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Hydrogen Storage and Transportation through Liquid Organic Hydrogen Carriers

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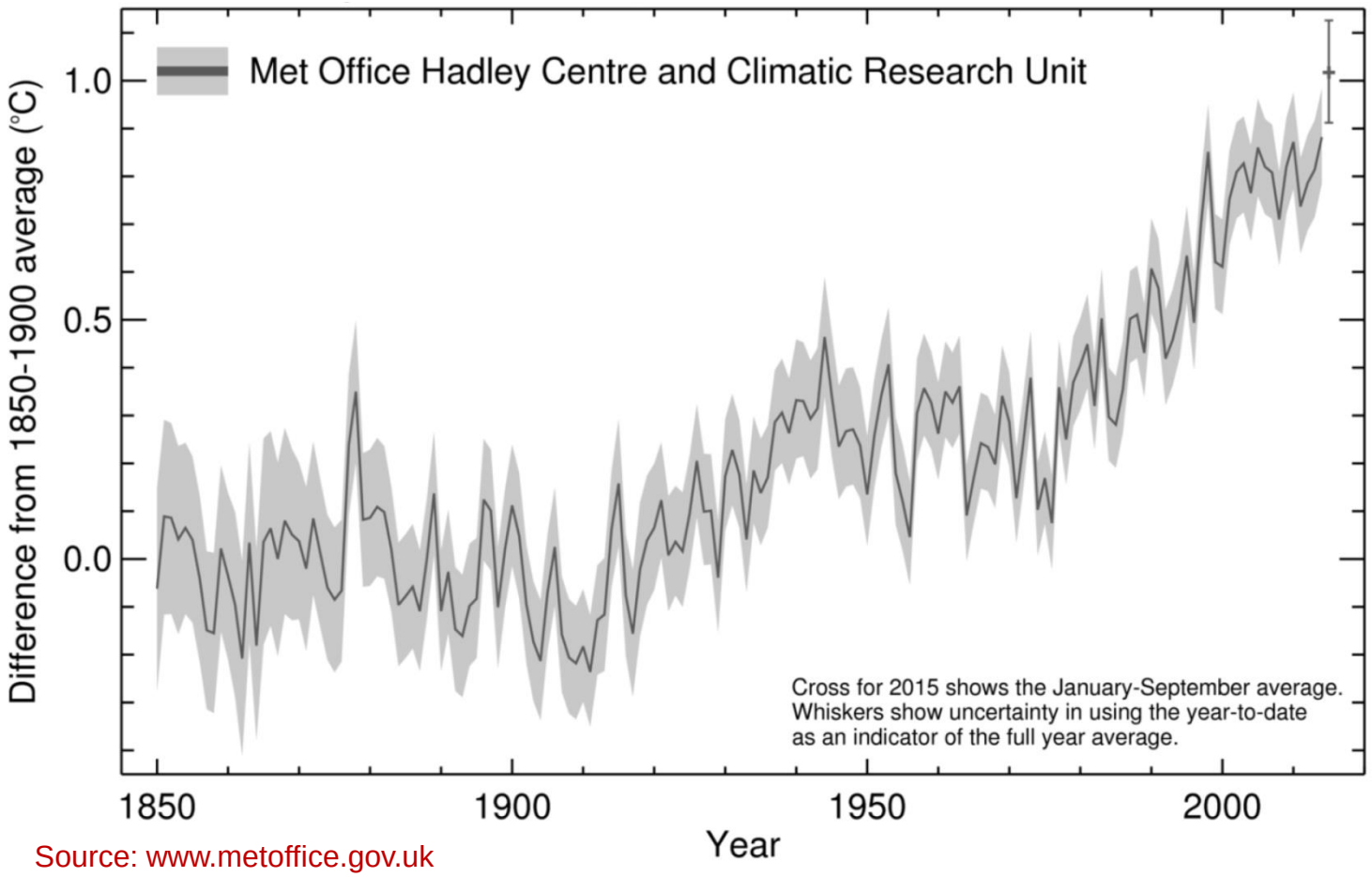
Overview

- CO_2 Emmissions and Climate Change
- Hydrogen Economy
- Methods of Hydrogen Storage
- Liquid Organic Hydrogen Carriers (LOHCs)
- LOHC Cycle
- Benefits of LOHC H_2 Storage
- Requirements for a Good LOHC
- Challenges with LOHCs
- Conclusion and Directions for Future Research

CO_2 Emissions and Climate Change

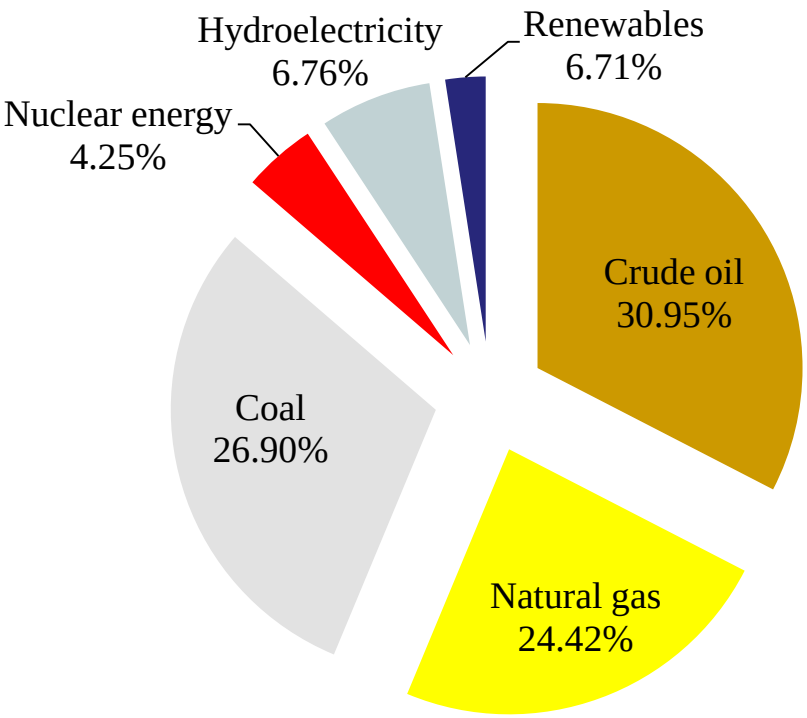
- CO_2 is probably the main reason for the climate change
- Before the industrial revolution CO_2 concentration was nearly 280 ppm, now it is more than 400 ppm
- In nearly 100 years the average global temperature has risen to more than 1°C
- Keeping the rise below 2°C can avoid dangerous effects of climate change
- In the Paris Climate Agreement 2015, governments agreed on a long term goal to work for keeping the temperature well below 2°C compared to the baseline of pre-industrial era

CO_2 Emissions and Climate Change



Source: www.metoffice.gov.uk

World Energy Consumption (2021)



Type	EJ
Crude oil	184.21
Natural gas	145.35
Coal	160.10
Nuclear	25.31
Hydro-electricity	40.26
Renewables	39.91
Total	595.14

Source: BP Statistical Review of World Energy 2021

Drawbacks of using Fossil Fuels

- ✓ Global warming (CO_2 emissions)
- ✓ Acid rain (SO_2 emissions)
- ✓ Human health (CO, hydrocarbons, air borne particles)
- ✓ Non-renewable
- ✓ Effect on aquatic life (oil spillage)
- ✓ Mining hazards (workers at coal mining)
- ✓ Low thermal efficiency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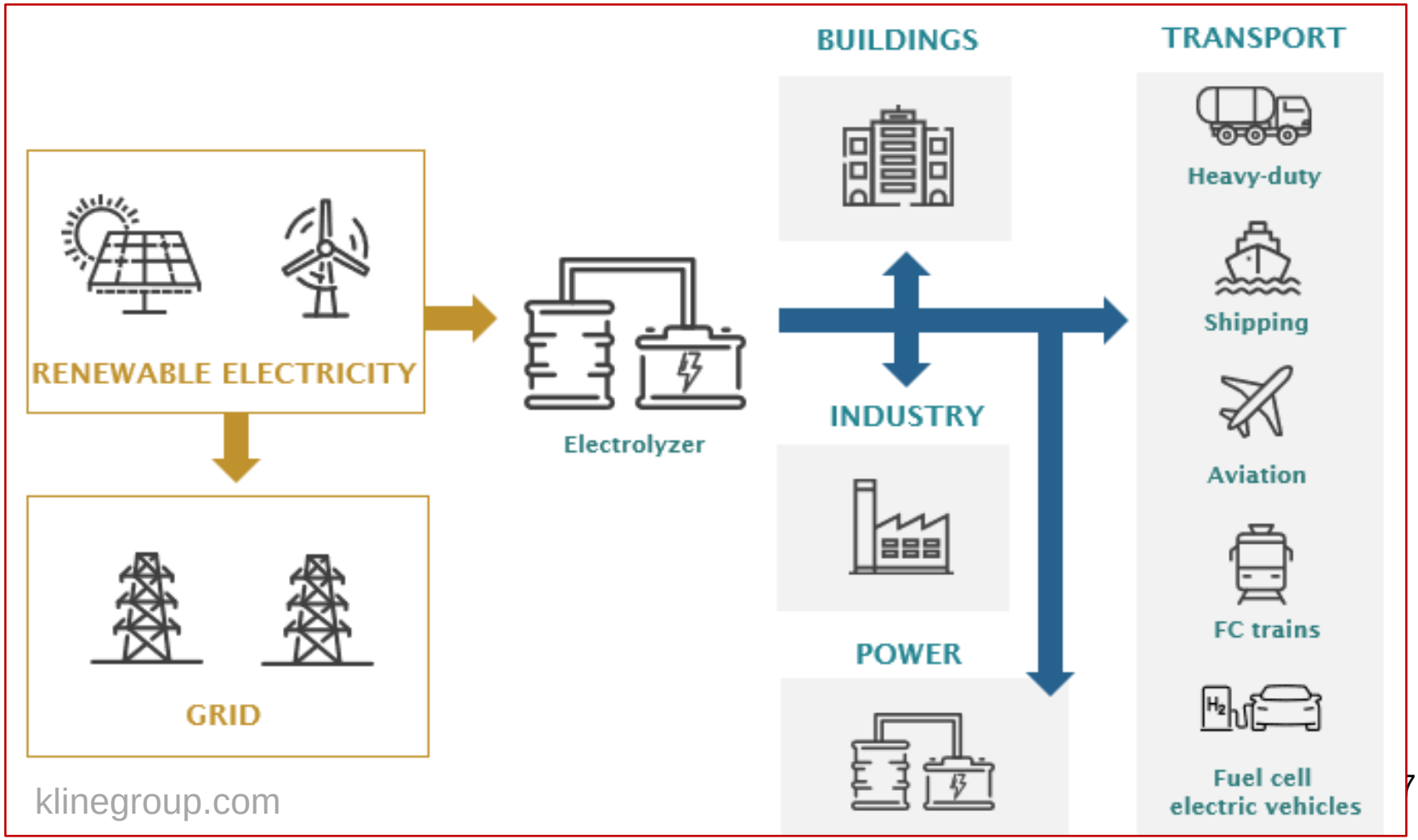
Hydrogen Economy: A Green Solution

Hydrogen economy is a commercial alternative energy infrastructure based on hydrogen



Hydrogen Economy: A Green Solution

- Unlimited supply of the raw material (water)
- Low carbon solution
- Less affected by politics among the countries
- Twice the more thermally efficient when used in fuel cells
- Non-toxic: no particles and hydrocarbons emissions
- H_2 energy can be stored and transported
- No engine noise (with fuel cell)
- Rate of combustion is far faster than gasoline
- More public acceptance

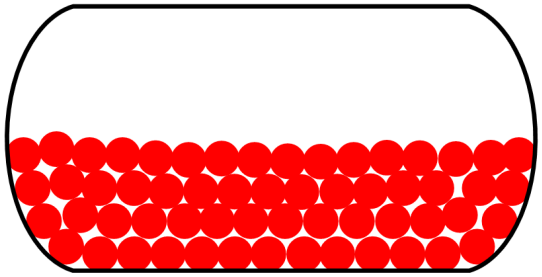
Elements of Hydrogen Economy

- Hydrogen generation
- **Hydrogen storage**
- Hydrogen transportation
- Hydrogen release

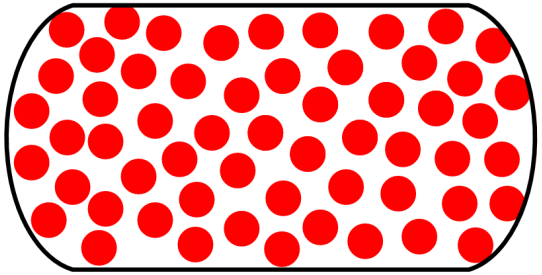
Hydrogen storage is perhaps the main hurdle in the success of hydrogen economy

Methods of Hydrogen Storage

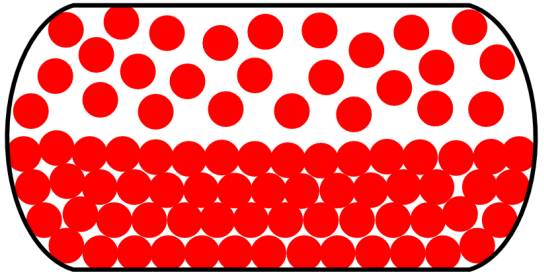
Liquefied Hydrogen



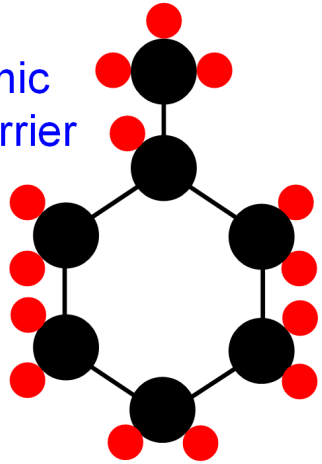
Compressed Hydrogen



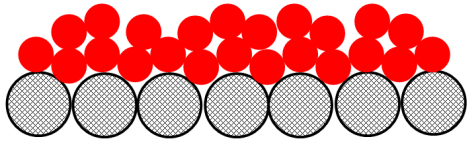
Cryocompressed Hydrogen



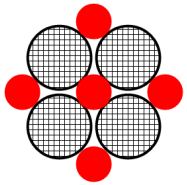
Liquid Organic Hydrogen Carrier



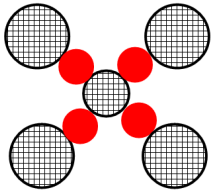
Physically Adsorbed Hydrogen



Metallic Hydride



Complex Hydride



Methods of Hydrogen Storage

Storage method	Hydrogen content (wt% H_2)	Volumetric density (g/L)	Volumetric energy density (MJ/L)
Compression			
1 bar, RT	100	0.0814	0.01
700 bar, RT	100	41.4	4.97
700 bar, RT, (inlc. Type IV tank)	5.7	40.8	4.9
Liquid hydrogen			
1 bar, –253°C	100	70.8	8.5
1 bar, –253°C (inlc. tank)	14	51	6.12
Cryo-compression			
350 bar, –253°C	100	80	9.6
Metal hydrides			
MgH_2	7.6	110	13.2
$FeTiH_2$	1.89	114	13.7
Complex hydrides			
$NaAlH_4$	7.5	80	9.6
Physical adsorbents			
Activated carbon @77 K and 30–60 bar	5.0	38.5	2.4
Liquid hydrogen organic carriers			
Methylcyclohexane/toluene	6.2	47.3	5.68
perhydro-benzyltoluene/ benzyltoluene	6.2	56.0	6.72

Usman, M.R. Hydrogen storage methods: Review and current status, Renew Sustain Energy Rev 167 (2022) 112743

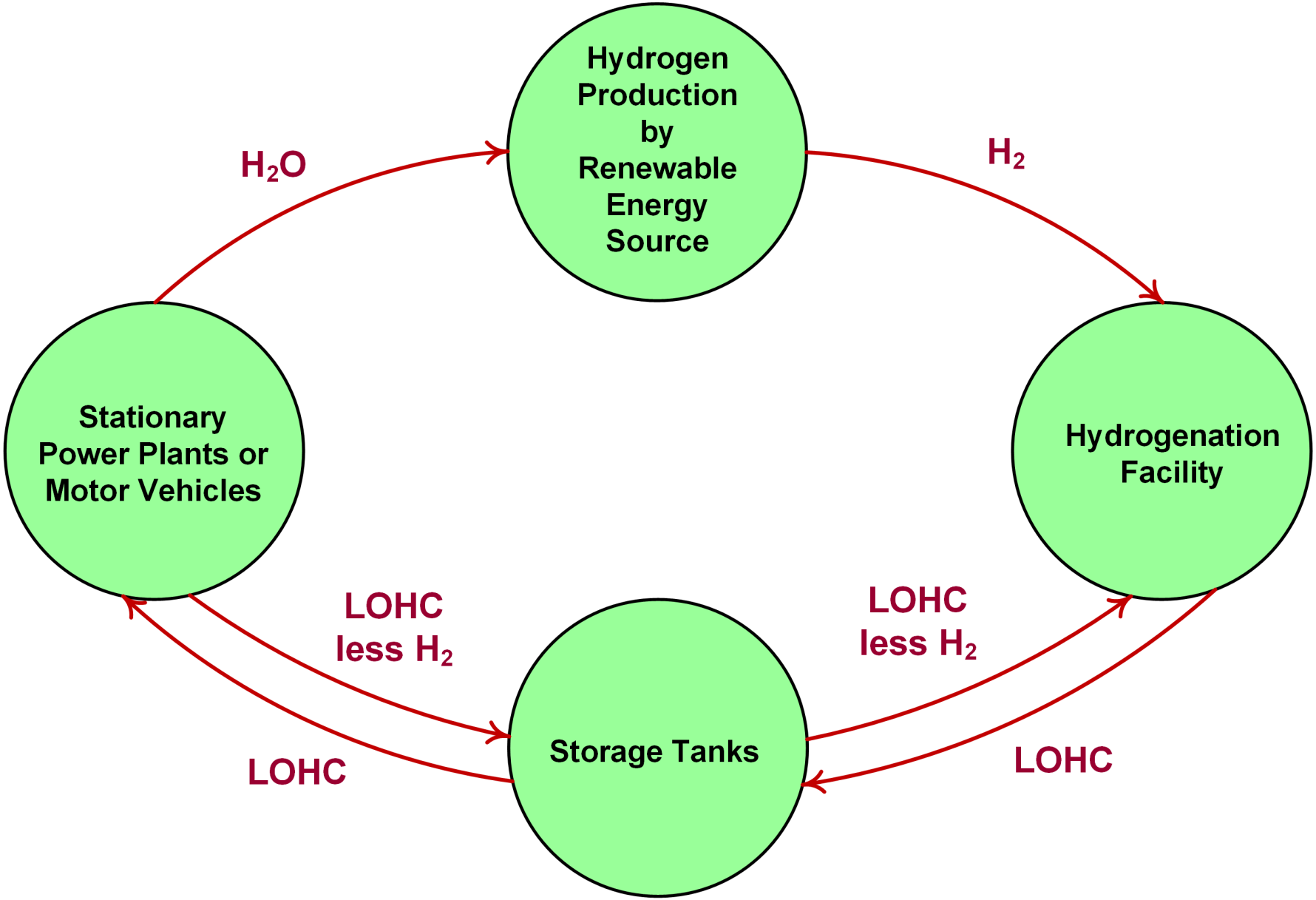
What is a Liquid Organic Hydrogen Carrier?

- An organic molecule that contains one or more recyclable hydrogen that can be released for an application
- Hydrogen is stored chemically by reacting with a hydrogen deficient organic molecule
- In the forward reaction hydrogen is releazed in a dehydrogenation reaction, whereas in the reverse reaction hydrogen is added in a hydrogenation reaction

Some of the Important LOHCs

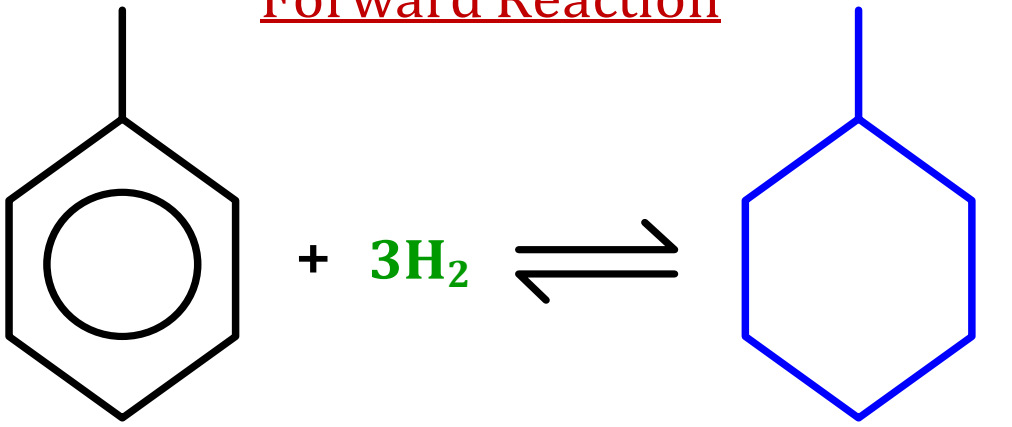
- Cyclohexane
- Methylcyclohexane
- Decalin
- Dodecahydrocarbazole
- Dodecahydro-N-ethylcarbazole
- perhydro-benzyltoluene
- perhydro-dibenzyltoluene

Concept of an LOHC Cycle

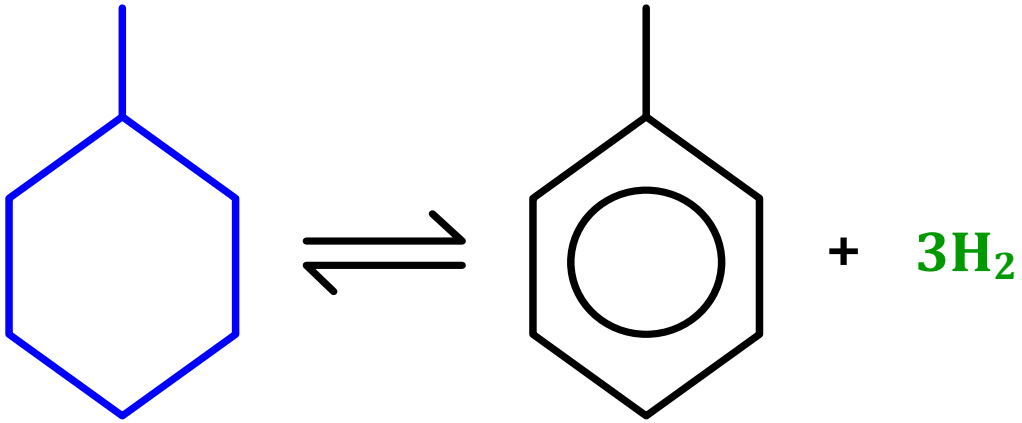


Methylcyclohexane as LOHC

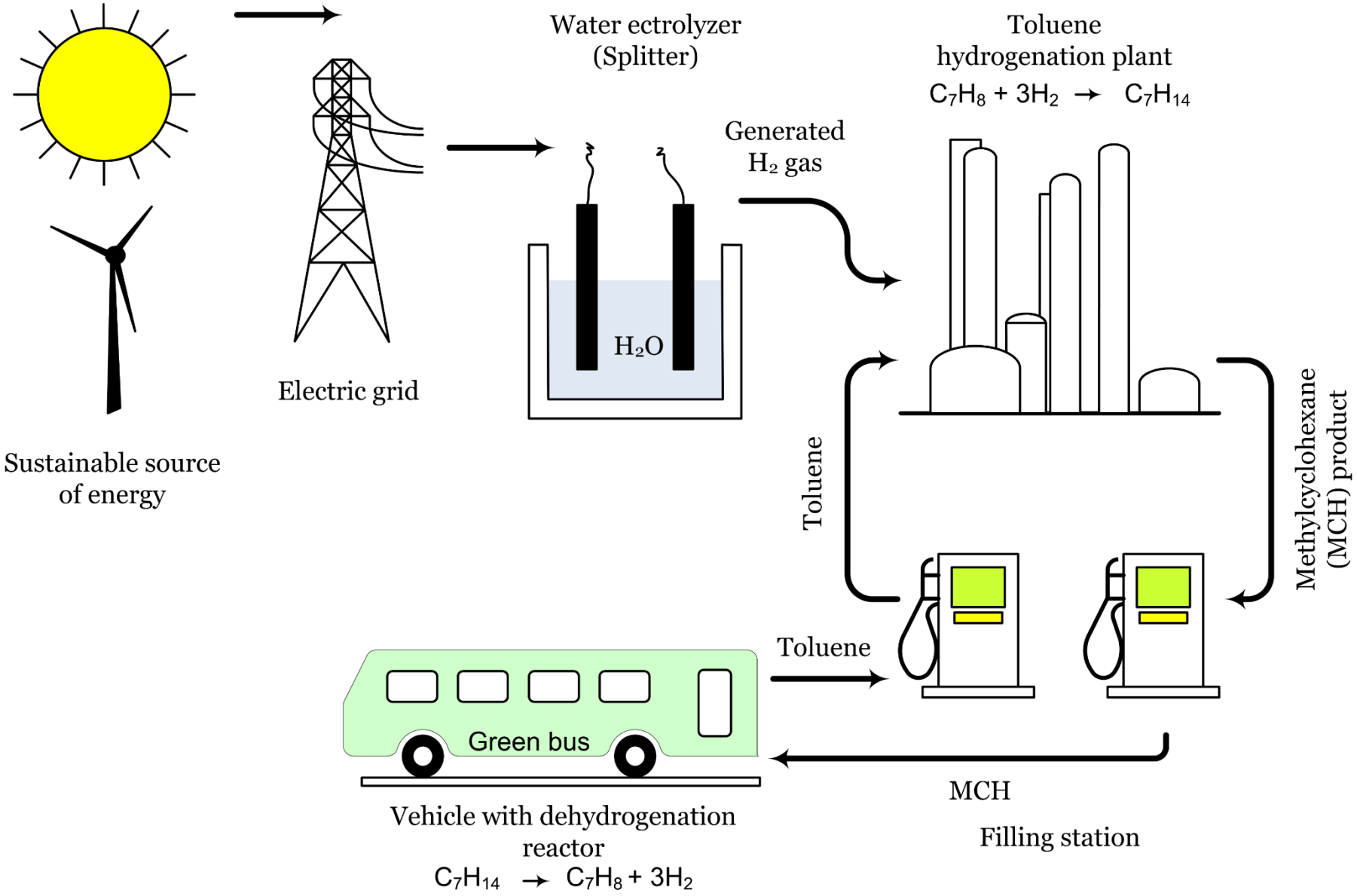
Forward Reaction



Reverse Reaction



Methylcyclohexane as LOHC: Concept for On-Vehicle System



Benefits of LOHC H_2 Storage

- Safer method of hydrogen storage and transportation
- The stored hydrogen can be utilized ex-situ and in a different season
- Unlike sun and wind, uninterupted supply of energy
- Properties like gasoline/diesel
- The current infrastructure of storage and transportation can be utilized
- Suitable for both stationary power production and on-vehicle system
- During the whole cycle, the carbon atom remains in the cycle and does not leave into the atmosphere
- No high pressure vessel and boil-off

Requirements of a Good Liquid Organic Hydrogen Carrier (LOHC)

- High hydrogen capacity
- Stable and having lower vapor pressure
- Non-toxic (not carcinogenic)
- Low dehydrogenation temperature
- Low heat of reaction
- Clean dehydrogenation/hydrogenation reactions, i.e., reduced amounts of by-products
- Moderate BPs for separation in a distillation column
- Low viscosity for easy transportation
- Cyclic manner so that C remains in the cycle

Liquid Organic Hydrogen Carriers (LOHCs)

Organic Hydride	Dehydrogenated product	H_2 capacity (wt%)	Energy (MJ/L)	Dehydroge. temperature (°C)	Dehydroge. enthalpy (kJ/mol H_2)
Cyclohexane	Benzene	7.2	6.67	325	68.8
Methylcyclohexane	Toluene	6.2	5.68	325	68.4
Decalin	Naphthalene*	7.3	7.57	325	66.5
Dodecahydrocarbazole	Carbazole*	6.7	10.4	170	51.1
Dodecahydro-N-ethylcarbazole	N-ethylcarbazole*	5.8	6.48	170	50.6
perhydro-benzyltoluene	Benzyltoluene	6.2	6.72	>270	71
perhydro-dibenzyltoluene	Dibenzyltoluene	6.2	6.96	>270	71
Indoline	Indole	1.7	2.17	110	51.9
1,2-BN-cyclohexane*	–	4.7	5.76	150	38.9
3-methyl-1,2-BN-cyclopentane	–	4.7	5.04	<80	–

*Solid at room temperature

Commercialization of LOHCs

- Chiyoda Corporation started bulk shipment of H_2 using methylcyclohexane as storage material

- Hydrogenious LOHC Technologies GmbH is using perhydro-dibenzyltoluene for hydrogen storage and transportation

- Covalian (Framatome) and H_2 Industries Inc. are also doing the LOHC business.

Challenges with LOHCs

- A highly efficient catalyst is required: active, selective, and stable
- The dehydrogenation reaction is highly endothermic and occurs mostly at high temperature
- An intensified reactor design is needed for managing heat effects
- As the dehydrogenated product has to be transported back to the hydrogenation facility, slight modification in the current infrastructure of transportation and storage is required
- Toxicology and biodegradability may need to be assessed
- Startup cost may also affect the overall economics

Conclusion

Future is moving towards hydrogen energy. Owing to the associated safety and high hydrogen capacity and due to the fact that the current infrastructure of transportation and storage can be effectively employed, liquid organic hydrogen carriers can play a vital role in the success of hydrogen economy.

Suggested Research Directions

Research is needed to synthesize more efficient hydrogenation/dehydrogenation catalysts that offers more importantly high selectivity

New LOHC-molecules are to be designed that have low heat of reaction and dehydrogenate at low temperature and fulfills the requirement of bulk production and transportation

Thank You