has been particularly favoured by both researchers and businesses (Wijayanta et al, 2019). One of the key reasons for this is the higher boiling point (111 ^oC for toluene and 101 ^oC for MCH) (Table 1).

[7] When ammonia is completely combusted, it only produces nitrogen and water without involving the production of NO_x: $4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$ (Kobayashi et al, 2019), However, in practice, ammonia combustion creates NO_x emissions, which are composed of the thermal NO_x (produced by the oxidation of N_2 at high temperature) and fuel NO_x (generated mainly by the oxidation of NH_3) (Li et al, 2021).

Table 1: Key characteristics of main potential hydrogen carriers

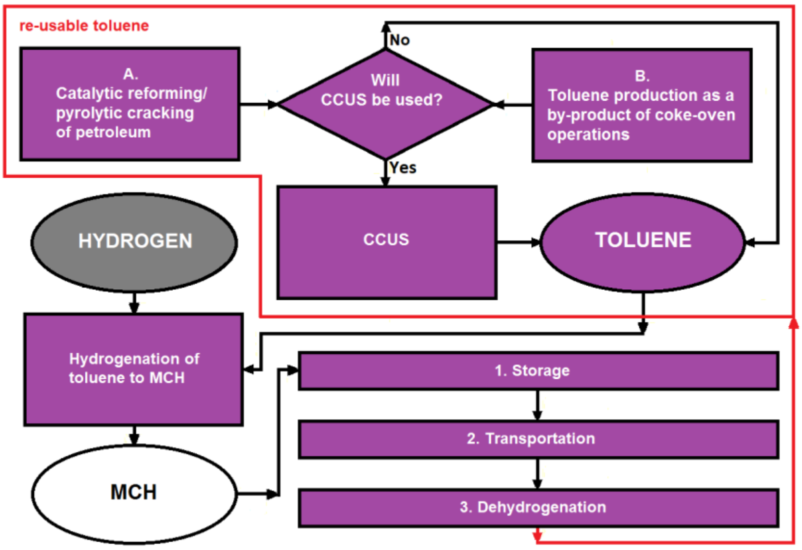
	Key characteristics	Hydrogen		Ammonia	Methylcyclohexane (MCH)	Methanol
	Chemical formula	H_2		NH_3	C_7H_{14} ($CH_3C_6H_{11}$)	CH_3OH
	Molecular weight (g/mol)	2.016		17.031	98.186	32.04
	Density under normal conditions (kg/m^3)[8]	0.08375		0.73	866.9	791.4
	Melting point (^oC)[9]	-259.16		-77.73	-126.3	-97.6
	Boiling point (^oC)[10]	-252.87		-33.34	101	64.7
Production	*Most popular production process*	Steam methane reforming	Coal gasification	Haber-Bosch process	Hydrogenation of toluene C_7H_8 ($C_6H_5CH_3$)	Carbon hydrogenation/ Methanation
Production	*Chemical reaction*	$CH_4 + H_2O \rightleftharpoons CO + 3H_2$	$3C + O_2 + H_2O \rightarrow H_2 + 3CO$	$N_2 + 3H_2 \rightleftharpoons 2NH_3$	$CH_3C_6H_5 + 3H_2 \rightarrow CH_3C_6H_{11}$	$CO + 2H_2 \rightleftharpoons CH_3OH$; $CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O$
Production	*Catalysts involved*	Usually Ni (but possible Ru/Rh/Pd/Ir/P)	K_2CO_3/ K_2S/ Na_2CO_3/ Na_2S	Fe-based catalyst	Ni-based catalyst (non-PGM)	Cu/ZnO/Al_2O_3 catalyst
Production	*Pressure (bar)*	3-25	<100	150	10	51
Production	*Temperature (^oC)*	700-1,000	>750	~375	~240	~250
Production	*BOG (%)*	~0.52		~0.025	~0.0005	
Storage and transportation (Liquid)	*Density under conditions suitable for storage/ transportation (kg/m^3)*	71.1		686	866.9	791.4
Storage and transportation (Liquid)	*Pressure for storage/ transportation (atm)*	1				
Storage and transportation (Liquid)	*Favourable temperature for storage/ transportation (^oC)*	<= -252.87		<= -33.34	20-25	
Storage and transportation (Liquid)	*Gravimetric energy density (MJ/kg)*	120		21.18-22.5	7.35	20.1-22.4
Storage and transportation (Liquid)	*Gravimetric H_2 content (wt%)*	100		17.65	6.1	12-12.5
Storage and transportation (Liquid)	*Volumetric energy density (Wh/L)*	8.49		12.92-14.4	5.66	11.40-11.88
Storage and transportation (Liquid)	*Volumetric H_2 content (kg_{H2}/m^3)*	70.8		107.7-120	47.1	95.04-99
Storage and transportation (Liquid)	*Explosive limit in air (vol%)*	>4		15-28	1.2-6.7	6.7-36
Decomposition	*Most popular process*	Heating/evaporation		High-temperature cracking	Dehydrogenation	Steam reforming
Decomposition	*Chemical reaction*	n/a		$2NH_3 \rightleftharpoons N_2 + 3H_2$	$CH_3C_6H_{11} \rightleftharpoons C_6H_5CH_3 + 3H_2$	$CH_3OH \rightleftharpoons CO + 2H_2$; $CO + H_2O \rightarrow CO_2 + H_2$
Decomposition	*Catalysts involved*			Ni catalyst	Pt/Al_2O_3 catalyst	Cu-based catalyst
Decomposition	*Pressure (bar)*			20	2	3
Decomposition	*Temperature (^oC)*	> -252.87		~800	~350	~290
Decomposition	*Enthalpy ΔH (kJ/mol)*	0.899-0.907		30.6	68.3-69.8	16.3-16.6

Source: Adapted from Chadwick, Highton, and Lindman (1987), Bobyloyov (2003), Beurden (2004), Yu et al (2012), Usman, Cresswell, and Garforth (2013), Usman, Alotaibi, and Aslam (2015), Hobson and Marquez (2018), Kurosaki (2018), Papadias, Peng, and Ahluwalia (2018), Aziz, Oda, and Kashiwagi (2019), Al-Breiki and Bicer (2020a), Aziz, Wiayanta, and Nandiyanto (2020), Letcher (2020), Lloyd's Register (2020), Wan et al (2021), CONCOA (2022), NIST (2022), US Department of Energy (2022).

[8] According to NIST (2022) standard, normal temperature and pressure are 20°C (293.15 K, 68 °F) and an absolute pressure of 1 atm (14.696 psi, 101.325 kPa).
[9] The melting point could be generally defined as the temperature at which the solid and liquid forms of a pure substance can exist in equilibrium (Helmenstine, 2019).
[10] The boiling point of a pure substance is the temperature at which the substance transitions from a liquid to the gaseous phase (ibid).

Normally produced either through catalytic reforming and pyrolytic cracking of petroleum or as a by-product of coke-oven operations (Figure 5), toluene is mainly used as a precursor to several chemicals (e.g. benzene, phenol, toluene diisocyanate), as a solvent for paints and coatings or as an octane booster in gasoline and thus is utilized primarily as a feedstock for the production of higher-value commodities (Papadias, Peng, and Ahluwalia, 2018). Toluene is a product with a well-established infrastructure that is not new to the market, and therefore handling toluene-MCH is unlikely to require significant infrastructure adjustments nor a completely new legislative framework to regulate it, compared to hydrogen (ibid).

Figure 5: Simplified value chain flow chart for MCH as hydrogen carrier



Source: Adaptation from Papadias and Ahluwalia (2020), CSIRO (2022)

On the other hand, compared to the other fuels viewed in this analysis (liquid hydrogen, ammonia, and methanol), MCH has the lowest gravimetric and volumetric energy densities as well as the lowest gravimetric and volumetric H_2 content (Table 1). This means that, despite its many advantages, if used as a hydrogen carrier, toluene-MCH will deliver the lowest quantity of H_2 out of all four substances. Consequently, given that its density is the highest of the four fuels (866.9 kg/m^3), using it to transport H_2 will mean incurring significant energy losses and costs that would not be associated with value generation – i.e., hydrogen transport. In fact, they will be related to the transportation of the toluene itself.

In addition, although shipping and storage of LOHCs can be done under ambient conditions using existing systems for hydrocarbons, toluene-MCH as well as other most efficient carriers do have high capital costs (Rao and Yoon, 2020). Furthermore, after dehydrogenation of MCH, often the unloaded toluene (or other carrier molecule) needs to be returned to the energy supplier for hydrogenation (Salmon and Bañares-Alcántara, 2021). Given the high density and thus weight of toluene and its alternatives, this, again, will generate additional costs.

II.4. Methanol

Another promising candidate for hydrogen storage and long-distance delivery is methanol (CH_3OH). Although it is traditionally produced from natural gas, coal, or even biomass via steam reforming and gasification, there is an option to generate e-methanol from ‘green’ hydrogen and captured CO_2[11] (Figure 6). While this type of methanol is still several times more expensive than the conventionally synthesized CH_3OH, its adoption strongly correlates with the idea of power-to-product (P2X), which utilizes surplus electricity to produce chemical fuels (Bowker, 2019). While the same idea lies behind

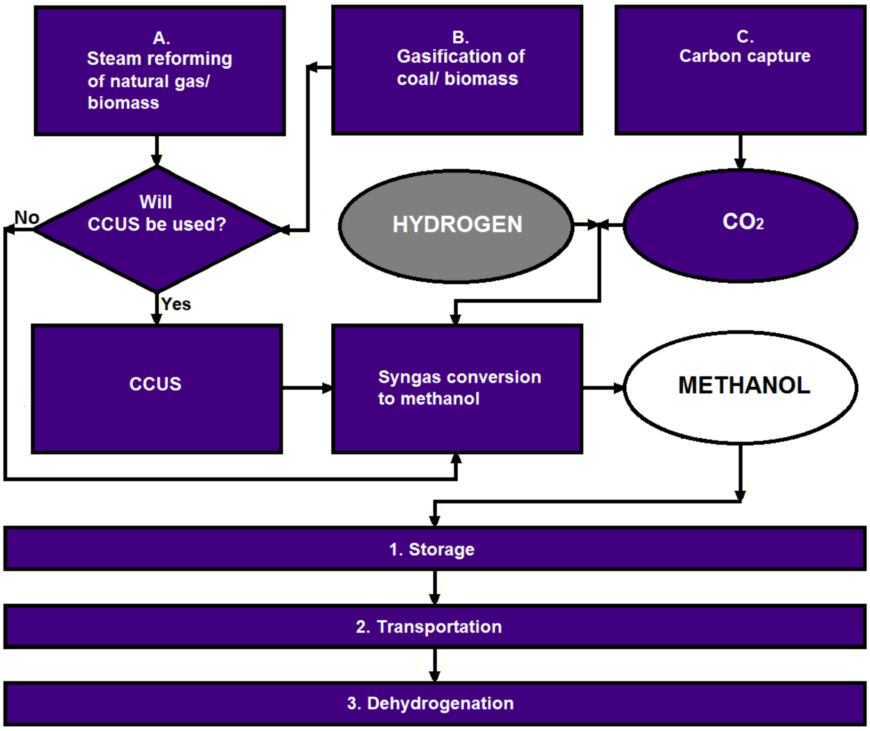
[11] Although the idea of using captured or industrially-generated carbon dioxide for the production of e-methanol has been actively promoted, it still faces a number of technical and economic challenges, as CO_2 capture technologies have not been fully commercialised and thus their cost will increase the price of e-methanol making it less competitive.

‘green’ hydrogen and ammonia development, in contrast to those fuels, methanol is liquid under ambient conditions and thus is easier to store and deliver.

Out of the four fuels under consideration in this paper, methanol is the second densest substance (791.4 kg/m_3) after MCH (Table 1). In addition its volumetric energy density and H_2 content (11.40-11.88 Wh/L and 95.04-99 kg_{H2}/m^3, respectively[12]) are second only to liquid ammonia. This generally means that methanol will be a more effective H_2 carrier in terms of transported volume than MCH and liquid hydrogen itself. Additionally, as it is liquid under ambient conditions, methanol will experience less significant thermodynamic losses and will not require additional costs for conversion (liquefaction) and temperature maintenance like ammonia or hydrogen.

A further point in its favour is that, like ammonia, apart from being just a cargo that carries hydrogen, methanol could potentially perform the function of a low-emission marine fuel that could be used by a methanol tanker. The concept of methanol fuel cells is being actively developed (Methanol Institute, 2022), and CH_3OH appears to be a decent substitute for most of the combusted marine propellants. Although when incinerated it will generate carbon dioxide,[13] in contrast to most popular conventional fuels, combusted CH_3OH will not be associated with the emission of sulphur oxides (SOx), nitrogen oxides (NOx) and particulate matter (Methanex, 2022).

Figure 6: Simplified value chain flow chart for methanol as hydrogen carrier



Source: Adapted from Hobson and Marquez (2018), IRENA (2021)

While ammonia-powered marine vessels have only recently gained significant attention, methanol-fueled ships have already been successfully operating for almost a decade[14] (Offshore Energy, 2020b). In fact, Finnish technology company Wärtsilä, Swedish ferry company Stena Line, and the Canadian supplier of methanol Methanex Corporation have successfully converted the Stena Germanica – a ferry originally using bunker fuel – into a vessel capable of running on CH_3OH in 2015 (ibid). This type of vessel was better prepared for the 2020 restrictions of the International Maritime Organization which forced a dramatic limit in SOx emissions from maritime transport (ibid).

[12] Since both indicators depend on such variables as temperature and pressure, they are represented as a range

[13] Combustion of methanol: $2CH_3OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(l)$.

[14] Alcohol fuels (e.g. methanol and ethanol), in general, have been long successfully used in conventional gasoline-powered vehicles by blending or pure combustion, since they generally improve engine performance and reduce pollutant emissions (Li et al, 2022).

It is worth highlighting that, if methanol's combustion is incomplete, formaldehyde is formed [15] (Ninomiya, Golovoy, and Labana, 1970 and Lervold et al, 2021). Apart from creating additional pollution concerns, this will also generate a significant threat, as formaldehyde is a colourless, flammable, and highly toxic gas, which is easily absorbed by the lungs, gastrointestinal tract, and skin (ATSDR, 2014). While inhalation of formaldehyde gas in even small quantities is usually followed by bronchitis and pneumonia, exposure to larger quantities may result in severe systemic toxicity, leading to metabolic acidosis, tissue and organ damage, and coma (ibid). That is why the safe use of methanol as a fuel for marine vessels will require significant effort from engineers to construct highly efficient engines with maximum combustion levels.

In addition to the above, despite all its potential advantages, methanol has further drawbacks. Within the context of global decarbonization, its major issue relates directly to the structure of its molecule which contains carbon. As a result, towards the final stage of its use as a hydrogen carrier, at the point when methanol needs to be decarbonized, the very process of extracting H_2 will ultimately be associated with carbon emissions[16] (Table 1). Although these could potentially be avoided through carbon capture, utilization, and storage (CCUS) applications, the technological maturity of such projects is still not at a level which allows for their full commercialization and large-scale use (Kearns, Liu, and Consoli, 2021).

As a result, while using methanol as a hydrogen carrier may have technical and economic backing, thinking of this fuel as a completely carbon-free alternative to other H_2 drivers will require additional adjustments to the dehydrogenation process and thus additional associated costs.

III. Thermodynamic and conversion losses and costs

III.1. Thermodynamic and conversion losses and ultimate quantities of hydrogen delivered

As demonstrated in the previous section, each of the four hydrogen carriers has its advantages and disadvantages. For instance, while some fuels could potentially eliminate carbon from their value chain (ammonia and hydrogen itself), others will need technological solutions that would either minimize their carbon footprint or completely eliminate it (toluene/MCH and methanol). Although it is primarily their attractive chemical properties that would allow them to be used as hydrogen transporters, their diverging physical features differentiates each of them in terms of how efficient they would be in performing this function. In this context, it is worth comparing the approximate thermodynamic as well as energy losses encountered by each of the substances at the key stages in their value chains (Table 2).

Predictably, the fuels that are liquid under ambient conditions (toluene/MCH and methanol) experience lower BOG losses along the value chain until reconversion (dehydrogenation) comes into play. They also do not require additional energy to be preserved in a liquid form. At the conversion point, however, all the fuels except liquid H_2 need a lot of energy to be dehydrogenated (MCH and methanol) whereby hydrogen is released for further use. Here, out of the three alternatives (ammonia, MCH, and methanol), ammonia is the one incurring lower thermodynamic and energy losses in this 'pre-deployment' process. At the same time, at the final stage of the value chain, due to no energy and thermodynamic losses, liquid hydrogen is the most efficient option of these four in terms of costs and losses associated with reconversion.

These estimates, however, do not demonstrate how much H_2 could ultimately be delivered by each fuel to the end user, which is perhaps the main function that an H_2 carrier should perform. That is why it seems reasonable to compare the amounts of hydrogen that the end user will get at the end of the value chain via each of the transportation options. To do so, two hydrogen delivery routes that are likely to become popular in the future will be examined: Australia – Japan and Morocco – The Netherlands. Here, Gladstone (Australia's possible point of hydrogen export) and Yokohama, one of Japan's most important ports, will serve as the start and end points for the first route. Similarly, the Moroccan port of Nador West Med, a potential hydrogen hub that is currently under construction

[15] Partial oxidation of methanol: CH_3OH (g) + ½ O_2 → CH_2O (g) + H_2O (g).
[16] Dehydrogenation of methanol: $CH_3OH \rightleftharpoons CO + 2H_2$; $CO + H_2O \rightarrow CO_2 + H_2$.

(European Council on Foreign Relations, 2022) and Rotterdam will perform the same functions for the second route.

Table 2: Approximate energy consumption and BOG rates along the hydrogen, ammonia, MCH, and methanol supply chains[17]

	Hydrogen	Ammonia	MCH	Methanol
Energy required for liquefaction/storage (MJ/ kg)	15.1-57	>6.73[18]	n/a	n/a
BOG of storage (%/day)	0.06-0.4	0.024-0.1[19]	0.00416-0.065	0.00032-0.005
Energy required for loading/ unloading (MJ/kg)	~0.00196			
BOG of loading/ unloading (%)	0.0814-3.6	0.022-1.2	>0.034	>0.01667
Energy required for reconversion (dehydrogenation) (MJ/kg)	n/a	>30,67	>43.38	>32
BOG of dehydrogenation (%)	n/a	>1.377	>2.52	>2.47
Total – **Energy (MJ/kg)**	15.1-57	>37.4	>43.4	>32
Total – **BOG (%)**	0.1414-4	1.42-2.677	2.56-2.62	2.48-2.49

Source: Adapted from Bossel and Eliasson (2003), Vervondern (2008), Teichmann (2015), Juangsa et al (2018), Papadias, Peng, and Ahluwalia (2018), Niermann et al (2019), Wijayanta et al (2019), Salmon and Bañares-Alcántara (2021), Schorn et al (2021), Al-Ghafri et al (2022), Smith, Glantonas, and Mastorakos (2022).

This will mean that the approximate distance to cover by tankers will be around 3,367 nm (6,791 km) in the case of Australia-Japan and about 1,438 nm (2,747 km) in the case of Morocco-Netherlands (Table 3). With an average tanker speed of 14 knots, it will take roughly 9.5 days to deliver cargo from Gladstone to Yokohama and 3.8 days to ship it from Nador West Med to Rotterdam. Bearing this in mind and incorporating a typical storage volume for long-distance tankers (160,000 m^3) into the calculations, gives the following results represented in Table 3.

The table shows that although the transported volume will be the same for each of the options (liquid hydrogen, liquid ammonia, MCH, and methanol), the cargoes will differ significantly in terms of their mass due to the varying density of the fuels transported (kg/m^3) (Table 3). Here, using each of the H_2 carriers' density as well as the ship's capacity (160,000 m^3), the nominal capacity (nominal cargo's weight in kg) can be calculated as follows:

Nominal capacity (kg) = Ship's capacity (m^3) X Fuel's density under conditions suitable for storage/transportation (kg/m^3)

The results, however, will not demonstrate the real capacity, as the BOG losses associated with loading should also be included:

Real capacity (kg) = Nominal capacity (kg) – Nominal capacity (kg) X BOG for loading (%)

As seen from the table, these calculations demonstrate that the MCH cargo will be the heaviest followed by methanol and then liquid ammonia, whereas liquid hydrogen itself will be the lightest. This will generally be reflected by additional costs incurred by the transporting entity, as a heavier cargo will result in greater consumption of fuel and thus additional expense. At the same time, if all the thermodynamic losses for each stage along the value chain are included, the pre-dehydrogenation

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[17] The estimates are provided for a storage volume of 160,000 m^3. Commonly, the volume of cryogenic tanks used to store the four liquids being assessed ranges from 80,000 - 160,000 m^3 (Al-Breiki and Bicer, 2020b) Also, the storage capacity of the majority of tankers used for long-distance transportations ranges between 120,000 m^3 and 160,000 m^3, with some exceptions being of up to 270,000 m^3 (ibid).

[18] This number represents the minimum amount of energy required for liquefaction provided in the literature.

[19] At the moment, ammonia BOG is minimised with the help of condensers that are normally part of an industrial refrigeration system and dissipate all the heat that is extracted from a refrigerated space to the outside (Intersam, 2022).

quantity of each fuel will also differ from the starting point. Here, although only transportation, loading and 3-day storage were included for the sake of simplicity, the BOG losses were shown to be highest for liquid hydrogen and ammonia and lowest for methanol and MCH for both routes (Australia-Japan and Morocco- Netherlands).

Table 3: Approximate thermodynamic and conversion losses for selected marine transportation routes of liquid hydrogen, ammonia, MCH, and methanol[20]

#	Indicators	Liquid hydrogen	Liquid ammonia	MCH	Methanol
	Ship capacity (m^3)	160,000			
	Nominal capacity (tonnes)[21]	11,376	109,760	138,704	126,624
	Real capacity (tonnes)[22]	~11,375.8	~109,757.8	~138,701.3	~126,621.5
1	***Australia-Japan (Gladstone-Yokohama)***				
Distance and time	Distance (nautical miles)	3,667			
	Distance (km)	6,791			
	Sailing time (days)[23]	9.5			
Transportation	Delivered quantity (tonnes)	11,310-11,330	108,715-109,508	137,845-138,646	126,561-126,618
Unloading	Pre-storage quantity (tonnes)	10,904-10,922	107,411-109,484	137,798-138,599	126,540-126,597
3-day storage	Pre-dehydrogenation quantity (tonnes)	9,726-10,913	107,088-109,405	137,529-138,582	126,521-126,595
Dehydro-genation	**Final H_2 quantity (tonnes)**	**9,726-10,913**	**18,901-19,310**	**8,389-8,454**	**15,183-15,824**
2	***Morocco – the Netherlands (Nador West Med – Rotterdam)***				
Distance and time	Distance (nautical miles)	1,483			
	Distance (km)	2,747			
	Sailing time (days)	3.8			
Transportation	Delivered quantity (tonnes)	11,203-11,350	109,341-109,658	138,359-138,679	126,597-126,620
Unloading	Pre-storage quantity (tonnes)	10,800-11,341	108,029-109,634	138,312-138,632	126,576-126,599
3-day storage	Pre-dehydrogenation quantity (tonnes)	10,670-11,320	107,705-109,555	138,042-138,615	126,557-126,598
Dehydro-genation	**Final H_2 quantity (tonnes)**	**10,670-11,320**	**19,010-19,336**	**8,421-8,456**	**15,187-15,825**

Source: Calculations made on the data obtained from Seddon (2006), Al-Breiki and Bicer (2020a), Port World (2022).

The most important task, however, is to identify the ultimate amount of hydrogen that will be available for direct use after all the steps in the value chain have been passed – i.e. after cracking of ammonia and dehydrogenation of MCH and methanol. This can be calculated using each of the fuels' gravimetric H_2 content (wt%) (Table 1)*:*

Final H_2 quantity (kg) = Pre-dehydrogenation fuel quantity (kg) X Fuel's gravimetric H_2 content (%)

As the table demonstrates, in both cases (Australia-Japan and Morocco-Netherlands), liquid ammonia is capable of delivering more hydrogen than the remaining three alternatives, over two times higher than that transported by MCH and almost two times the quantity of H_2 shipped in liquid form. Here, methanol is the runner-up, as it delivers slightly less hydrogen than liquid ammonia, but around 1.5 times more than liquid H_2 and two times more than MCH.

[20] Given the reconversion losses, it might be more useful to utilize ammonia and methanol directly rather than dehydrogenate them. This paper, however, provides the calculations illustrating how both can be used as H_2 carriers.
[21] Nominal capacity (kg) = Ship capacity (m^3) x Density under conditions suitable for storage/ transportation (kg/m^3).
[22] Real capacity (kg) = Nominal capacity (kg) – Nominal capacity (kg) X BOG for loading (%).
[23] Sailing time (hours) = Distance (miles) / (Speed (knots) X 1.15). 1 knot = 1.15 miles/hour (Metric Conversions, 2022). Average speed of a vessel transporting gases over long distances is 14 knots (JWN Energy, 2017).
Sailing time (days) = Sailing time (hours) / 24.

If we compare the same hydrogen carriers in terms of how much energy they could ultimately transport, the situation would look in quite a similar way (Table 4). Specifically, MCH again appears to be the option capable of transporting the lowest energy quantity among all the viewed alternatives. It is then followed by liquid hydrogen, which is still substantially lagging behind liquid ammonia and methanol that, if put in the same volume, are capable of ultimately deliver almost twice as much energy as H_2 itself.

Table 4: Comparison of approximate energy delivered by each hydrogen carrier for both routes (in EJ)[24]

Indicators	Liquid hydrogen	Liquid ammonia	MCH	Methanol
Ship capacity (m^3)	160,000			
Energy before shipping (EJ)	~1.4	~2.5	~1.0	~2.8
Australia-Japan (Gladstone-Yokohama)				
Energy delivered (EJ) before dehydrogenation (if applicable)	1.2-1.3	2.4-2.5	~1.0	~2.8
Energy delivered (EJ) after dehydrogenation (if applicable)		~2.3	~1.0	1.8-1.9
Morocco – the Netherlands (Nador West Med – Rotterdam)				
Energy delivered (EJ) before dehydrogenation (if applicable)	1.3-1.4	2.4-2.5	~1.0	~2.8
Energy delivered (EJ) after dehydrogenation (if applicable)		~2.3	~1.0	1.8-1.9

Source: Calculations made on the data obtained from Seddon (2006), Al-Breiki and Bicer (2020a), Port World (2022)

In summary, while MCH will represent the heaviest cargo, it will also be the fuel that will deliver the lowest quantity of H_2. On the other hand, while liquid hydrogen will be the lightest, it will be the second in terms of lowest effectiveness in delivery. Finally, while liquid ammonia and methanol generally appear to be similar in terms of how heavy they will be and how much H_2 they could carry, NH_3 will ultimately be more effective, as, with its lower weight, it will ship more hydrogen (Table 3).

III.2. Cost comparison and further considerations

While the consideration of thermodynamic and conversion losses is important, identifying the approximate costs associated with the use of each fuel for hydrogen delivery is crucial for the creation of a sound business case. In this sense, it is useful to compare the minimum average costs associated with crucial stages in the value chain for the viewed fuels (Table 5).

Although the generation phase for each option appears to be crucial in defining its life cycle, it does not seem to be the core cost component along the value chain for all the fuels viewed in this study. For instance, when hydrogen is considered, the share of its production expenses is amongst the lowest if compared to the costs associated with the remaining stages. Here, shipping, liquefaction, and specifically storage, are the most capital-intensive parts of the life cycle. In fact, even without any capital losses related to reconversion, the total cost of transportation for liquid hydrogen inclusive of all elements across the value chain is likely to be several times higher than that for the other fuels.

Quite predictably, both MCH and methanol will have zero direct costs associated with their storage, and would incur most of the expenses associated with their life cycles when they are produced and reconverted to hydrogen. At the same time, it should be noted that, due to the high weight of MCH, its transportation costs will be higher than those of methanol and would, in fact, approach those of liquid hydrogen. This is without including the costs associated with transporting the toluene regained after dehydrogenation back to the MCH producer. Hence, given the low volume of hydrogen delivered by this carrier, adding all these costs might make this H_2 delivery option less attractive.

[24] 1 EJ (Exajoule) = 10^{12} MJ (Megajoules).

Table 5: Approximate minimum levelized costs[25] for the key stages in the value chains for hydrogen, ammonia, MCH, and methanol (USD/kg-H_2)

Focus fuel	Production	Conversion		Storage	Shipping[26]	Reconversion	Sum of the components[27]
H_2	>1	Liquefaction	1.7-3.6	>4.57	1.7-2.6	n/a	**>8.97**
Ammonia	>2.20	Liquefaction	0.75-1.5	>0.5	0.56-0.82	0.30-1.6	**>4.31**
MCH	>1.35	n/a		n/a	1.37-2.07	0.54-1.22	**>3.26**
Methanol	>1.22	n/a		n/a	0.68-0.87	0.43-1.12 (dehydrogenation) + >0.6 (CCS)	**>2.93**

Source: Adapted from Ammonia Energy Association (2020), BloombergNEF (2020), IRENA (2021), Papadias, Peng, and Ahluwalia (2021), SG H2 Energy (2021), ChemAnalyst (2022), Johnston et al (2022), KPMG (2022), Zhao, Kamp, and Lukszo (2022).

As a result, both liquid ammonia and methanol would appear to offer better hydrogen delivery options in terms of the final quantity of H_2 transported to the end user as well as approximate minimum costs. Liquid hydrogen and MCH, in turn, are likely to be the fuels with highest total minimum costs and lowest shipped H_2 quantity, respectively. Although the data provided in Table 5 for the expenses associated with each stage in the value chain represent the minimum amounts indicated in the current literature, it is quite possible that, due to technological improvements as well as various external factors, these figures will change. For instance, since the ultimate decarbonization of the methanol value chain would most likely require applying CCUS at the dehydrogenation phase (when these technologies are ready for commercial use), these costs will have to be added to the total expenses related to using CH_3OH as a hydrogen carrier? In addition, while Table 5 shows the average minimum production costs which reflect conventional generation methods on a large scale, in the overall decarbonization scenario, these figures are likely to be replaced with ones reflecting the expenses of the synthesis of these fuels using renewable energy.

IV. Other aspects to consider

While both the ultimate total costs and the quantity of delivered hydrogen are crucial for creating a business case for long-distance hydrogen delivery, they should not be the only factors to consider when deciding which specific option to rely on for shipping H_2 overseas. In fact, none of the four fuels appears to be flawless (Table 6). For example, while fuels such as liquid hydrogen and ammonia as well as methanol seem more attractive from a purely techno-economic perspective, all of them raise significant safety considerations as they are either highly toxic (ammonia, MCH, and methanol) and/or flammable (hydrogen, MCH, and methanol). This means that, apart from creating the need for additional precautionary measures, the use of these H_2 carriers is likely to raise the issue of customer/public acceptance, which, in turn, may push the issue into the socio-political arena.

While perhaps not being the decisive issue that will ultimately determine whether the development of the hydrogen carriers under consideration will be successful, social acceptance of projects related to these chemicals will still most likely be extremely important. In fact, even with the technical possibility of guaranteeing the safe operation of H_2 production, storage, and delivery, public opposition to such initiatives may cause substantial challenges. It should be remembered that several European CCS pilots had to be terminated in countries like Germany and Poland due to the strong resistance of local

[25] The minimum levelized costs for each stage in the value chain could be generally defined as the minimum price at which this stage makes sense for the entire process to break even.

[26] These numbers are approximate and provided for distances over 1,000 km.

[27] Here, since 1 kg of H_2 contains 33.33 kWh of usable energy (H2Data, 2022), these results could be converted to USD/kWh for each fuel and would be >0.269 (hydrogen), >0.129 (ammonia), >0.098 (MCH), and >0.088 (methanol).

communities (Patonia, 2022), so evaluating public perception of hydrogen delivery in all its forms is important.

Another important factor to consider will be the necessity of creating or adjusting the existing legal and regulatory frameworks associated with the specific fuel option that is ultimately decided upon. Here, the use of ammonia and methanol as separate products with already relatively well-developed value chains that presuppose their production, storage, and delivery over long distances will make the take-up of these fuels as H_2 carriers less complicated and time-consuming when compared to liquid hydrogen. Similarly, using toluene – a fuel that has long been utilized by chemical industries and is easily storable compared to hydrogen – is likely to require only insignificant adjustments from a legal and regulatory perspective.

Table 6: Summary of the main advantages and challenges of the hydrogen carriers in question: liquid hydrogen, liquid ammonia, MCH, and methanol

	Hydrogen	Ammonia	MCH	Methanol
Advantages	• High purity • Carbon free • No need for dehydrogenation and purification • No/minimum energy losses in regasification • Commercialized liquefaction	• Possibility for direct use • High energy density and H_2 content • Not highly flammable • Carbon free • Possibility to utilize propane infrastructure/existing ammonia infrastructure • Low transport losses • Partially existing regulation	• Possibility to reuse toluene after dehydrogenation • Liquid storage without cooling • Existing storage infrastructure • Possibility to utilize existing gasoline infrastructure • Existing regulations	• Can be stored as liquid under ambient conditions • No need to largely adjust infrastructure in both storage and transportation (it is mostly in place)
Challenges	• Highly flammable • Need for extremely low temperature for liquefaction • High energy requirements for cooling and liquefaction • Difficulty for long-term storage • Requires boil-off control (0.2-0.3%/d in well-insulated tanker and up to 3%/d in truck) • Risk of leakage • Need for further development and scale-up of H_2 infrastructure	• Toxic and corrosive • Lower reactivity compared to hydrocarbons • Treatment and management by certified engineers • High energy use for dehydrogenation • Need for H_2 purification • Potential NOx emissions when used as shipping fuel and not completely combusted	• Toxic and corrosive • Highly flammable • Contains carbon • Toluene produced primarily as a by-product of oil refining • Expensive catalysts (Pt) used for dehydrogenation • Needs high temperature and large volumes of energy for dehydrogenation • Need for further H_2 purification • Additional costs for 'returning' toluene to the hydrogenation site	• Toxic and corrosive • Highly flammable • Contains carbon • Immature technology for renewable methanol production • Carbon (CO and CO_2) release during decomposition (steam reforming) • Need for further H_2 purification • Incomplete combustion/ incineration creates formaldehyde

By comparison, the development of a hydrogen value chain with liquid H_2 as its carrier may be a lot more challenging. Although H_2 has already been widely produced at an industrial scale in many locations, its consumption has mostly been localized. This means that hydrogen has so far been mainly consumed either next to its production site or within a relatively short distance from it. Indeed, the longest hydrogen pipeline in Europe, owned by Air Liquide, extends for just 250 miles from Northern France to Belgium, compared to the Yamal-Europe natural gas pipeline delivering Russian gas to the EU which is more than ten times longer at 2,608 miles (Argonne National Laboratory, 2008 and Forbes, 2011). To propose new and adjust the existing hydrogen-related regulatory framework will likely pose additional challenges of time and efforts that could have been saved for a more rapid lift-off of the sector.

Each hydrogen producer and exporter will also have to consider such issues as specific industries already developed in the country as well as the infrastructure available for their use. Here, for example, actors operating in countries with well-developing production of some fuels will end up in a disadvantaged position if they decide to rely on other hydrogen carriers that are relatively new to their economies. Similarly, nations with no particular predisposition towards the use of any specific fuel will be more flexible in this respect but will have to incur significant costs associated with the development of infrastructure from scratch. That is why, given that some of the options are quite similar (e.g., ammonia and methanol), the ultimate decision as to which hydrogen carrier to prefer is likely to be taken on a case-by-case basis.

For instance, in Chile, a country perennially involved in large-scale mining, building hydrogen export via the ammonia vector is likely to be a natural choice. This is because NH_3 is utilized as a feedstock for the production of explosives that are indispensable for the extraction of minerals that the country is so rich in (Figure 3). There, companies like Enaex – one of the world's leaders in blasting services, ammonium nitrate production, and products for fragmentation solutions – could become the drivers of H_2 build-up via NH_3 export (Enaex, 2022). Similarly, with the Methanex company having its methanol generation sites in Chile's Region of Magallanes as well as the Chilean Antarctic (Methanex, 2022), the country could also further expand the sector's CH_3OH export for follow-up hydrogen extraction in the key H_2 consuming regions of the world. Here, in the Chilean context, pursuing both ammonia and methanol options is likely to be more economically and technically sensible than developing an entire liquid hydrogen supply chain from scratch.

From a purely business perspective, building up industries with significant commercial potential outside of pure hydrogen use will entail fewer risks and thus is likely to attract a greater number of investors. In this sense, creating a hydrogen niche around those industries may also be viable. For example, exporting MCH to Germany or other countries with a well-developed chemical industry and leading in some specific markets such as the production of paints may make sense even if MCH seems to be a less efficient hydrogen carrier than the three remaining alternatives. In this case, shipping MCH to such destinations will mean simultaneous delivery of two products for follow-up use: toluene and hydrogen. While the hydrogen will then be consumed directly, toluene could be used as a feedstock for the production of paints, lacquers, glues, adhesives, etc. (US EPA, 2022).

In general, apart from existing industries that may further benefit from including hydrogen and its derivatives on their agenda, the consideration of country-specific factors such as the availability of human capital and experience in research and development as well as the management of specific technologies and projects may play a crucial role in promoting a certain H_2 carrying option. Similarly, a favourable economic environment and targeted policies as well as direct support to the related sectors are also likely to play their part in making specific carriers more preferable than other. In fact, in the case of competing H_2 delivery options with characteristics that are alike (e.g. liquid ammonia and methanol), these factors are likely to become decisive.

Finally, and significantly, those decision makers identifying which hydrogen carrier to rely on should consider the commercialization of other decarbonization technologies that could potentially dramatically change the overall approach towards H_2 delivery. Here, for example, the spread of large-scale use of CCUS, if successful, is likely to bring a major change not only to the very concept of shipping hydrogen overseas but also to the use of H_2 as a feedstock and energy source. Indeed, while some nations with extremely low cost hydrogen generation may still consider deploying H_2 overseas, countries that can successfully capture and store or use CO_2 will most likely not need hydrogen to the extent that the exporters originally planned. Instead, the already well-established 'conventional' fuels (e.g. LNG, coal) could be used at lower storage and shipping costs, while their emissions could be abated via CCUS at the very first (production) and last (utilization-e.g., production of hydrogen or direct use of methane) stages in the value chains. This, however, remains subject to the speed and peculiarity of technological progress as well as other external factors.

V. Conclusion

While creating a hydrogen economy is generally viewed as an important step towards comprehensive decarbonization, governments, businesses, and researchers are still largely uncertain about whether the hydrogen economy will become truly global or whether it will remain a largely local or regional phenomenon At the same time, if geographical and other country-specific factors continue to determine the costs of hydrogen production, delivery of H_2 over long distances including those of a transoceanic nature might make sense when the cost of import (i.e., production and delivery) is lower than that of domestic production. In these circumstances, choosing the most appropriate hydrogen carrier will be extremely important, as it will help to make the entire H_2 value chain more economical and efficient.

Out of all the long-distance hydrogen delivery options, liquid hydrogen and ammonia, methylcyclohexane, and methanol have gained the most attention in the literature and have already been tried by industries as H_2 carriers. Although each of these fuels has its own advantages and offers a special set of benefits, none of them is flawless or possess the characteristics of a perfect hydrogen shipping solution. This paper thus first focused on comparing the approximate thermodynamic and conversion losses that would be associated with each of the four mentioned options. It then focused on juxtaposing the approximate minimum levelized costs for the key stages in the value chains for liquid hydrogen and ammonia, MCH, and methanol. Finally, it highlighted additional issues that should be taken into consideration when comparing options for the purposes of choosing the optimal hydrogen shipping variant.

Having compared boil-off gas and conversion losses along the entire value chain for each of the analysed H_2 carriers, the paper identified liquid ammonia to be the most effective substance to deliver hydrogen over transoceanic distances out of the four under consideration. In fact, if hydrogen is converted to NH_3 which is then liquefied, the carrier ship will be able to deliver almost twice as much H_2 than if it was shipping liquid hydrogen itself. If the effectiveness of hydrogen delivery is looked at from this perspective only, methanol will then be the second choice, as it is potentially capable of transporting a slightly lesser amount of H_2 than liquid ammonia but almost twice as much as MCH, which will ultimately be viewed as the least effective carrier in these conditions.

At the same time, when it comes to the comparison of costs, methanol and MCH will most likely represent the cheapest alternatives. This is so primarily because of their relatively low production costs and no need of liquefaction. Since the ultimate expenses associated with the use of liquid ammonia will be nearing those of the two mentioned options, NH_3 could still be viewed as a relatively cost-effective means of delivering H_2. Paradoxically, liquid hydrogen itself is likely to be the most expensive hydrogen carrier out of the four.

On the other hand, thermodynamic and conversion losses as well as direct costs are not likely to be the only factors that will determine which of the shipping substances will be used in the end (if at all). In fact, stemming from issues of safety that relate to each of the viewed fuels' toxicity or flammability, the general challenge of public acceptance as well as legal and regulatory constraints may come into play when hydrogen delivery projects focus on a specific H_2 carrier. Another factor that would need to be taken into account is the availability of the industries and infrastructure already developed around any of the studied chemical substances as well as their potential industrial applicability beyond hydrogen. Finally, technological progress in other decarbonization applications and, most importantly, full commercialization of CCUS solutions is likely to dramatically change the approach towards long-distance H_2 transportation.

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