MefHySto

Metrology for Advanced
Hydrogen Storage Solutions

Metrology for Advanced Hydrogen Storage Solutions

WWW.MEFHYSTO.EU

EMPIR EURAMET

The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

IN MEMORIAM:

Dr. rer. nat. habil. Michael Maiwald

The MefHySto consortium mourns the sudden and unexpected loss of our esteemed colleague, Dr. rer. nat. habil. Michael Maiwald, who passed away in August, 2023.

As Project-Coordinator, Michael's dedication to the MefHySto Project and the consortium was unparalleled. His tireless efforts and visionary leadership were instrumental in advancing the project's goals within the consortium. His commitment and contributions have left a lasting impact.

With the passing of Michael Maiwald, the research community have lost an outstanding and respected colleague. He will always be remembered for his remarkable work and his friendly, open personality. Our thoughts and deepest sympathies are with his family and friends.

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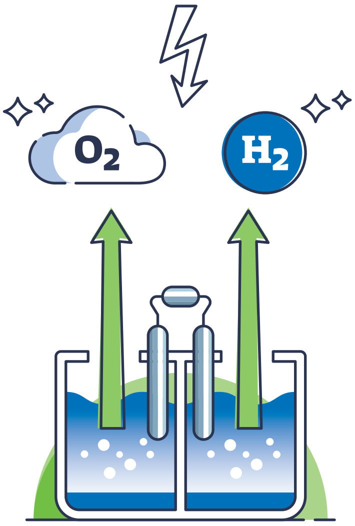

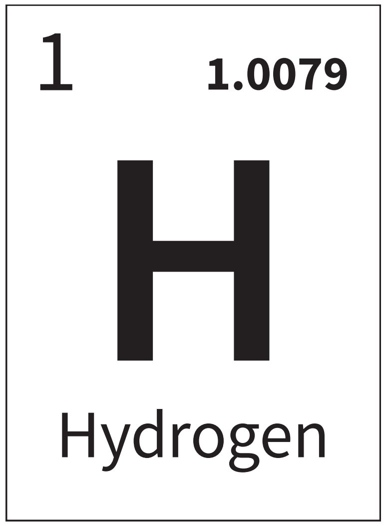

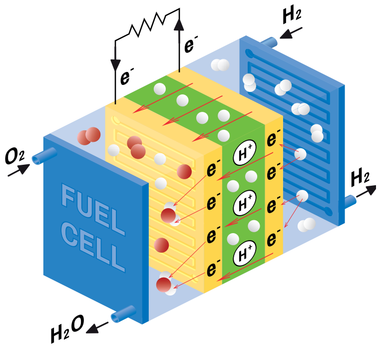
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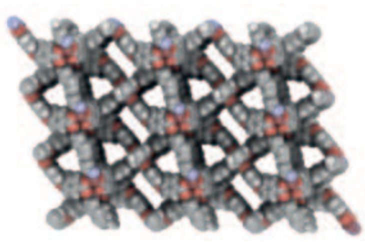
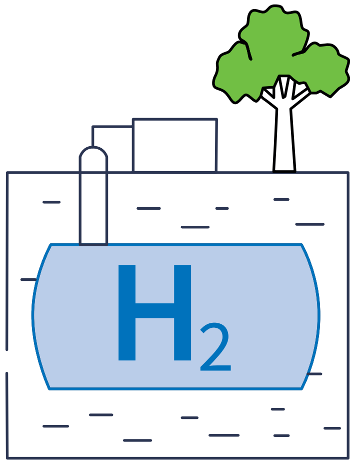



H_2

1 Introduction to the MefHySto Project

The "Metrology for Advanced Hydrogen Storage Solutions" (MefHySto) project is a European initiative addressing the need for large-scale energy storage solutions, that is crucial for the successful transition to renewable energy sources. The main objective of this project was to develop and provide metrological standards and validated techniques for the storage and utilization of hydrogen. Hydrogen is increasingly recognized as an important component in the future energy system due to its ability to store and supply energy during peak demand periods when renewable sources, such as solar and wind, are not generating power.

The MefHySto project was structured around several specific objectives to ensure a reliable and safe hydrogen storage infrastructure. These objectives included:

- **Metrology for Hydrogen from Power-to-Hydrogen (Work Package 1):** This involved assessing the quality of hydrogen produced through proton-exchange membrane (PEM) water electrolysis during varying operational conditions, using online gas analysers to measure key impurities.

- **Thermophysical Properties of Hydrogen (Work Package 2):** Improving reference equations of state (EoS) for hydrogen injection into natural gas grids, providing precise density measurements to accurately determine the calorific values of energy gases.

- **Metrology for Hydrogen from Back Conversion; Hydrogen-to-Power (Work Package 3):** Investigating the sustainability and reliability of fuel cells, which converted hydrogen back into electrical power, and how impurities in hydrogen and air affected their performance.

- **Metrology for Reversible Hydrogen Storage (Work Package 4):** Developing validated methods for measuring the heat conductivity of hydrogen absorbed in intermetallic or porous materials, and creating harmonized procedures with minimal uncertainty.

- **Metrology for Large-Scale Storage (Work Package 5):** Tackling the metrological and thermodynamic challenges associated with large-scale hydrogen storage in underground gas storages (UGS), particularly during the transition from natural gas to hydrogen.

- **Creating Impact (Work Package 6):** Facilitating the adoption of the project's technologies and measurement infrastructure by relevant stakeholders, including manufacturers, standardization bodies, end users, and the energy research community.

By achieving these objectives, the MefHySto project aimed to support the EU's ambitious renewable energy targets for 2030, as outlined in the Renewable Energy European Directive 2018/2001. The MefHySto project has received funding and support from the European Union, reflecting the EU's commitment to advancing hydrogen technologies and achieving its ambitious renewable energy targets. Through this funding, the EU aimed to facilitate the development of advanced hydrogen storage solutions, ensuring that these technologies are reliable, safe, and effective. The financial and institutional backing from the EU underscores the strategic importance of hydrogen in the future European energy landscape and supports the collaborative efforts needed to drive innovation and standardization in this field.

1.1 | Importance of Hydrogen (H_2) Storage for the Energy Transition

Integrating hydrogen into gas grids and storages represents a critical strategy for decarbonization and advancing the energy transition towards a more sustainable and decarbonized energy system. Hydrogen, and especially green hydrogen as a decarbonized energy carrier, offers several advantages for reducing greenhouse gas emissions and enhancing the flexibility and reliability of energy systems.

One of the primary reasons for integrating hydrogen into existing natural gas infrastructures is its potential to significantly reduce carbon dioxide (CO_2) emissions. When hydrogen is produced from renewable sources, such as wind or solar power through water electrolysis, it results in CO_2 emissions close to zero. By blending hydrogen with natural gas, the overall carbon intensity of the gas supply can be reduced, leading to lower emissions from heating, industrial processes, and power generation.

Moreover, hydrogen can address the intermittency issues associated with renewable energy sources. Solar and wind power generation are inherently variable, depending on weather conditions and time of day. Hydrogen provides a solution to this challenge by acting as a large-scale energy storage medium. Excess renewable energy can be used to produce hydrogen during periods of low demand or high generation, which can then be stored and later injected into the gas grid or converted back into electricity during peak demand periods. This enhances grid stability and ensures a continuous supply of clean energy.

The existing natural gas infrastructure can be utilized to transport and store hydrogen, offering a cost-effective and efficient pathway to integrate hydrogen into the energy system. This approach leverages the extensive and well-established gas grid network, minimizing the need for new infrastructure investments. However, it also necessitates advancements in metrology to ensure the safe and efficient operation of hydrogen-enriched gas grids. Reliable standards and reference methods are essential to address the unique properties and behaviours of hydrogen, such as its lower energy density and potential for material embrittlement.

Furthermore, the integration of hydrogen into the gas infrastructure aligns with the EU's broader energy policy objectives, including the European Green Deal, which aims to achieve climate neutrality by 2050. Hydrogen is seen as a key enabler of this transition, supporting sectors that are difficult to decarbonize, such as heavy industry, transportation, and heating. The development of advanced hydrogen storage solutions and accurate metrological techniques, as pursued by the MefHySto project, are important components in realizing the full potential of hydrogen in the energy transition.

1.2 | Project Partners

The MefHySto project brought together a diverse consortium of partners, each contributing expertise to the development of advanced hydrogen storage solutions. The consortium consisted of the following partners:

Bundesanstalt für Materialforschung und -prüfung (BAM)

The BAM (Federal Institute for Materials Research and Testing) with about 1600 employees is a senior scientific and technical federal institute with responsibility to the Federal Ministry for Economic Affairs and Climate Action in Germany. The BAM is an internationally recognized centre of excellence for safety in technology and chemistry, with competence in the areas: testing, analysis, and licensing of material, transfer of know-how and technology to the industry, and as counsellor of the German Federal Government. For the field of analytical chemistry, this defines the competence and tasks with main emphasis on (1) development and provision of certified reference materials (CRM) for chemical analysis, (2) development and validation of analytical methods, (3) methods for the assessment of analytical laboratories, (3) complex analytical problem solutions, and (4) establishing and fostering national and international networks committed to the assurance of quality, reliability and comparability in analytical chemistry.

In MefHySto, BAM coordinates and manages the research project, contributes to the production of high-precision gas standards with its facilities for gravimetric preparation and instrumentation for gas analysis, and is involved in the development of methods and reference materials for hydrogen cryoadsorption storage.

www.bam.de

Fundación para el Desarrollo de las Nuevas Tecnologías del Hidrógeno en Aragón (FHa)

FHa is a private, non-profit research centre that has been boosting hydrogen as an energy source since 2003. The initiative was promoted by the regional Government of Aragón and initially supported by 28 key entities from various sectors of the Aragonese economy. With continuous backing, it now celebrates its 20th anniversary, boasting a board of trustees exceeding 91 members. Focused on integrating Aragón into the global hydrogen economy, its objectives include fostering employment and wealth through strategic projects, establishing a collaborative industrial network for sustainable energy ventures, and implementing a comprehensive regional strategy outlined in its pioneering Hydrogen Master Plan, now in its fourth edition since 2007.

Within the project, FHa was responsible for the project coordination and administrative tasks. Additionally, FHa had a technical role in two work packages, focusing on the design, construction, and operation of the hydrogen admixing test platform, including the testing of different gas grid components. FHa also assisted with research on the potentials of hydrogen injection in the EU.

www.hidrogenoaragon.org

Commissariat à l'Énergie Atomique et aux Énergies Alternatives (CEA)

The French Alternative Energies and Atomic Energy Commission (CEA) is a key player in research, development and innovation in four main areas: defence and security, low-carbon energies (nuclear and renewable energies), technological research for industry, fundamental research in the physical sciences and life sciences. Drawing on its widely acknowledged expertise, the CEA actively participates in collaborative projects with a large number of academic and industrial partners.

CEA will be involved in the MefHySto project through its Liten institute, which is devoted to the development of innovative technologies for the energy transition. CEA-Liten has a staff of 975 people, an annual budget of 138 million euros, and has more than 200 industrial partners from a wide range of market segments: energy, transport, aerospace, construction, civil engineering, environmental, and IT industries, amongst others. Intellectual property forms a major part of CEA-Liten activities, with a portfolio of 1,600 international patents.

In MefHySto, CEA will, besides others, use the H2PAC platform, which is a large research infrastructure (LRI) located in Grenoble, France.

www.cea.fr

Czech Metrology Institute (CMI)

The Czech Metrology Institute (CMI) is a medium size national metrology institute. It develops and maintains standards realizing most of the SI base units and provides calibrations traceable to them down to the shop floor level. The department of flow, heat and wind speed measurements of CMI is involved in calibrations of flow meters for water and hydrocarbons, heat-meters and wind speed meters and in research and development of measurement standards in these fields including mathematical modeling of flow and processes in fluids using the OpenFOAM software at CMI's computing cluster.

In the MefHySto project, CMI will use a CFD simulation to model how changing parameters of the medium (density, viscosity or compressibility) during the conversion process from storage of natural gas to hydrogen affect the flow measurement and its optimal installation setup.

www.cmi.cz

Deutsches Brennstoffinstitut (DBI)

DBI is a medium-sized company active in the field of gas storage, gas transport and gas distribution. This applies to research on the one hand, but also to the implementation of services for the gas industry. DBI deals with gases, such as natural gas, biogases and increasingly hydrogen and mixtures thereof. Part of the tasks is the control of the gas quality and the measurement of trace components even under high pressure.

DBI brings this experience into the MefHySto project. The focus is on gas quality measurements in combination with underground storage of hydrogen.

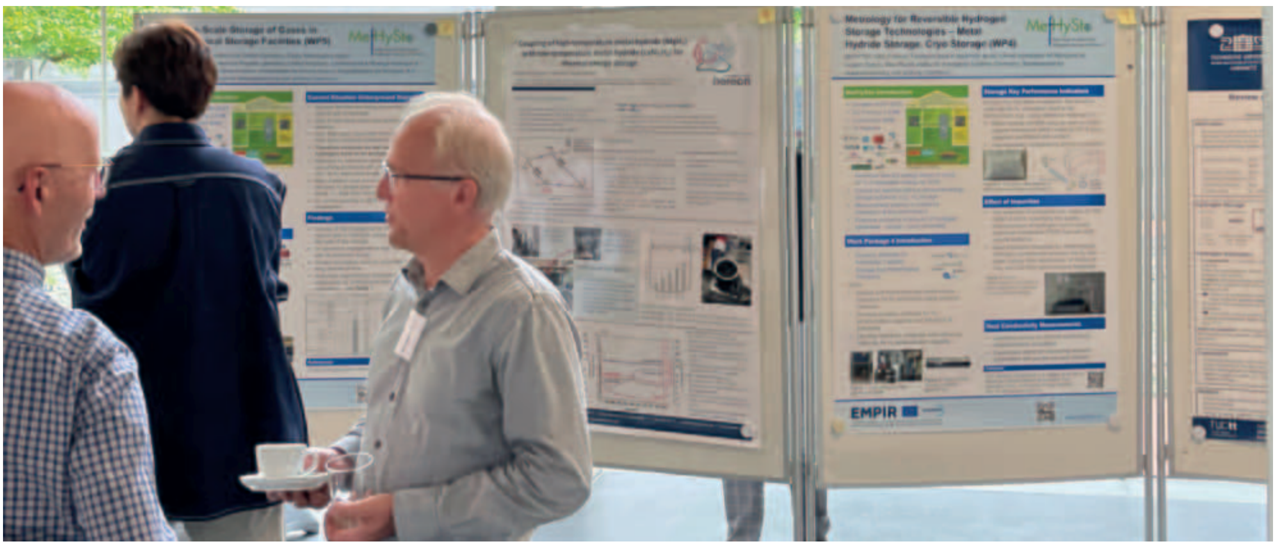
www.dbi-gruppe.de

German Technical and Scientific Association for Gas and Water (DVGW)

DVGW – German Technical and Scientific Association for Gas and Water has been working for the gas and water industry as an independent and unbiased technical scientific association since 1859, the objective being to create a basis for the safe and technologically flawless supply of gas and water. It is the reference German institution for the development of technical rules, the associated pre-normative research and certification of gas and water related appliances. Regulations merely constitute the basis of the services the DVGW has to offer its members. The practical work in the gas and water sector is based on the technical rules of DVGW. The association has excellent laboratories for the testing of gas related processes, an unbiased view on renewable gases, power to gas and related technologies.

DVGW led two work packages, one on legal, regulatory and technical aspects and one on a pathway towards integrating hydrogen in European gas networks. Herein, DVGW focused on mapping the current state of regulations, codes and standards (RCS) and on a technical inventory of high-pressure gas grids, providing updated information on pre-normative research activities. Furthermore, DVGW elaborated the set of recommendations towards integration of higher levels of hydrogen in the EU and assisted with the design of the test platform.

www.dvgw.de



European Research Institute for Gas and Energy Innovation (ERIG)

ERIG is a European research and development network that guides gas in the transition process towards a future renewable-based energy system. It is a non-profit network for European cooperation in research and innovation in the field of sustainable and innovative gas technologies and the use of natural gas with renewable energies. ERIG members represent national technical and scientific gas organizations and associations that represent in particular the new requirements of energy and gas in Europe. The research portfolio of ERIG members covers all aspects from the production of gas through to gas utilization in different markets.

Within the project, ERIG was responsible for the work package "Creating Impact (WP6)", which included communication and dissemination of project activities and results as well as network activities to transfer gained knowledge.

www.erig.eu

MAHYTEC

MAHYTEC is a French company founded in 2008 specialized in hydrogen storage. With its team of 25 people, MAHYTEC is specialised in the design and manufacturing of hydrogen storage systems for mobile, stationary and nomadic applications. MAHYTEC is the only European company developing high-pressure storage as well as solid storage through metal hydrides. MAHYTEC offers certified products based on both technologies for stationary use and transport of hydrogen. MAHYTEC also supplies fully integrated system to store renewable energy based on hybrid storage (batteries/hydrogen).

In MefHySto, MAHYTEC is responsible for the work package "Metrology for Reversible Hydrogen Storage Technologies (WP4)".

www.mahytec.com

Max Planck Institute for Intelligent Systems (MPI)

The Max Planck Society is Germany's most successful research organization and, in MefHySto, represented by the Max Planck Institute for Intelligent Systems in Stuttgart. This Institute has world-leading expertise in micro- and nano-robotic systems, haptic perception, human-robot interaction, bio-hybrid systems, and medical robotics. In the department of Modern Magnetic Systems, the Hydrogen Storage Group is specialized in characterising porous materials for over 20 years.

In MefHySto, the Hydrogen Storage Group of the MPI for Intelligent Systems is mainly involved in the development of methods and reference materials for hydrogen cryoadsorption storage.

www.mpg.de

National Physical Laboratory (NPL)

NPL is the UK's National Metrology Institute, developing and maintaining the national primary measurement standards. Our world-leading measurement solutions are critical to business and government, accelerating research and innovation, improving quality of life and enabling trade. We ensure our cutting-edge measurement science has a positive impact in the real world.

NPL are the Work Package 1 leader and will contribute expertise in humidity generation, gas metrology and testing of electrolysers to the delivery of various activities in the MefHySto research project.

www.npl.co.uk

Physikalisch-Technische Bundesanstalt (PTB)

The Physikalisch-Technische Bundesanstalt (PTB) is the national institute for science and technology and the highest technical authority of the Federal Republic of Germany for the field of metrology and certain sectors of safety engineering. The PTB comes under the auspices of the Federal Ministry for Economic Affairs and Climate Action. It is a fundamental task of the PTB to realize and maintain the legal units in compliance with the International System of Units (SI) and to disseminate them, above all within the framework of legal and industrial metrology.

PTB is one of the leading institutes in Europe in laser-based infrared spectroscopy. With its working group of Spectrometric Gas Analysis, PTB has experience in the development and usage of laser spectrometers for different applications including natural gas and biomethane monitoring. In the MefHySto project, PTB will use a laser-spectroscopic gas analyser to develop a metrologically compatible method for fast measurements of H_2O impurities in H_2 gas. Recommendation on H_2O detection in H_2, based on the developed measurement method, will be shared and seek to find its way into standardisation like ISO 14687-2/3.

www.ptb.de

Universidade da Coruña (UDC)

UDC is a public Spanish university with research expertise on air quality, water quality, marine environment and food safety. The Institute of Environmental Science (IUMA) at UDC is ISO 17025-accredited for the determination of the PM10 mass concentration of suspended particulate matter in ambient air; it has extensive experience on implementing validated analytical methodologies for a wide range of chemicals, volatile compounds, persistent and emerging pollutants, trace metals and organometallic species in environmental and industrial samples.

In MefHySto, UDC contributes to metrology for hydrogen quality through analytical characterisation of key-halogenated compounds and impurities from hydrogen production devices and ground storage systems.

www.udc.es

Universidad de Valladolid

The University of Valladolid (UVa)

The University of Valladolid, UVa, is a public university with a long tradition going back almost 800 years, making it one of the oldest universities in the world. It is located in Castilla y León, a region with a rich cultural heritage. The research group TERMOCAL at UVa has been working in the experimental determination of thermophysical properties of liquids and gases for more than 25 years. Its main research areas are the thermodynamic modelling of alternative fuels from the experimental determination of their thermophysical properties with the highest available accuracy; the research in metrology in the fields of temperature, pressure and humidity, as the main variables involved in the determination of the thermodynamic properties; and the energy and exergy analysis of systems and processes involved in the sustainable use of energy. TERMOCAL is part of the Bioeconomy Research Institute of the UVa.

In MefHySto, UVa-TERMOCAL is responsible for the work package two "Thermophysical properties", which includes the investigation of the properties of hydrogen obtained from electrolysis, hydrogen injected in the gas grids and hydrogen under geological storage conditions.

www.universityofvalladolid.uva.es

The partners in MefHySto collaborated closely to achieve the project's objectives with their combined expertise to advance the state-of-the-art in hydrogen storage technologies and support the broader goals of the EU's energy transition.

2 New Metrology for Hydrogen Quality from Power-to-Hydrogen

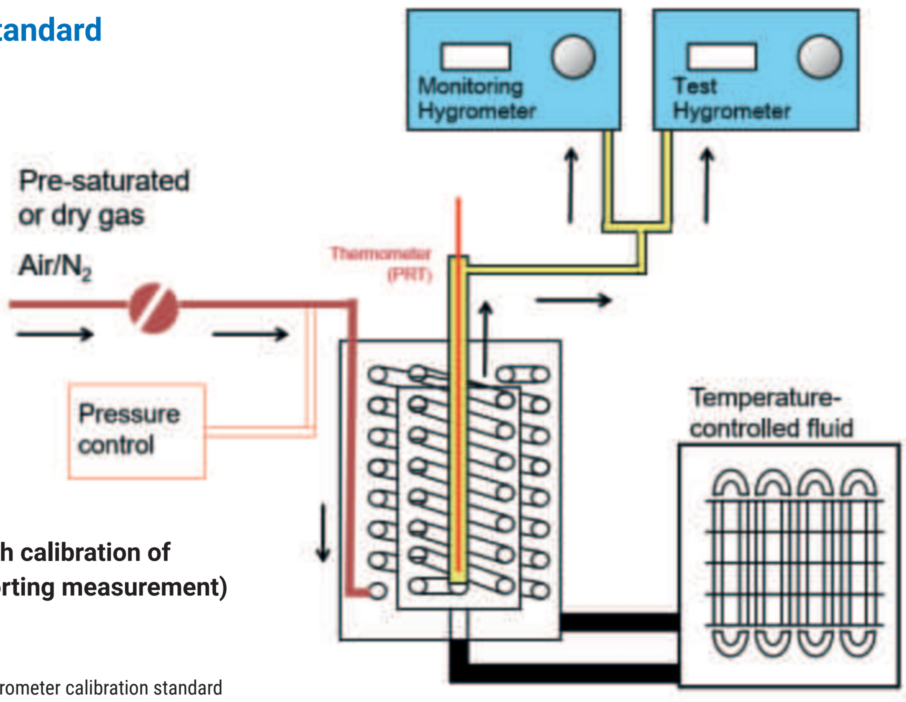
- *Hydrogen purity is crucial for fuel cell performance and durability.*
- *Oxygen sensors calibrated in different balance gases (nitrogen or helium) showed significant response variations, highlighting the need for hydrogen-specific calibration.*
- *Primary Reference Materials (PRMs) for water and oxygen can be reliably prepared and used for consistent hydrogen quality assessment.*
- *Sensors tested at different pressures showed varying measurement biases, indicating the need for pressure-specific calibration.*
- *Advancements in real-time hydrogen quality measurement with proper calibration greatly enhance PEM water electrolysis performance and reliability.*

2.1 | Improving Hydrogen Purity: Advancements in Measuring Impurities

Hydrogen purity is a critical factor in the performance and durability of fuel cells and other hydrogen-based technologies. As the demand for hydrogen as a clean energy carrier grows, so does the need for precise and reliable methods to measure impurities in hydrogen. This chapter delves into the advancements made in measuring key impurities, specifically water vapour and oxygen, in hydrogen produced through proton-exchange membrane (PEM) water electrolysis.

PEM water electrolysis is a widely used method for producing hydrogen. It involves using electricity to split water into hydrogen and oxygen. However, during transient periods of operation, such as rapid changes in electricity demand and supply, the quality of the hydrogen produced can be significantly affected by the presence of impurities. Water vapour and oxygen are particularly concerning, as they can degrade the performance of fuel cells when hydrogen is used as a fuel.

Primary dew point standard (single-pressure)



Traceable to the SI through calibration of thermometers (and supporting measurement)

Figure 1: Schematic of dew-point hygrometer calibration standard

To address these challenges, new metrological techniques have been developed to assess the response time of online gas analysers that measure these impurities. The ability to generate fast changes in the concentration of impurities is crucial for testing the response times of these instruments, ensuring they can accurately track and respond to rapid variations in hydrogen quality.

One significant advancement was the development of a laser-spectrometric measurement method based on cavity ring-down spectroscopy (CRDS). This highly sensitive technique allows for the detection of water vapour in hydrogen down to the nanomolar range. The method was validated against reference gas mixtures and demonstrated excellent repeatability, showcasing its potential for precise quality control in hydrogen production.

Additionally, a step-change facility was developed to apply rapid changes in water content within hydrogen, enabling the assessment of various hygrometers' (Figure 1 and Figure 2) response times. These tests revealed a wide range of response times, highlighting the importance of selecting appropriate instruments for online hydrogen quality measurement. Instruments with slower response times could delay critical feedback to process control systems, potentially compromising hydrogen quality.

Overall, these advancements in impurity measurement techniques are essential for ensuring the production of high-purity hydrogen, which is important for the efficient and reliable operation of hydrogen fuel cells and other applications.

2.2 | Ensuring Clean Hydrogen: New Techniques for Quality Assessment

Ensuring the cleanliness of hydrogen is paramount for its successful integration into the energy sector. The presence of impurities, even at trace levels, can have detrimental effects on the performance and longevity of hydrogen fuel cells and other systems. This section explores the innovative techniques developed for quality assessment of hydrogen produced through PEM water electrolysis, focusing on real-time monitoring and validation of sensor technologies.

Real-time quality assessment of hydrogen involves continuous monitoring of impurity levels during production. This is particularly important during transient periods, such as start-up and shutdown phases, where impurity concentrations can fluctuate. To meet this need, new facilities capable of inducing rapid changes in impurity levels were developed. These facilities allow for the testing and validation of online gas analysers under realistic operating conditions.

One of the key techniques employed is the use of CRDS for water vapour measurement. CRDS offers high sensitivity and precision, making it ideal for detecting low levels of water vapour in hydrogen. The method was validated against reference materials, ensuring traceable and reliable measurements. The ability to perform measurements in real-time provides a significant advantage, enabling immediate corrective actions to maintain hydrogen quality.

For oxygen measurement, a fast-step change facility was developed to evaluate the performance of oxygen sensors. This facility can induce rapid changes in oxygen concentration, allowing for the assessment of sensor response times and accuracy.

Figure 2: Saturator component of an NPL-designed dew- and frost-point primary generator

The results highlighted the importance of calibrating sensors under conditions that reflect their actual use in hydrogen production processes. Sensors calibrated in different balance gases, such as nitrogen or helium, exhibited significant variations in response, underscoring the need for hydrogen-specific calibration.

Moreover, the stability and shelf-life of calibration gases were examined, particularly for reactive compounds like oxygen. Ensuring the stability of these gases is crucial for maintaining accurate and traceable measurements. The project demonstrated that primary reference materials (PRMs) for water and oxygen can be reliably prepared and used for calibration, supporting consistent and accurate hydrogen quality assessment.

These advancements in quality assessment techniques are instrumental in maintaining the purity of hydrogen throughout its production and supply chain. By ensuring accurate real-time monitoring and validation of sensors, the industry can achieve higher standards of hydrogen quality, paving the way for its broader adoption as a clean energy source.

2.3 | Measuring Hydrogen Quality in Real Time: Enhancing PEM Water Electrolysis

The intermittent nature of renewable energy sources, such as wind and solar power, necessitates reliable and efficient methods for storing and converting energy. PEM water electrolysis plays a crucial role in this context, enabling the production of hydrogen from excess renewable electricity. However, maintaining the quality of hydrogen during rapidly changing operating conditions is a significant challenge. This section discusses the enhancements made in measuring hydrogen quality in real-time, focusing on the role of online gas analysers in PEM water electrolysis.

During PEM water electrolysis, the production of hydrogen can be affected by transient use periods, characterized by sudden changes in electricity supply and demand. These fluctuations can lead to variations in impurity levels, which need to be accurately monitored to ensure the quality of hydrogen. Online gas analysers, capable of providing real-time measurements, are essential tools for this purpose.

The project developed and validated a fast-step change facility capable of applying rapid changes in impurity concentrations within seconds. This facility was used to test the response times of various hygrometers and oxygen sensors, providing valuable insights into their performance under dynamic conditions. The ability to quickly detect and respond to changes in impurity levels is critical for maintaining hydrogen quality and preventing damage to fuel cells and other downstream equipment.

For water vapour measurement, the CRDS method proved to be highly effective. Its sensitivity and precision enable the detection of low levels of water vapour, ensuring that even minor impurities are identified and addressed. The method's validation against reference materials confirmed its reliability, making it a robust tool for real-time hydrogen quality assessment.

Oxygen sensors were similarly tested using the fast-step change facility. The results highlighted the importance of sensor calibration in the actual gas matrix used in hydrogen production. Sensors calibrated in alternative gases, such as nitrogen or helium, showed significant discrepancies in response when used in hydrogen. This finding underscores the necessity of a hydrogen-specific calibration to ensure accurate measurements.

The study also revealed the impact of pressure changes on sensor performance. Sensors tested at different pressures exhibited varying degrees of measurement bias, indicating the need for pressure-specific calibration. Accurate calibration across a range of pressures ensures reliable measurements under different operating conditions, enhancing the overall quality control of hydrogen production.

In conclusion, the advancements in real-time hydrogen quality measurement techniques significantly enhance the performance and reliability of PEM water electrolysis (Figure 3). By employing advanced metrological methods and ensuring accurate sensor calibration, the industry can achieve higher standards of hydrogen purity, supporting the broader adoption of hydrogen as a key component in the clean energy transition.

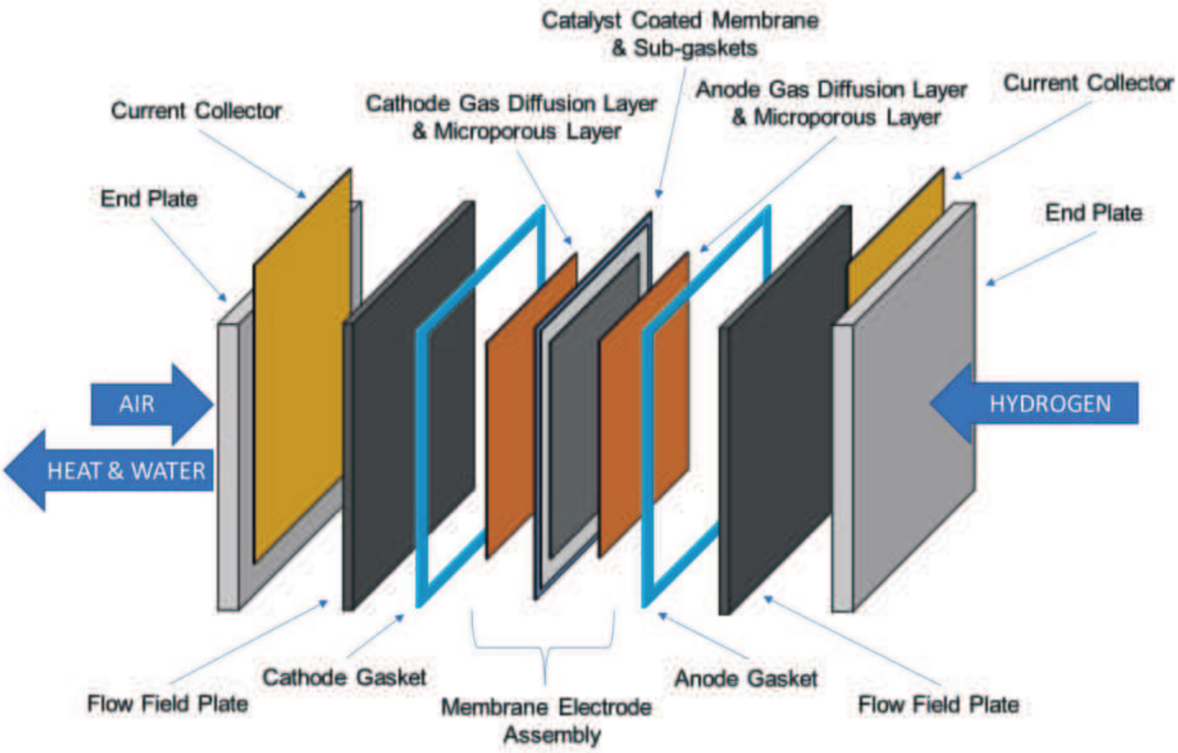


Figure 3: General components with a single cell PEMFC

Find out more in the final project reports under:

New metrology for the measurement of key impurities in hydrogen
https://mefhysto.eu/mefhysto-d1/

Trials of rapid response analysis of key impurities in hydrogen from electrolysis
https://mefhysto.eu/mefhysto-d2

3 Thermophysical Properties of Hydrogen Blends

- *Accurate prediction of the thermophysical properties of hydrogen-enriched gas mixtures is essential for their effective utilization in energy systems.*
- *Deviations from the Standard Helmholtz Energy Equation of State (GERG-2008) occur for H2/natural gas blends, particularly at lower temperatures and higher hydrogen concentrations.*
- *Significant phase behavior changes with increased hydrogen content simplify hydrogen extraction from underground storage.*
- *Density measurements of hydrogen-enriched natural gas mixtures reveal deviations from GERG-2008 EoS, especially at lower temperatures.*

3.1 | Understanding Energy Storage: The Role of Hydrogen in Gas Grids and Geological Storages

The integration of hydrogen into gas grids and geological storages is critical for advancing energy storage solutions. As renewable energy sources like solar and wind become more prevalent, the need for efficient energy storage methods intensifies. Hydrogen, with its high efficiency, transportability and versatility, is an ideal candidate for large-scale energy storage, capable of bridging the gap between variable renewable energy generation and steady energy demand.

Hydrogen can be injected into existing natural gas grids, leveraging the extensive and mature infrastructure already in place. This blending of hydrogen with natural gas offers a pragmatic approach to decarbonizing the gas supply and reducing greenhouse gas emissions. It also facilitates the storage of excess renewable energy, converting it into hydrogen via electrolysis during periods of low demand and high renewable generation. This hydrogen can later be utilized to meet peak energy demands, thereby enhancing grid stability and reliability.

Geological storages, such as underground gas storages (UGS), offer another dimension for large-scale hydrogen storage. These storages, including depleted oil and gas fields, aquifers, and salt caverns, provide vast capacities for hydrogen, ensuring long-term energy security and resilience. The MefHySto project focused on addressing the metrological and

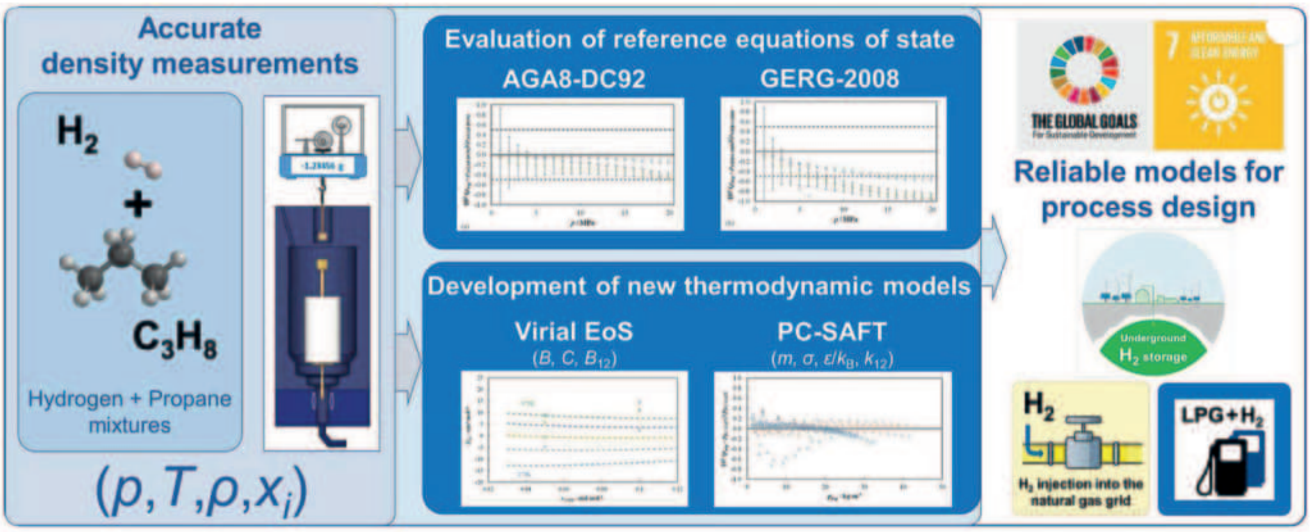


Figure 4: Graphical abstract of the thermodynamic characterization of a hydrogen (H_2) and propane (C_3H_8) mixture

thermodynamic challenges associated with such storages, particularly during the transition from storing natural gas to hydrogen.

The benefits of hydrogen integration into gas grids and geological storages extend beyond energy storage. Hydrogen can act as a crucial energy carrier, enabling the decarbonization of sectors that are difficult to electrify directly, such as heavy industry and long-haul transportation. By ensuring the availability of high-purity hydrogen, the MefHySto project supports the broader adoption of hydrogen technologies, contributing to the EU's ambitious climate targets and the overall goal of achieving a sustainable energy future.

3.2 | Equations of State: Unlocking the Secrets of Hydrogen-Enriched Gas Mixtures

The accurate prediction of the thermophysical properties of hydrogen-enriched gas mixtures is essential for their effective utilization in energy systems. Equations of state (EoS) play a critical role in this context, providing the necessary theoretical framework to describe the behaviour of gas mixtures under various conditions. The MefHySto project has made significant progress in refining these equations to better accommodate the unique properties of hydrogen.

Hydrogen-enriched gas mixtures exhibit distinct phase behaviours compared to traditional natural gas. The addition of hydrogen alters the solubility and interaction of hydrocarbons, affecting the overall thermodynamic properties of the mixture. For instance, as the hydrogen content increases, the solubility of heavier hydrocarbons decreases, which simplifies the processing required for hydrogen withdrawal from geological storages.

Experimental density data for hydrogen-enriched synthetic natural gas mixtures have been measured across a range of temperatures and pressures. These data reveal deviations from the Standard Helmholtz Energy Equation of State (GERG-2008), particularly at lower temperatures and higher hydrogen concentrations. Such deviations highlight the need for further refinement of existing models to ensure accurate predictions. The project also explored the phase behaviour and condensation phenomena

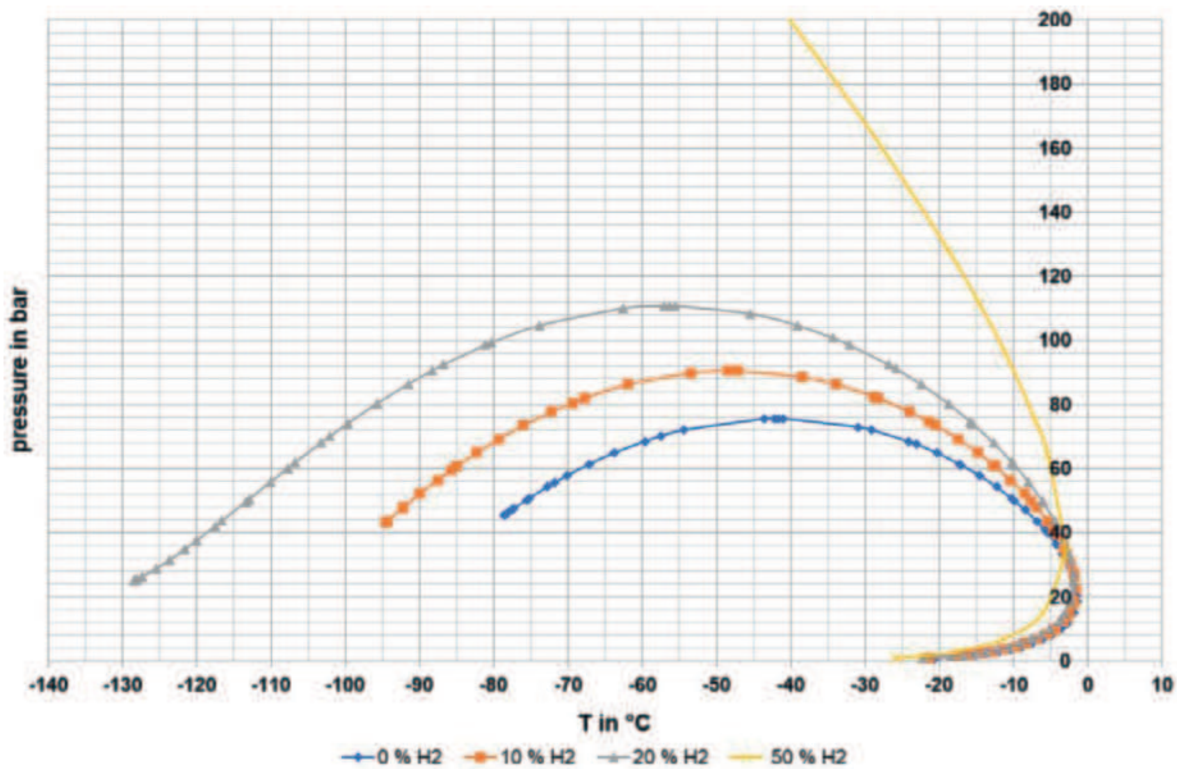


Figure 5: Phase envelope (p – T diagram) of a Russian-type natural gas mixture (0 % H_2), and the same sample with 10 %, 20 % and 50 % H_2 concentrations. SRK EoS predicted values.

of these mixtures, providing valuable insights into their stability and potential applications (Figure 5). Understanding these properties is crucial for optimizing the storage and transport of hydrogen-enriched gases, ensuring their efficient and safe use in energy systems.

The development of accurate EoS for hydrogen-enriched mixtures supports various applications, from industrial processes to residential heating and power generation. By improving our understanding of these mixtures, the MefHySto project enhances the feasibility of integrating hydrogen into existing energy infrastructures, paving the way for a cleaner and more sustainable energy landscape.

3.3 | Summary and Outlook for Equations of State

The current reference equation of state for hydrogen was proposed in 2009 (Leachman et al., 2009). The equation of state is explicit in the Helmholtz free energy, with 14 terms, and is valid for temperatures from the triple point (13.957 K) to 1000 K and for pressures up to 2000 MPa. Another important equation of state for hydrogen, with reference quality, was developed in 2000 (Klimeck, 2000) specifically designed for the development of the multicomponent GERG-2008 equation of state (Kunz and Wagner, 2012). This equation of state was developed by using multi-property fitting and optimization methods. It has an individually optimized structure with 14 terms. This equation is valid for temperatures of (14 to 700) K and pressures up to 300 MPa. Only the methane + hydrogen binary system, of the 20 possible binary mixtures of hydrogen with the rest of the components considered (Kunz and Wagner, 2012), has a binary specific departure function included in the current GERG-2008 EoS. A recent study (Beckmüller et al., 2021) has developed four equations of state for the binary systems of hydrogen with methane, nitrogen, carbon dioxide, and carbon monoxide. Nevertheless, the authors recognized that new highly accurate data for these systems are still required for further

improvements and a more comprehensive validation, especially for the binary system hydrogen + carbon monoxide. For the rest of the binary systems, the amount of experimental data available is very limited and of disputed quality. New experimental data will enable the development of new generalized departure functions and reducing functions of the mixture density and temperature, dependent on the composition, for several H_2 binary mixtures.

There is a real need for density and speed of sound data for the binary systems of hydrogen with water, hydrogen sulphide, helium, and argon, as well as all the linear hydrocarbons from ethane to decane, including iso-butane and iso-pentane. Accurate prediction of the fluid-liquid phase equilibrium and dew point calculations for mixtures, including heavier hydrocarbons and hydrogen, is crucial as well.

Besides the experimental data of binary mixtures, which are relevant for the development of new equations of state, it is also important to check the capability of the current or newly developed EoS with multicomponent mixtures containing hydrogen. In this sense, it is important to determine the density, speed of sound or phase equilibrium properties of ternary or multicomponent mixtures containing hydrogen.

It is necessary to obtain high-quality experimental data of binary mixtures of hydrogen with other components at high pressures (over 70 MPa) or at very low temperatures (below 20 K), respectively. Studying the effect of traces and small amounts of impurities in the behaviour of pure hydrogen or hydrogen mixture is also needed.

Find out more in the final project report and the corresponding research paper under:

Equations of state (EoS) used for modelling hydrogen injection
https://mefhysto.eu/mefhysto-d3/

Thermodynamic characterization of the ($H_2 + C_3H_8$) system significant for the hydrogen economy: Experimental (p, ρ, T) determination and equation-of-state modelling
https://doi.org/10.1016/j.ijhydene.2022.11.170

4 Metrology for Hydrogen-to-Power

- *Contaminants and oxygen (air) in hydrogen can significantly affect the power output, efficiency, and lifespan of fuel cells.*
- *In MefHySto, complex mixtures of impurities, simulating worst-case permissible contamination scenarios, were studied.*
- *The proton pump effectively detects low hydrogen contaminant concentrations, maintains stability under pure hydrogen flow, and quickly recovers after exposure to contaminants.*
- *At 1% contaminant concentration, voltage decay in single-cell PEMFCs is similar to that with pure hydrogen. However, at 5%, immediate cell deterioration occurs, especially at the electrochemically active surface area at the cathode.*
- *No significant differences were observed between synthetic and technical air during both short-term and long-term tests, with consistent results from testing two identical short-stacks at different labs.*
- *Halogenated VOCs in ambient air and hydrogen supplies were minimal, and purification systems were effective.*
- *A cutting-edge humidity sensor monitored hydrogen production in a commercial electrolyzer, confirming high-quality hydrogen production.*
- *Real-world tests demonstrated the robustness of MefHySto metrological tools and procedures, ensuring PEMFCs maintain high performance and durability even under challenging conditions.*

4.1 | Ensuring Clean Power: Investigating the Quality of Hydrogen for Fuel Cells

The MefHySto project dedicated substantial efforts to research metrology to help ensure the quality of hydrogen supplied to proton-exchange membrane fuel cells (PEMFCs). Recognizing the sensitivity of PEMFCs to contaminants, the research aimed to investigate the impact of various impurities in hydrogen on the short-term performance and long-term durability of these cells. PEMFCs operate below 100 °C using hydrogen and oxygen from air. Contaminants in either supply can significantly affect the power output, efficiency, and lifespan of the fuel cells. Previous research predominantly focused on binary or ternary mixtures of contaminants. However, the study adopted a novel approach by using complex mixtures of impurities, mimicking worst-case, yet still permissible, contamination scenarios.

The selection of hydrogen contaminants was guided by the ISO 14687:2019(D) standard and considered potential compound interactions when prepared in a

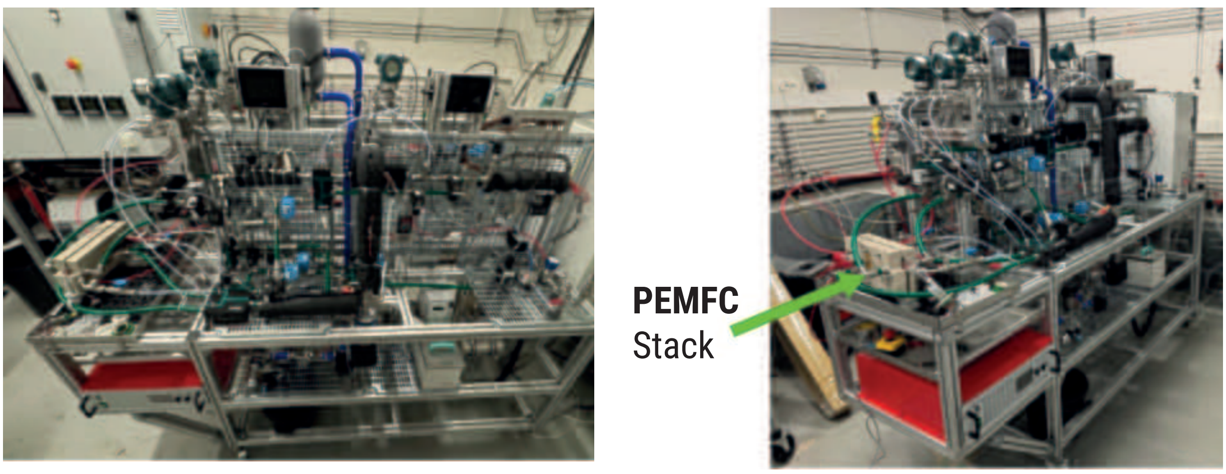


Figure 6: ALPIX Test bench for 1 kW PEMFC stack installed on SENEPY Platform (air circuit side on the left, front side on the right)

cylinder. Air contaminants and their concentrations were based on real-world averages from urban and suburban areas in the UK and EU, ensuring a realistic representation of ambient air quality.

Key findings from our investigation include:

- The proton pump proved highly effective in detecting low concentrations of hydrogen contaminants, maintaining stability under pure hydrogen flow and showing quick recovery after exposure to contaminants.
- In single-cell PEMFCs, voltage decay at 1% contaminant concentration was indistinguishable from intrinsic decay with pure hydrogen. However, at 5% contaminant concentration, immediate cell deterioration occurred.
- The degradation of the electrochemically active surface area (ECSA), particularly at the cathode, was identified as a key factor in performance loss during fuel cell duty cycle (FC-DLC) tests.
- No significant differences were observed between synthetic air and technical air during both short-term and long-term tests, indicating robustness in various air quality conditions.
- Consistent results were obtained from testing two identical short-stacks at different labs, validating our methodologies and findings.

These results underscore the importance of maintaining high hydrogen purity to ensure the reliability and efficiency of PEMFCs, highlighting the critical need for advanced metrological techniques to monitor and control hydrogen quality.

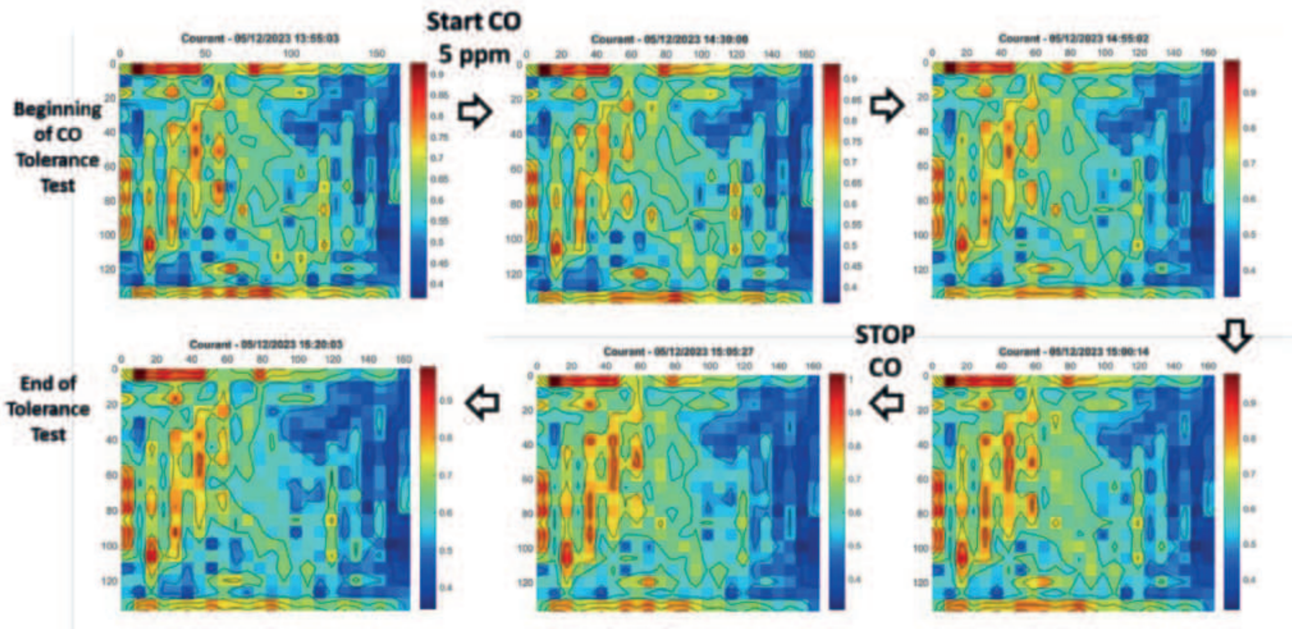


Figure 7: Current density distribution maps measured using a segmented plate (S++®) placed in the middle of the stack. CDDM reported at different times during a CO tolerance test from BoT until the EoT, indicating the moments when the shift is performed between pure hydrogen to mixture with 5 ppm CO (= START CO) and the reverse (= STOP CO).

4.2 | The Science of Sustainable Energy: Monitoring Hydrogen and Air for Fuel Cell Performance

A core focus was also monitoring the effects of hydrogen and air quality on PEMFC performance. Fuel cells are highly susceptible to impurities, which can poison the catalysts necessary for the chemical reaction between hydrogen and oxygen, thereby reducing efficiency and longevity.

The study encompassed the detection and analysis of various contaminants, particularly halogenated volatile organic compounds (VOCs), which, even at trace levels, can degrade PEMFC performance. Using state-of-the-art techniques, such as in-tube extraction dynamic headspace coupled to gas chromatography-mass spectrometry (ITEX-DHS-GC-MS), we developed robust protocols for gas sampling and analysis.

The methodology was validated through applications on different gas lines and ambient air at the SENEPY demonstration platform, achieving the following:

- Identification and quantification of up to 39 halogenated VOCs.
- Development of protocols for sampling both air and hydrogen.
- Validation of the purification systems for air and hydrogen, ensuring the removal of harmful organic halogenated impurities.

Our findings indicated that the levels of halogenated VOCs in ambient air and hydrogen supplies were minimal and unlikely to affect PEMFC performance significantly. The purification systems implemented were effective, ensuring the high purity required for optimal fuel cell operation.

Additionally, we conducted humidity measurements in the hydrogen stream produced by a commercial electrolyzer. Using a cutting-edge humidity sensor, we characterized the sensor's response and compared it to other measurement methods. The results confirmed that the water content in hydrogen remained within acceptable limits (< 5 µmol mol^{-1}) across all tested operating points, as detailed in the deliverables D1 and D2.

4.3 | Reliability in Action: Real-World Testing of Fuel Cell Systems

The MefHySto project's real-world testing of fuel cell systems was important in validating our findings and methodologies. By simulating realistic contamination scenarios and using complex mixtures of impurities, we ensured that our results were applicable to actual operating environments.

Key activities and results from our testing included:

- Measurement of local current density during 5 ppm CO contamination, revealing that the anode active area near the hydrogen inlet suffered more severe contamination, shifting cell operation towards the outlet.
- Effective recovery of cell performance through a shutdown procedure that included an air cleaning phase, successfully mitigating CO poisoning at the anode.
- Analysis of voltage degradation profiles on short stack PEMFCs, which suggested that CO contamination was the primary cause of performance loss, corroborating similar decay profiles for both the contaminant mixture and single-CO contamination.

These real-world tests demonstrated the robustness of our metrological tools and procedures, ensuring that PEMFCs can maintain high performance and durability even under challenging conditions. The consistency of results across different laboratories further validated our approach, providing a solid foundation for future advancements in hydrogen fuel cell technology.

Find out more in the final project reports under:

The impact of contaminants in hydrogen and air on PEMFC
https://mefhysto.eu/mefhysto-d4/

Metrological chain for gas quality measurement at a H_2 demonstration platform level
https://mefhysto.eu/mefhysto-d5/

5 Metrology for Reversible Hydrogen Storage Technologies

- *Accurate assessment of heat conductivity is essential for predicting the storage capacity and efficiency of hydrogen storage systems in in metal hydrides and metal-organic frameworks (MOFs).*
- *In MefHySto, methods for measuring and calculating hydrogen ad- and desorption in metal hydrides and metal-organic frameworks (MOFs) were developed.*
- *The crystal metal-organic framework, ZIF-8, was validated as a reference material for hydrogen storage in MOFs.*

5.1 | Hydrogen Storage: Measuring Heat Conductivity and Quality for Sustainable Technology

The MefHySto project developed advanced hydrogen storage technologies, particularly focusing on the accurate measurement of heat conductivity and hydrogen quality in storage systems. One of the key outcomes was the establishment of a robust methodology for measuring and calculating the heat conductivity of hydrogen absorbed or adsorbed in intermetallic materials or porous substances, such as metal hydrides and metal-organic frameworks (MOFs). This methodology considers various factors including temperature, pressure, hydrogen absorption capacity, and rate, all while accounting for the impact of dynamic heat flux. The process of hydrogen storage involves complex thermodynamic interactions, where heat conductivity plays a crucial role. Accurate assessment of this parameter is essential for predicting the storage capacity and efficiency of hydrogen storage systems. This is, besides others, important due to heat management: Hydrogen storage involves exothermic and endothermic reactions during absorption and desorption. Efficient heat management is essential to maintain optimal storage conditions and prevent overheating or insufficient cooling, which can impact storage capacity. Despite two decades of research, the dynamic methods for H_2 adsorption need to be harmonised, e.g., using reference materials.

Figure 8: Test tank assembled at MAHYTEC to carry out thermal conductivity tests with the selected method, MAHYTEC designed the test tank with FHa support, which takes care of the assembly of the test bench in parallel.

A notable achievement was validation of ZIF-8, a crystalline metal-organic framework, as a reference material. ZIF-8 was chosen due to its exceptional hydrogen uptake capacity, mechanical stability, and hydrophobic properties, which minimize water adsorption and enhance measurement accuracy. The high reproducibility of hydrogen uptake by ZIF-8, demonstrated across 15 different experimental setups, underscored its reliability as a reference material. This development is expected to significantly aid the advancement of hydrogen storage technologies by providing a standard for future research and commercial applications.

5.2 | Understanding the Science of Hydrogen Storage: Impacts of Temperature and Purity

Gas temperature and purity are two critical factors influencing the performance of hydrogen storage technologies. The MefHySto project extensively studied the thermodynamic parameters affecting hydrogen storage, including heat conductivity, enthalpy of absorption and desorption, and the dynamic impact of heat flux.

The correct assessment of thermodynamic parameters, like heat conductivity and enthalpy changes during hydrogen absorption and desorption, is important for accurate forecasting of storage capacity. The project's research showed that as temperature varies, so does the efficiency of hydrogen storage and release processes. This understanding allows for better design and optimization of storage systems to operate effectively under different thermal conditions.

Additionally, the purity of hydrogen has a significant impact on storage capacity and system longevity. Impurities in hydrogen can degrade the performance of storage materials, leading to reduced storage capacity and shorter operational life. The MefHySto project developed methods and experiments (Figure 9 and Figure 10) to assess the influence of hydrogen pollutants on storage systems. By studying the effects of different pollutants and their concentrations, the project provided valuable insights into maintaining high-purity hydrogen, thus ensuring the durability and efficiency of storage technologies. The analysis showed that an excess of CO_2, O_2 and H_2O pollutants does have a stronger effect than an excess of N_2 or CO.

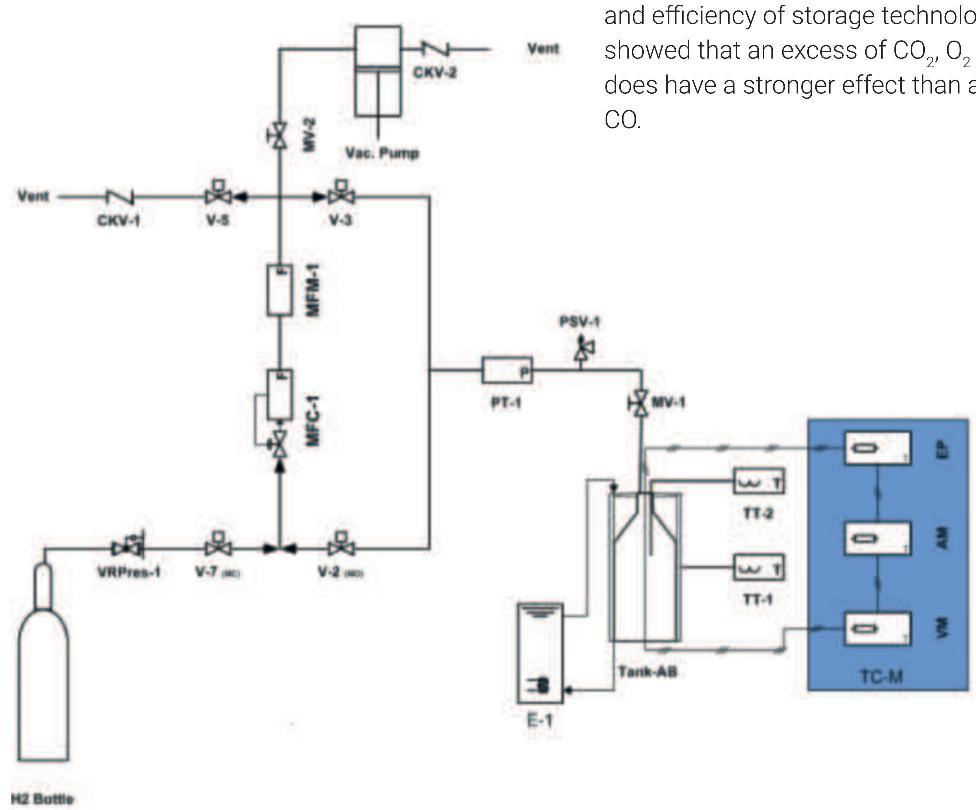


Figure 9: P&ID scheme of set-up built of the testbench at FHa's facilities

5.3 | Reliable Hydrogen Storage: Advancements in Measurement and Assessment

The advancements in measurement and assessment techniques developed by the MefHySto project have paved the way for more reliable hydrogen storage solutions. One of the primary goals was to develop a validated method for measuring heat conductivity of hydrogen in intermetallic and porous materials, which was successfully achieved with less than 1% uncertainty.

Despite initial plans to develop reference materials and methods for hydrogen adsorption and absorption capacity with precision better than 1%, it was found that current knowledge and technologies in hydride systems did not support this level of precision. However, the project made progress in understanding the role of pollutants in hydrides, both in terms of concentration and cycling effects. This research is crucial for the commercial implementation of hydride-based hydrogen storage solutions, as it ensures the systems can maintain performance and longevity in real-world conditions.

The validated methods developed include dynamic storage methods for hydrogen adsorption and desorption, as well as assessing the impact of pollutants using metal hydride assemblies. The selection of ZIF-8 as a reference material has proven to be a significant milestone. Its consistent performance across various experimental setups highlights its potential to serve as a standard for future hydrogen storage research and development.

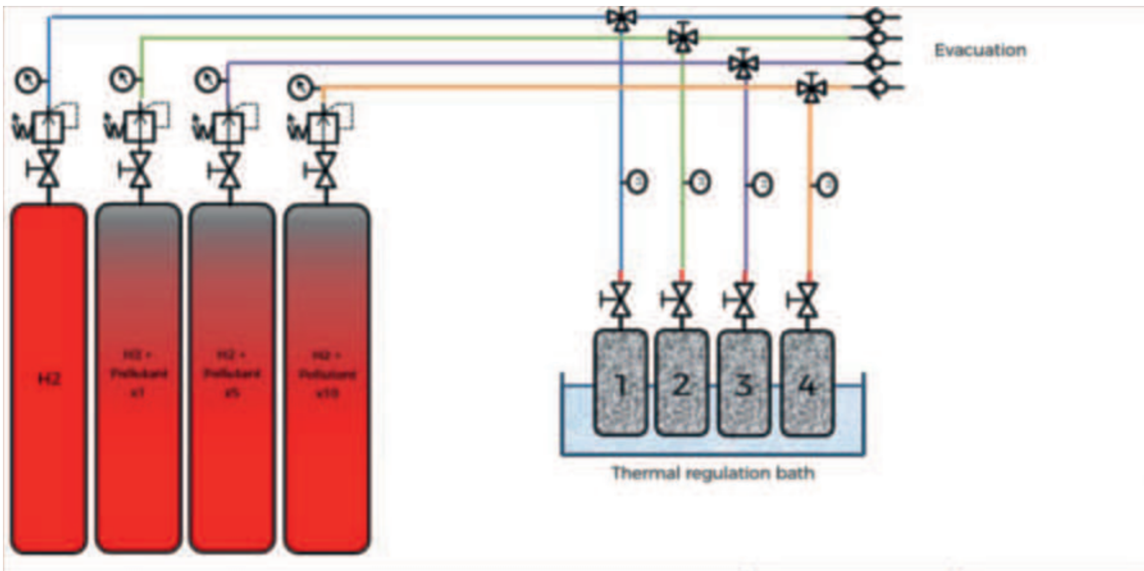


Figure 10: Schematic of the test bench for measuring the influence of pollutants in hydrogen gas

The harmonized method for measuring heat conductivity and the use of ZIF-8 as a reference material developed in MefHySto in regard to reversable hydrogen storage sets new standards for accuracy and reliability in the field.

Future work could focus on further reducing uncertainties in measurements and expanding the range of materials tested. Exploring other MOFs and intermetallic compounds could reveal additional candidates with desirable properties for hydrogen storage. Moreover, integrating advanced computational models with experimental data could enhance the predictive capabilities for storage system performance under various conditions.

The impact of hydrogen purity on storage systems also warrants ongoing investigation. Developing more sophisticated purification technologies and contamination-resistant materials will be essential as hydrogen production and storage scale up. Understanding the long-term effects of pollutants and repeated cycling on storage materials will help in designing systems with extended lifespans and improved resilience.

Find out more in the final project report and the corresponding research paper under:

Measuring and calculating heat conductivity of hydrogen ab/adsorbed in an intermetallic material or porous materials
https://mefhysto.eu/mefhysto-d6/

ZIF-8 Pellets as a Robust Material for Hydrogen Cryo-Adsorption Tanks
https://pubs.acs.org/doi/pdf/10.1021/acsaem.2c03719

Experimental Volumetric Hydrogen Uptake Determination at 77 K of Commercially Available Metal-Organic Framework Materials
https://www.mdpi.com/2311-5629/8/1/5

A database to select affordable MOFs for volumetric hydrogen cryoadsorption considering the cost of their linkers
https://erig.eu/wp-content/uploads/2023/10/d3ma00315a.pdf

6 Metrology for Large-Scale Underground Hydrogen Storage

- *Projections suggest a global demand of 17,000 TWh of hydrogen by 2050 and a capacity of 580–600 billion m³ (10-12% of total demand) underground storage is anticipated.*
- *Existing storage facilities must undergo conversion from natural gas to hydrogen and the demand for storage capacity will surpass the existing volume, necessitating at least an equivalent amount.*
- *Operational changes in storage facilities are anticipated, with increased frequency expected, involving daily fluctuations between injection and withdrawal.*
- *The filling of former natural gas fields and storage facilities implies prolonged trading of natural gas/hydrogen mixtures.*
- *MefHySto showed that Gas Chromatography with Barrier Ionization Discharge detector (GC-BID), could lower the detection limits for gases and hydrocarbons, enabling a thorough analysis of the stringent requirement for high-purity hydrogen from underground storage.*
- *Existing sensors are capable of accurately measuring the dew point in hydrogen, but only when appropriately calibrated.*
- *Findings of the diffusion process of hydrogen align with theoretical considerations and support the assertion that gravity segregation is not a significant factor for hydrogen-methane mixtures within reasonable dimensions and timeframes.*

6.1 | Underground Gas Storage: A Vital Component of Energy Transition

Hydrogen is widely recognized as an essential energy source for the future. Numerous countries beyond Europe have established explicit targets for incorporating hydrogen into their energy strategies. To ensure the security of the supply chain, there is a growing emphasis on underground hydrogen storage. Considerable global expertise in storing natural gas to meet medium-term demand is available, and some of this knowledge can be effectively applied to hydrogen storage as well.

There are two main storage options for hydrogen in the geological subsurface:

- pore storage (aquifers or depleted natural gas reservoirs) and
- underground cavern storage (salt caverns or rock caverns).

The porous storage structures are differentiated between depleted gas fields and deep (saline) aquifers.

Currently, there are 662 operational Underground Gas Storage (UGS) facilities worldwide, with 72% located in depleted hydrocarbon reservoirs, 15% in salt caverns, and another 15% in deep aquifers. In Europe alone, there are more than 100 existing underground gas storage facilities. As of 2019, the global storage capacity in UGS was approximately 483 billion cubic meters of working gas.

The distinctive role of underground gas storage facilities arises from the demand for natural gas, which experience significant increases in winter compared to summer. Concurrently, natural gas production remains relatively stable in comparison.

Underground storage is not limited to natural gas; it also encompasses helium, propane, butane, ethene, and historically, town gas (a mixture of CO, CH_4, N_2, and H_2).

6.2 | Transitioning to Hydrogen: The Role of Underground Storage Facilities

The future need for renewable hydrogen is indisputable, yet the forecasted quantity remains uncertain. Projections suggest a global demand of 17,000 TWh of hydrogen by 2050. To accommodate 10 – 12% of this volume in storage capacity, a requisite capacity of 580 – 600 billion m³ is anticipated. Consequently, the following conclusions were drawn within the project:

- The demand for storage capacity will surpass the existing volume, necessitating at least an equivalent amount.
- Existing storage facilities must undergo conversion from natural gas to hydrogen, or alternatively, the construction of new storage facilities, which is both technically and regulatory complex.
- Porous storage facilities, challenging to convert to hydrogen, will also be imperative for accommodating hydrogen storage needs.
- Operational changes in storage facilities are anticipated, with increased frequency expected, involving daily fluctuations between injection and withdrawal.
- The filling of former natural gas fields and storage facilities implies prolonged trading of natural gas/ hydrogen mixtures.

The subsequent application of hydrogen will dictate the required quality. While household applications or burners in the steel and cement industries can function with hydrogen of quality group A (98 mol-%) and its associated compounds without issues, applications in the chemical industry and fuel cells demand higher H_2 qualities. Analytical distinctions must be made, encompassing:

- Hydrogen content, with discussions involving concentrations of 98, 99.5, and 99.97 mol-%.
- Trace components (e.g., sulfur components, H_2O) and accompanying gases (e.g., CO_2, N_2, CO) present in the hydrogen.

Owing to their historical background, geological characteristics, or microbiological processes, underground storage facilities (UGS) play a role in introducing diverse substances into hydrogen. Beyond storage installations, hydrogen may also encounter contamination from deposits within pipelines. The measurement technology employed in underground storage facilities needs to be adapted to these overarching conditions.

6.3 | Challenges and Solutions: Metrology for Large-Scale Hydrogen Storage in Geological Reservoirs

Requirements for measurement results arise from various aspects, including:

- Technical specifications mandated by the storage operator to ensure storage integrity and operational processes.
- Criteria outlined by gas providers for acceptance.
- Fiscal and financial considerations.

Hydrogen exhibits notable differences from methane in terms of viscosity, density, and calorific value. Moreover, its explosive nature necessitates adherence to safety protocols akin to those for natural gas. This underscores the importance of minimizing emissions during measurements.

Measurements can be conducted either in-line (e.g., H_2O) or separately post-depressurization in a dedicated measuring facility (e.g., gas chromatography measurements). Presently, there is no predefined technical standardization for measurements, and assessing components is often optional. Unlike natural gas UGSs, where site-specific measurements are commonplace, standardisation is challenging due to the diverse range of products.

Water content or water vapor dew point after gas drying is typically the standard measurement for natural gas UGS. Gas chromatographs, capable of assessing 11 or 16 components and calculating combustion parameters, are employed for quality checks. However, hydrogen is not routinely measured. Occasional measurements include:

- Oxygen levels, especially at the storage facility entrance.
- Sulfur compounds.
- Hydrocarbon condensation point.

UGS gas treatment involves gas drying and occasionally hydrocarbon dew point adjustment through cooling or silica gel adsorption. Desulfurization is typically unnecessary in natural gas UGS, except in cases of microbiological processes during underground storage.

Beyond oxygen, measuring sulfur compounds becomes technically necessary. Discussion surrounds the potential measurement of hydrocarbons (glycols, blanket, etc.), with uncertainties regarding gas treatment possibilities. Laboratory-based measurement

of these long-chain hydrocarbons may be considered after enrichment sampling.

Within the framework of Work Package 5 in the MefHySto project, the emphasis was placed on specific components and substance categories. This encompassed the measurement of trace compounds in hydrogen, assessment of water content, and consideration of thermodynamic factors.

An inquiry was conducted to assess whether the utilization of a GC-BID[1], an exceptionally sensitive detector, could effectively reduce detection limits for gases and hydrocarbons, thereby validating its capabilities. Table 1 shows the detection limits for selected compounds achieved through the application of this advanced detector. The investigation aimed to ascertain if the deployment of a GC-BID, a novel and highly sensitive detector, could lower the detection limits for gases and hydrocarbons, enabling a thorough analysis of the stringent requirement for high-purity hydrogen. This hypothesis was substantiated. The ensuing table illustrates the detection limits of various compounds using this innovative detector.

Analyt	Limit of detection (ppm)
Hydrogen	0.1
Argon	1.2
Oxygen	1.1
Nitrogen	1.9
Methane	0.03
Carbon monoxide	0.1

Table 1: Detection limits for selected compounds

[1] Gas Chromatograph with Barrier Ionization Discharge detector

On one hand, this process facilitated the verification of user requirements for high-quality hydrogen, as well as the monitoring of any potential introduction of components from the storage tank into the hydrogen. The introduction of water into all gases, due to geological reasons, necessitates the drying of gases and careful control of their water content. Within the project, NPL conducted measurements on the saturation of hydrogen and hydrogen/natural gas mixtures with water. Simultaneously, sensors were tested in these gases.

Figure 11 illustrates deviations observed in a gas moisture measuring device. These discrepancies can be rectified through an adjusted calibration, specifically calibrated at the appropriate pressure. In summary, it was observed that existing sensors are capable of accurately measuring the dew point in hydrogen when appropriately calibrated.

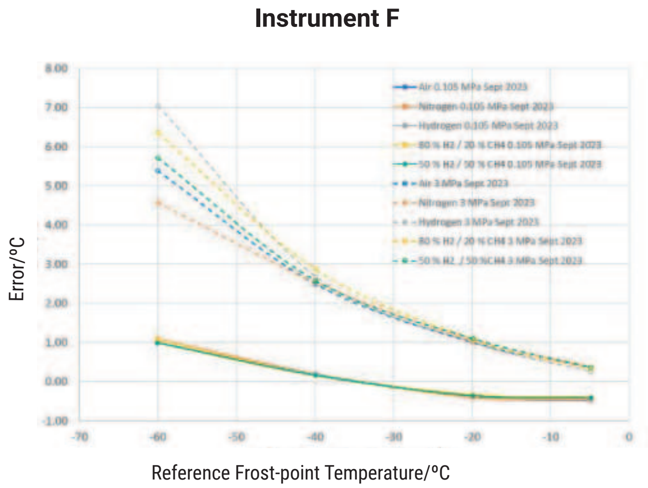


Figure 11: Deviations measured in gas moisture measuring device

The water content was measured based on pressure and the defined dew point, with correction values determined using Hardy's formulae. Within the MefHySto project, emphasis was placed on simulating the mixing process of hydrogen and methane. Various mixture mass compositions were tested, including ratios of 50:50 and 80:20.

Figure 12 illustrates the hydrogen volume fraction in the streamwise direction at the central axis of the pipeline (depicted in green), as well as at 25% (red) and 75% (blue) height of the pipeline. In this scenario, simulations were conducted for a 50D long pipe at a pressure of 5 bar, considering both a 50:50 initial hydrogen/methane mixture (a) and an 80:20 mixture (b).

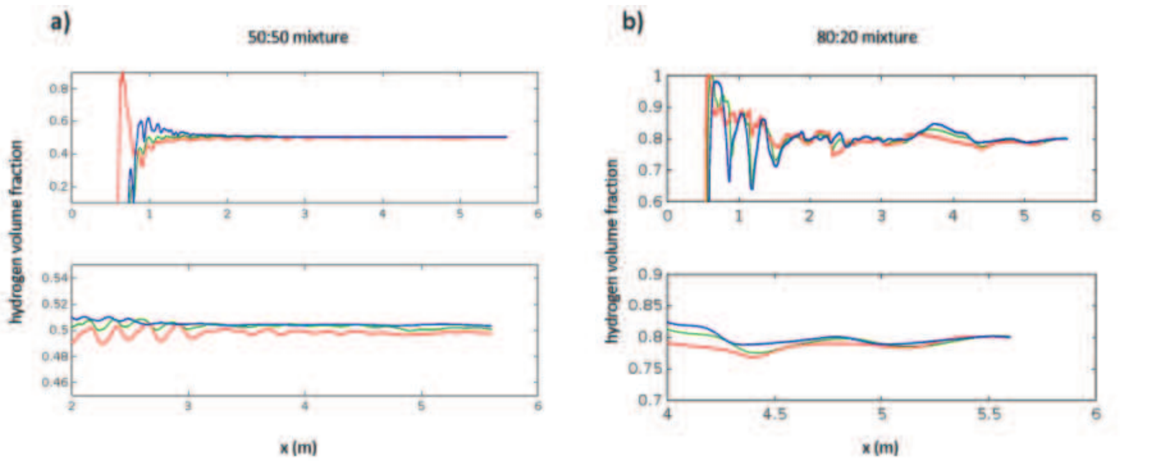


Figure 12: Hydrogen volume fraction in the streamwise direction

Observations revealed that, as a result of the diffusion process, hydrogen was effectively distributed throughout the entire space within the pipe, with no discernible stratification observed over a timeframe spanning 2,000 seconds. These findings align with theoretical considerations and support the assertion that gravity segregation is not a significant factor for hydrogen-methane mixtures within reasonable dimensions and timeframes.

The technical relevance of hydrocarbon solubility in hydrogen was explored. Simulation studies were conducted utilizing thermodynamic programs to assess the solubility of different hydrocarbons in hydrogen and other gases, as shown in Figure 13. Solubility in methane significantly increases with increasing pressure at 50 bar and higher. It remains at a concentration level below 20 ppm for hydrogen and nitrogen.

Solubility of n-dodecane (C12)

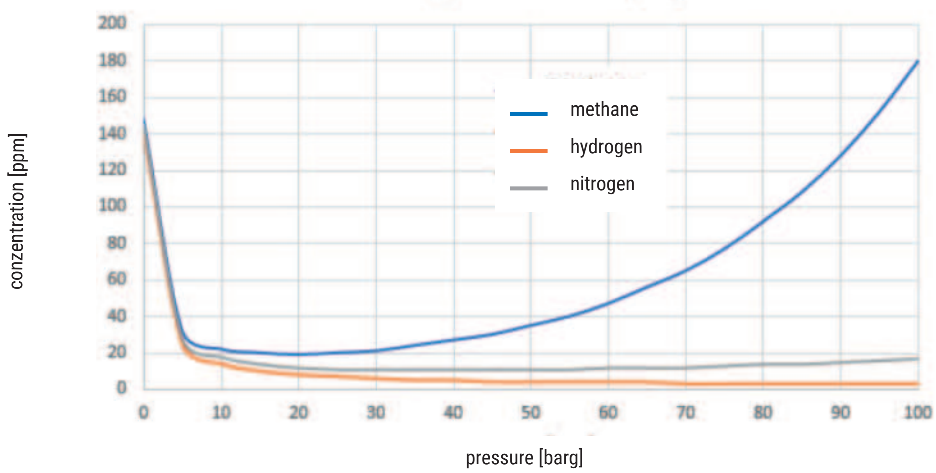


Figure 13: Simulation for solubility of n-dodecane in methane, hydrogen, and nitrogen

Find out more in the final project reports under:

Metrology for Hydrogen Quality from Electrical Energy Storage (HEES) by Hydrogen Back Conversion (Gas-to-Power)
https://mefhysto.eu/mefhysto-d7/

Large-Scale Storage of Gases in Geological Storage Facilities
https://mefhysto.eu/mefhysto-d8/

7 Outlook

The European project focused on addressing the imperative need for large-scale energy storage solutions, particularly through the utilization of hydrogen. With the fluctuation of renewable energy sources, the project's primary aim was to ensure metrological traceability and provide validated techniques and reference standards for hydrogen storage across the entire supply chain—from water electrolysis (power-to-hydrogen) to storage in various forms (reversible chemical, cryogenic, and underground gas storage) and finally to its conversion back into power via fuel cells.

The project's achievements include:

- **Advanced Measurement Techniques:** The development of new measurement methods for key impurities (water vapor and oxygen) in hydrogen production through electrolysis. This included a metrologically compatible laser spectrometer based on cavity ring-down spectroscopy (CRDS) for determining trace humidity in hydrogen.
- **Thermophysical Property Data:** High-precision traceable measurements of thermophysical properties, such as density and phase equilibria, feeding into improved reference equations of state (EoS) for hydrogen-enriched natural gases. This ensured accurate determination of calorific values for energy metering.
- **Fuel Cell Performance and Reliability:** Comprehensive studies on the impact of contaminants on proton-exchange membrane fuel cells, providing specifications and recommendations for air quality sensors and improving protocols for gas sampling and gas quality measurement.
- **Reversible Hydrogen Storage:** Development of validated methods for measuring thermal conductivity and hydrogen absorption in materials like metal hydrides and cryogenic adsorbents. This included an interlaboratory comparison that identified ZIF-8 as a suitable reference material for hydrogen storage.
- **Large-Scale Storage Solutions:** Addressed metrological and thermodynamic issues related to underground gas storage (UGS) and the transition of these systems from natural gas to hydrogen. This involved defining relevant impurities and developing measurement protocols adaptable for field conditions.

7.1 | Future Opportunities for Further Research and Development

While the project achieved its determined milestones, several areas present opportunities for further research and development:

- **Enhanced Measurement Accuracy:** Further refining measurement techniques for detecting impurities in hydrogen and improving the sensitivity and reliability of these methods under varying operational conditions will ensure even greater precision and safety in hydrogen storage and utilization.
- **Advanced Materials for Storage:** Exploration of new materials for hydrogen storage, including innovative metal hydrides and porous materials, could offer higher storage capacities and better efficiency. Research into the dynamic behaviors and long-term stability of these materials is essential.
- **Integration with Renewable Energy Systems:** Developing robust systems that seamlessly integrate hydrogen production, storage, and conversion with renewable energy sources like

wind and solar power. This involves optimizing the intermittent operation of electrolysis and enhancing the efficiency of energy conversion processes.

- **Environmental and Economic Impact Studies:** Conducting comprehensive studies to understand the long-term environmental and economic impacts of large-scale hydrogen storage and its role in the broader energy infrastructure. This includes life-cycle assessments and cost-benefit analyses of different hydrogen storage technologies.

- **Safety and Standardization:** Ongoing efforts to standardize measurement methods and safety protocols across different regions and applications. Collaboration with international standardisation bodies to harmonize regulations and guidelines will be crucial for the global adoption of hydrogen technologies.

7.2 | Continued Collaboration and Knowledge Sharing Among Stakeholders

To ensure the sustained growth and development of hydrogen storage technologies, ongoing collaboration and knowledge sharing among stakeholders are vital. Key aspects that still require focused efforts include:

- **Cross-Disciplinary Research:** Promoting collaboration between researchers in metrology, materials science, engineering, and environmental science to address complex challenges in hydrogen storage and utilization. Joint research projects and interdisciplinary conferences can facilitate the exchange of ideas and innovations.

- **Industry-Academia Partnerships:** Strengthening partnerships between academic institutions and industry players to translate research findings into practical applications. This includes pilot projects, technology transfer agreements, and collaborative development of new hydrogen storage solutions.

- **Policy and Regulatory Support:** Engaging with policymakers to advocate for supportive regulations and incentives that promote the adoption of hydrogen technologies. This involves providing evidence-based recommendations and participating in policy dialogues to shape a conducive regulatory environment.

- **Public Awareness and Education:** Raising awareness about the benefits and challenges of hydrogen storage through public outreach and educational programs. Informing the general public and stakeholders about the role of hydrogen in achieving sustainable energy goals will garner broader support and investment.

- **Continuous Improvement and Feedback:** Establishing mechanisms for continuous feedback and improvement of measurement techniques and standards. This includes regular updates to guidelines based on new research findings, industry feedback, and technological advancements.

By addressing these aspects, stakeholders can ensure that the advancements made in hydrogen storage technology are effectively leveraged to build a sustainable and resilient energy future.

MefHySto

Metrology for Advanced Hydrogen Storage Solutions

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