

Asia Industrial Gases Association

(Webinar # 15, 08 Dec 2022 from 1 30 to 3 30 pm SG/SH time)







"An Overview on H2 Production Processes and Safe Use of H2 in Mobility"



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Agenda

- ❖ Welcome and Webinar Rules by Claudia Wang, AIGA China Sec General
- ❖ AIGA Antitrust and Disclaimer by Claudia Wang
- ❖ Brief Introduction about AIGA by Du Pu, AIGA TC Member (Messer Asia)
- ❖ Webinar Objectives by Du Pu
- ❖ Session 1: An Overview of H2 Production Processes and Key Safety Aspects
 - H2 Production Process by Sandeep Kamat(Linde)
 - Hydrogen Venting, Lessons Learnt for Safe Design and Operation by Amy Shen (AP)
- Session 2: An Overview on Safe Use of H2 in Mobility
 - Hydrogen Refueling Station (HRS) Introduction by Wayne Guan (Linde)
 - Engineering Safe Practice for HRS by Esdala Wang (AP)
 - Safety of Hydrogen System in Fuel Cell Vehicle by Darcy Qin (AL)
- ❖ Wrap Up/Role of AIGA in Supporting Safe Use of H2- by Chen Xing (AL)
- Q&A Moderator Chen Xing (AL)



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- 3. profits and profit margins;
- 4. output and sales;
- 5. market shares and sales territories;
- 6. investments and marketing plans;
- 7. bidding or refraining from bidding;
- 8. credit conditions or any other terms or conditions of sale;
- 9. selection, rejection, or termination of customers or suppliers.

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Moderator



Ms. Claudia Wang Secretary General AIGA China

Opening Address



Mr. Du Pu Technical Director Messer Asia AIGA TC member

Closing Comments and Q&A



Mr. Chen Xing
H2E Head
Air Liquide China
AIGA H2 Task Force Chair



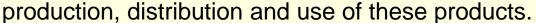
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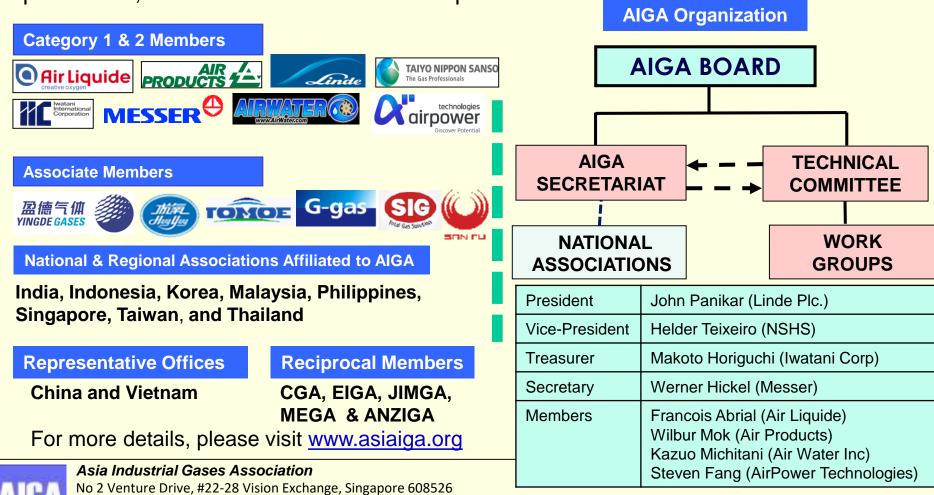
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AIGA Board and Key Members

About AIGA: Formed in <u>Dec 2002 in Singapore as a non profit association</u> to represent the majority of Industrial Gas companies in the countries in Asia.

Mission: To promote better safety, health, environmental awareness and security in





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AIGA Technical Committee Focus

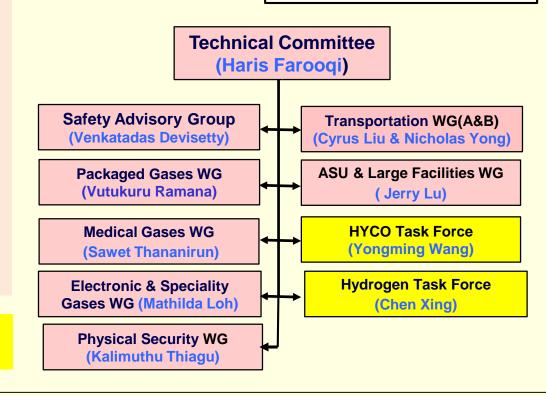


AIGA TC is currently focused on 9 priority areas:

- SAG (General Safety & sharing of incidents/ learnings)
- 2. Packaged Gases
- 3. Medical Gases
- 4. Electronics & Specialty Gases
- Transportation of Packaged & Bulk Gases
- 6. ASU & Large Facilities
- 7. HYCO
- 8. Physical Security
- 9. H2 Mobility/Clean Energy

AIGA TC is responsible for driving all technical work of the association

Technical Committee Members: Haris Farooqi (Air Products) Vicky Dobson (Air Liquide) Noriyuki Murata (Air Water) Steven Yee (Iwatani) MVS Ramakrishna(Linde Plc) Du Pu (Messer) Takeshi Yamanishi (Nippon Sanso)





Technical Committee: Major Deliverables



- AIGA Publications (available on AIGA website: > 180 in nos.)
 - > 120 Standards/ Guidelines/ Codes of Practices
 - > 28 Training Packages
 - > 25 Safety Bulletins
 - Several Safety Posters and Position Papers
- Co-hosting of multiple Safety Seminars every year with National Associations
- Engagement with National Associations and Representative Offices
- Actively promote AIGA activities and publications
- Participation in global harmonization of standards at IHC
- Sharing of learning from safety events and analysis of safety data
- Collaborate with non-AIGA Associations AIIGMA (India) & CIGIA (China)
- Communicate and cooperate with IOMA Global Committee and Regional Associations (CGA,EIGA,JIMGA)

Please visit <u>www.asiaiga.org</u> for more details



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Webinar Objectives



Background:

- H2 has many current applications and usage but it is also fast developing as 'fuel for the future' and clean(green) energy source
- Use of H2 in Mobility is fast gaining momentum in all over the world and also in Asia.
- Also, new manufacturing processes are being evolved to support the 'net zero' commitment of Governments and Industrial Gases(IG) Companies
- IG Industry have been safely manufacturing and distributing H2 over more than 100 years and thus have "thought leadership"

The objective of this webinar is to create

- a general awareness about the various production processes of H2 and key safety challenges/ future trends
- Use of H2 in mobility: how and why/advantages and key safety challenges
- What role AIGA is playing to support the safe production, transport and use of H2





Session - 1

An Overview of H2 Production Processes and Key Safety Aspects



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Presenters





Mr. Sandeep Kamat

Head of HyCO Operations (APAC-Center of Excellence) Linde Gas. Chem Engineer 29 years of experience in operations & process dept. Worked with leading industries in fertilizer complex, refineries and now with Linde Gas since Jun 2011.



Dr. Amy Shen

Senior Principal Process Safety Engineer, Central Process Safety, Air Products. Ph.D. in chem engineering, actively involved in hydrogen and oxygen safety; skilled in advanced modeling of gas dispersion, fire and explosion hazards.





Hydrogen... What Do You Know About It?

Is it the Bad Boy of the Gas World?



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HYDROGEN SAFETY



HYDROGEN BOMB





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HYDROGEN SAFETY-HINDENBURG CASE YEAR 1937

THE FIRE

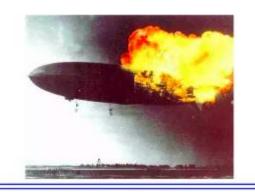


HINDENBURG



NHA NEWS

Fabric, Not Filling, to Blame
Hydrogen Exonerated in Hindenburg Disaster



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HYDROGEN SAFETY- SPACE CHALLENGER CASE YEAR 1986

SPACE SHUTTLE CHALLENGER



O RING FAILURE





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HYDROGEN SAFETY

HYDROGEN FACTS

Chemical Symbol: H₂

CAS Registry Number: 1333-74-0

DOT Classification : Flammable Gas

DOT Label : Flammable Gas

Transport Canada Classification: 2.1

UN Number : UN 1049 (compressed gas)

UN 1966 (refrigerated liquid)

HHPHYSICAL PROPERTIES

- Gas at atmospheric temperature and pressure
- Extremely flammable
- Colorless
- Odorless
- Tasteless

HHPHYSICAL PROPERTIES cont.

- Smallest molecule
- Lightest specific density (14 times lighter than air)
- Non-toxic, simple asphyxiant
- Non-corrosive
- Metallurgical: hydrogen embrittlement
- Normal boiling point: -423.0 °F

HHPHYSICAL PROPERTIES cont.

- Cryogenic Burns: Damage can result from exposure to cold gases
- Lightest of All Chemical Elements: Most abundant substance in the universe
- Our sun is a nuclear reactor in which hydrogen continuously fuses into helium. Fusion process creates heat which warms our earth.



HYDROGEN SAFETY ASPECTS

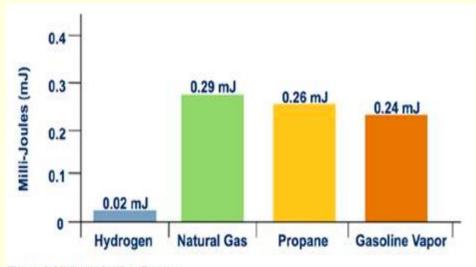
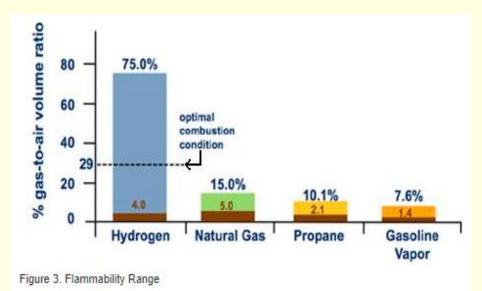
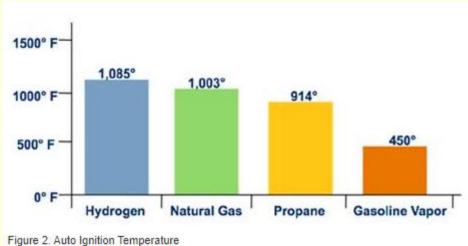


Figure 4. Minimum Ignition Energy





Relative to Air 2-1.52 1-0.55 0.07 0 **Natural Gas** Hydrogen Propane Figure 1. Relative Vapor Density

5

3-



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4.0

Gasoline Vapor

H₂ Production Process



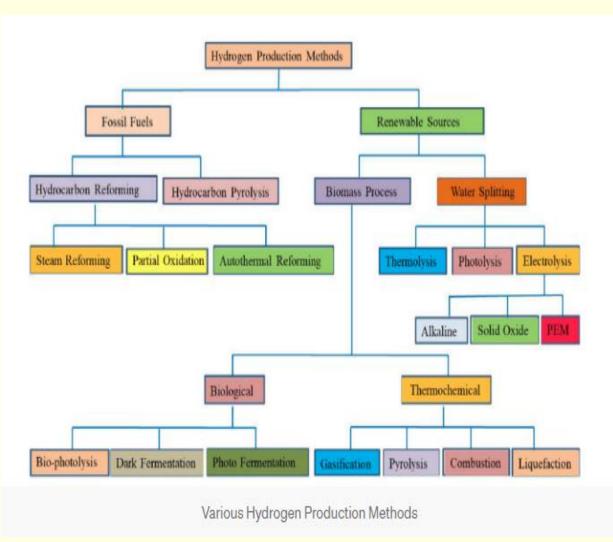


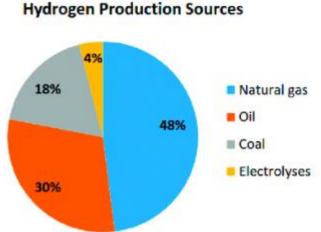


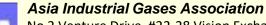
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HYDROGEN PRODUCTION PROCESS









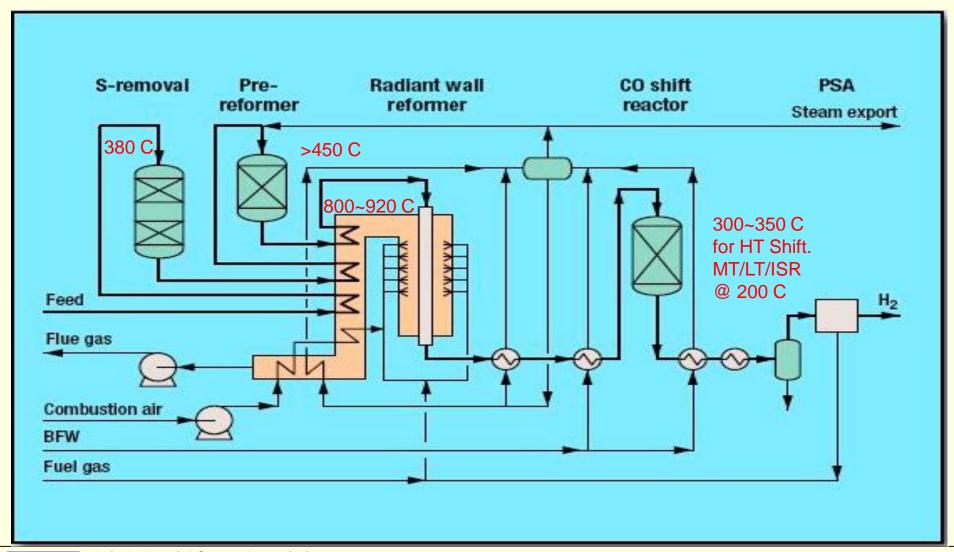
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STEAM METHANE REFORMING PROCESS (SMR)







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Few aspects of SMR process



Basic Chemical reactions

- CH4 + H2O CO + 3H2 Endo (STEAM REFORMING REACTION)
- CO + H2O ← CO2 + H2 Exo (WGS)

Main process parameters

- Temp out : up to 800~ 920 C
- Pressure : up to 40 bars
- Syngas Composition (31.95 bar and 870°C) with NG
 - ♦ H₂
 47.23 %
 - ◆ CO 9.234 %
 - ◆ CH₄ 4.454 %
 - ◆ CO₂ 5.392 %
 - ◆ H₂O 33.516 %
 - ◆ N2 0.173%

Licensors : Linde, Technip, TKIS, Foster wheeler, Haldor Topose, Caloric, Mahler, Hydro chem



Hydrogen Production technologies



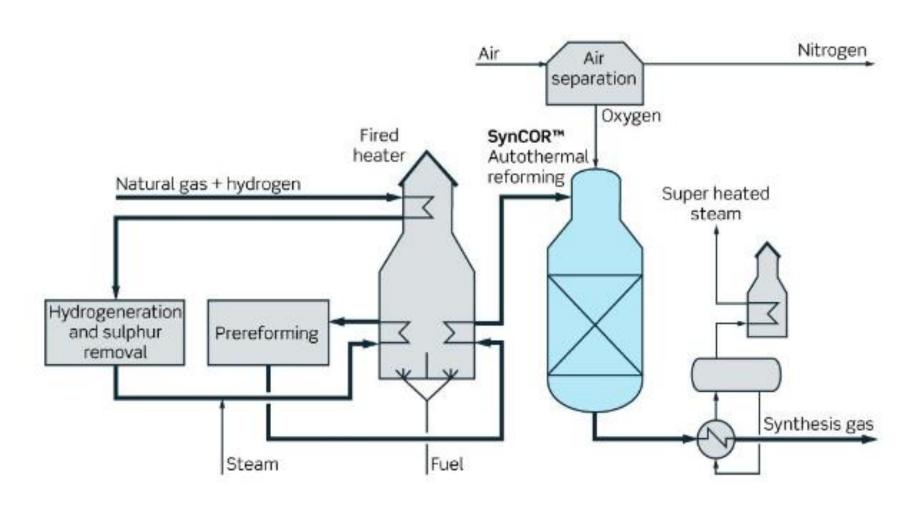
Autothermal Reforming

- Low carbon Hydrogen production process at scale.
- Catalytic process
- Feed stock
 - Light hydrocarbons: natural gas up to naphtha
 - Requires O₂
- Low H₂/CO ratio available
- A few licensors : HALDOR Topsoe, LURGI, Linde



AUTOTHERMAL REFORMING (ATR)







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Few aspects of Autothermal reforming process



Basic Chemical reactions

- CH4 + 1.5 O2 ← CO + 2H2O (1) Exo
- CH4 + H20 ← CO +3H2 (2) Endo
- CO + H20 ← CO2 +H2 (3) Exo
- Temp out : up to 1400 °C
- Pressure : up to 70 bars
- Syngas Composition (21 bar and 1050°C) with NG
 - ◆ H₂ 52.0 %
 - ◆ CO 26.0 %
 - ◆ CH₄ 0.3 %
 - ◆ CO₂ 5.4 %
 - ◆ H₂O 16.3 %
- CO2 from syn gas is also recycled back after recovery and it is called dry reforming producing then Blue H2.



Hydrogen Production technologies



Partial Oxidation

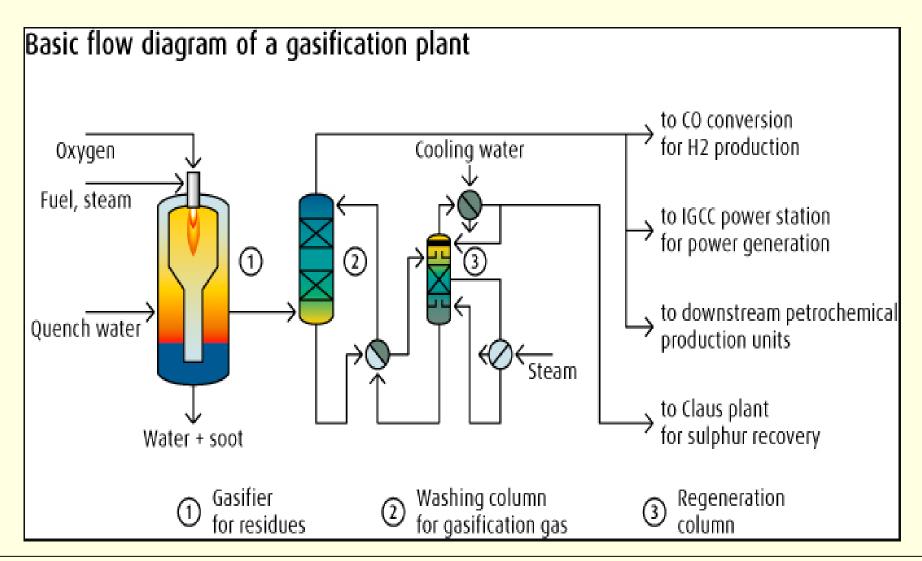
- Non catalytic process
- Feed stock
 - Light to very heavy hydrocarbons (residual oil, coal or coke)
 - Requires O₂
- Size of plants
 - Medium and large
- Three licensors for gasifiers
 - TEXACO/GE
 - SHELL
 - LURGI



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PARTIAL OXIDATION PROCESS (POX)







Few aspects of Partial oxidation process



Basic Chemical reactions

- CH4 + 1/2 O2 ← CO + 2H2 (1) Exo
- CH4 + 202 ← CO2+2H2O (2) Exo
- CO + H20 ←→ CO2 +H2 (3) Exo
- Temp out: up to 1400 °C
- Pressure : up to 80 bars
- Syngas Composition (38 bar and 1240°C)

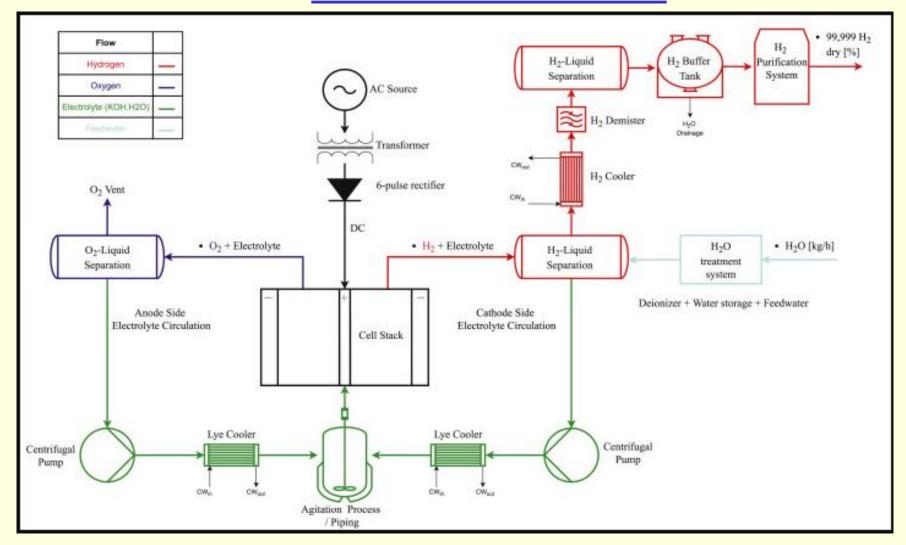
◆ H ₂	59.1 %
◆ CO	32.5 %
◆ CH ₄	0.6 %
◆ CO ₂	1.3 %
♦ H ₂ O	6.5 %



Hydrogen Production technologies



ALKALINE ELECTROLYZER





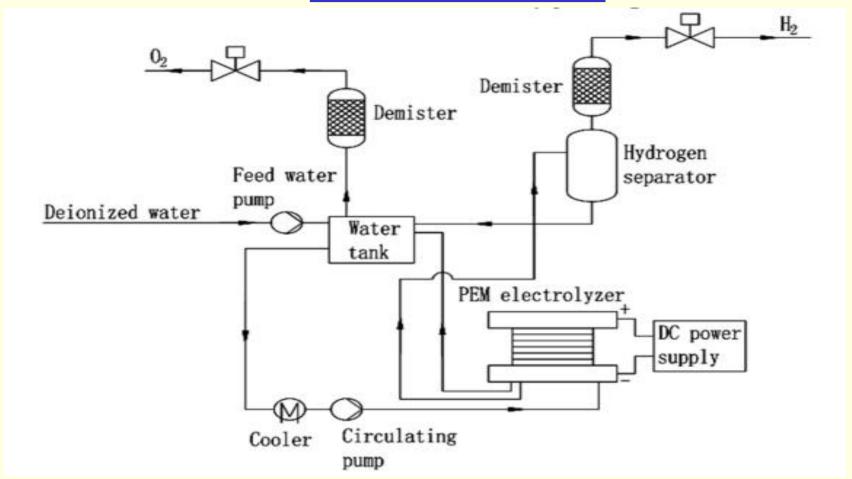
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Hydrogen Production technologies

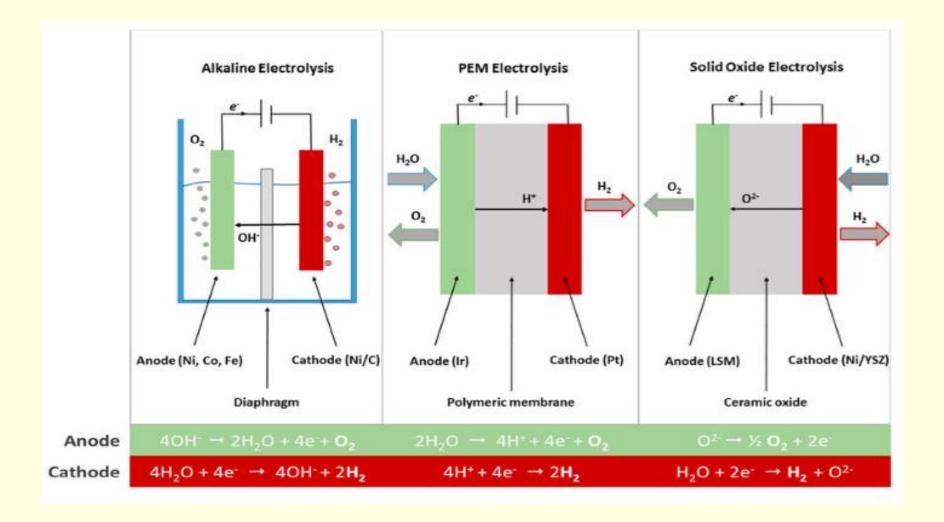


PEM ELECTROLYZERS



AEL/PEM/SOLID OXIDE ELECTROLYSIS EQUATIONS







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Hydrogen Production technologies



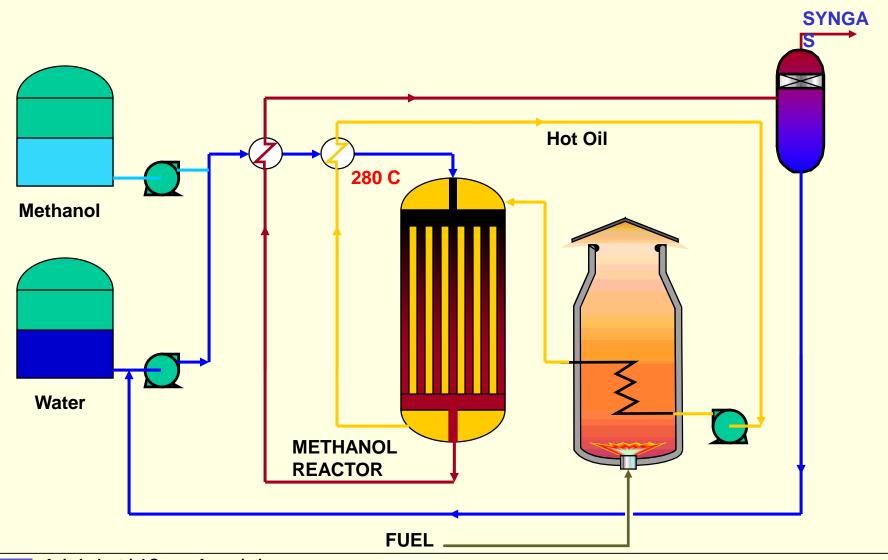
Methanol Reforming

- Catalytic process
- Feed stock
 - Pure Methanol
 - Methanol + Alcohols mixture
- Size of plants
 - Small Hydrogen, Carbon monoxide plant





Methanol Reforming





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Few aspects of Methanol cracking process



Basic chemical reaction

- CH3OH ←→ CO + 2H2O (1) Endo
- CO + H2O ← CO2 + H2 (2)Exo
- CH3OH +H20 ←→CO2+2H2 (3) Endo
- Temp out : 250 °C to 300 °C
- Pressure : 25 to 30 bars (up to 60 bars)
- H₂O/CH₃OH: 1.5 ~ 2
- Syngas Composition

♦ H ₂	74.5	%
◆ CO	1.7	%
◆ CO ₂	23.5	%
◆ CH ₃ OH + CH ₄	6.5	%

Licensors: Hydro chem, Caloric



GREY/BLUE/GREEN HYDROGEN



Grey hydrogen

Hydrogen is produced from fossil fuels, notably natural gas, and the CO2 is emitted.



Blue hydrogen

Hydrogen is produced from fossil fuels, notably natural gas, and the CO2 emissions are captured and stored (hydrogen with CCS).



Green hydrogen

Hydrogen produced with electrolysers that use green electricity like hydropower, wind and solar power.





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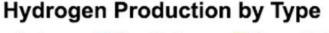
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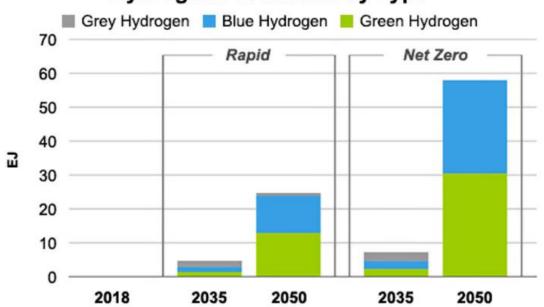
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Hydrogen Production by type as of today and future projection







Source: BP plc

Blue hydrogen follows the same processing route as grey hydrogen to produce molecules, but the carbon dioxide (CO2) emissions are captured during production, so they're kept out of the atmosphere. According to the Global CCS Institute, grey hydrogen – which uses more carbon-intensive steam methane reforming – makes up approximately 98% of current hydrogen production, while blue hydrogen accounts for just 1%.

Source: Gas world News



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Challenges in H2 production process



- Most hydrogen production process from fossil fuels are in extremely challenging operating condition, high temperature, sour conditions, and reducing atmosphere etc lead to various metallurgical challenges like damage to material of construction by following phenomena:
 - High temperature Hydrogen attack (HTHA)
 - Hydrogen embrittlement
 - Metal dusting
 - acidic corrosion
 - Creep
- Green Hydrogen production is still a challenge due to higher specific unit cost of production/sourcing of Renewable Energy (RE), limitation in getting continuous availability of RE.
- Modulation of process and conceptualization of green hydrogen production process as per RE availability is also a challenge.



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Hydrogen Venting, Lessons Learnt for Safe Design and Operation

Amy Shen
Air Products



Liquid hydrogen tank vent fire



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Hydrogen Vent vs. Flare



Vent





Flare



Figure 1. Overview of hydrogen plant, & flare highlighting near and far field data collection locations.



A continuous inert purge or the ability to add a purge to extinguish the flame on an atmospheric vent could be required due to special considerations.





Types of Hydrogen Vent

Process vent

Lower velocity

- H2 purifier purge gas
- PHG H2 product vent during commissioning or excess production rate
- PSA H2 vent when purity is not met
- H2 trailer purge gas

Emergency vent

Higher velocity

- PRD release for HyCO/PHG/H2
 PSA/H2 trailer/tank etc.
- PSA control valve opens when system pressure is higher than set pressure
- ..

What's the difference between a process vent and an emergency vent?

A process vent may occur in normal operation, an emergency vent should not!

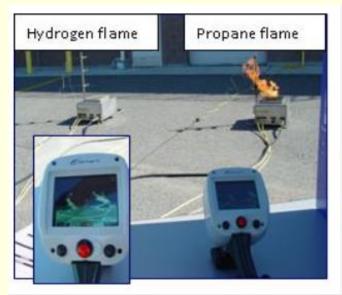


Hydrogen Flammability



- Wide flammable range and low ignition energy
- Burns with low luminosity flame, almost invisible in the daytime (easier to observe at night)

Hydrogen flame vs. propane flame





Be careful of working around the hydrogen vents. Potential invisible fire!

Hydrogen and Propane Flames in Daylight

Hydrogen and Propane Flames at Night

^{*}Pictures from https://h2tools.org/bestpractices/hydrogen-flames

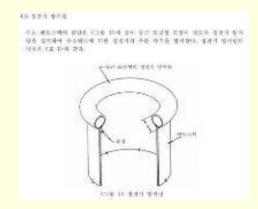


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Ignition suppression?

- Potential ignition sources should be minimized but CANNOT BE ELIMINATED
- Devices exist that claim to control ignition potential
 - Avoid static discharge onto the tip of the vent
 - Static can come from rust particles, atmospheric static etc.
- Investigated by NASA in late 1960's for low velocity releases.



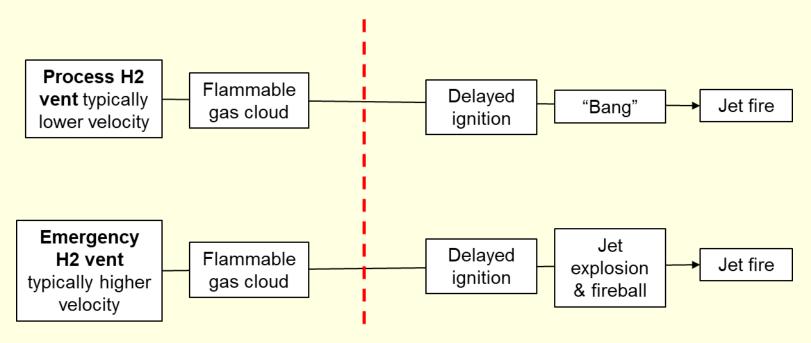


Toroidal ring Korea OSHA guideline









Most of the time, vents do not ignite, but we should not be surprised if they do. Even if they ignite, vents are designed to be safe.

Jet fire



2009 Spadeadam Large scale jets

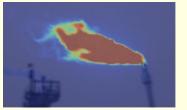






2014 Garyville Full scale flare test



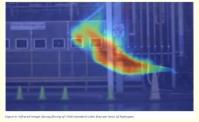




2015 R&D 2 H2 mixtures







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High-pressure H2 vent incident



- Large relief valve lift, 11 kg/s
- 16" diameter, 50 ft high vent stack
- Broken glass. No injury
- Security video: explosion, fireball, vertical jet fire (reflected in water puddle).
- Model developments ongoing:
 - Sub-sonic jet explosion
 - New hazard, downward fireball

3rd party video from ~ 3,000 ft



Video from ~ 1,500 ft





Hydrogen vent design for safety

- Vent elevation, diameter, release direction based on:
 - Flammable cloud (all vents)
 - II. Jet fire (all vents)
 - III. Jet explosion & fireball (emergency vents)





H2 vent safe operation

- Trainings are critical
- May think
 - H₂ vents never light off
 - H₂ vents always light off
 - If vent is on fire, there is something wrong, fire should be put out



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Incident: H2 purifier vent fire

- H₂ purifiers used at some customer sites
 - Some H₂ vented
 - Typically vent above building roof line
- In this example
 - Vent lit off
 - Customer saw flame, asked the operator to put fire out
 - Operator went up on roof with CO₂ fire extinguisher
 - Failed to put fire out





Lessons

- Educate customer and operator that occasionally H₂ vents light off. This is normal and quite safe.
- Operators should not attempt to put fire out
 - Resulting vented H₂ could reignite and cause injury
- Safe actions:
 - Do nothing, let it burn
 - Turn off H₂ source, if practical





LH2 Vent Fire



Liquid hydrogen tank vent fire

Being very careful NOT to get water in the vent line! That could cause a freeze block and subsequent tank/trailer overpressure and explosion!





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What might happen with wrong response?

Unexpected hazards!

☐ Higher thermal radiation
☐ Unexpected fire or explosion due to delayed ignition
☐ If emergency services put water on a LH2 vent, the vent line can be frozen and blocked with ice which might lead to tank/trailer overpressure and explosion
☐ Wrong firefighting technique might worsen the fire





Conclusion

- H₂ venting is relatively common
- It is safe to vent H₂
- Design vents based on the specific hazards of H₂
- Train everyone associated with hydrogen operation on what can happen when H₂ vents
 - what to do, and not do
- There is always more to learn about H₂





Session – 2

An Overview on Safe Use of Hydrogen in Mobility



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Presenters





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Driving Tomorrow's Fuel TodayHydrogen Refueling Station (HRS) Introduction

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Hydrogen Value Chain of Hydrogen Mobility









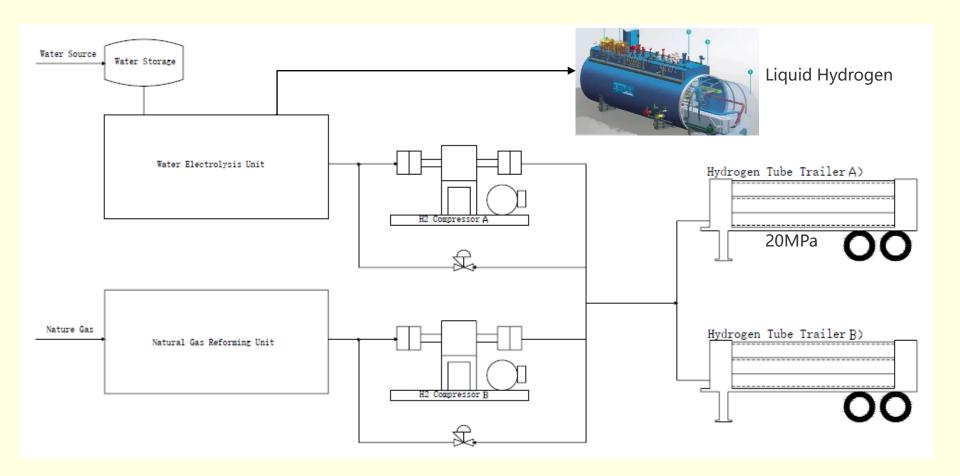
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Technology overview



Basic Concept for Typical H2 Supply & Transportation





Technology overview



H2 Specification of HRS: ISO-14687-2019

Components	Specification
H2	≥99.97%
СО	≤ 0.2 ppm
CO2	≤ 2.0 ppm
N2/Ar	≤ 300.0 ppm
O2	≤ 5.0 ppm
Не	≤ 300 ppm
Sulfide	≤ 0.004 ppm
Halogen ion	\leq 0.05 ppm
NH3	≤ 0.1 ppm
Total hydrocarbon (as per methane)	≤ 2.0 ppm
H2O (liquid)	≤ 5.0 ppm
Maximum particle content	$\leq 1 \text{ mg/kg}$



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Technology overview H2 Supply to HRS







Bulk supply (5 MPa)

Trailer supply (30 MPa)

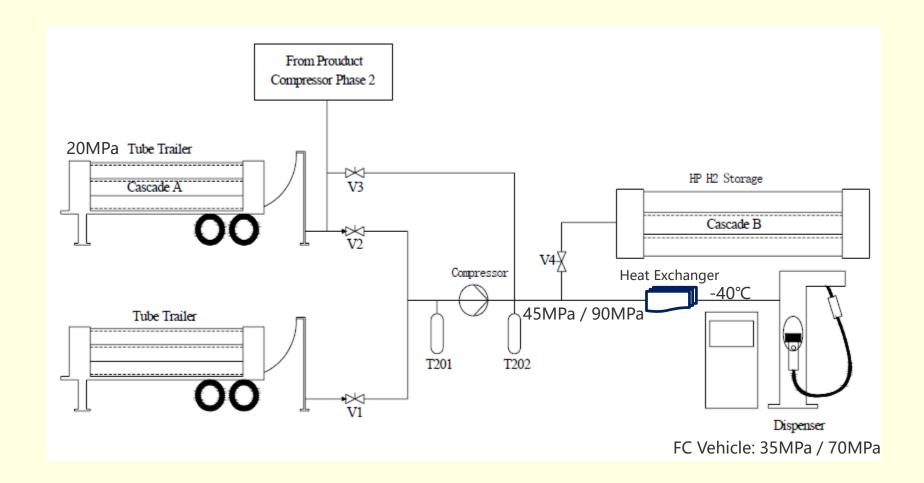
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Technology overview

Basic Concept for Typical HRS







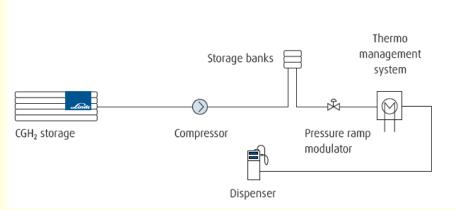
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Technology overviewBasic concept for HRS

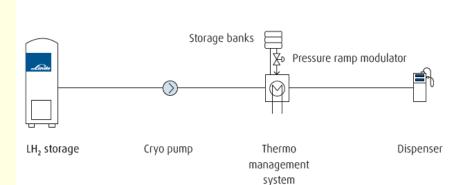


Basic concept: Ionic compressor system





Basic concept: Cryo pump system







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Hamburg Germany



35/70 MPa, 2 sets of ionic compressors, 2 sets of on-site electrolysis





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High capacity on small footprint

Linde H2 Station in Oakland, California







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Engineering Safety Practice for HRS

Air Products

Esdala Wang





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Let's discuss:





HRS Safety Distance – Different HRS Requirement



HRS Safety Facilities – F&G Detecting System



HRS Safety Facilities – Firefighting System



HRS Safety Assessment – Fire & Explosion



HRS Safety Distance – Different HRS Requirement

DIFFERENT HRS TYPE OF AIR PRODUCTS:

INDIVIDUAL HRS

INTEGRATED HRS

--- H2 resource is outside supplied

--- HRS system is stand-alone

--- Nothing is to share with other

--- HRS + Package Gas

--- HRS + H2 Plant

--- HRS + OIL/CNG/etc.

Different HRS is to follow different Codes. It is the first and important step of HRS safety evaluation.







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HRS Safety Distance – Different HRS Requirement

APPLICABLE CODE:

ISO 19880 Gaseous hydrogen — Fuelling stations

AIGA 045/07 Gaseous hydrogen stations

Safety distance is smaller than GB

Can cover cylinder\bundle\railcar\trailer\roadvehicle filling

NFPA 2 Hydrogen technologies code

GB 50516 Technical code for hydrogen fuelling station

(LHY STORAGE TANK = GHY STORAGE VESSEL)

Safety distance to outside facilities are not allowed to be reduced by firewall

GB 50177 Design code for hydrogen station



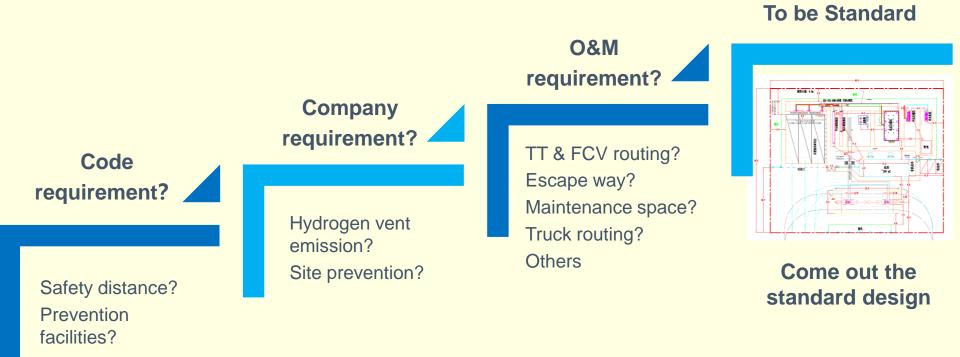
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HRS Safety Distance – Different HRS Requirement



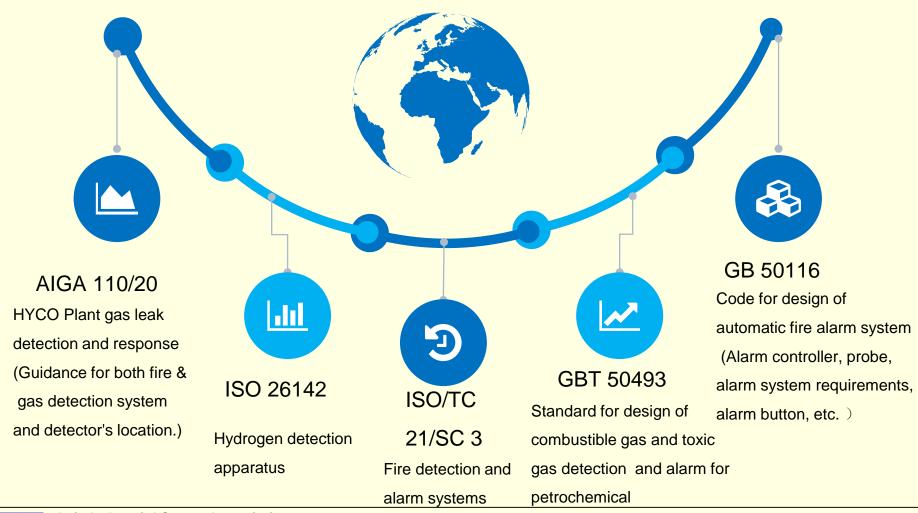


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HRS Safety Facilities – F&G Detecting System





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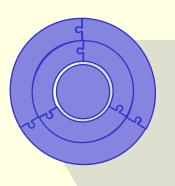
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HRS Safety Facilities – F&G Detecting System

Aligned company base practice:



GHY HRS	TT stanchion	Compressor	H2 storage bottles	FCM Manifold	Other valve Manifold	H70 cooling block	Dispenser
	1 detector for 1 stanchion	1 detector for 1 compressor	1 detector	1 detector for 2 closed manifolds		s 1 detector	1 detector for 1 dispenser
LHY HRS	LHY carrier unloading point	СНС	LHY storage tank (with vent vap.)	FCM Manifold	Other valve Manifold	Vaporizers	Dispenser
	1 detector	1 detector for 1 CHC pump	1 detector	1 detector for 2 closed manifolds		2 detectors	1 detector for 1 dispenser

Detector height:

1. open area: 0.5~1.5m from H2 release point;

2. with a canopy: 0.5~1.5m from H2 release point; at the possible H2 accumulated.

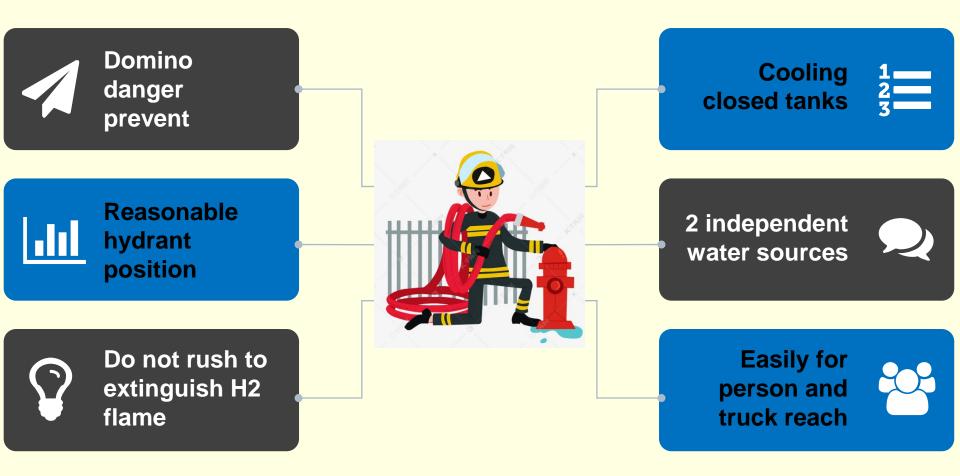


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HRS Safety Facilities - Firefighting system





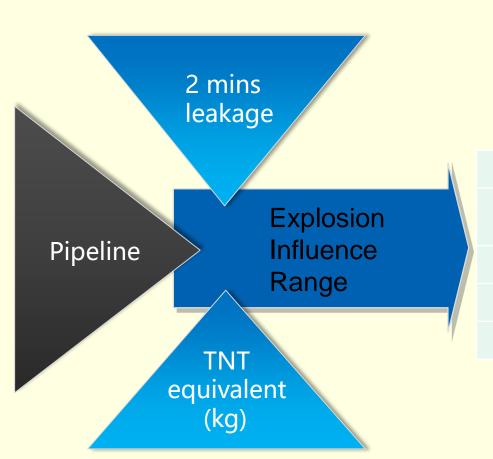
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HRS Safety Assessment – Fire & Explosion



H2 vapor cloud Explosion damage radius							
(m)							
Death	Serious injury	Minor injury					

7.62

2.68



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13.67



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Leak Ignition Test by Dr. Swain from the Miami University of the United States



1- Ignition start

Two cars were fueled with H2 and Gasoline separately, and then subjected to leak ignition tests

2- After igniting 3 s

Car with Fuel H2

The flame produced by the high-pressure H2 sprays directly above.

Car with Gasoline

Catches fire from the lower part of the car.

3- By 1 min.

Car with Fuel H2

Only the leaked H2 is burning in the car, and the car has no major problems.

Car with Gasoline

Has long been burning, become a big fireball and burn up completely.

Justification

The volatile nature of H2 is beneficial to the safety of automobiles compared with ordinary gasoline vehicles.







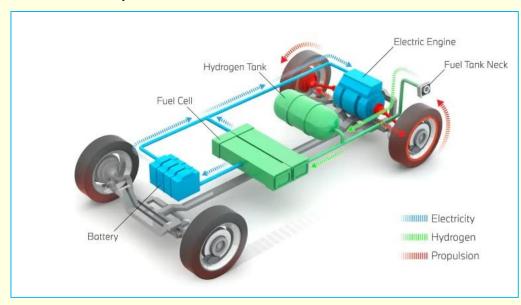
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- The H2 safety of fuel cell vehicles mainly refers to the safety of on-board H2 systems during the operation of fuel cell vehicles, mainly including:
 - Safety of high pressure H2 supply systems
 - Fuel cell power generation systems
- In order to ensure the safety of the on-board H2 system, various enterprises mainly carry out **prevention and control** from the aspects of
 - Material selection
 - H2 leakage monitoring
 - Electrostatic protection
 - Explosion-proof
 - Collision protection, etc.



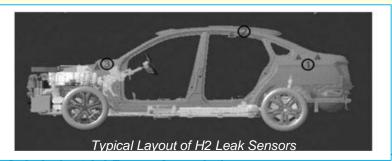


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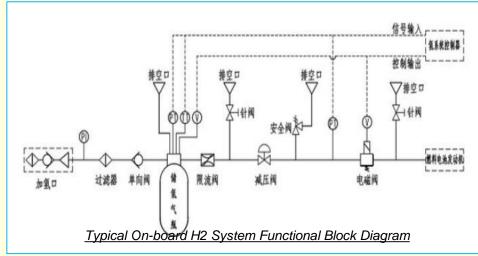
- **Protective measures** for the H2 system mainly include:
 - Material Selection (H2 Material Compatibility)
 - High pressure H2 storage cylinders (Type III or Type IV)
 - Fuel pipelines & valves: SS316L, Aluminum alloy, Polymers, etc.
 - Electrical components: Ex-proof, Anti-static, Flame-retardant, Waterproof, Salt-spray-proof materials.
 - Safety design for high-pressure H2 storage cylinders and H2 pipelines, and installation of various safety facilities.
 - Safety protection system
 - Safety monitoring system

H2 leak, H2 filling, Temperature of H2 storage cylinders, Pressure of H2 pipelines, Short circuit of electrical components, etc.











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- Control Measures for H2 system mainly include:
 - Anti-collision Ability of key components;
 - Layout Optimization, example as follows:
 - High-pressure H2 storage cylinder generally placed on the front top of the vehicle
 - Fuel cell module placed on the rear top of the bus
 - Power battery placed under the floor
 - Front H2 storage cylinder connected to the fuel cell system at the rear of the vehicle through the pipeline on the top of the vehicle.

Fixed device protection

- Integrated with a special H2 storage system fixing bracket of sufficient strength;
- Supported by steel belts to ensure that the dynamic displacement of the high-pressure H2 cylinder will not be too large during the collision.

Redundant design of the Inertia switches

 At least two are installed in different parts of the vehicle body.



(1) H2 system (3) Fuel cell engine system



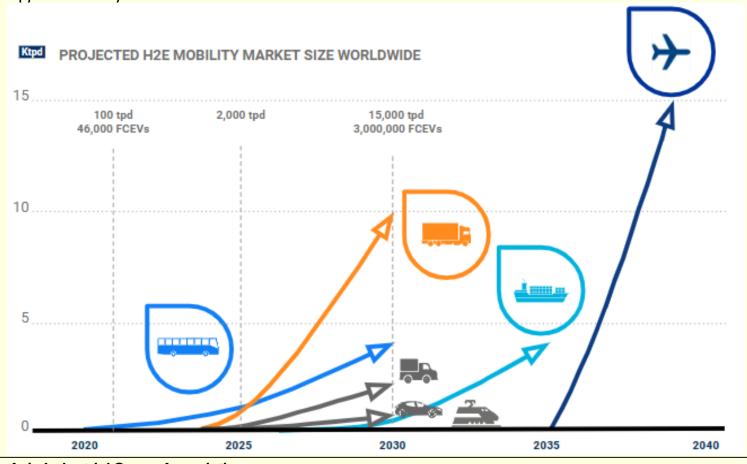


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Hydrogen will play an important role in energy transition and mobility will be a key field for H2E deployment, given fuel cell's techno maturity and synergies with existing industry infrastructure.





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Fuel cell electrical vehicle (FCEV) is recognized as a clean and safe transportation option, got fast deployment in Asia and is scaling up, that requires a well-designed H2 refueling station and equipment being built and operated in an efficient and safe manner.









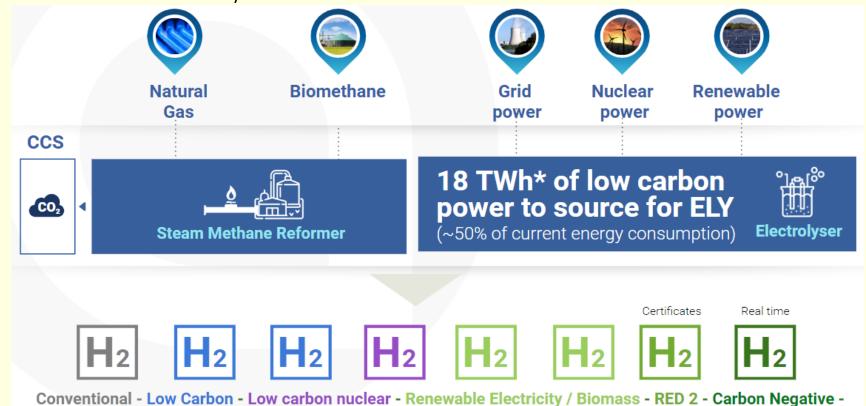




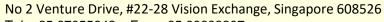




To realize the above goals, we need low carbon intensity hydrogen (blue) instead of fully fossil based hydrogen (grey), that means existing processes should equip with carbon solution "CCU" or "CCS", and our goal is green H2 produced from renewables via electrolysis.







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Bear in mind that safety is fundamental to H2 production and FCEV deployment, gas industry and association (like AIGA) will proactively share H2 safety knowledge (engineering design, lesson learnt, best practice, ISO and standardization) to stakeholders (authority, institution and civilians), to ensure H2 can contribute its value to the environment and society.





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