

Hydrogen safety, liquid and gaseous, issues and knowledge gaps

Laurent Allidières, Simon Jallais



Let's start with a (short) safety moment !

Safety Tips For Changing A Tire On A Busy Road

1. If you don't have to change the tire, don't. Only change it if you have no other option.
2. Get As Far Off The Road As You Can
3. Clearly Mark That There's An Emergency
4. Make Sure You Have Solid, Flat Ground For Your Jack
5. Be Aware of Your Surroundings



2,000 fatal accidents occur along the shoulder of roads each year! (in the US)

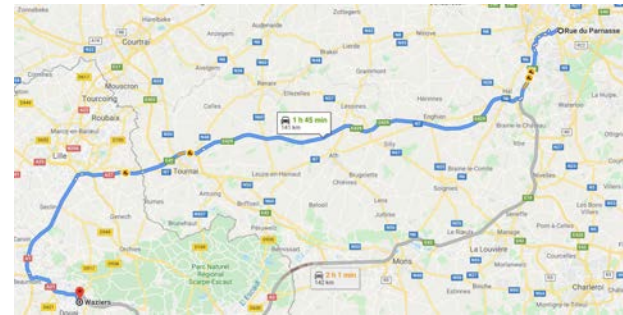
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Hydrogen safety, liquid and gaseous, issues and knowledge gaps

LH₂ and Air Liquide

- Engineering & Operations of liquefiers & loading bays
 - Waziers (1986, 10 tpd) + Bécancour (1986, 10 tpd) + Kourou (1986, 2.3 tpd)
 - Calvert City (2016, 9.1 tpd)
 - Nevada (in-construction, 30tpd)
 - + third party liquefiers sold (*5)
- LH₂ used for Space Industry & Industrial Merchant customers
- Technology provider + operator on the whole LH₂ supply chain
- Key equipments mastered & core to AL
 - Proprietary turbo-expanders with gas bearing technology
 - TB cycle expertise (methane)
 - Cold box design and manufacture
 - Boil-off optimization
 - Ortho-para conversion: optimization



R&D key figures



5

Campuses



60%

R&D projects are conducted in partnerships with laboratories, start-ups, industrial players and customers



18

Essential
Small
Molecules



60%

R&D portfolio is devoted to reduce CO2 emissions*



567

Employees

*by reducing the carbon content of Air Liquide products or those of its customers

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4

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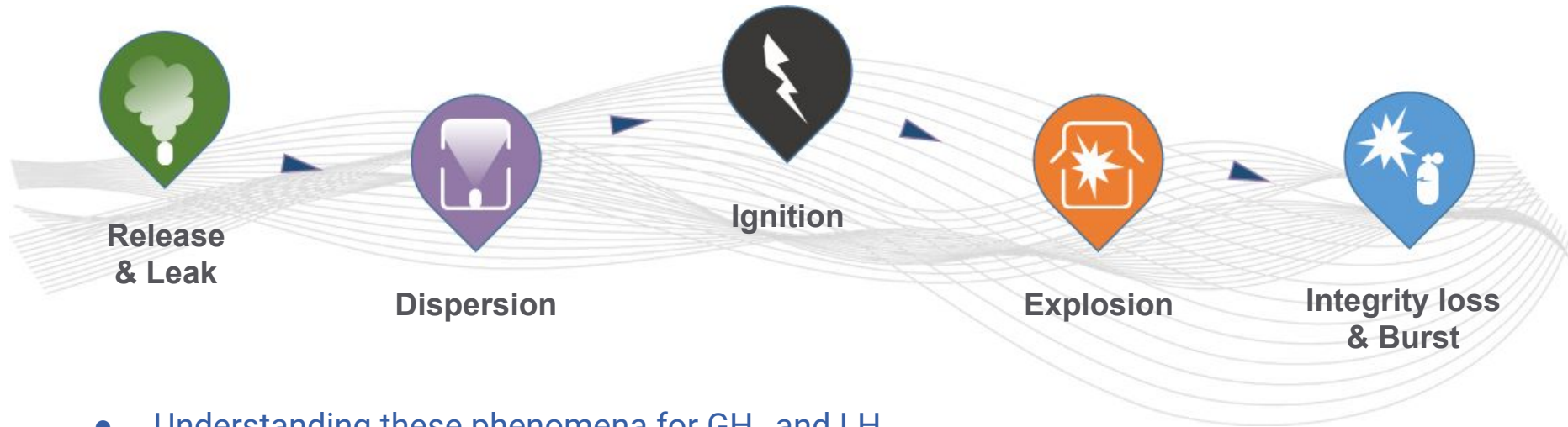
Safety Lab

TOOLS and
Methods for risk
and
consequences
assessment

SUPPORT for
deployment,
permitting,
design...

TRAININGS

Accidental kindling chain



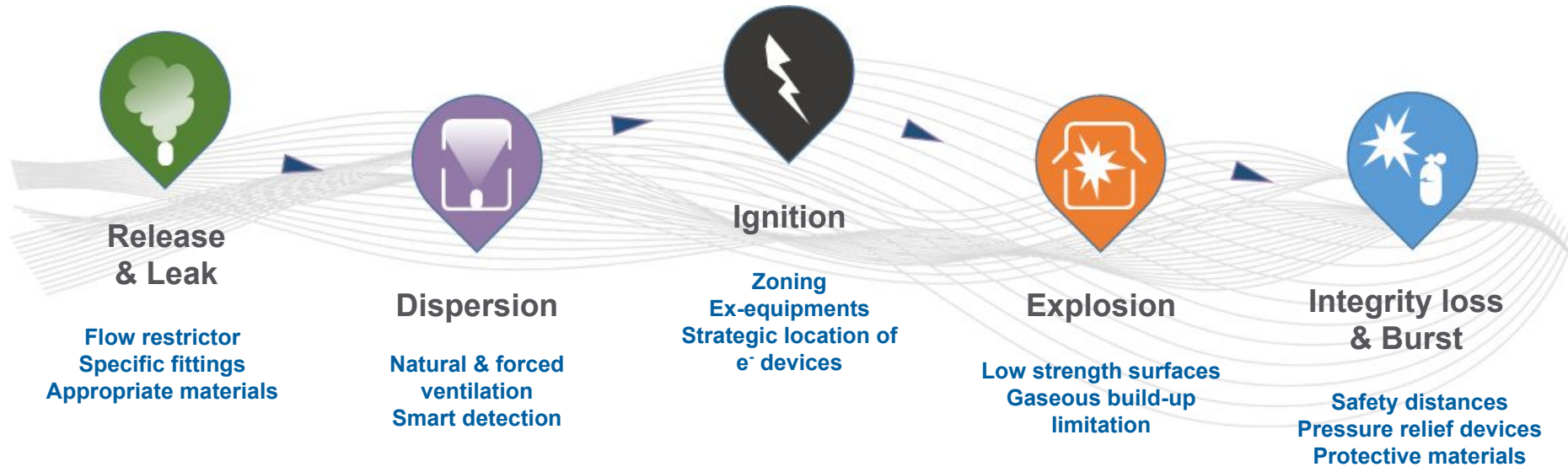
- Understanding these phenomena for GH_2 and LH_2
- Accurate and adapted tools and methods for consequences calculations
- Development of technical barriers to manage frequencies and consequences

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Example of mitigation



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Previous GH₂ projects (2007 - 2018) : a long history ...

- Pre-normative research FCHJU :
 - Hyindoor : Pre-normative research on safe indoor use of fuel cells and hydrogen systems
 - HySEA : Improving Hydrogen Safety for Energy Applications through pre-normative research on vented deflagrations
 - HyResponse : European hydrogen emergency response training program for first responders
- Safety French funded:
 - Hydromel : Safety of hydrogen/natural gas mixtures by pipelines
 - Dimitrhy : Data and instrumentation for hydrogen risk mitigation in public applications of fuel cell systems
 - BARPPRO : Protection of industrial facilities against explosion blast wave
 - Horizon Hydrogen Energy : safety of hydrogen energy applications
 - Mithygene : Hydrogen safety in nuclear applications

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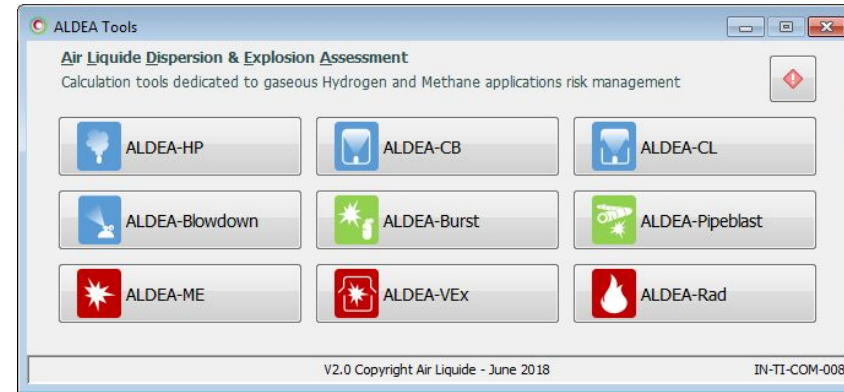
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Development of consequence models

- ALDEA software tools : Air Liquide Dispersion and Explosion Assessment
 - High pressure releases & flammable cloud formation
 - Delayed ignition and associate overpressure
 - H₂ build-up in confined zones
 - Jet fires and radiation
 - Vented explosions
 - Pressure Vessel Burst

- Based on AL R&D and open publications



- Methods published in international conferences and peer review journals

- Benchmark with tools of other groups :
 - Sandia National Lab (HYRAM)
 - INERIS, FM Global, NetTools, HySAFER tools...

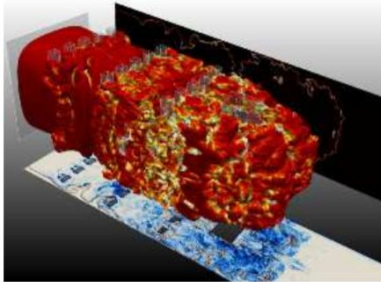
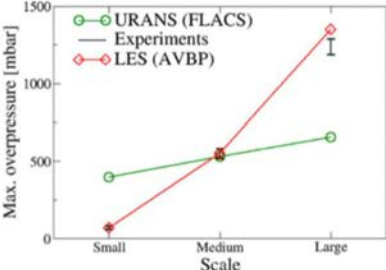
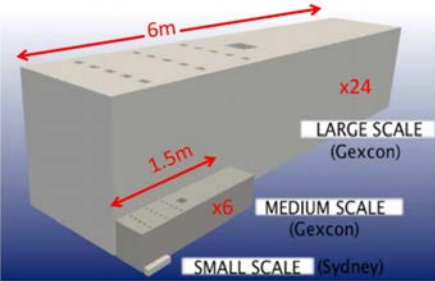
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Remaining Gaps for GH₂



- Very confined environment :
 - HyTunnel FCHJU on going project (2019-2021)
 - Focus on tunnels and underground parkings
 - Leader : Ulster University

- CFD modelling of explosion
 - HYSEA outcome : poor predictability of CFD codes
 - LEFEX : on going JIP with CERFACS, AL / TOTAL / GRTGaz
 - Objective : Development of a high fidelity modeling solution (AVBP LES code) able to model large scale realistic explosions (GH₂ or LH₂)



Current LH₂ projects (2018 - onwards)



- Pre-normative research FCHJU and JIPs :
 - PRESLHY : Pre-normative research for the safe use of liquid hydrogen
 - SH2IFT : Safe hydrogen fuel handling and use for efficient implementation
 - Marhsafe JIP : Maritime hydrogen safety
- Phenomena investigated :
 - Pressurized LH₂ releases
 - LH₂ pool vaporisation
 - LH₂ jet-fire
 - Explosion of cold flammable cloud
 - BLEVE (Boiling Liquid Expanding Vapor Explosion)
 - RPT (Rapid Phase Transition)
- Experiments on going (HSE, KIT, INERIS, GEXCON, ...)
- All the experiments, data analysis, developed models will be published
- Developpement of modelling tools with partners
- Modelling tools will be implemented in ALDEA softwares



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H2 Regulations, Codes & Standards



International
Organization for
Standardization

- Air Liquide is involved in most Regulatory bodies (ISO, CEN, SAE, NFPA, KHK...) to develop & improve the proper framework for H2 Energy applications:
 - HRS standards
 - H2 Quality and Quality Assurance
 - Refueling Protocols
 - Metering
 - Safety distances
 - Safety factors on HP storages
 - LH2 regulations
 - Guarantees of Origin for Low-CO2 H2 (e.g. CertifHy)

Constituent	Characteristics
Hydrogen fuel index (minimum mole fraction) ^a	99.97 %
Total non-hydrogen gases	300 µmol/mol
Maximum concentration of individual contaminants	
Water (H ₂ O)	5 µmol/mol
Total hydrocarbons ^b (Excluding Methane)	2 µmol/mol
Methane (CH ₄)	100 µmol/mol
Oxygen (O ₂)	5 µmol/mol
Helium (He)	300 µmol/mol
Nitrogen (N ₂)	300 µmol/mol
Argon (Ar)	300 µmol/mol
Carbon dioxide (CO ₂)	2 µmol/mol
Carbon monoxide (CO) ^c	0.2 µmol/mol
Total sulfur compounds (H ₂ S basis)	0.004 µmol/mol
Formaldehyde (HCHO) ^d	0.2 µmol/mol
Formic acid (HCOOH) ^d	0.2 µmol/mol
Ammonia (NH ₃)	0.1 µmol/mol
Total halogenated compounds ^e (Halogenate ion basis)	0.05 µmol/mol
Maximum particulates concentration	1 mg/kg

For the constituents that are additive, such as total hydrocarbons and total sulfur compounds, the sum of the constituents are to be less than or equal to the acceptable limit.

^a The hydrogen fuel index is determined by subtracting the "total non-hydrogen gases" in this table, expressed in mole percent from 100 mole percent.

^b Total hydrocarbons include oxygenated organic species. Total hydrocarbons shall be measured on a carbon basis (µmolC/mol).

^c Total of CO, HCHO, HCOOH shall not exceed 0.2 µmol/mol

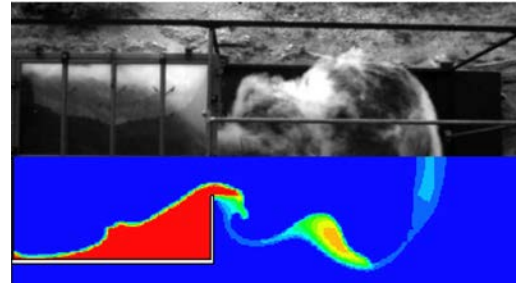
^d Total halogenated compounds include, for example, hydrogen chloride (HCl), and organic halides (R-X). Species will be checked according Quality Assurance



Our Objectives & Means

Manage risk of H₂ Energy Markets
with strategic partners, in particular H₂ Mobility
and Industry

Maintain leadership across the full value chain
from H₂ production to delivery at the point of use



ANALYTICAL
and
NUMERICAL
approaches



EXPERIMENTS



Worldwide
STRATEGIC
PARTNERSHIP

Some public references

D Houssin-Agbomson, D Jamois, Ch Proust, J Daubech, S Ruban, S Jallais - **Study of potential leakage on several stressed fittings for hydrogen pressures up to 700 bar** - International Journal of Hydrogen Energy, 2012, 37(22), pp 17509-17516

S Jallais, D Houssin-Agbomson, B Cariteau - **Application of natural ventilation engineering models to hydrogen build-up in confined zones** - ICHS5 conference, Brussels, September 2013

D Houssin-Agbomson, JY Letellier, Ph Renault, S Jallais - **An experimental study on the influence of helium on helium build-up and concentration distribution inside a 1-m³ semi-confined enclosure considering different conditions of use** - ICHS6, Yokohama (Japan), 2015 October, Lecture.

G Bernard-Michel, D. Houssin-Agbomson - **Comparisons of helium concentration measurements at different flow rates and for two diameters of pipes** - ICHS6, Yokohama (Japan), 2015 October, Lecture.

B Fuster, D Houssin-Agbomson, S Jallais, E Vyazmina... - **Guidelines for the design of hydrogen storage systems** - International Journal of Hydrogen Energy, 2016, in press

E. Vyazmina, S. Jallais, - **Validation and recommendations for FLACS CFX for hydrogen explosions: Effects of concentration, obstruction vent area and ignition position** - International Journal of Hydrogen Energy, 2016, in press

E. Vyazmina, S. Jallais, J. Daubech, J. Hebrard, A. Duclos, L. Gastaldo, N. Daudey, - **Delayed explosion in highly obstructed geometry** -, ICHS, Hamburg, Germany, September, 2017.

E. Vyazmina, S. Jallais L. Krumenacker, A. Tripathi, A. Mahon, J. Commanay, S. Kudriakov, E. Stude, - **Vented Explosion of hydrogen/air mixture: an inter comparison benchmark exercise** -, ICHS, Hamburg, Germany, September, 2017.

Contribution to the French Ministerial working group on H2 forklifts in warehouse - **Arrêté n°4715 du 26/11/2015**

More than
20
publications
in peer reviewed
journal

More than
50
communications
in scientific
conferences



H₂ gets things moving

Thank you

Questions

Development in Hydrogen for our customers

Production & Supply chain

Production

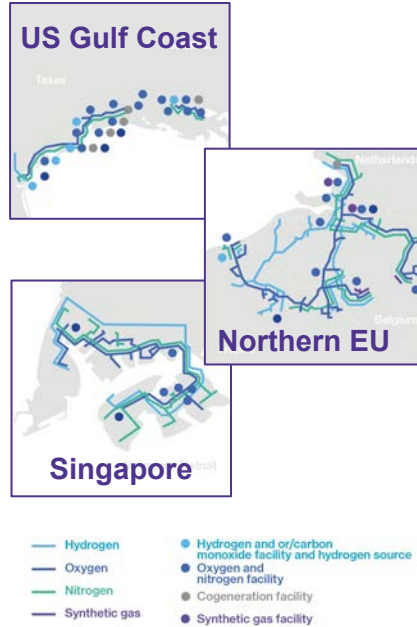


Supply-chain



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Distribution Networks



Markets Segments

Process industries

Oil & Gas



Steel, Glass



Electronics



Transportation Space



Key Figures

14 bn m³ / yr
1,25 Mt / yr
0,18 ExaJ / yr

3500 t / d

1,850 km H₂
pipelines

~ 50 large H₂/CO
plants

~ 40 electrolysers

Air Liquide already started to invest for mobility



Mobility for Professionals
US+EUROPE
9 HRS



Mobility for Consumers
US North-East
12 HRS
+ Supply chain



Mobility for Consumers
California
4 HRS



Mobility for Consumers
Japan
6 HRS



Mobility for Consumers
Dubai
1 HRS



Mobility for Consumers
Korea
1 HRS



Power to Gas
Denmark
5 HRS
+ 1 Electrolyzer



Mobility for Consumers
Germany
11 HRS



Mobility for Consumers
Paris, Brussels and Rotterdam
6 HRS



120 H₂ stations installed by AL² in the world

60 stations invested and operated by AL

Hydrogen mobility markets: Ready to scale TODAY

Paris :

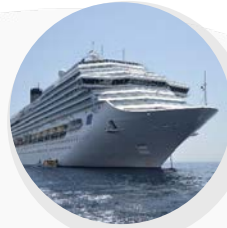
- 150 H₂ Taxis HYPE
- 3 H₂ stations



Ferries
1 t/day



Cruise ships
10 t/day



Material handling forklifts (20 000)
100 kg/day per site



Trucks (few)
100 kg/day per truck



Cars (10 000)
100-200 kg/day per station



Buses (200)
20 kg/day per bus

Trains (1+)
150 kg/day per train



Airplanes Applications



Bicycles & scooters

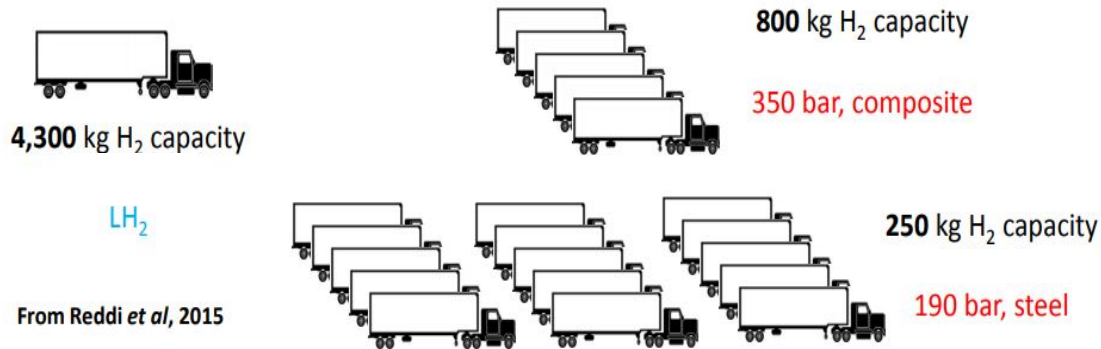


Drones



Why Liquid Hydrogen?

Higher density \Rightarrow Improved logistic and allow higher throughput



Lower foot print (factor 2) for car refueling stations

Synergies with others applications : planes, trucks, trains, boats, ...

R&D skills applied to H₂ Mobility

0 Production

1 H₂ storage- (on board and supply chain)

2 Compression (case Isobar reservoir)

3 H₂ material compatibility (HE/HEF/LBB)

4 H₂ Quality Assurance

5 Refuelling protocols

6 SAFETY

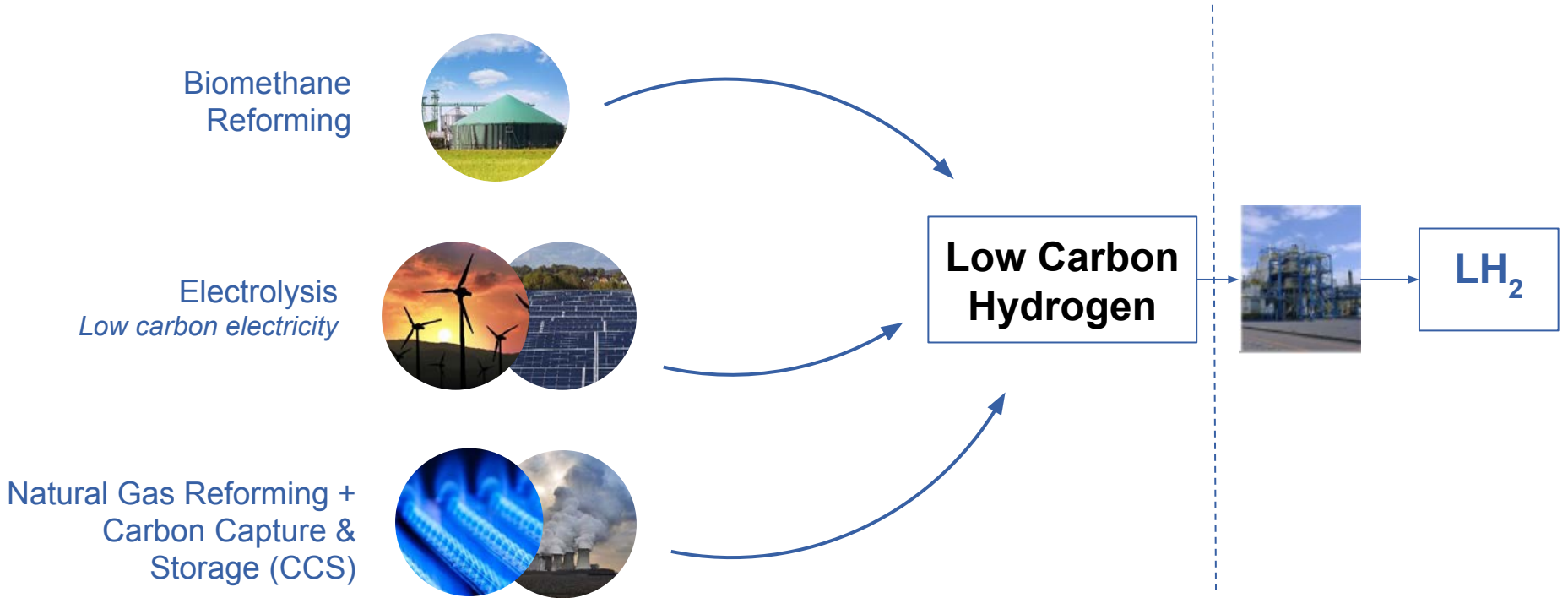


ATEX

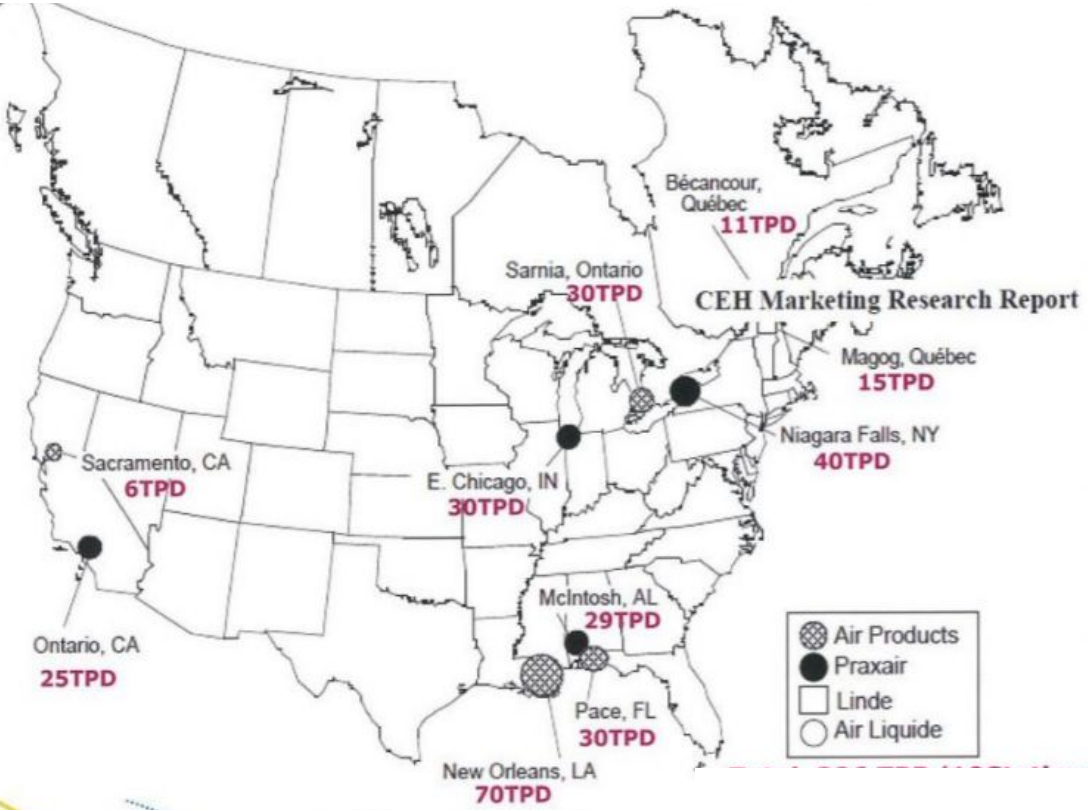
7 Logistic studies



H₂ Production



“Large scale” liquefiers in operation (from 1960 to now)



2018 :

- AirGas (AL) 10 tpd - Calvert City, KY
- Hydrogen United 10 tpd - Charleston, TN

Europe :

- Air Products 5 tpd - Rozenburg NL
- Linde 4 tpd - Ingolstadt GE
- 6 tpd - Leuna GE
- Air Liquide 10 tpd - Waziers FR
- 2 tpd - Kourou - Guyana

Liquefiers announcements : an amazing acceleration end 2018

AIR LIQUIDE	Nov 2018 Fev 2019	30 tpd 20 MW PEM (8t/d)	McCarran, Nevada Becancour, Canada
AIR PRODUCTS	Sept 2018 Janv 2019	30 tpd XX tpd	La Porte, Texas California
PRAXAIR	Nov 2018	30 tpd	La Porte, Texas
LINDE	Oct 2018	10 tpd	Leuna, Germany

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H₂ related projects (1 / 2)



PRESLHy (FCHJU) project :

- State of the art analysis on LH₂ hazards (public report, see PRESLHy website)
- PIRT (Phenomena Identification Ranking Table) (public report)
- Experimental and simulation WP on release, ignition and combustion phenomena
- Chapter on LH₂ safety in Handbook of Hydrogen Safety
- Guidelines for safe design and operation of LH₂ systems and infrastructure
- Recommendations for relevant Regulations, Codes and Standards (RCS)

SHIFT project :



- Experiments and simulations of BLEVE, RPT and GH₂ jet fires
- Safety of hydrogen technology, especially focusing on consequences of handling and use of large volumes and within closed and semi-closed environments and in maritime transport.
- Development of Guidelines for use of H₂ in industry and transport.

H₂ related projects (2 / 2)

HEAVEN (FCHJU) project :

- High power density FC System for Aerial Passenger VEHICLE fueled by liquid Hydrogen

ENABLEHy H2020 project :

- ENABLING cryogenic Hydrogen based CO₂ free air transport

