TRABAJO FINAL DE INGENIERÍA QUÍMICA

ANÁLISIS COMPARATIVO DE LOS ASPECTOS ENERGÉTICOS Y TÉCNICOS DE LOS MÉTODOS DE ALMACENAMIENTO DE HIDRÓGENO

Autor: *Di Bartolo, Zoe Federica*

zoefedericadb@gmail.com

Directores: *Castañer, Julieta*

García de la Mata, Manuel

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PROYECTO FINAL PARA OPTAR AL GRADO DE INGENIERO/A QUÍMICO/A

UNIVERSIDAD NACIONAL DE MAR DEL PLATA
FACULTAD DE INGENIERÍA
DEPARTAMENTO DE INGENIERÍA QUÍMICA Y EN ALIMENTOS

MAR DEL PLATA, 06 DE DICIEMBRE DE 2024

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INSTITUT FÜR ENERGIEVERFAHRENSTECHNIK UND CHEMIEINGENIEURWESEN

TU BERGAKADEMIE FREIBERG · TUBAF Die Ressourcenuniversität. Seit 1765.

RESUMEN DE CONTENIDO

El presente proyecto analiza y compara diversos métodos de almacenamiento de hidrógeno, un combustible esencial para la transición hacia una economía sostenible y descarbonizada. Se examinan aspectos energéticos y técnicos de tecnologías como el almacenamiento físico y basado en materiales, incluyendo un método experimental con pellets de mineral de hierro mediante reacciones redox. Asimismo, se contextualiza el rol del hidrógeno en los esfuerzos globales para mitigar el cambio climático y cumplir con los objetivos del Acuerdo de París.

Los objetivos principales de este estudio son:

1. Evaluar diferentes métodos de almacenamiento de hidrógeno.
2. Determinar la densidad de almacenamiento de los pellets de mineral de hierro.
3. Comparar los métodos de almacenamiento según criterios energéticos y técnicos.

Se abordan métodos como el almacenamiento en gas comprimido (GH2), hidrógeno líquido (LH2), adsorción en materiales específicos, hidruros metálicos, portadores orgánicos líquidos y compuestos químicos. Además, se evalúan los requisitos clave de los sistemas de almacenamiento de energía, como una elevada densidad energética, una baja o nula producción de carbono, seguridad, mínimas pérdidas de energía con el tiempo, versatilidad, disponibilidad y capacidad de ser reciclables, en respuesta con la transición de combustibles tradicionales a energía limpia.

El hidrógeno se presenta como una alternativa prometedora gracias a su alta densidad de energía por masa, aunque su baja densidad volumétrica plantea importantes desafíos. El hidrógeno es el elemento más ligero de la tabla periódica muestra una alta reactividad a temperaturas elevadas. Aunque ofrece una densidad gravimétrica alta, su baja densidad volumétrica exige tecnologías avanzadas para optimizar su uso.

Entre los métodos evaluados se encuentran el almacenamiento como gas comprimido (GH2), como líquido criogénico a -253 °C (LH2), en materiales adsorbentes como MOFs o carbón activado, mediante hidruros metálicos reversibles, en compuestos químicos como amoníaco, metanol o metano, y a través de portadores orgánicos líquidos (LOHCs).

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Además, se evaluó el almacenamiento energético en pellets de mineral de hierro sometidos a reacciones redox. Bajo atmósferas de dióxido de carbono e hidrógeno, los pellets demostraron ser una alternativa segura y eficiente para el almacenamiento a largo plazo con ligeras pérdidas energéticas. En el experimento, los pellets de hematita con magnetita y silicato de calcio se redujeron a 892 °C y presión atmosférica en una corriente de H_2, y después se oxidaron con CO_2. El procedimiento incluyó la preparación de los pellets en un reactor bajo gas inerte (argón), el cambio a una atmósfera reactiva durante una hora y la medición de la pérdida de masa de los pellets y del agua generada.

Los resultados indicaron densidades energéticas de 2,11 kWh/L en condiciones ideales y de 1,99 kWh/L en experimentales. Además, se determinó que la energía almacenada fue de 0,024 kWh y la energía liberada, de 0,023 kWh. Entre las ventajas de este método destacan la ausencia de pérdidas durante el almacenamiento y la seguridad del método respecto a otros.

La comparación de las densidades energéticas volumétricas indicó que los pellets de hierro son una opción más segura, estable y viable que otros métodos.

El hidrógeno se consolida como un elemento clave para lograr un futuro energético sostenible. Aunque los métodos actuales presentan limitaciones, el avance tecnológico podría superarlas. Los pellets de hierro destacan como una alternativa prometedora para el almacenamiento y el transporte, y la combinación de múltiples métodos podría ser la estrategia óptima para transición energética generalizada.

Zoe Federica Di Bartolo

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A mi familia, amigos y docentes.

Zoe Federica Di Bartolo

INSTITUT FÜR ENERGIEVERFAHRENSTECHNIK UND CHEMIEINGENIEURWESEN

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COMPARATIVE ANALYSIS OF ENERGY AND TECHNICAL ASPECTS IN HYDROGEN STORAGE METHODS

STUDENT: ZOE FEDERICA DI BARTOLO (ID: 69060)

Submission Date: 07.05.2024

Location: Institute of Energy Process Engineering and Chemical Engineering, TU Bergakademie Freiberg

Reviewer: Prof. Dr.-Ing Martin Gräbner

"Creo que un día se empleará el agua como combustible, que el hidrógeno y el oxígeno que la constituyen, utilizados aislada o simultáneamente, proporcionarán una fuente de calor y de luz inagotable, de una intensidad que el carbón no puede; dado que las reservas de carbón se agotarán, nos calentaremos gracias al agua. El agua será el carbón del futuro".

'La isla misteriosa', Julio Verne (1874)

SWORN STATEMENT

I hereby declare that I have independently composed this work and have relied solely on the specified aids. Any ideas derived from external sources, whether directly or indirectly, have been appropriately attributed. This statement also encompasses the depictions and tables.

Heilbronn, 07.05.2024

Zoe Federica Di Bartolo

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LIST OF ABBREVIATIONS

C	Carbon
$CaSiO_3$	Calcium Silicate
CO	Carbon Monoxide
CO_2	Carbon Dioxide
COP28	UN Climate Change Conference
DR	Direct reduction
Fe	Iron
Fe_2O_3	Hematite
Fe_3O_4	Magnetite
GH_2	Compressed gas hydrogen
H_2	Hydrogen
H_2O	Water
HFTO	Office's Hydrogen and Fuel Cell Technologies
IEA	International Energy Agency
LH_2	Liquid hydrogen
LOHC	Liquid Organic Hydrogen Carriers
MOFs	Metal-organic frameworks
N_2	Nitrogen
SDGs	Sustainable Development Goals
TiO_2	Titanium dioxide
SiC	Silicon Carbide
TRL	Technology Readiness Level
UNO	United Nations Organization

INTRODUCTION

As global efforts intensify to combat climate change and shift towards cleaner energy alternatives, understanding hydrogen storage methods becomes increasingly crucial. This project aims to explore the complexities of different hydrogen storage technologies, assessing their energy efficiency, technical feasibility and potential impact on the global energy landscape.

As the climate crisis intensifies, the world stands at a crucial crossroads. The year 2023 will be the warmest on record, with a near-surface global average temperature surpassing 1,45°C above pre-industrial levels. (UNO, 2024) Despite being a readily available source of stored solar energy, fossil fuels are unsustainable in the long term, given their carbon dioxide emissions contributing to climate change. There is also concern that conventional crude oil production will peak. (Bergthorson, 2018)

The Paris Agreement, implemented in 2015, aims to significantly reduce global greenhouse gas emissions and limit the temperature rise to below 2°C above pre-industrial levels. However, the United Nations Climate Change Conference (COP28) in 2023 acknowledged that current efforts are insufficient to meet these goals. (Worth, 2023)

The urgency to transition to a low-carbon or zero-carbon society is undeniable. Achieving net-zero carbon emissions from energy and transport systems is essential to mitigate climate change. This transition requires diverse clean energy solutions to replace fossil fuels in the global economy, with hydrogen emerging as a potential solution. (Bergthorson, 2018)

In this context, hydrogen presents itself as a potential game changer in the race to decarbonize the planet. It can serve as an alternative to fossil fuels in various sectors, including energy and transport, or, for example, to produce ammonia. (Gielen, Lathwal, & Lopez Rocha, 2023) The adoption of hydrogen as a global energy solution is becoming increasingly urgent. (Hydrogen Council, McKinsey & Company, 2023)

While hydrogen boasts the highest energy per mass of any fuel, its low ambient temperature density poses a challenge, necessitating the development of advanced storage methods with higher energy density. Overcoming this challenge is crucial for establishing a hydrogen economy. (Hydrogen and Fuel Cell Technologies Office, n.d.)

This study compares different hydrogen storage methods based on criteria such as storage density, considering both mass and volume. The methods under analysis include direct storage of hydrogen in liquid form (LH_2), as compressed gas (GH_2 - at 200, 700, and 1.200 bar), storage using metal hydrides, organic liquids (e.g., carbazole or formic acid), and chemical compounds (e.g., ammonia, methanol, methane, gasoline, or through the steam-iron process).

The study incorporates an experimental component aimed at theoretically and experimentally determining the storage density of iron ore pellets. Subsequently, a comparison will be made between direct hydrogen storage (LH_2 and GH_2) and the use of iron ore pellets. This report aims to provide an analysis of the energy and technical aspects of various hydrogen storage methods.

LITERATURE REVIEW

GLOBAL CONTEXT: THE PATH TO A SUSTAINABLE FUTURE

The Paris Agreement, adopted at COP21 in 2015, stands as a testament to the world's unified resolve in mitigating climate change by substantially reducing greenhouse gas emissions and constraining temperature escalation to well below 2°C, with a striving ambition to cap it at 1,5°C. This landmark treaty establishes a framework for a five-year cycle of increasingly ambitious climate endeavors, that culming in the inaugural "global stocktake" convened at COP28 in 2023. (UNO, n.d.)

The conclusion of the UN Climate Change Conference (COP28) represents a critical juncture, signaling the onset of a post-fossil fuel era. Anchored by an accord emphasizing profound emissions reductions and amplified financial commitments, nations stand poised to embark on a just and equitable transition toward a sustainable future. (Worth, 2023)

SDG 7: AFFORDABLE AND CLEAN ENERGY

The Sustainable Development Goals (SDGs), also known as the Global Goals, emerged as a universal call to action endorsed by all United Nations Member States in 2015. These 17 interconnected goals aim to eradicate poverty, safeguard the planet, and foster global peace and prosperity by 2030. Recognizing the intricate interplay between social, economic, and environmental factors, the SDGs underscore the imperative of balanced development across all areas.

The "Our Common Agenda" report serves as a blueprint for expediting SDG implementation, based on the necessity to realign the world with the shared objectives of the 2030 Agenda. (UNO, n.d.)

Figure 1. SDG 7.

SDG 7: Affordable and Clean Energy aims to provide access to affordable, reliable, sustainable, and modern energy for all. "Our Common Agenda" underscores the criticality of transitioning towards sustainable energy as the axis to safeguard the planet and its inhabitants.

The primary objective of SDG 7 is to enhance energy efficiency and facilitate universal access to energy resources. Through the expansion of infrastructure and the deployment of innovative technologies to deliver cleaner and more efficient energy services worldwide, economic growth can be stimulated while concurrently realizing environmental benefits. (United Nations Development Program, n.d.)

This aligns with the objectives of the project, which endeavors to contribute to the attainment of SDG 7 by exploring more effective and sustainable energy storage methodologies.

HYDROGEN'S ROLE IN THE TRANSITION TO A SUSTAINABLE FUTURE

As the world navigates this transition, hydrogen emerges as a cornerstone in the drive for decarbonization. Despite significant investments in clean hydrogen, expedited decision-making and deployment are imperative to align with ambitious net-zero targets set for 2050. The hydrogen industry's robust growth, with over 1.000 project proposals worldwide, underscores its potential to revolutionize energy storage and expedite the transition to a sustainable economy. (Hydrogen Council, McKinsey & Company, 2023)

Hydrogen plays a key role success of the energy transition and climate mitigation efforts. Hydrogen, as a versatile fuel and energy carrier, holds the capacity to transport and store vast quantities of renewable energy over prolonged durations. (European Comission, n.d.) Its efficacy in efficiently storing renewable energy addresses the intermittency challenge of renewables, thus laying the foundation for a dependable and resilient energy ecosystem. Furthermore, hydrogen can help drive the decarbonization of entire industrial sectors such as steel or iron production and heavy-duty transportation. (Bruch, 2022)

As nations strive toward achieving carbon neutrality by 2050, hydrogen emerges as a catalyst for realizing this ambitious objective. By leveraging advanced storage methodologies and innovative technologies, the hydrogen economy presents a viable pathway toward sustainable development, economic prosperity, and climate resilience.

Hydrogen, often hailed as the 'fuel of the future,' assumes a pivotal role as an energy carrier and electrofuel in the global pursuit of decarbonization. With its capacity to store vast amounts of renewable energy over extended periods, hydrogen stands as a linchpin in the journey toward achieving net-zero emissions by 2050. Bergthorson's research (Bergthorson, 2018) underscores hydrogen's potential as an electrofuel, highlighting its ability to supplant hydrocarbon fuels in transportation and power generation, thereby facilitating the transition from a fossil fuel-centric economy to a hydrogen-based one. Through electrolysis, clean primary electricity transforms water into hydrogen and oxygen, offering a closed-loop energy cycle with minimal environmental repercussions. This transition not only holds promise for decarbonizing multiple industries but also heralds sustainable job creation, the establishment of new value chains, and the emergence of a thriving global market.

PROPERTIES AND CHARACTERISTICS OF HYDROGEN (H_2)

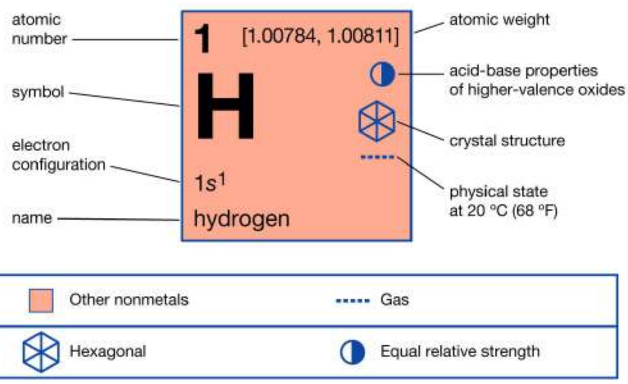

Figure 2. Information diagram of the element hydrogen from Britannica. (Lee Jolly, 2024)

Hydrogen, represented by the symbol H, holds the distinction of being the lightest element in the periodic table, boasting an atomic number of 1. First identified and isolated by H. Cavendish in 1766, hydrogen exists primarily as the diatomic molecule H_2, characterized by its colorless, odorless nature and relative inertness at room temperature unless catalyzed. However, its reactivity escalates significantly at elevated temperatures.

Atomic hydrogen exhibits a density of 0,08988 kg/m^3, while compressed hydrogen gas showcases densities ranging from 23 to 27 g/L at a pressure of 350 bar and 38 to 40 g/L at a pressure of 700 bar. (Platzer, 2021)

Although hydrogen is rarely found in its pure form and is typically bound to other elements, such as carbon in plants, petroleum, or natural gas, or as part of water where it combines with oxygen, extraction requires an energy source. Various methods, including extraction from natural gas, water, biomass, or coal, can be employed, with energy sources like wind, solar, coal, natural gas, or nuclear power facilitating the separation process. Once extracted, hydrogen serves as a versatile energy carrier, capable of providing heat and electricity through combustion or fuel cell reactions, following the oxidation reaction:

$$2\,H_2 + O_2 \rightarrow 2\,H_2O \qquad [1]$$

However, hydrogen's extreme flammability poses significant safety concerns. It readily forms explosive mixtures with air and is lighter than air, making it susceptible to rapid diffusion. Elevated concentrations of hydrogen in the air can result in oxygen deficiency, potentially leading to unconsciousness or fatalities. Notably, there are no odor warnings for toxic hydrogen concentrations (TÜV Nord Group, n.d.).

Despite safety challenges, hydrogen boasts the highest gravimetric energy density among energy sources. However, its volumetric energy density remains low, requiring methods such as compression, liquefaction, or bonding with other substances to enhance storage efficiency. Compression proves effective for increasing volumetric energy density over short durations, given hydrogen's gaseous state under practical conditions. Liquefaction necessitates cryogenic refrigeration due to hydrogen's critical temperature and pressure, while storing hydrogen in its usable form minimizes the need for additional subsystems to maintain storage conditions. (Platzer, 2021)

Hydrogen's physical and chemical properties underscore its unique characteristics. Transparent to visible, infrared, and ultraviolet light, hydrogen exhibits exceptional diffusion properties owing to its low molecular weight. Reactivity-wise, hydrogen dissociates into atoms under sufficient energy, with atomic hydrogen displaying significant reactivity, forming hydrides with most elements, and reducing metallic oxides. Moreover, hydrogen can react explosively with chlorine and oxygen under specific conditions, presenting both challenges and opportunities for various industrial applications. (Lee Jolly, 2024)

In summary, the distinct properties and versatile applications of hydrogen highlight its significance as an essential component of future energy systems.

ENERGY STORAGE SYSTEMS

Definition

An energy storage system encompasses an energy technology device that involves three fundamental processes: charging, storing, and discharging.

Figure 3. Steps in storage systems.

Furthermore, an energy carrier represents a substance containing stored energy, typically housed within the storage unit of an energy storage device. (Sterner, 2014)

Subcategories of energy storage systems

Energy storage systems are divided into primary and secondary categories, as well as sectoral and cross-sectoral variations.

Categorization of energy storage devices according to the frequency of discharge cycles:

- **Primary energy storage devices** are energy storage devices with a single charge and discharge cycle.
- **Secondary energy storage systems** are energy storage systems that support multiple charge and discharge cycles.

Categorization of energy storage systems by sector of use:

- **Sectoral energy storage systems** are energy storage systems that limited to a single energy sector, are used in one energy sector. These systems facilitate bidirectional injection and withdrawal within the same sector.
- **Cross-sectoral energy storage systems** are energy storage systems that are used in one or more energy sectors and operate uni- and/or bidirectionally, with injection and withdrawal not necessarily confined to a single sector.

Classification

Apart from the delineation and categorization of energy storage systems, their classification based on diverse properties offers a comprehensive overview.

Table 1. Classification of energy storage systems. (Sterner, 2014)

Classification				
physical	energetic	temporal	spatial	economic
• Electrical • Electrochemical • Chemical • Mechanical • Thermal	• Power • Energy	• Short-term • Long-term • Discharge time • Cycle times	• Central • Decentralized • Stationary • Mobile	• Markets • Capital costs • Operating costs

Need for energy storage and tradeable energy commodities

A wide range of clean, low-carbon power-generation technologies exist, making the transition to a low-carbon power grid appear feasible, albeit a formidable undertaking. (Clack, et al., 2017) However, the power output of many clean energy sources, such as solar and wind, fluctuates significantly over various timescales, from diurnal to seasonal.

In regions characterized by high population density or challenging geographic conditions, local production of sufficient low-carbon energy may be unattainable, necessitating the importation of clean energy from distant sources. (Mackay, 2008) Additionally, fossil fuels not only serve as fuels for transportation and power generation but also facilitate the global trade of energy, playing a key role in the global economy.

Requirements for energy storage

To meet the diverse energy demands of society, there is a need for abundant, carbon-free, globally tradable sustainable energy commodities that possess several key characteristics:

- provide the high energy densities and convenience of fossil fuels,
- can be created using low-carbon primary-energy sources,
- can be safely exported over long distances,
- can be safely stored indefinitely with minimal loss,
- can be used for transportation and stationary power generation at various power levels,
- are available in large quantities, and
- are recyclable (Auner & Holl, 2006)

Presently, the predominant high-carbon energy commodities traded globally include coal, oil, and natural gas, transported across the globe via tanker ships, oil and gas pipelines, railway networks, and trucks with minimal losses during transit and storage. Any sustainable energy commodity replacing fossil-derived hydrocarbon fuels must emulate similar energy density, safety, and transportability to meet society's energy requirements. (Bergthorson, 2018)

TRL: TECHNOLOGY READINESS LEVELS

Technology Readiness Levels (TRL) are a type of measurement system used to assess the maturity level of a particular technology. Each technology project is evaluated against the parameters for each technology level and is then assigned a TRL rating based on its current level of development. (Manning, 2023)

The TRL scale consists of nine levels. Each level characterizes the progress in the development of a technology, from the idea (TRL 1) to the full deployment of the product (TRL 9):

TRL 1 Basic principles observed and reported.
TRL 2 Technology concept and/or application formulated.
TRL 3 Analytical and experimental critical function and/or characteristic proof-of-concept.
TRL 4 Component and/or breadboard validation in a laboratory environment.
TRL 5 Component and/or breadboard validation in a relevant environment.
TRL 6 System/subsystem model or prototype demonstration in a relevant environment.
TRL 7 System prototype demonstration in an operational environment.
TRL 8 Actual system completed and qualified through test and demonstration.
TRL 9 Actual system proven through successful mission operations.

This way, TRL provides a systematic metric for tracking the progress of a technology and can aid in the decision-making process when developing or investing in innovative technologies. It is important to note that achieving a high TRL does not necessarily mean the technology is commercially viable or will be successful in the market. Other factors such as cost, performance, and market demand must also be considered.

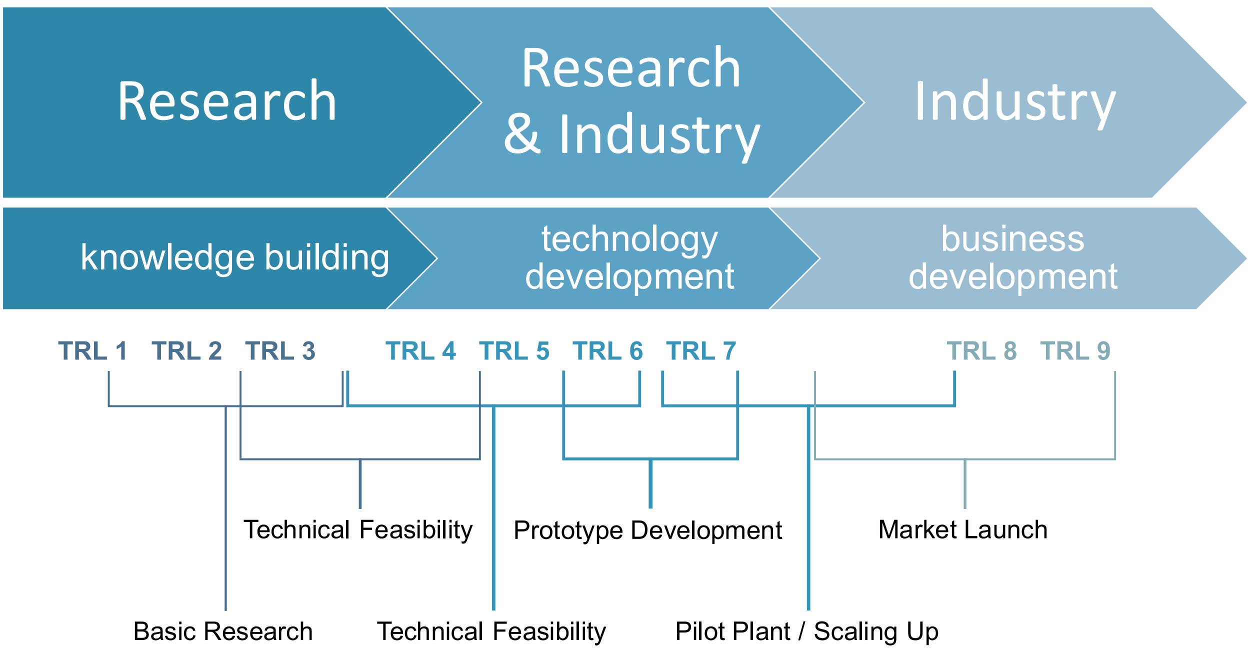

Figure 4. Progress of a technology using TRL.

HYDROGEN STORAGE METHODS

Hydrogen storage systems can be broadly categorized into two main types: physical-based and material-based storage. Physical-based storage involves altering the physical state of hydrogen, typically by increasing pressure (compressed gaseous hydrogen storage, GH2) or reducing temperature below its evaporation point (liquid hydrogen storage, LH2). On the other hand, material-based storage utilizes additional materials known as 'carriers' that can bond with hydrogen molecules or atoms, either physically or chemically, thereby enhancing storage density and safety compared to physical-based systems. (Yang, Hunger, & al, 2023)

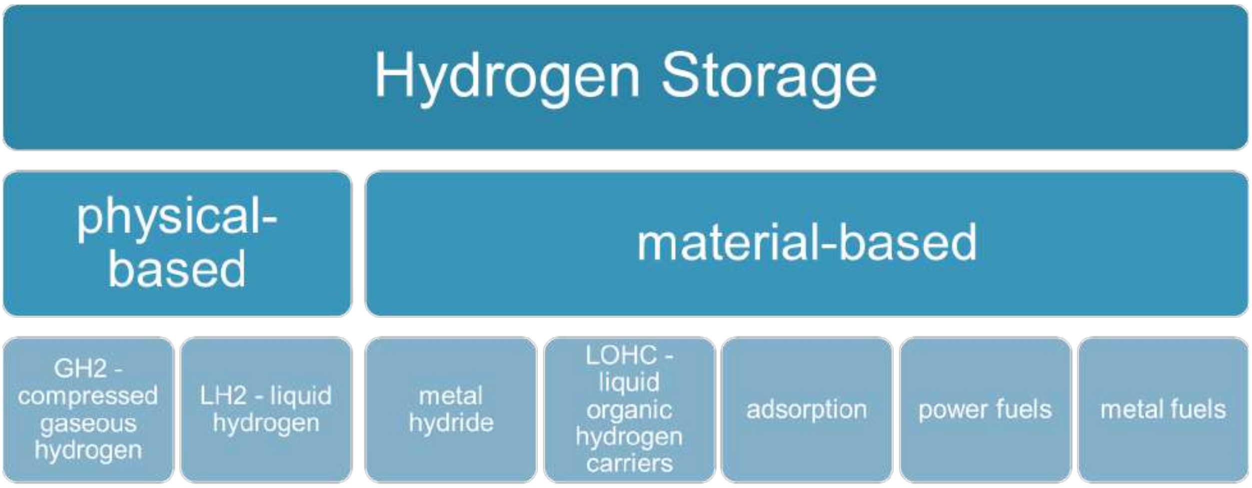

Figure 5. Overview of storage technologies.

While material-based storage technologies show promise, many are still in the laboratory and demonstration phases, awaiting commercial scalability. (Yang, Hunger, & al, 2023) Continued research and development are essential to bridge this gap.

Hydrogen storage methods are continuously studied and compared for their efficiency, safety, and suitability for various applications. Physical-based storage systems, such as high-pressure gas cylinders and cryogenic tanks, offer advantages in terms of simplicity and proven technology. Material-based storage methods, including adsorption, absorption, and chemical bonding, hold potential for higher storage densities but often require further development for practical implementation. (Züttel, 2014)

Despite significant advancements, challenges remain in developing hydrogen storage systems with high energy density, reversibility, and safety. Addressing these challenges is critical for realizing the full potential of hydrogen as a clean energy carrier. Additionally, establishing efficient distribution and storage infrastructure is essential for building a robust hydrogen supply chain, which is pivotal for the widespread adoption of hydrogen based. (Linde Engineering, n.d.) (Hydrogen and Fuel Cell Technologies Office, n.d.)

Each storage method presents its own set of advantages and disadvantages, that influence the technological effort, cost and associated risks. Understanding these nuances is vital for informed decision-making in the pursuit of sustainable energy solutions.

Let's now take a closer look at the storage methods covered by the previously mentioned classification.

Physical-based

Hydrogen's vast potential as a clean and energy-rich fuel makes it a viable fuel for a wide range of uses. However, its low density poses a significant challenge for storage in large volumes. Compression emerges as a key technique to address this issue, with two primary methods: mechanical compression and cryogenic compression.

- **Mechanical compression** employs compressors or pumps to physically condense hydrogen gas, a method known for its cost-effectiveness and ease of operation. However, it does come with higher energy demands and may necessitate temperature regulation due to the heat generated during compression.
- **Cryogenic compression** on the other hand, requires hydrogen gas to be liquefied at temperatures typically below -253°C before compression. While this method boasts lower energy requirements and achieves superior storage densities, it also entails greater operational complexity and expenses due to the specialized cryogenic equipment needed.

Despite the potential benefits, both compression methods face significant challenges and limitations. Ensuring safety and reliability while achieving high compression ratios poses a primary concern, given hydrogen's reactivity and potential for leakage. Moreover, issues like "boil-off" can arise during prolonged storage, leading to hydrogen loss and safety hazards as stored hydrogen evaporates with increasing container temperatures.

Nonetheless, compression remains a viable option for hydrogen storage. Future research endeavors are expected to concentrate on enhancing the safety, efficiency, and reliability of compression systems, alongside the development of innovative materials and techniques for hydrogen storage and release. (Tuan Le, Sharma, & al, 2024)

Overall, while compression holds promise as a hydrogen storage strategy, substantial research and development efforts are imperative to address existing challenges and constraints.

GH_2: Compressed gaseous hydrogen storage

Hydrogen can be efficiently stored through compression in large tanks, without the need for liquefaction, especially when the gaseous supply is economically favorable. Alternatively, underground salt caverns offer bulk storage options but requiring gas purification and compression before injection. (Linde Engineering, n.d.)

By compressing the hydrogen gas, the volume required for a defined amount of energy can be reduced. Hydrogen is most stored as a gas today - and it is estimated that this will continue to be the case in the future. This compression method requires minimal technical effort. (Frey, 2023)

- **High-pressure gas cylinders:** Commonly utilized, these cylinders maintain pressures ranging from 20 MPa (200 bar) to 80 MPa (800 bar), providing a volumetric density of approximately 36 $kg{\cdot}m^3$, nearly half that of its liquid state. However, increased pressure leads to thicker cylinder walls, resulting in reduced gravimetric hydrogen density. Safety concerns, particularly in densely populated areas, are pertinent.
- **Compression Methods:** Standard piston-type mechanical compressors are typically employed.
- **Gaseous Hydrogen Storage:** Widely employed, gaseous hydrogen storage, usually at pressures around 200 bar in industry and up to 700 bar for vehicles, is economically viable.

- **Tank Designs and Transport:** Tanks of diverse designs, cylindrical or spherical, cater to diverse needs, with spherical tanks minimizing surface area per unit volume and evenly distributing pressure load on tank structures.
- Additionally, global hydrogen transport **via pipelines** spanning up to 3.000 km (USA) showcases the versatility of gaseous storage. (Züttel, 2014)
- **Pressure Vessels:** Compression into pressure vessels remains the most straightforward method, with four types available, each offering a different compromise between technical performance and cost.
- **Underground Hydrogen Storage:** Utilization of salt caverns, aquifers, and depleted gas reservoirs for compressed gaseous hydrogen storage presents promising solutions for medium- to long-term storage, albeit with distinct challenges and advantages based on geological criteria. Salt caverns offer excellent sealing, while depleted gas reservoirs offer larger volumes. Aquifers, abundant yet challenging, pose potential leakage and biochemical reaction risks. (Yang, Hunger, & al, 2023)

LH_2: Liquid hydrogen storage

Liquid hydrogen (LH_2) is stored under ambient pressure at extremely low temperatures (-253°C), offering significant advantages in terms of energy density and space efficiency, making it an attractive option for various applications. LH2 is liquefied hydrogen stored in specially insulated tanks designed to withstand the low temperatures and high pressures required for storage. (Linde Engineering, n.d.) Stored within specially insulated cryogenic tanks, LH_2, or liquefied hydrogen, maintains its form under extreme conditions, ensuring its viability for long-distance transportation, medicine, semiconductor manufacturing, food production, aerospace applications. (Züttel, 2014)

Key characteristics of LH_2 storage include the utilization of cryogenic tanks, available in both vertical and horizontal configurations, equipped with vacuum-insulated containers ranging in capacity from 3.000 to over 100.000 Liters. Additionally, the availability of transportable LH_2 containers, featuring active cooling mechanisms, extends storage windows while prioritizing safety. (Linde Engineering, n.d.)

The advantages of LH_2 storage are multifaceted. Firstly, its density surpasses that of compressed gaseous storage. Moreover, the economic feasibility of transporting large quantities of hydrogen over long distances is facilitated by LH2's high density, contributing to its widespread adoption. (Frey, 2023) Additionally, the low reactivity of liquid hydrogen at low temperatures enhances safety during handling and transportation.

However, LH_2 storage also presents significant challenges. The energy-intensive process of liquefying hydrogen demands substantial resources, resulting in high costs and energy consumption. Moreover, boil-off losses during storage and transportation pose significant concerns, leading to hydrogen losses and safety risks. Additionally, the handling of LH_2 presents challenges due to its extremely low temperature, necessitating specialized equipment and procedures to ensure safe operations. (Züttel, 2014)

In summary, while liquid hydrogen storage offers compelling advantages in terms of density and safety, it also presents notable challenges related to energy consumption and handling. These factors must be carefully considered in evaluating the suitability of LH_2 storage methods.

Storage on metal hydrides

Metal hydrides, metals capable of chemically bonding with hydrogen atoms, are being extensively investigated for hydrogen storage due to their many advantages over alternative methods. They offer high-density storage, allowing a smaller volume of material to store the same amount of hydrogen as larger volumes of compressed gas or liquid (Sunku Prasad & Muthukumar, 2022); (Karmakar, Mallik, Gupta, & Sharma, 2021). This feature makes them particularly suitable for space-constrained applications such as automobiles (Ga Bui, Minh Tu Bui, Tuan Hoang, & al, 2021). In addition, (complex) metal hydrides can release hydrogen at low temperatures and pressures, reducing the energy and infrastructure required for storage and distribution (Kumar, Raju, Muthukumar, & Selvan, 2019). Furthermore, their stability and reduced risk of leakage or explosions make them safer to handle and transport than compressed gas or liquid hydrogen.

Research into metal hydrides for hydrogen storage includes different forms, including complex metal hydrides, lightweight metal hydrides, and intermetallic hydrides. Complex metal hydrides consist of a metal ion and a ligand capable of forming bonds with hydrogen atoms. (Tuan Le, Sharma, & al, 2024) Meanwhile, lightweight metal hydrides, such as magnesium hydride, offer stable hydrogen storage with high gravimetric and volumetric densities.

However, before metal hydrides can be economically viable for hydrogen storage, several challenges need to be overcome. Some metal hydrides require high temperatures or pressures to release hydrogen, which can be energy intensive and costly. In addition, the degradation of some metal hydrides over time reduces their hydrogen storage capacity. Complex hydrides, on the other hand, release hydrogen at lower temperatures and are easier to refill, although they have a lower hydrogen storage capacity than metal hydrides.

Despite these challenges, metal hydrides remain a promising hydrogen storage technologies and ongoing research aims to overcome current limitations and enable their widespread use in fuel applications. One of the notable advantages of chemical hydrides is their ability to release hydrogen on demand, making them suitable for applications such as fuel cells that require a constant supply of hydrogen.

In conclusion, chemical hydrides offer high energy density and on-demand hydrogen release, but further research is needed to overcome challenges and improve their suitability for real-world applications. (Tuan Le, Sharma, & al, 2024) For example, challenges such as high release temperatures, slow kinetics, and the use of expensive or toxic materials need to be addressed to improve their practicality.

Metal hydrides have the advantage of extremely high volumetric densities of hydrogen atoms present in the host lattice, making them effective for storing large amounts of hydrogen in a safe and compact manner. They offer reversible hydrides that operate at ambient temperature and atmospheric pressure, although the gravimetric hydrogen density is limited to <3 mass%. Research into the properties of lightweight metal hydrides remains challenging. (Züttel, 2014)

Complex hydrides, such as $NaAlH_4$, $LiAlH_4$, and $LiBH_4$, are particularly promising due to their potential to achieve higher gravimetric hydrogen storage densities, despite the multi-step process required for their hydrogenation. (Yang, Hunger, & al, 2023)

Metal-organic frameworks (MOFs) represent another avenue for hydrogen storage, using their porous structure to adsorb hydrogen. While both metal hydrides and metal-organic frameworks find applications primarily in synthesis, catalysis, and other technical fields, hydrogen storage remains only one aspect of their utility. (Frey, 2023)

Storage by adsorption

Storage methods using adsorption, such as those employing materials with high internal surface areas such as zeolites or carbon nanotubes, offer a promising route to hydrogen storage. These materials attract hydrogen molecules to their surfaces through weak van der Waals forces or similar interactions, effectively retaining the hydrogen within their porous structures. Upon decreasing pressure or temperature, the stored hydrogen molecules are released. (Züttel, 2014)

Additionally, unconventional materials such as glass have shown potential for hydrogen storage due to their remarkable properties, including high tensile strength and low density. When structured in capillary form, glass can withstand high pressures, allowing storage pressures of up to 700 to 1.000 bar.

Nanotubes, particularly TiO_2 or SiC nanotubes, are still in the laboratory phase for hydrogen storage. Similarly, plastic nanotubes are also in the early stages of development. (Frey, 2023)

The adsorption process relies on materials with large surface areas, that can absorb significant amounts of hydrogen at low pressures. Materials such as activated carbon, MOFs, and zeolites are commonly used for this purpose. Each material offers distinct advantages based on factors like pore size and surface area, making them suitable for different hydrogen storage conditions.

While adsorption-based storage methods offer the advantage of potentially higher volumetric energy density compared to high-pressure systems, challenges remain. These include the need for materials with high storage capacities and fast kinetics for efficient hydrogen adsorption and desorption. In addition, concerns about material degradation over time may limit the effectiveness of these systems. Nevertheless, with further research and development, adsorption-based hydrogen storage holds promise. (Tuan Le, Sharma, & al, 2024)

LOHCs: Liquid Organic Hydrogen Carriers

LOHCs represent an innovative approach to hydrogen storage and transport. These energy carriers, such as dibenzyltoluene, carbazole, and formic acid, reversibly store hydrogen in a liquid medium through catalytic reactions. In essence, they act like a "thermal oil," chemically bonding hydrogen to carbon atom chains. This enables them to be handled similarly to traditional liquid fuels such as diesel or gasoline, making them easier to store and transport.

In addition to dibenzyltoluene, other materials such as N-ethylcarbazole, methylcyclohexane, and formic acid can also be used to store hydrogen in LOHC systems. The challenge is to ensure that the bound hydrogen can be easily released from the carrier material. Recyclable materials are preferred to enable multiple uses of the carrier material for storage. (Frey, 2023)

While hydrogen storage in liquid form has a long history, it requires high temperatures for hydrogenation or dehydrogenation, which leads to energy consumption. Moreover, liquid energy carriers tend to degrade over time, often due to incomplete dehydrogenation reactions. There's been limited commercialization of such storage technologies. (Züttel, 2014)

In recent years, there has been growing interest in material-based hydrogen storage, with LOHCs emerging as promising candidates. These organic substances, which can be liquid or semi-liquid at ambient temperatures, chemically bind hydrogen through exothermic hydrogenation reactions. The reversible nature of these reactions enables the release of hydrogen through endothermic dehydrogenation under appropriate conditions.

The design of effective LOHC materials requires consideration of several factors, including safety, storage density, stability, and integration into existing fuel infrastructures. Although extensive research has been carried out since the 1980s, no LOHC perfectly satisfies all the criteria. The focus has primarily been on two classes of materials: homocyclic and heterocyclic compounds.

Homocyclic LOHC systems such as methylcyclohexane (MCH)/toluene and decalin/naphthalene offer promising hydrogen storage densities, albeit with challenges such as energy demands and material decomposition. Meanwhile, heterocyclic LOHCs like perhydrophenazine/phenazine exhibit solid-state properties at room temperature, presenting unique advantages and challenges in terms of hydrogenation and dehydrogenation processes. (Yang, Hunger, & al, 2023)

Power fuels: storage in chemical compounds

Storage in chemical compounds offers a variety of methods for hydrogen storage, including the use of methanol, methane, ammonia, gasoline, or employing processes such as the steam-iron method. (Linde Engineering, n.d.) These chemical energy carriers play a key role in long-distance energy trade, remote power generation, and robust machinery and transportation equipment, given their superior energy density compared to mechanical and thermal counterparts. This category includes chemical combinations of hydrogen with elements such as chlorine, methane, ammonia, water, or other compounds.

Another approach, the conversion method, involves processes like Power-To-Gas, which allows methane to be produce from H_2 and CO_2, methanol to be synthesized from H_2, ammonia to be produce from H_2 and N_2, or coal to be hydrogenated. Even water itself can act as a hydrogen store, with H_2 released through water splitting, albeit requiring energy input. Simple combustion can then convert H_2 back to water, releasing significant energy. (Bergthorson, 2018)

There exists a unique class of material-based carriers, known as 'power fuels' or 'e-fuels', which are capable of binding and releasing hydrogen molecules while serving as fuels themselves. Examples encompass electrochemically synthesized methane, Fischer-Tropsch fuels, methanol, and ammonia.

Ammonia, mainly produced by the Haber–Bosch process, emerges as a versatile hydrogen carrier with synthesis energy demands ranging from 7.78 to 9.06 kWh/kg ammonia. Alternatively, electrolysis offers a greener route, albeit with slightly higher energy demands. Ammonia's ability to liquefy at relatively low temperatures enables various storage methods, including pressure and reduced pressure vessels.

Methanol, another significant hydrogen carrier, undergoes synthesis through carbon dioxide hydrogenation. Its reversible nature allows for use as an industrial feedstock and fuel. The exothermic hydrogenation of carbon dioxide facilitates methanol distillation, and subsequent reactions like methanol steam reforming offer efficient hydrogen release methods. (Yang, Hunger, & al, 2023)

Metal fuels

Metal fuels offer a promising avenue for storing hydrogen indirectly, presenting a potential solution for clean energy carriers in a low-carbon future economy. They possess high energy densities and are integral components within various batteries, energetic materials, and propellants. The combustion of metal fuels generates solid metal-oxide products that can be efficiently captured and recycled using zero-carbon electrolysis processes powered by clean energy sources. However, the widespread adoption of metal fuels faces technological challenges, particularly in developing clean and efficient combustor/reactor/engine technologies to harness their chemical energy effectively.

Within the realm of metal fuels, an intriguing prospect lies in their utilization as zero-carbon, recyclable electrofuels. These metals can be oxidized by either water or air, providing versatile options for energy generation. Metals, compared to other elements, exhibit the highest volumetric heat production when burned in air, making them exceptionally energetic chemical fuels. Certain metals, such as boron, demonstrate specific energies surpassing current options, particularly when considering the mass of the required hydrogen-storage system. Moreover, metals like silicon, aluminum, and iron, being abundant elements in the Earth's crust, offer practical choices for electrofuel applications.

The concept of a metal-fuel cycle envisions metals being utilized as recyclable zero-carbon electrofuels, providing a sustainable energy solution consistent with the principles of a circular economy. Metal fuels, upon combustion, produce solid metal-oxide products that can be collected and recycled using clean primary energy sources, ensuring minimal environmental impact and an effectively infinite recycling capability.

Metal fuels offer a pathway towards high-energy-density storage and transport solutions, presenting a viable alternative to traditional hydrocarbon fuels. While challenges exist, including the development of efficient recycling processes and high-energy-cycle efficiencies, continued research and development in this area hold promise for enabling a transition to a low-carbon economy reliant on metals as both energy carriers and materials for various applications. (Bergthorson, 2018)

EXPERIMENT: REDOX FROM IRON ORE PELLETS

For the energy transition to effectively take root, the efficiency, compactness, and cost-effectiveness of H_2 storage and transport must be improved. Current technologies, including GH2, LH2, and LOHC, fall short in terms of storage volume, energy demand, and efficiency (AMBARtec, 2024).

A transition to a low-carbon society requires the eradication of fossil fuels from all metallurgical processes, as metal production stands as a significant contributor to global carbon dioxide emissions (Allanore, 2013) (Fray, 2013) . Since the dawn of the Iron Age, carbon has traditionally been utilized to reduce metals. However, the concept of utilizing hydrogen for metal oxide reduction and energy storage in metals presents a compelling alternative.

The development, scaling up, and commercial deployment of various low-carbon metal smelting technologies are essential for fostering a low-carbon economy, irrespective of the metal-fuel concept. In fact, the metal-fuel concept offers the advantage of leveraging existing infrastructure for metal production, storage, and transport, with enabling retrofitting to reduce carbon dioxide emissions, rather than necessitating the construction of entirely new infrastructure. (Bergthorson, 2018)

In terms of the regeneration process, the proposition of a 'recyclable metal-fuel concept' introduces an innovative method for efficient 'hydrogen storage' during the metal oxide reduction process. (COMETNANO, 2012)

Iron emerges as a compelling recyclable fuel due to its widespread availability, affordability, non-toxic nature, and recyclability without CO_2 emissions using current technology. The combustion of iron yields flame temperatures akin to hydrocarbons and generates large oxide particles, simplifying collection due to iron's heterogeneous combustion process. Moreover, the relatively low combustion temperatures in iron flames result in lower thermal-NOx emissions. (Bergthorson, 2018)

Figure 6. Industrial iron ore pellets. Illustration from AMBARtec. (AMBARtec, 2024)

This experiment investigates the direct reduction (DR) of a sample of iron ore pellets under an atmosphere of hydrogen (H_2) at a temperature approximate of 900°C at atmospheric pressure.

Previous studies have analyzed the porosities and the swelling behavior of the pellets under an atmosphere of H_2 at temperatures between 800°C and 1100°C at atmospheric pressure. The performance of the technology, including the reduction rate, metallization degree, and behavior of the iron ore, significantly varies depending on the reducing atmosphere and temperature. A comprehensive understanding of the role of the reducing gas composition and temperature on the process is crucial for achieving appropriate reduction efficiency and product quality. The reduction rate is higher under H_2 atmosphere due to the small size and high diffusion rate of the H_2 molecules penetrating deeper into the crystal structure of iron oxide, resulting in a greater degree of metallization. Other aspect is the reduction rate increases as the temperature rises. (Scharm & al, 2022)

The DR of iron ore stands as one of the methods for energy storage. This technology includes a range of processes employing diverse reducing agents, oxidant agents, and reactors. In this study, hydrogen (H_2) serves as the reducing agent, complemented by carbon dioxide (CO_2) or water (H_2O) as oxidant agents. The source of hydrogen crucially impacts carbon emissions, with CO_2 as an oxidant agent potentially offsetting total carbon emissions.

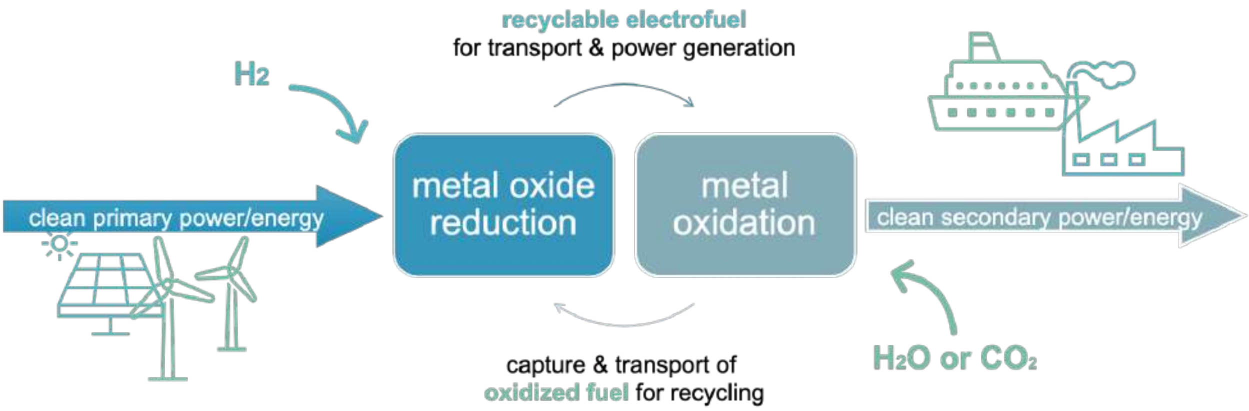

Figure 7. Schematic of the reduction-oxidation cycle characteristic the iron pellets.

For instance, in industrial settings, iron oxide undergoes reduction during storage loading via added hydrogen. Steam produced can be recycled through electrolysis. During discharge, steam is fed at the point of use, sourced potentially from the exhaust gas of a regeneration unit, oxidizing iron, and providing H_2. (AMBARtec, 2024)

MATERIALS

The sample of pellets consists predominant of hematite (Fe_2O_3, 92% m/m) with a lower content of magnetite (Fe_3O_4, 5% m/m) and 3% of calcium silicate ($CaSiO_3$). The diameter of the iron ore pellets ranges from 4 to 6 mm. The total weight of the sample is 20,1 g.

The redox reaction of iron ore pellets is studied in a quartz glass tube reactor equipped with a hinged furnace. To measure the performance of the reaction, a condenser and a water collector have been installed at the reactor outlet.

Experimental setup and procedure

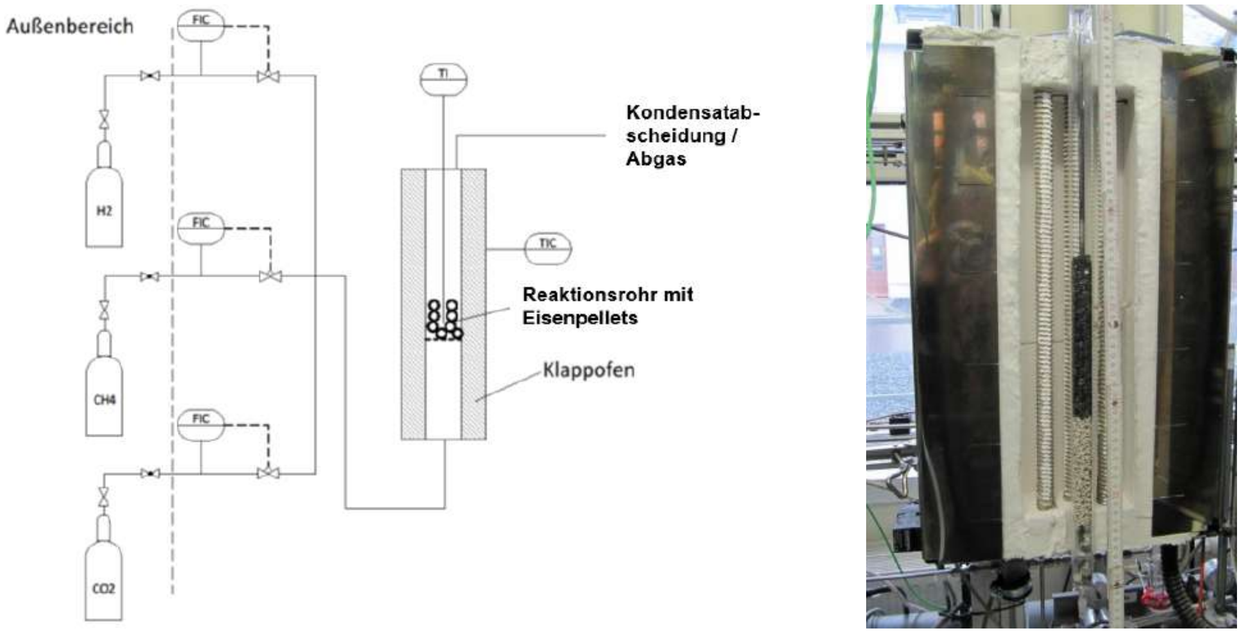

Figure 8. Reactor Setup.

Reduction reaction procedure

In the present study, iron ore pellets are reduced under H_2 atmosphere at an isothermal operating temperature of 892°C at 1 bar under defined flow conditions (30L/h). The sample is fixed and placed in the tray of the reactor.

The reactor is heated up to the operating temperature under an inert gas (Argon). Before switching to a reactive gas atmosphere (H_2 - 30L/h), the operating temperature is held for 10 minutes to reach a steady state (isothermal conditions). The flow of the reactive gas is sustained for one hour, until the volume of released H_2O shows no further change. Subsequently, the mass of releases and condensed water, along with the sample of pellets is weighed.

Finally, the reactor is rinsed with Argon.

Oxidation reaction procedure

The iron pellets are oxidized under CO_2 atmosphere at an isothermal operating temperature at 1 bar under defined flow conditions (30L/h) using the same reactor. The sample is fixed and placed in the tray of the reactor.

Like the reduction reaction procedure, the reactor is heated up to an operating temperature under an inert gas (Argon). Before transitioning to a reactive gas atmosphere (H_2 - 30L/h), the operating temperature is held for 10 minutes to reach a steady state (isothermal conditions). The flow of the reactive gas is maintained for one hour.

Subsequently, the sample of pellets is weighed, and the released energy is calculated. Finally, the reactor is rinsed with Argon.

Moreover, oxidation can take place in the presence of a H_2O atmosphere, facilitated by the inclusion of a steam generator within the system.

Operating conditions

- Temperature: 892°C (isothermal conditions)
- Pressure: 1 atm
- H_2-flow rate: 30L/h
- Operation time: 1 hour (end of reactions)

Reduction

The pellets have been reduced from Fe_2O_3 and Fe_3O_4 to Fe under the H_2 atmosphere. However, due to transport limitations through the porosity, reduction occurs primarily via solid diffusion, potentially resulting in incomplete reduction. (Lu & al, 1999) Previous studies, such as the one conducted by Scharm et al., demonstrated nearly complete reduction of pellets to metallic Fe by H_2 at 800°C, without deposition of carbon on the pellet surface. Moreover, as temperatures increase, the reduction progression accelerates, leading to complete reduction. For the purposes of this study, it is assumed that the sample undergoes full conversion.

The reduction reactions are as follows:

$$Fe_2O_3 + 3\ H_2 \rightarrow 2\ Fe + 3\ H_2O \qquad \Delta H_{R,298}\ [kJ/mol] = 99{,}182 \qquad [2]$$

$$Fe_3O_4 + 4\ H_2 \rightarrow 3\ Fe + 4\ H_2O \qquad \Delta H_{R,298}\ [kJ/mol] = 151{,}075 \qquad [3]$$

It is evident that all the iron oxide will be converted into iron metal and water.

Table 2 displays the initial composition of the entire sample of pellets, with a total weight of 20,1g. The sample of pellets consists predominant of Fe_2O_3 (18,492 g) with a lower content of Fe_3O_4 (1,005 g) while $CaSiO_3$ remains inert, with a constant mass of 0,603 g. Additionally, theoretical results of a total conversion due to reduction and the experimental ones are found.

A slight difference in the remaining pellet sample masses, of less than 0.3 g, is observed. Discrepancies may arise from incomplete conversion, water evaporation or spillage, or measurement errors.

Table 2. Iron ore pellets sample composition before and after the reduction.

Composition [g]				
Sample		sample after reduction		
pellets	**20,1**		theoretical	experimental
Fe_2O_3	18,492	pellets	**14,264**	**14,53**
Fe_3O_4	1,005	Fe	13,661	13,927
$CaSiO_3$	0,603	H_2O	6,571	5,24
Mass lost after reduction			5,836	5,570

Oxidation

The oxidation reaction occurring in a steam atmosphere is represented by:

$$2\ Fe + 3\ H_2O \rightarrow Fe_2O_3 + 3\ H_2 \quad \Delta H_{R,298}\ [kJ/mol] = 24{,}301 \qquad [4]$$

Similarly, in a CO_2 atmosphere, the oxidation reaction is:

$$2\ Fe + 3\ CO_2 \rightarrow Fe_2O_3 + 3\ CO \quad \Delta H_{R,298}\ [kJ/mol] = -99{,}182 \qquad [5]$$

The ratios of reactants to products remain identical in both reactions, resulting in the same composition of the sample.

Initially, it is presumed that iron completely converts to iron oxide with the higher oxidation state (Fe_2O_3), resulting in the maximum released energy amount ($Ev = 2{,}11\ kWh/Lpellets$). Incomplete oxidation may lead to the formation of Fe_3O_4 resulting in reduced energy release ($Ev = 1{,}94\ kWh/Lpellets$). An analysis is necessary to determine the composition of the pellets.

Table 3 indicates that the oxidation process has not fully reverted to its original state, with the sample's weight decreasing from 20,1 g to 19,03 g. It is evident that energy loss occurs during the process.

Table 3. Comparison between original iron ore pellets sample and after the reduction.

	Composition (g)	
	original sample	after oxidation
pellets	**20,1**	**19,03**
Fe_2O_3	18,492	18,427
Fe_3O_4	1,005	-
$CaSiO_3$	0,603	0,603

During the oxidation process, an amount of H_2 equivalent to 0,6979 g is released.

Released Energy

The lower heating value of hydrogen is 33,33 kWh/kg (Linde Gas GmbH, 2022). By calculating the mass of hydrogen released during the oxidation, one can determine the energy density provided by this metal-fuel process.

$$E\ (kWh) = Hu\left(\frac{kWh}{kg}\right) \cdot m_{H_2}(kg) \qquad [6]$$

$$Em\ \left(\frac{kWh}{kg\ pellets}\right) = \frac{E\ (kWh)}{m_{pellets}\ (kg)} \qquad [7]$$

$$Ev\ \left(\frac{kWh}{L\ pellets}\right) = \frac{E\ (kWh)}{m_{pellets}\ (g)/\rho_{bulk}\left(\frac{g}{L}\right)} \qquad [8]$$

The results:

Table 4. Energy comparison between ideal situation and experimental.

Energy		
	theoretical	experimental
m pellets [g]	20,100	19,030
H2 [g]	0,738	0,698
E [kWh]	0,025	0,023
Em [kWh/kg pellets]	1,224	1,157
Ev [kWh/L pellets]	2,110	1,994
ΔEv [kWh/L pellets]	**0,116**	

A small difference between the energy density is observed ($\Delta Ev = 0{,}116\ kWh/Lpellets$). Several reasons could account for this, including the reduction reaction producing less iron than theoretically expected and potential losses during iron oxidation, such as incomplete oxidation from the iron.

DISCUSSION & COMPARISON OF RESULTS

In the context of physical-based hydrogen storage methods (GH_2 and LH_2), volumetric energy density (kWh/L) calculations were also performed to facilitate comparison with the iron pellets experiment.

Initially, energy density values were estimated assuming gaseous hydrogen behaved ideally across the analysis range (200, 700, and 1.200 bar). Subsequently, the real gas factor (Z) was considered. The results, depicted in Figure 9, show that at elevated pressures, gases significantly deviate from ideal behavior, indicating that such simplifications can lead to notable discrepancies from actual conditions.

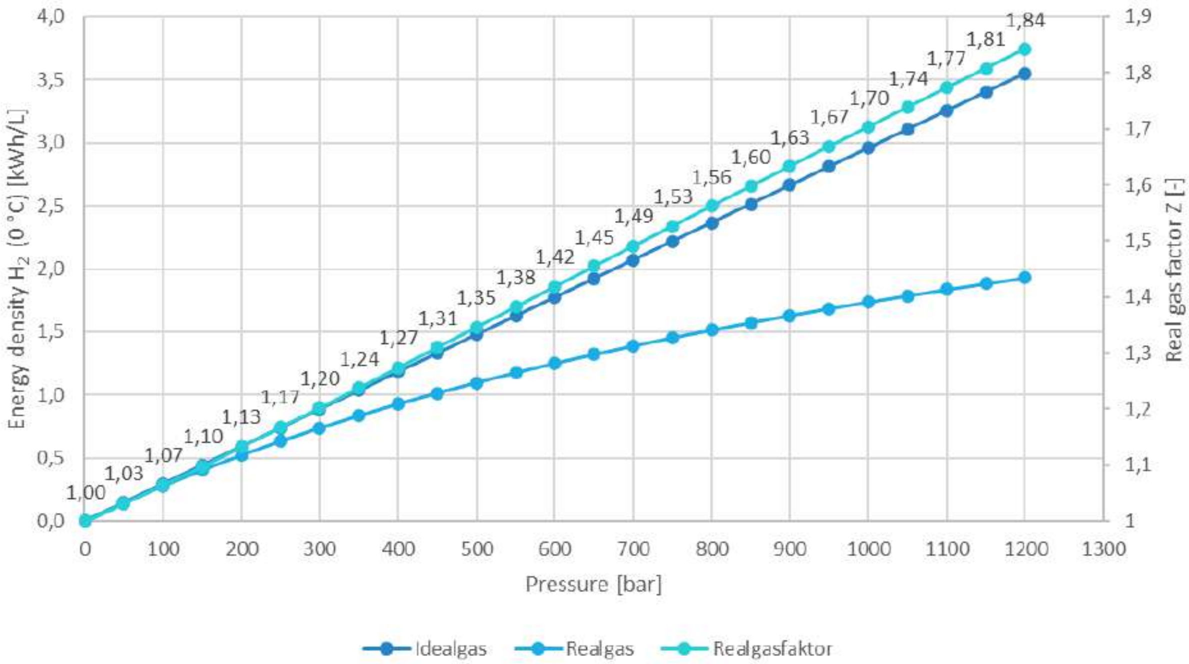

Figure 9. Energy density to ideal gas and real gas (1 - 1200 bar, 0 °C).

Table 5 reveals that at a pressure of 200 bar, the variation is minimal ($\Delta Ev = 0{,}07\ kWh/L$). In contrast, at 1.200 bar, the actual energy density is considerably lower than the ideal predictions. This suggests that utilizing such high pressures for hydrogen storage is impractical, as the marginal increase in energy density does not justify the risks. Therefore, alternative storage methods that avoid the safety concerns associated with high pressures are recommended.

Table 5. Compressed gaseous hydrogen compared to ideal gas and real gas (0°C).

GH2						
P [bar]	**200**		**700**		**1.200**	
m/V [kg/m3]	18		62		107	
Z	1	1,133	1	1,491	1	1,842
Ev [kWh/L]	0,59	0,52	2,07	1,39	3,55	1,93

For LH2, the analysis of three standard tank pressures for cryogenic liquids shows that the variation with respect to pressure is minimal. This suggests a low dependence of both volumetric density and energy density on pressure. At -253°C, the energy density consistently stays within the range of 2,40-2,50 kWh/L.

Table 6. Liquid hydrogen properties at different pressures (-253°C).

LH2			
P [bar]	**18**	**22**	**36**
ρ [kg/m3]	73,16	73,59	74,98
Ev [kWh/L]	2,44	2,45	2,50

Table 7 illustrates a higher volumetric energy density for LH2 compared to GH2, as the literature said. The energy density of iron pellets falls in between. However, due to the disadvantages associated with LH2, with evaporative losses during storage and transport. It's conceivable that iron pellets could be a safer and more efficient alternative for long-distance transportation or long-term storage, as there would be no energy losses over those periods.

Table 7. Summary of Energy Densities for Different Storage Processes.
Source TRL-Levels: Yang, M., Hunger, R., & al, e. (2023)

	GH2			LH2 (20,15 K, 18-36 bar)	iron pellets (theoretical)
	200 bar	**700 bar**	**1.200 bar**		
m. energy density [kWh/kg]	33,34				1,22
v. energy density [kWh/L]	0,52	1,39	1,93	2,44 - 2,50	2,11
energy losses [%]	3-8	3-10	n.d.	18-30	13
TRL	9		4-6	9	6-7

Figure 10 illustrates a comprehensive comparison of energy densities among various energy storage methods, spanning both conventional and hydrogen-based approaches. Currently, diesel and gasoline demonstrate superior energy densities, followed by methanol, metal hydrides, and complex hydrides. Additionally, GH2 (200 bar), despite being a simple storage technique, falls significantly behind the rest of the methods. However, it's notable that certain technologies such as LOCHs and MOFs require further development to reach their full potential.

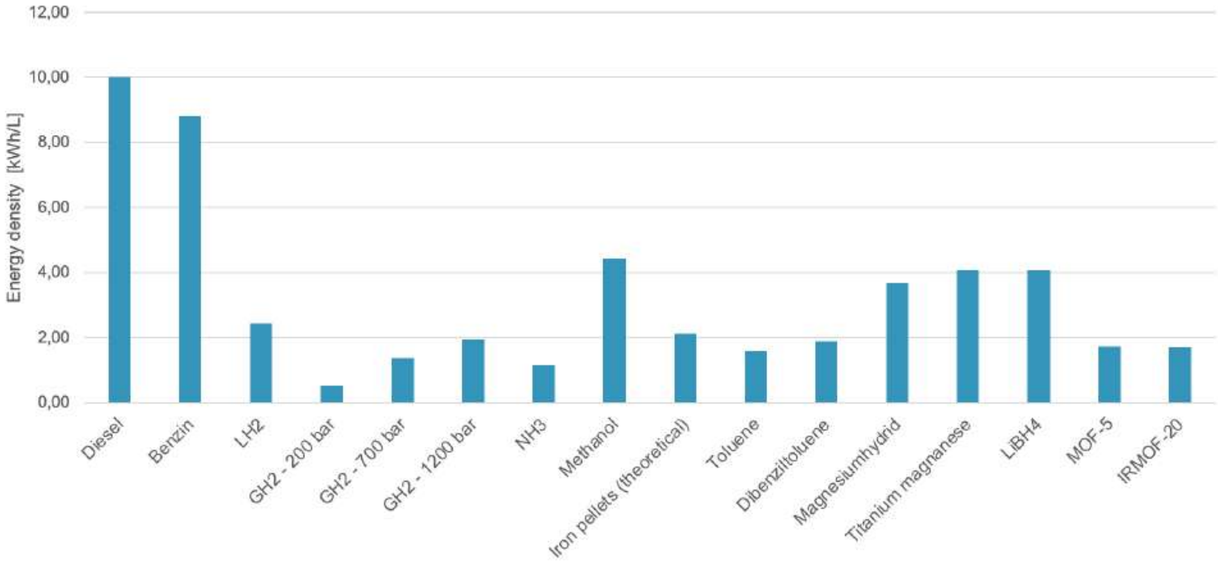

Figure 10. Volumetric energy density of different storages systems.

Hydrogen is emerging as a promising energy carrier due to its abundant availability, high energy content, and potential for emissions reduction. However, effective storage systems are crucial for its utilization as a fuel, prompting a comparative analysis of different hydrogen storage technologies. Let's compare hydrogen storage systems, including compression (GH_2), liquefaction (LH_2), adsorption, metal hydrides, power fuels, and metal fuels, considering their advantages, limitations, prospects, and challenges.

GH_2 storage presents an economically feasible solution, facilitating global transportation via pipelines and underground salt caverns for long-term storage. Nevertheless, certain methods entail purification alongside gas compression, while safety concerns arise from high pressure.

Although, LH_2 storage offers heightened energy density and enhanced safety compared to GH2 but demands substantial energy for liquefaction, coupled with evaporative losses during storage and transport.

Adsorption presents a low-pressure storage option with potentially vast capacity, yet it may be constrained by the capabilities of adsorbent materials and sluggish hydrogen adsorption and desorption rates.

While offering secure and reversible storage, metal hydrides may exhibit sensitivity to temperature and pressure fluctuations, thereby limiting practical application. Chemical hydrides offer a compact and safe storage solution, although their capacity is restricted, and they might generate undesirable byproducts.

Organic hydrogen carriers mimic conventional liquid fuels in terms of storage and transport, featuring recyclability of carrier materials and heightened safety. Nevertheless, they encounter challenges regarding energy consumption and decomposition over time.

Chemical compound storage (Power Fuels) boasts high energy density and on-demand hydrogen release; however, energy is consumed during production and conversion of chemical compounds, while capturing and recycling carbon emissions present challenges.

Lastly, metal fuels offer remarkable energy density and recyclability, leveraging abundant metals. Nonetheless, they confront technological hurdles in efficient combustion and metal recycling, alongside potential energy losses during the reaction process.

Table 8. Extend Summary of Energy Densities for Storage Processes.
Source TRL-Levels: Yang, M., Hunger, R., & al, e. (2023)

Hydrogen Storage Methods	physical-based				material-based			
	GH2			LH2 (20,15 K, 18-36 bar)	power fuels			
	200 bar	700 bar	1200 bar		NH3	CH3OH	iron pellets (theoretical)	iron pellets (experimental)
m. energy density [kWh/kg]	33,34				1,33	5,47	1,22	1,16
v. energy density [kWh/L]	0,52	1,39	1,93	2,44 - 2,50	1,14	4,44	2,11	1,99
energy losses (%)	3-8	3-10	n.d.	18-30	44-59	20	13	
TRL	9		4-6	9	9	9	6-7	

In essence, each system has its own advantages and disadvantages. However, ongoing advancements in materials science and engineering hold promise for enhancing these technologies. A blend of multiple storage systems may represent the optimal approach for realizing the practical and widespread utilization of hydrogen as a fuel.

CONCLUSION

In summary, hydrogen is emerging as a promising synthetic fuel for the future, boasting a significant calorific value and the potential for renewable energy integration within a closed cycle.

While existing hydrogen storage methods demonstrate efficiency and safety, and despite current advancements in hydrogen production, storage, and conversion technologies, the field remains open to further enhancements and breakthroughs.

The comparative analysis presented here outlines two overarching categories (physics-based and materials-based) and examines several hydrogen storage methods and one experimental storage method (Redox from iron ore pellets). Ongoing scientific research and technological advances are expected to yield materials with increased volumetric and gravimetric hydrogen densities.

It is noteworthy that no singular form of hydrogen storage has monopolized the entire value chain to date. Rather, the method of storage varies depending on specific application requirements, transportation organization, and end-use scenarios. Consequently, adaptable infrastructure systems may be necessary to accommodate diverse application contexts.

For applications necessitating medium- to long-term hydrogen storage, material-based storage technologies emerge as favorable options due to their superior volumetric density, chemical stability, and safety profiles. Also, metals offer markedly higher energy densities compared to natural gas or petroleum, making them attractive for energy stockpiles and international trade.

Power and metal fuels present a compelling solution, offering recyclable resources capable of providing high-intensity OnDemand power across various applications. However, the widespread adoption of metal fuels faces a key technological obstacle: the development of efficient power-generation equipment capable of harnessing the chemical energy stored in metals at rates suitable for compact power applications.

Among power fuels, iron stands out as a promising candidate, given its widespread availability, affordability, non-toxic nature, and recyclability without CO2 emissions using existing technology.

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