

Offene Fragen beim sicheren Umgang mit Wasserstoff

Dr.-Ing. Detlev Markus



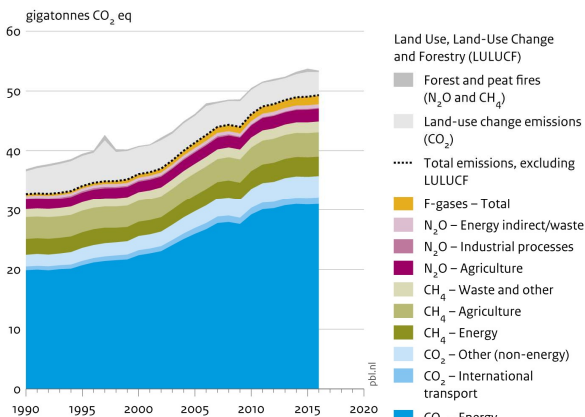
18. Seminar für Ex-Sachverständige
28. August 2024



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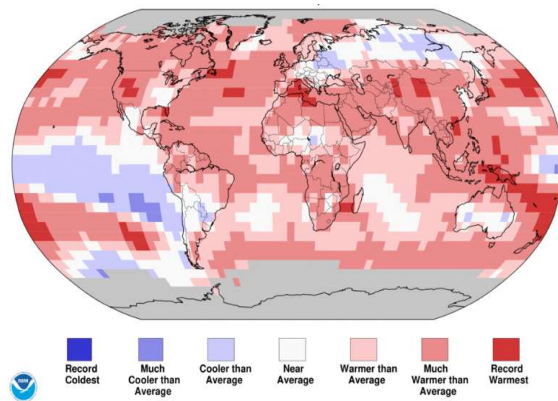
Challenges of today | Climate change - greenhouse gases

Global greenhouse gas emissions, per type of gas and source, including LULUCF



Source: EDGAR v4.3.2 (EC-JRC/PBL 2017); Houghton and Nassikas (2017); GFED 4.1s (2017)

Land and Ocean Temperature Percentiles September 2022 ©



Warning of a forthcoming collapse of the Atlantic meridional overturning circulation.

Ditlevsen, P., Ditlevsen, S., Nat Commun 14, 4254 (2023). <https://doi.org/10.1038/s41467-023-39810-w>



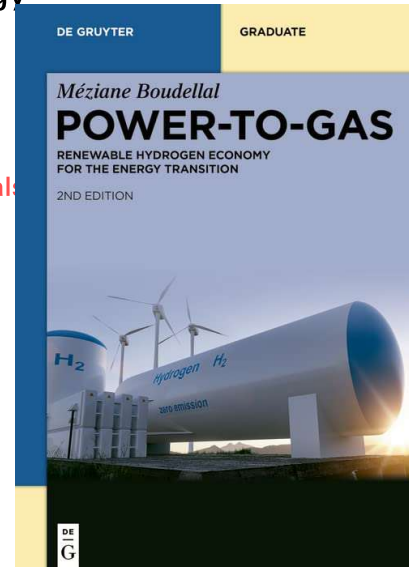
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Challenges of today | Renewable energy

- Change **towards climate neutrality and sustainability**
 - Framework for circular economy
 - **Methods for reducing greenhouse gases**
 - ▶ **EU Green Deal & UN sustainable development goals**
 - **Renewable energy is energy that is obtained from natural sources**
- How can **hydrogen** contribute?
 - **Power to Gas**
 - Energy storage & energy networks
 - About **twenty countries**, which together account for almost half of the world's GDP, have already adopted **hydrogen strategies** or intend to do so.



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Contents | Research on hydrogen safety



Safe handling of hydrogen in the process industry
Safety characteristic data, explosion protection



Challenges to implementing a hydrogen economy
Key to the future energy system



New processes require new safety concepts
Safer production, storage, distribution and use of hydrogen in all application sectors



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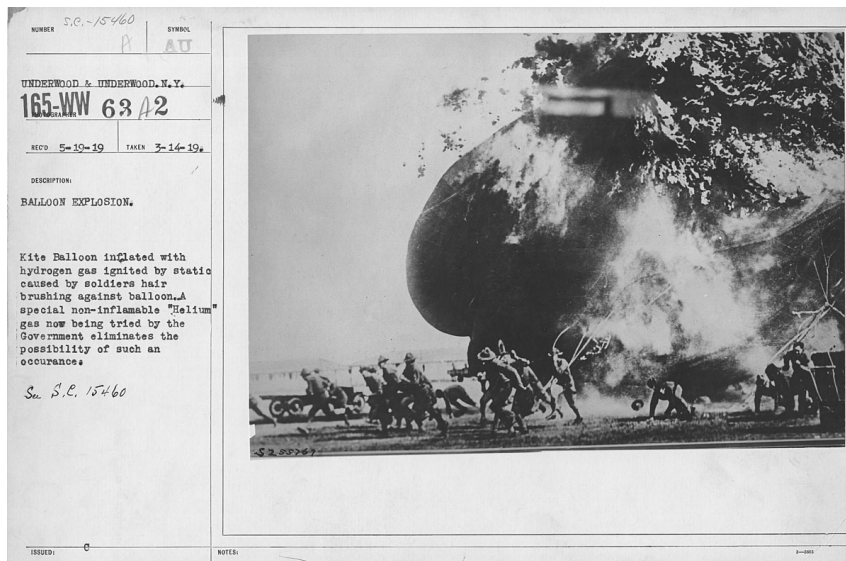


**Safe handling of hydrogen
in the process industry**
Safety characteristic data, explosion protection

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Safe handling of hydrogen | Hydrogen explosion (?)



National Archives and Records Administration, Public domain, Wikimedia Commons

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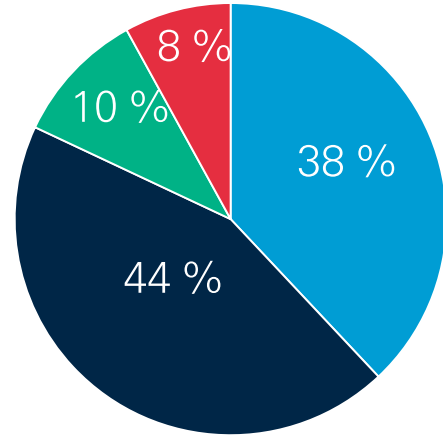
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Safe handling of hydrogen | Production and Usage

World hydrogen demand

- Hydrogen sources (2021, www.irena.org)
 - 47% of is from natural gas
 - 27% from coal
 - 22% from oil (as a by-product)
 - 4% comes from electrolysis
 - ▶ Assuming a global average renewable share of about 33% for electricity, only about 1% of global hydrogen output is produced with renewable energy.

- Global Hydrogen production
 - 75 Mt H₂/yr as pure hydrogen
 - additional 45 Mt H₂/yr as part of a mix of gases



■ Ammonia ■ Refining ■ Other ■ Other chemical products

Mansilla, C. et al: Hydrogen Applications: Overview of the Key Economic Issues and Perspectives, in: Hydrogen Supply Chains, Elsevier, 2018, pp. 271–292.



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Safe handling of hydrogen | Process safety



BASF SE, Ludwigshafen.

- ATEX Directives 1999/92/EU and 2014/34/EU
- The existing regulations of process safety fully cover hydrogen
- Currently, hydrogen is produced and used on a large scale in centralized plants where well-trained personnel follow high safety requirements

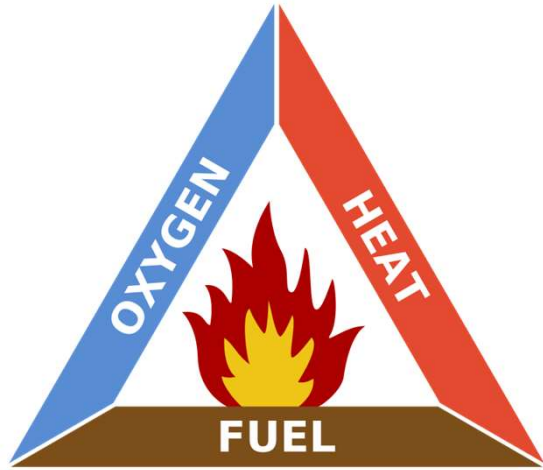


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Safe handling of hydrogen | Explosion protection



https://commons.wikimedia.org/wiki/File:Fire_triangle.svg
 User:Gustavb, CC BY-SA 3.0 <<http://creativecommons.org/licenses/by-sa/3.0/>>, via Wikimedia Commons



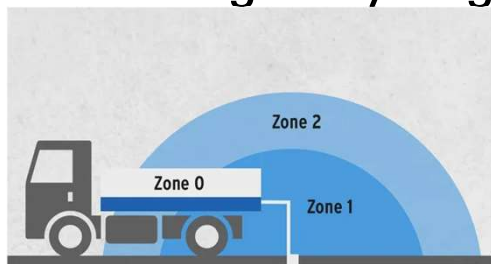
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- Primary explosion protection
 - measures prevent the formation of hazardous explosive atmospheres
- Secondary explosion protection
 - measures to prevent the ignition of potentially explosive hazardous atmospheres
- Tertiary explosion protection
 - measures shall reduce the effects of an explosion to a harmless level.

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Safe handling of hydrogen | Classification of areas



- **Zone 0/20**
permanently or frequently hazardous over long period
- **Zone 1/21**
occasionally hazardous
- **Zone 2/22**
rarely or temporarily hazardous
- **Safe Area**



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Ex-Area	Zone	Explosion protected equipment Category
Gas	0	1 G
	1	2 G
	2	3 G
Dust	20	1 D
	21	2 D
	22	3 D

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Safe handling of hydrogen | Explosion group

Explosion group	Area	MESG	MIC ratio	MIE
I	Methane and coal dust Mining only	> 1.0 mm	1.0	> 0.25 mJ
IIA (e.g. propane)	Gas atmospheres	≥ 0.9 mm	> 0.8	> 0.20 mJ
IIB (e.g. ethylene)		> 0.5 mm	≥ 0.45	> 0.05 mJ
	
IIC (e.g. hydrogen and acetylen)	Surface Industries	< 0.9 mm	≤ 0.8	< 0.8
		≤ 0.5 mm	< 0.45	≤ 0.05 mJ
IIIA	Dust atmospheres	combustible flyings (e.g. cotton fibers)		
IIIB		non-conductive dust (e.g. flour)		
IIIC		conductive dust (e.g. metal dust)		



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Safe handling of hydrogen | Temperature category

Explosion group	Temperature category (max. permissible surface temperature)					
	T1 (450°C)	T2 (300°C)	T3 (200°C)	T4 (135°C)	T5 (100°C)	T6 (85°C)
Ignition temp.	> 450°C	300–450°C	200–300°C	135–300°C	100–135°C	85–100°C
	> 842°F	572–842°F	392–572°F	275–572°F	212–275°F	185–212°F
I	methane					
IIA	acetone	isoamyl acetate	amyl alcohol	acetaldehyde		
Ignition energy more than 0.18 mJ	ammonia	n-butane	benzine			
	benzene	n-butanol	diesel fuel			
0.18 mJ	ethyl acetate	1-butene	heating oil			
	methane	propyl acetate	n-hexane			
	methanol	i-propanol				
	propane	vinyl chloride				
	toluene					
IIB	hydrogen	1,3-butadiene	dimethyl ether	diethyl ether		
Ignition energy 0.06 to 0.18 mJ	cyanide					
	coal gas	1,4-dioxane	ethylglycol			
		ethylene	hydrogen sulfide			
	ethylene oxide					
IIC	hydrogen	acetylene				carbon disulfide
Ignition energy less than 0.06 mJ						



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Safe handling of hydrogen | Safety characteristic data



IEC 60079-20-1

Edition 1.0 2010-01

**INTERNATIONAL
STANDARD**

**NORME
INTERNATIONALE**

- No material constants
- Quantitative information about material properties
- Not independent of the determination method
- Most standardized determination procedures have been developed for atmospheric conditions

■ <https://www.chemsafe.ptb.de>

Explosive atmospheres –
Part 20-1: Material characteristics for gas and vapour classification – Test
methods and data



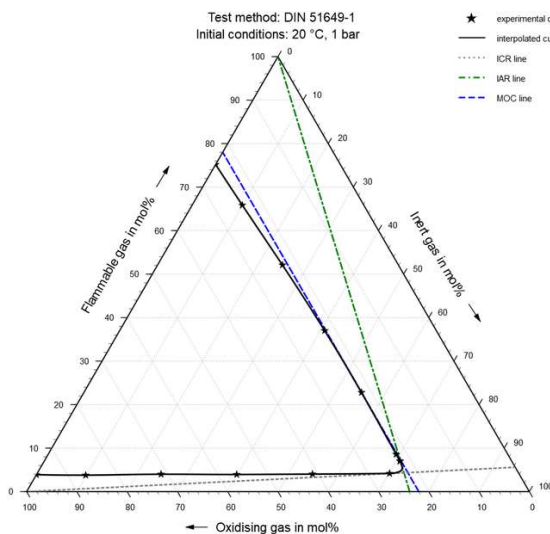
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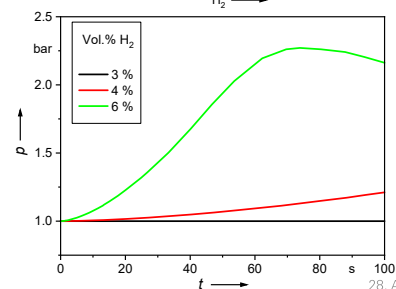
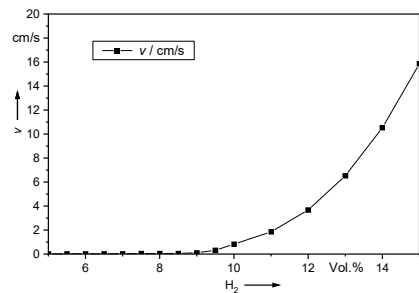
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Safe handling of hydrogen | Explosion limits

Explosion region
Hydrogen/nitrogen/air mixture



Laminar burning velocities of lean H₂/air mixtures (T = 293 K, p = 1bar)



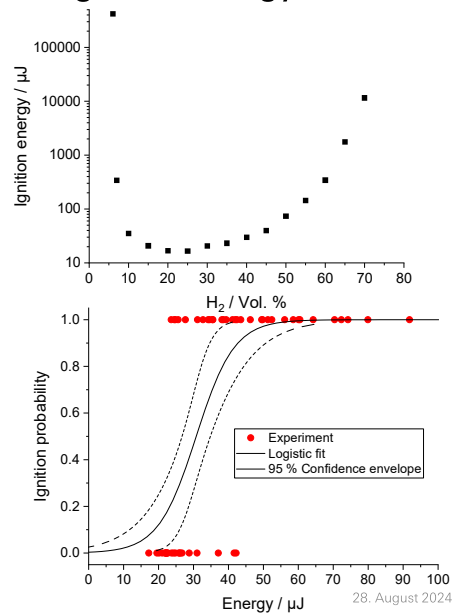
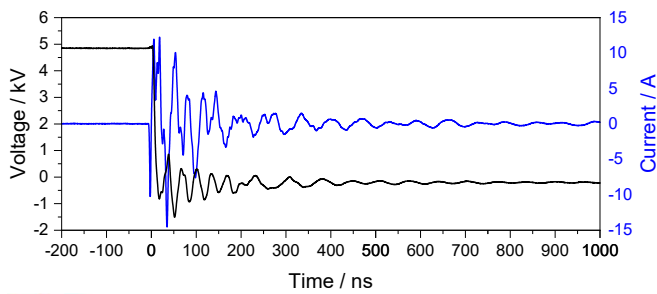
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Safe handling of hydrogen | Minimum ignition energy

- High voltage capacitive discharges
- Duration: ~ 50 ns (pure breakdown discharge)
- Electrode distance: 0.5 mm at minimum ignition energy (MIE)



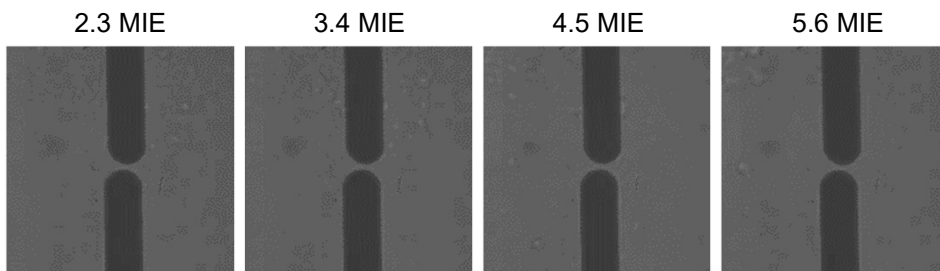
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Safe handling of hydrogen | Early flame propagation near MIE

23.3 vol. % hydrogen/air mixture



$P_{ign} = 99.0\%$

$P_{ign} = 100\%$

$P_{ign} = 100\%$

$P_{ign} = 100\%$

Recording: 62500 frames/s
 Playback: 15 frames/s
 Duration: 1.78 ms



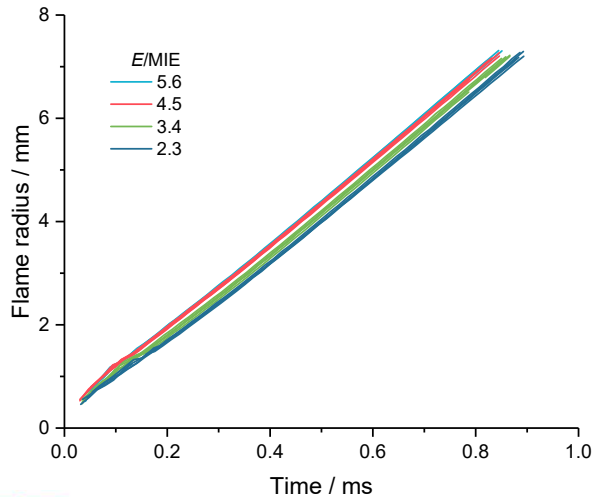
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Safe handling of hydrogen | Flame radius over time

23.3 vol. % hydrogen/air mixture



- Lewis number of hydrogen mixture $Le < 1$
- Curvature enhances flame propagation
- Tested energies relatively high, high ignition probabilities (99%...100%)

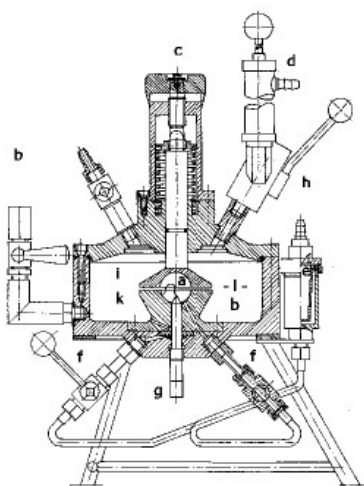


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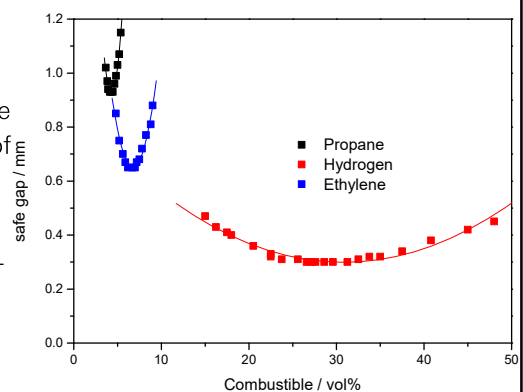
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Safe handling of hydrogen | Maximum experimental safe gap (MESG)



- The MESG is the distance of a annular gap (length: 25 mm) which at each concentration of the explosive flammable mixture just prevents transmission of a flame
- Test apparatus in accordance with IEC 60079-20-1
- MESG is approx. half of the quenching distance



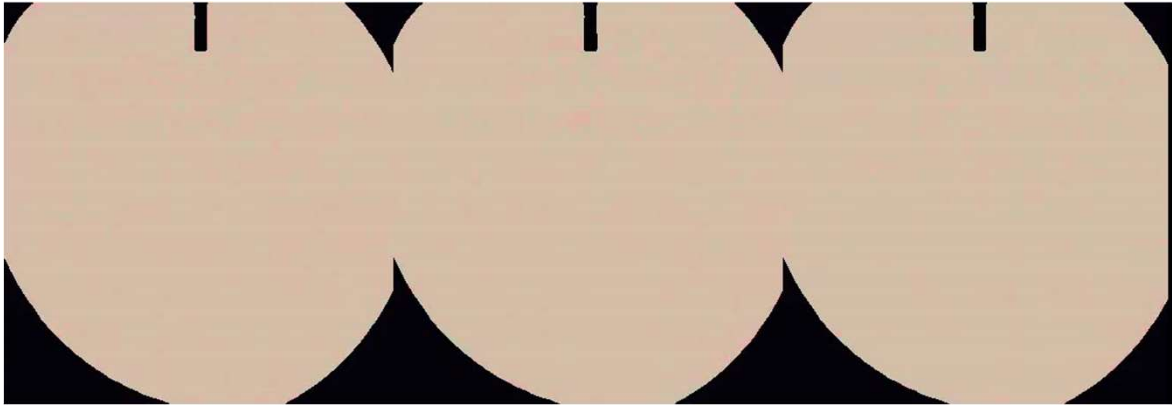
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Safe handling of hydrogen | Flame transmission

Identical initial conditions: Nozzle: 0.7 mm inner diameter, 25 mm long, 28% H₂ in air



Immediate re-ignition (0.2 ms)
close to nozzle

Re-ignition after long time (2 ms)
far away from nozzle (3 cm)

No re-ignition
at all

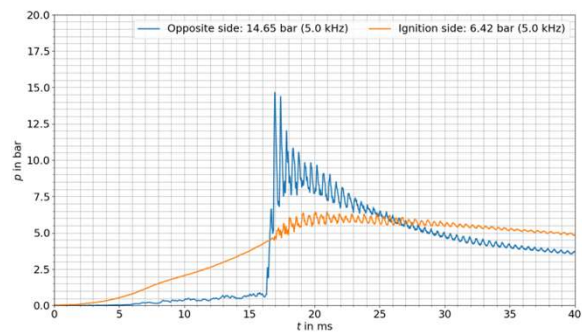
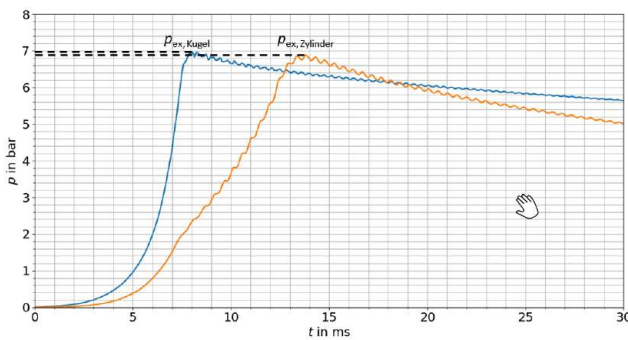
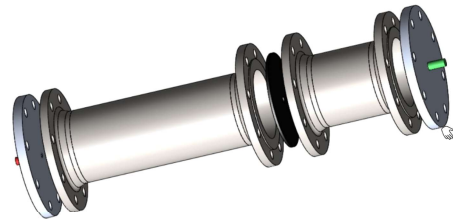


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Safe handling of hydrogen | Explosion pressure (31 Vol.% H₂ in air)



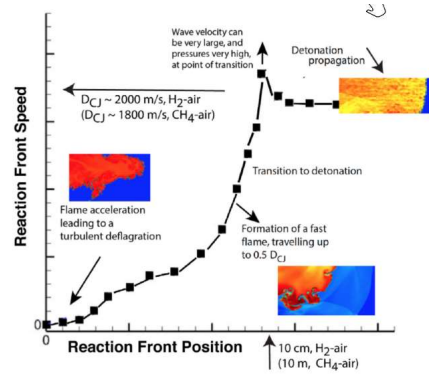
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Safe handling of hydrogen | Detonation

Fukushima 2011



Oran, E.S., Chamberlain, G., Pekalski, A. Mechanisms and occurrence of detonations in vapor cloud explosions. Prog. Energy Combust. Sci. 2020, 77, 100804. <https://doi.org/10.1016/j.pecs.2019.100804>.

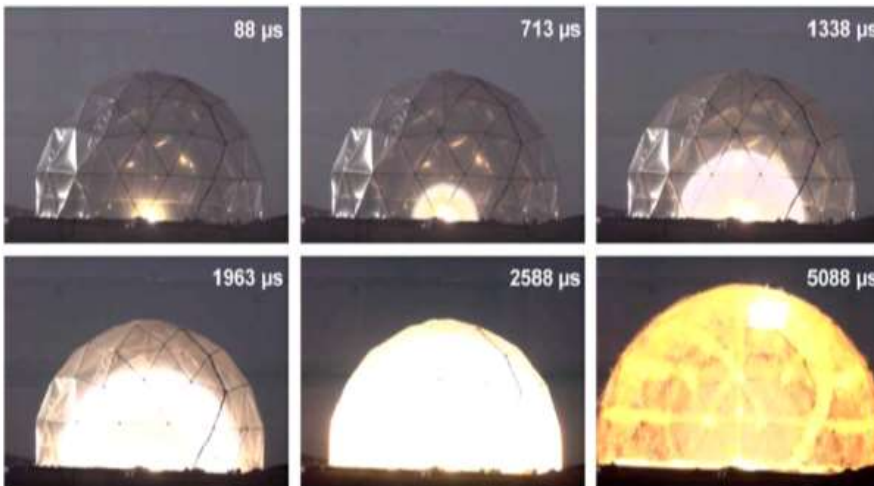


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Safe handling of hydrogen | Detonation



The ability of a hydrogen-air mixture to direct initiation of detonation is greater than that of hydrocarbons

The TNT equivalent of hydrogen is high: 28.65, i.e. 28.65 g of TNT is energetic equivalent of 1 g of hydrogen

www.hysafe.org

Hemispherical detonations of hydrogen-air mixture (30 vol. %) in a polyethylene balloon (radius 5.23 m)

Groethe, M, Merilo, E, Colton, J, Chiba, S, Sato, Y and Iwabuchi, H (2005). Large-scale hydrogen deflagrations and detonations, Proceedings of the 1st International Conference on Hydrogen Safety, 8-10 September 2005, Pisa, Paper 120105

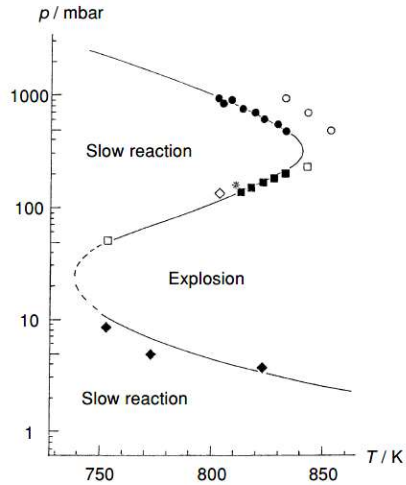


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Safe handling of hydrogen | Ignition temperature



- Thermal explosion limit
 - Competition between heat production and heat losses

Warnatz, J., Maas, U., Dibble, R.W.
Combustion, 4th ed., Springer:
Berlin, 2009.

Fig. 10.3. Ignition limits in the hydrogen-oxygen system (p - T explosion diagram); points: experiments, lines: simulations (see Maas and Warnatz 1988)



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Challenges to implementing a hydrogen economy

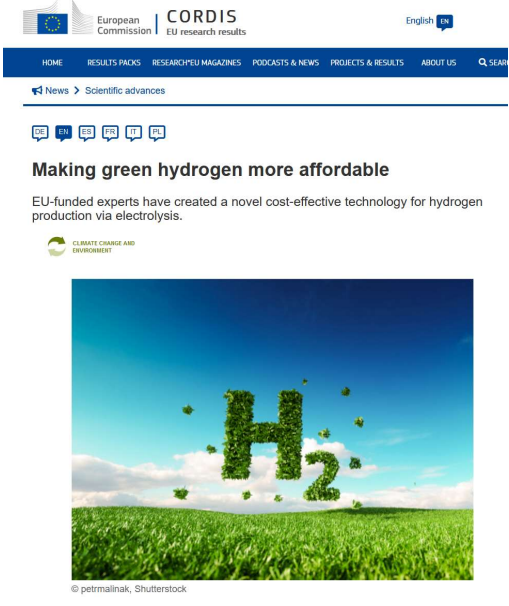
Key to the future energy system



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Challenges | Obstacles

- Public acceptance
- Regulatory requirements
- Infrastructure
- Standardisation
- Education/Training



Making green hydrogen more affordable
 EU-funded experts have created a novel cost-effective technology for hydrogen production via electrolysis.


<https://cordis.europa.eu/article/id/421850-making-green-hydrogen-more-affordable>

© peirmalmak, Shutterstock

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Challenges | Education



10 important questions

- 01 | What is hydrogen?
- 02 | How does the energy density of hydrogen compare to other fuels?
- 03 | How dangerous is the use of hydrogen?
- 04 | Is hydrogen explosive?
 No. Hydrogen-air mixture is combustible, but not explosive. Hydrogen-oxygen (oxyhydrogen) is explosive.
- 05 | Is hydrogen a clean fuel?

„Werden in Luft bei normalem atmosphärischem Druck circa 4 % Wasserstoff eingemischt, lässt sich dieses Gemisch mit einer Zündquelle entzünden. Explosionsgefahr herrscht jedoch noch nicht. Diese ist erst ab einer Wasserstoffkonzentration von 18 % gegeben.“

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Challenges | Public acceptance / Regulatory requirements



- Sandvika, Norway, 2019
- Large leakage in a storage cylinder, normally operating at 950 bar
- Explosion of 1.5 – 3 kg H₂
- Several subsequent fires

Headline: “Hydrogen refuelling plant explodes in Norway”



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Challenges | Regulatory requirements

- US: H.R. 5376, The Inflation Reduction Act of 2022
 - The climate and clean energy provisions in the budget reconciliation bill build on the BIL programs by providing \$369 billion in tax credits and additional funding for zero-emissions vehicles and technologies, building efficiency and resilience, home energy efficiency and appliance electrification rebates, and reducing air pollution and greenhouse gas emissions overall, with many programs targeting low-income and disadvantaged communities.
- EU: 14.02.2023: EC published a proposed revision to Regulation (EU) 2019/1242, setting CO₂ performance standards for heavy-duty vehicles (HDVs)
 - Heavy duty vehicles will be mandated to reduce their emissions by 45 % by 2030 and 90 % by 2040
 - City buses will have to be zero emission by 2030
- EU: 13.02.2023: EC finally published the delegated act on additionality to determine compliance with the targets of the Renewable Energy directive 2009/28/EC
 - „It has taken over three years to provide a framework that defines renewable-based hydrogen and hydrogen-based fuels” (Hydrogen Europe)
- EU: 31.10.2023: Revision of the Renewable Energy Directive (RED III)

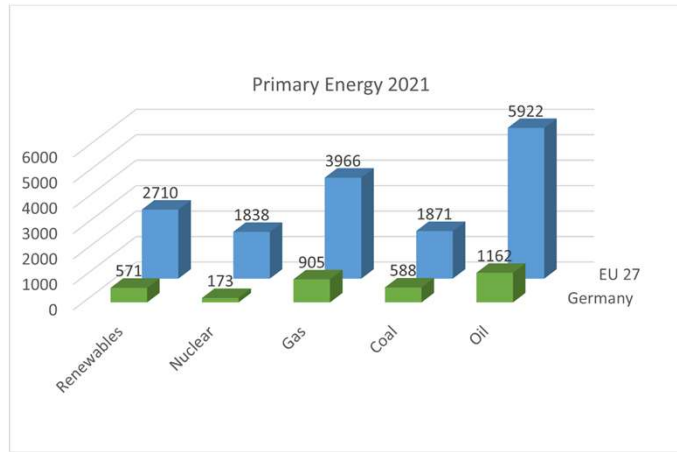
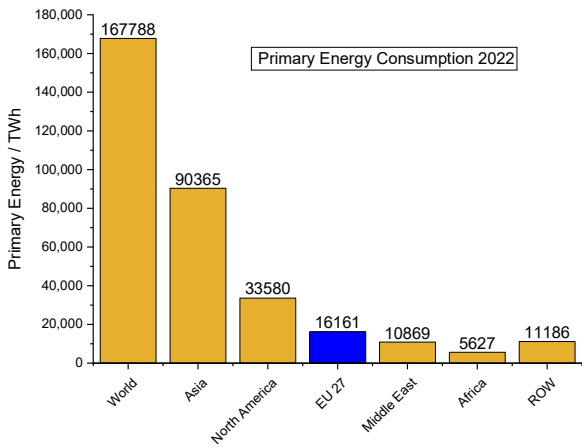


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Challenges | The numbers



<https://ourworldindata.org>



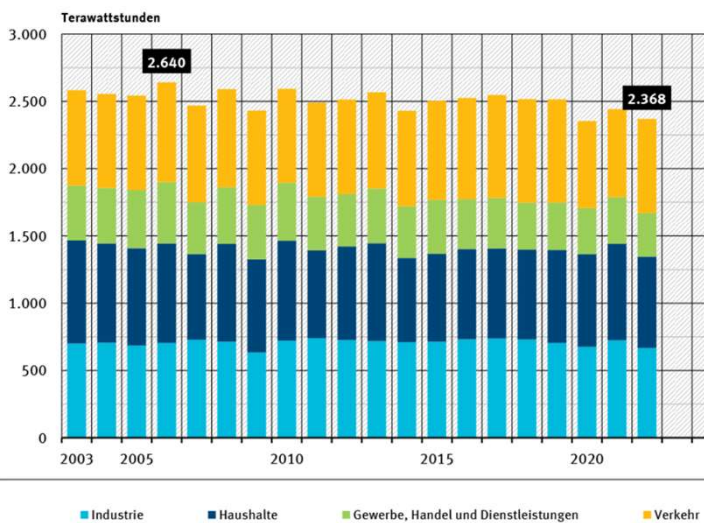
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Challenges | Final energy

Endenergieverbrauch nach Sektoren



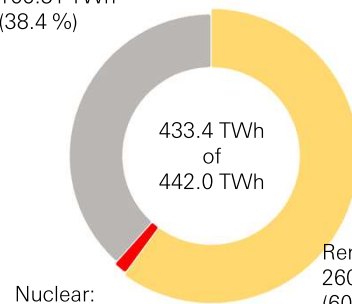
Quelle: Umweltbundesamt auf Basis AG Energiebilanzen: "Auswertungstabellen" (Stand 11/2023)



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Public net electricity generation in Germany in 2023

Fossil: 166.31 TWh (38.4%)



Nuclear: 6.73 TWh (1.6%)

Renewables: 260.34 TWh (60.3%, 192 TWh from wind and solar)

Energy-Charts.info, Datenquelle: ENTSO-E, AGEE-Stat, Destatis, Fraunhofer ISE, AG Energiebilanzen; Letztes Update: 12.03.2024, 18:42 MEZ



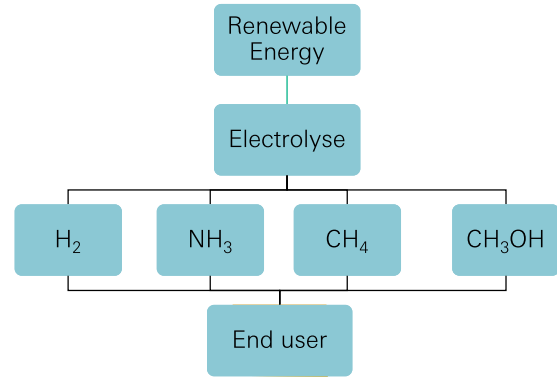
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Challenges | Energy carrier

- ❑ Assumption: Germany needs 2000 TWh for NZE
 - Approx. 60 Mt/yr H₂
- ❑ 1 Mt H₂ needs 50 TWh renewable energy (67 % efficiency)
 - 3000 TWh
- ❑ Assuming 5000 h/yr working time
 - 600 GW electrolysis is needed
- ❑ The National Hydrogen Strategy (revision)
 - Installation of 10 GW electrolysis by 2030
 - 1 Mt/yr H₂ (today in Germany we produce 1.8 Mt/yr H₂, mainly fossil)



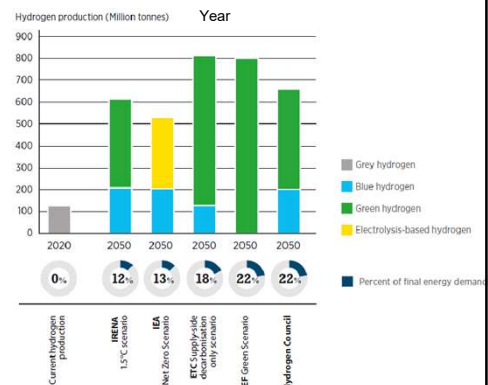
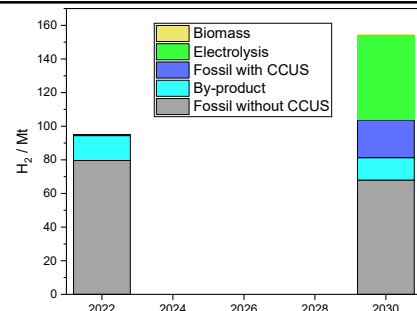
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Challenges | Hydrogen demand

- ❑ EU (until 2030)
 - 10 Mt/a production
 - 10 Mt/a import
- ❑ Worldwide (bis 2050)
 - 500 – 800 Mt/a (depending on the scenario)
- ❑ Trillions of euros of investment required for infrastructure and transport by 2050



Top: IEA, <https://www.iea.org/data-and-statistics/charts/global-hydrogen-production-by-technology-in-the-net-zero-scenario-2019-2030-3>
 Bottom: <https://www.irena.org/publications/2022/Jan/Geo-politics-of-the-Energy-Transformation-Hydrogen>



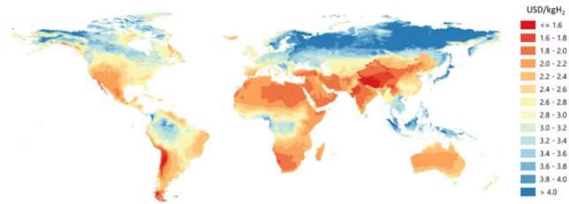
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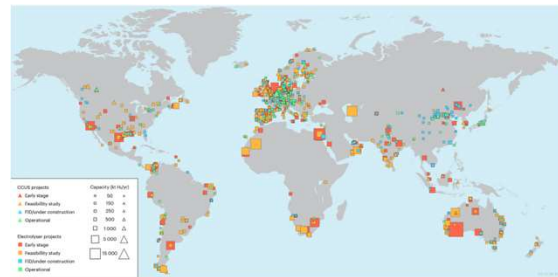
Challenges | hydrogen production

- 65% of global hydrogen demand is concentrated in North America, Europe and East Asia
- Significant difference between the cheapest and most expensive production locations
- 400 Mt/a transportation over long distances (2050)
- e.g. Call for tenders according to H2Global:
 - Hydrogen, ammonia, methanol etc.
 - Regional (e.g. Europe) or country-specific; global award procedure
 - Product requirements and sustainability criteria for production, transportation and acceptance

Hydrogen costs from hybrid solar PV and onshore wind systems in the long term



IEA (2019), *The Future of Hydrogen*, IEA, Paris
<https://www.iea.org/reports/the-future-of-hydrogen>



IEA (2023), *Global Hydrogen Review*, IEA, Paris
<https://www.iea.org/data-and-statistics/data-product/hydrogen-production-and-infrastructure-projects-database>

How is certification and safety ensured?



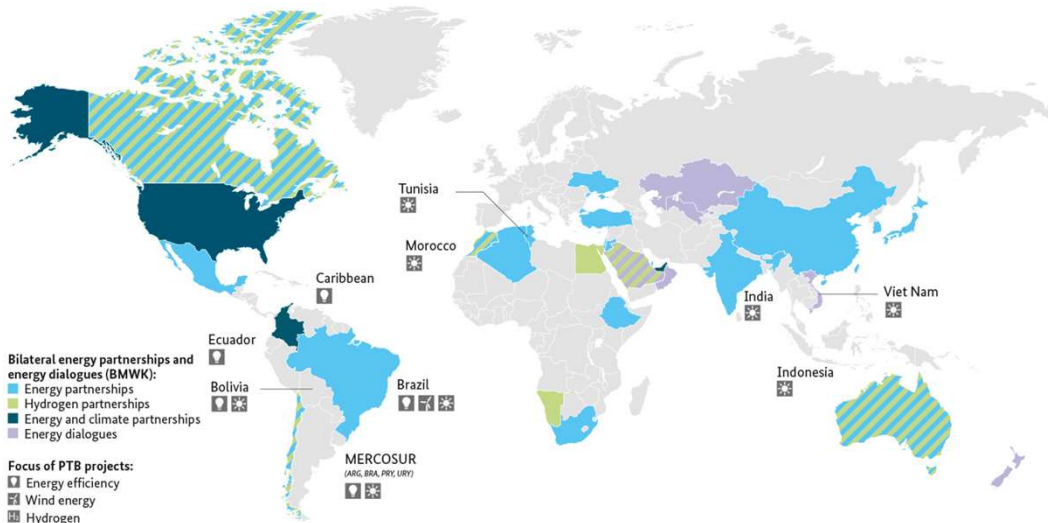
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International cooperations of PTB |

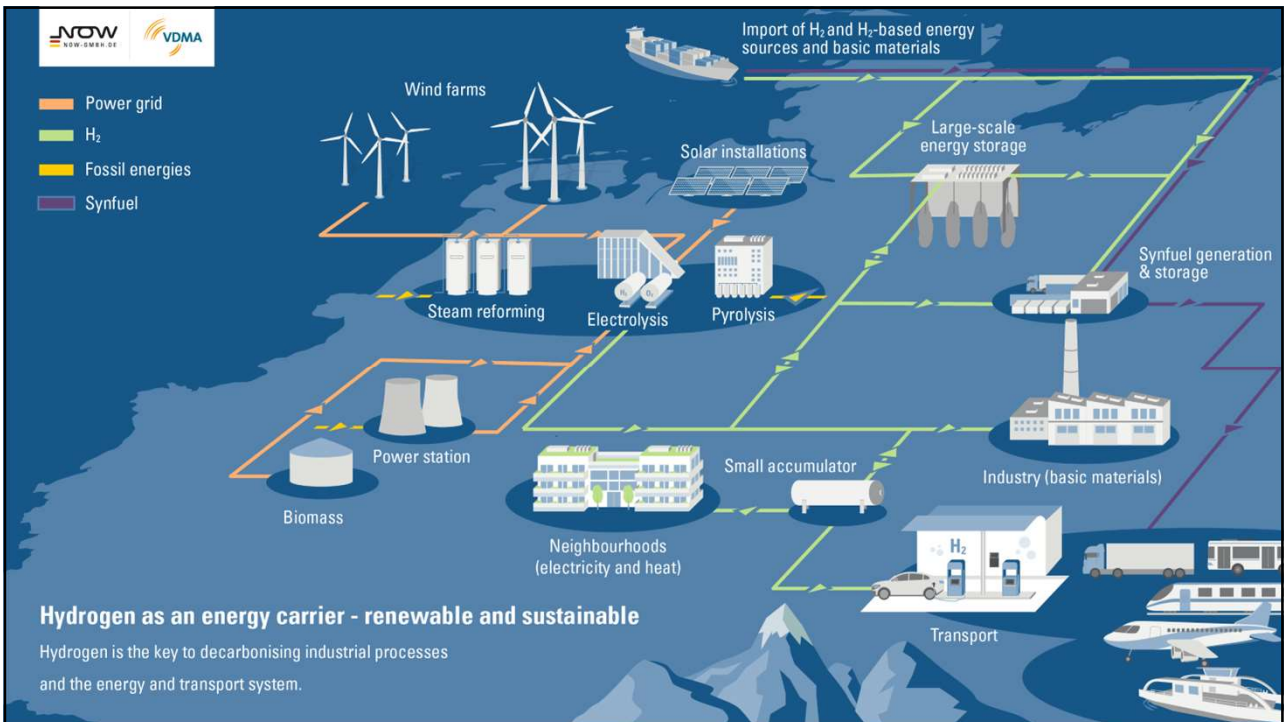
Bilateral energy partnerships (BMWK) und projekts with an energy focus (BMZ)



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28. August 2024

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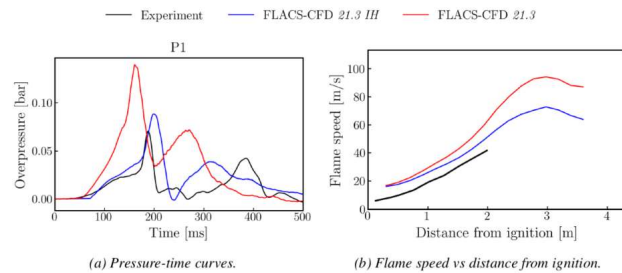
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New processes require new safety concepts
 Safer production, storage, distribution and use of hydrogen in all application sectors

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New processes | Large scale explosions



(a) Pressure-time curves. (b) Flame speed vs distance from ignition.

Fig. 6: FM Global test with 18 vol.% hydrogen.

- Development of consequence models
- Effect of H₂ on generated explosion overpressure
- DDT Prediction for large systems?
- Fundamental Mechanisms of Detonation Initiation
- Quenching a Detonation
- Safety characteristic data

Top: Skjold et al.: Blind-prediction: Estimating the consequences of vented hydrogen deflagrations for inhomogeneous mixtures in 20-foot ISO containers. *J. Loss Prev. Process Ind.* 2019, 61, 220–236. <https://doi.org/10.1016/j.jlp.2019.06.013>.
 Bottom: Lucas et al.: CFD modelling of hydrogen and hydrogen-methane explosions – Analysis of varying concentration and reduced oxygen atmospheres. *J. Loss Prev. Process Ind.* 2023, 83, 105012. <https://doi.org/10.1016/j.jlp.2023.105012>.

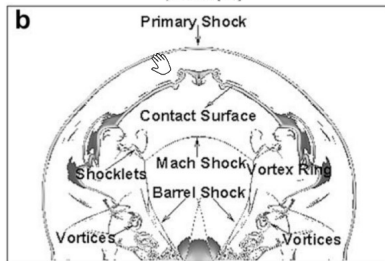
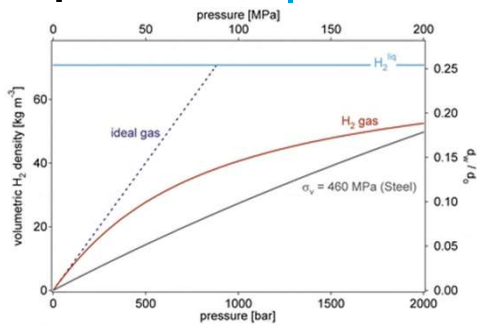


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New processes | High pressure Premixed combustion



- Further model developments for the description of transient large-scale flame phenomena with confinement and obstruction
- Coupling combustion with blast waves
- Ignition
 - Development of statistical models
 - Investigation of spontaneous ignition processes (Shock Diffusion Ignition in realistic configurations, etc..)
- Material properties
 - Tanks, pipes etc.
 - Transport, storage
- Safety characteristic data

Top: Züttel, A. Hydrogen storage methods. *Die Naturwissenschaften* 2004, 91, 157–172. <https://doi.org/10.1007/s00114-004-0516-x>.
 Bottom: Xu et al.: The effect of pressure boundary rupture rate on spontaneous ignition of pressurized hydrogen release. *J. Loss Prev. Process Ind.* 2009, 22, 279–287. <https://doi.org/10.1016/j.jlp.2008.07.007>.



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New processes | Cryogenic/liquid hydrogen



Figure 11: Fireball development after the failure of an MLI-insulated vessel positioned horizontally filled with LH2 as seen from an UAV flying over the H2TA



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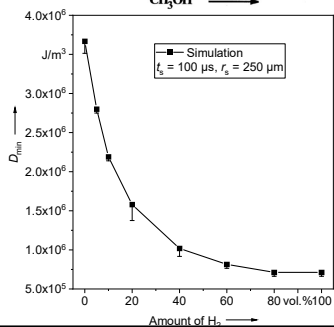
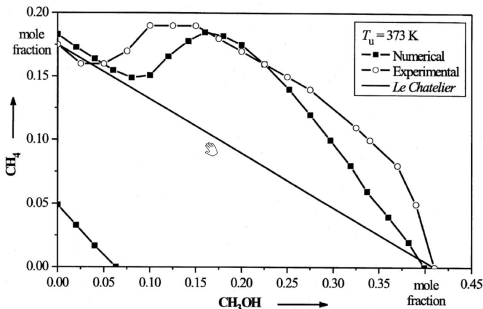
Combustion

- Multiphase mixtures
- O₂ enrichment
- Transient combustion properties of the cold, premixed systems (80 K < T < 250 K)
- Kinetics
- Mitigation
 - Design, sensors, ventilation
- Material properties
 - Tanks, pipes etc.
 - Transport, storage
- Safety characteristic data

Top: Houssin, D., Brennan, S., Van Esbroeck, T., Bouix, D. European Train the Trainer Programme for Responders: Fuel Cells and Hydrogen Joint Undertaking Grant Agreement Number 875089: Deliverable D1.1 Report on hydrogen safety aspects of technologies, systems and infrastructures pertinent to responders, 2020. Bottom: Kluge et al: Large-scale tests to investigate the consequences of exposing cryogenic storage vessels containing liquid hydrogen to a fire load. Proceedings of the 14th international Symposium on Hazards, Prevention and Mitigation of Industrial Explosions, 2022.

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New processes | Mixtures with energy carriers



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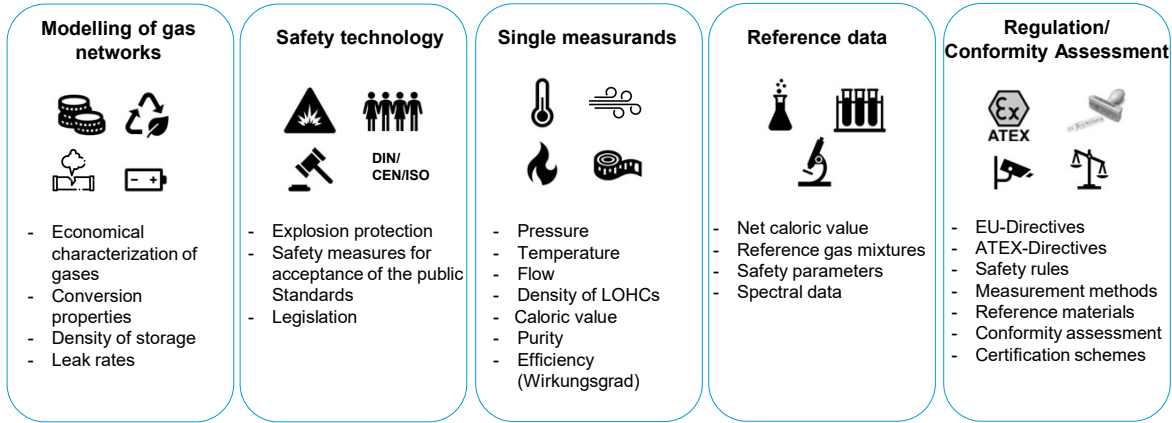
- Mixtures with HCs
 - Up to 20 % H₂ without problems
- Mixtures with NH₃
 - MIE NH₃: 14 mJ (H₂: 17 μJ)
 - Reaction kinetics
 - Premixed combustion
- Material properties
 - Tanks, pipes etc.
 - Transport, storage
- Safety characteristic data

Top: D. Markus, H.-P. Schildberg, W. Wildner, G. Krdzalic, U. Maas, Flammability limits of premixed methane/methanol/air flames, Combust. Sci. Technol. 175 (2003) 2095–2112. Bottom: D. Markus, C. Yu, S. Essmann, R. Schießl, U. Maas, Ignition of ammonia/hydrogen/air mixtures by electrical discharges, in: 1st Symposium on Ammonia Energy, 2022, Cardiff.

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Hydrogen Metrology needs for Green Hydrogen

H₂

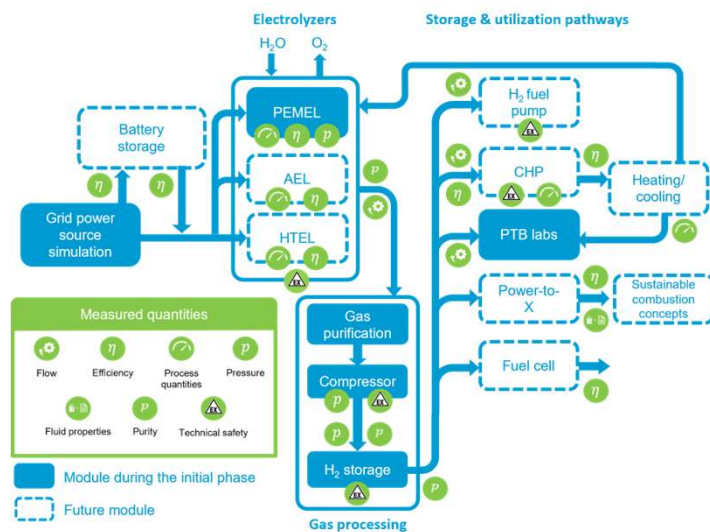


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New processes Metrology



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- Systemic plant concept from the production of green hydrogen to gas processing, storage and utilisation via different paths
- Manufacturer-independent testing of measurement technology, methodology and safety technology
- Development of services related to the evaluation of measurement technology of individual processes, but also in the overall system under real conditions

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New processes | National Hydrogen Safety Alliance



Bundling decades of application-related expertise from science and education, standardization and regulation, networking, ...



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Hydrogen: New safety requirements | Conclusion

- Explosion hazards arise along the entire chain from production to transport to storage or consumption
- The existing standards of explosion protection cover hydrogen completely at atmospheric conditions
 - Hydrogen may be produced and consumed simultaneously centrally and decentrally in heterogeneous grids. A great need for training is already apparent.
- The new applications require additional studies of
 - Reaction kinetics
 - Safety characteristic data
 - Material properties
 - Measurement devices
- Standardisation is important to ensure uniform safety standards worldwide. This requires preliminary research!



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Hydrogen: New safety requirements | Acknowledgement

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