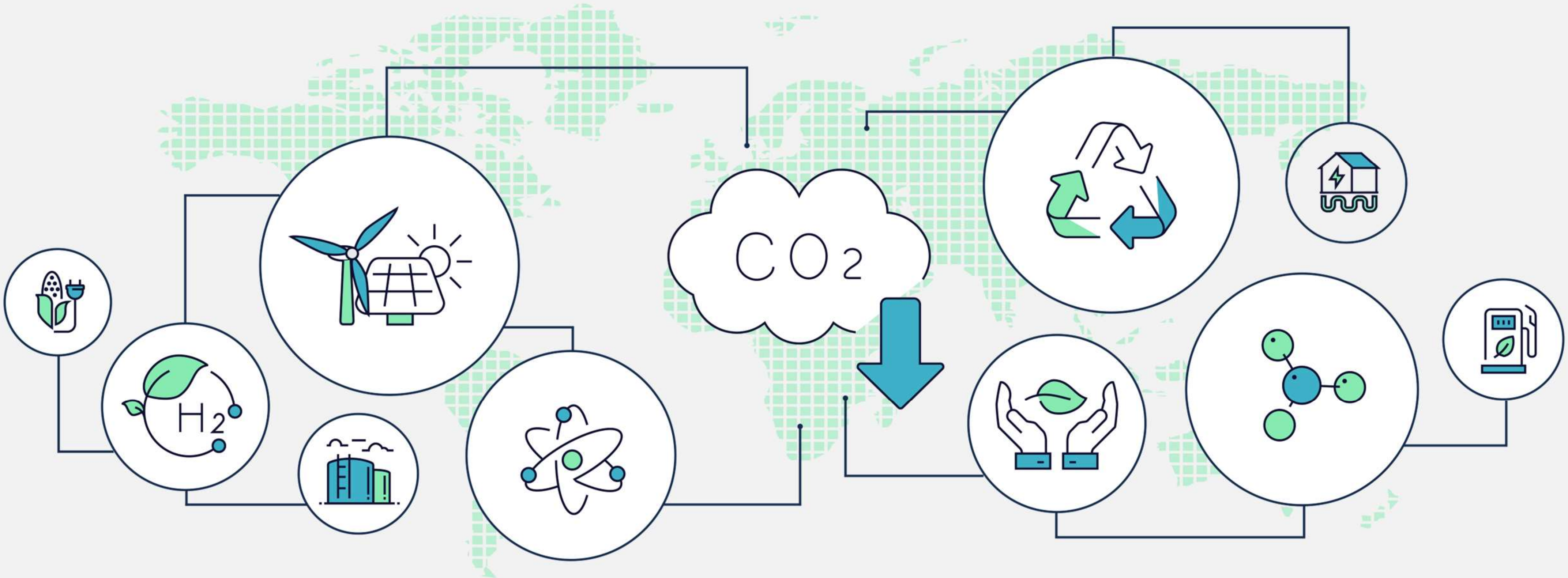


RINA

Storage di H2 tramite liquidi organici

Giornate Sicurezza, 15 Novembre 2022

ANTONIO LUCCI

Who we are

RINA

Marine

Rules, technologies and innovative services to manage transport and pleasure vessels

Certification

Solutions to support products, people and processes on their way to excellence

Real Estate & Infrastructures

The path to the next generation of infrastructure and buildings by ensuring their safety and efficiency

Energy & Mobility

Energy solutions from O&G to renewables, taking care of sustainability and environmental impacts

Industry

Materials, Industry 4.0, innovation & research, Space & Defence, Cyber Security

Energy transition & Decarbonization

Agenda

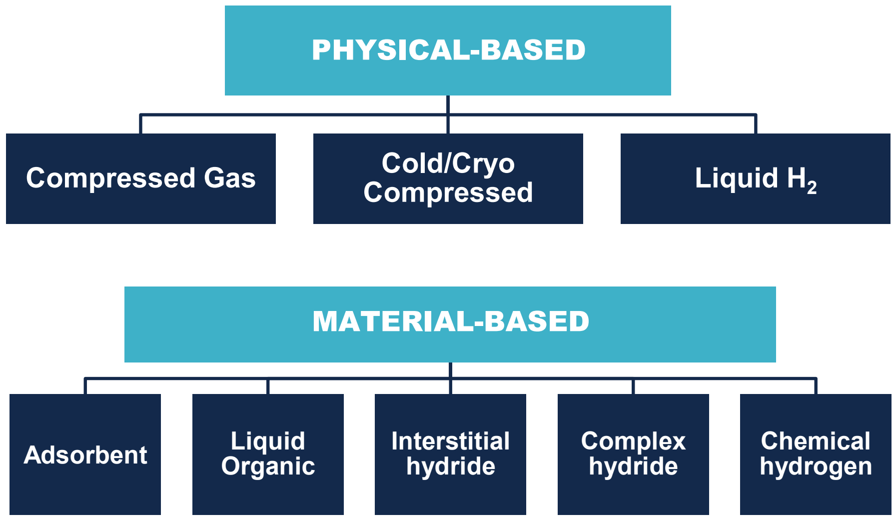
- Transporting Hydrogen
- Introducing LOHC
- Solutions for transport: balancing Distance and Capacity
- Comparing Costs in the future scenario
- Strengths and Weaknesses of LOHC
- Overview on technical data for various types of LOHC
- CONCLUSION

Transporting Hydrogen

Focus on solutions for transport

Main types of storage of H_2 are mainly:

- Physical storage of **compressed hydrogen gas** (CGH_2) in high pressure tanks (up to 700 bar)
- Physical storage of **liquid hydrogen** (LGH_2) and cold/compressed in insulated tanks
- **Storage in materials**: metal hydrides and other chemical compounds, liquids (LHC), ultra-micro-porous materials, ammonia



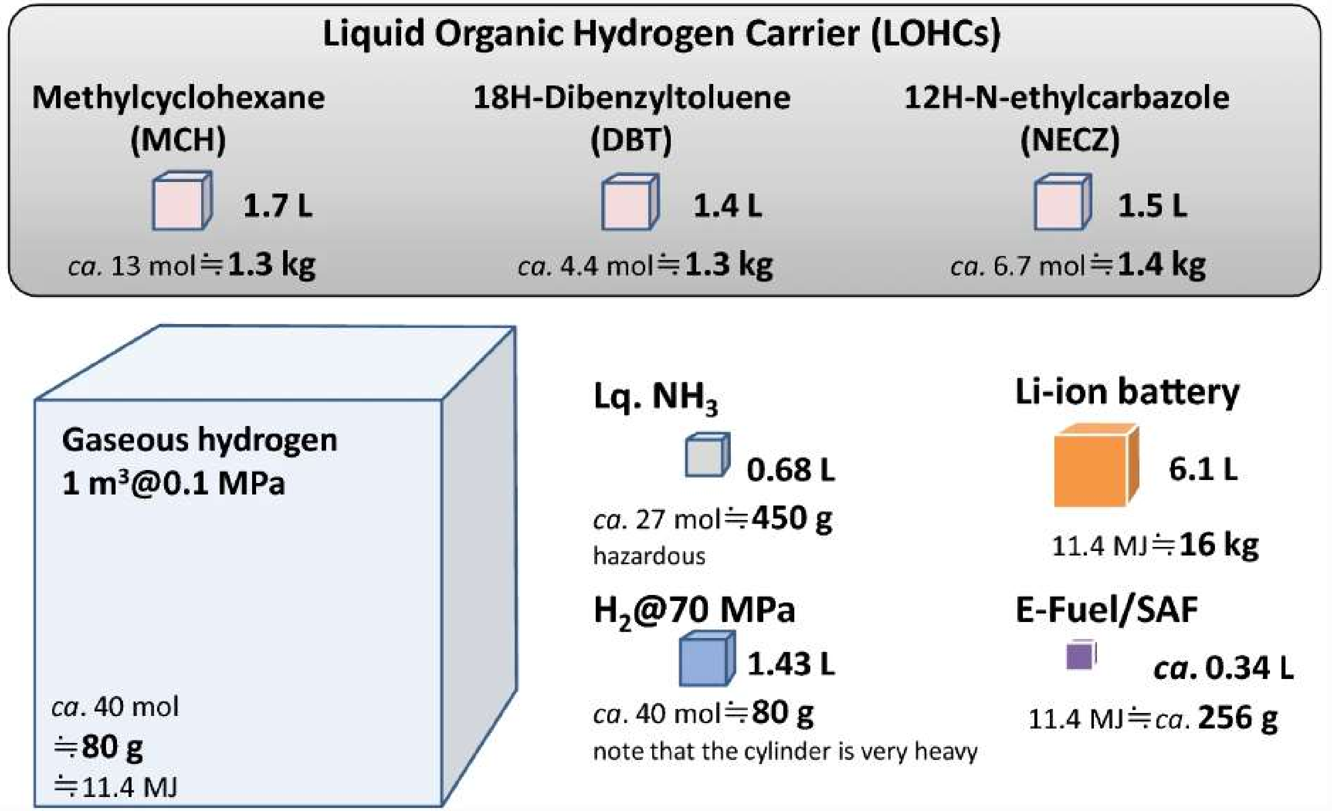
A fourth option is to convert Hydrogen in Ammonia

- Operation **advantages**: High storage capacity, mature value chain, except for cracking process
- Operational **disadvantages**: additional purification step needed and high energy requirements for cracking process
- **Safety Issue**: Acute Toxicity, flammable, explosive under heat, toxic to aquatic life

Volume per Energy

11.4 MJ = 1 Nm³ of hydrogen

From: Recent Trends on the Dehydrogenation Catalysis of Liquid Organic Hydrogen Carrier (LOHC): A Review

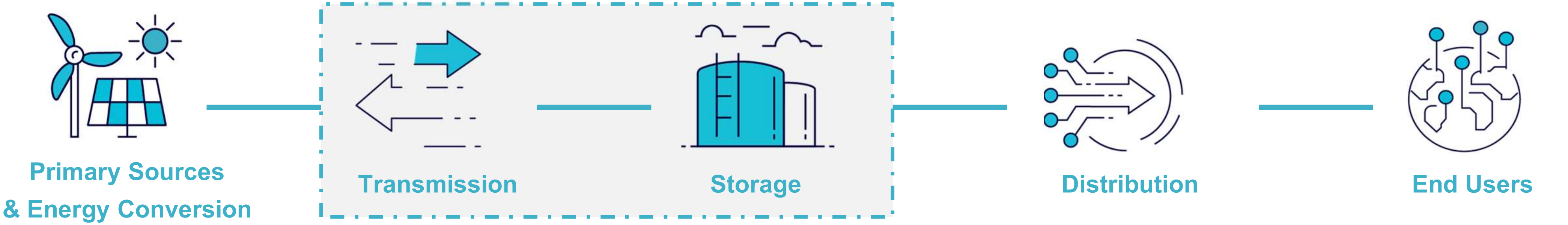


A comparison of the same amount of energy; all of these are equal to be 11.4 MJ = 1 Nm³ of hydrogen [1, 2]

Liquid Organic Hydrogen Carrier

Why and Technological Status

Liquid organic hydrogen carriers (LOHC) are compounds that can react with hydrogen and be used multiple times

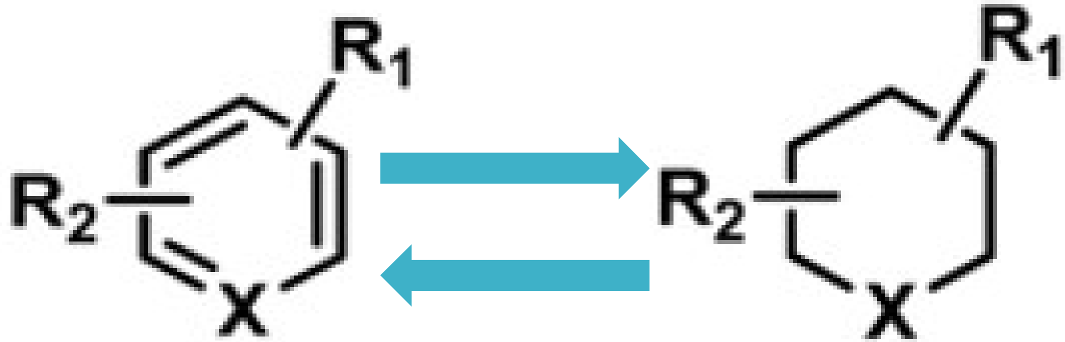


- **Technology** is **not** carried out **on a large scale** currently
- **Conversion** and **reconversion** steps still **need demonstration** before reaching commercial scale
- There is a **wider gap in capacity** (compared to ammonia or liquid hydrogen) **to satisfy largescale demand** in the future
- The largest plant in the world is being constructed in Germany (Chempark Dormagen) with a capacity of 5 t/d and funding has been received for a 24 t/d plant.

Liquid Organic Hydrogen Carriers (LOHC)

What are they

Liquid-organic hydrogen carriers (LOHCs) are organic substances in liquid or semi-solid states that store hydrogen by catalytic hydrogenation and dehydrogenation processes over multiple cycles



HYDROGENATION

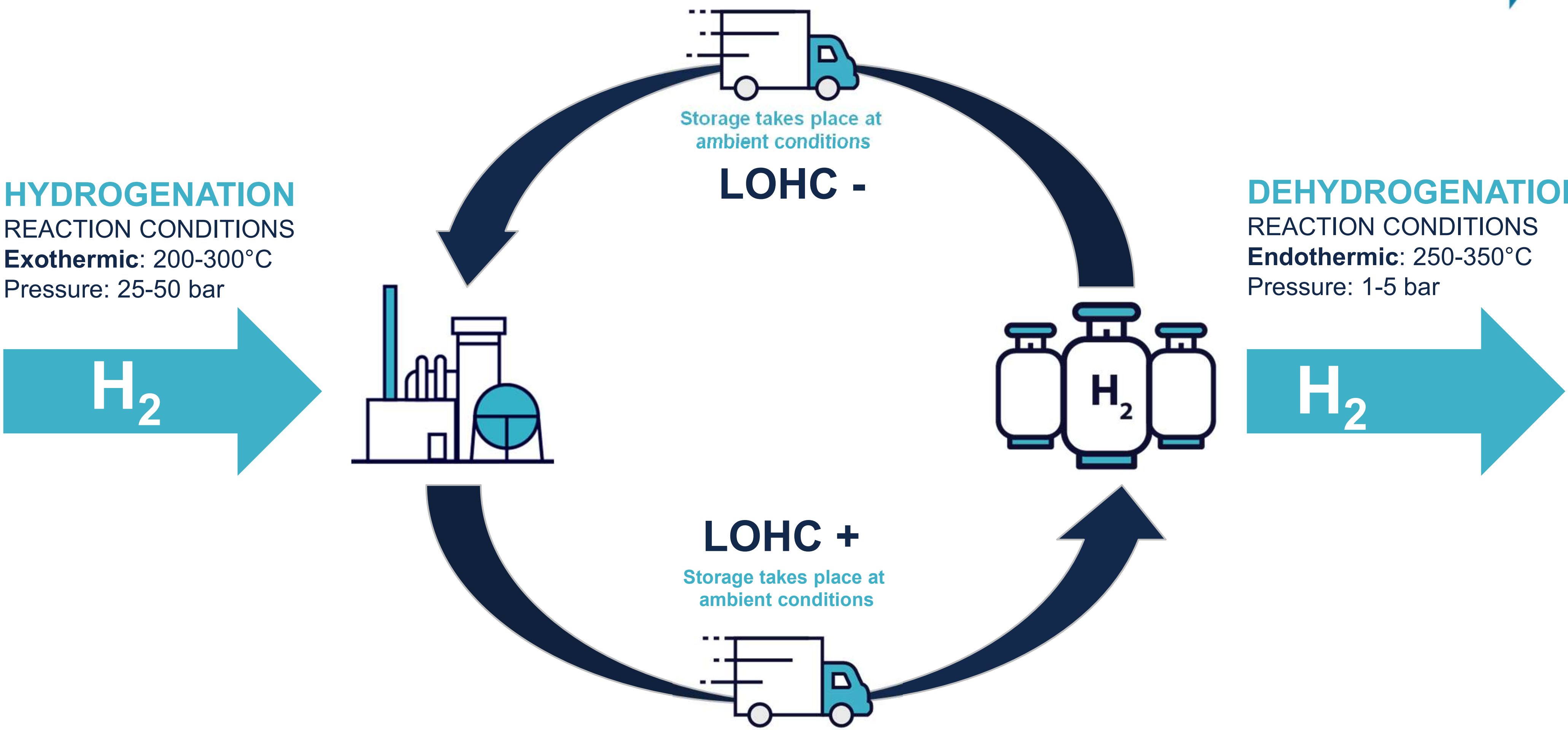
hydrogen is chemically bonded to the carrier medium (lean LOHC) **@30-50 bar** and **ambient temperature** resulting in the rich LOHC and **releasing heat**. It can be performed close to centralized hydrogen production sites

DEHYDROGENATION

the **hydrogen is dissolved from the carrier medium by the application of heat**. It needs to be easily obtained locally for different applications

Liquid Organic Hydrogen Carriers

How they work



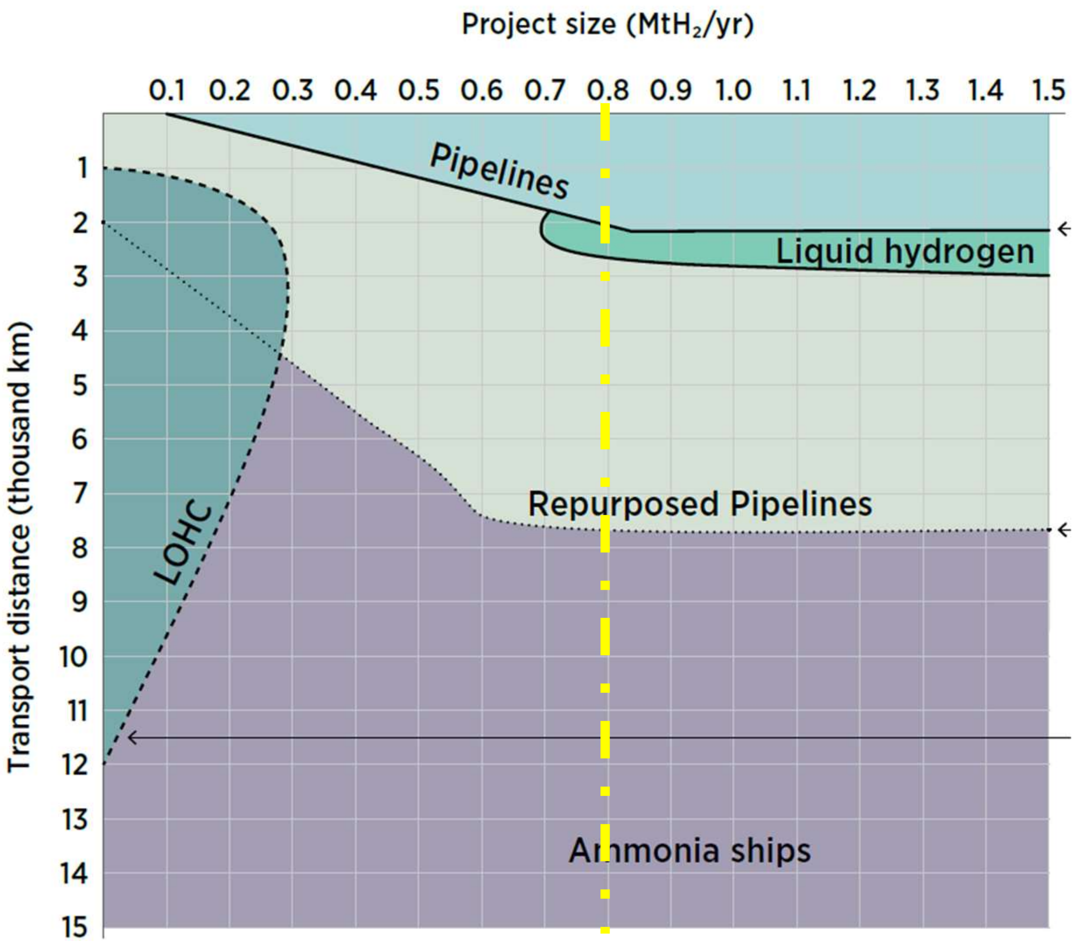
Distance and Capacity
Technology scenario

1 MtH_2/year would be equivalent to:

- **10 GW** electrolyzers running for about **60%** of the year

or

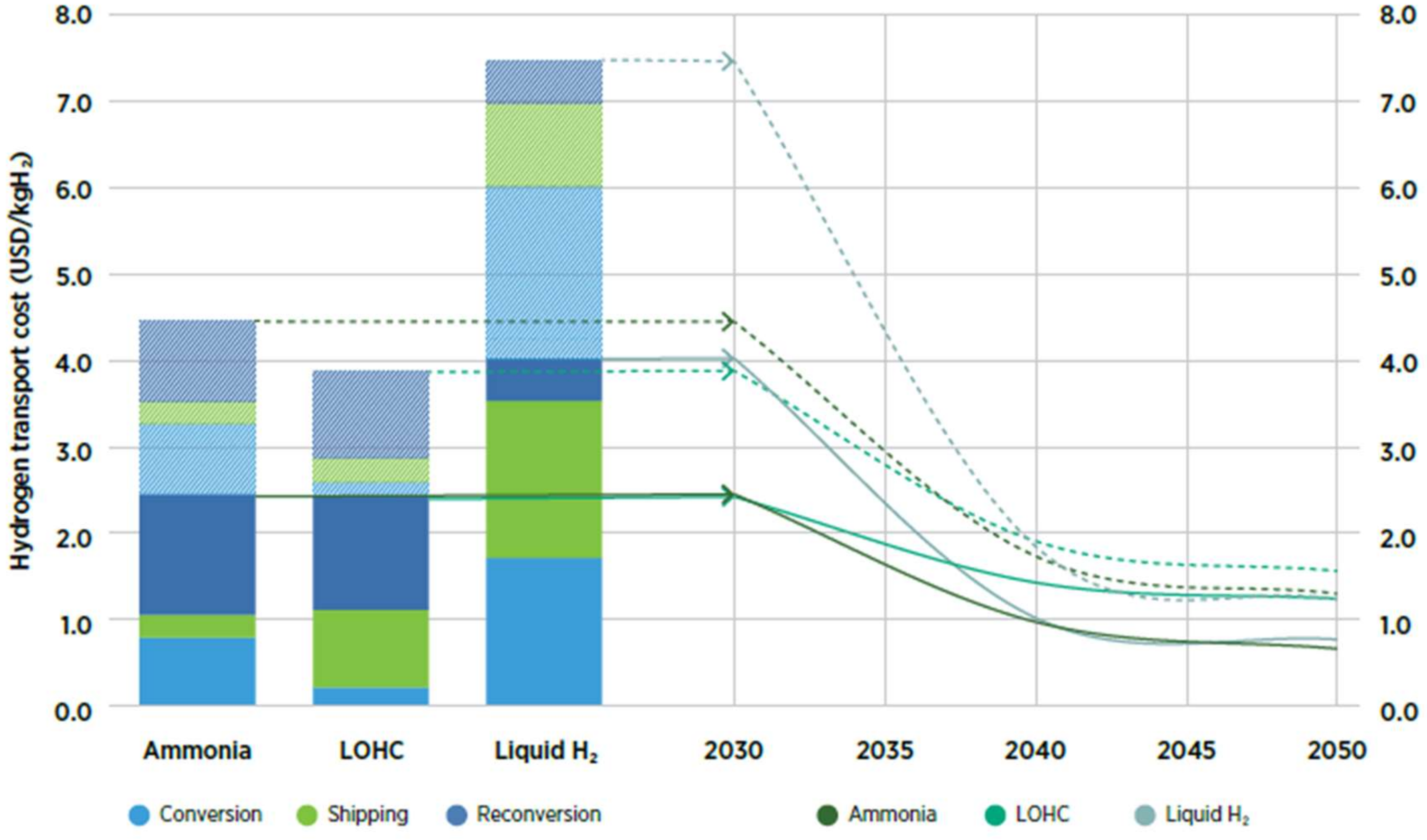
- the hydrogen consumption of **5** commercial ammonia plants (500 t/d)



Source: IRENA 2022

Costs

Comparing hydrogen carriers in the next decades



Source: IRENA 2022

Liquid Organic Hydrogen Carrier

Strength & Weakness

STRENGTH

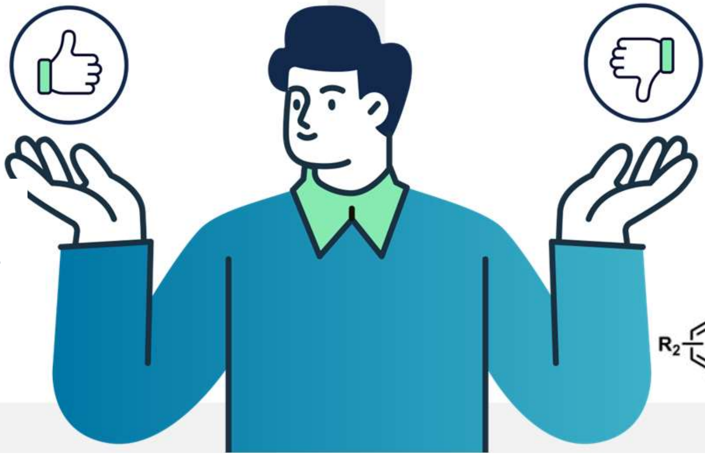
High storage density

Simple handling: liquid phase at ambient conditions

Can be transported as oil today using existing infrastructure, making it suitable for multi-modal transport

Non-toxic and non-falmmable if LOHC is appropriately selected

Stable compounds and no boil-off losses during transport or storage



WEAKNESS

Need of a dedicated infrastrucure for reactions $H2^{+} \rightleftharpoons H2^{-}$

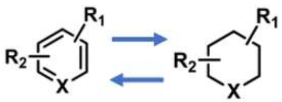
High LOHC costs

Low hydrogen content: 4-7% by weight

Pressure requirements for hydrogenation

Heat for dehydrogenation corresponds to 30-40% of the energy contained in the hydrogen

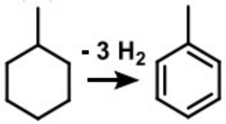
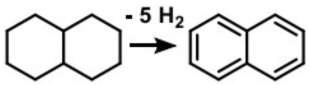
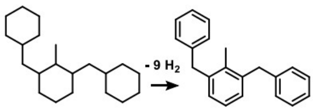
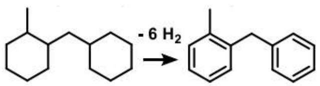
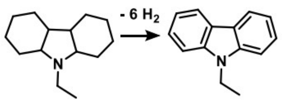
Limited LOHC production capacity



Losses per cycle of 0.1%

Overview on types of LOHC

Flash Point (°C)
Gasoline -20 ° C
Diesel 55 ° C

	Formula	Storage Density ($KgH_2/KgLOHC$)	Entalpia (kJ/mol H2)	Flash Point (°C)	Boiling Point (°C)	Health Hazard (NFPA Classification)
Toluene		6.1	68.3	4.4	111	2
Naftalene		7.3	63.9	88	80	2
Dibenziltoluene		6.2	65.4	200	380	0
Benziltoluene		6.2	63.5	132	270	n.a.
N-etil carbazolo		5.8	50.6	186	218	2

Current pipeline of advanced projects

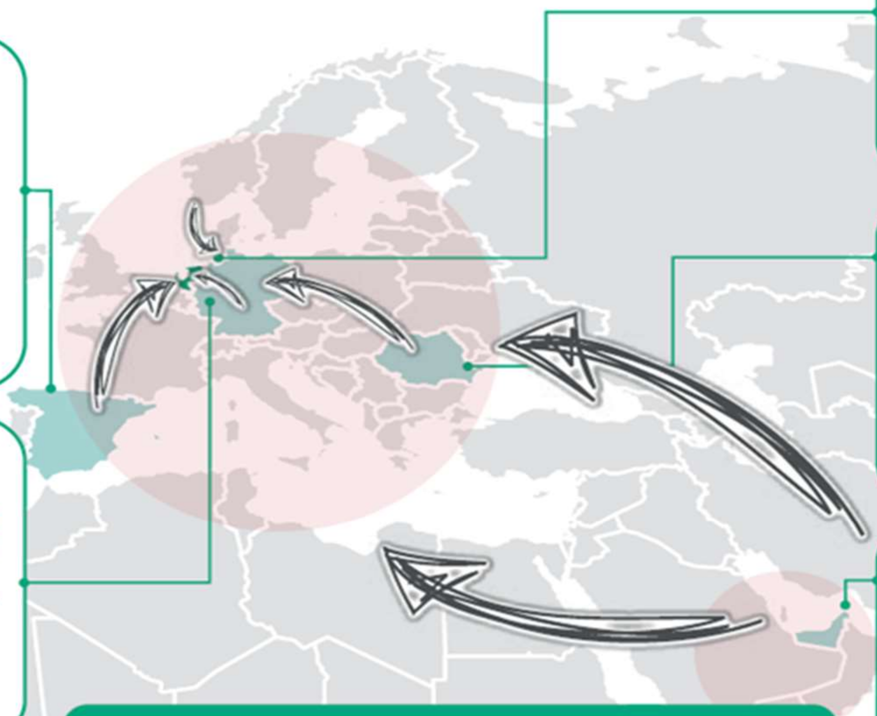
Some projects are for **domestic hydrogen** transport or storage, but three are related to **international trade**

Green Crane (IPCEI)

- **Hydrogen production from renewables** in **Northern Spain**, storage in LOHC and transport via ship to the **Netherlands**. Distribution to off-takers in the region with possible extension along the Rhine river to **Germany**
- 12 tpd **storage plant** and **release plant** as first development step
- enagas, Vopak, Naturgy

Hector/Puffin

- Storage of **by-product hydrogen** from Covestro site in Western **Germany** in LOHC and transport via truck to Vopak in the **Netherlands**
- **5 tpd storage plant** and **1.5 tpd release plant** as first development step



Creating a first industrial reference case through Puffin and Pre-project Blue Danube will be the key milestone for further industrialization of our technology

AquaVentus (AquaPortus)

- **Hydrogen production from offshore wind energy** located in the North Sea
- Storage plant located at Helgoland and release plant in the port of Hamburg

Green Hydrogen @ Blue Danube (IPCEI)

- **Hydrogen production from renewables** in **Romania**, storage in LOHC and transport via ship to off-takers in **Austria** and **Germany**
- **Blue Danube** demonstrator in first development step. **Several storage plants** in initial stage, **and release plants**
- Verbund

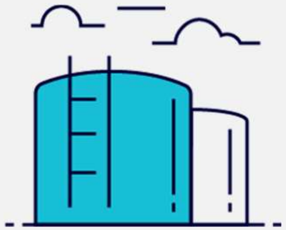
Green H_2 from Middle East

- Cooperation with ESCO in **UAE** to develop **green hydrogen export business**
- Large-scale storage plants
- ESCO

Project description · Capacity · Key partner(s)

Source: IRENA 2022and Hydrogenius

Hydrogen for a sustainable development

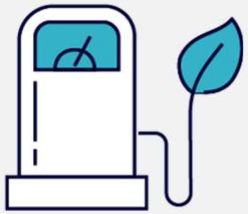


SAFETY

LOHC are oil derivatives and could build upon existing facilities with no boiloff losses and a liquid state at ambient conditions. Nowadays are produced in limited quantities.

IMPROVEMENT

While the carrier is recycled, there are losses (about 0.1% per cycle) that would require compensating.

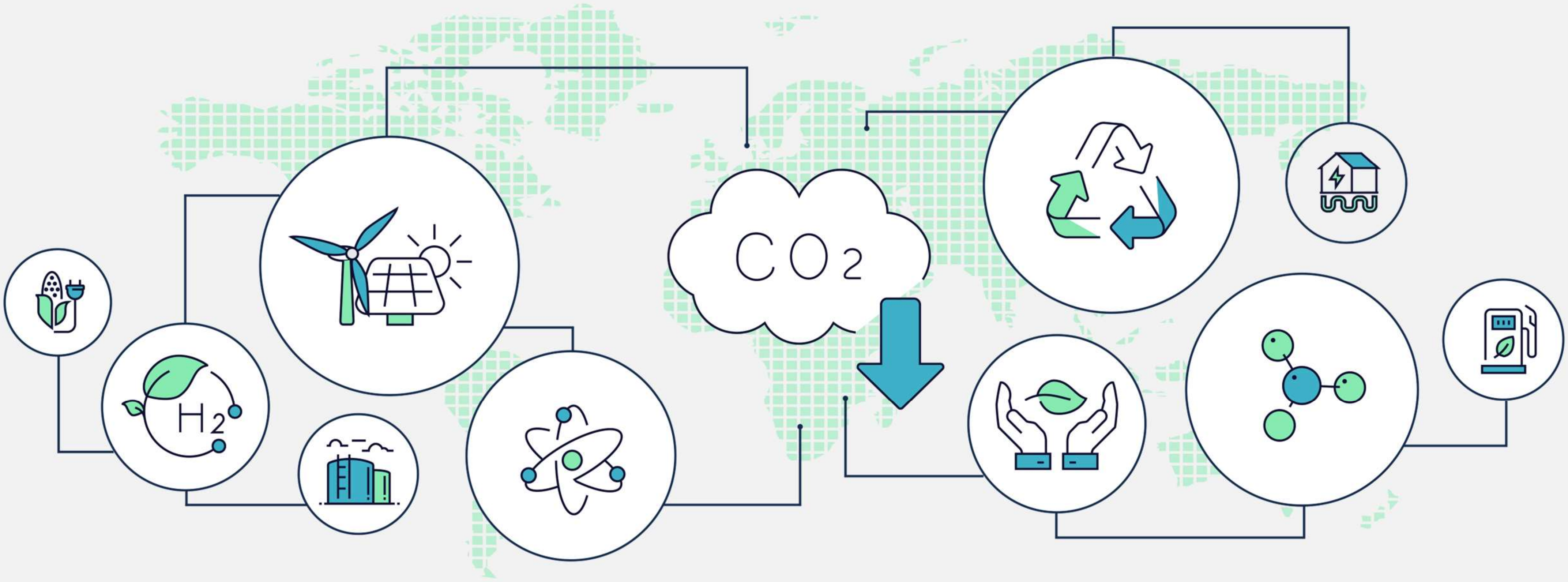


VOLUME

All LOHC have a relatively low hydrogen content (4-7% weight), which translates into a large mass of LOHC to be transported and increases the share of the cargo that is consumed as fuel

LIMITATIONS

One of the main limitations of this pathway is the heat required at a medium temperature level (270-320°C) to recover the hydrogen from the carrier. This energy consumption is equivalent to 30-40% of the energy contained in the hydrogen and is limited by thermodynamics



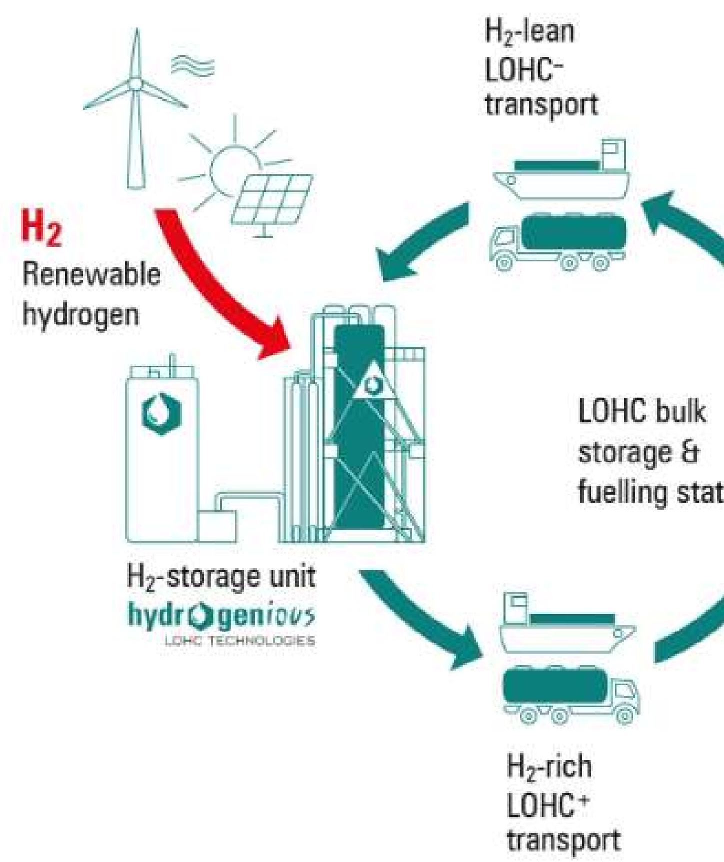
Make it sure, make it simple.

LOHC in ecosistema portuale (HyNjord) - LOHC Maritime

Projects

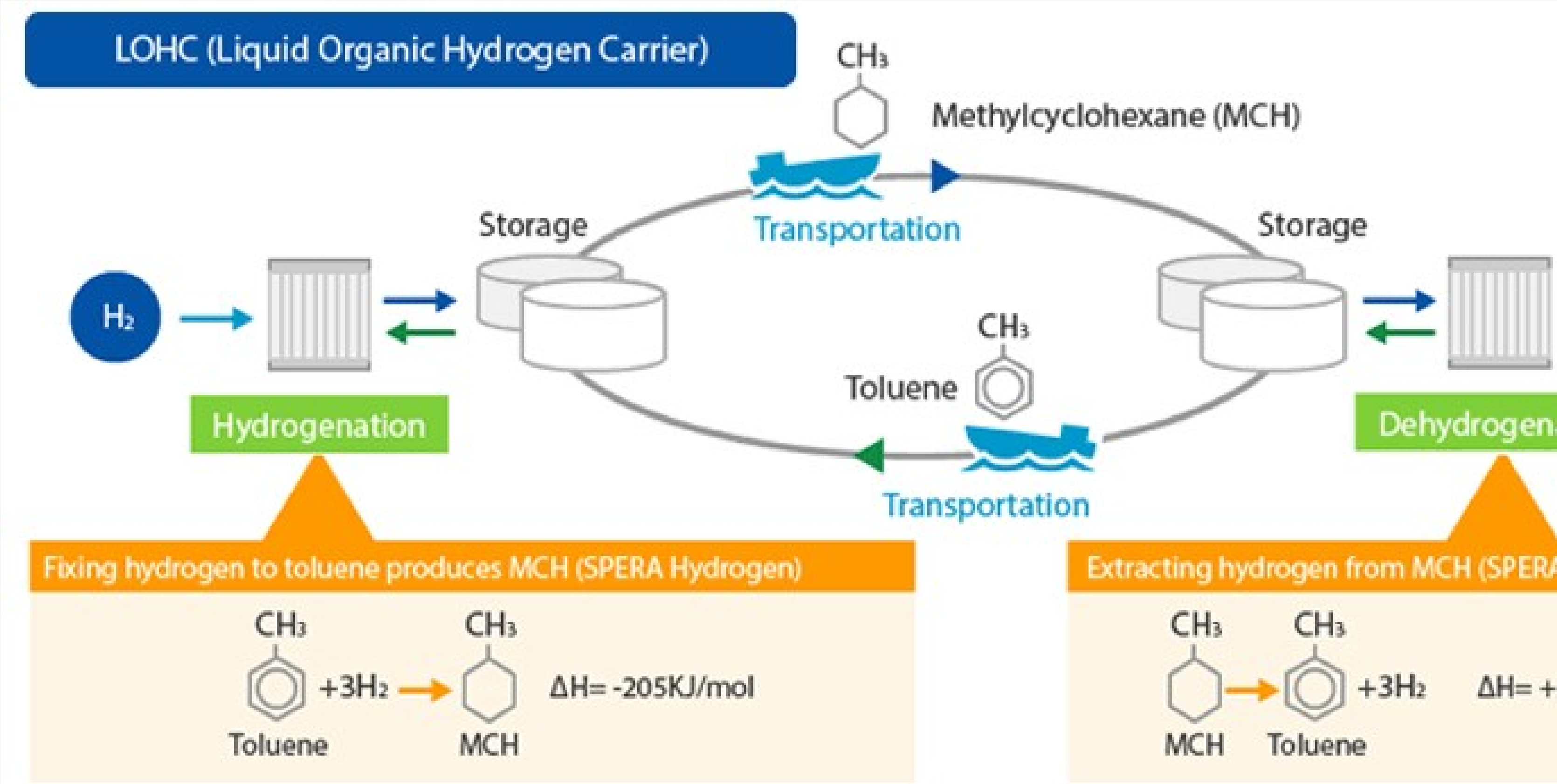
Il progetto **HyNjord** si concentra sullo sviluppo di un pilota da **200 kW** di un innovati LOHC/cella a combustibile.

- Il lancio di un prodotto commerciale su scala megawatt è previsto per il 2025.
- L'applicazione prevista prevede la combinazione di tre componenti principali a bordo della nave:
  - interfaccia con il sistema di gestione dell'energia della nave
  - una cella a combustibile
  - unità di rilascio LOHC, che rilascia idrogeno dal LOHC vettore organico liquido benziltoluene su richiesta.



Projects

Progetto dimostrativo Advanced Hydrogen Energy Chain Association for Technology D



- AHEAD ha completato con successo le prove della prima spedizione internazionale di MCH e dell'estr

Liquid Organic Hydrogen Carriers

What are they

Typical conditions for hydrogenation and chemical properties of LOHC

		NEC	DBT	BT	AB	FORMIC ACID	METHANOL	NAP	BENZENE	TOLUENE
Hydrogenation	Pressure (bara)	50	50	30	10	50	50	69	10-50	20
	Temperature (°C)	150	150	220	80	50	250	200	200	200
	STY (g/(L*hr))	388	279	296	78	8	220	218	-	467
Heat of reaction (kWh/kgH$_2$)		7.4	9.1	8.8	5.0	4.3	2.3	9.2	9.5	9.5
Price (USD/kg)		44	4.4	4.4	110	0.55	0.3	0.66	1	0.88
Market size (Mt)		<0.1	0.009	<0.01	<0.01	1.1	100	1	65	30
Amount needed for 10 MtH$_2$/yr[36]		15.7	14.7	14.7	13.0	20.7	7.3	12.5	12.6	14.9
Storage density (kgH$_2$/kgLOHC)		5.8%	6.2%	6.2%	7%	4.4%	12.5%	7.3%	7.2%	6.1%
Health hazard		1	0	-	-	3	1	2	2	2
Flammability		0	1	-	-	2	3	2	3	3
Flash point (°C)		186	200	132	23	69	11	88	-11	4.4

Typical conditions for dehydrogenation and chemical properties of LOHC

TABLE 4.5. Typical conditions for dehydrogenation and chemical properties of

	NEC	DBT	BT	AB	FORMIC ACID	METHANOL	NA
Dehydrogenation							
Pressure (bara)	1	1-2	1	1	1	1	1
Temperature (°C)	270	310	260	80	60	420	28
STY (g/(L*hr))	163	28	32	27	0.2	45	1
Conversion (%)	90	97	99	99	100	100	9

Molecola	Fo
Metilcicloesano ->	

Tecnologia LOHC per lo stoccaggio ed il trasporto di Idrogeno

Caratteristiche del LOHC:

- *Deve essere atossico e sicuro, con un profilo ecotossicologico accettabile durante il trasporto e l'utilizzo.*

- *Per evitare la necessità di infrastrutture per combustibili a base solida e l'aggiunta esterna di solventi, i sistemi LOHC devono avere punti di fusione bassi con valori < - 30°C*

- *Il punto di ebollizione del sistema LOHC deve essere elevato (>300 ◦C) per semplificare la purificazione dell'idrogeno. idrogeno e richiedere una bassa viscosità dinamica per facilitare il pompaggio.*

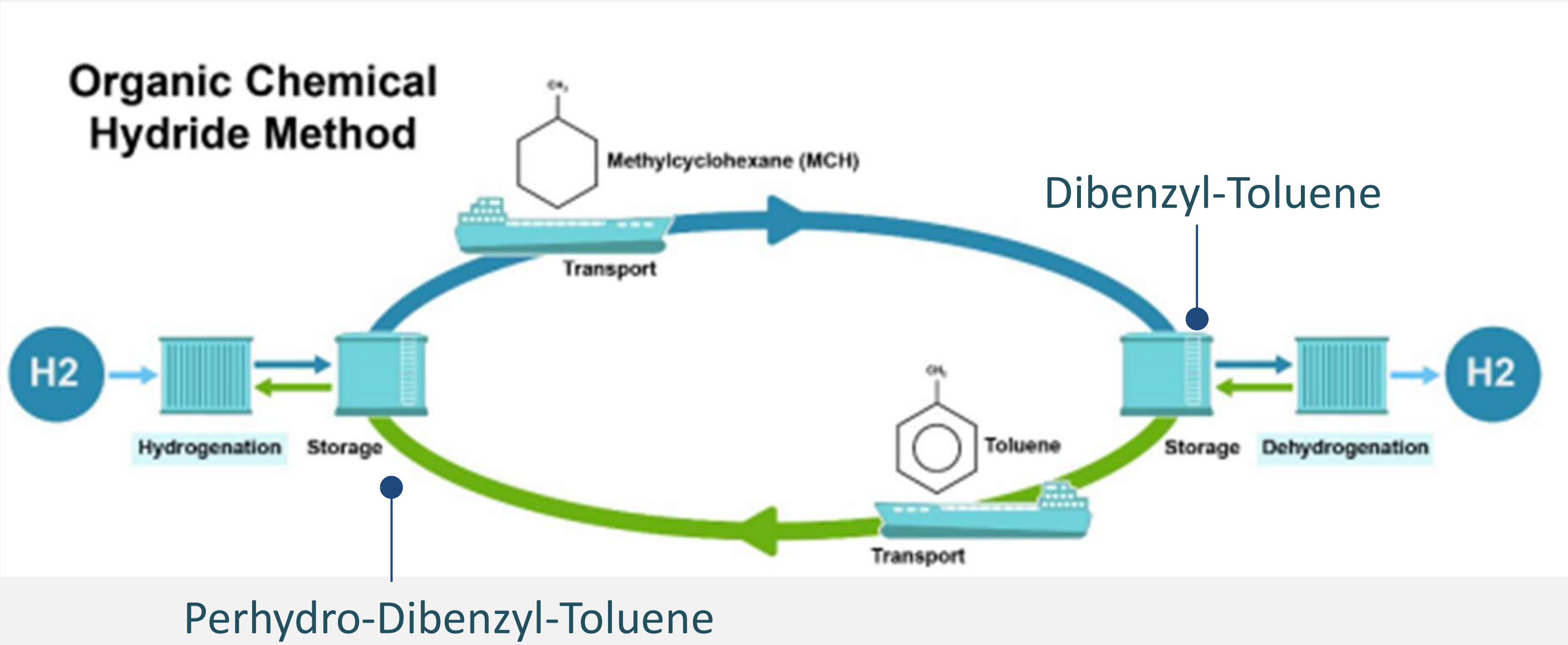
- *Al fine di definire un sistema LOHC efficiente in termini di trasporto di gas idrogeno, sono richieste capacità di stoccaggio volumetriche (>55 kg/m3) e gravimetriche (>6 wt%) ragionevolmente elevate.*

- *Al fine di raggiungere una elevata stabilità delle molecole LOHC e ottenere temperature di deidrogenazione sufficientemente basse (<200 ◦C a 100 kPa di pressione H_2) tali da evitare massivi utilizzi energetici nel processo di recupero del gas idrogeno, l'entalpia di legame desiderata tra idrogeno e molecola carrier dovrebbe essere nell'intervallo di 40-70 kJ/mol H_2*

- *il sistema deve essere in grado di produrre idrogeno molto puro in reazioni catalitiche di idrogenazione/deidrogenazione molto selettive durante molti cicli, ed evitare la decomposizione della struttura molecolare di trasporto*

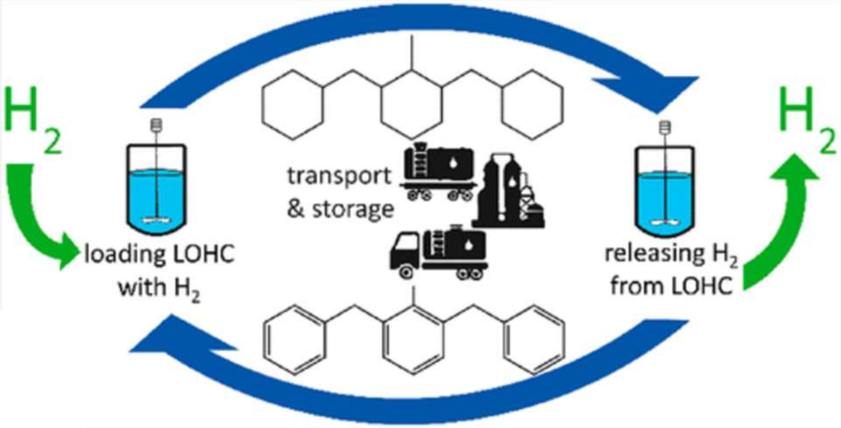
- *Deve essere compatibile con le attuali infrastrutture di rifornimento per abbassare i costi di produzione*

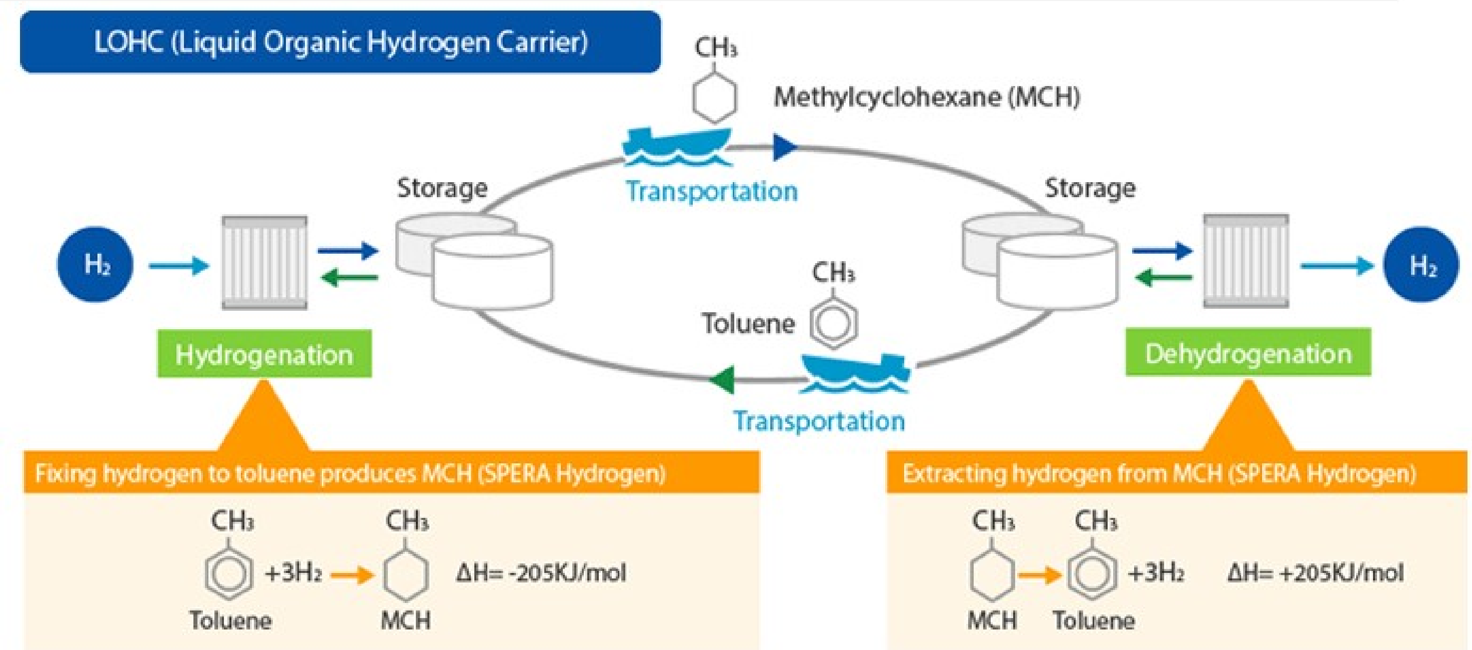
Source: Purna Chandra Rao et.al. Potential Liquid-Organic Hydrogen Carrier (LOHC) Systems: A Review on Recent Progress, Energies 2020, 13, 6040



- Low toxicity
- Good Stability: up to 200°C - hydrogen can be stored and transported similarly to Diesel fuel
- Not categorized toxic and environmental hazardous like Ammonia
- Not flammable and explosive like Methane

AHEAD project

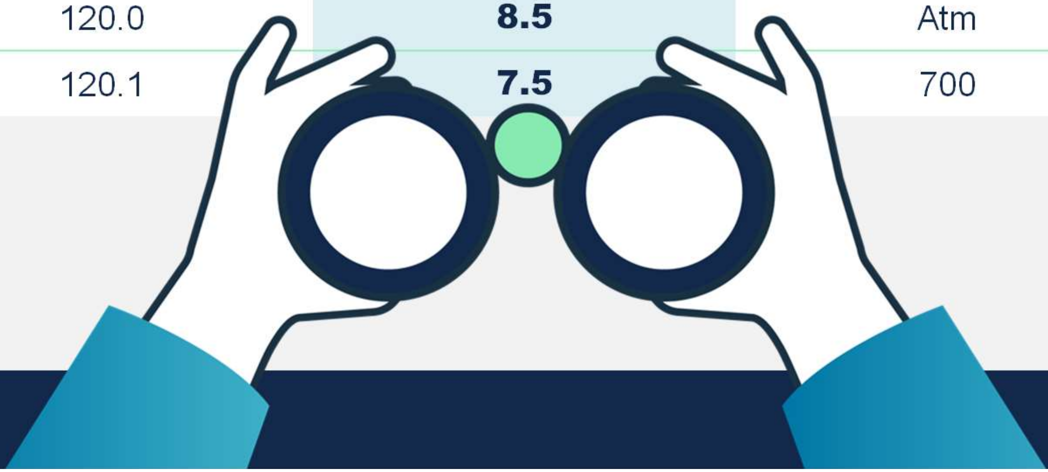




Hydrogen

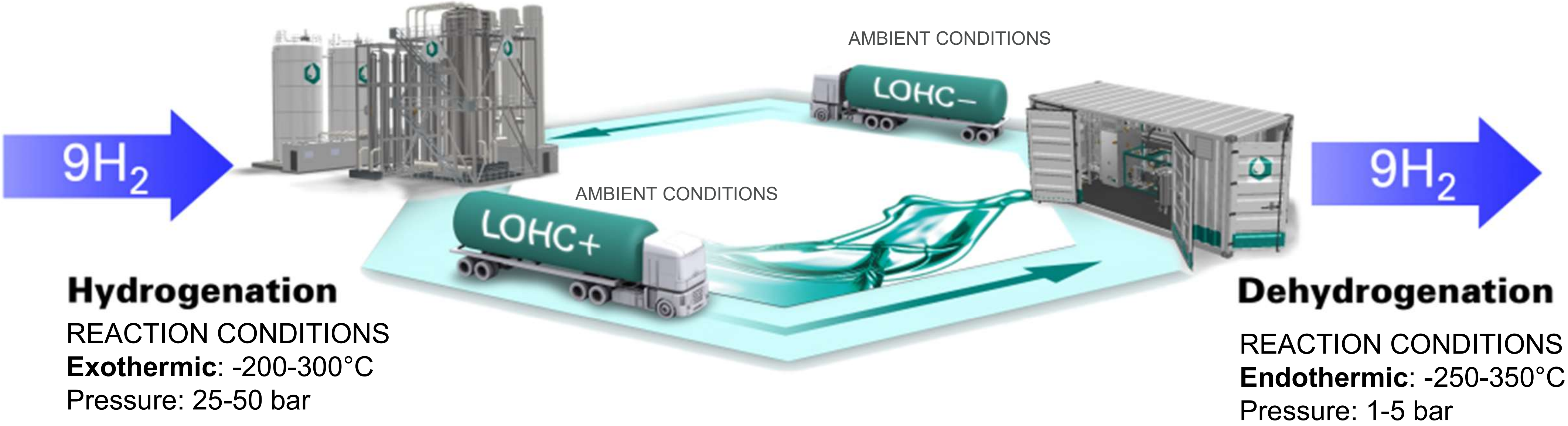
Physic-chemical characteristics

FUEL TYPE	ENERGY DENSITY [MJ/kg]	VOLUMETRIC ENERGY DENSITY [GJ/m³]	STORAGE PRESSURE [bar]	STORAGE TEMPERATURE [°C]
Marine Gas Oil	42,8	**36,6**	Atm	Ambient
Liquid Methane	50.0	**23,4**	Atm	-162
Ethanol	26.7	**21.1**	Atm	Ambient
Methanol	19.9	**15.8**	Atm	Ambient
Liquid Ammonia	18.6	**12,7**	Atm up to 10	-34 or 20
Liquid Hydrogen	120.0	**8.5**	Atm	-253
Compressed Hydrogen	120.1	**7.5**	700	Ambient



Liquid Organic Hydrogen Carriers

How they work

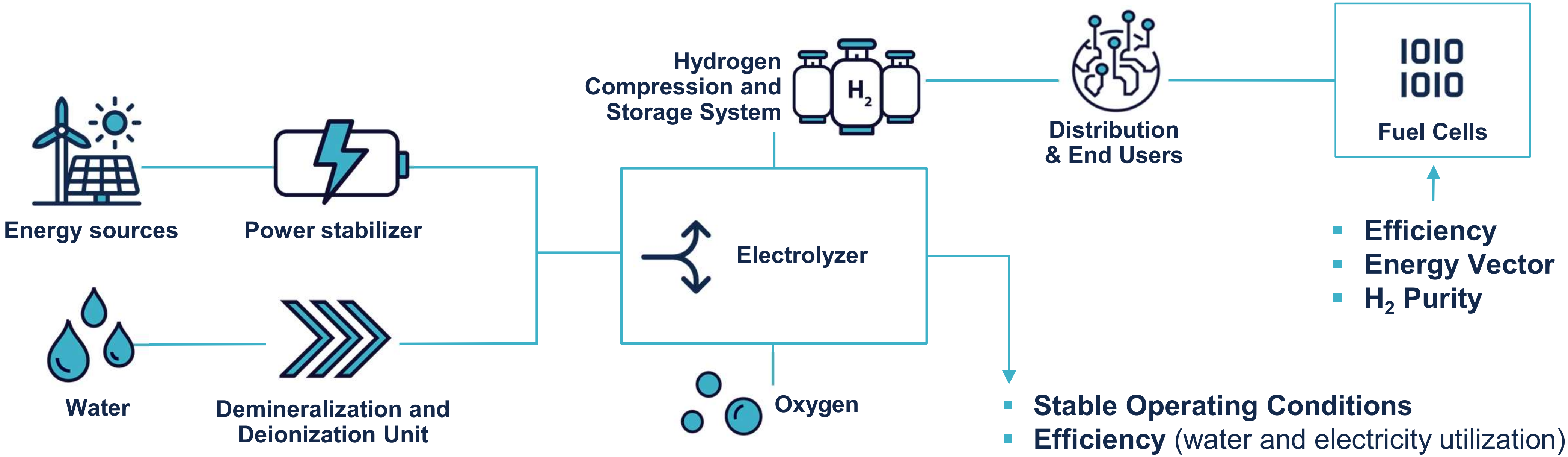


Source: Hydrogenious

Green Hydrogen Production

The critical role of Technologies and Primary Sources

Technologies: electrolyzers and Fuel Cell
Primary Sources: Renewables + demineralized and deionized Water



Stoccaggio ad alta pressione

160-700bar

- Tecnologia matura e largamente conosciuta
- Velocità e facilità di rifornimento veicoli nelle stazioni
- Disponibilità immediata di idrogeno
- Bassa densità di stoccaggio
- Alti costi di CAPEX (acquisto nuovi impianti) ed OPEX (mantenimento)
- Necessità di ampia zona di sicurezza

Stoccaggio liquido

-253 °C

- Alta densità di stoccaggio
- Costi energetici molto alti per liquefazione e mantenimento di tale condizione.
- Costi molto alti di CAPEX ed OPEX
- Non adatto per stoccaggio a lungo termine (perdite di gas)
- Necessità di ampia zona di sicurezza

LOHC

H2+ ⇌ H2-

- Alta densità di stoccaggio
- Handling facilitato (liquido a condizioni di pressione e temperatura ambiente)
- Possibilità di utilizzo delle attuali infrastrutture (serbatoi stazioni di distribuzione carburanti, navi per il trasporto di petrolio..)
- LOHC opportunamente selezionato è non tossico, non pericoloso e non esplosivo
- Necessità di infrastruttura dedicata per reazioni catalitiche **H2+ ⇌ H2-**