



UNIVERSITY OF WEST ATTICA SCHOOL OF ENGINEERING MSc in Oil and Gas Process Systems Engineering Dissertation

Title:HYDROGEN COMPATIBILITY ASSESSMENT IN
NATURAL GAS INFRASTRUCTURES

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ΔΗΛΩΣΗ ΣΥΓΓΡΑΦΕΑ ΜΕΤΑΠΤΥΧΙΑΚΗΣ ΕΡΓΑΣΙΑΣ

Ο/η κάτωθι υπογεγραμμένος/η Κουζούπης Σπυρίδων του Ηλία, με αριθμό μητρώου 20200051 φοιτητής του Προγράμματος Μεταπτυχιακών Σπουδών «Βιομηχανικά Συστήματα Πετρελαίου και Φυσικού Αερίου» του Τμήματος Μηχανολόγων Μηχανικών του Πανεπιστημίου Δυτικής Αττικής, δηλώνω ότι:

«Είμαι συγγραφέας αυτής της μεταπτυχιακής εργασίας και ότι κάθε βοήθεια την οποία είχα για την προετοιμασία της, είναι πλήρως αναγνωρισμένη και αναφέρεται στην εργασία. Επίσης, οι όποιες πηγές από τις οποίες έκανα χρήση δεδομένων, ιδεών ή λέξεων, είτε ακριβώς είτε παραφρασμένες, αναφέρονται στο σύνολό τους, με πλήρη αναφορά στους συγγραφείς, τον εκδοτικό οίκο ή το περιοδικό, συμπεριλαμβανομένων και των πηγών που ενδεχομένως χρησιμοποιήθηκαν από το διαδίκτυο. Επίσης, βεβαιώνω ότι αυτή η εργασία έχει συγγραφεί από μένα αποκλειστικά και αποτελεί προϊόν πνευματικής ιδιοκτησίας τόσο δικής μου, όσο και του Ιδρύματος.

Παράβαση της ανωτέρω ακαδημαϊκής μου ευθύνης αποτελεί ουσιώδη λόγο για την ανάκληση του πτυχίου μου».

Επιθυμώ την απαγόρευση πρόσβασης στο πλήρες κείμενο της εργασίας μου μέχρι και έπειτα από αίτηση μου στη Βιβλιοθήκη και έγκριση του επιβλέποντα καθηγητή.

Ο/Η Δηλών/ούσα Κουζούπης Σπυρίδων

ABSTRACT

Man's progress during the years of his existence on Earth is remarkable. From the discovery of fire until today, technology is constantly developing and so are the needs of man. From the industrial revolution (1750-1840) onwards and especially from the beginning of the first world war (1914-1918), industry developed rapidly, and of course the extraction and use of hydrocarbons. The first fuels were coal and oil, while now we refer to fuels such as natural gas, ammonia and hydrogen. Now beyond the capacity of our global energy needs, where it is a matter of resolution, the use of milder forms of energy is intensified, according of course to the laws and directives of global organizations and states. Natural gas is a milder fuel compared to other hydrocarbons and is a transition fuel towards greener forms of energy. A green form of energy, subject to conditions in the way it is produced, is hydrogen (green). Hydrogen being a fuel with potential (production, lots of storage, quality of combustion products, etc.) and energy content, it is considered one of the fuels of the future. For this reason, it has generated a lot of interest in the energy field, on how we can exploit its reaction with oxygen (O_2) and produce large amounts of energy, store it, produce it with zero pollutants, and transport it. In this work, reference is made to the issues that arise during the blending of hydrogen into natural gas pipelines, as it constitutes a wide network, ready for use.

Keywords: Hydrogen; Natural Gas; Pipeline; Transmission; Blending; Embrittlement

ΠΕΡΙΛΗΨΗ

Η πρόοδος του ανθρώπου μέσα στα χρόνια ύπαρξής του στην Γη, είναι αξιοσημείωτη. Από την ανακάλυψη της φωτιάς μέχρι και σήμερα η τεχνολογία αναπτύσσεται συνεχώς και μαζί και οι ανάγκες του ανθρώπου. Από την βιομηγανική επανάσταση (1750-1840) και μετά και ιδίως από τις αρχές του πρώτου παγκοσμίου πολέμου (1914-1918), η βιομηγανία αναπτύχθηκε ραγδαία, και φυσικά η εξόρυξη και η χρήση των υδρογονανθράκων. Τα πρώτα καύσιμα ήταν ο άνθρακας και το πετρέλαιο, ενώ πλέον αναφερόμαστε σε καύσιμα όπως το φυσικό αέριο, η αμμωνία και το υδρογόνο. Πλέον πέρα από την ικανοποίηση των παγκόσμιων ενεργειακών αναγκών μας, όπου είναι ένα ζήτημα προς επίλυση, η χρήση ηπιότερων μορφών ενέργειας εντείνεται, σύμφωνα φυσικά με της νομοθεσίες και της οδηγίες παγκόσμιων οργανισμών και κρατών. Το φυσικό αέριο αποτελεί ένα ηπιότερο καύσιμο σε σύγκριση με τους λοιπούς υδρογονάνθρακες και αποτελεί ένα μεταβατικό καύσιμο προς τις πιο πράσινες μορφές ενέργειας. Μία πράσινη μορφή ενέργειας, υπό ορισμένες προϋποθέσεις στον τρόπο παραγωγής του είναι το υδρογόνο (πράσινο). Όντας το υδρογόνο ένα καύσιμο με πολλές δυνατότητες (παραγωγής, αποθήκευσης, ποιότητας προϊόντων καύσης κ.ο.κ.) και ενεργειακό περιεχόμενο, θεωρείται ένα από τα καύσιμα του μέλλοντος. Για το λόγο αυτό, έχει προξενήσει μεγάλο ενδιαφέρον στον τομέα της ενέργειας, για το πώς μπορούμε να εκμεταλλευτούμε την αντίδρασή του με το οξυγόνο (O2) και την παραγωγή μεγάλων ποσοτήτων ενέργειας, την αποθήκευσή του, την παραγωγή του με μηδενικούς ρύπους, και την μεταφορά του. Στην παρούσα εργασία, γίνεται η αναφορά στα ζητήματα που προκύπτουν κατά την εισαγωγή αυτού στους αγωγούς φυσικού αερίου, μίας και αποτελεί ένα ευρύ δίκτυο, έτοιμο προς χρήση.

Λέξεις – Κλειδιά: Υδρογόνο; Φυσικό Αέριο; Αγωγοί; Μεταφορά; Ανάμιξη; Ευθραυστότητα

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GLOSSARY OF TERMS AND ACRONYMS

AHW AlO4 API ASTM Americ.	Atomic Hydrogen Welding Oxidoperoxy(oxo)alumane American Petroleum Institute an Society for Testing and Material
ATEX	Atmosphere Explosive
ATR	Autothermic Reformer
AVL	Adelson-Velsky Landis
BCC	Body Centred Cubic
Bcm	Billion cubic meters
BM	Base Metal
CAPEX	Capital Expenditure
CCS	Carbon Capture Storage
CCUS	Carbon Capture Utilization Storage
CO_2	Carbon Dioxide
COx	Carbon Oxygen compound
CV	Calorific Value
d	diameter of pipe
DME	Dimethyl Ether
DMFC	Direct Methanol Fuel Cell
E	Energy
EEPR	European Energy Program for Recovery
EHB	European Hydrogen Backbone
ESA	Electrical Swing Adsorption
f	Darcy-Weisbach friction factor
FCC	Face Centred Cubic
FCEV	Fuel Cell Electric Vehicle
FCGR	Fatigue Crack Growth
GfC	Gas for Climate
h	Planck's constant
H+ H-	Hydrogen ions
H0	Atomic Hydrogen
H1,2,3	Isotopes of Hydrogen, protium, deuterium, tritium
H_2O	Water
H_2S	Hydrogen Sulfide
HAZ	Heat Affected Zone
HCD	Hexagonal Close-Packed
HDPE	High density Polyethylene
HHV	High Heating Value
HIC	Hydrogen Induced Cracking
HSC	Hydrogen Stress Cracking
HSM	Hydrogen Storage Material
HTHA	High Temperature Hydrogen Crack
Hz	Hertz
ICE	Internal Combustion Engine
IEA	International Energy Agency
IMP	Integrity Management Program
ISO	International Organization for Standardization
K	Intensity factor
kWe	kilo Watt electric
kWh	kilo Watt hours
LCA	Life Cycle Analysis

LED	Light Emitting Diode
LEL	Lower Explosive limit
LH	Liquid Hydrogen
LHV	Low Heating Value
LNG	Liquid Natural Gas
LPG	Liquid Petroleum Gases
Lt	litters
m	Mass
М	Metal Element
MDPE	Medium density Polyethylene
Me	Transitional Metal
MIE	Minimum Ignition Energy
mJ	milli Joule
MN	Methane Number
Mt	Megatons
MTBE	Methyl tert-butyl ether
Mtoe	Megatons of equivalent energy
MWe	Mega Watt electric
N	Fatigue cycles
NASA	National Aeronautics and Space Administration
NG	Natural Gas
NOx	Nitrogen Oxygen compound
Ω_2	Oxygen
OPEX	Operational Expenditure
P	Permeation Coefficient
n	Pressure
PAC	Paris Agreement Compatible
PF	Polyethylene
PFFC	Polymer electrolyte fuel cells
PFM	Proton Exchange Membrane
ΡΗΜSΔ	Pipeline & Hazardous Materials Safety Administration
ΡςΔ	Pressure Swing Adsorption
PTFF	Polytetrafluoroethylene
PVC	Polyvinylchloride
PWHT	Post Weld Heat Treatment
RFM	Remote Telecom Stations
RES	Renewable Energy Systems
SCC	Stress Corrosion Crack
SiO	Silicate
SMR	Steam Methane Reformer
SOFC	Solid Oxide Electrolysis Cells
SOLCS	Sulphur Oxygen compound
SSR	Slow Strain Rate
T	Temperature
1 f	Tones
ι Τς λ	Temperature Swing Adsorption
15A	Velocity
u UFI	Unper Explosive limit
V	Laskage rate
VSA	Vacuum Swing Adsorption
V SA WE NET	World Enorgy Notwork
	Wolding Motol
vv 1V1 v	Stoichiometry of hydride
A V	Grade of Steels
л- 7	Compressibility Easter
L	Compressionity ractor

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- Crack size α
- Width barrier energy of particle Intensity factor range Enthalpy difference δ
- ΔK
- ΔH
- Intensity Factor Range ΔK
- De Broglie Wavelength λ

CHAPTER 1: INTRODUCTION TO HYDROGEN ENERGY

1.1Background and motivation for the work

The current author attended the Polytechnic School of the University of Patras to pursue a degree in Mechanical and Aeronautical Engineering from his undergraduate years. On the third year, author chose direction as a Mechanical Engineer, concentrating on fluids and energy. His diploma thesis was on "NUMERICAL SIMULATION OF SUBSEA OIL SPILL IN THE WEST OF KATAKOLO." All of this motivated him to continue in the same industry, specifically in hydrocarbon processing, in the postgraduate program "Oil and Gas Process Systems Engineering" at the University of West Attica, Department of Mechanical Engineering. The current dissertation focuses on "Evaluation of hydrogen compatibility in natural gas infrastructures". Natural gas is a transition fuel toward greener forms of energy because it is a milder fuel than other hydrocarbons. Hydrogen (green) is a green energy source when certain conditions are met during its production process.

As a fuel with numerous options (production, storage, quality of combustion products, etc.), hydrogen, it is thought to be one of the future fuels. Because of this, there has been a lot of interest in the energy industry in finding ways to use its reaction with oxygen (O₂) to produce a lot of energy, store it, produce it without using any pollutants, and transport it. The manner in which all of this should be carried out still is of great interest, particularly in the decade (2010-2022), when the issue of energy becomes a global one, with national governments and legislation promoting the cleanest forms of energy while simultaneously global crises of all kinds-social, economic, and cultural-have a direct impact on the energy sector. Naturally, the issue of global warming (also known as the greenhouse effect) plays a significant role in energy policy decisions made by politicians and will continue to do so in the years to come. Therefore, hydrogen is a promising fuel, provided that it is produced from renewable energy sources, in order to achieve the European and global targets of producing specific amounts of carbon dioxide (CO₂) annually and limit the increase in the average temperature of the Earth's surface. Therefore, hydrogen's safe transportation and environmentally friendly production are two issues. Since we are aware of the significance of this fuel right now, we concentrate on the issues that arise during its transportation and, more specifically, its integration into the existing natural gas pipelines, both globally and nationally (Greece) (Zohuri, 2019).

1.2 Dissertation structure

This master thesis concerns the way to introduce hydrogen into natural gas transmission facilities and the problems that will have to be addressed to make this possible. Therefore, the structure of the present is based on the following sections:

- Summary of the thesis.
- Structure of the thesis
- Introduction to hydrogen fuel and its properties.
- Global interest and investment in hydrogen.
- Method of production of hydrogen.
- Hydrogen purification
- Hydrogen transfer.
- Uses of hydrogen, its importance, and its interchangeability with natural gas.
- Legislative framework.
- Natural gas transmission system in Greece, Europe
- Conclusions from this thesis.
- Possibilities of development of the diplomatic work.
- Definitions.

1.3 Introduction to hydrogen energy

From the moment he was born, man wanted to create and advance in accordance with his time. After years and securing his livelihood, this progress was about making his life on Earth easier and more comfortable. He was able to accomplish this by developing machines and tools, observing and comprehending the world more deeply over time, and expressing it through equations, theorems, and other similar methods. However, in order for the machines to function, they required an energy source, which at first was the air (wind energy). However, as people's needs grew, wind energy became insufficient, and they turned to alternative sources of energy. Hydrocarbons, for example, are sources.

As can be seen from their name, hydrocarbons are a chemical combination of carbon and hydrogen. Oil and natural gas are the two most well-known forms of hydrocarbons currently in use. Methane, which makes up the majority of natural gas (70-90% by volume), ethane (5-7%), propane (5% by volume), butane (0.2-2% by volume), and other hydrocarbon chemical compounds are just a few examples. Natural gas composition changes depending on where it comes from, where it is shipped, how it is transported, and international regulations that make it easy to buy and sell.



Figure 1. Chemical compount of Natural Gas.

Oil and natural gas are the main fuels that internal combustion engines use to run. These engines still make it easy to move around in cars today, but they also heat and cook food. Since their discovery, both of these applications of hydrocarbons have improved human life. As a result, we could say that oil and natural gas are one of the fundamental goods that humans receive from the planet Earth. But first, these fuels need to be taken out of the ground and processed (the refining process).

Additionally, when burned, fossil fuels can produce chemicals that are harmful to people and the environment in addition to providing energy. Chemical elements like carbon (CO_x), nitrogen (NOx), sulfur (SOx, H₂S), and so on are the basis of these compounds. They cause a lot of problems, and these gaseous pollutants will get worse as man's needs and goals grow. As a result, despite the fact that the objective was to develop without restrictions up until a few years ago, the use of fuels like coal/lignite, oil, and natural gas (widely available and simple to use with the technology at the time), the resulted pollution and the need for improved people's quality of life prompted global directives, policies, and legislation to reduce emissions of air pollutants. Survival from climate change, which is largely caused by the excessive use of fossil fuels, the release of pollutants into the atmosphere, and water contamination, is one of these needs. Consequently, we have reached the point where we are looking for milder forms of energy. Examples include wind power (wind turbines), solar power (photovoltaics, thermal panels), natural gas (a transitional fuel to replace oil and coal), and hydrogen (brown, blue, and green). These primary energy sources can be used to generate electricity. Hydrogen as a fuel, on the other hand, is the technology that is just starting to attract attention and has many applications (Zohuri, 2019).

One of the largest worldwide programs for the production of electricity and fuel is Hydrogen. Depending on how it is produced, hydrogen can be gray, blue, or green—the point

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being that it is green. When the energy used to produce it comes from environmentally friendly sources like photovoltaic or wind power, it is considered green. This ensures that no gaseous pollutants are produced during the production and "burning" of hydrogen. Pure water (H₂O) is especially produced during its "burning" in hydrogen engines. Therefore, hydrogen is an excellent option for combating climate change, reducing air pollution, and reducing people's general reliance on harmful fossil fuels. As a result, it is regarded as a crucial energy carrier for a more cost-effective, reliable, and sustainable energy future. Nevertheless, hydrogen technology is still in its infancy, and research and development of the technology, both for its production and use (see hydrogen cars), requires a significant number of financial resources. Consequently, its production and final application are two obstacles that must be gradually overcome, but they are not the only ones. The development of a transportation system that is both dependable and financially viable is one of the most significant issues. Figure 2, shows the types of hydrogen based on their color classification, which is a symbol of their production process.



Figure 2. Types of Hydrogen. (Source: www.klimaschutz-niedersachsen.de and www.klimaandmore.de)

The hydrogen, when it will be produced, will have to be stored somewhere and then supplied to its final use points. The problem that arises in addition to the others, therefore, is the way it will be able to reach the consumer safely and economically, so that the development of this technology is sustainable. Hydrogen can be transported by:

- High pressure tank truck
- Cryogenic transportation of liquid hydrogen via shipping
- Railway transportation
- Cryogenic liquid tanker trucks
- Compressed hydrogen tube trailer
- Pipelines
- Chemical carriers

In order to understand how important an element is to humanity and to life in general in the universe, it is useful to do a brief historical review of hydrogen.

1.3.1 Historical data of hydrogen

Hydrogen, a highly flammable gas, was discovered by Henry Cavendish in 1766, but Antoine Lavoisier gave it its name. Hydrogen derives from the Greek words' hydros, meaning "water," and gonos, meaning "seed" (Zohuri, 2019).

Due to its location towards the top of the periodic table, hydrogen is an essential element. The fundamental reason for this is because it is a vital component of water (H₂O). Its properties are crucial to several chemical, biological, and physical processes. Our universe started with the Big Bang, the rapid expansion of an endlessly dense and very energy "Singular state." During the Planck epoch, which started 13.3 to 3.9 billion years ago, hydrogen was formed and its theoretic description commenced. "The parameters at the time were T = 1032 K (Planck temperature) and d = 1093 g/cm³ (Planck density) (Gavrilyuk, 2013). In addition to a high energy density, temperature, and pressure, the early universe was also very uniform" (Zohuri, 2019).

"As the universe expanded and cooled, the particle system experienced a series of phase changes. At this period, elementary particles possessed higher energy than can be produced using particle accelerators on Earth. The universe was very hot. 10e⁻³⁵ seconds after the Planck epoch, a phase change initiated the exponential growth known as "cosmic inflation"" (Zohuri, 2019).

"After the conclusion of the cosmic inflation era, the universe was composed of a quark-gluon plasma. The third phase transition, baryogenesis, occurred as temperatures continued to plummet. Protons, the first known species of hydrogen, were created when quarks and gluons combined to form baryons" (Zohuri, 2019).

"After cooling, physical forces and elementary particles assumed their modern forms. During this period, deuterium, Helium-4, and other light isotopes were produced in nuclear reactors by the fusion of protons and neutrons. As the universe continued to expand and cool, gravity finally emerged as its fundamental driving force" (Zohuri, 2019). "After the Big Bang, it took about 380,000 years for the temperature to drop enough for hydrogen atoms to form. Prior to this, ionization of hydrogen atoms and recombination of their component protons and electrons existed in dynamic equilibrium" (Zohuri, 2019).

"After the formation of neutral hydrogen, the decoupling of matter and radiation resulted in the discharge of cosmic microwaves. Since then, the color temperature of decoupling radiation has continuously decreased and is presently below 2,725 K. As a result of cosmic expansion, the temperature is falling. According to the Big Bang theory, the radiation that we detect now emerges from a spherical surface known as the "last scattering surface"" (Zohuri, 2019).

The development of the universe throughout these three eras after the Big Bang is seen in Figure 3. Hydrogen initially arose during the second stage, whereas protons were produced during the third stage, around 380,000 years after the appearance of hydrogen (Zohuri, 2019).

The offspring of the Big Bang, hydrogen atoms, celebrated their birthday by emitting cosmic microwaves. This provided a difficult difficulty for future scientists to address. However, after 13.7 billion years, this extraordinary riddle has been solved. Arno Penzias and Robert Woodrow Wilson of Bell Telephone Laboratories documented this cosmic background in 1965; they were given the Nobel Prize in Physics in 1978 for their achievements (Zohuri, 2019).



Figure 3. Evolution of the universe after the Big Bang. (NASA/WMAP Science Team) (Gavrilyuk, 2013).

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As a consequence of the decoupling of matter and radiation, a significant development in the form of microwave radiation known as the "hydrogen line" occurred (Gavrilyuk, 2013). "This radiation is strongly connected with the abundance of hydrogen atoms in the universe. To understand more about this radiation, the electron structure of hydrogen atoms must be

dissected". Figure 4 depicts the elements of chemistry in their periodic table arrangement (Gavrilyuk, 2013).

"After the formation of hydrogen atoms, matter began to organize, giving birth to the first stars, galaxies, quasars, galaxy clusters, and superclusters. Hydrogen comprises 88.6 percent of the universe, making it the most abundant element by mass, and 93 percent of all atoms in the universe are composed of hydrogen" (Gavrilyuk, 2013). Hydrogen fusion was important for the chemical evolution of stars, since hydrogen was the primary constituent of their plasma states . Hydrogen exists in interstellar space as molecules, atoms, and ions, and it may condense into clouds of varying size, density, and temperature (Gavrilyuk, 2013).

Hydrogen is one of the universe's first elements, since it was produced shortly after the Big Bang (Gavrilyuk, 2013).

Using the first telescope, Nicolas-Claude Fabri de Peiresc captured these images of hydrogen in the universe Figure 5. In addition, Figure 6 illustrates a more precise hydrogen map of the Milky Way, which was constructed by a team of scientists using data from the most powerful telescopes.



Figure 5. NGC 604, a magnificent H II area inside the Triangulum Galaxy.



Figure 6. This HI4PI map Image credit: Benjamin Winkel / HI4PI Collaboration.

The creation of this HI4PI map involved utilizing data gathered from two radio telescopes: the 100-m Max-Planck radio telescope located in Effelsberg, Germany, and the 64-m CSIRO radio telescope situated in Parkes, Australia. The colors depicted in the image represent gas moving at various velocities. Running horizontally across the center of the image is the plane of the Milky Way Galaxy, while the lower right portion reveals the presence of the Magellanic Clouds.

Hydrogen Energy Pros

Renewable energy source

Hydrogen possesses numerous qualities that make it a valuable energy source, but its abundant availability stands out as the primary factor. Unlike any other energy source, hydrogen is virtually boundless, ensuring an inexhaustible supply. While harnessing hydrogen may demand substantial resources, this fundamental characteristic sets it apart from other energy sources, guaranteeing its perpetual availability (Zohuri, 2019).

Practically a clean energy source

The byproducts of hydrogen combustion are absolutely harmless, with no adverse consequences documented to date. Interestingly, hydrogen is employed as a replacement for drinking water in the aviation industry. After hydrogen has served its intended purpose aboard spacecraft and space stations, it is often recycled into potable water for humans (Zohuri, 2019).

Hydrogen is non-toxic

This indicates that it does not harm human health in any way. Because of this, it is preferred to other fuel sources like natural gas and nuclear energy, which are extremely risky and difficult to harness safely. Additionally, it permits the use of hydrogen in locations where other fuels may be prohibited (Zohuri, 2019).

Hydrogen surpasses other energy sources in terms of efficiency

Hydrogen is an extraordinarily efficient energy source due to its extraordinary energycarrying capacity per unit of fuel weight. This demonstrates indisputably that a car driven by hydrogen will go farther than a gasoline-powered vehicle of comparable capacity. In other words, the mileage potential of hydrogen-powered automobiles is boosted (Zohuri, 2019).

Hydrogen energy is an ideal fuel for both space exploration and future hydrogen-driven cars due to its exceptional power and efficiency. It is suitable for spacecraft propulsion on exploratory expeditions thanks to its high power-to-weight ratio. Hydrogen energy is a safe and effective alternative to gasoline and other fossil fuel-based fuels because it is three times more potent (Zohuri, 2019).

Hydrogen is the principal fuel used by NASA's current space program. The propulsion system of space shuttles and rockets is liquid hydrogen, whilst electrical systems are fuelled by hydrogen fuel cells. Additionally, hydrogen fuel cells provide a significant portion of the crew's clean drinking water (Zohuri, 2019).

Hydrogen's adaptability in transportation may be advantageous to vehicles, ships, airplanes, and even permanent fuel cell systems. Due to the necessity to store the fuel in cryogenic or high-pressure tanks, there are logistical issues with utilizing hydrogen in automobiles (Zohuri, 2019).

Fuel cells, which convert the chemical energy of hydrogen into electricity, have several benefits. In addition to providing heat and water, they have no impact on the environment. Additionally, fuel cells are two to three times more efficient than traditional combustion systems (Zohuri, 2019).

In the future, autos, buses, marine vessels, and trucks might all be driven by fuel cells. Fuel cells might potentially power a vast array of transportable devices. Hydrogen might have a big influence on the future of transportation by replacing costly imported petroleum used in vehicles (Gavrilyuk, 2013). (Zohuri, 2019). Fuel cells are used to produce energy during space shuttle missions (Zohuri, 2019).

Disadvantages of Hydrogen Energy

Hydrogen energy offers a number of benefits, but it has not yet gained universal acceptance as a viable alternative energy source. The high volatility of hydrogen in its gaseous form offers hazards and challenges in its handling and use. Its intrinsic volatility may be advantageous in some settings, but it also has substantial disadvantages. Below are the downsides of hydrogen energy (Zohuri, 2019)

Expensive energy production methods

Costs connected with the two principal methods of producing hydrogen—steam reforming and electrolysis—present the largest obstacle to its widespread usage. As a result, hydrogen energy has not been broadly adopted in a variety of areas. Hydrogen-powered hybrid vehicles do exist, but there is still more work to be done before they can be used in a practical and cost-effective manner. Until such advancements are made, hydrogen energy will be inaccessible to all but the wealthiest individuals (Zohuri, 2019)

Inadequate storage

The significant difference in density between hydrogen and gasoline also distinguishes hydrogen. Compressing hydrogen into a liquid state and storing it at lower temperatures improves its dependability and use as an energy source. This also explains why hydrogen cannot be transported or used in its normal condition and must constantly be moved under great pressure (Zohuri, 2019)

Not the most trustworthy power source

Never underestimate hydrogen's explosive capability. The flammability and possible risks of hydrogen get a tremendous deal of attention, yet gasoline offers a larger threat to the environment. Hydrogen's odorlessness makes it difficult to detect leaks without the installation of specially designed sensors (Zohuri, 2019)

Tough to maneuver

In contrast to oil, which can be safely transported via pipelines, and coal, which can be easily transported in dump trucks, the lightness of hydrogen makes it difficult to transport.

Transporting large quantities of hydrogen has distinct obstacles, which is why the element is often transported in smaller quantities (Zohuri, 2019)

Energy derived from hydrogen is insufficient for human survival.

Hydrogen has not been widely used due to the high expense of extracting it, despite its universal availability. It is difficult to challenge the current energy model, which is built on the use of fossil fuels. Moreover, there is no present overall structure that ensures future access to inexpensive and ecological hydrogen energy for typical automotive drivers. Hydrogen will become the primary energy source in the future, but it will take a very long time and a large expenditure to get there. This is because automobiles and gas stations would need to be upgraded to satisfy hydrogen infrastructure standards (Zohuri, 2019).

Hydrogen energy may be safely categorized as a renewable resource due to its broad availability and little environmental impact. Nevertheless, commercial hydrogen separation procedures often depend on fossil fuels such as coal, natural gas, and oil for energy. Hydrogen energy has the potential to reduce our dependency on fossil fuels, notwithstanding the difficulty of its implementation (Zohuri, 2019).

Hydrogen is a major source of power, but its generation and processing efficiency might be significantly enhanced with the aid of contemporary technology. Hydrogen, which can be produced from green technologies, may soon compete with electricity as a vital energy carrier. As an aviation fuel, heat source, energy generator, and propulsion system for "zero-emission" cars, it shows promise (Zohuri, 2019).

1.3.2 Hydrogen atom structure and hydrogen line

Hydrogen's structure is simple, consisting of a core proton and an orbital electron. Because electrons are quantum particles, a stable orbit for an electron is only feasible around a proton. Absorption or generation of photons is necessary for these orbital transitions. "Therefore, the absorption spectra of hydrogen are unique and contains several bands. These spectra are the result of photon-induced transformations between energy levels of electrons in their various orbits" (Gavrilyuk, 2013). These spectrum are called after the scientists who are credited with discovering them. Figure 7 illustrates the possible electron transitions.



Figure 7. Electron transitions, hydrogen wavelengths. (Gavrilyuk, 2013)



Figure 8. Structure of Hydrogen Isotopes. (Source: Google).

1.3.3 Introduction to the properties of hydrogen

"Hydrogen unlike any other material in the periodic table due to its distinctive properties, which will be discussed in this section. There are several chemical reactions and physical processes in which these properties play a crucial role" (Gavrilyuk, 2013).

There are three hydrogen isotopes found in nature (¹H, ²H, and ³H). Protium, deuterium, and tritium are these. Included among stable isotopes are proton and deuterium. The nucleus of deuterium is composed of both a proton and a neutron. "All the deuterium in the universe is believed to have been created in the early stages of the Big Bang and has remained unchanged since then. Deuterium is commonly utilized in daily life due to its lack of radioactivity and low toxicity" (Gavrilyuk, 2013).

"Heavy water is water in which a portion of the hydrogen has been replaced by deuterium. Deuterium and its derivatives are employed as non-radioactive labels and solvents for 1H-nuclear magnetic spectroscopy, respectively, in the area of chemistry". "Using heavy water, neutrons can be regulated and nuclear reactors can be cooled. Also being investigated is the use of deuterium as a fuel for industrial nuclear fusion" (Gavrilyuk, 2013).

$${}_{1}^{3}T \to {}_{2}^{3}He^{+} + e^{-} + v_{e}$$
 (1)

"Another hydrogen isotope, tritium (³H) has a nucleus composed of one proton and two neutrons. It decays into helium-3 by beta decompose, a radioactive process. The half-life is expected to be 12,32 years" (Gavrilyuk, 2013).

"Hydrogen is the first element in the periodic table and the element with the lowest mass, having an atomic number of 1. The average atomic mass of hydrogen is 1.00794 u. (1.007825 u for the most common isotope, H^0). Atomic hydrogen (H^0) has the smallest covalent radius of all chemical elements, measuring around 0.37". "Hydrogen is the lightest and smallest atom in nature, which is an essential characteristic for its mobility. Under certain conditions, hydrogen's low mass also makes it appropriate for use in tunneling techniques" (Gavrilyuk, 2013).

Hydrogen's remarkable chemical and physical properties derive from its simplicity. This gives rise to three common oxidation states: +1, 0 (equivalent to $1s^0$), and -1. (corresponding to $1s^1$ and $1s^2$ electronic configurations). "During the transitions from H⁰ to H⁻ and H⁰ to H⁺, the total number of electrons around the nucleus changes by 1e, or 100 percent. This is the greatest possible change in the periodic table, and it has had profound consequences on the basic chemical and physical properties of these three elements" (Gavrilyuk, 2013).

"Protium, which has just one proton and no neutrons, is the most abundant hydrogen isotope. This makes up almost 99.98 percent of all hydrogen. Since it is energetically

advantageous for H^0 to either completely fill its 1s shell or undergo ionization to create an Hor H^+ ion, H^0 is in an extremely unstable state. When hydrogen comes into contact with other atoms or molecules, it ionizes rapidly. The proton (H^+) has a radius of around 10⁻⁵, which is much smaller than the radius of other singly charged ions, which is normally 1" (Gavrilyuk, 2013).

"During chemical reactions, hydrogen loses one electron, transforming into a proton that aggressively seeks electron density from other atoms and molecules" (Gavrilyuk, 2013). "Due to its tiny size and lack of an electron shell, the proton may induce a substantial polarization in its surroundings. Due to the fact that this particle has few steric constraints, it may exist freely in a variety of surroundings, earning it the label "ubiquitous"" (Gavrilyuk, 2013).

Since of this, it is feasible to categorize a wide range of processes as proton transfer reactions, which, at first glance, may seem to be simple because they involve the mobility of a small nucleus without its electron shell. Hydrogen atoms, not protons, are transferred in a number of processes, most often when radiation or high-energy particles are present. Due to its low mass, hydrogen is extremely mobile in many different solids and liquids. "The proton has a high affinity for accepting a pair of electrons and demonstrates a very potent Lewis's acidity. Since the bare proton spontaneously eliminates electron density from even the weakest Lewis acids, which retain considerable Lewis's acidity even after partial solvation, the bare proton is never found in solution or inside solids" (Gavrilyuk, 2013). In addition, hydrogen has a unique feature known as a hydrogen bond, which is often seen in chemistry and may be observed in the structure of objects such as curly hair (Gavrilyuk, 2013).

Hydrogen may form covalent connections with several different elements. "Due to their small mass and strong static forces, these bonds have much greater vibrational frequency values than other types of bonds. Higher vibrational quantum energy and vibrational zero-point energy (1/2 hv) are the equivalent quantum mechanical notions" (Gavrilyuk, 2013).

Previously, "the discovery of subatomic particles was considered a very distant prospect. Hydrogen tunneling has been shown to be a widespread phenomenon. The de Broglie wavelength of an atomic particle with mass m and velocity u (and, thus, energy E = 0.5 mu 2) must be equal to the energy barrier width δ for the particle's wave properties to become apparent" (Gavrilyuk, 2013).

$$\lambda = \hbar / \sqrt{2mE} \tag{2}$$

where \hbar Planck's constant divided by 2π .

In addition, the altitude of the energy difference E must be much greater than kbT, where kb is the Boltzmann constant and T is the temperature, in order to prevent classical transitions over the barrier from occurring too quickly and to limit the likelihood of tunneling (Gavrilyuk, 2013). To ensure that single-particle tunneling transitions prevail over Arrhenius transitions above the barrier, the following inequality must be satisfied (Gavrilyuk, 2013):

$$\frac{\lambda}{d} > \frac{k_b T}{E} \tag{3}$$

And so,

$$T < \hbar/k_b \sqrt{2} d\sqrt{E/m} \tag{4}$$

"Below a particular temperature Tt, known as the "tunneling temperature," Arrhenius tunneling transitions may thus prevail. At temperatures below Tt, tunnel changes predominate over Arrhenius transitions, and vice versa above Tt" (Gavrilyuk, 2013). Goldanskii calculated the tunneling temp as the Arrhenius temp at which exponentially dominating tunneling transitions occur:

$$T_t = \left(\frac{\sqrt{2\hbar}}{k_d d}\right) \sqrt{E/m} \tag{5}$$

To calculate the tunneling temps, we use the conventional barrier height and width values E = 1 eV and d = 1 respectively. It is established that the tunneling temp (Tt) for protons is 320 K and for deuterium, 240 K. (Gavrilyuk, 2013). It may seem that these temperatures are excessive, but tunneling is always an issue when dealing with hydrogen, so don't disregard it just because they look excessive. Tunneling in hydrogen processes is feasible (Gavrilyuk, 2013).



Figure 9. The graph depicts the dependency of the electronic energy of the Hn species on the oxidized form of hydrogen, represented by n. The dashed lines show the hardness, which is the gradient of energy corresponding to electron density. The graph illustrates the link between energy but also electron density for various hydrogen oxidation states. (Gavrilyuk, 2013)

Hydrogen's unique qualities make it an essential component in several energy-related activities. These characteristics include its diminutive size, low weight, and propensity to shed its electron shell and then become an ionized proton. Hydrogen's properties make it suitable for energy conversion. It is capable of directly converting light or chemical energy into electrical energy, as well as breaking and creating chemical bonds. Hydrogen plays an active part in Earth's energy cycles. Presently, scientists and engineers are investigating the use of hydrogen in refineries and diesel engines, such as those used in automobiles (Gavrilyuk, 2013).

Property	Hydrogen	Comparison
Density (gaseous)	0.089 kg/m ³ (0°C, 1 bar)	1/10 of natural gas
Density (liquid)	70.79 kg/m ³ (-253°C, 1 bar)	1/6 of natural gas
Boiling point	-252.76°C (1 bar)	90°C below LNG
Energy per unit of mass (LHV)	120.1 MJ/kg	3x that of gasoline
Energy density (ambient cond., LHV)	0.01 MJ/L	1/3 of natural gas
Specific energy (liquefied, LHV)	8.5 MJ/L	1/3 of LNG
Flame velocity	346 cm/s	8x methane
Ignition range	4–77% in air by volume	6x wider than methane
Autoignition temperature	585°C	220°C for gasoline
Ignition energy	0.02 MJ	1/10 of methane

Table 1. Differences in properties of hydrogen and natural gas. (IEA, 2019)



Figure 10. Comparison of specific energy versus volumetric density. (Zohuri, 2019)

1.3.4 Molecular properties of hydrogen

Hydrogen occurs naturally as the H_2 particle, a highly combustible diatomic gas. Enthalpy of the H-H bond in H_2 is substantial, at 436 kJ/mol or 4.52 eV. (Gavrilyuk, 2013). This number is substantially greater than the bond enthalpies of other diatomic molecules, such as Li₂ (110,2 kJ/mol, 1.14 eV) and Cl2 (242.6 kJ/mol, 2.52 eV), and is relatively near to that of the tightly linked O₂ molecule (498,4 kJ/mol, 5.17 eV).

$$2H_{2(gas)} + O_{2(gas)} \rightarrow 2H_2O_{liquid} + 572 kJ$$
(6)
(286 kJ/mol per one Hydrogen atom)

One of the reasons why hydrogen is such a promising fuel is its high combustion energy per unit weight. Hydrogen combustion generates a great deal of useable energy, and the only byproduct is water, so it's beneficial for the environment (Gavrilyuk, 2013). Because of this, hydrogen is an excellent rocket fuel, particularly for rockets with several stages.

"However, challenges must be overcome for hydrogen fuel infrastructure to become practical and inexpensive" (Gavrilyuk, 2013). The section on hydrogen storage and transport elaborates on these obstacles.

Hydrogen gas must be handled with care since, within small concentration ranges (4-74%), it interacts explosively with air (ATEX). Certain mixtures may explode when exposed to a spark, heat, or sunlight (Gavrilyuk, 2013).

In addition to atomic hydrogen, orthohydrogen and parahydrogen are two spin isomers of the diatomic hydrogen (H₂) atom (H⁰). "In orthohydrogen, the two protons have parallel spins, resulting in a triplet state, while in parahydrogen, the two protons have antiparallel spins, resulting in a singlet state" (Gavrilyuk, 2013). "The ortho form of hydrogen does have a higher energy level and accounts for about 25% of hydrogen gas at standard temperature and pressure. Parahydrogen accounts for the remaining 75%. In the equilibrium ratio at very low temperatures, parahydrogen predominates over orthohydrogen" (Gavrilyuk, 2013). Since the rate where the ortho and para H₂ are changed to one another increases with temperature, liquid hydrogen must be stored and managed with care (Gavrilyuk, 2013).

"The thermal properties of parahydrogen differ greatly from those of normal hydrogen, mostly due to its greater rotational heat capacity. Even while the difference between the ortho and para forms of water and methylene is not as pronounced in terms of their thermal properties, the same holds true for other hydrogen-containing molecules and functional groups" (Gavrilyuk, 2013).



Figure 11. Image of Spin isomers of molecular Hydrogen (1/2). (Source: Google).



Figure 12. Spin of isomers of molecular Hydrogen (Source: Jim Farris).

1.3.5 Hydrogen in chemical Industry

In addition to its use as a fuel and transporter of clean energy, hydrogen has other significant uses. It plays a significant role in the chemistry of hydrocarbon-based energy resources such as mineral oil and methane gas.

As a solution to issues such as energy shortages, pollution, and the greenhouse effect, renewable energy is gaining popularity. Hydrogen is soon becoming a viable alternative to petroleum products as a clean energy carrier for many mobile and stationary applications (Gavrilyuk, 2013).

Hydrogen is present in water and organic molecules, and it may react with a variety of other elements to form new compounds. Proton exchange between solute molecules is vital to acid-base chemistry, where it serves a crucial role (Gavrilyuk, 2013).

"Significant quantities of hydrogen are required by sectors such as the petrochemical and chemical industries. It is used in several processes, including the production of ammonia, hydrodealkylation, hydrodesulfurization, and hydrocracking. Hydrogen is utilized as a hydrogenating agent to increase the saturation level of unsaturated fats and oils. Hydrogen is also required for the production of methanol and hydrochloric acid. When coupled with ores, hydrogen also acts as a reducing agent" (Gavrilyuk, 2013).

Hydrogen's importance in energy materials and industrial applications is enhanced by its participation in a vast array of chemical processes.

1.3.6 Hydrogen in engineering

"Hydrogen (H_2) is an element having several applications in chemistry, physics, and technology. Helium is utilized as a shielding gas in welding techniques such as atomic hydrogen welding and as a coolant in the rotors of electric generators in power plants due to its high

thermal conductivity. Liquid hydrogen is necessary for the investigation of superconductivity and other cryogenic phenomena. Hydrogen may be utilized as a lift gas in airships and balloons due to its low density" (Gavrilyuk, 2013).

"Hydrogen is also used as a tracer gas for leak detection in a variety of different industries, including the automotive, chemical, power generation, aerospace, and telecommunications industries" (Gavrilyuk, 2013).

"Compounds such as hydrogen copper (HxMemOn), where Me represents the transition metal, are generated as a result of the fact that hydrogen is so small that it fits well inside transition metal oxides. Hydrogen is soluble in all metals, including transitional, nanocrystalline, amorphous, and rare-earth metals. This solubility must be taken into consideration when designing pipelines and storage tanks, notwithstanding the challenges caused by hydrogen embrittlement in metals" (Gavrilyuk, 2013).

"Hydrogen's wide range of applications may be due to its unique properties, such as its small size, low mass, and electron-poor shell. Hydrogen is necessary for the "hydrogenation" of our planet owing to the many ways in which its effects may be perceived. The following part will examine hydrogen storage, transportation, and the challenges of putting it into existing natural gas pipelines" (Gavrilyuk, 2013).

1.4 Methods of storing hydrogen

First, we will provide an overview of how hydrogen is kept, and then we will discuss how it is delivered. "The phrase "hydrogen storage" refers to the materials used to retain hydrogen rather than hydrogen itself. Hydrogen's distinctive properties have a major impact on storage solutions. Consequently, the focus of materials research has turned to the discovery of the best material for hydrogen storage" (Gavrilyuk, 2013).

"Materials intended for hydrogen storage, whether for atomic or molecular hydrogen, serve as "boxes" with the objectives of improving hydrogen density and ease of release" (Gavrilyuk, 2013).

"It is impossible to exaggerate the significance of hydrogen storage to the hydrogen energy system. As a consequence, economic considerations have a substantial impact on the scientific and technological approaches to tackling this critical issue. As a portable energy carrier for applications such as automobile fuel cells, much research on hydrogen storage has concentrated on lightweight and tiny hydrogen storage types" (Gavrilyuk, 2013).

Therefore, it makes sense to begin with tried-and-true storage methods, such as highpressure storage and cryogenic applications. Later, we will explore cutting-edge approaches in materials science and storage technology, such as physiochemical storage in compounds that emit H₂ reversibly upon heating (Gavrilyuk, 2013).

1.4.1 General methods of hydrogen storage based on its phase

Liquid Phase Hydrogen

"Like space shuttles, hydrogen fuel cell cars operate most efficiently with liquid hydrogen (LH)". Its energy storage capability is about 2.6 times larger than that of gasoline per unit mass. This sort of energy storage requires around four times as much room as other types of energy storage to store the same amount of energy. Since it has a lower energy density per volume than hydrocarbon fuels like gasoline, liquid hydrogen is not as efficient. One liter of gasoline contains about 64 percent more hydrogen (116 g) than one liter of pure liquid hydrogen, emphasizing the density issue with pure hydrogen (71 g). Carbon in gasoline also contributes to energy release during combustion (Gavrilyuk, 2013).

"Because liquid hydrogen boils at a very low temperature of around 20.3 K (-253°C), cryogenic storage is necessary. In addition, there is a high energy cost related to producing fluid or highly compressed hydrogen (due to the liquefaction cost and the requirement for solid cryogenic tanks that are impermeable to minute H_2 molecules) and there are potential safety concerns associated with certain applications" (Gavrilyuk, 2013).

Compressed Gaseous Phase Hydrogen

Hydrogen gas is capable of being compressed and stored at very high pressures. Storage of compressed hydrogen differs from that of liquid hydrogen. Typically, hydrogen is used in hydrogen automobiles and maintained in hydrogen tanks at pressures between 350 bar and 700 bar. As a gas, hydrogen has a high energy density per mass, but a low energy density per area compared to hydrocarbons. Consequently, more room is required to store the same amount of energy in a tank. In addition, "large hydrogen tanks are often heavier than small hydrocarbon tanks that store the same amount of energy, everything else being equal. Higher gas pressure improves the energy density per unit volume, allowing for the use of smaller tanks without compromising storage capacity. Approximately 2.1% of the energy content of compressed hydrogen is lost during compression, mostly as heat in the compressor" (Gavrilyuk, 2013). When more gas is compressed, resulting in a reduced volume, if the energy is not recovered simultaneously, more energy is lost. Typically, infiltration rates in compressed hydrogen storage tanks are rather low (Gavrilyuk, 2013).

Hydrogen storage in underground Facilities – Geological storage

In salt domes, abandoned oil and gas fields, and subterranean caves, hydrogen is stored. The Imperial Chemical Industry has safely stored enormous quantities of hydrogen gas in caverns for decades. Gas is currently stored in these facilities because to the enormous economies of scale and high operational efficiency given by the rapid storage and retrieval of massive volumes of gas. Additionally, this storage system has a modest footprint and low yearly operating costs. Significant quantities of hydrogen must be stored underground as grid energy storage in salt domes, aquifers, excavated rock caverns, or converted mines in order to make hydrogen and other fuels or gases, such as natural gas or carbon dioxide, economically feasible. Through the use of a turboexpander, the electrical input for compressed storage at 200 bar may be decreased to 2.1% of the energy content. Geological storage provides outstanding possibilities for long-term and large-scale gas storage, but it is not an economically feasible choice for short-term or small-scale gas storage because to the massive amount of space it requires and the low operating pressure. In such cases, tanks and other analogous solutions are used (IEA, 2019).



Figure 13. Different types of caverns for underground hydrogen storage. (Source: Web).

1.4.2 Physical hydrogen storage

Physical storage is the most widely adopted method for hydrogen storage. In the realm of automotive applications, compressed gas vessels, commonly referred to as "tanks," are the prevailing technology for on-board hydrogen storage. These tanks operate at nominal working pressures of 350 and 700 bar (5000 and 10,000 psi). Although low-pressure liquid hydrogen, which has a boiling point near 20 K, is commonly used for large-scale transportation and storage of hydrogen, limited efforts have been dedicated to its development for automotive usage. However, researchers are exploring the potential of "cold" and "cryogenic" compressed hydrogen storage, which involves maintaining compressed hydrogen at temperatures below
ambient (150 K and below), as this approach enables higher hydrogen densities to be achieved through lower temperatures (Zohuri, 2019).

1.4.3 Hydrogen storage in solid state phase

Requirements for solid state storage

Solid-state storage is the preferred technique for hydrogen storage owing to its perfect safety and excellent efficiency ratings. Hydrogen storage materials have been the subject of substantial investigation because of the significance of this technical and scientific issue to society (HSMs). "As an example of a country that has embraced hydrogen storage, the United States has set targets for a 6.5 kg H₂ storage system, with even more severe goals set for 2015: 9.0 percent weight percentage and 81 kg H₂ per m³, which are in accordance with automotive industry expectations. The density of liquid hydrogen at 20 K (1 atmosphere) is only 70,8 kg/m³, making it difficult to attain these goals, while 5 kilograms of hydrogen gas occupy 56 m³ under typical conditions" (Gavrilyuk, 2013) (Basile, et al., 2017).

A good HSM must be able to successfully absorb and release hydrogen between 25 and 120 degrees Celsius, store large quantities of hydrogen in a reversible manner, and have a low molecular weight (to reduce the size of the storage tank). However, there is currently no material that fits all of these requirements. "High storage capacity (minimum 6.5 wt. percent hydrogen abundance and minimum 65 g/L hydrogen availability), thermal decomposition temperature of approximately 60-120°C for a hydrogen-charged material, reversibility of thermal absorption/desorption cycle with low temperature and pressure requirements, cost-effectiveness, and low toxicity with non-explosive and potentially inert hydrogen properties are all required for a solid HSM to be useful in real-world applications. The aforementioned objectives cannot be generalized to the HSM but only to the hydrogen storage system "(Gavrilyuk, 2013).

Hydrogen Storage in Porous Materials

"This process includes the storage of molecular hydrogen (dihydrogen) in extremely porous, purpose-built materials. Hydrogen molecules retain their chemical integrity and are adsorbed and desorbed without breakdown" (Gavrilyuk, 2013).

"For automotive applications, the exploitation of hydrogen physisorption in porous materials is a main strategy under investigation. The goal is to store considerable amounts of hydrogen at temperatures and pressures close to ambient. These materials must meet the volume, mass, and speed criteria for hydrogen gas charging and discharging. To enhance the adsorption capacities of porous materials, it is essential to comprehend why hydrogen does not naturally diffuse into the pores of the material" (Gavrilyuk, 2013; Zohuri, 2019).

The following are important metrics for this application: (i) the quantity of hydrogen adsorbed as a function of pressure. (ii) The temperature dependence of adsorption, which may be determined using isotherms and isobaric curves across a variety of temperatures. (iii) The adsorption enthalpies. (iv) The properties of adsorption and desorption.

The comparison of adsorption isotherm curves permits the estimation of the quantities adsorbed, while isotherms and isobaric curves may be used to determine the temperature dependence. These properties are crucial in establishing the hydrogen's charging and discharging behavior. In addition, the kinetics of adsorption and desorption must be measured in order to fulfill the need for rapid hydrogen charging and discharging (Gavrilyuk, 2013).

"The majority of porous materials explored for the physical absorption and storage of hydrogen are microporous. Frequently observed are ultra-micropores with diameters less than 0.7 nm, which roughly resemble the size of a single hydrogen molecule. Microporous materials are an important study topic in the realm of hydrogen storage materials (HSMs). The presence of micropores increases the hydrogen density inside the pore network relative to the gas phase, notably at temperatures below ambient conditions and at relatively low temperatures" (Gavrilyuk, 2013).

Zeolites

"Microporous aluminosilicate minerals comprised of AIO4 and SiO4 tetrahedra. Their distinctive characteristics, including as ion exchange, molecular sieving, and catalytic capabilities, make them very adaptable for a variety of practical applications. Zeotypes are comparable structures produced from elements such as P, Ga, Ge, B, and Be. These substances have varied crystallographic structures. Their crystalline structure results in microporous cavities and pores of uniform size, making them potential candidates for hydrogen storage. Zeolite structures are stiff, have large pore volumes, and have high specific surface areas" (Gavrilyuk, 2013).

Carbons

"As prospective hydrogen storage materials, a variety of microporous carbons, including activated carbons, carbon nanotubes (CNTs), nanofibers, and, more recently, microporous carbons, are being explored. Carbon has advantageous qualities as a host material, such as its low molecular weight, chemical stability, and diversity in synthesis. Particularly advantageous are porous carbons, which are widely accessible in commercial quantities and inexpensive for a variety of applications" (Gavrilyuk, 2013).

1.4.3 Interstitial hydrides

Formation of Hydrides

"Numerous metals often react with molecular hydrogen (H₂), resulting in the creation of metal hydrides. Different metals undergo these reactions at differing temperatures and pressures. Beginning with the adsorption of H₂ on the metal surface and concluding with the creation of hydrides, Figure 14 depicts the sequential processes involved in the interaction between hydrogen and a metal surface. Metal hydrides are compounds of the binary or higher level formed by the interaction of metallic elements or compounds with hydrogen gas. Hydrogen molecules disintegrate into hydrogen atoms at the surface of the host material, and then diffuse into the interstitial spaces of the host metal lattice. Understanding the process of hydride production through hydrogen adsorption on the metal surface and subsequent absorption of dissociated atomic hydrogen inside the metal structure necessitates the study of crucial aspects. These considerations help to clarify the complex interaction between hydrogen and metals" (Gavrilyuk, 2013).



Subsurface hydrogenSolid solution (a-phase)Hydride (b-phase)Figure 14. Hydrogen absorption in metals. Copyright (2008) American Chemical Society.

"The process of hydrogen absorption in metals can be divided into six distinct states. In the upper left-hand side, the metal and hydrogen gas exist as separate phases. At low temperatures, hydrogen molecules can be found in the physisorbed state, where they interact with the electrons on the metal surface. Subsequently, the hydrogen molecules dissociate and bind to the metal atoms at the surface, forming the chemisorbed state. The hydrogen atoms can then diffuse into a subsurface layer and further penetrate the metal host lattice, resulting in a solid solution known as the a-phase. Finally, as the hydrogen-hydrogen interaction becomes significant, leading to volume expansion, the hydride phase (b-phase) is formed" (Zohuri, 2019).

Hydrogen Storage in Hydrides

Hydrogen is absorbed by dissociating hydrogen molecules at the surface of the host material into hydrogen atoms and then diffusing these atoms via interstitial sites into the metal lattice. Nevertheless, "binary hydrides (MH_x , where M is a metal element and x are the stoichiometry of the hydride) often exhibit either excessive instability or excess stability, leaving them unsuitable for practical hydrogen storage". At practical temperatures, the pressures required for the hosting metal to reversibly absorb and release hydrogen are impractically high for the former and impractically low for the latter. "This is shown by the formation or breakdown enthalpy difference H being relatively large (negative) in the first case and relatively small (positive) in the second" (Gavrilyuk, 2013).

"When two or more metallic elements are combined, an alloy or intermetallic compound is more likely to generate a hydride of intermediate stability, particularly when one of the elements forms a stable hydride while the other does not. The initial event in the study of metal hydrides was the discovery of the hydrogen-absorbing properties of palladium around 150 years ago (Pd)" (Gavrilyuk, 2013).

1.4.4 Conclusions on hydrogen storages methods

Many assume that "solid-state hydrogen storage is the solution to the challenging problem of hydrogen storage. It is envisaged that the development of nanomaterials and nanosystems-based cutting-edge technologies would facilitate advancement in this sector". Numerous approaches, materials, and technologies have been evaluated so far in the effort to establish a hydrogen storage system with commercial feasibility. A challenge, however, is the great diversity of materials and methods utilized to do this. Hydrogen storage is a difficult issue that requires in-depth research and the capacity to synthesize data from a variety of sources (Gavrilyuk, 2013).

1.5 Production methods of hydrogen

Hydrogen production can be achieved through various methods. Currently, the predominant method involves utilizing fossil resources. However, electrolysis, a process where water is electrolyzed to generate hydrogen, has played a relatively minor role in global hydrogen production, despite being the primary method between 1920 and 1960. Initially, hydroelectric plants provided the energy for electrolysis, but they were eventually replaced by natural gas. As the cost of energy from renewable energy sources (RES) such as wind and photovoltaics continues to decline, the focus has shifted towards water electrolysis. The produced hydrogen can then be converted into hydrogen-based fuels or used in applications such as synthetic hydrocarbons and ammonia. These alternative forms of hydrogen are considered more compatible with existing technologies and infrastructures compared to simple hydrogen. This section examines the different methods of hydrogen production and its associated products (IEA, 2019).



Figure 15. Value chain of hydrogen. (IEA, 2019)

1.5.1 Today's hydrogen production and CO₂ emissions

As mentioned previously, hydrogen can be produced from hydrocarbons, biomass, water, or a combination of these sources. In 2019, approximately 275 million tonnes of oil equivalent (Mtoe) of energy were used for hydrogen production, accounting for just 2% of global primary energy demand. The primary source for hydrogen production is natural gas, particularly through a process called steam methane reforming. This method is employed in ammonia and methanol units, as well as in refineries where hydrogen plays a crucial role in various chemical processes. Natural gas accounts for about three-quarters of the annual global hydrogen production of approximately 70 million tons (Mt) of hydrogen, using around 205 billion cubic meters (bcm) of natural gas. This amount of natural gas represents 6% of its global consumption. Following natural gas, coal is the second largest contributor to primary energy for hydrogen production, mainly due to its extensive use in China. Coal power accounts for 23% of global hydrogen production, requiring 107 Mt of coal, which constitutes 2% of global

coal consumption. As of 2021, the production distribution was approximately 47% from natural gas, 27% from coal, 22% from oil, and 4% from electrolysis (IEA, 2019).

The reliance on natural gas and coal for hydrogen production results in significant carbon dioxide (CO₂) emissions. Specifically, natural gas production generates around 10 tons of CO₂ per ton of hydrogen (tCO₂/tH₂), while petroleum products contribute 12 tCO₂/tH₂, and coal contributes 19 tCO₂/tH₂. Consequently, the total CO₂ emissions amount to 830 million tonnes per year, equivalent to the combined emissions of Indonesia and the United Kingdom. Although most of this CO₂ is released into the atmosphere, ammonia/urea plants capture and utilize condensed CO₂ streams from steam methane reforming to produce urea fertilizer, accounting for approximately 130 million tonnes of CO₂ emissions each year (IEA, 2019).

The majority of natural gas is transformed to hydrogen by steam methane reforming (SMR). Several methods exist for reforming, but the three most prevalent are steam reforming, partial oxidation, and autothermal reforming (ATR). Hydrogen may be recovered from natural gas, LPG, and naphtha by methods of steam reforming. Through partial oxidation, hydrogen may be produced from heavy fuel oil and coal. When producing pure hydrogen, a synthesis gas comprising mostly carbon monoxide and hydrogen is produced, which is then converted to hydrogen and carbon dioxide. Gasification, in which feedstocks such as coal or biomass are turned to syngas, which is subsequently converted to hydrogen and carbon dioxide, and electrolysis, in which water is separated into hydrogen and oxygen, are two more techniques of creating hydrogen. However, electrolysis is no longer the primary way of creating hydrogen in the chlor-alkali industry.(IEA, 2019).



Figure 16. Producing hydrogen and hydrogen-based products. (IEA, 2019)

"The dashed lines in the figure depict the flow of synthesis gas, a mixture of hydrogen and carbon monoxide, created from hydrocarbon fuels and subsequently used in processes such as coal-to-liquids and gas-to-liquids to make synthetic hydrocarbons. In terms of emissions (particularly when paired with carbon capture, utilization, and storage - CCUS) or costs, converting hydrocarbons directly into synthesis gas has advantages over producing pure hydrogen from petroleum products and then combining it with CO_2 to produce synthetic hydrocarbons, especially when the CO_2 contribution is derived from fossil sources" (IEA, 2019).

However, the extraction and utilization of natural gas, coal, and oil as sources for hydrogen production result in the emission of greenhouse gases during their combustion. This applies to both the production and transportation phases, as turbines may burn natural gas from the transported product for their operation and to power compressors. To establish hydrogen as the energy carrier of the future, it is crucial to minimize these pollutants by adopting alternative production methods that do not emit CO₂, such as electrolysis powered by renewable energy sources, or by implementing carbon capture and storage (CCS) techniques. Figure 17 below illustrates the carbon dioxide emissions per gram of hydrogen production and how this is expected to change by 2030.





1.5.2 Production of hydrogen from natural gas

Although autothermal reforming (ATR) is also used, steam methane reforming (SMR) is the predominant and most extensively used process for producing hydrogen from natural gas. Along with water, natural gas acts as both a fuel and a raw material in this process. Approximately 30-40 percent of the natural gas is used as a fuel, resulting in the production of a "dilute" carbon dioxide (CO₂) stream, while the remainder is decomposed to create hydrogen and a more concentrated "process" CO₂ stream. It is anticipated that "SMR will continue to dominate large-scale hydrogen production in the near future owing to its advantageous economics and huge number of operating SMR units". "Nonetheless, Carbon Capture, Utilization, and Storage (CCUS) technology may be used to reduce the carbon dioxide emissions connected with this operation" (IEA, 2019).

CCUS may also be implemented into SMR and ATR hydrogen generation operations. Carbon emissions may be decreased by up to 90 percent by using CCUS in SMR units, when applied to both the process and energy streams. Several SMR-CCUS plants are now operational and produce around 0.5 million tons of hydrogen annually. In an SMR unit, CO₂ collection may be accomplished by numerous means. Separating CO₂ from the stream of high-pressure syngas may reduce emissions by up to 60 percent. Based on 2019 European natural gas prices, this method generally incurs a cost of around USD 53 per ton of carbon dioxide (tCO₂) for commercial installations (excluding ammonia or methanol production). Alternately, CO₂ may be extracted from the more diluted furnace exhaust gases, resulting in a decrease in emissions by at least 90 percent. This strategy boosts costs to roughly USD 80 per tCO₂ in commercial plants and USD 90-115 per tCO₂ in integrated ammonia/urea and methanol facilities, which produce CO₂ streams that are more diluted. Figure 18 demonstrates the process of producing hydrogen from natural gas using CCUS (IEA, 2019).



Figure 18. Process from gas to hydrogen with CCUS. (IEA, 2019)

Figure 19 compares the cost of producing hydrogen from natural gas with and without carbon capture, utilization, and storage (CCUS). "Across all areas, fuel expenses account for between 45 and 75 percent of overall production costs". Reduced natural gas prices in regions such as the Middle East, the Russian Federation, and North America result in comparatively lower hydrogen production costs. Depending on the design, "the incorporation of CCUS into SMR units often results in a 50 percent increase in capital expenditures (CAPEX) and a 10 percent rise in fuel expenses on average. In addition, operating expenditures (OPEX) tend to increase as a result of CO₂ transportation and storage costs. However, in the most promising places, the cost of producing hydrogen from SMR with CCUS ranges between \$1.4 and \$1.5 per kilogram of hydrogen, making it one of the most cost-effective low-carbon methods for hydrogen generation" (IEA, 2019).

The following section describes the chemical processes involved in steam methane reforming (SMR) (Melaina et al., 2013):

(

$$CH4 + H_2O \rightarrow CO + 3H_2 \text{ (re - forming)}$$
(7)

$$CO + H_2O \rightarrow CO_2 + H_2 \text{ (shift)} \tag{8}$$

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2 \text{ (overall)}$$
(9)





Figure 20. Hydrogen production process via steam reforming. (Stolten & Emonts, 2016)

1.5.3 Hydrogen production based on water and electricity

"The electrochemical technique known as water electrolysis may be used to recover hydrogen and oxygen from water. Currently, less than 0.1% of all hydrogen is generated using water electrolysis, and this method is mostly used in high-purity hydrogen applications such as electronics and polysilicon production. In addition, the production of chlorine and caustic soda by chlor-alkali electrolysis produces around 2% of the world's hydrogen output" (IEA, 2019).

In recent years, attention in electrolysis-based hydrogen production has surged owing to the dropping cost of electricity from renewable sources, particularly solar photovoltaic and wind. Depending on the used technology and load factor, "the efficiency of electrolysis systems may range between 60 and 81 percent. Approximately 3,600 terawatt hours (TWh) of energy would be required to produce the current dedicated hydrogen production of 69 million metric tons (Mt) from electricity, which is more than the annual energy output of the European Union" (IEA, 2019).

Moreover, 1 kilogram of hydrogen needs around 9 liters of water, and 8 kilograms of oxygen are created during the electrolysis process. In addition to its potential industrial use, the oxygen byproduct has possible medicinal applications. Currently, "steam methane reforming (SMR) uses 345 million cubic meters (m³) of water to produce 52 million tons (Mt) of hydrogen; if all of today's dedicated hydrogen production of around 70 million tons (Mt) were obtained through electrolysis, the water demand would be 617 million cubic meters (m³), which is approximately 1.3% of the global energy sector's water consumption" (IEA, 2019).

However, in water-scarce regions, a lack of easily accessible fresh water may cause problems. In rare circumstances, saltwater may be a viable choice, particularly near the coast. Reverse osmosis desalination is one method, albeit it consumes around 3 to 4 kWh per m^3 of water and costs between \$0.7 and \$2.5 per m^3 . Desalination has a minor impact on the cost of water electrolysis, contributing between 0.01 and 0.02 USD/kgH₂ to the ultimate cost of hydrogen production (IEA, 2019).

Electrolysis technology options

Currently, there are three primary electrolyte technologies available:

- 1. Alkaline electrolysis,
- 2. Proton Exchange Membrane (PEM) electrolysis, and
- 3. Solid Oxide Electrolysis Cells (SOECs).

Since the 1920s, the fertilizer and chlorine industries have used alkaline electrolysis because it is a proven and economically viable process. The efficiency range for these electrolyzers is between 10 and 100 percent. "Large-scale alkaline electrolyzers with outputs of up to 165 MWe have already been constructed in countries with accessible access to hydroelectric electricity, such as Canada, Egypt, India, Norway, and Zimbabwe. In the 1970s, when steam methane reforming and natural gas became the norm for hydrogen production, the majority of these electrolyzers were shut down. Alkaline electrolysis facilities have lower capital costs than competing electrolyte methods because they use less expensive materials" (IEA, 2019; IEA, et al., 2022).

In the 1960s, General Electric developed PEM electrolysis devices as an alternative to alkaline electrolysis to overcome some of the latter's operating limitations. Since pure water is used as the electrolyte solution in these systems, there is no need to collect and recycle the potassium hydroxide electrolyte commonly used in alkaline electrolysis. As PEM electrolyzers need less room, they may be more suitable for application in densely populated cities. The ability of fueling stations to create high-pressure hydrogen is advantageous to decentralized production and storage (achieving pressures of 30-60 bar without an additional compressor and up to 100-200 bar in some systems, compared to 1-30 bar for alkaline electrolysis devices). PEM electrolysis is also highly versatile in terms of its applications. In comparison to alkaline electrolysis, they are currently more costly and used less often. (IEA, 2019; IEA, et al., 2022).

Despite the fact that various companies are making strides in commercializing SOECs, they remain the least developed electrolysis technology. Since ceramics are utilized as the electrolyte in SOECs, cheaper components are required. They can operate in very hot settings with excellent electrical efficiency. As steam is used in the electrolysis process, they need a heat source. If the generated hydrogen is utilized for the creation of synthetic hydrocarbons (energy-to-liquid and energy-to-gas), then the waste heat from processes such as Fischer-Tropsch synthesis and methanation may be used to generate steam to support more SOEC electrolysis. Other heat sources, such as nuclear power plants, solar thermal systems, and geothermal systems, may also be used in high-temperature electrolysis (IEA, 2019). In contrast to alkaline and PEM electrolytes, SOEC electrolytes may serve as fuel cells in reverse mode, enabling hydrogen to be turned back into energy. This characteristic enables hydrogen storage facilities to offer grid balancing services, hence increasing the potential use of both types of technology. Controlling material degradation brought on by high operating temperatures is a significant barrier to the development of SOEC electrolytes (IEA, 2019).

Table 2 shows the key technical and cost elements of different electrolyte techniques.

	Alkaline electrolysis			PE	PEM electrolysis			SOEC electrolysis		
	Today	2030	Long term	Today	2030	Long- term	Today	2030	Long term	
Electric efficiency (%, LHV)	63–70	65–71	70–80	56–60	63–68	67–74	74–81	77–84	77–90	
pressure (bar)	1–30			30–80			1			
temperature (°C)	60–80			50–80			650 - 1 000			
lifetime (operating hours)	60000 - 90000	90000 - 100000	100000 - 150000	30000 - 90000	60000 - 90000	100000 - 150000	10000 - 30000	40000 - 60000	75000 - 100000	
Load range (%, relative to nominal load)	10–110			0–160			20–100			

Table 2. Technical and Economic characteristics of electrolysers (IEA, 2019).

MSc Oil and Gas Process Systems Engineering HYDROGEN COMPATIBILITY ASSESSMENT IN NATURAL GAS INFRASTRUCTURES

Plant footprint (m²/kWe)	0.095			0.048					
Electrical efficiency (%, LHV)	63–70	65–71	70–80	56–60	63–68	67–74	74–81	77–84	77–90
CAPEX (USD/kWe)	500 - 1400	400 - 850	200 - 700	1 100 - 1 800	650 - 1 500	200 - 900	2 800 - 5 600	800 - 2 800	500 - 1 000



Notes: CAPEX = USD 800/kW₄; efficiency (LHV) = 64%; discount rate = 8%. Source: IEA analysis based on Japanese electricity spot prices in 2018, JEPX (2019), Intraday Market Trading Results 2018.

1.5.4 production of hydrogen relying on coal

"In the chemical and fertilizer sectors, coal gasification for hydrogen production has been a well-established process for decades, especially in China, where it is widely used for ammonia synthesis. China is home to far more than 80% of the world's coal gasification plants, with more than 130 now operational. However, coal-based hydrogen production creates far more carbon dioxide than natural gas-based hydrogen production, around 19 metric tons of CO_2 each metric ton of hydrogen produced" (IEA, 2019).

Due to the high CO_2 emissions associated with its production, "hydrogen generated from coal cannot be included in a low-carbon energy system without carbon capture equipment. The low hydrogen-to-carbon ratio of coal (0.1:1 vs. 4:1 for methane) and higher levels of pollutants (sulfur, nitrogen, and metals) impede the widespread application of CCUS" (IEA, 2019).

"China produces the majority of coal-based hydrogen and employs coal gasification for ammonia synthesis. China has discovered that manufacturing hydrogen from coal is the most cost-effective method, with costs average between 0.6 and 0.7 Chinese Renminbi per cubic meter (about 1 USD per kilogram of hydrogen)" (IEA, 2019). CHN Energy, the largest energy provider in China, also generates the most hydrogen of any company in the world. "Its 80 coal gasifiers have a yearly production capacity of around 8 million metric tons of hydrogen, which is equivalent to approximately 12 percent of the world's exclusive hydrogen production. Coal with CCUS is currently the most cost-effective technique for producing cleaner hydrogen

Figure 21. Hydrogen productions costs from electrolysis using grid electricity. (IEA, 2019)

in China, with current technologies achieving CO_2 emissions as low as 2 kg CO_2 /kg H_2 and advanced technologies reaching as low as 0.4 kg CO_2 /kg H_2 " (IEA, 2019).



information on the underlying assumptions is available at <u>www.iea.org/hydrogenzo1g</u>. Source: IEA 2019. All rights reserved.

Figure 22. Hydrogen production cost using electrolysis, SMR- Natural gas and coal gasification in China (2019). (IEA, 2019)

1.5.5 Hydrogen production based on biomass

There are several ways to extract hydrogen from organic materials. "Biochemical processes use bacteria to convert organic resources into usable products, such as biogas, through anaerobic digestion or a fermentation byproduct consisting of acids, alcohols, and gases. Similar to coal gasification, biomass may be transformed into a gaseous mixture of carbon monoxide, carbon dioxide, hydrogen, and methane by thermochemical gasification. Anaerobic digestion for biogas production is the most established of these techniques, and it may be used to a number of waste streams, including sewage sludge, food industry waste, domestic garbage, and even some energy crops. However, the cellulose component of some plants may be degraded by fermentation. Lignin in biomass is particularly responsive to gasification units have been constructed throughout the world, but tar formation, which may contaminate the catalyst, remains an outstanding issue (Ericsson, 2017). The produced gas must always be treated further to eliminate hydrogen" (IEA, 2019).

In the foreseeable future, "until 2030, fossil fuels are expected to maintain their cost advantage in most regions, resulting in natural gas hydrogen without carbon capture, utilization, and storage (CCUS) having a cost range of USD 1-2/kgH, depending on local gas prices" (IEA, 2019). "With the exception of coal-based hydrogen production, fuel costs constitute the largest portion of hydrogen production expenses. Therefore, the future cost of hydrogen will be significantly influenced by the prices of electricity and natural gas, as well as factors that impact these costs, such as conversion efficiency. The cost of electrolysis production can also be affected by the capital expenditure (CAPEX) requirements, particularly when the units operate for a limited number of hours at maximum capacity" (IEA, 2019).



1.5.6 Hydrogen production cost between technologies



Figure 23. Hydrogen production costs. (IEA, 2019)

1.5.7 Hydrogen as by-product

In all the above hydrogen production methods, the desired product is not the main derivative but the by-product. In steam reforming we produce carbon dioxide with hydrogen as a by-product and correspondingly in electrolysis we produce oxygen without carbon dioxide, in pyrolysis of methane we produce carbon without carbon dioxide, pyrolysis of methane we hydrogen without CO_2 . In general, which technology to use for hydrogen production ultimately depends on the feedstock, energy, final desired price and production quantity of the main product. Below are the chemical reactions for the various hydrogen production methods.

Steam Reformer:
$$2 kg CH_4 + 4.5 kg H_2 O \rightarrow 32MJ$$
 energy (10)

$$\rightarrow 1 \ kg \ H_2 + 5.5 \ kg \ U_2$$

$$Electrolysis: 9 \ kg \ H_2 \ O \rightarrow 142 MJ \ energy \rightarrow 1 \ kg \ H_2 + 8 \ kg \ O_2 \tag{11}$$

$$Plasmolysis: 4 \ kg \ CH \rightarrow 19 \ MI \rightarrow 1 \ kg \ H_2 + 3 \ kg \ C \tag{12}$$

$$Plasmolysis: 4 kg CH_4 \rightarrow 19 MJ \rightarrow 1 kg H_2 + 3 kg C \qquad (12)$$

$$Plasmolysis: 5.3 kg CH_4 \rightarrow 63MJ \rightarrow 1 kg H_2 + 4.3 kg HC \equiv CH \qquad (13)$$

1.5.8 Other production processes

1) Steam reforming of alcohols (ethanol)

- 2) steam reforming of biogas (-//-)
- 3) Biological hydrogen production (fermentative) biophotolysis HBP
- 4) Gasification
- 5) Ammonia cracking
- 6) hydrogen production from algae
- 7) Nuclear production

1.6 Benefit of using hydrogen

In this section, some of the benefits of using hydrogen are presented as well. In general, beyond the fact that the use of hydrogen supports RES investments (to the extent that its production relies on them), the introduction of hydrogen into gas pipelines offers an efficient way of storage as a solution to the existing extensive natural gas network and facilities thereof.

Initially, we could divide the benefits of using hydrogen into four categories, as presented below:

- 1) Environmental benefits
- 2) Social benefits
- 3) Financial benefits
- 4) Other benefits

Incorporating hydrogen into the natural gas system may significantly decrease greenhouse gas emissions, particularly if the hydrogen is generated using low-carbon energy sources such as biomass, solar, wind, or hydrocarbons with carbon capture and storage (CCS) technology (Melaina, et al., 2013). Natural gas and its combination with hydrogen should get credit for the social and environmental benefits of sustainable hydrogen development in proportion to the amount of hydrogen present in the gas mixture. Hydrogen created from natural gas and utilized in FCEVs may help improve air quality by reducing hazardous pollutants like as sulfur oxides, nitrogen oxides, and particulate matter, and subsequently reducing the need for fossil fuels such as gasoline and oil (Melaina, et al., 2013).

Blending hydrogen with natural gas may provide consumers a renewable natural gas product with many of the same benefits as the introduction of biogas into the natural gas distribution network (Melaina, et al., 2013). Additional measures, like as the "adoption of a credit system, may be used to boost the fuel's social acceptability. Similar to the present renewable energy credit system in the power sector, a credit trading system for natural gas with a certain proportion of renewable hydrogen may be established" (Melaina, et al., 2013). "If appropriately organized, this credit system might incentivize the use of limited renewable energy resources for hydrogen generation, therefore enhancing the efficiency of current renewable power plants and enhancing the dependability of the nation's natural gas supply. The creation of such a system in Germany will give important empirical data for determining how renewable energy credits interact with hydrogen and natural gas" (Melaina, et al., 2013).

"In the "NaturalHy Project-Work Package 1," a life cycle analysis and socio-economic analysis were done to explore the potential benefits of integrating hydrogen into the natural gas network. Cogent Europe (Belgium), The Energy Research Center (Netherlands), Instituto de Soldadura e Qualidade (ISQ) (Portugal), Planungsgruppe Energie und Technik GbR (Germany), SAVIKO Consultants Ltd. (Denmark), and Technische Universität Berlin (Germany) all took part in this study led by Loughborough University (United Kingdom)" (Melaina, et al., 2013). According to Melaina et al., adding hydrogen to the current natural gas infrastructure offers several benefits (2013).

- 1. Significant reduction in greenhouse gas emissions when hydrogen is produced from renewable sources.
- 2. Potential benefits in automotive applications, such as reducing oil consumption and improving air quality by reducing emissions of sulfur dioxide, nitrogen oxides, and particulates.
- 3. "Green natural gas" when a hydrogen/natural gas mixture is used in existing devices for heat and electricity generation, similar to increasing the share of renewable generation in the electricity grid without requiring significant equipment changes.
- 4. Reduction in greenhouse gas emissions through hydrogen production from fossil fuels with CCS, although it does not reduce primary energy demand or limit the use of energy resources.
- 5. Potential benefits from selective hydrogen extraction, depending on the efficiency of separation technology and subsequent hydrogen and tail gas utilization.
- 6. Potential improvement in air quality by reducing emissions of sulfur dioxide, nitrogen oxides, and particulates when hydrogen is used in transportation to replace conventional diesel fuel.
- 7. Potential benefit of "greening" natural gas by directly using the hydrogen/natural gas mixture in existing devices for heat and power generation. To comprehensively understand the cost-benefit trade-offs of integrating hydrogen into the US natural gas



pipeline system, further extensive analysis and research would be required, beyond the scope of the European assessment (Melaina, et al., 2013).

Figure 24. Natural Gas transmission and distribution pipelines.

As a feedstock, "renewable natural gas is in great demand, especially in the United States. Through the Self-Production Incentive Program, California offers unique state incentives for energy generation, including \$4,500 per kilowatt (kW) for biogas systems and \$2,500 per kW for natural gas fuel cell systems (SGIP). Interestingly, California does not require the direct use of biogas in fuel cell systems, but it does permit the selling of credits. A methane-producing water treatment facility, for instance, has the option of purifying the methane and injecting it into the natural gas pipeline system, therefore obtaining certifications for sustainable natural gas production" (Melaina, et al., 2013). These certificates may be sold to a foreign firm that can then use the credits to define natural gas as renewable. This entity may then use the gas in a fuel cell system and receive credits as if the fuel cell system were powered by renewable gas. "Renewable methane is often priced between \$12 and \$14 per million British thermal units (MMBtu) in such contracts (GSE 2011). Correspondingly, a credit trading system may be established for the incorporation of renewable hydrogen into the natural gas system, giving equivalent possibilities" (Melaina, et al., 2013).

1.6.1 Environmental benefits of using hydrogen

In terms of environmental benefits, there is a large reduction in the environmental footprint of both natural gas infrastructure and in general all gas-powered transport and other applications that use natural gas. Specifically, by making the natural gas grid greener by reducing the intensity of coal generation (by "blending" natural gas and green hydrogen), environmental performance is improved for efficient gas-based power and heat production, helping decarbonization. By introducing hydrogen into natural gas facilities, there is improved flexibility in the electricity system, supporting the integration of renewable energy into it. The introduction of green hydrogen into the natural gas grid enables environmental benefits from the ever-increasing potential for green electricity, which can also impact other sectors linked to natural gas infrastructure, e.g. industrial sector for electricity and heat production, and in the transport sector.

1.6.2 Social benefits of using hydrogen

For the society itself, a stability and security in the energy supply is created, through the medium-term and long-term storage of hydrogen in natural gas pipelines. Of course, as hydrogen enters the pipeline, it becomes more and more socially acceptable, since any fears about its use disappear, with its use in fuel cells, as a larger element of an integrated energy system (Zohuri, 2019).

1.6.3 Economic benefits of using hydrogen

The transition of energy distribution to natural gas pipelines offers several advantages, including a reduced need for expanding the electricity grid and the utilization of existing natural gas infrastructure, especially in regions of Europe with a dense gas network. This shift enables efficient storage options for short-term, medium-term, and seasonal energy needs (Stolten & Emonts, 2016).

1.6.4 Further benefits of using hydrogen

Further promotion of renewable energy sources as they are used to produce hydrogen, which is injected into the gas grid and an overall higher capacity of the electricity/gas system to absorb changes in renewable electricity generation (Stolten & Emonts, 2016).

1.7 Hydrogen end uses

Hydrogen is extensively explored as a possible "energy carrier for applications such as fuel cell electric vehicles (FCEVs) and renewable energy storage" (Melaina, et al., 2013). Additionally, it may be used as a source of energy in static fuel cell systems for residences, backup power, and distributed generation. "Hydrogen blending into the current gas pipeline network is one suggested way for enhancing renewable energy sources, such as big wind farms. This strategy is possible when the concentration of hydrogen stays relatively low, often between 5 and 15 percent by volume. The implementation of this plan does not considerably enhance hazards associated with the use of gas mixtures in end-use devices, public safety, or the resilience of the current natural gas pipeline network" (Melaina, et al., 2013). However, "the appropriate hydrogen content may vary based on particular pipeline systems and natural gas composition, requiring a case-by-case review. Once hydrogen has been transferred, it must be used for a variety of purposes" (Melaina, et al., 2013).

Initially, hydrogen finds primary usage in refinery and chemical industries before extending its application in other sectors such as transportation, electricity production, ammonia production (e.g., as a green fuel in ships), synthetic fuels, infrastructure development, and pipeline operations. As the global community aims for zero greenhouse gas emissions, the utilization of green fuels, including hydrogen, is expected to increase its share of the total global energy consumption. The chart below illustrates the hydrogen penetration targets for 2025 and 2030, which represent significant milestones for the global energy community, leading toward the ultimate goal in 2050 (Stolten & Emonts, 2016).



Figure 25. Hydrogen consumption prediction for years 2025 and 2030. (IEA, 2020)

1.7.1 Hydrogen use in refineries

Incorporating hydrogen into refinery processes is a major technological development of the 20th century that is now commonplace. Both destructive and non-destructive hydrogenation techniques are used in the creation of hydrogen for use in the processing of petroleum fractions and products (Stolten & Emonts, 2016).

Hydrotreating, or simple hydrogenation, is a kind of non-destructive hydrogenation used to improve product quality without significantly affecting the boiling range. This method uses relatively "modest conditions to extract the volatile components". "Hydrogen reacts with compounds of nitrogen, sulfur, and oxygen to produce ammonia, hydrogen sulfide, and water, respectively. Gum- or insoluble-prone unstable chemicals are changed into more stable molecules" (Stolten & Emonts, 2016).

"Destructive hydrogenation, also known as hydrogenolysis or hydrocracking, transforms the raw material's greater molecular weight components into lower boiling point, higher value products" (Stolten & Emonts, 2016). "High hydrogen pressures and stringent operating conditions are required to reduce the likelihood of coke formation from unfavorable polymerization and condensation processes" (Stolten & Emonts, 2016).

"The addition of hydrogen during the thermal reaction of petroleum feedstock prevents the formation of coke and increases the yields of gasoline, kerosene, and jet fuel, all of which have lower boiling points. Optimal production of valuable petroleum products may be achieved by refineries by carefully controlling the role of hydrogen in the process" (Stolten & Emonts, 2016).

HYDROGEN APPLICATIONS IN REFINERIES				
Naphtha hydrotreater	Hydrogen is employed for the desulfurization of naphtha obtained through atmospheric distillation, requiring the hydrotreatment of the naphtha prior to its transfer to a catalytic reformer unit.			
Distillate hydrotreater	Hydrogen is utilized to desulfurize distillates following atmospheric or vacuum distillation. In			

 Table 3. Hydrogen applications in a refinery. (Speight, 2020)

	certain units, the hydrogenation of aromatics is conducted to convert them into cycloparaffins or alkanes.
Hydrodesulfurization	Sulfur compounds undergo hydrogenation to convert them into hydrogen sulfide, which serves as the feed for Claus plants.
Hydro isomerization	Straight-chain paraffins are transformed into iso- paraffins through a conversion process aiming to enhance the properties of the end product, such as the octane number.
Hydrocracker	Hydrogen is utilized to enhance the quality of heavier fractions by converting them into lighter and more valuable products.

1.7.2 Hydrogen use in chemical Industries

"As the largest producer and consumer of hydrogen in the world, the chemical industry plays a crucial role. Many steps of the chemical value chain are dependent on hydrogen. It is mostly used as a chemical intermediary in the production of organic and inorganic chemicals. It may be employed as a reactant or coupled to other molecules to expedite the creation of a desired product. Ammonia production for nitrogen-based fertilizer is one of the most crucial hydrogen-dependent global activities" (Stolten & Emonts, 2016).

"Hydrogen could also be generated via chemical processes. In the chlor-alkali process, for instance, high-purity hydrogen is produced in massive quantities using chlorine. Depending on the viability and economics of separation and purification, side streams with a high concentration of hydrogen and other unwanted elements may be used as fuel for process heat generation" (Stolten & Emonts, 2016).

"Molecular hydrogen has several uses in the chemical and metal industries as a reducing agent. Beneficial for transforming raw materials such as ores and metals into their final forms. This aptitude for reduction also assists in the removal of contaminants from the surfaces of semiconductors and sulfur-containing chemicals from mixtures. In addition, hydrogen is employed extensively in the chemical industry to regenerate catalysts. The following image illustrates how hydrogen is used in several economic areas" (Stolten & Emonts, 2016).



Figure 26. Hydrogen application in various industries and sectors. (Stolten & Emonts, 2016)

1.7.3 Hydrogen usage for ammonia

"As the greatest consumer of hydrogen, ammonia is essential to several businesses. In 2012, the global ammonia output reached 166 million metric tons, necessitating the generation of around 29 million metric tons of hydrogen". This need continues to increase in tandem with the world's growing population, as a result of the demand for nitrogen fertilizers. A considerable amount of the produced ammonia is converted to urea using the CO_2 byproduct of the hydrogen-producing steam reforming process. In 2012, worldwide urea output was projected at 162 million tons, with Europe producing roughly 17 million tons. In addition, ammonia acts as a precursor for a number of organic nitrogen molecules. Nitric acid, a crucial byproduct, is created by oxidizing ammonia with air over a platinum catalyst, a process known as the Ostwald procedure" (Stolten & Emonts, 2016). "For ammonia manufacturing, the Haber-Bosch process, a catalytic reaction involving high temperature (300-550 °C) and pressure (15-25 MPa, 150-250 bar), is mostly utilized globally" (Stolten & Emonts, 2016).

1.7.4 Hydrogen use for methanol

In the chemical sector, "methanol is very important since it is the second greatest user of hydrogen". Formaldehyde, methyl tert-butyl ether, acetic acid, and fuels may all be made from methanol using procedures such as the methanol-to-gasoline or methanol-to-olefin pathways. "About 48 million tons of methanol were produced worldwide in 2010, with Europe producing about 1.6 million tons of that total. Natural gas is utilized as the principal feedstock in methanol manufacturing, making up around 75% of the total". Coal is also a major contributor, as are other feedstocks such as naphtha and heavy oil. Methanol has been offered as an alternative fuel for vehicles and a significant component in the chemical industry's value chains. "Methanol is a key component in the manufacturing of many different chemicals and has the potential to disrupt present value chains in the chemical sector" (Stolten & Emonts, 2016).

As was previously noted, steam reforming and coal gasification are two examples of syngas generation techniques necessary for methanol manufacturing. The following explanation is based on the LurgiMegaMethanol Process, which is the current gold standard for producing methanol at industrial scale (Stolten & Emonts, 2016).



Figure 27. Process scheme for methanol production. (Stolten & Emonts, 2016)

1.7.5 Hydrogen use in FCEV

"Fuel selection is crucial for both mobile and stationary applications, and although hydrogen is regarded the best fuel for fuel cells, its infrastructure-wide availability is restricted at present. Hydrogen gas may be held at 70 MPa in automotive systems and utilized as fuel for polymer electrolyte fuel cells (PEFCs)" (Stolten & Emonts, 2016). "Car stacks fitted with PEFCs can provide 50 to 70 kWe of electricity to an electric motor for propulsion, allowing for a theoretical range of 400 to 500 kilometers. For future developments, however, major expansion of the hydrogen infrastructure and the development of sustainable hydrogen generation sources are required" (Stolten & Emonts, 2016). "The power densities of present hydrogen storage devices, both in terms of mass-specific and volumetric features, do not fulfill the needs of large fuel cell systems utilized in mobile applications such as trucks, ships, and aircraft. Liquid hydrogen storage systems may serve as an intermediate option for mediumsized aircraft systems with electrical power between 10 and 100 kWe. As more room may be accommodated to a certain amount on aircraft, mass concerns become more essential than volumetric needs in this instance" (Stolten & Emonts, 2016). This is owing to the fact that greater fuel consumption is precisely proportional to a 0.16 kg per 1 kg rise in mass weight. However, bigger fuel cell systems (>150 kWe) will need liquid energy carriers in the long term. Hydrogen is not a viable energy carrier for long-haul vehicles owing to the difficulties connected with lengthy distances and the driver's need to handle extra fuels. Alternative fuels such as LPG, LNG, and DME are being studied in addition to diesel, the predominant fuel in heavy transport. LPG is considered a superior option to gas oil and heavy fuel oils in maritime applications compared to hydrogen. For ferries and small boats working in close proximity to shores and ports, hydrogen is the fuel of choice. Methanol is another alternative for sailing yachts, since it may be utilized directly in direct methanol fuel cells (DMFCs). Propane-butane (LPG) combination is envisioned as a viable energy carrier for recreational applications, such as camping gas. Lastly, natural gas is the most common source of hydrogen for fixed home heating systems, followed by kerosene (in Japan) or EL heating oil (in Europe) (Stolten & Emonts, 2016).

1.7.6 Other uses of hydrogen

• <u>Agricultural</u>

Hydrogen finds widespread use in the agricultural sector, particularly in the form of ammonia, also known as anhydrous ammonia, which serves as a crucial component in fertilizers. Additionally, hydrogen in the form of ammonia can be utilized as a refrigerant, commonly referred to as R-717, offering efficient cooling capabilities.

• Food Industry

Hydrogen is employed in the process of converting unsaturated fats into saturated oils and fats, which includes the production of hydrogenated vegetable oils such as margarine and butter spreads.

• <u>Metalworking</u>

Hydrogen finds applications in various processes, including metal alloying and iron production through methods like flash smelting.

• <u>Welding</u>

Hydrogen is employed in Atomic Hydrogen Welding (AHW), a specific type of arc welding that utilizes a hydrogen atmosphere.

• Flat Glass Production

A mixture of hydrogen and nitrogen is employed to safeguard against oxidation and mitigate potential defects during the manufacturing process.

• <u>Electronics manufacturing</u>

Hydrogen serves as a highly effective reducing and etching agent in the production of semiconductors, LEDs, displays, photovoltaic components, and other electronic devices.

• <u>Medical</u>

Hydrogen gas is utilized in the production of hydrogen peroxide (H_2O_2) . Additionally, in recent times, hydrogen gas has gained attention for its potential therapeutic applications in treating various diseases.

• <u>Space exploration</u>

Liquid hydrogen (LH₂) fuel has been a significant factor in space exploration since its introduction during NASA's Apollo program, primarily in the secondary stage of Saturn rockets. Presently, the utilization of LH2 is growing to encompass a wider range of government and commercial entities, including United Launch Alliance, Boeing, and Blue Origin.

• <u>Aviation</u>

A number of experimental initiatives have employed hydrogen fuel cells in endeavors such as the Pathfinder and Helios unmanned long duration aircraft. More recently, Airbus has introduced its "ZEROe" aircraft concepts that incorporate liquid hydrogen as a fuel source to power modified gas turbine engines.

• <u>Public transportation</u>

Hydrogen fuel cells are indeed being investigated as a possible energy source for trains, buses, and other modes of public transportation. Notable cities, including Chicago, Vancouver, London, and Beijing, have tested hydrogen-powered buses. Germany has already installed hydrogen-powered trains, and comparable models are expected to be implemented over the next five years in the United Kingdom, France, Italy, Japan, South Korea, and the United States.

1.8 Hydrogen separation/extraction methods

Due to the existence of many coexisting gaseous by-products that might limit the yield of hydrogen, "the separation of hydrogen is a key problem in industrial operations". "It is essential to distinguish between the "separation" and "purification" processes, with the former focused on initial hydrogen concentration and the latter on hydrogen upgrading" (Basile, et al., 2017).

"Processes for hydrogen separation are classified according to several parameters. Conventional techniques for hydrogen separation include cryogenic methods and adsorption techniques such as Pressure Swing Adsorption (PSA), Vacuum Swing Adsorption (VSA), Temperature Swing Adsorption (TSA), and Electrochemical Swing Adsorption (ESA), which are explained in more detail in the following sections" (Basile, et al., 2017).

1.8.1 Cryogenic process separation

"The cryogenic or partial condensation procedure used to separate hydrogen depends on the differential in volatility between the components of a gas mixture existing at low temperatures. This results in the condensation of some components while hydrogen stays in gaseous form, allowing for the separation of hydrogen from other contaminants. Hydrogen is highly volatile; however its volatility is affected by operating pressure" (Basile, et al., 2017). "The cryogenic process progressively lowers the temperature, producing the condensation of water vapor, fuels, CO, and N_2 since they are less volatile than hydrogen. Consequently, hydrogen, which is more volatile, persists in the gaseous form, enabling its separation from other gaseous contaminants. The success of the cryogenic process is contingent on variables such as operating temperature, pressure, and input gas composition" (Basile, et al., 2017).

"As with any other technique, the cryogenic process has limits. One drawback is the need to use compressors to boost the low pressure of the gas mixture. In the cryogenic process, reaching very low working temperatures and compressing the incoming gas mixture are both expensive and energy-intensive tasks. Furthermore, the combustible and poisonous character of cryogenic fluids, as well as the possibility of equipment blockage owing to the freezing of water or CO_2 in the intake mixture, create additional hurdles for this operation" (Basile, et al., 2017).

1.8.2 Pressure Swing Adsorption

"PSA is perhaps the most used method for separating hydrogen. This method, which was developed in the 1930s and used in the 1960s, involves varying the pressure at different stages during the operation. owing to the fact that distinct compounds have different physical adsorption affinities for the same adsorbent under circumstances of constant temperature. Hydrogen is removed from the original gas mixture because to its high volatility and low polarity, whereas pollutants such as N_2 , CO_2 , CO, hydrocarbons, and water vapor are adsorbed to the surface of the adsorbent. Gas component, adsorbent material, gas component partial pressure, and operating temperature all influence adsorption" (Basile, et al., 2017).

"The key steps of a PSA process are adsorption of a gas component, pressure balancing, desorption of the gas (regeneration), and repressurization. First, the adsorbent absorbs the gas's contaminants; next, the adsorbent's surface becomes saturated and cannot absorb any more gas molecules. In this situation, the adsorbent must be refreshed by desorpting the gases by reducing the pressure to slightly above atmospheric. When the working pressure is once again increased to the adsorption level, the cycle is complete" (Ruthven, et al., 1994; Basile et al., 2017).

The scientific community has highlighted the following PSA drawbacks as the most significant (Basile et al., 2017):

- 1. High production cost due to low recovery rates.
- 2. Significant production of CO_2 as a pollutant, attributed to its greenhouse effect.
- 3. Elevated noise levels resulting from successive compressions and expansions during the cycle.
- 4. Challenges related to valve leakage during the opening and closing stages.
- 5. Reduction in adsorbent capacity and difficulties in the desorption process due to temperature changes over time and position in the exothermic adsorption stage.
- 6. Absence of universally applicable design rules for PSA units, owing to the complex nature of the process and the multitude of decision parameters involved.

1.8.3 Vacuum Swing Adsorption

VSA (Vacuum Swing Adsorption) can be accurately described as a subset of the broader PSA (Pressure Swing Adsorption) category. The core principle of the VSA process is the separation of hydrogen from a gas mixture based on varying levels of adsorption on the adsorbent, which aligns with the fundamental principle of the PSA process. However, the VSA unit operates at temperatures and pressures that are near ambient or below atmospheric pressure, setting it apart from other processes. Additionally, unlike PSA, VSA utilizes a vacuum to propel the gas through the separation process, while PSA typically vents to atmospheric pressures and employs a high-pressure gas mixture as a feed. Despite these differences, VSA and PSA share common adsorbents (Basile, et al., 2017).

1.8.4 Temperature Swing Adsorption

The TSA (Temperature Swing Adsorption) mechanism is cyclical, like Pressure SA and Vacuum SA. In contrast to TSA, temperature rather than pressure determines adsorbent renewal in TSA. In order to enhance gas consumption, adsorption happens at a low temperature, while regeneration occurs at a higher temperature (Basile, et al., 2017). A TSA adsorbent must have a wide surface area, comparable to that of a PSA adsorbent, in order to be effective. There are isotherm values for common adsorbents such as activated carbon, silica gel, alumina, and zeolite in the literature (Basile, et al., 2017).

TSA has more upfront costs than PSA, but it saves money and decreases stress in the long term. TSA is not widely used, however, because to its high energy consumption and the need for considerable adsorbent stocks. Because the heating and cooling operations take so long, the cycle time is so lengthy and more absorbent is required. TSA becomes the preferred approach when PSA fails to achieve an acceptable degree of product purity (Basile, et al., 2017).

1.8.5 Electrical Swing Adsorption

Fabuss and Dubois were the first to propose ESA (Electric Swing Adsorption) in 1971. ESA is a specific type of TSA process that eliminates the need for transporting or heating the adsorbent, as well as large temperature and pressure changes or system concentration, by generating heat in-situ (Basile, et al., 2017). This is achieved through the use of a highly conductive adsorbent material called "carbon-bonded activated carbon fiber," which relies on the Joule effect and an applied electric current. The ESA process allows for rapid desorption of adsorbed gases with low-voltage electrical current, while maintaining constant system pressure and slightly altering the temperature (Basile, et al., 2017).

ESA procedures offer several advantages over conventional TSA methods. These include faster heating rates, resulting in smaller systems, and improved heating efficiency due to direct energy delivery to the adsorbent. The effects of thermal and gas diffusion contribute to better desorption through similar heat and mass fluxes, regardless of the heat capacity of the heat source and the heating rate to heat transfer rate between the source and the adsorbent (Basile, et al., 2017).

1.8.6 Membrane technology

Traditional processes may be difficult to use on an industrial scale owing to their primary constraints. These processes are not only time-consuming and expensive, but they also pose security hazards. A new generation of membrane-based approaches for hydrogen separation has recently emerged (Basile, et al., 2017).

"A membrane is a semipermeable barrier that allows passage of just certain substances. Consequently, it is an excellent process for eliminating undesirable elements from a gas or liquid mixture while retaining the desired ones. Other forms of separation processes may be driven by concentration, temperature, or electrical potential gradients. Partial pressure drives the majority of gas separation procedures" (Basile, et al., 2017).

The yield of a separation process is governed by the permeability and selectivity of a membrane. The first indicates the percentage of a component that will flow through the membrane, while the second reveals the percentage of a mixture that will be separated by the membrane. Permeation across a membrane is related to its thickness and influenced by a variety of variables, including pressure gradient, gas solubility inside the membrane, and gas diffusivity across the membrane (Basile, et al., 2017). The permeation flow of a component is influenced by the membrane material, microstructure, and operating temperature (Basile, et al., 2017).

As separation methods, "membrane-based gas separation techniques use molecular sieving, solution-diffusion, surface diffusion, viscous flow, and Knudsen diffusion" (Basile, et al., 2017).

Tan (2015) asserts that membranes may be classified based on a variety of features, including their thickness, phase, symmetry, and polarity. However, membranes are often classified according to the materials from which they are made. Organic (polymeric), inorganic

(metal, metal alloy, zeolite, carbon molecular sieve, and ceramic), and composite (hybrid) membranes will be investigated in further detail in the subsequent sections (Basile, et al., 2017).

1.9 Dissertation basis

On the basis of the previous sections, a thorough grasp of hydrogen's importance has been developed. Hydrogen's methods of manufacturing, techniques of purification, methods of storage, and ultimate uses have been addressed. To create a smooth relationship between production and consumption, however, a safe route of conveyance from the production site to the final consumer must be devised. In the part that follows, we will examine the transportation of hydrogen via natural gas pipelines, as well as the difficulties faced during its integration and the appropriate mitigating strategies. This research focuses mostly on the basic issues of incorporating hydrogen into existing natural gas transmission networks.

Whenever hydrogen levels in natural gas are relatively low, it may be necessary to make only minimal modifications to the operation and maintenance of the pipeline network (Melaina, et al., 2013). The natural gas and hydrogen combination may be employed directly in end-user systems, or the hydrogen can be purified and used in applications such as automobile fuel cells. According to current research, concentrations of less than 5 to 15 percent hydrogen (by volume) pose only minimal problems (Melaina, et al., 2013). However, the location of the pipeline and the composition of the natural gas (which changes depending on production and state restrictions) must be taken into account. Concentrations ranging from 15 to 50 percent provide more issues and demand the implementation of suitable safeguards. Examples include modifying household appliances to accommodate larger quantities of hydrogen (due to the different auto-ignition and fire point temperatures between hydrogen and natural gas) or rising compression capacity along the distribution network for industrial users (as hydrogen is transported in smaller quantities per delivery volume) (Melaina, et al., 2013).

Mixtures containing more than fifty percent hydrogen provide considerably more complicated issues, including pipeline material concerns, safety considerations, and modifications necessary for end-use devices and other applications (Melaina, et al., 2013).

"Hydrogen blending is a possible means of boosting the production of renewable energy sources such as wind farms, since it enables the storage and delivery of hydrogen at many places". "Using the wide reach and scale of the existing natural gas infrastructure, even minor blending ratios (below 3–5 percent) may absorb considerable quantities of surplus or commercially unviable wind or solar electricity. By mixing renewable hydrogen (green hydrogen) with natural gas, the final natural gas product distributed to customers may be made more environmentally friendly" (Melaina, et al., 2013). However, this strategy requires further study and analysis, and its viability may be limited by location-specific considerations. However, it has potential as a realistic long-term scenario.

"Hydrogen pipeline delivery is regarded as a cost-effective way for carrying hydrogen over long distances and in huge quantities; nevertheless, the development of an enormous dedicated hydrogen pipeline system is very costly and might take several decades to complete" (Melaina, et al., 2013). As a market matures, different forms of transportation may be implemented. In a developed hydrogen infrastructure, tankers or on-site manufacturing may supplement pipeline deliveries during the early phase. "If hydrogen blending with natural gas and subsequent separation proves economically viable in the early market phase, it might possibly function as an extra and sustainable method of transportation in the long run" (Melaina, et al., 2013).

CHAPTER 2: TRANSPORTATRION OF HYDROGEN VIA NATURAL GAS INFRASTRUCTURE

Starting this chapter, we will first refer to some basic elements for hydrogen transport and some technical characteristics. Then, we will present what is happening at the global and European level, in terms of its transfer, as well as in the limitations of the respective networks. We will also mention the projects that are either at the stage of the idea and cooperation agreements or at the stage of Basic Engineering, FEED or at the stage of their implementation. Finally, we will reach the pipeline network of Greece, its future development, and the plans for the integration of hydrogen into the Greek economy. In the first section of the chapter, we will describe the modes of hydrogen transport.

2.1 Hydrogen transportation methods

To begin with, hydrogen transport is not an issue that has arisen in the last decade but as early as the 1930s there have been attempts to transport it by pipelines. Nevertheless, the transfer of hydrogen can be done in various ways such as:

1) With pipelines (either natural gas or exclusively for hydrogen, gaseous form).

2) Compressed in tanks and containers, transport by trains or trucks (gaseous form or liquid form).

3) In liquid form via ships.



Figure 28. Supply chain of natural gas.

These can be classified into two broad categories: 1) continuous transfer (pipelines) and 2) batch (other methods). Each mode of transportation also has specific limitations. When it comes to transporting hydrogen by trains and trucks, only small quantities and distances of up to approximately 1100 km are feasible, beyond which the costs become prohibitive. This method of transport is not widely favored, particularly for ammonia transportation. In contrast, transport pipelines play a crucial role in carrying hydrogen continuously and in large quantities over distances ranging from 1000 km to 4000 km. It is worth noting that there are already gas pipelines exceeding 4000 km in length. Subsequently, transport ships take the lead by carrying substantial amounts of liquefied gas over distances exceeding 4000 km. Due to the high shipping costs, it is not advisable to transport hydrogen in its gaseous form due to its low energy content per volume. To make it more cost-effective, hydrogen is transported either in liquefied form or in the form of ammonia, as they have higher energy content. However, it is important to recognize that shipping ammonia incurs greater costs due to reconversion losses. Therefore, ammonia is suggested to be better suited for decarbonizing sectors where it can be directly used as a without necessitating conversion of fuel or feedstock (Gerboni, 2016).

2.1.1 Hydrogen gas and liquid are transported via road and trail

These means of transport are widely used, especially with tanks built to resist high pressure. "Larger containers (>150 liters) are hauled on tube trailers, although industrial-sized tanks (50 to 150 liters) are also available. Typically, smaller containers are bulk-filled and

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packaged at central production facilities before being sent to retailers and consumers. Without access to other forms of hydrogen infrastructure, such as pipelines or local production facilities, tube trailers fill dispersed storage at demand sites or serve as permanent storage at refueling stations" (Gerboni, 2016). In a typical configuration, "nine pipes holding a total of 20,000 liters would be used. Although greater pressures are achievable and essential to improve the economic sustainability of this step of the hydrogen cycle, the typical filling pressure for these cylinders is between 18 and 25 MPa" (Gerboni, 2016). Cylinders that can bear pressures of up to 70 MPa are available, however they are mainly intended for on-board vehicle storage rather for hydrogen transportation. Manufacturers of cylinders have chosen the more expensive Type II, Type III, and some Type IV cylinders to meet the need for greater pressure levels. as reported by (Gerboni, 2016).

Increasing the internal pressure to 40-70 MPa, however, may minimize the cost per MJ of transported hydrogen. "Type I cylinders or transfer containers are often used on tube trailers. As of the year 2020, the US Department of Energy (DOE) has mandated a maximum filling pressure of 52 MPa for tube trailers. The possibility of using composite materials for pipe production is also being explored" (Gerboni, 2016). "Valve and safety device components, as well as transfer cylinders, should be made from 34CrMo4 alloy steel. Since there is a large temperature difference between the outside and inside surroundings, transporting the liquid from the tank to the end destination is a crucial stage in the process" (Gerboni, 2016). There is a risk of injury to personnel as well as property and environmental damage as a consequence of flashing caused by this temperature disparity. In addition to the danger of flashing, cargo is lost throughout all stages of transporting liquid hydrogen due to normal boiling. When moving hydrogen from one tiny dewar to another, around 20% is lost, but when moving from a trailer, about 10% is lost. Therefore, we utilize storage and transportation containers interchangeably wherever we can. as reported by (Gerboni, 2016).

"Tanker capacities range from 20,000 to 50,000 liters, while vessels carrying as much as 4,000 kg of liquid hydrogen have been seen. Tank interior pressure is typically modest, falling between 0.6 and 1 MPa. By using rail and tanks the same size as those used for trailers, liquid hydrogen may be moved across the country. Liquid hydrogen is often transported by railroad, especially in the petrochemical sector (refineries)" (Gerboni, 2016). While on-site production and consumption of hydrogen is becoming more common, pipelines with intermediate storage stations are still the standard in the industrial sector. as reported by (Gerboni, 2016).



Figure 29. Hydrogen tube trailer.



Figure 30. Type IV pressure vessel for hydrogen.

2.1.2 Ocean transportation via shipping LH₂

From the late 1980s until the late 1990s, two research groups with largely overlapping aims did extensive study on marine hydrogen transportation as said by Gerboni, (2016). The major objective was to create a method for transferring hydrogen across great distances from low-cost production plants to high-demand locations. Despite the high energy investment necessary for liquefaction and its lower energy density compared to its nearest rival, LNG, liquid hydrogen was the dominating option (Gerboni, 2016).

"As part of the Euro-Quebec Hydro-Hydrogen Pilot Project, the first complete research on marine hydrogen transportation was conducted (EQHHPP). This project, backed by the European Commission (JRC Ispra), the Government of Quebec, and a number of industrial partners, including a number of German firms, attempted to capitalize on Quebec's difficult-tostore excess hydroelectric power" (Gerboni, 2016). "Initial research revealed that liquid hydrogen would be the most cost-effective option, particularly when the targeted product at the destination was liquid hydrogen itself (as methylcyclohexane releases hydrogen gas, necessitating liquefaction at the port of arrival)" (Gerboni, 2016). When all the hidden costs associated with gasoline, such as maintenance fees, environmental protection owing to leaks and accidents, and unanticipated climate impacts are included, the cost gap between hydrogen per kW and gasoline would be little, according to the research. ExternE and NEEDS, sponsored by the European Union, aimed to quantify these hidden costs and proved that they should not be ignored (Gerboni, 2016).

"The Japanese government began the second research as part of a long-term initiative (1993-2020) to assess the viability of hydrogen as an energy carrier for Japan. One of the stages of the World Energy Network (WE-NET) research project includes the creation of liquid hydrogen tankers for worldwide transport. The Japanese ship's capacity surpassed that suggested in the Euro-Canadian proposal and was more comparable to that of a conventional LNG tanker (approximately 200,000 m³)" (Gerboni, 2016). Different storage structures (spherical and prismatic containers) and tanker designs were offered by the researchers (single or twin hull). In contrast to prior research that ignored boil-off during simulated journeys, the Japanese study accounted for boil-off and proposed using the hydrogen evaporation as fuel for the ship. In reality, the boil-off was deemed necessary to provide adequate fuel for the travel to the destination (estimated at 0.2-0.4 percent per day). The lightweight nature of hydrogen, even

in liquid form, necessitated the adoption of a double-hull design for LH_2 ships, which needed ballast and a double-hull for stability guarantee (Gerboni, 2016).



Figure 31. Worlds first liquid hydrogen carrier by Japan's Kawasaki Heavy Industries, Ltd.

2.2 Hydrogen transportation via pipelines

As stated, this paper investigates the technological challenges associated with the transport of hydrogen through natural gas pipelines. "Pipelines are ideal for concurrently distributing hydrogen to many sites or transporting it between cities in gaseous form. Employing the natural gas pipeline infrastructure is vital to Europe's hydrogen transition, since the network of natural gas pipes can be converted for hydrogen transport. Transporting hydrogen via pipes is the most logical and technically straightforward technique" (Gerboni, 2016).

There are three alternatives for the pipeline transportation of hydrogen: 1) the construction of new pipeline infrastructures designed specifically for hydrogen transfer, adhering to hydrogen standards and codes, 2) the repurposing of established gas pipelines to handle hydrogen exclusively, ensuring they can handle 100 percent hydrogen, or 3) the adoption of hydrogen blending, in which hydrogen concentrations are pumped into the natural gas stream. However, it is vital to remember that the capacity and locations of the current infrastructure restrict the repurposing of pipes. In circumstances where it is anticipated that demand for hydrogen will exceed the capacity of existing pipelines, the building of additional pipes devoted to 100 percent hydrogen should also be considered. In our case scenario, we will analyze only the transport via existing natural gas pipelines, as we focus on the problems rising when we blend hydrogen to NG infrastructures. For reference, however, there are independent hydrogen transport systems in both Europe and America. In the Figure 32 below, we see the goal that Europe has set for the creation of a pipeline exclusively for the transport of hydrogen by 2040. Specifically, for 2030 we hope for a pipeline system of 6800 km, connecting all major hydrogen production plants. In the second and third stages, the pipeline network will be expanded, starting in 2035 until 2040, reaching a total of 23000 km of hydrogen pipelines. For 2040, some additional pipelines are also planned where they are depicted with red dotted lines, one of which also passes through Greece. For 2050, further expansion of the pipelines is foreseen, while there will be two transport systems in parallel, 1) a pipeline system exclusively for hydrogen and 2) a pipeline system exclusively for the transport of biomethane.

"Regarding the natural gas infrastructure in Europe, it consists of pipelines of various sizes, ranging from 20 inches to 48 inches or more in diameter. The future hydrogen backbone,

primarily based on repurposed existing pipelines, will reflect this diversity. Converted 36- and 48-inch pipelines, commonly used for long-distance gas transportation within the EU, have the potential to carry approximately 7-13 GW of hydrogen per pipeline, with a lower heating value, across Europe. This highlights the significant potential of utilizing the natural gas infrastructure for hydrogen transport in the EU's future zero-emission energy system. Operating hydrogen pipelines below their maximum capacity is deemed more attractive, leading to substantial savings in compressor investment and operating costs, including energy consumption" (Wang, et al., 2020).

Several large industrial gases firms, such as Praxair, Air Liquide, and Air Products, lead the hydrogen pipeline terrain, while other companies maintain smaller networks inside their production sites or share shorter lines covering a few kilometers. Hydrogen transportation primarily serves refineries and large chemical plants; however, certain specialized facilities, such as goldsmiths, that require hydrogen for their production have begun to establish local networks supplied with centrally produced hydrogen, typically generated through electrolysis. Nevertheless, household distribution of hydrogen remains restricted. The bulk of Europe's hydrogen network is owned by France, Germany, and the Benelux states, but Sweden and the United Kingdom have shorter hydrogen pipes. Ongoing initiatives seek to link the Netherlands with Sweden (Gerboni, 2016).

Existing pipes are made using ordinary steels acceptable for general construction, and their usage has not been linked to any known concerns. Operating pressures vary between networks, but commonly range between 0.34 and 10 MPa, with diameters between 10 and 300 mm. Typically, the working pressure is between 1 and 2 MPa, and the diameters are between 25 and 30 cm (Gerboni, 2016).

"The anticipated total investment necessary for a unique European hydrogen backbone is between \notin 27 billion and \notin 64 billion, assuming that 75% of converted natural gas pipelines and 25% of new pipeline segments are used. This cost is much less than prior approximate estimates and is quite small in the perspective of the European energy transition as a whole. The variance in the estimate is mostly attributable to uncertainty in compressor costs, which are very location-dependent" (Wang, et al., 2020).

It is vital to note that the estimations for the cost of hydrogen transportation differ based on three import scenarios: low, medium, and high.

	LOW	MEDIUM	HIGH
Levelized cost (100% new infrastructure) (€/kg/1000km)	0.16	0.20	0.23
Levelized cost (100% retrofitted infrastructure) (€/kg/1000km)	0.07	0.11	0.15
Levelized cost (EHB, 75% retrofitted) (€/kg/1000km)	0.09	0.13	0.17

 Table 4. Calculated cost for 3 import scenarios. (Wang, et al., 2020)



Figure 32. European hydrogen pipeline. (Wang, et al., 2020)

2.2.1 European natural gas infrastructure

The natural gas network of Europe is constantly expanding, with the aim of greater penetration of natural gas in the final energy consumption. Alongside the development of this network, support for the European Union's plan for hydrogen, for its transport, is accelerating. In the Image, we see the gas network of Europe as it is configured for the year 2020. Due to the fact that Europe has an extensive network of natural gas pipelines, it makes the use of hydrogen more accessible and easier than if it were not possible to transport it by conduits. The network is constantly being expanded, with the aim of introducing, primarily, natural gas, to all households and industries (under the consideration of the delignification of Europe, and correspondingly also of Greece, and finally at the stage of Net Zero Emissions).



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2.2.2 Hellenic natural gas infrastructure

The Greek National Natural Gas Transmission System, as outlined by DESFA in 2022 (desfa, 2022), comprises several key components:

- 1. Main transmission pipelines and distribution networks
- 2. Measuring stations located at entry points from other countries, specifically Sidirokastro near Serres and Evros Gardens
- 3. Compression stations situated in Nea Mesimvria Thessaloniki
- 4. Natural Gas Metering and Regulating Stations
- 5. Natural Gas Control and Dispatching Centers at Patima Magoulas near Athens and Nea Mesimvria near Thessaloniki
- 6. Operation and Maintenance Centers in Sidirokastro Border Station, Northern Greece, Eastern Greece, Central Greece, and Southern Greece
- 7. Remote Control and Communication System.

These elements collectively form the comprehensive infrastructure of the Greek National Natural Gas Transmission System.

The Greek National Natural Gas Transmission System is also connected to some international natural gas infrastructure projects, such as:

1) Interconnector Greece – Bulgaria

- 2) Trans Adriatic Pipeline
- 3) Trans Balkan Pipeline
- 4) Other Interconnectors



Figure 34. Hellenic National Transmission pipelines. (Source: Desfa)

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In the future, the further interconnection of the Hellenic National Natural Gas Transmission System is foreseen (desfa, 2022), with pipelines of common interest, which will play a critical role in Europe's energy sufficiency and in general in its energy mix. Figure 34, shows the transmission pipelines of Greece. These pipelines are:

- 1) East Mediterranean Pipeline
- 2) Poseidon Pipeline Project (onshore & offshore)

EastMed Pipeline

The EastMed interconnector pipeline, which is designed to transmit gas first from Eastern Mediterranean regions to the European Natural Gas System through Greece, is a significant initiative. Initial capacity of the pipeline is 10 billion cubic meters of natural gas per year. It starts with an underwater segment linking Cyprus to Crete, followed by a route around the shore of Crete. From there, it continues across the Peloponnese and Western Greece to the coast of Thesprotia before reaching Italy. In Florovouni, Thesprotia, the EastMed pipeline might link with the POSEIDON pipeline project, which would further integrate the EU energy market with the recently found gas deposits in the Levantine region (DEPA, 2019).

Since July 2014, the operation of the EastMed project has been the responsibility of DEPA's subsidiary "YAFA - POSEIDON." In compliance with European Regulation 347/2013, this cross-border project has been classified as a Project of Common Interest (PCI) by the European Union since 2013. (DEPA, 2019).

General Characteristics			
Length	1900 χλμ.		
Capacity	10 bcm/year		
Diameter	24"- 26"- 42"		
COD	2025		

 Table 5. Characteristics of EastMed.

Poseidon Pipeline

"Two independent portions comprise the Poseidon pipeline project created by the Greek business IGI Poseidon S.A. (50 percent DEPA and 50 percent Edison). Beginning at the Greek-Turkish border in Kipi and continuing through Greece until it reaches Florovouni in the Thesprotia area, the first segment is an approximately 760-kilometer-long onshore road. The second segment is a 210-kilometer-long offshore road linking the coasts of Thesprotia to the area of Otranto, Italy" (DEPA, 2019).

"Designed exclusively for Italy, the Poseidon pipeline has an initial capacity of 12 billion cubic meters per year. It has the possibility for future extension up to 20 billion cubic meters per year, enabling the transfer of natural gas when it becomes available at Greece's borders. The Poseidon Pipeline helps to Europe's energy security by developing linkages and integration across European markets and by diversifying routes and sources of gas from the Caspian area, the Middle East, and the Eastern Mediterranean Basin" (DEPA, 2019).

"The offshore part of the Poseidon pipeline project is already on the list of Projects of Common Interest (PCI) maintained by the European Union, and therefore benefits from faster processes given by EU Regulation 347 of December 2013. Funds from the TEN-E (Trans-European Networks - Energy) initiative and the European Energy Program for Recovery (EEPR) were used to co-finance a number of related research" (DEPA, 2019).

General characteristics			
Length	970 χλμ.		
Capacity	12-20 bcm/year		
Diameter	32"-36"-48"		
COD	2022-2023		
Reverse Flow Capacity	Yes		

Table 6. characteristics of Poseidon pipeline.



Figure 35. Natural Gas pipelines passing through Greece.

2.2.3 Key infrastructure components

A natural gas pipeline network consists not only of its pipelines, but also of other extremely important infrastructures. This is how we should refer to the compression stations, the metering stations, the valves (valve stations) and the reception stations in the cities.

Compression Stations

The compression stations control the pressure drop along the pipelines and ensure that the gas will remain under pressure, for its smooth and optimized transportation. The distance between two stations can vary, and can be from 40 to 100 miles. Compression is done with a turbine, motor, or engine. The energy they need is covered by the natural gas they transport, consuming a very small percentage of it. Nevertheless, there are compressors that are driven by an electric motor, so in this case natural gas is not used at all. Centrifugal compressors are usually used, where the power varies in thousands of horsepower. This station also contains valves, pipelines, and condition control systems. These stations are generally fully automated. The space they occupy is approximately 60000-90000 m². Compression stations also produce a lot of noise during their operation.



Figure 36. Typical compression station. (Source: Web)

Metering Stations

Metering stations are strategically positioned at transit and exit points to enable Transmission System Operators (TSOs) to effectively monitor, manage, and accurately account for the flow of gas within their pipelines (Wang, et al., 2020).

Transmission Pipelines

Transmission pipelines transport gas from the injection points to customers utilizing high-pressure, large-diameter steel pipes. (Wang, et al., 2020).



Figure 37. Typical configuration of transmission pipeline. (Source: Web) *Valve stations*

Valves serve as crucial access points strategically positioned at intervals of 8-30 kilometers along the pipeline, allowing for safe and efficient daily operations and maintenance activities. (Wang, et al., 2020).


Figure 38. Typical valve station configuration. (Source: Web) City Gate Stations

City gate stations play a vital role in reducing gas pressure levels and facilitating the transfer of gas to end-use systems, typically through the distribution network, where applicable.

At this point we should mention the reason for mentioning all these main elements of a natural gas infrastructure. In this thesis, as previously mentioned, the problems during the introduction of hydrogen into the gas pipelines are highlighted. Therefore, hydrogen will pass through the same infrastructures (either in new ones specifically for hydrogen), and potentially, it will create technical issues in them, which need to be resolved. So it is considered a use to know where the hydrogen finally passes, until it reaches the final consumer.

2.3 Limits on hydrogen blending

The process of adding H_2 to CH_4 -rich gases that are being transported in natural gas networks is referred to as "hydrogen blending" or "grid-level blending." These admixtures are theoretically possible and have already been utilized in a number of projects, however, their application is not unlimited. It is important to note that the maximum blending limit for hydrogen-natural gas mixtures is not universally standardized. The upper limits are determined by the tolerances and requirements of different gas consumers or customers within a network area. Additionally, the blending limits are influenced by the sensitivity and tolerance of the gas infrastructure itself. The ability to accommodate hydrogen also depends on the gas properties of the methane-rich gases in the system. These blending limits, which are outlined in technical standards and regulatory documents, may vary across European countries (ENTSOG, et al., 2021).

Within standard EN 16726 from 2019 it is stated: "At present, it is not possible to establish a limit value for hydrogen that is universal for all areas of European gas infrastructure, and therefore a case-by-case analysis is recommended."

The maximum concentration of hydrogen that can be utilized is heavily influenced by the structure, pressure variations, and any flaws that are already present. The majority of people, on the other hand, are aware that certain blending percentages—such as 2% to 10% in volumetric terms—are technically feasible for some grid sections with a few modifications in some European Member States.

Even though more tests are required, operators consider 20% to be the upper bound due to the need to adapt downstream users beyond this point (see Figure 39). In terms of technical regulation, a few Member States explicitly acknowledge hydrogen blending (ENTSOG, et al., 2021).

None of the three scenarios (EU, PAC, and GfC) explicitly take into account the combination of hydrogen and methane. In general, hydrogen blending is mostly talked about as a new technology for the market's ramp-up phase. Therefore, it is extremely helpful to ascertain

the potential volumes in question for 2030. Figure 40 depicts the hydrogen volumes needed to blend all of the methane consumed in the PAC, EU, and GfC scenarios in 2030 by volume of 5%, 10%, 15%, and 20%, respectively (Bard, et al., 2022).



Figure 39. The existing natural gas infrastructure and end-use systems have established test results and regulatory limits regarding the admission of hydrogen. (ENTSOG, et al., 2021)



Figure 40. The comparison between the hydrogen (H2) required for blending purposes and the targeted supply of green hydrogen, as well as the scheduled demand for 2030, is an important consideration (Bard, et al., 2022)

The European Commission's target of 40 GW for water electrolyzers has the potential to generate 130 TWh of green hydrogen. Based on the previous illustration, approximately 5% or almost 40% of this green hydrogen would be consumed through hydrogen blending. In the case of high blending volumes of 20%, as much as 90% of the green hydrogen would be utilized.

Even at very moderate levels of mixing, green hydrogen has high absorption capability, according to these studies. In addition, according to the hydrogen plan of the European Commission, the overall demand for "no-regret" hydrogen surpasses the 130 TWh generating capacity for green hydrogen in all three scenarios. The industrial sector alone would need 147 TWh of hydrogen under the GfC scenario. Green hydrogen might replace 120 TWh of grey hydrogen used in ammonia production under the EU scenario. "In the PAC scenario, the industrial sector could absorb 159 TWh of hydrogen by 2030, while the transportation sector could absorb 129 TWh on its own" (Bard, et al., 2022).

Regarding the hydrogen requirements of end users, the limitations depicted in Figure 41 pertain to specific gas infrastructure components and utilization options. The current state of knowledge is depicted in dark green, and the various other colors indicate what is required to achieve hydrogen blending (Bard, et al., 2022).



Figure 41. There are limitations on the rates at which hydrogen (H2) can be blended with selected components of the gas infrastructure, as well as restrictions on utilization options. (Bard, et al., 2022)

The color-coded categorization of the limitations for hydrogen blending rates and utilization options can be summarized as follows:

- Dark green: No significant issues or limitations.
- Light green: Some modifications or additional measures may be required.
- Yellow: Conflicting references or information found, further research and clarification are needed.
- Orange: Technically feasible, but significant modifications, additional measures, or replacement may be necessary.
- Red: Currently not technically feasible.
- White: Insufficient information available, further research and development is required to determine feasibility.

CHAPTER 3: HYDROGEN INDUCED PIPELINE INTEGRITY AND SAFETY ISSUES

Pipeline networks for gas transportation and distribution are quite complex and heterogeneous, depending on the location. The transportation of natural gas itself is risky, considering that the operating pressures range from 50-70 bar, usually at 70, while now the scenario of 150 bar is being considered, for economic reasons (larger quantities of gas are transported - kg per cubic meter). Hydrogen addition to natural gas results into its direct contact with transmission systems and other infrastructure elements, which, however, have been designed and studied for the transport of natural gas only (it does not concern independent hydrogen transport networks). The introduction process is called hydrogen blending, with the hydrogen entering existing pipelines of natural gas or gases in general.

"Hydrogen's incorporation into the global energy system is constrained by a number of factors, most notably the inherent dangers of gas and, to a lesser degree, technical impediments. The following sections offer an overview of the safety, structural integrity, and energy efficiency problems posed by hydrogen transportation. It is essential to remember that these dangers depend on the percentage of hydrogen in the final gas combination" (Gerboni, 2016).

3.1 Natural gas - H₂ mixtures

Each country, depending on the existing pipeline network it has and its energy needs, as well as its legislative framework, allows different hydrogen quotas, mainly for safety reasons. In addition, it depends on the pressure fluctuations, the operating conditions, the pipeline itself from a construction point of view, and possible defects of the network elements, while many times the most limiting factor is the efficiency of the boilers and turbines and not so much on the compatibility of materials. In general, for some gas networks, from 2-10% hydrogen content is technically possible. For example, we list the following countries with the corresponding acceptable hydrogen contents in their national gas transmission systems, up to and including the year 2017.

	Table 7. Allowable hydrogen blend in natural gas systems per country.							
Country	Volume/ molar percent	Mass percent (%)						
	(%)	-						
Belgium	0	0						
UK	0	0						
Sweden	0.4	0.06						
Switzerland	4	0.6						
Austria	4	0.6						
Germany	5-10	0.8-1.5						
France	6	0.9						
Netherlands	12	1.85						
Italy	0.5	0.08						
New Zealand	0	0						
US	0	0						
Czech Republic	2	0.3						
Canada	4	0.6						
Spain	5	0.8						

The regulatory limits for imported hydrogen vary significantly among European countries. Even within a single country like Germany, there are limitations on hydrogen content, such as at supply points with compressed natural gas where the hydrogen content is restricted to 2% by volume. This restriction is in place due to the type II CNG tanks used in cars. The energy content of the mixture in the pipeline is influenced by this limit, which is

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crucial for the final utilization of the mixture, including burners and other applications. Figure 42 (Gondial, 2016) presents two profiles of hydrogen-natural gas mixtures (for rich and lean natural gas) at low pressures. It may be determined that mixes of up to 40 percent hydrogen and natural gas may not need major adjustments in energy transmission. The Wobbe index varies from 41 to 47 for Lean NG mixes and 48 to 58 for Rich NG combinations (Gondial, 2016).

It is important to recognize that the development of a hydrogen economy requires time for such a large-scale project to unfold. It is not reasonable to expect an immediate replacement of all heat engines and boilers with fuel cells overnight. Instead, "a natural progression is necessary to achieve the full market penetration of fuel cells and hydrogen in general" (Gondial, 2016) (Stetson, et al., 2016).



Figure 42. H₂ addition per relative energy flow of Natural Gas. (Stetson, et al., 2016)

Studies have demonstrated that hydrogen mixtures of up to 17% by volume in natural gas do not pose significant issues. However, when considering "higher percentages of hydrogen, several factors need to be taken into account, including linepack, pressure drop, and the Wobbe index" (Gondial, 2016) (Stetson, et al., 2016). The Wobbe index, or Wobbe number, is calculated by dividing the High Heating Value (or Low Heating Value) of the gas by the square root of its specific gravity relative to air. A higher Wobbe number indicates a greater calorific value and the ability of a specific quantity of gas to flow through a given-sized opening in a specified time. This index serves as a measure of gas interchangeability and can also be applied to domestic end-use applications. The equation provided below represents the formula used for calculating the Wobbe index (Gondial, 2016) (Stetson, et al., 2016):

$$W_s = \frac{H_s}{\sqrt{d}} \tag{14}$$

$$W_{s_{mix}} = \frac{H_{s_{mix}}}{\sqrt{d_{mix}}} = \frac{HHV \text{ of } NG + HHV \text{ of } H_2}{\sqrt{sp. gravity \text{ of } NG + sp. gravity \text{ of } H_2}}$$
(15)

Equation is for mixtures of $H_2 - NG$.

"The Wobbe number for common natural gas burners ranges between 48 and 58 MJ/Nm³ for rich natural gas and 41 and 47 MJ/Nm³ for lean natural gas. Figure 42 demonstrates that lean natural gas burners can tolerate up to 98 percent by volume of hydrogen injection, but rich natural gas burners can tolerate up to 45 percent by volume. To accommodate user convenience and assure compatibility with both low and high calorific value fuels, the whole spectrum of 41–58 percent hydrogen/natural gas mixes should be considered. This facilitates

the use of the whole spectrum of energy content with equal ease. To solve problems about flame detection, burner heads, and sealings, it is advised to employ multipurpose devices that can operate with the complete spectrum of hydrogen/natural gas mixes" (Gondial, 2016) (Stetson, et al., 2016).

Based on the data shown in Figure 43, it is obvious that the Wobbe index for low calorific value gas (lean gas) reaches its lowest point at a 72 percent volume combination. In contrast, the performance range with the lowest outcomes for high calorific value gas (rich gas) is between 75 and 85 percent by volume (Gondial, 2016) (Stetson, et al., 2016).



Figure 43. Wobbe index behavior. (Gondial, 2016) (Gondal & Sahir, 2012) (Stetson, et al., 2016)

3.2 Energy issues

"The pipeline transmission of hydrogen differs from that of natural gas in many ways. Hydrogen may attain greater velocities and flow rates in a pipeline of a given diameter and internal pressure drop due to its reduced viscosity. However, hydrogen has a lower energy density per unit volume than natural gas, resulting in a compression process that requires four times more energy. Consequently, a natural gas pipeline can transport more energy than a hydrogen pipeline" (Nexant, 2008; Gerboni, 2016).

Typically, "hydrogen pipelines are shorter than the vast energy corridors used to carry natural gas from Russia to Europe. Rarely are intermediate compression stations necessary for hydrogen pipelines. Hydrogen is recompressed at the ultimate destination after high-pressure production, which may be accomplished by high-pressure electrolysis or steam reforming. Compressing hydrogen from 20 to 70 bar needs around 2.4 MJ of energy, while liquification requires 55-65 MJ/kg" (Nexant, 2008; Gerboni, 2016).

In addition, the Wobbe index measures the substitutability and energy content of gases during burning. Bigger energy content and thermal efficiency correspond to a greater Wobbe index. As the hydrogen concentration in a gas mixture grows, the Wobbe index decreases linearly, as seen in Figure 43. This drop is up to 85% for rich natural gases and up to 75% for lean natural gases. In comparison to natural gas, hydrogen has a lower density and energy content per unit volume. The energy density of hydrogen is 0.01 MJ/L (LHV), whereas that of natural gas is 0.03 MJ/L (LHV) (LHV). In order to convey the same amount of energy, it is necessary to compress three times as much hydrogen as natural gas. In the Wobbe index diagram, where methane, biomethane, and medium-rich LNG represent three distinct gaseous fuels, the reactivity of hydrogen can also be noticed.



Figure 44. Wobbe indexes. (Altfeld & Pinchbeck, 2013)

$$Q = C * \frac{T_b}{P_b} * D^{2.5} * e * \sqrt{\frac{P_1 - P_2^2}{L * G * T_a * Z_a * f}}$$
(16)

Όπου,

 $Q = flow rate\left(\frac{m}{s}\right)$ C = Constant D = pipe diameter (m) E = pipe efficiency f = Darcy - Weisbach friction factor G = gas specific gravity L = pipeline length (m) Pb = pressure base (Pa) $P_1 = inlet pressure (Pa)$ $P_2 = outlet pressure (Pa)$ Ta = average temperature (K) Tb = temperature base (K) Za = compressibility factor

Additionally, depending on the conditions of the pipeline, the amount of "stored" gas inside the pipeline (line pack) is also affected. The gas supply affects the linepack, inversely proportionally, that is, with a reduced supply, the stored gas increases, while with an increased supply, the stored gas decreases. From Equation 17 we can see the relationship between the two quantities.

$$V_{storage_{,n}} = V_{geom} \left[\frac{P_m}{K_m} - \frac{P_{m'}}{K_{m'}} \right] * \frac{T_n}{P_n * T}$$
(17)

Όπου,

Pm = upper mean pressure (Pa) Pm' = lower mean pressure (Pa) Km = compressibility factor Vstorage, n = storage volume at normal temperature and pressure (273oK and 1 bar)(m³) Vgeom = volume of pipeline (m³)

Taking into account the aforementioned statistics and assuming normal flow conditions in a gas transmission network, the line pack for hydrogen gas normally ranges from 65 to 71

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percent, while that for natural gas is between 63 and 74 percent. Hydrogen's energy capacity in a pipeline with the same diameter and pressure drop is often 20 to 30 percent lower than that of natural gas. Despite the fact that hydrogen has a substantially lower volumetric energy density, its greater flow rate compensates for this. The quality of natural gas, such as its origin (e.g., Russian, American, Algerian), also plays a part in these issues. The transmission of energy via a liquid or gaseous fuel must correspond to national standards controlling chemical and mechanical qualities (e.g., the amount of methane in natural gas) and satisfy client demand specifications. The energy content of hydrogen in this context is about one-fourth that of natural gas. This discrepancy creates obstacles for securing a safe energy supply. Figure 45 depicts line pack values for different combinations ranging from 0% to 100% hydrogen (Dodds & Demoullin, 2013; Gondial, 2016).



Figure 45. Line pack. (Gondal & Sahir, 2012)

3.2.1 Methane number (MN)

"The Methane Number (MN) defines the knocking tendency of combustible gases in internal combustion engines (ICE) and is impacted by the gas's composition, specifically the presence of higher hydrocarbons (C_3 , C_4 , C_5) and the amount of hydrogen in the fuel gas. For example, the methane number for pure methane is 100, whereas the hydrogen number is 0. According to the AVL technique, the methane number varies from 65 to 70 for rich liquefied natural gas (LNG). The graphic below depicts the change in methane concentration when a gaseous fuel, such as hydrogen, is added to a mixture" (Altfeld & Pinchbeck, 2013).

Again in the case of the methane number, we can conclude that the difference in MN between the gases is greater compared to the difference that the introduction of hydrogen to the gaseous fuels causes in the methane number. Moreover, it is worth noting that by adding H_2 into NG mixtures, it can bring about a reduction in MN enough so that the final number is below the limit, for use in gas engines, on the part of the operators (e.g. high-efficiency cogeneration plants, natural gas vehicles). Despite the discussion made in this paper, and the fact that the methane number plays an important role in gaseous fuels, many states of the EU have not set a limit for it in fuels. But this tends to change based on CEN TC 234, where it sets a quality limit for gaseous fuels in Europe, within which the methane number is also estimated.



Figure 46. Methane number. (Altfeld & Pinchbeck, 2013)

3.2.2 Laminar flame speed

Regarding hydrogen energy, it is essential to recognize that hydrogen's combustion properties vary from those of natural gas. "Flame speed, which is influenced by elements such as flashback and flame stability, plays a crucial function. It is possible to define both laminar and turbulent flame speeds, but measuring them precisely is difficult, resulting in the lack of norms or standards for these characteristics" (Altfeld & Pinchbeck, 2013).

Based on experimental evidence addressing the speed of laminar flames, several research have produced contradictory findings. Nevertheless, a general tendency suggests that the addition of hydrogen increases flame speed. "A 10 percent hydrogen impurity, for instance, may result in a 5 percent increase in laminar flame speed. This pattern holds true for all air-to-fuel ratios and combustion circumstances" (Altfeld & Pinchbeck, 2013).

"Regarding gas turbines, turbulent flame speed is a crucial element. Unfortunately, there is a dearth of pertinent data on this subject. However, simulations indicate that hydrogen has a greater effect on turbulent flame speed. A 10 percent hydrogen admixture, for instance, may cause a 10 percent increase in turbulent flame speed" (Altfeld & Pinchbeck, 2013).



Figure 47. Laminar flame speed vs hydrogen admixture in methane. (Altfeld & Pinchbeck, 2013)

3.3 Safety issues

Production, storage, transport, and delivery of hydrogen raise serious safety problems. Existing natural gas pipeline networks are mainly intended for natural gas transmission, and the related dangers to the general public and pipeline system are well established and controlled. The introduction of hydrogen into these pipes, however, poses an elevated safety concern owing to the possibility of pipeline rupture and the increased chance of gas ignition. The accidental release of a combination of hydrogen and natural gas also offers fire and explosive concerns. GTI has reviewed NaturalHy Project and Greenhouse Gas R&D Programme (IEA) publications to evaluate these hazards (Melaina, et al., 2013).

In general, risk is the combination of an event's probability and its effects. Typically, lowering the possibility of an occurrence takes precedence over addressing the severity of its repercussions. On the basis of the aforementioned investigations, the following conclusions have been drawn about the effect of adding hydrogen on the probability and effects of events.

3.3.1 The Influence on the Probability of incident

"When comparing ng pipelines with hydrogen additions of up to 50% using an appropriate integrity management system, pipeline failure rates remain unchanged" (Melaina, et al., 2013). However, the introduction of hydrogen into the gas mixture brings about notable changes in ignition characteristics. This is attributed to a significant decrease in the minimum energy required for ignition (known as Minimum Ignition Energy or MIE) and an increase in the upper flammability limit. Consequently, mixtures of hydrogen and natural gas have a higher probability of igniting. The LEL and UEL for these gases, considering the chemical properties of methane as the primary component of natural gas, are presented in Table 8 below. For comparison, the flammability of hydrosulfide compound, a highly flammable gas, is also included. The following equations are employed to calculate the flammability limits of a gas mixture.

Compounds	Flammability	V Limits in air
Compounds	LFL, %v/v	UFL, %v/v
Hydrogen (pure)	4	75
H_2S	4	44
Methane	5	15

$$LFL_{mixt} = \left(\frac{1}{\sum_{i=1}^{n} \frac{c_i}{LFL_i}}\right)$$
(18)
$$UFL_{mixt} = \left(\frac{1}{\sum_{i=1}^{n} \frac{c_i}{UFL_i}}\right)$$
(19)

Where,

LFLi = LFL of the i component of the mixture (% of volume) $Ci = the concentration (% of volume) of the i component (<math>\Sigma ci = 100$) N = number of flammable componets in the gas mixture

The temperature has an effect on the limits for flammables. By decreasing LEL and increasing UEL, increasing the liquid temperature increases the flammable area. The rate for the gases of interest is shown in the Table 9 below for the minimum ignition energy. Shoes can make 22 mJ of electricity produced via friction exclusively by strolling in a protected region.

Table 9. Minimum Ignition Energy of Hydrogen and Methane	
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Substance	MIE (mJ)
Methane	0.29
Hydrogen	0.015-0.03

3.3.2 The significance on the Severity of an Incident

"The behavior of gas accumulation resembles that of natural gas. The concentration of gas accumulation increases somewhat when hydrogen is added to natural gas, up to 50 percent hydrogen addition. Nonetheless, large increases in gas accumulation concentration occur when the hydrogen level surpasses 50 percent, and especially when the hydrogen addition exceeds 70 percent. In the event of a vented explosion, a 20 percent hydrogen addition has no effect on the explosion's severity, however additions of 50 percent or more enhance the explosion's severity owing to overpressure" (Melaina, et al., 2013).

"In confined places, the intensity of explosions caused by gas accumulation rises somewhat up to 30 percent hydrogen addition, but dramatically at 40 percent hydrogen addition or more. Effective interventions, such as boosting ventilation or decreasing structural confinement, may greatly alleviate overpressure difficulties caused by high hydrogen mixtures. In addition, the fire threat decreases somewhat when hydrogen is added" (Melaina, et al., 2013; Melaina, et al., 2015).

3.3.3 Risk Assessment

GTI developed a risk assessment tool that evaluates the risk associated with different levels of hydrogen in natural gas by analyzing the likelihood and severity of potential incidents as said by Melaina et al., (2013). The findings indicate that the addition of hydrogen in natural gas pipelines increases the risk to individuals located near the pipeline, but it reduces the extent of the hazardous region (Melaina, et al., 2013).

To assess the impact of adding hydrogen up to 25% in natural gas on hazards, the changes in gas properties were evaluated and compared to standard natural gases. The results

are summarized in Table 10 (Melaina, et al., 2013). "According to the assessment conducted by the Greenhouse Gas Programme of the International Energy Agency (IEA), the addition of hydrogen up to 25% increases the risk of explosions and the probability of fire in confined spaces. However, the same study concludes that the use of hydrogen-blended natural gas, under well-regulated conditions, does not pose a higher risk of explosions compared to unblended natural gas" (Melaina, et al., 2013).

	Main Hazardous Hazards						
Properties /Phenomena	Effect of Hydrogen Addition	Rupture	Explosion	Fire	Burns	Suffocation	Poisoning
Density	Lower					х	
Viscosity	Lower					х	
Velocity of Dispersion	About the same		х	х		х	
Hydrogen Component	Higher	х					X
Household Gas Pipe Leak Rate	Higher		x	+		X	
Lower flammability limit	About the same level		х	х			
Higher Flammability Limit	t Higher		+				
Flammability Range	Wider		х				
Detonability Range	Wider		х				
Explosive Energy/Volume	Lower		x	х			
Explosive Energy/Mass	Higher		X	X			
Minimum Energy for Ignition	Lower		X	х			
Auto Ignition Temperature	Lower		x	+			
Uncontrolled Ignition	Easier		х	х			
Severity of Explosive Damage	Lower		х				
Explosion Risk in Confined Room	Higher		+				
Explosion Risk in unconfinedRoom	Lower		-				

Table 10.	Hydrogen	effects when	n adding ir	n NG.	(Source:	(Melaina,	et al	2013) (I	EA, 2003)
	1				((,	/ (,,

In the context of hazard assessment, the impact of hydrogen addition in natural gas can be categorized as follows: for hazard indicators marked with " \times ," the presence of hydrogen up to 15% does not alter the existing hazard; for indicators marked with "+," the hazard increases with the presence of hydrogen; and for indicators marked with "-", the hazard reduces with the presence of hydrogen. These classifications provide insights into how the introduction of hydrogen influences specific hazards and aids in evaluating the overall safety considerations associated with hydrogen-blended natural gas.

It is considered useful, to mention the equation to calculate the potential risks posed to the public by natural gas distribution pipelines (the same equation applies to all risks) (Melaina, et al., 2013), i.e.:

$$Risk = Probability (pipeline failure) * Severity$$
(20)

MSc Oil and Gas Process Systems Engineering HYDROGEN COMPATIBILITY ASSESSMENT IN NATURAL GAS INFRASTRUCTURES

The primary failure modes observed in natural gas distribution pipelines predominantly involve leaks. Statistical data published in the 2007 annual report by the Department of Transportation (DOT) classify leak incidences into eight distinct failure modes. These failure modes provide valuable information for understanding the nature and patterns of leaks in natural gas distribution pipelines, contributing to the development of effective strategies for mitigating risks and ensuring the integrity of the pipeline system. (date for USA) (Melaina, et al., 2013). Although, these statistics are for USA, and material may differ to Europe based on their %, these gives as a general understanding of the failure mechanisms. As shown in the Table 11 below, Corrosion, Excavation and Other are the main mechanisms of failure in NG pipelines.

Foilure Mechanisms	Mai	ns	Services		
r anure mechanisms	Number	%	Number	%	
Corrosion	55553	36.42	71963	21.64	
Component Imperfection	10645	6.98	37124	11.16	
External Influence	12924	8.47	11305	3.40	
Earthwork	23475	15.39	82814	24.90	
Other forces	2834	1.86	13141	3.95	
Machinery	10293	6.75	42279	12.71	
Procedure	3866	2.53	8557	2.57	
Other	32956	21.60	65386	19.66	
Total	152546	100.00	332569	100.00	

Table 11. Failure mechanisms on distribution mains and services. (Melaina, et al., 2013)

1) Corrosion-induced leaks

"Corrosion-induced leaks constitute a failure mode within the distribution system, encompassing both external corrosion of bare steel pipes, coated/wrapped steel pipes, and castiron pipes, as well as internal corrosion. The occurrence of leaks arising from corrosion defects in the distribution system can lead to the accumulation of gas in enclosed spaces, thereby posing a potential hazard of fire or explosion" (Melaina, et al., 2013).

2) Component imperfection

"Material defects in pipes can be categorized into two types: manufacture-related defects and construction-related defects. Manufacture-related defects encompass issues such as defective materials, pipe seams, or other components used in piping. On the other hand, construction-related defects pertain to flawed pipe girth welds, faulty fabrication welds, stripped threads, broken pipes or couplings in the case of steel pipes, and defective fusion, installation errors, and improper backfill in the case of plastic pipes" (Melaina, et al., 2013).

The occurrence of these defects can lead to the slow release of gas, which in turn poses a fire or explosion hazard, particularly when the leak transpires in a confined space (Melaina, et al., 2013).

3) Natural Force

Natural forces encompass the various external forces exerted on a pipeline due to earth movements, such as landslides, washouts, subsidence, frost heave, earthquakes, and other related phenomena. These forces have the potential to cause substantial damage to the pipeline infrastructure and may lead to significant gas release (Melaina, et al., 2013).

4) Excavation Damage

This refers to the detrimental effects on pipes that occur during excavation activities, typically resulting in either a leakage or a rupture of the pipeline (Melaina, et al., 2013). **5) Other Outside Force**

This pertains to the damage caused by external forces, excluding natural forces or excavation activities (Melaina, et al., 2013).

6) Equipment Malfunction

This failure occurs due to equipment malfunction, which includes failures in gaskets or O-rings, control/relief equipment, seals, and piping components, among others (Melaina, et al., 2013).

7) **Operation**

This failure arises from improper operational practices, such as deviations from correct operational procedures by the operator (Melaina, et al., 2013).

Corrosion and excavation are the leading causes of distribution system leaks. The introduction of hydrogen into the system is not anticipated to appreciably impact the likelihood of these failure scenarios. The presence of hydrogen in natural gas, however, may enhance the risk and severity of fire and explosion occurrences as said by Melaina et al., (2013). The risks connected with fire or explosion threats in natural gas distribution systems are classified into six categories (range from no hazard (0) to severe (50)) depending on the possible dangers presented to the general public in the case of pipeline breakdown. Refer to Table 12 for further information (Melaina, et al., 2013).

Importance of Hazards	Rank
Severe	50
Moderate to Severe	40
Moderate	30
Minor to Moderate	20
Minor	10
None	0

Table 12. Rank of the Hazards in NG Systems. (Melaina, et al., 2013)

Table 13. The risk factor associated with different pipe material categories and the overall risk factor for each failure mode in distribution mains (Melaina, et al., 2013)

	Pipe Material Categories and Their Percentage in Distribution Mains						
Failure Mode	Steel	Cast Iron	PE	Other Plastics	Other	Overall Risk	
	46.55%	3.14%	48.12%	2.06%	0.13%	Factor	
Corrosion	50	40	0	0	10	24.54	
Material Defect	30	10	40	30	10	34.16	
Natural Force	30	50	20	20	10	25.58	
Excavation	50	50	50	50	50	50.00	
Other Outside Force	10	10	10	10	10	10.00	
Equipment	30	30	30	30	30	30.00	
Operation	30	30	30	30	30	30.00	
Other	10	10	10	10	10	10.00	
Total	240	230	190	180	160	214	

Pipe Material Categories and Their Percentage in Service Lines							
Failure Type	Steel	Cast Iron	PE	Other Plastics	Other	Overall Risk	
Tunure Type	32.68%	0.17%	63.05%	0.42%	3.69%	Factor	
Corrosion	50	40	0	0	10	16.77	
Material Defect	30	10	40	30	10	35.53	
Natural Force	30	50	20	20	10	22.95	
Excavation	50	50	50	50	50	50.00	
Other Outside Force	10	10	10	10	10	10.00	
Equipment	30	30	30	30	30	30.00	
Operation	30	30	30	30	30	30.00	
Other	10	10	10	10	10	10.00	
Total	240	230	190	180	160	205	

 Table 14. The risk factor associated with pipe material categories and the overall risk factor for each failure mode in service lines. (Melaina, et al., 2013)

The final column represents the overall risk factors for each failure mode in the natural gas pipeline system of the USA. These factors are calculated by multiplying the risk factor of each material type by the percentage of that material type in the system, and then summing the results (Melaina, et al., 2013):

$$RF_{Overall} = \Sigma_{i=1 \ to \ 5} [RF_i * P_i] \tag{21}$$

RFoverall: the overall risk factor

RFi: risk factor for each material category (total of five categories) Pi: percentage of each type of material in distribution mains or service lines

The comprehensive risks associated with each failure mode in Table 13 and 14 are evaluated in greater detail for hydrogen/natural gas mixtures at three distinct hydrogen concentration levels: less than 20%, 20 to 50%, and greater than 50% as said by Melaina et al.,(2013). These levels are determined based on research conducted in the NaturalHy project and other relevant literature, which have examined the impact of hydrogen content on the likelihood of fire or explosion in hydrogen/natural gas mixtures, as well as the severity of associated hazards (Melaina, et al., 2013).

|--|

	Probability ^a	Risk Factor						
Failure Mode	(%)	NG ^b	< 20% H ₂ ^c	20 to 50% H_2^{c}	>50% H ₂ ^c			
Corrosion	36.42	24.54	29.54	29.54	44.54			
Material Defect	6.98	34.16	39.16	39.16	54.16			
Natural Force	8.47	25.58	35.58	35.58	45.58			
Excavation	15.39	50.00	60.00	70.00	70.00			
Other Outside Force	1.86	10.00	15.00	15.00	30.00			
Equipment	6.75	30.00	35.00	35.00	50.00			
Operation	2.53	30.00	35.00	35.00	50.00			

Other	21.60	10.00	15.00	15.00	30.00
Total	100.00	214	264	274	374

	Т	otal Risks	
NG ^b	<20% H ₂ ^c	20 to 50% ${\rm H_2}^{\rm c}$	>50% H ₂ ^c
8.94	10.76	10.76	16.22
2.38	2.73	2.73	3.78
2.17	3.01	3.01	3.86
7.69	9.23	10.77	10.77
0.19	0.28	0.28	0.56
2.02	2.36	2.36	3.37
0.76	0.89	0.89	1.27
2.16	3.24	3.24	6.48
26	33	34	46

Table 16. Risk Assessment for Distribution Services. (Melaina, et al., 2013)

Failure Mode	Probability ^a	Risk Factor						
i unure moue	(%)	NG ^b	$<20\%$ H $_2$ $^{\rm c}$	20 to 50% ${\rm H_2}^{\rm c}$	>50% H ₂ ^c			
Corrosion	21.64	16.77	26.77	26.77	36.77			
Material Defect	11.16	35.53	45.53	45.53	55.53			
Natural Force	3.40	22.95	42.95	42.95	42.95			
Excavation	24.90	50.00	70.00	90.00	100.00			
Other Outside Force	3.95	10.00	20.00	20.00	30.00			
Equipment	12.71	30.00	40.00	40.00	50.00			
Operation	2.57	30.00	40.00	40.00	50.00			
Other	19.66	10.00	20.00	20.00	30.00			
Total	100.00	205	305	325	395			

	Tot	al Risks	
NG ^b	< 20% H ₂ ^c	20 to 50% ${\rm H_2}^{\rm c}$	>50% H ₂ ^c
6.11	9.75	9.75	13.39
2.48	3.18	3.18	3.88
1.94	3.64	3.64	3.64
7.69	10.77	13.85	15.39
0.19	0.37	0.37	0.56
2.02	2.70	2.70	3.37
0.76	1.01	1.01	1.27
2.16	4.32	4.32	6.48
23	36	39	48

 $\Delta RF=05$: minor increase $\Delta RF=10$: minor to moderate increase $\Delta RF=20$: moderate to significant increase $\Delta RF=40$: significant increase $\Delta RF=50$: significant increase at higher degree

"The bulk of distribution mains pipes are regarded to be in a vented state. The addition of hydrogen to natural gas enhances gas accumulation near pipelines, however the change in gas accumulation behavior is minor up to 50 percent hydrogen concentration. The addition of up to 20 percent hydrogen to natural gas does not considerably enhance the risks associated with delayed gas release, such as corrosion-caused leaks or manufacturing faults. However, these dangers rise dramatically at increasing hydrogen concentrations, notably over 50 percent hydrogen content" (Melaina et al., 2013). In the event of pipeline breakdown caused by external factors such as excavation damage or natural forces, the presence of hydrogen heightens the explosion danger, and the risk factor increases dramatically when hydrogen levels surpass 50 percent. Tables 15 and 16 illustrate the effect of hydrogen on the risk factor for each failure mode and the total risk at three hydrogen concentration levels, said by Melaina et al., (2013). The overall risk, computed using the formula (risk = probability * severity), demonstrates that the addition of hydrogen to natural gas increases the overall danger in distribution mains. The increase in risk is low up to 50 percent hydrogen, but becomes considerable when hydrogen levels beyond 50 percent (Melaina et al., 2013).

In contrast to distribution mains, "many distribution services pipes are located in limited places, such as inside buildings. In such instances, the gas cannot be immediately evacuated, resulting to a buildup of gas in tight places and an increased risk of fire or explosion" (Melaina et al., 2013). The addition of hydrogen to natural gas raises the likelihood of all pipeline failure scenarios. The total danger is greatly enhanced at all hydrogen concentrations, and becomes severe over 20 percent hydrogen (Melaina et al., 2013).

To estimate individual risk, which is the possibility of a person dying owing to transmission pipes in a given year, three factors are considered: 1) the frequency of pipeline failure, 2) the probability of ignition, and 3) the consequences of resultant fires or explosions. Failure of pipelines, whether caused by corrosion or other processes, was recognized as the greatest risk factor. As previously indicated, increasing the proportion of hydrogen in natural gas-hydrogen blends raises the danger closer to the pipeline axis and reduces the risk farther from the pipeline compared to natural gas. This impact is shown in Figure 48, which demonstrates that adding hydrogen to a long, high-pressure pipeline decreases the danger at distances between 265 and 400 meters, while increases the risk at distance between 0 and 275 meters. For a concentration of 25% hydrogen, the maximum danger distance decreases to around 25m, but increases near the leak. This action gets more intense as the concentration of hydrogen rises (Melaina et al., 2015).

Hydrogen mixtures scatter more quickly than natural gas, resulting in decreasing hydrogen mixture concentrations as distance from the pipeline increases (Melaina et al., 2015).



Figure 48. The risk to an individual per year is influenced by the distance from the pipeline. The risk presented here represents the likelihood of a person experiencing a fatality within a specific year. (Melaina, et al., 2015)

Increasing the diameter of transmission pipes increases risk, but the risk-relationship remains the same independent of the existence of hydrogen mixes. This connection is shown in Figure 49, which illustrates pipes with diameters of 273, 508, 762, and 914 millimeters. Due to a lower estimated pressure, the distinct pattern exhibited for the 508 mm pipe diameter was noted. In all pipe diameters, the mixes are comprised of 75% natural gas and 25% hydrogen (Melaina, et al., 2015).

The Greenhouse Gas R&D Programme of the International Energy Agency also studied the risk involved with mixing hydrogen with natural gas. It was discovered that with a 75/25 mixture, the hazards of unburned gas igniting in the air and burns connected with gas and open flame equipment rose (Haines, et al., 2004). Adding hydrogen, however, lowered the hazards of explosion from unburned gas in the air, suffocation from unburned gas in the air, asphyxia from malfunctioning flue gas systems, and poisoning from heated media. These results contrast the conclusions of another research, which indicated an increase in overpressure in confined explosions with 20 percent hydrogen concentrations and venting. These disparate outcomes demonstrate the complexity and context-specific nature of risk evaluations for hydrogen mixtures. It is essential to recognize that dangers in the actual world might vary greatly based on location and circumstances (Melaina, et al., 2015).

In addition, the Greenhouse Gas R&D Programme determined that the addition of hydrogen had no impact on the risks associated with ten additional dangers (Melaina, et al., 2015).



Figure 49.Risk per distance for 75/25 hydrogen blend in different pipe diameters.

3.3.4 Other aspects of safety

Safety considerations are crucial when it comes to hydrogen transportation, whether in its pure form or as a mixture with natural gas. "While hydrogen is generally considered safer than methane or gasoline as a fuel, it is important to address the specific safety concerns associated with hydrogen transport. Table 17 provides an overview of the safety comparison between hydrogen, methane, and gasoline, highlighting some key aspects that need to be taken into account" (IEA, 2019).

Properties		Rankings of different fuels	
	Gasolines	Methane/NG	Pure Hydrogen
Toxicity of Fuel	3	2	1
Toxicity of Combustion	3	2	1
Density	3	2	1
Diffusion Coefficient	3	2	1
Specific het ignition	3	2	1
Limit ignition energy	1	2	3
Ignition temperature	2	1	3
Flame temperature	3	2	1
Explosion energy Flame	3	1	2
Total Emissivity	3	2	1
Safety factors	3	2	1
	30	20	16
	0.53	0.8	1

Table 17. Characteristics of Gasoline, Methane and Hydrogen.

1. Safest, 2. Less safe, 3. Least safe.

"To maintain the safety of the distribution network, specialized hydrogen pipeline networks need modifications to their leak detection systems. Timely detection and repair of leaks produced by cracks, corrosion, embrittlement, and diffusion are essential. In addition, the development of specialized sensors for detecting leaks and fractures is necessary if hydrogen and natural gas are delivered together" (Gondial, 2016).

GTI did a quantitative risk analysis of natural gas distribution infrastructure in the United States for carrying hydrogen-enriched natural gas. This study was based on data from NaturalHy and other studies that explored the possible dangers associated with hydrogen transport in current natural gas networks as said by Melaina, et al., (2013). "Using fatal incident data from US distribution systems between 1990 and 2002 and survey findings on severe risks, baseline risk factors for each failure mode in natural gas service were established. The effect of hydrogen was examined based on research results from NaturalHy and other studies, resulting

in the identification of risk factors for each failure mode at three concentrations of hydrogen explored in the literature" (Melaina, et al., 2013).

"Introducing hydrogen into natural gas distribution networks raises the total risk compared to the present natural gas condition. The magnitude of this effect is dependent on the hydrogen content of the gas mixes" (Melaina, et al., 2013). When introducing less than 20 percent hydrogen, the total danger is not greatly increased. However, service lines are more susceptible since they are often put in limited places. In these situations, the inclusion of hydrogen concentration in natural gas surpasses 20 percent, the total risk in service lines may considerably rise, posing grave dangers. In contrast, distribution mains may still provide a moderate overall danger up to 50 percent, both distribution mains and service lines encounter a significant rise in hazards relative to natural gas, making the entire risk in the distribution system undesirable" (Melaina, et al., 2013).

3.3.5 Safety of hydrogen use in buildings

Hydrogen has the potential to be utilized in residential applications such as water heating and cooking. Therefore, it is important to address safety considerations related to household applications. However, there is limited knowledge regarding the risks associated with hydrogen as a consumer fuel in residential and service sector buildings. The hazardous potential of a hydrogen leak into buildings is determined by three main factors, as outlined by Dodds and Demoullin (2013):

- 1. Confinement level: The level of confinement affects the risk of gas accumulation. Confined spaces can include rooms within a building, wall partitions enclosing pipes, as well as spaces created by air currents, open doors, and obstructions that allow hydrogen build-up to reach ignition concentrations.
- 2. Detection of hydrogen: The ability to detect hydrogen is crucial both before ignition to initiate dispersion and after ignition to prevent injuries. Effective hydrogen detection systems are necessary to ensure prompt action in case of a leak.
- 3. Tolerability of ignition and explosion: The safety record of natural gas is used as a reference for assessing the tolerability of hydrogen ignition and explosion. It is essential to understand the comparative risks associated with hydrogen in relation to natural gas.

"In domestic rooms, it takes longer for hydrogen to reach flammable concentrations in confined spaces compared to natural gas. This is due to the higher volumetric release rate of hydrogen, which is offset by its increased dissipation rate resulting from its higher buoyancy in air. However, the overall risk of gas ignition is likely higher for hydrogen than for natural gas in residential buildings. Safety precautions for hydrogen use involve either installing hydrogen technologies outdoors or implementing preventive measures such as detection systems and proper ventilation for indoor applications" (Dodds & Demoullin, 2013).

Worker Safety

Lower Explosive Limit (LEL) values for hydrogen are lower than those for natural gas, suggesting a greater chance of igniting in the case of a gas leak. However, this problem is not anticipated to be relevant at low hydrogen concentrations (below 10 percent). For concentrations of hydrogen up to 10 percent, the current techniques for maintaining worker safety continue to be relevant without change. This information is based on the Australian National Hydrogen Policy, which complies with applicable GPA legislation and standards (2019).

In conclusion, "all energy systems, regardless of their means of transmission or energy storage, pose inherent dangers to both humans and the environment. In comparison to coal, crude oil, nuclear, and hydropower systems, natural gas systems have a reduced risk of catastrophic mishaps. However, they could still pose more dangers than solar and wind energy systems" (Melaina, et al., 2015).

3.4 Leakage issues

"Hydrogen, as the smallest element and the first element in the periodic table, has a greater potential to escape than natural gas. Due to its reduced molecule size, it diffuses typically four to five times quicker than natural gas. In order to reduce safety risks, pipeline network components must be constructed with mechanisms to prevent leakage from valves, seals, gaskets, and other fittings. In some instances, new seals, gaskets, valves, and fittings may be required to address the diffusion of hydrogen gas in accordance with regulatory regulations. Due to its low viscosity and tiny size, existing fittings may let hydrogen molecules to diffuse. In addition, hydrogen may infiltrate and be trapped into the pipeline's walls" (Gondial, 2016).

"Although hydrogen leaking may result in larger volumetric losses, the related energy losses are far smaller. The rate of hydrogen leakage is mostly determined by the material of the pipeline, such as plastic, iron, or alloy. Due to hydrogen's lower molecular size, its leakage rate through pipe walls and joints may be greater than that of methane, which presents economic and safety issues over total gas loss (Melaina, et al., 2013). Cast iron and fibrous cement pipes are more susceptible to leaking. Distribution networks often use polyethylene pipes. According to research, the yearly hydrogen loss due to leakage is predicted to be between 0.0005-0.001% of the total volume delivered" (Gondal & Sahir, 2012; Stetson, et al., 2016).

3.4.1 Leakage through pipe walls

GTI undertook a detailed analysis of several papers, including those from the NaturalHy project, which mainly researched the permeability properties of polyethylene (PE) and polyvinyl chloride pipe materials (PVC). In addition, GTI analyzed the report from the IEA Greenhouse Gas R&D Programme and other pertinent sources of data addressing gas leakage in natural gas distribution pipelines, with a particular emphasis on hydrogen services as outlined by Melaina, et al., (2013).

Assessment of Permeation Loss by NaturalHy Project (Work Package 3)

"Gaz de France examined the permeation loss of natural gas via plastic pipes in the gas distribution network as part of work package 3 of the NaturalHy project. Real pipes and assemblies were tested with a hydrogen/methane mixture to compare the penetration characteristics of hydrogen and methane" (Melaina, et al., 2013).

"The investigation utilized three distinct polyethylene grades (PE 63, PE 80, and PE 100) with various diameters and operating pressures within the normal range for natural gas networks. Tests were done at temperatures ranging from 5 to 25 degrees Celsius. In the testing, pure methane and a 10 percent hydrogen/methane mixture were employed to compare penetration characteristics" (Melaina, et al., 2013).

Table 18 displays the permeation coefficients of hydrogen and methane as well as the expected gas loss for a 32 mm (1.26") PE 80 pipe based on experimental data at various test pressures. The conclusions of the research may be stated as follows:

- Methane has an incubation period for diffusion through the pipe, but hydrogen has an incubation time that is close to zero.
- Both methane and hydrogen penetration rates increase as internal pressures rise.
- In a combination of hydrogen and methane, the permeation coefficient of hydrogen is four to five times larger than that of methane, despite the fact that hydrogen has a lower partial pressure than methane.
- The predicted methane loss for the three kinds of PE pipe is much less than the extrapolated data.
- Under the experimental circumstances, the aging of the pipes had no effect on the permeation coefficients (Melaina, et al., 2013).

Gas	s Pressure Time-Lag (psig) (day)		⊿ag	Permeation Coefficient (×10 ⁻³ ft ³ - mil/ft ² /day	Gas (ft³/mile/year)		Loss	
		CH ₄	H ₂	CH ₄	H_2	CH ₄	H_2	Total
Pure CH ₄	58	6.46	NA	0.18	0	54.07	NA	54.07
90% CH ₄	58	4.31	0	0.09	0.34	25.90	10.59	36.49
+ 10% H ₂	116	6.39	0	0.12	0.50	67.03	31.04	98.07
	174	5.69	0	0.12	0.52	101.91	48.54	150.45

Table 18. The permeation coefficient and the gas loss computed from a 32 mm PE80 Pipe at 58 psig (4 bar) and174 psig (12 bar) (Melaina, et al., 2013)

This study also included PVC-CPE (chlorinated polyvinyl chloride) as another type of PVC material. The hydrogen leakage rate from both PE and PVC pipes was calculated at an operating pressure of 2.9 psig (200 mbar) when distributing 100% hydrogen (Melaina, et al., 2013):

• PE100: 5.0 liter/km/day.

• PVC: 13.2 liter/km/day.

The leakage rates of methane and hydrogen were calculated from PE disc samples under a mixture of 80% natural gas and 20% hydrogen at a pressure of 58 psig (4 bar) are:

- Methane: 1.1 liter/km/day.
- Hydrogen: 2.3 liter/km/day.
- Pure Methane: 1.4 liter/km/day

Gas Leakage from Systems Made of Steel or Ductile Iron

Leakage in systems made of steel or ductile iron often occurs at threads or mechanical joints. GTI observations of gas distribution system leakage indicate that the volume leakage rate for hydrogen is around three times greater than that of natural gas as outlined by Melaina, et al., (2013).

Plastic Pipe and Elastomer Gas Leakage

In the IEA Greenhouse Gas Program, experimental tests were performed to estimate the hydrogen permeability coefficient in a variety of plastic pipes. The findings of the experiment are summarized in Table 19, which also incorporates data from the literature. In this work, the total hydrogen loss was computed using experimental data gathered from a sample of Dutch grid material. The anticipated yearly gas loss is 26103 m³ when 17 percent hydrogen is added into this gas distribution system (918,182 ft³). This gas loss accounts for just 0.0005% of the hydrogen transported. Consequently, the gas loss caused by hydrogen penetration is deemed insignificant and is not anticipated to constitute a substantial concern (Melaina, et al., 2013).

Table 19. Permeation Coefficient (10⁻³×ft³-mil/ft/day/psig) of Hydrogen Gas for Plastic Pipe Materials at 20 C*. (Melaina, et al., 2013)

Material	Experimental studies	References
PE80	1.50	1.99
MDPE	1.63	1.10
PE100	1.46	0.00
PEXa	3.37	0.00
PVC	0.91	0.69

Ductile PVC 0.97 0.00

The bulk of plastic pipes used in natural gas distribution networks in the United States are constructed of polyethylene, namely medium-density polyethylene (MDPE) and high-density polyethylene (HDPE) (HDPE). Less often, polyvinyl chloride (PVC) pipes are also used. Despite having differing material identification techniques, these materials are equivalent to those used in natural gas distribution networks in Europe (Melaina, et al., 2013).

Table 20 provides an overview of the hydrogen and methane penetration coefficients in typical US distribution system plastic pipes and elastomeric materials. The hydrogen permeability coefficient recorded in plastic pipe materials of US quality is comparable to IEA data. It is obvious that the penetration coefficient of hydrogen in plastic pipes is five to six times that of methane. Notably, the hydrogen permeability coefficients of natural rubber and Buna S are 26 and 21 times greater than HDPE, respectively. This implies that owing to their hydrophilic character, these materials are more sensitive to hydrogen penetration (Melaina, et al., 2013).

Material	Hydrogen	Methane
MDPE (PE2708) a	1.43	0.29
HDPE (PE3608) a	1.09	0.16
HDPE (PE4710) a	1.09	0.16
PVC a	0.95	NA
Natural Rubber b	28.39	NA
Butyl Rubber b	4.27	NA
Buna S (SBR) ^b	23.02	NA
Neoprene (CR) ^b	7.67	NA
Buna N (NBR) ^b	9.12	NA

 Table 20. Permeation Coefficient (10⁻³×ft³-mil/ft/day/psig) of Hydrogen in Plastic Pipe and Elastomeric Materials. (Melaina, et al., 2013)

To estimate gas leakage over the whole gas distribution system, the gas leakage rate is computed based on plastic pipes, which have a substantially greater surface area than seals. Using the permeation coefficient, one may calculate the rate of gas leakage (V) via plastic pipes (P), as indicated by Melaina, et al., (2013):

$$V = P * \left(\frac{A}{t}\right) * \Delta p \tag{22}$$

A: pipe surface area (m) t: pipe wall thickness (m)

 Δp : the pressure difference between internal and external surface of pipe (Pa)

For the computation, it was used an HDPE pipe with a diameter of 1 and a wall thickness of 0.1, which is a standard size for electrical distribution systems. The hydrogen permeation coefficient and predicted methane leakage rate are shown in Table 21. Due to its high penetration rate, the addition of hydrogen increases the overall gas loss. At a hydrogen concentration of 20%, the gas loss from the gas combination is almost double that of methane. However, "at low pressures of 3 psig (210 mbar) and 0.25 psig (17.2 mbar), the gas loss for a 1 HDPE pipe is negligible, with values of 5.3 ft³/mile/year and 0.4 ft³/mile/year at 3 psig and 0.25 psig, respectively" (Melaina, et al., 2013).

Hydrogen Content	ogen Content At 60 psig		At 3 psig			At 0.25 psig			
	H_2	CH ₄	Total	H ₂	CH ₄	Total	H_2	CH ₄	Total
0%	0.0	49.4	49.4	0.0	2.5	2.5	0.0	0.2	0.2
10%	32.9	44.5	77.4	1.6	2.2	3.9	0.1	0.2	0.3
20%	65.9	39.5	105.4	3.3	2.0	5.3	0.3	0.2	0.4
50%	164.7	24.7	189.4	8.2	1.2	9.5	0.7	0.1	0.8
100%	329.3	0.0	329.3	16.5	0.0	16.5	1.4	0.0	1.4

 Table 21. The Calculated Gas Loss Rate (ft³/mile/year) Based on Literature Data for HDPE Pipes at the Operating Pressures of 60 psig, 3 psig and 0.25 psig*. (Melaina, et al., 2013)

"Hydrogen displays greater permeability than methane in a variety of polymer materials, such as plastic pipes and elastomeric seals used in typical gas distribution systems, as evidenced by GTI and the NaturalHy project's scientific investigations and published literature" (Melaina, et al., 2013). "With a penetration coefficient that is four to five times greater than that of methane, hydrogen has a much higher permeation rate through ordinary gas distribution pipes" (Melaina, et al., 2013). In comparison to other elastomers, natural rubber and Buna S have a lesser hydrogen-sealing capacity than other elastomers as outlined by Melaina, et al., (2013).

To calculate gas loss through the pipe wall in gas distribution systems, computations are based on a standard polyethylene pipe, whose surface area is greater than that of seals and gaskets as mentioned by Melaina, et al., (2013). Literature data on hydrogen and methane permeability coefficients in polyethylene pipe indicate that the bulk of gas losses occur in main distribution networks operating at or above 60 psig (4.1 bar) (Melaina, et al., 2013). "Adding 20 percent hydrogen to a natural gas pipeline system will increase gas loss by 40 million cubic feet per year from a distribution network with a total pipe length of 414,830 miles of polyethylene pipe with a diameter of less than 2 inches. However, this gas loss is regarded economically minor, and the addition of hydrogen to natural gas may decrease methane leakage and greenhouse gas emissions by a little amount" (Melaina, et al., 2013).

It should be noted that published data on hydrogen permeation coefficients may exaggerate gas loss in a pipe system with a low hydrogen content, particularly at lower working pressures. This is due to the fact that published data are often tested in pure hydrogen and thin polymer films, but practical systems include a combination of hydrogen and methane and have pipes with larger walls (Melaina, et al., 2013). "To correctly quantify gas loss in distribution systems, particularly under operating circumstances characteristic of hydrogen mixing in natural gas pipelines, further study is required" (Melaina, et al., 2013).

Leaks from electrical lines are economically insignificant, but leaks in restricted locations may lead to the buildup of hydrogen, which poses a safety issue. In this context, elastomeric seals with increased hydrogen permeability rates are also an issue. The behavior of hydrogen penetration in plastic pipes and elastomeric materials under anticipated operating circumstances for hydrogen services needs more research, including the development of novel pipe and gasket materials, as stated by Melaina, et al., (2013). This will inform the requirement for leak detection and monitoring systems by aiding in the estimation of gas leaks and assessing possible safety issues in confined areas (Melaina, et al., 2013).

3.5 Durability issues & Hydrogen Embrittlement

For high-pressure gas transmission pipes, it is common knowledge that tough engineering alloys are necessary. In addition, it is widely knowledge that hydrogen may corrode metallic pipe materials. Depending on a variety of factors, including the type of metal, the concentration of hydrogen, and the operating conditions, hydrogen can cause damage to metals (Melaina, et al., 2013). Although metallurgical concerns also play a role, metals' hardness is largely influenced by their composition. It is essential to determine the maximum amount of

hydrogen that can be added to natural gas without reducing the infrastructure's service life (EIGA, 2004; EIGA, 2014).

"Hydrogen damage occurs when hydrogen interacts with residual or applied tensile stress to produce breakdowns helped by the environment. Hydrogen damage can manifest in numerous ways in various alloys, ranging from cracking and blistering to hydride formation and loss of tensile ductility" (Adler, et al., 2003).

Some failure modes related with hydrogen do not exhibit the traditional characteristics of embrittlement (i.e., stress reduction or failure below the load-bearing or yield point), but the term "hydrogen embrittlement" has been used to describe these types of failures for some time (Adler, et al., 2003).

Hydrogen, the lightest and smallest element, can escape through valves, seals, gaskets, and pipelines with greater ease than natural gas. The harmful accumulation of hydrogen gas in enclosed places. A gas meter is the typical instrument for monitoring natural gas use. All of these issues stem from the material degradation that occurs when hydrogen is added to natural gas (Melaina, et al., 2013).

"Commissariat à l'Energie Atomique, CMI, CSM, DBI-GUT, DEPA, École Nationale des Ingénieurs de Metz, GASUNIE, Institut Français du Pétrole, IGDAS, ISQ, STATOIL, TNO, TOTAL, and TUBITAK all contributed to the success of Work Package 3 of the NaturalHy Project, which was directed by GDF SUEZ. This endeavor's principal study objective was to determine the effect of hydrogen on the long-term dependability of natural gas infrastructure (from pipes to appliances)" (Melaina, et al., 2013).

3.5.1 Initiation and growth of defects

"Hydrogen embrittlement of steel pipes is a serious issue in the context of high-pressure natural gas transmission pipelines, especially in the case of existing defects such as corrosion defects and acute defects in the welds. According to the aforementioned investigations, the addition of up to 50 percent hydrogen to gas transmission pipelines might not even result in catastrophic collapse" (Melaina, et al., 2013). However, the allowable level of hydrogen in high-pressure pipelines varies on the type of steel employed. Because distribution systems operate at significantly lower pressures and are built with lower-grade steels, the NaturalHy project did not analyze the potential of hydrogen embrittlement on distribution steel and other metallic pipes, as cited by Melaina, et al., (2013).

Several variables have been consistently recognized as influencing factors in crack growth rate and metal toughness for corrosion fatigue phenomena (Adler, et al., 2003; EIGA, 2004; EIGA, 2014; Zohuri, 2019):

- 1. Stress-intensity range (SIR)
- 2. Load frequency
- 3. Stress ratio
- 4. Aqueous environment electrode potential
- 5. Environment
- 6. Metallurgical variables
- 7. Grain size
- 8. Microstructure
- 9. Type of impurity in the metal structure
- 10. Heat treatment history of steel

Metallurgical variables can play a crucial role in controlling alloy chemistry, inclusion shape, microstructure, and other factors that influence the susceptibility to corrosion fatigue. Measures such as using fine-grained microstructures, killed steels, low carbon equivalents, and microalloying can help mitigate the effects of corrosion fatigue.

It is important to note that "the effects of temperature, pipeline history, load history and waveform, stress rate, and environment composition can vary depending on the specific materials and environmental conditions" (Adler, et al., 2003).



Figure 50. Schematic showing SCC (stress corrosion cracking), corrosion fatigue, and hydrogen embrittlement. (Wei & Shim, 1983) (Adler, et al., 2003)

The influence of hydrogen on different substances varies. Hydrogen can affect the characteristics of steel materials when it comes into intimate interaction with clean metal surfaces. This interaction can have a negative impact on the fatigue characteristics and tensile strength of steels typically used in gas transportation. Hydrogen-induced deterioration leads in accelerated fracture propagation and can potentially trigger the production of new cracks. The influence of a hydrogen atmosphere on the resistance of pipe steel to crack formation under fatigue loading is depicted in Figure 51.



Ritchie, 2012)

da/dN: Crack growth rate

 ΔK : Fracture toughness amplitude applied in fatigue testing (MPa * $m^{\frac{1}{2}}$) R: Ratio of Kmin/Kmax v: Frequency of cycling (Hz)

Mechanism of crack growth in HE

Depending on the particular combination of materials and environment, stress corrosion-induced cracking can be a form of subcritical crack formation influenced by hydrogen. Hydrogen-induced subcritical crack formation can be the primary method of stress fracture propagation in some materials when anodic reactions necessitate equivalent cathodic reactions as cited by Adler et al., (2003).

With cathodic hydrogen, the features of hydrogen-driven subcritical fracture development are comparable to those caused by gaseous or internal hydrogen. Once a substance has absorbed hydrogen, the effects of gaseous and cathodic sources are comparable. This has been observed in a variety of materials and attributes. However, there are three significant distinctions between the gaseous hydrogen and cathodic absorption processes. Initially, cathodic hydrogen is adsorbed as atomic hydrogen on the surface, whereas gaseous hydrogen is in molecular form and must dissolve into atomic hydrogen. In some instances, "the dissociation phase can be the rate-determining step, while the absorption of loosely bound molecular hydrogen is comparatively simple" (Adler et al., 2003).

Even for the same hydrogen activity, the emission and uptake of gaseous hydrogen from the cathode might differ dramatically. Depending on the velocity of the anodic reaction, the activity of hydrogen produced by cathodic hydrogenation can be quite high (up to thousands of pounds per square inch), whereas hydrogen gas pressures are often much lower. Moreover, under electrochemical corrosion circumstances, the surface characteristics of materials at crack tips can vary significantly in the presence of hydrogen gas, which may contain considerable quantities of other gases such as oxygen (O_2) and carbon monoxide (CO_2) (Adler et al., 2003).

It has been suggested that **hydrogen-induced crack growth** is the primary stress corrosion mechanism in ferritic steels, nickel-based alloys, titanium alloys, and aluminum alloys, with ferritic steels offering the greatest evidence for this mechanism. In accordance with the trend reported in hydrogen gas embrittlement, the crack growth behavior of ferritic materials in aqueous settings is influenced by yield strength, impurity segregation, and temperature. Figure 52(a) represents the fracture growth rate of 3-percent Ni steel in water as a function of temperature, whereas Figure 52(b) depicts the crack growth rate of 4340 steel in gaseous hydrogen. The maximal rate of crack growth occurs at approximately 20 degrees Celsius (70 degrees Fahrenheit) and reduces at higher and lower temperatures. However, anodic stress corrosion processes become active for steels tested in water at temperatures above 100°C (212°F). Similar tendencies are observed for the effects of impurity segregation on hydrogen-induced crack propagation, with cathodic hydrogen and gaseous hydrogen producing practically identical outcomes, as cited by Adler et al., (2003).



Figure 52. Schematic of crack growth rate versus temperature. (Adler, et al., 2003)

A unique mechanism for subcritical crack development generated by cathodic hydrogen has not been fully explained. This is because, in general, it was believed that the presence of hydrogen alone sufficed to identify the source of the fissures. A hypothesized mechanism, however, implies that grain boundary impurities function as recombinant hydrogen poisons, hence enhancing cathodic hydrogen uptake. This mechanism is depicted schematically in Figure 53; tin and antimony deposited at nickel borders increase the rate of hydrogen uptake (Adler et al., 2003). This process does not provide a new mechanism by which hydrogen generates cracks; rather, it focuses on how impurity sequestration can improve hydrogen uptake. Such mechanisms can upset the equilibrium between anodic and cathodic processes or accelerate the formation of cracks to levels that are observable or practically important. However, when the combined effects of impurity diffusion and hydrogen embrittlement are considered, boundary impurities accelerate fracture formation through linked grain-boundary embrittlement processes, rather than through increased hydrogen absorption. It has been determined that the behavior of hydrogen and hydrogen gas is identical. Materials having impurities such as sulfur, phosphorus, antimony, and tin deposited near grain boundaries are vulnerable to various kinds of hydrogen, including cathodic, gaseous, and internal hydrogen (Adler, et al., 2003).



Figure 53. Schematic illustrating the effect of certain contaminants on the proposed mechanism by which intergranular embrittlement of nickel occurs at cathodic potentials. (Adler, et al., 2003)

3.5.2 Hydrogen damage of Metals – Hydrogen embrittlement

General aspects of hydrogen embrittlement

Hydrogen damage causes environmental failure when hydrogen interacts with residual or applied tensile tension (Melaina et al., 2013). Hydrogen embrittlement refers to a variety of failure mechanisms, including but not limited to cracking, blistering, hydride formation, and tensile ductility loss (ASM Vol. 13a). Hydrogen damages metals at lower stress levels than

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those seen in environments devoid of hydrogen. The microstructure, strength, stress, strain rate, and temperature of the material, in addition to the hydrogen's purity, all have a role (Melaina et al., 2013).

"Types of hydrogen damage have been identified to facilitate the investigation and formulation of theories about the mechanisms behind the occurrence of hydrogen damage" (Adler et al., 2003). In Volume 13A of the ASM Handbook, "the initiation locations, materials susceptible to damage from hydrogen, sources of hydrogen, failure conditions, and typical failure scenarios are all discussed in depth". Due to their vulnerability to hydrogen damage, the materials, forms of damage, hydrogen sources, and typical failure situations listed in Table 22 are included (Melaina et al., 2013; Adler et al., 2003).

The first three categories are utilized to show ordinary **hydrogen embrittlement** since they are characteristic of environmental-driven cracking. Several forms of damage are the result of corrosion processes generated by environmental stress (Adler et al., 2003). "Since hydrogen damage requirements for iron and copper pipes may not apply to natural gas distribution systems, hydrogen damage to these materials is not a serious problem" (Adler et al., 2003; Melaina et al., 2013).

Hydrogen embrittlement is a potential issue for steel pipes, albeit its severity depends on the material. Hydrogen-induced cracking is more prevalent in high strength steel (tensile strength > 100 ksi), while low strength steel loses tensile ductility to a great extent (Melaina et al., 2013). Table 22. Classifications of processes of hydrogen degradation of metals. (Adler, et al., 2003)

ing Shatter cracks, Microperforation Degradation in flow Metal	flakes, fisheyes form	pper, Steels (forgings and Steels (compressors) Iron, Steels, nickel-base V, Nb, Ta alloys	en Water vapor m, reacting with Gaseous hydrogen hydrogen hydrogen corrosion, g, molten steel corrosion	en 1-10 ppm hydrogen content 0.1 to 100 Mp y Precipitation of t to dissolved ingot 2 to 8*1066 Mpa at 20 Mpa gaseous hydrogen 100 °C (various metals, T> 0.5 0.1 to 100 hydrogen a 02 cooling 100 °C metting point) (various metals, T> 0.5 20 exceed solubi			sfect Internal defect Unknown	en n, ,and Hvdrosen diffrision ,and Hvdrosen diffrision
II IANTION I I I I I I I I I I I I I I I I I I		arbon and low-alloy steels steels aluminu	Hydroge sulfide corrosion electroly charging gaseous	Hydroge activity p to 10e2 Mpa ar 200-595 °C equivalent 0.2 to 1*1 Mpa at 0-15			Surface (decarburization), internal carbide interfaces Internal de nethane bubble formation)	Hydroge Carbon diffusion diffusion diffusion hydrogen nucleation
	Loss in tensile ductility	Steels, nickel-base alloys, Be-Cu bronze, aluminum alloys	Gaseous hydrogen, internal hydrogen from electrochemical charging	0.1 to 10 ppm total hydrogen content range of gas pressure exposure	Observed at -100 to 700 °C	Occurs in absence of effect on yield stress, strain rate important	Surface and/or i internal effect (r	Surface or (c
gen embrittlement	Hydrogen stress cracking	Carbon and low-alloy steels	Thermal processing, electrolysis, corrosion	0.1 to 10 ppm total hydrogen content	Observed at -100 to 100 v °C most severe near 20 °C	Strain rate important, embrittlement more severe at low strain rate, always more severe in notched or precracked specimens	internal crack initiation	Internal diffusion to stress
Hydro	Hydrogen environment embtitlement	Steels, Nickel-base alloys, metastable stainless steel, titanium alloys	Gaseous H2	10e-12 to 10e2 Mpa gas pressure	Observed at -100 to 700 °C most severe near 20 °C	Strain rate important, embrittlement more severe at low strain rate, generally more severe in notched or precracked specimens	Surface or internal initiation, incubation period not observed	Surface or subsurface
		Typical materials	Usual source of hydrogen (not exclusive)	Typical conditions			Failure initiation	Mechanisms

MSc Oil and Gas Process Systems Engineering HYDROGEN COMPATIBILITY ASSESSMENT IN NATURAL GAS INFRASTRUCTURES The strain rate influences embrittlement in hydrogen conditions, which happens when alloys experience plastic deformation when in contact with hydrogen-containing gases or undergoing corrosion processes. At low strain rates, high hydrogen pressures, and high hydrogen purities, the mechanical characteristics of ferritic steels, nickel-based alloys, titanium alloys, and metastable austenitic stainless steels degrade the most (Adler, et al., 2003).



Figure 54. Hydrogen-induced blistering (left) and cracking (HIC) (right). (Szummer, et al., 1999)

"Hydrogen stress cracking (HSC) or else Hydrogen induced cracking (HIC), also known as hydrogen-induced cracking or static fatigue, is the brittle fracture of usually ductile alloys under persistent hydrogen stress". Figure 54 depicts the microstructure of blistering and cracking failure in an atmosphere containing hydrogen. It does not apply to steels over 150 °C, however "hydrogen attack" might replace it at high temperatures. Failure often happens under prolonged stress below the yield point of the material. This mechanism is dependent on the hydrogen volatility, material strength, heat treatment/microstructure, stress applied, and temperature. "Numerous steels have a voltage threshold below which hydrogen stress cracking cannot occur. This threshold is dependent on the steel's strength and the unique hydrogencontaining environment" (Adler, et al., 2003; EIGA, 2004; EIGA, 2014). Therefore, the hydrogen stress cracking critical stress or stress intensity is not considered a material attribute. "In general, the critical stress of an alloy reduces as its yield strength and tensile strength rise. Hydrogen stress cracking is characterized by hydrogen absorption and a delayed time-to-failure (incubation period) for hydrogen diffusion into areas with high triaxial stress. Hydrogen stress cracking may encourage a particular style of alloy failure, as opposed to the kind often found in benign settings" (Adler, et al., 2003; EIGA, 2004; EIGA, 2014). Thus, all fracture mechanisms have been seen in the majority of commercially available alloy systems. "However, hydrogen stress cracking often creates acute, distinct fractures, while stress corrosion cracking is characterized by extensive branching (SCC). Sulphide stress cracking, the catastrophic cracking of steel in hydrogen sulphide (H₂S) conditions, is a subtype of hydrogen stress cracking" (Adler, et al., 2003; EIGA, 2004; EIGA, 2014).

Loss of tensile ductility is one among the early signs of hydrogen damage to be identified. When exposed to hydrogen, the elongation and necking of steels, stainless steels, nickel-based alloys, aluminium alloys, and titanium alloys decrease significantly. This form of failure is often encountered in low-strength alloys, and the degree of tensile ductility loss is proportional to the hydrogen concentration of the material. Loss of tensile ductility is strain rate dependent and gets more evident as strain rate lowers (Adler, et al., 2003).

Hydrogen attack is a high-temperature type of hydrogen damage caused by prolonged exposure of soft and low-alloy steels to high-pressure hydrogen at high temperatures. Hydrogen diffuses throughout steel and interacts with carbon in solution or as carbides to produce methane gas. This may result in the production of fractures and fissures or the decarburization of the steel, resulting in a loss of alloy strength. This kind of damage is temperature-dependent, with a temperature threshold of around 200 degrees Celsius (400 degrees Fahrenheit) (Adler, et al., 2003).

Hydrogen-induced blistering occurs when large concentrations of absorbed hydrogen atoms recombine into hydrogen molecules at exceptional places. This generates pressure that squeezes the grid, therefore expanding the area. This mechanism, however, only happens at very high absorption rates. This occurs when metals are subjected to high hydrogen concentrations. For instance, it is induced by chemical charging or pickling. Even at pressures of up to 700 bar, the concentration of gaseous hydrogen is insufficient to absorb this quantity (Adler, et al., 2003).

Hydrogen is injected into metals during forging, welding, or casting, resulting in cracking due to the **precipitation of internal hydrogen**. These occurrences use high temperatures to extract hydrogen from water. When the metal re-cools, hydrogen separates and forms fissures and so-called fisheyes. This may be avoided by keeping all weld ports and weld regions as dry as possible. However, this approach of incorporating hydrogen into metals is more production-oriented than application-oriented. Therefore, adding hydrogen to a gas network does not enhance the incidence of hydrogen precipitation-related cracking (Adler, et al., 2003).

Cracking from hydride production happens when hydrogen combines with certain rare earth, alkaline earth, or transition metals to generate hydrides. This occurs most often in titanium, zirconium, and tantalum. The following reactions produce titanium hydride:

$$Ti + H_2 \rightarrow TiH_2$$
 (23)

Hydrides are chemicals that decrease the ductility and dielectric strength of metals due to their brittleness. With the exception of trace quantities of titanium, the metals generally used to create transport pipes are not susceptible to hydride formation. In addition, the reaction mentioned above prefers temperatures between 300°C and 500°C. Hydrogen-induced cracking due to hydride formation poses no new safety risks when adding hydrogen into gas networks.

3.5.3 Theory of hydrogen damage

As indicated by the several classes of hydrogen damage, there are multiple reasons and ideas for the various types of deterioration found in hydrogen damage. Pressure theory, surface adsorption, deagglomeration, improved plastic flow, hydrogen assault, and hydride creation are the prominent hypotheses. These models have been widely developed and researched, and additional ideas are often modifications or expansions of these essential notions (Adler, et al., 2003).

Hydrogen damage, the pressure theory of hydrogen embrittlement, which is one of the oldest theories, proposes that hydrogen penetration into the metal results in its concentration at interior surfaces or spaces, leading to the creation of molecular hydrogen. At these microstructural discontinuities, the increased hydrogen concentration generates high internal pressures that encourage void expansion and crack initiation. This hypothesis explains blistering and some features of tensile ductility loss; however it does not account for all hydrogen stress cracking data (Adler, et al., 2003).

The surface adsorption hypothesis postulates that hydrogen adsorbs to the free surface of the crack tip, decreasing its surface free energy and, hence, the work of fracture. This decrease in effort of fracture promotes crack propagation at stress levels below those commonly observed in a moderate environment. However, there are objections to this model, such as the underestimating of fracture effort and the inability to account for the discontinuous crack development found in hydrogen stress cracking (Adler, et al., 2003).

The theory of **decohesion** addresses the influence of hydrogen on the cohesive forces between atoms in the matrix of an alloy. It shows that hydrogen concentrations sufficiently high ahead of a crack tip may diminish cohesive forces, leading to fracture when the local maximum tensile stress perpendicular to the crack plane exceeds the lattice cohesive force (Adler, et al., 2003).

Group Vb metals (niobium, vanadium, tantalum), zirconium, titanium, and magnesium create hydrides when exposed to hydrogen environments. It is characterized by the development of brittle metal hydrides near the fracture tip. The hydride precipitates, followed by either crack arrest in the more ductile matrix or continuous fracture propagation between hydrides due to ductile rupture (Adler, et al., 2003).

Hydrogen attack, which is unique to high-temperature hydrogen damage, appears as either surface or interior decarburization. At extreme temperatures, hydrogen diffuses through steel and interacts with solid solution carbon or carbides to produce hydrocarbons, including methane. This chemical reaction is characterized thermodynamically and is temperature and hydrogen partial pressure dependent (Adler, et al., 2003).

Hydrogen entrapment refers to the attachment of hydrogen atoms to impurities, structural flaws, or microstructural components in an alloy. These traps may display reversible or irreversible trapping behavior and may be movable (e.g., dislocations, stacking faults) or stationary (grain boundaries, carbide particles). While trapping has been studied mostly in steels, comparable trapping behavior has been seen in face-centered cubic alloys, albeit to a lesser extent than in steels (Adler, et al., 2003).

These many hypotheses and methods provide light on the complicated nature of hydrogen damage and add to our comprehension of the variables affecting the deterioration of materials in the presence of hydrogen. (Adler, et al., 2003; Melaina, et al., 2015).

3.5.3.1 Hydrogen Damage in Iron-Base Alloys

Pure Irons: Hydrogen damage may occur in comparatively pure irons, such as Ferrovac E and other magnetically soft irons, resulting in either transgranular or intergranular fracture, depending on parameters such as heat treatment and the presence of impurities and solutes (carbon, oxygen, nitrogen). Hydrogen may diminish the yield strength and flow stress at normal temperature or cause hardening in iron of high purity. However, with impure iron, under circumstances of low hydrogen fugacity, the yield strength may be lowered while the flow stress can be enhanced (Adler, et al., 2003).

Numerous variables impact the behavior of ferrous alloys in environments containing hydrogen. The susceptibility to hydrogen embrittlement is influenced by the hydrogen concentration, temperature, heat treatment, microstructure, applied and yield stress levels, solution composition, and surrounding environment. The influence of hydrogen concentration on the time to failure of high-strength steel is shown in Figure 55. In general, increasing the content of hydrogen in an alloy decreases the time to failure and the stress level at which failure occurs. The period of baking might change the amount of residual hydrogen in the steel matrix, consequently changing its behavior (Adler, et al., 2003).



Figure 55. Static fatigue curves for various hydrogen concentrations obtained by different baking times at 150 °C. (Adler, et al., 2003)

The amount of hydrogen in an alloy is affected by the fugacity, which approximates the amount of hydrogen at the exposed surface. Therefore, hydrogen embrittlement is affected by the hydrogen gas pressure or pH of the environment, as well as other environmental elements that favor or impede the entrance of hydrogen into the alloy. Temperature is also an important factor in the hydrogen embrittlement of ferrous alloys. Due to differences in hydrogen diffusivity and trapping, the severity of embrittlement is greatest at room temperature and decreases as the temperature rises or falls (Adler, et al., 2003)

Hydrogen damage in **low strength steels** with a yield strength of 700 MPa or less appears predominantly as a loss in tensile ductility or blistering. In the US natural gas distribution system, metallic pipes constructed of low strength steels such as API 5L A, B, X42, and X46 are not vulnerable to hydrogen-induced embrittlement or hydrogen-induced failures under typical operating circumstances. Other metallic pipes used in distribution systems, such as ductile iron, cast and wrought iron, copper pipes, and certain plastics like as PE and PVC, provide low risk of hydrogen damage under normal working circumstances. Most distribution system elastomeric materials are also compatible with hydrogen (Adler, et al., 2003)

In contrast, **high strength steels** with yield strengths over 700 MPa (or beyond 900 MPa according to other sources) are more vulnerable to fracture, either in an intergranular or quasi-cleavage manner, depending on the stress intensity. Under prolonged loading, these steels often demonstrate an incubation period prior to fracture initiation, which is generally linked with areas of high triaxial stress. Fracture initiation in these steels occurs internally owing to the generation of triaxial strains at notch roots or under circumstances of plane strain. Steels' resistance to hydrogen embrittlement may be considerably affected by their metallurgical structure. For instance, a quenched and tempered fine grain microstructure is often more resistant to cracking than a normalized or bainitic steel, especially when compared at equal levels of strength. Typically, the most resistant microstructure is a highly tempered martensitic structure with equiaxed ferrite grains and uniformly dispersed spheroidized carbides throughout the matrix. It is vital to evaluate both heat treatment and composition parameters, since they



impact microstructure and resistance to embrittlement and are interdependent (Adler, et al., 2003)

Figure 56. How a refinement in grain size increases resistance to hydrogen failure, as assessed by the time to failure of two strengths of AISI 4340 steels, is described. (Adler, et al., 2003)

Stainless Steels: The behavior of stainless steels in hydrogen-bearing environments is primarily influenced by their strength level. Ferritic stainless steels exhibit excellent resistance to hydrogen embrittlement due to their low strength and increased ductility. However, if these steels undergo cold working, they can become susceptible to cracking in hydrogen environments. Similarly, austenitic stainless steels show high resistance to hydrogen cracking when in the annealed or lightly cold-worked condition, but their susceptibility increases significantly when heavily cold worked. This increased susceptibility to hydrogen cracking with increasing yield strength from cold working is similar to the behavior observed in carbon and low-alloy steels (Adler, et al., 2003).

Duplex stainless steels, which consist of a two-phase structure of ferrite and austenite, exhibit unique behavior in hydrogen environments. The solubilities and diffusivities of hydrogen differ significantly between the austenite and ferrite phases, leading to distinct responses in the overall duplex alloy compared to ferritic or austenitic stainless steels (Adler, et al., 2003).

Hydrogen attack is the only form of hydrogen damage that can occur at high temperatures, primarily affecting ferritic steels. Factors such as time, temperature, and hydrogen pressure influence hydrogen attack. Chromium-molybdenum steels have demonstrated cost-effective resistance to hydrogen attack and have gained extensive industrial experience in this regard (Adler, et al., 2003).

3.5.3.2 Hydrogen damage in Nickel alloys

Nickel and its alloys exhibit vulnerability to hydrogen damage in both aqueous and gaseous hydrogen conditions. The same parameters that determine the susceptibility of iron alloys to hydrogen embrittlement are also significant for nickel alloys, although to a lower level. In general, automotive metals are less susceptible to hydrogen degradation than bcc (body-centered cubic) materials owing to their greater lubricity and lower solute diffusivity. Similar to iron alloys, hydrogen may cause intergranular, intragranular, and quasi-cleavage cracking in nickel and its alloys. These materials may look brittle on a macroscopic scale, but on a microscopic scale, they demonstrate a high degree of local flexibility and flow near the crack
tip, indicating that hydrogen may actually strengthen the material in specific locations (Adler, et al., 2003).

3.5.3.3 Hydrogen damage in Aluminum alloys

Recent research indicates that hydrogen may cause aluminum to become brittle. Until recently, all environmental cracking in aluminum and its alloys was attributable to stress corrosion cracking (SCC). Recent studies done in certain hydrogen settings have shown, however, that aluminum is sensitive to hydrogen damage. Hydrogen damage in aluminum alloys may emerge as intergranular or intragranular fractures, as well as blistering. Blistering is a typical occurrence in aluminum smelting and heat treatment operations that create hydrogen via water vapor reactions. Frequently, hydrogen blisters are linked to grain boundary precipitation or the creation of tiny voids. Notably, aluminum blisters are distinct from those found in iron-based alloys in that they often entail the creation of several near-surface spaces that ultimately merge into a single big bubble (Adler, et al., 2003).

Similar to iron-based alloys, hydrogen diffuses into the aluminum lattice and accumulates in internal flaws. This diffusion process is most likely to occur prior to age hardening during air furnace annealing or solution heat treatment. Similar to the phenomena reported in iron- and nickel-based alloys, the hydrogen permeability also influences the development of fractures in aluminum exposed to hydrogen. The permeability of hydrogen and the rate of fracture formation are dependent on the potential, with a higher negative potential resulting in increased sensitivity to hydrogen embrittlement. Furthermore, the ductility of aluminum alloys in the presence of hydrogen is affected by temperature, with negligible ductility loss reported at temperatures below 0 °C (32 °F). This behavior is similar to that of other face-centered cubic (FCC) alloys (Adler, et al., 2003).

3.5.3.4 Hydrogen damage in copper alloys

Vapor embrittlement has been known for a long time as a prevalent type of hydrogen damage in copper, but it only happens when oxygen is present. When hydrogen penetrates a metal, it interacts with oxygen in solid solution or on oxide inclusions, producing water. At temperatures over the water's critical temperature, steam is produced, causing pressure that may lead to the production of microvoids and fractures. The equation for this reaction is Cu2O + 2H = 2Cu + H2O(g) (Adler, et al., 2003). Copper annealing in a hydrogen environment often results in vapor embrittlement, which is not a worry at lower temperatures when vapor production is restricted. Copper without oxygen reduces the likelihood for vapor embrittlement substantially. Nonetheless, when oxygen-free copper is subjected to extreme cold working, grain boundary inclusions may occur and contribute to hydrogen embrittlement when hydrogen is injected (Adler, et al., 2003).

3.5.4 Hydrogen diffusion via Plastic Pipes

The rate of hydrogen diffusion through the walls of polyethylene (PE) pipes is typically four to five times greater than that of methane. However, it is crucial to highlight that the total gas permeation loss, including hydrogen, remains very low and within acceptable limits from the viewpoints of safety, economics, and environmental effect (Melaina, et al., 2013).

3.5.5 Reliability of Gas meters for Hydrogen service

Hydrogen blending with natural gas may affect the accuracy of current gas meters. The magnitude of this effect is dependent on the meter's design, and it has been shown that the decrease in accuracy is acceptable if recalibration is conducted within a range of less than 4 percent when measuring gas mixtures containing less than 50 percent hydrogen. Meters working with hydrogen concentrations below 50% may not need calibration. When the hydrogen production system does not create pure hydrogen, however, it is essential to undertake durability tests to evaluate the possible consequences of contaminants that may enter the network if the system does not produce pure hydrogen. Based on the US distribution system,

these data give useful insights into the link between gas meters and hydrogen (Melaina et al., 2013; Melaina, et al., 2015).

In the NaturalHy Projects-Work Package 3 investigation, three gas meters with polymer membranes made by Gallus (France), Dresser (Italy), and Elster (Germany) were assessed using two gas mixtures: 100% methane and a combination of 50% hydrogen and 50% methane. The Dresser meter showed a positive deviation from 100 percent methane, but the Gallus and Elster meters demonstrated a negative deviation. However, for each of the measured meters, the variations were less than 2 percent and reduced as flow rates declined (Melaina, et al., 2013).

3.5.6 Crystal structure

The most significant engineering alloys include face-centered cubic (FCC), bodycentered cubic (BCC), and hexagonal close-packed crystal structures (HCP). Certain alloys may undergo allotropic transformations under appropriate circumstances, such as quenching or welding, and generate martensite, which has a body-centered square lattice. In rare instances, martensite may be induced by strain. In terms of toughness, FCC structures demonstrate the greatest level of toughness, followed by BCC structures and HCP structures. BCC-structured carbon steel is extensively utilized for high-pressure gas transport. In contrast, nickel alloys normally have an FCC structure, but some may become embrittled in the presence of hydrogen (H₂). (EIGA, 2004) (EIGA, 2014).

3.6 Integrity

Preexisting faults exist in pipe materials or weld seams, and the addition of hydrogen to a pipeline network may modify the operating environment, resulting in accelerated crack propagation and fatigue failure from existing defects. This may effect pipeline integrity negatively. Certain faults that may be tolerated under present integrity control standards may be worsened in hydrogen-containing settings as a result of changes in material characteristics (Melaina, et al., 2013).

In the United States, the Pipeline and Hazardous Materials Safety Administration (PHMSA) has developed integrity control rules for hazardous liquids and gas transit lines, but gas distribution lines lacked comparable regulations. In 2009, however, the PHMSA issued a final rule, which went into effect on February 2, 2010, establishing integrity control standards for gas distribution pipeline systems. The deadline for operators to execute a distribution pipeline system health program was extended to August 2011 (Melaina, et al., 2013).

Natural gas pipelines have been the primary subject of studies examining the appropriateness of the Hydrogen Service Integrity Program. Compared to high-pressure transmission lines, integrity issues in medium- to low-pressure distribution systems are deemed less dangerous if the permitted level of hydrogen in the high-pressure pipeline does not pose a significant threat to the operation of the much lower-pressure distribution system. It is inappropriate to immediately adapt a transmission system integrity program to a distribution system since they are designed with different materials and function under different pressures and environmental conditions. GTI evaluated natural gas distribution and identified fourteen possible hazards based on a survey of utility operators done by the American Gas Foundation in order to assess the potential dangers associated with adding hydrogen into the distribution system. GTI reevaluated each hazard in light of the circumstances under which the system will carry hydrogen/natural gas combinations, with the NaturalHy project integrity analysis acting as the basis for determining distribution system integrity threats (Melaina, et al., 2013).

Under the "NaturalHy Project Work Package 4" directed by DBI-GUT, an inquiry was done into modernizing the existing Integrity Management Program (IMP) for delivering hydrogen/natural gas mixes. TNO Science & Industry, Computational Mechanics BEASY, GDF SUEZ, PII Ltd., Istanbul Gas Distribution Co. Inc. (IGDAS), N.V. Nederlandse Gasunie, Instituto de Soldadura e Qualidade (ISQ), Turkish Scientific and Technical Research Council (TUBITAK), StatoilHydro, and Total participated in this project (Melaina, et al., 2013).

3.6.1 Defects in Natural Gas network

Work Package 4 of the NaturalHy Project gives insight into the permissible flaws in natural gas pipeline systems, as specified by the integrity program and based on characteristics such as the amount, kind, distribution, and form of defects. Concerning hydrogen service, the stresses that build across the defect and the pace at which the defect propagates after the stress exceeds the threshold value for crack propagation are of fundamental importance (Melaina, et al., 2013).

Corrosion and similar faults do not cause considerable pressures. Nonetheless, acute flaws, such as fractures, may cause large stresses, particularly under normal pipeline fatigue loads. Hydrogen may expedite the formation of fractures, making them more severe than corrosion-induced flaws (Melaina, et al., 2013).

3.6.2 Hydrogen impact on defect criticality

Based on past research, it is obvious that the allowable beginning crack size is altered, especially for axial flaws. Back-calculating using an expected design life and taking into account the crack development rate in a particular environment may establish the critical size of the defect. Under the assumptions established for hydrogen/natural gas mixes comprising up to 50 percent hydrogen, the effect of hydrogen on defect criticality is determined to be small. A technique for calculating the likelihood and failure rate of faults leading to pipeline failure has been created (Melaina, et al., 2013).

To establish an integrity management system for gas pipelines, threats need to be classified for the distribution infrastructure. ASME Standard B31.8S provides a classification of threats, including the following:

- 1. Time-Dependent Threats:
 - External corrosion
 - Internal corrosion
 - Stress corrosion cracking (SCC)
- 2. Stable Threats:
 - Manufacturing related defects (e.g., defective pipe seam or pipe)
 - Construction related defects (e.g., defective girth weld, wrinkle bend, or buckle)
 - Equipment related issues (e.g., gasket or O-ring failure, control/relief equipment malfunction)
- 3. Time Independent:
 - Third-party/mechanical damage
 - Incorrect operations (e.g., incorrect operation procedure)
 - Weather-related/outside force damage (e.g., cold weather, lightning, heavy rains, floods, earth movements)

These hazards are largely outlined for high-pressure natural gas transmission systems made mostly of coated, jacketed, or bare high-strength steel. However, distribution systems are not susceptible to all dangers, such as stress corrosion cracking. Distribution systems, particularly water distribution pipes, run at lower pressures and are thus less susceptible to stress corrosion cracking. Distribution systems use a variety of materials, including steel, polyethylene, cast iron, wrought iron, various polymers, and copper (Melaina, et al., 2013).

Due to the diversity of materials and event reasons, the nine categories of hazards identified for transmission pipes have been increased to fourteen for distribution systems. Unlike transmission pipes, the top two hazards to distribution pipelines are weather-related external force damage to cast iron and excavation/mechanical damage, as opposed to the time-dependent corrosion concerns that are prevalent in transmission pipelines. This is owing to the fact that the distribution pipes are underground in densely inhabited regions and are regularly damaged by external forces. The addition of hydrogen to natural gas distribution networks has

no substantial effect on the risk of hazards. However, if hydrogen is present, the severity of the risk may rise in the event of events leading to leaks (Melaina, et al., 2013).

Threat Priority	Threat	% of Respondent
1	External Pressure/Weather Cast Iron Pipe	90
2	Excavation/Mechanical Destruction	87
3	Corrosion-External Bare Steel Pipe	86
4	Cast Iron Pipe External Corrosion (Graphitization)	71
5	Externally Coated and Wrapped Corrosion-Proof Pipe	69
6	Related to Construction Defects Plastic Pipe	57
7	External Pressure/Weather Steel Pipe	49
8	Related to Construction Defects Steel Pipe	48
9	Incorrect Procedures and Operator Error	35
10	Equipment Malfunction	35
11	Plastic Pipe with Manufacturing Defects	30
12	External Pressure/Weather Plastic Pipe	26
13	Internal Corrosion	22
14	Plastic Pipe with Manufacturing Defects	22

 Table 23. Operator Perceptions on threat significance. (Melaina, et al., 2013)

In conclusion, the emphasis of the NaturalHy project integrity analysis was on high voltage transmission pipes. The research suggests that hydrogen may be transported over existing natural gas pipelines with minimum modifications to present integrity control processes. Depending on the hydrogen content and particular operating circumstances of each pipeline, the necessary changes will vary. For pipeline hydrogen concentrations below 50 percent, modifications to the present integrity program are deemed minimal. However, a thorough analysis of each case and changes to the maximum concentration of hydrogen are required (Melaina, et al., 2013).

GTI has also remarked on this research, emphasizing that the danger of hydrogen to distribution system integrity is quite modest compared to transmission pipes. Natural gas distribution systems vary greatly from transmission systems, and maintenance strategies intended for transmission systems cannot be transferred simply to distribution systems. Considering the frequency and severity of fires and explosions in populated regions, it may be necessary to reevaluate the permissible quantity of hydrogen in transmission pipes for distribution systems (Melaina, et al., 2013).

Moreover, gas leaks in distribution systems are more worrisome than those in transmission lines, particularly in service locations with limited space. Leak detection/monitoring devices or sensors may be necessary for the health management of hydrogen service distribution networks. Notably, there are presently no known odorants for hydrogen, highlighting the need for more research in this field (Melaina, et al., 2013; Melaina, et al., 2015).

3.7 End use issues

3.7.1 Separation

The separation of hydrogen from the gas mixture at the end-use site is one of the primary obstacles of delivering hydrogen using existing natural gas networks. In refineries, pressure swing adsorption (PSA) is a well-established method for producing ultrapure

hydrogen. However, this method needs big units and is best successful when working with mixtures containing at least 50 percent hydrogen content. In the case of natural gas pipelines, smaller separation devices are required to extract hydrogen from mixtures with lower hydrogen concentrations, often below 25 percent (Melaina, et al., 2013).

In addition, the extracted hydrogen purity must fulfill the standards of the desired application. Hydrogen-selective membranes have emerged as a potential method for recovering hydrogen from input streams with modest quantities of hydrogen (30 percent). These membranes can effectively isolate hydrogen from mixes of natural gas and hydrogen (Melaina, et al., 2013). Work Package 5 of the NaturalHy project has focused on the development of enhanced hydrogen-selective membranes for this purpose. This project was conducted by the University of Oxford, with assistance from the Norwegian University of Science and Technology (NTNU) and Compagnie Européenne des Technologies de l'Hydrogène (CETE) (Melaina, et al., 2013).

In general, there are two kinds of membranes: dense membranes (such as metallic membranes) and microporous membranes (such as carbon molecular sieves). In the NaturalHy research, both kinds of membranes were evaluated (Melaina, et al., 2013).

Electroless plating of palladium and carbon molecular sieves (CMS) have the capacity to separate hydrogen from hydrogen/natural gas mixes carried via natural gas pipeline networks, according to the research. Palladium membranes can create hydrogen with a high degree of purity, but they are costly and need operation at temperatures of 300 degrees Celsius. CMS membranes, on the other hand, are cost-effective and function at temperatures between 30°C and 90°C, with a maximum hydrogen concentration of around 98 percent (Melaina, et al., 2013).

A separation system that combines palladium and CMS technology is regarded as the most promising method. This hybrid system, which employs CMS cones with palladium, provides an economical alternative. The study's cost analysis indicates that hybrid systems with extra accessories might be more cost-effective than PSA alone. While smaller PSA systems are now being developed, the extraction of hydrogen from streams containing less than 40 percent hydrogen causes difficulties. Incorporating extra PSA or CMS membranes in the first stage may thus assist in removing hydrogen content and concentrating the input for effective separation (Melaina, et al., 2013).

3.7.2 Adaptation of end-use systems and concerns of quality

As indicated by the Wobbe index and calorific value, the study's analysis reveals that the quality of the downstream gas continues to meet legal criteria (Melaina et al., 2013; Melaina, et al., 2015).

The adaption of end-use natural gas networks to accept significant amounts of hydrogen blends is an additional factor to consider. Typically, end-use regulations set the toughest limitations on the hydrogen content in natural gas. Concerns must be alleviated by ensuring compliance with these standards in order to guarantee safety and material integrity while combining hydrogen (Florisson, 2009; Melaina, et al., 2015).

Numerous studies have addressed the maximum allowable hydrogen concentration for different end-use systems, including residential boilers, stoves, industrial operations, and power generation (Schmura & Klingenberg, 2005; De Vries, et al., 2007; De Vries, 2009). It has been proven that it is safe to utilize amounts of hydrogen up to 28 percent in well maintained current appliances. However, after a 15-year period, the compatibility of equipment with combinations of hydrogen and natural gas remains unknown (De Vries, 2009). Considering the inertia involved with changes in end-user equipment and industrial operations, the introduction of hydrogen blending is likely to begin with relatively low concentrations and grow gradually as the adjustments required to handle greater concentrations are completed. Notably, improperly tuned devices are unsuitable for hydrogen mixtures (Florisson, 2010). In addition, the natural gas composition in a particular pipeline must be considered (Zachariah-Wolf et al., 2007; Melaina, et al., 2015).

3.8 Hydrogen effect on various components

3.8.1 Effect of hydrogen on Pipework Material and Weld

This section provides an overview of the behavior of pipework when exposed to an environment containing less than 10 percent by volume of hydrogen gas. Hydrogen embrittlement, which degrades the mechanical characteristics of vulnerable alloys including ferritic steels, nickel-base alloys, titanium alloys, and metastable austenitic stainless steels, is the primary problem associated with steel in contact with hydrogen (Adler, et al., 2003). Variables including strain rate, hydrogen pressure, and hydrogen purity affect the pace at which mechanical properties degrade, with higher degradation recorded at low strain rates, high hydrogen pressures, and high hydrogen purities. Hydrogen embrittlement is caused by a complex interaction between the environment, the materials, the welding, and the stress or mechanics applied to the material (EIGA, 2004; EIGA, 2014).

When exposed to extended hydrogen concentrations, metals, steels, and other alloys may deteriorate significantly. The ASM Materials Handbook (Adler et al., 2003) describes a variety of hydrogen deterioration processes that may result in a significant loss of mechanical characteristics in metallic components. Hydrogen embrittlement poses particular safety problems when hydrogen gas is transported via pipelines (Adler, et al., 2003).

Hydrogen adsorption onto the metal surface is the first step in the process of hydrogeninduced damage. Prior to its absorption into the metal lattice, hydrogen molecules dissociate, and the pace of hydrogen adsorption is reliant on the degree of breakdown at the surface, which is determined by surface conditions. Hydrogen may fill interstitial sites within the lattice or other unusual locations like as grain borders, vacancies, or lattice flaws. Due to its size, hydrogen cannot fit into interstitial sites and prefers to pick exceptional spots where lattice dilatation has already happened. Hydrogen is highly mobile inside the lattice and able to switch locations. As the pressure produced by hydrogen alters the lattice structure, the concentration of hydrogen in a given location correlates to the degree of degradation (Terenzi, 2022).

Hydrogen embrittlement differs from other forms of hydrogen-induced damage in that it does not involve a phase transition or chemical reactions. This makes hydrogen embrittlement particularly challenging to detect and comprehend. It is a delayed fracture process, where hydrogen slowly decomposes within the metal, leaving no easily identifiable properties (Terenzi, 2022). The following steps describe the progression of hydrogen embrittlement:

- 1. Hydrogen atoms are introduced to the metal during production, welding, or usage.
- 2. The absorbed hydrogen migrates to extraordinary sites where lattice dilation has occurred.
- 3. In new components, extraordinary sites are randomly distributed, resulting in the random distribution of absorbed hydrogen throughout the component.
- 4. When the component is put into service and experiences stresses, certain locations in the component, such as flanges, sharp edges, or connecting lines, undergo localized stress concentration.
- 5. Hydrogen preferentially accumulates in these stress-concentrated regions, leading to the formation of small cracks due to the pressure exerted by hydrogen on the lattice.
- 6. The cracks cause further lattice dilation, promoting crack propagation.
- 7. Hydrogen continues to relocate to these cracks, sustaining their growth until they reach a critical size and the component fails. Hydrogen embrittlement may cease before component failure if the hydrogen concentration is not high enough to induce further lattice dilation (Terenzi, 2022).

This embrittlement process and its effects have been documented in metals, steels, and other alloys of varying strengths. Intergranular fracture is widely employed as a sign of embrittlement; however the presence or absence of grain breaking does not conclusively imply that a component has been weakened. In addition, the lack of grain breaking does not always indicate the absence of embrittlement. The fracture pattern is influenced by variables such as the metal's composition, exposure temperature, stress distribution, and hydrogen content (Terenzi, 2022).

The primary problem in the context of gas pipes is the incorporation of hydrogen into the metal during the production or welding operations. Even with minor amounts of hydrogen contamination, which may occur when hydrogen is supplied to the gas network, hydrogen embrittlement can occur in gas pipes. Hydrogen embrittlement is a gradual process, and even modest quantities of hydrogen may have a negative effect (Terenzi, 2022). Hydrogen's behavior in mixed-gas settings might vary. Some gases, like O₂ and CO, seem to inhibit embrittlement, while others, including CO₂ and H₂S, may operate as accelerators. The effects of methane (CH₄) and nitrogen (N₂) are insignificant. The embrittlement impact of hydrogen in methane/nitrogen mixtures is principally linked to the partial pressure of hydrogen, which may be estimated by multiplying the total gas pressure by the mole percentage of hydrogen in the mixture (GPA, 2019).

3.8.1.1 Hydrogen embrittlement in carbon steel pipes

The addition of hydrogen may cause the mechanical characteristics of steel in the tube to deteriorate, especially in higher-grade steels. Option A and Option B are two design alternatives for piping and piping break control provided by ASME B31.12, a widely acknowledged standard for hydrogen pipeline engineering.

Option A utilizes a prescriptive design method with a maximum design factor of 0.5 times the yield strength of the line pipe. The "Material Performance Factor" for pipe grades above X52 is less than 1, resulting in a lower design factor. Option A piping systems feature lower stress levels than normal oil and gas designs, but all other criteria are the same (Terenzi, 2022).

Option B permits a design factor larger than 0.5, with a maximum value of 0.72. Even for steels greater than X52, the "material performance factor" is always 1. This option guarantees appropriate hydrogen gas fracture safety. In accordance with Article KD-10 of the ASME BPV Code, Section VIII, Division 3, the fracture toughness value (KIH) of manufactured tubing must be at least 55 MPa m^{1/2}. Option B additionally needs pipe fatigue testing in accordance with ASME B31.12 section PL-3.7. It permits the same design considerations as conventional oil and gas systems (GPA, 2019; Terenzi, 2022).

Hydrogen absorbed by steel may build in its microstructure, resulting in hydrogen embrittlement. This embrittlement diminishes the material's toughness and tensile ductility, making the steel more susceptible to pipeline failure and more severe failure modes, such as rupture as opposed to leaking (Terenzi, 2022).

Hydrogen embrittlement is comparable to water entering and freezing in pavement cracks, causing the fissures to enlarge. As a tiny molecule, hydrogen may migrate through microcracks in materials, causing damage by enlarging the fissures (cracking/blistering) or interacting with the substance (hydrogenation) under changing pressures (Terenzi, 2022).

Depending on the heat treatment and chemical content of the material, the crystal formations and morphologies of metal pipework might vary (Terenzi, 2022).

In general, hydrogen embrittlement has no effect on the yield strength or ultimate tensile strength of steel, but it does diminish the material's fault tolerance, requiring a drop in the maximum permitted working pressure.

As seen in Figure 57, existing hydrogen pipe systems usually utilize low-strength steel. These systems are intended to fulfill the low transport performance criteria for transporting natural gas in terms of operating pressure and capacity. Option B of ASME B31.12 permits system optimization and the use of high-strength steel without sacrificing wall thickness.

MSc	Oil	and	Gas	Process	Systems	Engineering	Ş

g HYDROGEN COMPATIBILITY ASSESSMENT IN NATURAL GAS INFRASTRUCTURES

AGEC, Alberta, Canada Gr. 290 (American Air Liquide API 5LX	Pipeline Material	Operation	Diameter (mm)	(km)	Pressure (kPa) and Gas Purity (%)	Experience Reported	Status
ICARS/LOUISING USA	(5LX X42) (42, X52, X60 and others	Since 1987	273 x 4.8 WT 3" to 14"	3.7	3.790 kPA-99.9 5100 kPa (740 PSI)	No Yes	Operational Operational
Air Products, Texas Carbon S	Steel	Since 1967	50-450(2"-18")	357 (222 m)	1825-10030 kPa	No	Operational
Air Products, Louisiana ASTM 1 Air Products, Samia Carbon S (Dour to Thome educt)	106, Carbon Steel Steel	1983 Since 1981	101.6-304.8 150-300 (2"-6")	(m101) [631 9 app.	5514 5514 4238-10030 kPa	5% X	Operational Operational
Air Products, Cleveland Ohio Carbon S Air Products, Cleveland Ohio Steel, set Air products, CA	Steel hedule 40	Since 1979 Since 1982	50& 100 (2" & 4" 150-250 (6"-10"))3.5 17.4 45 Em	1136 6651-15407 kPa-Pure H2 0hosenheet = 50 toos/dav)	Yes Yes	Operational Operational
Chemische Werke Huis Seamless	s equipment to	Since 1938	168.3-273	215	to 2,500: raw gas	Yes	Operational
Cominco B.C., Canada Carada Caraboa S 210 casar	10 Steel Steel (ASTM	Since 1964	5 x 0.8125 WT	90	(unoughput = 300 x 100 m) >30,000.62 to 100% pure H2	°N N	Standby
Gulf Petroleum Cnd, Carbon S (Petroscost, Varmae) Soh 40	Steel, somiess,		168.3	16	93.5% H2; 7.5% methane	°N N	Operational
Hawkeye Chemical, Iowa ASTM A KCI Billinoham, UK Cerbon S	NSJ Gr. B. Strel	£ .	152.4	32	2.757.6 30.000 kPa. eure	No.	Operational
L'Air Liquide, France, Carbon S	Steel, seamless,	Since 1966	since up to 12"	879	6,484 - 10,000 kPa; pure	No.	Operational
LASL, N.M. ASME A LASL, N.M. S Cz M Los Alarros, N.M. 5 Cz M Gr. 5)	v357-Gr. 5 Vio (ASME A357	. 8~	25.4 30	6.4 6	atos tew 13,790 pure	Ya	Abandonod Abandonod
Linde, Germany				1.6-3.2			
NASA-KSC, Fla 316 SS (NSA-MSPC Al- ASTWA A	(austinitic) A 106-B	>16	50	1.6-2	42,000 kPa 34470	23	Operational
Phillips Petroleum ASTM A Praxair, Golf Coust, Tx, Carbon S Indiana, California,	N524 Steel	4	203.2	20.9 450 Km	12,133-12,822 Commercial Purity H2 (500 MSCFD)	, s	Operational
Automin, Louissins, microgen Rockwell International S. South Africa		01<	250	. 8	>100,000 kPa; ultra pure	Å	

Figure 57. Summary of hydrogen pipelines operating worldwide.

Fatigue analysis for carbon steels

13 July 2023

The fatigue crack growth rate (FCGR) for a crack size α can be represented as da/dN, where N is the number of fatigue cycles. It is measured as a function of the stress intensity factor range ΔK , which is defined as the difference between the maximum stress intensity factor per cycle (Kmax) and the minimum stress intensity factor (Kmin). The ratio between Kmax and Kmin, referred to as the R ratio, can be expressed as R = Kmax / Kmin. The Paris law equation is commonly used to describe the FCGR: (Terenzi, 2022):

$$\frac{d_a}{d_N} = C(\Delta K)^m \tag{24}$$

Where C and m are material constants.

The equation mentioned above can be divided into three distinct regions. In Region I, where the stress intensity factor range ΔK is small, the crack propagation is slow. As ΔK increases and enters Region II, the growth rate of the crack accelerates, and the curve exhibits a linear relationship on a logarithmic scale. As ΔK continues to increase, the crack growth becomes rapid and unstable in Region III, where the Paris law is no longer applicable. Recent measurements for both low-grade and high-grade steels show that for ΔK values less than or equal to 7 MPa*m^{1/2}, the material's behavior in a hydrogen environment is similar to that in air. Therefore, below this threshold, there are no significant hydrogen-related effects on the material. (Terenzi, 2022).

$$\Delta K = Y \Delta \sigma \sqrt{\pi \alpha} \tag{25}$$

Where,

 $\Delta \sigma = applied pipe wall stress range (MPa * sqrt(mm))$ $\alpha = crack size (depth) (mm)$ Y = geometry factor associated with the crack structural geometry

$$\Delta \sigma_E = \left(\frac{\sum_i n_i \Delta \sigma_i^3}{\sum_i n_i}\right)^{1/3} \tag{26}$$

When a structure has a significant fracture, the crack will propagate or develop with each load cycle owing to some sort of damage, such as an environmental crack or weld flaw. If the rate of fracture propagation is high enough, the crack will continue to expand under cyclic loading until the component can no longer handle the applied stress, ultimately leading to failure (Terenzi, 2022).

Option B in ASME B31.12 permits the use of pipe materials having a grade above X52 without penalty factors. This implies that the design variables may be comparable to those used in conventional petroleum applications so long as fatigue crack growth rate (FCGR) analysis is performed using equations such as Equation 24 (Terenzi, 2022).

Notably, the correlation presented by ASME B31.12 was derived based on experimental data for materials subjected to a high-pressure, pure hydrogen environment. The application of this standard to pipe systems is often restricted to quantities of hydrogen more than 10 percent. In accordance with the restrictions defined in ASME B31.12, many sources believe a 10 percent hydrogen concentration to be the highest limit for the safe operation of hydrogen-natural gas mixes in transportation systems without the need for specific design considerations. However, there is continuous dispute and disagreement around this subject, since some other sources describe hydrogen embrittlement problems even at low hydrogen partial pressures (Terenzi, 2022).

For mixes of inert gas and hydrogen at low partial pressures, very little information is available. The X42 steel grade is related with a detailed data set compiled by Holbrook et al. The link between the FCGR ratio of hydrogen to inert gas and the hydrogen partial pressure is shown in Equation 25. For instance, a 10 percent hydrogen concentration in the mixture at 75 bar corresponds to a horizontal axis value of 0.9. Even with such a tiny hydrogen level, the fracture propagation rate is 10 times greater than in an inert liquid environment (Terenzi, 2022).

$$\frac{\left(\frac{d_a}{d_N}\right)H_2}{\left(\frac{d_a}{d_N}\right)N_2} = 1 + 2.2\left(P_{H_2}^{0.36}\right)(4)$$
(25)



Figure 58. Schematic of FCGR vs stress intensity factor range ΔK . (Che, 2018) (Ambriz & Jaramillo, 2014)

Figure 58, shows the schematic of a fatigue crack growth rate as a function of ΔK . It is easily shown the three regions as mentioned before. In Figure 59, Drexler et. al have studied and tested the effect of hydrogen on Grade X52 steel in fatigue crack growth. Firstly, we observe the similarity of the schematic for both air and hydrogen environments as the theoretical schematic shown in Figure 58. The difference between the two environments is that, for hydrogen the three regions are more distinctive and the gradient of region two is steeper than of air. This means that for the same intensity factor, crack is more grown for hydrogen than in air environment.



Figure 59. FCGR for Grade X52 steel, tested both in air and hydrogen environment for gas pressure of 5.5 MPa and 34 MPa (**Drexler, et al., 2018**)



Figure 60. FCGR for Grade X52 steel, tested both in air and hydrogen environment for gas pressure of 5.5 MPa and 34 MPa. (**Drexler, et al., 2018**)



Figure 61. Effect of hydrogen partial pressure on the ratio (da/dN)H2 / (da/dN)N2 for X42 steel. (Holbrook, et al., 1982)

Sievert's law is an equation that describes the relationship between hydrogen pressure and the concentration of hydrogen in steel under equilibrium conditions. The law can be expressed as follows (Gonzalez, et al., 2020):

$$C_H = k \sqrt{p_{H_2}} \tag{26}$$

Where,

 C_H = is the concentration of hydrogen in steel (ppm) p_{H_2} = is the amount of pressure of the hydrogen gas (Pa) k = is a constant (ppm¹/₂)

The fatigue crack growth rate (FCGR) for X42 steel with an R ratio of 0.25, a frequency of 0.1 Hz, and a stress intensity factor range of $\Delta K=22$ MPa*m^{1/2} has been found to exhibit a dependency of 0.36 instead of the expected 0.5. The influence of hydrogen at a pressure of 69 bars on the mechanical properties of the material is presented in Table 24. The observed differences in the mechanical properties are relatively small and can be considered acceptable. (Gonzalez, et al., 2020).

Table 24. Variation in basic material mechanical properties in the presence of H2. (Gonzalez, et al., 2020)						
% variation with H2 @ 69 bar,	X42	X52	X60	X65	X70	
room temperature, vs air*						
Yield Strength	-9.6	3.6	-1.2	0.4	-6.2	
Tensile Strength	-5.5	-2.0	-0.7	1.0	-1.5	
Elongation at fracture	-4.8	-21.1	-23.1	0.0	0.0	

The increase in crack growth rate due to higher pressure leads to a decrease in the number of cycles to failure, as depicted in Figure 62. Although the testing was conducted on X80 grade steel, which falls outside the materials considered in this section, it is reasonable to expect a similar behavior for X42-X70 grade steels. (**Gonzalez, et al., 2020**).



Figure 62. Cycles to failure versus hydrogen pressure.

The frequency of loading influences fatigue crack development depending on the frequency range. Multiple references imply a reliance above 0.1 Hz, but no substantial dependence has been seen below this threshold. As the number of cycles rises, crack growth tends to diminish each cycle. This phenomena may be linked to one or more frequency-dependent rate-limiting phases in hydrogen-assisted fatigue crack development (HA-FCG). These rate-limiting processes include hydrogen dissociation and adsorption, diffusion to the fracture tip plastic zone, and the formation of a new crack surface. It is hypothesized that above 0.1 Hz, hydrogen transport limits fracture formation, suggesting a transport-limited phenomena. Below 0.1 Hz, when equilibrium is reached in hydrogen transport, this phase is no longer rate-limiting. To completely comprehend these rate-limiting stages and identify the exact effect of frequency on fatigue crack formation, however, further study is required (Gonzalez et al., 2020).

3.8.1.2 Effect of hydrogen on Welding

The compatibility between hydrogen and circumferential welds poses a significant challenge in the transportation of hydrogen through new pipeline systems. To address this issue, design specifications for welds in hydrogen-conveying pipelines under pressure should be developed to prevent hydrogen input during the welding process. For instance, the use of filler metals with high hydrogen content, such as low-E7018/E7016/ER308L/ER316L and high-hydrogen bakeable filler metals/hydrogen-relief filler metals, should be avoided.

Both the cathodic protection (CP) bound aqueous solution and the low-pressure dry hydrogen gas within the pipeline expose piping systems to hydrogen. Hydrogen atoms may readily permeate and diffuse through the lattice structure of materials and welds, resulting in a phenomena known as "hydrogen embrittlement" This phenomena degrades the mechanical characteristics of metals, including ductility, fracture strength, fatigue resistance, and solderability. As a consequence, it may lead to unanticipated failures and substantial maintenance concerns, even when subjected to loads well below the design limits. Particularly sensitive to hydrogen embrittlement are metallic materials having a body-centered cubic (BCC) structure, such as ferritic steels (e.g. carbon steels, carbon manganese steels, and low alloy steels) (Hagen & Alvaro, 2020).

When evaluating the technical feasibility of hydrogen transport in onshore pipelines, it is necessary to evaluate the hydrogen sensitivity of three distinct microstructural regions: the base metal (BM), the welding metal (WM), and the heat-affected zone (HAZ). The presence of certain microstructural characteristics might facilitate hydrogen-induced failures. Band microstructures of tougher phases such as martensite, bainite, and pearlite have been found via research. Due to processing techniques, extra hard phases such as acicular ferrite and bainite may be present in ferritic steel microstructures (Hagen & Alvaro, 2020)

Due to the existence of geometric stress concentrators, weld defects, residual stresses, and microstructures sensitive to hydrogen embrittlement, especially in the HAZ, pipeline failures often originate at or near welds. The HAZ is of particular importance due to the fact that the greatest temperatures during welding result in considerable grain development and the production of microstructures (e.g. martensite and bainite) with locally decreased fracture strength and increased vulnerability to hydrogen embrittlement.

When building pipe systems, it is essential to adhere to certain design requirements, particularly for gas transmission. In nations of the European Union, oil and gas firms are normally obliged to adhere to the EN 1594 standard for gas infrastructure as the principal code, in addition to local norms and regulations, such as those for compressed air and gas stations. This code demands the adoption of welding and inspection standards such as EN 12732 and ISO 15614-1 (Hagen & Alvaro, 2020).

However, EN 1594 does not cover the piping in compressor stations, including pipes made of stainless steel for natural gas and fuel gas and pipes made of carbon steel for sealed exhaust pipes and atmospheric vents. These pipe systems must instead be constructed according to EN 13480 or ASME B31.3 (Hagen & Alvaro, 2020).

Currently, none of the aforementioned rules give explicit welding criteria for settings containing hydrogen. Nonetheless, the latest edition of EN 12732 contains a chapter addressing the hydrogen environment, which has been the subject of a public inquiry, and a formal vote is now underway. This standard will provide minimum hardness values for welding that are separate from those specified in ASME code B31.12, the only extant code that addresses the design of pipe systems and related welds for hydrogen transport (Hagen & Alvaro, 2020).

How to harmonize the requirements of EN 1594, EN 13480, and ASME B31.3 is a serious challenge.

3.8.2 Effect of hydrogen on Compressors

The majority of compressors used in existing natural gas networks are centrifugal or reciprocating in type. Compressors serve a critical function in gas transport infrastructure and are often regarded as the systems' beating heart. When huge amounts of gas need to be compressed, centrifugal compressors are often the best option. In contrast, reciprocating compressors are better suited for lesser quantities owing to their greater efficiency and operational flexibility (Gonzalez, et al., 2020).

However, when it comes to hydrogen transportation, the usage of centrifugal compressors, which are often used for enhancing natural gas pressure, might cause issues. The compression ratio of centrifugal compressors is highly dependent on the molecular weight of the gas being compressed. The diffuser converts head, which is responsible for increasing gas velocity to create kinetic energy, to pressure. Kinetic energy changes according to gas velocity and molecule mass (Terenzi, 2022).

In contrast, reciprocating compressors are not constrained by gas molecular weight and have been investigated for transporting pure hydrogen. They can compress both light and heavy gases efficiently. However, when working with gases of a very low molecular weight, there may be possible sealing difficulties.

Due to its low specific gravity, it should be emphasized that hydrogen is more difficult to compress than natural gas. According to reports, compressing hydrogen from 30 pressure to 100 bar needs up to 60 stages of centrifugal compression, but compressing natural gas requires just four or five stages on average. Conventional natural gas compression technology is impracticable for hydrogen pipeline networks due to the large number of steps necessary for centrifugal compression. As indicated by Leighty et al. in Figure 63, the limit for employing current gas centrifugal compressors in hydrogen blends is 10 percent.



Figure 63. Tolerance of selected existing elements of the natural gas network to hydrogen blend shares by volume. (IEA, 2019)

When using centrifugal compressors with natural gas/hydrogen blends, the following general considerations should be made:

1) A 10% hydrogen concentration reference limit can be established, primarily for compressor material compatibility as well as compression efficiency and sealing issues. The compressor could not achieve the required compression ratio by increasing the hydrogen content due to density reduction. Furthermore, high velocities within the compressor rotating section necessitate stringent material specifications.

2) New, more efficient centrifugal compressors will be developed to handle higher hydrogen concentrations. A hydrogen concentration limit for these new devices will be established.

3.8.2.1 Centrifugal compressors

Centrifugal compressors are developed specifically for each project in the energy industry, taking into consideration the fluid qualities of the process stream. As the asset ages, it is conceivable to combine new impellers with old compressors in order to achieve optimum efficiency in light of the asset's evolving working circumstances.

The design of centrifugal compressors is governed by flow rate, thermodynamic parameters of the gas, and the desired pressure ratio. Due to the low density and molecular weight of hydrogen, attaining a suitable pressure ratio necessitates either very high impeller tip speeds or an increased number of compression stages. This presents a problem for the designers of centrifugal compressors, since maintaining the essential structural integrity becomes challenging, particularly when utilizing high-strength metals that may not be compatible with high hydrogen concentrations. Hydrogen embrittlement in severely loaded impellers might pose a threat to safety. In situations where centrifugal compressors presently manage high hydrogen concentrations, such as hydrogen recycling in refineries or syngas, long shafts with many impellers are often used (Gonzalez, et al., 2020).

If a centrifugal compressor is to be repurposed for hydrogen use, a number of factors must be thoroughly evaluated, including:

- Compatibility of materials in contact with hydrogen at specific local pressure and temperature conditions.
- Impact on performance and operational range.
- Acceptability of hydrogen stream contamination with lubricants.
- Acceptability of fugitive losses through the seals.

Repurposing existing natural gas centrifugal compressors for hydrogen service has been deemed impractical, although concentrations of up to 10% volume have been considered non-critical. The optimization of centrifugal compressor technology for pure hydrogen service

is currently underway, driven by the increasing demand for large-scale hydrogen transportation and the challenges mentioned above. Transitioning to a 100% hydrogen pipeline would require the installation of new turbines or motors and dedicated compressors, as outlined by ENTSOG, GIE, and Hydrogen Europe (Gonzalez, et al., 2020) (ENTSOG, et al., 2021).

3.8.3 Effect of hydrogen on Gas engines and Turbines

Gas turbines and engines are another important component that must be considered. When compressor turbines employ natural gas as a fuel, combustion equipment may be exposed to a mixture of natural gas and hydrogen. This is contingent upon whether or not hydrogen is added to the gas stream upstream of the fuel gas off-take point. Primarily impacted are prime movers such as gas turbines, gas engines, and generator sets, although gas-fired heaters may also be affected (Gonzalez, et al., 2020).

3.8.3.1 Gas Engines

Hydrogen can be added to all motors up to 2% vol. To deal with fluctuations in hydrogen concentration above 2% vol, additional management systems are required. Engine wear, NOx production, and engine knocking are all possible outcomes of these fluctuations. The fluctuations may be controlled by modern systems. If the methane level remains above the minimum, the engine might be able to handle concentrations up to 10%. Because of the increased flame speed and reactivity, gas engines generally perform better and are more efficient (Gonzalez, et al., 2020).

3.8.3.2 Gas Turbines

In general, the most difficult component of integrating hydrogen into natural gas systems is the increased production of NOx in gas turbines as a result of the higher adiabatic flame temperature. When running with a lean mixture, one might anticipate fewer NOx emissions, but at the price of decreased power production owing to a fall in heat rate (Gonzalez, et al., 2020).

Typically, gas turbines stipulate a maximum hydrogen level of 1 percent, however it may be able to tolerate 5-10 percent hydrogen content with retuning. The variation in gas composition, however, poses a greater threat. If the hydrogen concentration varies, the gas-to-air ratio must be changed dynamically. For concentrations exceeding 1 percent, each turbine must be examined, and actions including combustor redesign, enhanced control systems with online composition assessment and control, and fuel heating must be adopted (Smith, et al., 2017).

With modifications and adjustment, gas turbines can take up to 10 percent volume hydrogen concentration. Some modern turbines may be able to handle concentrations of up to 15 percent hydrogen, while special syngas turbines are built to manage concentrations of up to 50 percent hydrogen (Gonzalez, et al., 2020).

The increased flame speed presented by the addition of hydrogen to the combustion process is the greatest technological obstacle. The flame speed of pure hydrogen is roughly 10 times that of natural gas, which increases the danger of flashback. Hydrogen may be used in lean premixed combustion, however the concentration limits for flammability are greater than for natural gas, increasing the likelihood of unintended combustion. Using catalytic converters, NOx emissions may be reduced to very low levels. However, further study is required to overcome concerns of ignition, flame stability, and emissions (Gonzalez, et al., 2020).

The majority of gas turbine manufacturers are either exploring retrofit solutions to tolerate greater hydrogen concentrations or already provide hydrogen-ready equipment (Gonzalez, et al., 2020).

3.8.4 Effect of hydrogen on Flow meters

The impact of introducing hydrogen into natural gas on flow meters is a significant concern due to the potential safety risks associated with faulty measurements. The addition of hydrogen alters the physical properties of the gas mixture. When hydrogen is incorporated into a natural gas composition, the following changes in fluid properties occur at the same pressure and temperature (Gonzalez, et al., 2020):

- Gas density decreases.
- Dynamic viscosity decreases, although the effect is small.
- Velocity of sound increases.
- Reynolds number decreases (at similar flow speed).
- Calorific value decreases.

The ratio of the calorific value of methane to hydrogen is 3. This means that the gas velocity must increase by a factor of three to transport the same energy flux. However, existing gas flow meters are not yet capable of achieving this factor. A study by Steiner (2018) investigated the impact of hydrogen addition on metering errors and uncertainties in volume (flow) measurement using an uncertainty budget model. The presence of natural gas and hydrogen mixtures exacerbates the uncertainties and measurement errors in metering data, leading to a decrease in the accuracy of billing values. Measurement errors worsen with higher concentrations of hydrogen (Gonzalez, et al., 2020).

Turbine flow meters

Hydrogen added to natural gas influences the operation of turbine meters, which rotate a turbine wheel in response to gas flow. The flow rate and velocity are inversely related to the wheel's rotating speed. The maximum gas velocity may be measured using turbine meters, which is an essential characteristic for monitoring the flow of hydrogen-natural gas mixes. Based on recent product specifications for a maximum bore diameter of 600 mm, the maximum flow rate for all gas types, independent of their composition, is 24,000 m3/h. Therefore, the maximum velocity is around 24 meters per second. The maximum velocity is restricted to minimize possible damage to the mechanical components of the turbine meter and erosion induced by high particle velocities in the gas. When delivering the same amount of energy with natural gas-H2 mixes or 100 percent hydrogen, however, speeds greater than 24 m/s are required (assuming the pipeline is operating at capacity with natural gas) (Gonzalez, et al., 2020).

The addition of hydrogen to natural gas also changes the minimum energy necessary to drive the turbine wheel, a key metric. The manufacturer-specified minimum pressure must be maintained, and the minimum flow rate must be raised following the addition of hydrogen. The addition of hydrogen to the natural gas mixture decreases the actual flow measurement range. Currently, the majority of manufacturers say that turbine meters are adequate for a maximum of 10 vol % hydrogen (Gonzalez, et al., 2020).

Ultrasonic flow meters

The measuring principle is based on the measurement of the time difference between ultrasonic signals flowing with the gas flow and in the opposite direction. The period between these two observations influences both the actual volume flow rates and the gas velocity. Existing flow meters have a maximum bore diameter of 600 mm and an actual maximum flow rate of 30000 m3/h in terms of the greatest flow velocity they are capable of achieving. This maximum flow rate applies to all gas types, regardless of their composition. As a result, the highest velocity is around 29 meters per second, which is inadequate to convey the same amount of energy as natural gas does currently (Gonzalez, et al., 2020).

At greater flow velocities, the measurement principle will encounter difficulties since the ultrasonic signal from the transmitting sensor may not reach the receiving sensor and instead strike the spool wall. Adding hydrogen to natural gas also modifies the measurement principle in a different manner. As H2 concentrations rise, the speed of sound rises and the signal-tonoise ratio falls, resulting in greater measurement errors that disrupt ultrasonic transmissions (Gonzalez, et al., 2020).

According to the majority of manufacturers, modern ultrasonic meters can only detect 10 vol percent hydrogen (Gonzalez, et al., 2020).

Coriolis flow meters

The measurement principle is based on the Coriolis principle. Utilizing actuators to vibrate two pipe elbows. In order to detect vibration signals, sensors are positioned at the inlet and outflow of the oscillating system. When there is no flow, both signals are in phase with one another. The Coriolis force generated by the fluid as it flows through the gadget generates a

phase change between the two signals. Inversely proportional to the phase shift is the mass flow (Gonzalez, et al., 2020).

The measurement principle itself is unaffected by the addition of hydrogen to natural gas. At the same velocity, larger amounts of hydrogen will result in a smaller phase shift. Coriolis meters are capable of measuring the gas flow of 100 percent hydrogen. To carry the same quantity of energy, gas velocities must be drastically increased. If high speeds are attained, erosion concerns will increase. It should be remembered that the measurement uncertainty is determined by the ratio between the mass of the tubes and the mass of the fluid within the vibrating tubes. Hydrogen has a lower density; hence this ratio is less advantageous for it (Gonzalez, et al., 2020).

In general, when current gas flow meters are intended for use with hydrogen (or concentrations of hydrogen), factors unrelated to the measurement itself must be considered (Gonzalez, et al., 2020). These factors consist of:

- Gas leakage
- Material embrittlement
- decreasing service life
- Lubrication (type and frequency of lubrication)
- Metrological approval not including 100% hydrogen
- High-pressure flowmeters using hydrogen as the flowing media cannot be calibrated wet.

Flow rate measurements are often used for invoicing, but they may also be utilized to regulate operations. In addition to the gas's composition and, thus, its calorific value, the flow rate is the only determinant of billing. A process gas chromatograph may be used to analyze the composition of a gas. Hydrogen concentrations might be challenging to determine using a process gas chromatograph. Process gas chromatographs typically use Thermal Conductivity Detectors, which detect the thermal conductivity of the gas components separated in the separation column. Helium is often used as a carrier gas. The thermal conductivity decreases when hydrogen concentrations of hydrogen can only be detected in small amounts. As a solution, a new carrier gas, such as argon, might be utilized. Actual gas quantities are converted to standard gas volumes for invoicing reasons. The compressibility of the gas is crucial for this conversion (Gonzalez, et al., 2020).

3.8.5 Effect of hydrogen on Valves

Lastly, preventing leakage to the surrounding air or across the valve is the primary concern that is unique to pure hydrogen service.

Packing and bonnet leaks, as well as casting leaks, account for the majority of ambient leaks. The following, or something similar, is suggested to reduce the likelihood of leaks (EIGA, 2004) (EIGA, 2014):

- Double seals or packing
- hydraulically leak test for each cast
- Valves used in hydrogen service require specific design features and considerations to mitigate risks associated with temperature, hydrogen concentration, and pressure. Various valve configurations and materials are recommended for different applications to ensure safety and reliability.
- For in-line automatic valves and automatic vents, it is recommended to use a soft seat in a metal retainer to achieve bubble tight shut off. In the case of in-line manual valves, a metal-to-metal seat or a soft seat in a retainer should be used along with a means of positive isolation to block flow during maintenance or inspection.
- When valve outlet blocking is required, a metallic seat can be used, and common arrangements include double valves, blind flanges, plugs, or caps.
- It is preferable to avoid through bolting, body flanges, or threaded connections in the valve body assembly.

• Mainline isolation valves should be of full port design, especially when pipeline pigging for inspection is anticipated (Zohuri, 2019).

In the study of risk for hydrogen service valves, temperature, hydrogen concentration, and pressure are key parameters. Hydrogen increases the likelihood of metallic material corrosion, including hydrogen attack, embrittlement, and blistering. Typically, end users choose metals based on their knowledge of the operating circumstances and industry norms stated in API 941 Recommended Practices (Zohuri, 2019).

To mitigate hazards in hydrogen service valves, it is vital to examine design elements such as rounded vs angular features and fabricated, forged, or cast methods. In hydrogen settings, advancements in gaskets, packing, heat treatment, and inspection procedures result in enhanced leak prevention capabilities. It is crucial for the end user to specify precise material specifications, taking into account the precise process parameters, hydrogen concentration, corrosive components, and exposure duration (Zohuri, 2019).

Although operating pressure and temperature are significant issues, they are subordinate to the wider process considerations and material selection based on the Nelson curves. To guarantee the optimal material selection, each of these criteria must be carefully analyzed in line with the unique needs of the process (Zohuri, 2019).

3.8.5.1 Typical design for valves

The incidence of hydrogen attack, embrittlement, and blistering may be considerably reduced by considering several design considerations. Sharp edges and abrupt angles concentrate stress and increase the likelihood of hydrogen embrittlement and cracking, thus they must be eliminated or minimized. At sharp edges, the thinning or tapering of metal provides stress-prone regions sensitive to hydrogen infiltration and deterioration. In order to prevent stress concentration, hydrogen service valves are built with wider radii and uniform stress distribution, using finite element analysis and stress estimates for the valve's essential sections (Zohuri, 2019).

The forming process itself has a substantial impact on the performance of valves in hydrogen operation. Both forged and cast steel have benefits and drawbacks that must be considered. Welding, a possible weakening site, should be reduced or removed. Casting has the benefit of eliminating the need for welds and often decreases stress concentrations and sharp edges. However, it is more susceptible to flaws like porosity, voids, and impurities than forged steel. Increasingly, foundries use casting simulations to reduce faults, and nondestructive testing is often done on cast valves to assure their quality and dependability (Zohuri, 2019).



Figure 64. Hydrogen service valves typically feature large radius to avoid stress concentrations. (Zohuri, 2019)

3.8.5.2 Leakage paths

There are two main routes that valve leakage takes. When the valve is closed, hydrogen can pass through the seat due to leakage. The gas is contained within the process thanks to this leak. Leakage through the stem, which may cause gas to escape into the atmosphere, is the most serious (Zohuri, 2019).

Seat leak

Metal-to-metal technology is preferred to prevent seat leaks. The hydrogen service technology uses a disk made of flexible, resilient metal that seals against a hard-faced satellite seat. The metal-to-metal construction produces a long-lasting, high-temperature seal that prevents leaks (Zohuri, 2019).

The most significant environmental leakage—the one that is the subject of legal scrutiny—occurs when media leaks into the atmosphere. Before getting into that kind of leakage, a few regulatory issues will be briefly discussed (Zohuri, 2019).

Stem leak

To ensure the prevention of stem leakage, several fundamental design factors need to be considered. These factors, as outlined by Zohuri (2019), include:

- 1. Implementation of live loaded packing to accommodate temperature variations effectively.
- 2. Preventing rotation of the packing material to maintain its integrity.
- 3. Provision of a highly efficient shaft seal to minimize the potential for leakage.
- 4. Incorporation of a smooth shaft surface to reduce friction and enhance sealing performance.
- 5. Ensuring that the packing segments maintain contact with both the stuffing box and the shaft simultaneously.
- 6. Utilization of independent PTFE and graphite packing materials to optimize sealing efficiency.

For these functions, the gaskets and packing are essential valve components. With the softer graphite commonly used for packing and gaskets, leak prevention is very successful in a wide variety of applications. But in hydrogen service, it creates a distinct difficulty. Because graphite is porous to the microscopic hydrogen atom, the soft substance cannot prevent leakage. Since PTFE, a synthetic fluoropolymer, has the ability to evaporate in a fire, impregnating graphite with it to reduce leakage is undesirable (Zohuri, 2019).

3.8.5.3 Post Weld Heat Treatment

Typically, post-weld heat treatment (PWHT) is used by manufacturers for hydrogen service valves. According to studies and industrial experience, PWHT strengthens the resistance of chromium-molybdenum and 0.5Mo steels to HTHA. By stabilizing alloy carbides, the PWHT reduces the amount of carbon accessible for combination with hydrogen. As a consequence of the treatment's decrease in residual stresses, the material becomes more ductile (Zohuri, 2019).

Manufacturers routinely treat all low-alloy steels with PWHT, but plain carbon steels are only treated at the request of end customers (Zohuri, 2019).

3.9 Suitable materials

There are several ways for determining a material's resistance to hydrogen gas embrittlement. These procedures, such as those defined in ISO 11114-4 and B4 standards, use various kinds of test specimens to assess the qualities of a material. Some of these techniques involve fracture mechanics specimens, while others utilize tensile test or disk specimens. These test procedures give useful information into the susceptibility of materials to hydrogen gas-induced embrittlement. (EIGA, 2004) (EIGA, 2014).

3.9.1 Pertinent test methods

Hydrogen embrittlement typically occurs due to two sources of hydrogen: electrochemical reaction-produced hydrogen and gaseous hydrogen in the environment. To assess the susceptibility of materials to hydrogen embrittlement, experimental studies are conducted under relevant operating conditions. The presence of hydrogen can significantly affect various mechanical properties, including tensile strength, elongation, fatigue life, fatigue crack growth rate, and fracture toughness. Evaluating these mechanical attributes can be achieved through experiments performed in hydrogen environments or by testing hydrogen pre-charged specimens. (EIGA, 2004; EIGA, 2014).

In recent years, several testing strategies have been developed to investigate hydrogen embrittlement. Established procedures for testing gaseous hydrogen and assessing resistance to stress corrosion cracking (SCC) can be applied to studying material behavior in a hydrogen environment, as hydrogen embrittlement shares similarities with SCC. The following descriptions outline typical tests conducted to assess hydrogen embrittlement. (EIGA, 2004) (EIGA, 2014):

3.9.2 Tensile and notched tensile properties

The vulnerability of a metal to hydrogen embrittlement may be determined by performing tensile tests on smooth or notched specimens in a hydrogen atmosphere at varying pressures. ASTM G 142-98 is a standard test technique for assessing the susceptibility to embrittlement of metals in hydrogen-containing environments, notably under high pressure, high temperature, or both. This test technique provides a reference for evaluating the influence of hydrogen on the mechanical characteristics of metals. (EIGA, 2004) (EIGA, 2014).

3.9.3 KIH test

The K_{1H} test is a fracture mechanics test that measures the stress intensity factor at the cracking threshold for hydrogen stress cracking. In this test, a specimen that has already been fractured is subjected to stress while being exposed to a hydrogen gas atmosphere. The

resistance to hydrogen-assisted cracking may be evaluated by calculating the minimum stress intensity factor (K_{1H}) necessary for crack propagation. The susceptibility of materials to hydrogen-induced cracking may be determined by adapting various ASTM or ISO test techniques (EIGA, 2004) (EIGA, 2014).

3.9.4 Slow strain rate (SSR) test

The strain rate sensitivity of materials in a hydrogen environment can be determined using a slow strain rate test, as hydrogen attack is a process that depends on time. The slow strain rate test is conducted at very low strain rates, typically around 10-7. This test can be performed either in environments filled with hydrogen or by pre-charging the specimen with hydrogen before testing it in hydrogen or air. ASTM G129-00, titled "Standard Practice for Slow Strain Rate Testing to Evaluate the Susceptibility of Metallic Materials to Environmentally Assisted Cracking," offers a general procedure for conducting slow strain rate tests (SSR tests) (EIGA, 2004) (EIGA, 2014).

3.9.5 Disk pressure test

The disk pressure test is employed to assess the vulnerability of metallic materials to hydrogen embrittlement under high-pressure hydrogen conditions. This test involves subjecting a thin disk sample to hydrogen and helium at elevated pressures within a test cell. The material's susceptibility to environmental hydrogen embrittlement is determined by calculating the ratio of the burst pressure with helium to the burst pressure with hydrogen. The "Standard Test Method for Determination of the Susceptibility of Metallic Materials to Gaseous Hydrogen Embrittlement" provides a well-established test procedure for conducting this assessment. (EIGA, 2004) (EIGA, 2014).

3.10 Energetic aspects

The fundamental purposes of pipeline networks intended for fuel or gas transfer are twofold. First, they permit the transmission of adequate energy to end customers in an effective manner. Second, these pipes function as gas storage tanks when the supply exceeds the current demand. Linepack is the popular term for the temporary storage of natural gas inside a pipeline. Linepack allows for the continual delivery of natural gas across the network, despite fluctuating demand patterns. Essentially, the linepack enables the demand side to alter gas absorption based on the amount of gas pumped into the network. A bigger linepack capacity affords more storage space, but needs higher pressure levels (Gondial, 2016).



Figure 65. Steady state flow in gas pipeline. (Gerboni, 2016)

As indicated in section 3.8.4, the substitution of natural gas with hydrogen necessitates transporting a larger volume of gas to meet the energy requirements of the end user. Specifically, the gas volume needs to be approximately three times greater compared to natural gas. Consequently, considering the flow Equation (27), the gas flow rate is expressed in terms of normal meters per hour (Nm³/h). This representation of flow rate accounts for the mass flow of gas rather than its volumetric flow (Gondial, 2016).

HYDROGEN COMPATIBILITY MSc Oil and Gas Process Systems Engineering ASSESSMENT IN NATURAL GAS INFRASTRUCTURES

$$Q = 1.1494 * 10^{-2} \left(\frac{T_b}{P_b}\right) * \left(\frac{P_1^2 - P_2^2}{f G T_a L Z_a}\right)^{0.5} D^{2.5}$$
(27)

Figure 65 assumes that the gas temperature Ta remains constant between sections 1 and 2 for isothermal flow, and Q is the gas flow rate under normal circumstances, which is affected by gas parameters such as density G and compressibility factor Z. If the specific gravity G is high, the flow rate will drop. Typically, when the compressibility factor increases, the flow rate decreases (Gondial, 2016). Similarly, the flow rate falls as the gas flow temperature Ta increases. In order to enhance gas flow, it is required to maintain a low gas temperature. In addition, the influence of pipeline length and diameter is evident. Increasing pipe length reduces the flow rate at P1 and P2 pressures. Consequently, increasing the diameter of a pipe increases its flow rate. The flow rate from upstream to downstream is dictated by the pressure differential (P12 - P22). There is obviously no flow when P1 and P2 are equal. Friction between the gas and the pipe walls causes a decrease in pressure (P1 P2). The amount of pressure loss is affected by the kind of flow—laminar or turbulent—and the friction factor "f," which indicates the pipe's interior condition. Equation 2 is met when the gas pipeline is horizontal, albeit this is not always the case (Gondial, 2016).

The roughness of the conduit and a factor known as the Reynold's number, which is given by (IEA, 2019):

$$Re = u * \frac{D}{\theta} \tag{28}$$

where, $\theta = viscosity \ o \ gas \ in \frac{m^2}{s}$ $u = speed \ of \ gas \ flow \frac{m}{s}$

To provide further clarity regarding the energy transport capacity of hydrogen in a pipeline, two terms require elaboration:

- The high heating value, also referred to as gross energy or gross calorific value, represents the amount of heat released by a specific quantity of fuel (initially at 25 °C) after complete combustion, with the combustion products being brought back to the same temperature (Gondial, 2016; Stetson, et al., 2016).
- Lower Heating Value (LHV): The lower heating value, also known as net calorific value • or net CV, denotes the amount of heat released when a specific quantity of fuel is burned (at a temperature of 25 °C or a reference state) and the resulting combustion products are brought back to 150 °C (Gondial, 2016; Stetson, et al., 2016).

Table 25. Comparison of hy	drogen and natural gas prope	erties (Gerboni, 2016) (IEA,	2019) (Stetson, et al., 2016)
Gas	$HH (MJ/Nm^3)$	Density (kg/m ³)	Specific gravity
			relative to air
Hydrogen	13	0.084	0.07
Natural gas	40	0.65	0.55

Considering Equation (28) and the previously mentioned High Heating Value (HHV), it becomes evident that the volume of hydrogen (H₂) required for transportation is three times that of natural gas to meet the same energy demand. However, due to the density of natural gas being approximately nine times that of hydrogen (9*0.084), the pressure drop for hydrogen and natural gas would be equal if the hydrogen flow rate is maintained at three times that of natural gas. It is noteworthy that pressure drop serves as a critical design parameter for piping infrastructure (Gondial, 2016; Stetson, et al., 2016).

Two variables, "Z" and "f," are influenced by the flow rate. Investigations have indicated that, for a constant pipeline and pressure drop, the energy flow achieved by hydrogen is 98% in comparison to lean natural gas and 80% in comparison to rich natural gas. Linepack,

which is a significant advantage of pipeline networks, is primarily influenced by the flow rate. The inverse relationship implies that a higher linepack is associated with reduced flow, while a higher flow rate results in diminished linepack or storage capacity (Gondal & Sahir, 2012) (Stetson, et al., 2016).

Figure 66 illustrates the fundamental concept of linepack, depicting the available space between the upper and lower pressure profiles.



3.11 Disadvantages of hydrogen pipeline

The network of hydrogen pipelines does not have intrinsic drawbacks; nonetheless, technical barriers and problems might be deemed disadvantages. However, as technology progresses, it is anticipated that these disadvantages will reduce, allowing hydrogen to join the energy industry. In the following sections, we will address the potential challenges a network of hydrogen infrastructure may face (Gondial, 2016).

Similar to power loss in electrical networks, hydrogen gas is similarly lost in the hydrogen transportation network. Therefore, the efficiency of hydrogen pipes must be continuously enhanced.

The natural gas distribution network works at low pressure, permitting the use of polymer materials rather than costly steel tubes. Hydrogen's low density, which is about oneeighth that of natural gas, necessitates that it be compressed to greater pressures to permit its rapid distribution. Inability to boost pressure would result in inefficient transmission of energy. Due to their large porosity, the polymer materials used in gas pipes are unsuitable for hydrogen transport tubes. Currently, the majority of hydrogen pipes are made from costly low-carbon steels. To establish a large-scale hydrogen economy, it is necessary to find inexpensive materials for the manufacturing of hydrogen pipes that will be deployed in an extensive network. Furthermore, hydrogen-induced embrittlement may greatly hamper the distribution and delivery of hydrogen by causing pipeline fractures (Chawla et al., 1986; Thompson, 1977; Zakaria and Davies, 1991) (Gondial, 2016).

3.11.1 Safety concerns

Production, storage, transport, and delivery of hydrogen are accompanied by severe safety concerns. Although hydrogen is a safer fuel than methane or gasoline, safety remains a key problem whether carrying hydrogen alone or in conjunction with natural gas (Gondial, 2016).

Adaptations must be made to pipeline networks' leak-detection systems developed expressly for hydrogen supply. To maintain the safety of the supply network, it is essential to rapidly detect and repair leaks produced by variables such as fractures, corrosion, embrittlement, and diffusion. If hydrogen is to be carried in a natural gas combination, it is also required to design sensors that can detect fractures and leaks in these mixes (Gondial, 2016).

3.11.2 Pig inspection

Pipelines with a diameter of at least 10 inches are inspected internally using "pigs," which are inspection tools. Additionally, these devices must be designed for use with hydrogen pipelines.

3.11.3 Sensors

Pipeline rupture can be caused by hydrogen embrittlement. New ultrasonic sensor technologies must be developed to enable earlier detection.

3.11.4 Diffusion losses

To stop hydrogen from spreading, new fittings, seals, gaskets, and valves need to be made. Because of its low viscosity and small size, the fittings currently in use permit the diffusion of hydrogen molecules. Pipe walls can also absorb hydrogen through permeation (Gondial, 2016).

3.11.5 Leak detection

Hydrogen leaks may be difficult to detect owing to its invisibility, odorlessness, and lack of color. Due to the presence of odorants such as organic sulfides and mercaptans, natural gas leaks may be detected more quickly. However, chemicals containing sulfur and mercaptans cannot be utilized to detect hydrogen in fuel cells. This is due to the fact that sulfur-containing compounds have the ability to negatively influence the catalysts in fuel cells, causing early failure and necessitating fuel cell replacement. Therefore, a non-sulfur chemical serving as an odorant for hydrogen must spread at the same rate as hydrogen itself (IEA, 2019).

3.11.6 Compressors

The majority of current natural gas network compressors are either centrifugal or reciprocating in design. In order to use hydrogen pipeline networks, new certification procedures and technology for hydrogen compression must be developed. Hydrogen is also incompatible with lubricants used in natural gas infrastructure. Hydrogen pipelines necessitate the development of oils intended for use in hydrogen-specific equipment (Gondial, 2016).

3.11.7 Cost

Establishing a dedicated pipeline transmission and distribution network exclusively for hydrogen poses a substantial financial hurdle due to the extensive infrastructure required to reach end users. Gas pipeline operators have traditionally shown limited interest in supporting research and development in this area. Consequently, governments may need to play a crucial role in providing financial support and fostering the development of suitable technologies specifically designed for hydrogen pipeline networks. (Gondial, 2016).

3.11.8 Energy density

Hydrogen has a lower volumetric energy density than other gases, such as natural gas, which reduces the amount of energy that can be carried. This is particularly true for combinations of hydrogen and natural gas. In order to satisfy the energy need, high-power compressors are required to support the greater volumetric flow rate required for hydrogen. In the case of natural gas, compressors use around 0.3 percent of the energy content of the supplied gas volume every 150 kilometers of pipeline length. However, the energy needed for compression of pure hydrogen rises to roughly 1,3% of the energy content of the supplied hydrogen for the same pipeline length (150 km) (Air Liquide: Hydrogen Delivery Technologies and Systems, 2003). If hydrogen is to be carried as a combination with natural gas in existing

pipeline networks, capacity derating is required. Specific restrictions and changes must be made based on the energy system and demand factors (Gondial, 2016).

CHAPTER 4: CONCLUSIONS

Hydrogen is one of the largest programs worldwide for its use as a fuel and electricity production. It is therefore considered a very important energy carrier. Despite all this, hydrogen technology is still at an early stage and many financial resources are required for research and development of the technology both for its production and its use. Hydrogen can be transported in many ways, including natural gas or hydrogen-only pipelines.

The hydrogen pipeline network does not have any inherent disadvantages. However, technological obstacles and challenges may be considered disadvantages. On the other hand, as technology improves, the drawbacks are likely to diminish, allowing hydrogen to enter the energy market. In the same way that electrical grids lose power, the pipeline network that transports hydrogen also loses hydrogen gas. As a result, hydrogen pipelines must be continuously improved to increase efficiency (Gondial, 2016).

Because the natural gas delivery network operates at a low pressure, pricey polymer materials can take the place of costly steel pipelines. Nevertheless, in order to speed up delivery, hydrogen must be compressed to a high pressure of 10–20 bars due to its low density, about one eighth of that of natural gas (Gondial, 2016).

However, the problems with the introduction of hydrogen into natural gas pipeline networks are multidimensional. Firstly, planning for a specific quota of hydrogen in natural gas should be done. The different energy content by weight and volume of these two gases should be taken into account, as in the same volume natural gas contains a greater energy content, and of course there are safety issues that arise. This is because, due to its small size, and the corrosion mechanisms of metals, hydrogen can enter the microstructure of metal pipes, and leak out of it, after a possible rupture of the pipe. The most well-known mechanism is that of hydrogen embrittlement, which has been mentioned extensively in chapter 3.5. So, there are issues of strength and integrity of the pipeline. Of course, hydrogen is transported by pipelines to reach the final consumer. This can be either industrial or domestic or for cars with hydrogen cells. Therefore, the means that will use hydrogen as a fuel should also be evaluated.

4.1 Future work

Based on several research studies, the widespread adoption and continuous advancement of fuel cell applications for stationary and mobile purposes are considered crucial for initiating the Hydrogen Supply Chain (HSC). Once there is a significant demand for hydrogen and its availability becomes more accessible to end users, the development of infrastructure, including hydrogen pipelines, would commence. It is essential to thoroughly examine and address all aspects related to HSC. This thesis highlights that while fossil fuels may serve as an intermediate step towards the full realization of a hydrogen economy, any future fuel supply chain aiming to tackle climate change, greenhouse gas emissions, and supply security must incorporate renewable resources. Although the establishment of hydrogen fueling stations has already commenced the transitional phase, the integration of hydrogen into the energy market is expected to take several decades. According to Zoulias and Lymberopoulos (2007), this transition will initially involve standalone hydrogen production units and gradually evolve into a fully functional hydrogen transmission and distribution network through pipeline infrastructure (Gondial, 2016).

Table 26. Development priorities for hydrogen infrastructure. (Gondial, 2016)

Issue	Importance
Safety-odorants, diffusion losses, materials	Very important
Operation and maintenance-leak detection, hydrogen metering,	Important
inspection, remote sensing, compression	
Transmission and distribution technology-Inspection, hydrogen	Very important
metering, compression	
Security	Very important

APPENDIX A: HELLENIC NATURAL GAS INFRASTRUCTURE

The Greek National gas transmission system (NNGTS) consists of the primary transmission pipeline with a total length of 512 kilometers and a design pressure of 70 barg, and stretches from the Greek-Bulgarian borderline at Promachonas to Attica (desfa, 2022). Natural gas is distributed to the provinces of Eastern Macedonia, Thrace, Thessaloniki, Platy, Volos, Trikala, Oinofyta, Antikyra, Aliveri, Korinthos, Megalopoli, and Attica through transmission branches with a total length of 953.2 kilometers (desfa, 2022). There are locations along the main transmission pipeline and its branches:

- Line valve stations for isolating a segment of the NNGTS in emergencies and scheduled maintenance.
- Scraper Stations for launching and receiving cleaning devices (scrapers) or interior inspection devices for the pipeline.
- Cathodic protection system of the pipeline from corrosion.
- Fiber Optic Cable for the remote supervision, control and communications system.

Operation and Maintenance center of Southern Greece

The Southern Greece Operations and Maintenance Center is located in Patima Magoulas in Attica. Included is the territory between the Viotia scraper station Mavroneri and the Mandra Line Valve. It also contains the high-pressure pipelines Antikyra, Aliveri, Lavrio, Keratsini, Oinofyta, Heron, and Thisvi (desfa, 2022).

The Operations and Maintenance Center maintains and operates 278 kilometers of 30inch diameter high pressure natural gas pipeline, 6 kilometers of 24-inch diameter high pressure natural gas pipeline, 127 kilometers of 20-inch diameter high pressure natural gas pipeline, and 20 kilometers of 10-inch diameter high pressure natural gas pipeline.

There are seventeen (17) Metering and/or Regulating Stations, twenty-two (22) Scraper Stations, twenty-one (21) Line Valve Stations, four (4) Remote Telecommunication Stations (REM), and one (1) Remote Telecommunication Station located in close proximity to the O&M Center.

In addition, the principal Gas Control and Dispatching Center for the national transmission system is located at the Operation and Maintenance Center of Southern Greece (desfa, 2022).

Operation and Maintenance center of Central Greece

The Central Greek Operation and Maintenance Center is located in the village of Farsala, close to Ambelia. Along the main transmission pipeline, it stretches from Pieria's Platamonas Scraper Station to Viotia's Mavroneri Scraper Station. It also contains high-pressure pipes in Volos and Trikala (desfa, 2022). The Operations and Maintenance Center maintains and operates a total of 206 kilometers of 30 inch diameter high pressure natural gas pipeline, 40 kilometers of 10 inch diameter high pressure natural gas pipeline in the Volos branch, and 72 kilometers of 10 inch diameter high pressure natural gas pipeline in the Trikala branch. The O&M Hub is in close vicinity to eight (8) Metering and/or Regulating Stations, five (5) Remote Telecommunication Stations (REM), and five (5) Scraper Stations (desfa, 2022).

Operation and Maintenance center of Northern Greece

Nea Mesimvria, not far from Thessaloniki, is home to the Operations and Maintenance Command Center for Northern Greece. Along the main transmission pipeline, it stretches from the Karperi Station in Serres to the Platamonas Scraper Station in Pieria. Also featured are EKO, Asvestochori, and Platy high-pressure pipes (desfa, 2022). The Operations and Maintenance Center maintains and operates 166 kilometers of 36inch-diameter high-pressure natural gas pipeline, 92 kilometers of 30-inch-diameter pipeline, 32.5 kilometers of 24-inch-diameter pipeline, and 10.5 kilometers of 10-inch-diameter pipeline (desfa, 2022).

In the vicinity of the O&M Center are a number of stations with varying purposes, including eight (8) Scraper Stations, six (6) Line Valve Stations, two (2) Remote Telecommunication Stations (REM), and seven (7) Metering and/or Regulating Stations. The Northern Greece Operation and Maintenance Center also houses the redundant Gas Control and Dispatching Center for the national transmission system (desfa, 2022).

Operation and Maintenance center of Eastern Greece

The Eastern Greece Operation and Maintenance Center is located on the second kilometer of the Diomedia-Lefki road, about 5 kilometers from Xanthi. This part of the Karperi-Kipi branch is covered between the Paleochori Line Valve Station and the Kipi Border Metering Station at the Greek-Turkish border (desfa, 2022).

The O&M Center's infrastructure includes high pressure natural gas pipes with a diameter of 36 inches and 147 kilometers with a diameter of 24 inches (desfa, 2022).

There are six (6) Scraper Stations, fifteen (15) Line Valve Stations, two (2) Remote Telecommunication Stations (REM), and seven (7) Metering and/or Regulating Stations within a reasonable distance of the O&M complex. Also maintained and managed by the Eastern Greece Operation and Maintenance Center is the Kipi Border Metering Station (desfa, 2022). **Operation and Maintenance center of Border Metering Station at Sidirokastro**

The Border Metering Station's Operation and Maintenance Center is located in Sindiki, a municipality close to Sidirokastro and barely 12 kilometers from the Greek-Bulgarian border. Included are the regions between the Promakhonas Scraper Station on the Greek side of the Bulgarian border and the Karperi Station in Serres, as well as the Karperi-Kipi branch between the Karperi Scraper Station and the Line Valve Station of Fotolivos near Drama (desfa, 2022).

The infrastructure of the center consists of a 33.3-kilometer-long, 36-inch-diameter natural gas pipeline and a 70.4-kilometer-long, 24-inch-diameter natural gas pipeline. A number of stations are located in the vicinity of the O&M Center, including 5 Scraper Stations, 4 Line Valve Stations, 2 REM (Remote Telecommunications Stations), and 2 Metering & Regulating Stations (desfa, 2022).

In addition, the Sidirokastro Operation and Maintenance Center operates and maintains the Sidirokastro Border Metering Station.

Operation and Maintenance center of Peloponnisos

Spathovouni in the city of Korinth serves as the region's Operations and Maintenance Hub for the Peloponnisos. It spans the principal transmission route between the LNG Terminal Scraper Station on Revythousa and the PPC Megalopoli Metering Station (desfa, 2022).

The Operations and Maintenance Center maintains and operates a total of 158 kilometers of 24 inch diameter high pressure natural gas pipeline and 58 kilometers of 30 inch diameter high pressure natural gas pipeline. In close proximity to the O&M Base are four Scraper Stations, six Line Valve Stations, and four Metering/Regulating Stations (desfa, 2022).

Border Metering Station of Sidirokastro at Serres

The Border Metering Station at Sidirokastro is located in the municipality of Sidiki next to the village of Sidirokastro, only 12 kilometers from the Greek-Bulgarian border (desfa, 2022).

The major function of the station is to monitor the quantity and quality of Bulgarian natural gas imports. In line with the Gas Control and Dispatching Center's program, the station also controls gas supply to the Greek network, warms with heat exchangers using hot water (when required), and eliminates solid and liquid particles with filters at the station's entry (desfa, 2022).

Since the station is manned by individuals who work in shifts around the clock, it is open 24/7.

Border Metering Station of Kipi at Evros

The Kipi Border Metering Station is located in the Ferres Municipality, next to the Greek-Turkish border and the Evros River, about 3.5 kilometers from the village of Peplo (desfa, 2022).

The major task of the station is to monitor and record the properties of Turkish natural gas. Filters at the station's entrance remove solid and liquid particles from the natural gas (desfa, 2022), and three (3) regulating lines control the gas supply to the Greek network in accordance with the Gas Control and Dispatching Center's program.

Without shift personnel, the station is continuously manned.

New Mesimvria Compression Station

At kilometer marker 414 on the main pipeline of the National Natural Gas Transmission System (NNGTS), when the diameter of the pipeline decreases from 36 inches to 30 inches, is where the compression station can be found (desfa, 2022).

With remote control and monitoring from the DESFA's main dispatching center in Patima Elefsina, the station may run without a human presence. The DESFA's Nea Messimvria Backup Dispatching Centre has a local Station Control Room (SCR). In December of 2012, the station officially began operations (desfa, 2022).

- Two compression units, each with a 7,7 MW gas turbine and a centrifugal compressor (SOLAR 453), make up the Compression Station's power supply.
- There are two condensate collectors and two separation filters (one active and one standby) for separating liquids and filtering/purifying natural gas.
- Gas temperature regulators installed at the compressor's discharge port.
- Full-fledged compressed-air setup.
- Diesel-powered generator used as a backup
- Ventilation
- (MT) Medium Voltage Substation (two thousand kilowatt-amperes) safeguards against power surges and surges from lightning.
- Power that doesn't go out (UPS)
- Cathodic defense
- System for detecting fire and gas leaks and putting out fires
- Reduced emissions to below 25 ppmV for CO, NOx, and UHC.
- At 1 meter, the noise level is 85 dB, whereas within the land station's boundaries, it drops to 65 dB.
- Station administration and monitoring using tools like DCS for the turbine and compressor, a performance map of the engines, and load balancing.

Part of the development plan 2022-2031 for the Greek NNGTS (desfa, 2022) (RAE, 2022)

NEW PROJECTS	COST (€)	MILESTONES
Expansion of NNGTS to Ioannina	156.000.000	Investment Decision: 07/2023 Start of operation:06/2026 Inclusion in the system: 09/2026
M/R Station to Veroia	2.500.000	Investment Decision: 07/2022 Start of operation: 10/2023 Inclusion in the system: 12/2023
M/R Station to Naousa	2.080.000	Investment Decision: 07/2022 Start of operation: 12/2023 Inclusion in the system: 02/2024

Expansion and Upgrade of M/R	3.000.000	Investment Decision: 07/2022
Stations of Exit Point to		Start of operation: $12/2023$ Inclusion in the
Distribution Network 'Athens'		system: 03/2024
		system: 03/2024
Keratsini branch rerouting (Mavri	425.000	Investment Decision: 12/2021
Ore stream)	1201000	Start of operation: 12/2022 Inclusion in the
		start of operation. 12/2022 metusion in the
		system: 12/2022
Construction of a new Metering &	2.200.000	Investment Decision: 07/2022
Degulating Station in Markonoulo	2.200.000	Start of operation: $12/2022$ Inclusion in the
		Start of operation. 12/2025 inclusion in the
Site to replace the existing temporary M/R		system: 03/2024
New electronic information system	350.000	Investment Decision: 12/2021 Start of operation:
for natural gas functionalities		12/2022
ungrada		Inclusion in the system: $12/2022$
upgrade		inclusion in the system. 12/2022
Development of an Information	500.000	Investment Decision: 12/2021 Start of operation:
System for DESFA to undertake the		10/2022
role of forecasting party for the		Inclusion in the system: $10/2022$
NINCTS		merusion in the system. 10/2022
New electronic information system	3.500.000	Investment Decision: 12/2021
for natural gas		Start of operation: 12/2023 Inclusion in the
		system: 12/2023
New project management system	1.200.000	Investment Decision: 12/2021 Start of operation:
upgrade		12/2022
		Inclusion in the system: 12/2022
Upgrade of Fire Fighting System &	800.000	Investment Decision: 10/2021
replacement of the pressure relief		Start of operation: 11/2022 Inclusion in the
valves at BMS Sidirokastro		system: 12/2022
Nitrogen injection system	2.530.000	Investment Decision: 12/2021
		Start of operation: 06/2023 Inclusion in the
		system: 09/2023
Pipeline Nea Mesimvria – Evzoni/	67.000.000	Investment Decision: 04/2022
Gevgelija and M Station		Start of operation: 12/2024
		Inclusion in the system: 12/2024
		2
Interconnection of IGR Pineline with	650.000	Investment Decision: Taken
the NNCS in Kometini	0.0000	Start of operation: 12/2021
uie mings in Aomouni		Start of operation: $12/2021$
		inclusion in the system: 03/2022

Connection of the FSRU of Alexandroupolis	13.000.000	Investment Decision: 09/2021 Start of operation: 10/2023 Inclusion in the system: 10/2023
Metering and Regulating Station for connecting with Dioryga Gas FSRU	9.900.000	Investment Decision 06/2022 Start of operation: 10/2023 Inclusion in the System: 12/2023
M Station at SALFA Ano Liossia	680.000	Investment Decision: Taken Start of operation: 12/2021 Inclusion in the system: 12/2021
M/R Station AdG III	2.000.000	Investment Decision: Taken Start of operation: 03/2023 Inclusion in the system: 04/2023
Connection with DEPA Commercial SA CNG Station in Komotini	1.300.000	Investment Decision: 12/2022 Start of operation: 09/2024 Inclusion in the system: 12/2024
Connection with DEPA Commercial SA CNG Station in Tripoli	2.350.000	Investment Decision: 12/2022 Start of operation: 09/2024 Inclusion in the system: 12/2024
Connection of Kavala Oil plant to the NNGTS	3.400.000	Investment Decision: 02/2023 Start of operation: 08/2024 Inclusion in the system: 11/2024
Metering Station at Agios Nikolaos Viotia (AdG IV)	1.870.000	Investment Decision: Taken Start of operation: 03/2023 Inclusion in the system: 04/2023
Connection of ELVAL plant of NNGTS in Inofyta	4.320.000	Investment Decision: 07/2021 Start of operation: 10/2022 Inclusion in the system: 12/2022
Connection with TERNA Power Plant to the NNTGS	4.950.000	Investment Decision: 11/2021 Start of operation: 03/2023 Inclusion in the system: 06/2023
Connection with ELPEDISON Power Plant to the NNTGS	2.910.000	Investment Decision: 11/2021 Start of operation: 09/2023 Inclusion in the system: 12/2023

Connection to ELVAL/HALCOK	2.010.000	Investment Decision: 11/2022 Start of operation: 05/2024 Inclusion in the
		system: 06/2024
Installation of M/R in Kavala	2.400.000	Investment Decision: Taken Phase 1 Start of operation: 10/2021 Inclusion in the system: 12/2021 Phase 2 Start of operation: 10/2024 Inclusion in the system: 12/2024
M/R Station at the prefecture of Poria	2.200.000	Investment Decision: 12/2021 Start of operation: 11/2022 Inclusion in the system:01/2023
CNG Station at the prefecture of Poria	1.000.000	Investment Decision: 12/2021 Start of operation: 11/2022 Inclusion in the system: 01/2023
M/R Station at the prefecture of Aspros	3.000.000	Investment Decision: 12/2021 Start of operation: 11/2022 Inclusion in the system: 01/2023
M/R Station in the region of Perdika Eordeas	is 4.200.000	Investment Decision: 12/2021 Phase 1 Start of operation: 09/2022 Inclusion in the system:11/2022 Phase 2 Start of operation: 11/2022 Inclusion in the system: 01/2023
M/R Station Livadia	2.300.000	Investment Decision: Taken Phase 1 Start of operation: 12/2021 Inclusion in the system: 03/2022 Phase 2 Start of operation: 10/2024 Inclusion in the system: 12/2024

Megalopoli M/R city gate station	2.700.000	Investment Decision: 06/2022 Stort of operation: 00/2023
		Start of operation: 09/2025
		Inclusion in the system: 12/2023
		Final Investment Decision of the temporary M/R:
		Taken
		Start of operation:09/2021
		Start of operation. 072021
		inclusion in the system of the temporary M/K :
		11/2021
Drimos/Liti M/R city gate station	2.800.000	Investment Decision: 12/2021 Phase 1
		Start of operation: 10/2022 Inclusion in the
	1	system: 12/2022 Phase 2
		Start of operation: 12/2023
	1	Inclusion in the system: 02/2024
	1 47 000 000	
High Pressure pipeline to West	147.000.000	Investment Decision: 12/2021
Macedonia		Start of operation: 08/2023 Inclusion in the
		system:09/2023
High Pressure Pipeline to Patras	98.000.000	Investment Decision: 05/2023 Start of operation:
		06/2025
		Inclusion in the system:09/2025
Korinthos M/R city gate Station	2.200.000	Investment Decision: 11/2021 Start of operation:
		09/2023
		Inclusion in the system $12/2023$
		merusion in the system. 12, 2023
Argos/Napflio M/R city gate Station	2.300.000	Investment Decision: 11/2021
		Start of operation: 09/2023 Inclusion in the
		suctom: $12/2023$
		System. 12/2023
Tripoli M/R city gate Station	2.300.000	Investment Decision: 11/2021 Phase 1
		Start of operation: 07/2022 Inclusion in the
		start of operation. 07/2022 metasion in the
		System.07/2022 Phase 2
		start of operation: 10/2024
		Inclusion in the system: 12/2024
Truck Loading Pilot (first) Station	7.500.000	Investment Decision: Taken Start of operation:
_		12/2021
		Inclusion in the system: 05/2022
New jetty for small scale LNG in	22.500.000	Investment Decision: Taken
Revithoussa		Start of operation: $10/2022$ Inclusion in the
	1	system: $01/2023$
		System. 01/2023
Compression station at Kini and	15.000.000	Investment Decision: 12/2021
Regulating Station in Komatini		Start of operation: 11/2022
Acgulating Station in Aonothin	1	Start of operation. $11/2023$
		inclusion in the system:01/2024
	72 000 000	
Compressor Station in Ampelia	/3.000.000	investment Decision: Taken
		Start of operation: 08/2023

		Inclusion in the system: 12/2023
Upgrade of Nea Messimvria compression station	18.200.000	Investment Decision: Taken Start of operation: 12/2022 Inclusion in the system: 03/2023
Booster Compressor for TAP in Nea Mesimvria	36.900.000	Investment Decision: 12/2021 Start of operation: 09/2023 Inclusion in the system: 12/2023
APPENDIX B: GLOBAL HYDROGEN PROJECTS OF COMMON INTEREST

Project name	Project promoters	Country	Timeline	Project maturity	Scope & goal
<u>2G's CHP fleet</u> retrofit	2G Energy AG	Germany	NA-NA	Project	Existing natural gas CHP plants can be easily retrofitted for the operation with hydrogen by moderate costs; by this means millions of tons of CO2 can be saved each year
<u>Aberdeen Vision</u> <u>Project</u>	SGN / NG / PBDE / DNVGL	United Kingdom	NA-NA	Project	The focus for the Aberdeen Vision project is the transport and use of hydrogen produced from reformed natural gas from StFergus in North East Scotland. Outline the possibility of using advanced hydrogen production at St Fergus. And to discuss the technology and safety requirements for the transportation and storage of CO2 from hydrogen production.
Accuracy of thermal gas meters	Adrian Dudek, Jacek Jaworski	Poland	2020-NA	Study	Test influence of up to 15% hydrogen on 4 thermal gas meters AERIUS (DIEHL Metering)
<u>Acorn Hydrogen</u>	Pale Blue Dot Energy	United Kingdom	2018-2028	Project	The Acorn Hydrogen project aims to construct a natural gas to hydrogen reformation plant at St Fergus where co-located. CCS facilities will transport captured CO2 offshore for sequestration with the produced hydrogen being injected into the NTS.
<u>AHLAS</u> Energéticas project	H2 Vector	Spain	2022-NA	Project	LOHC Optimization Studies for H2 Storage in Decentralised Applications / Buildings
AHMUR - H2 renewable production by electrolysis (100 MW)	Repsol, Engie, Enagás	Spain	2021-2025	Project	Repsol will promote the construction of a large-scale electrolyser in Cartagena, with a capacity of 100 MW in its first phase, with the aim of promoting the decarbonisation of the industries located in the Escombreras Valley. Thanks to this electrolyser, the emission of more than 167,000 tonnes of CO2 per year will be avoided and some 1,100 jobs could be created. The project has been recognized as IPCEI.
ALBA Project - Sines (4 MW)	Repsol	Portugal	2022-2025	Project	Hydrogen Generation Project to feed the new PP and PEL plants of the ALBA project
<u>Apeldoorn H2</u> boilers	BDR Thermea group	Netherlan ds	2021-NA	Project	Main scope of the demo was to confirm the perfect interchangeability with an Natural Gas boiler referring to installation, commissioning and operation.
<u>AquaDuctus</u>	GASCADE, Gasunie, RWE and Shell	Germany	2022-2035	Project	AquaDuctus is part of the project initiative AquaVentus and aims at transporting green hydrogen, which will be produced offshore in the German North Sea, to the island of Heligoland. At a later stage a connection to the German mainland and to the German national hydrogen network is foreseen.
Aquamarine	Hungarian Gas Storage Ltd (MFGT)	Hungary	2021-2023	Project	Establishing a 2.5 MW electrolizer and proper hydrogen compressor at Kardoskut Underground Gas Storage (HU).The hydrogen will be utilized within the Gas Storage Ltd.'s own gas-operated equipment as hydrogen blended natural gas and reducing its own CO2 emission. Furthermore, at withdrawal period the hydrogen blended natural gas will be injected into the gas transmission system. Other topics: development of material science, LOHC technologies and additional R&D program of hydrogen blended natural gas
<u>AquaPortus</u>	GASCADE, Gasunie, RWE, Shell, Island of Heligoland, Reuther, Vattenfall, Siemens, Parkwind and MHI Vestas	Germany	NA-NA	Project	AquaPortus is the name given to the incremental expansion of Heligoland's port infrastructure to make the island the main hydrogen hub in the North Sea. In addition to maritime research and the complete decarbonisation of the island, including maritime traffic, the focus is also on the regional supply of users along the German North Sea coast with green hydrogen. Furthermore, Heligoland is to become the main hub for a Pan-European H2 pipeline grid.

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<u>AquaPrimus</u>	GASCADE, Gasunie, RWE, Shell, Island of Heligoland, Reuther, Vattenfall, Siemens, Parkwind and MHI Vestas	Germany	NA-NA	Project	The AquaPrimus pilot project benefits Germany as a hydrogen nation in several ways. In terms of industrial policy, the prototype of a decentralised generation unit that is ready for serial production is developed here and tested for the global market. At the same time, all parties involved gain valuable experience with the prototype in Sassnitz (HyStarter) as well as with the first pilot plants on Heligoland and contribute the first 42 MW towards building the required capacities by 2025.
<u>AquaSector</u>	Equinor, Gasunie, RWE and Shell	Germany	2022-2028	Project	The AquaSector project intends to install approx. 300 megawatt (MW) electrolyser capacity to produce up to 20,000 tons per year of green hydrogen offshore. The green hydrogen is planned to be transported via a pipeline, called AquaDuctus, to Heligoland starting in the year of 2028. The partners regard the AquaSector project also as a 'proof of concept' for the realisation of the AquaVentus vision of producing up to 10 gigawatts of green hydrogen offshore by 2035 and transporting it via an extended pipeline to mainland Germany.
<u>AquaVentus</u>	GASCADE, Gasunie, RWE, Shell, Island of Heligoland, Reuther, Vattenfall, Siemens, Parkwind and MHI Vestas	Germany	2020-2035	Project	The project portfolio associated with the AquaVentus initiative includes various sub-projects along the value chain from the production of hydrogen in the North Sea to transportation to customers on the mainland. These coordinated projects synchronise demand and production, thereby facilitating market roll-out. T
<u>astora H2</u>	astora GmbH	Germany	2023-2030	Project	Construction of H2 storage by retroffitting existing cavern(s)
<u>ATC PLANT AT</u> LOWER BRIGHOUSE	ETGAS, Yorkshire Water	United Kingdom	2020-NA	Project	Production of H2 from biomass
<u>BayH2</u>	Vattenfall Innovation; Bayernoil	Germany	NA-NA	Project	Decarbonising refinery industry
<u>BIG HIT</u>	Twelve partners from Denmark, France, Italy, Malta, Spain and the UK. Coodination by Foundation for the development of new hydrogen technologies in Aragon	United Kingdom	NA-NA	Project	BIG HIT (Building Innovative Green Hydrogen Systems in Isolated Territorie) will demonstrate the Orkney Islands of Scotland as a replicable Hydrogen Territory, using curtailed renewable energy generated locally to produce hydrogen which can then be used as a clean energy vector to store and use valuable energy for local applications.
<u>BioH2_project</u>	NG distribution	United Kingdom	2016-2017	Project (R&D)	Investigate the potential for hydrogen production from waste through potential conversion of the BioSNG plant that gasifieswaste into syngas, possible with relatively minor modifications to the plant.
<u>Black Horse</u>	Bioway, major oil and refineries company, OEMs, factories, member states representatives and others involved in the hydrogen economy	Slovakia	NA-NA	Project	Construction of renewable power plants, production of green hydrogen for transport sector, rollout of large scale, state of the art hydrogen powered trucks, build HRS infrastructure for HDV, but also for passenger cars and buses.

MSc Oil and Gas Process Systems Engineering HYDROGEN COMPATIBILITY ASSESSMENT IN NATURAL GAS INFRASTRUCTURES

<u>BLUE DANUBE</u>	Verbund (electric utility), ElringKlinger (tier 1 auto supplier), DB Schenker (logistics), ÖBB (rail), Siemens (industrial), Hydrogenious (LOHC), Chemgas Shipping (inland barges and sea), Danube Commission (river management)	Germany	NA-NA	Project	 With an electrolysis capacity of around 1.5 GW, over 80,000 tons of green hydrogen per year are to be produced in South-East Europe at competitive prices from around 2 GW of renewable energy and will bei import to Austria and Germany by our Liquid Organic Hydrogen Carrier (LOHC) technology. 2 GW wind and solar-based hydrogen production, transportation by barges on River Danube, supply to industry and mobility hubs in the InterReg Danube Transnational Region. SOFC unit on 100% hydrogen network
<u>Blue Dolphin</u>	Fincantieri (shipbuilder)	Italy	NA-NA	Project	50 ships and ship power generation systems, from liquid hydrogen cargo to passenger ships, powered by hydrogen and the required infrastructure
<u>Blue Mackerel</u>	Ei-H2	Ireland	2021-2024	Project	The Blue Mackerel project aims to establish a 50 MW early market Green Hydrogen Production Plant in Aghada, Co. Cork. It will aim to produce 22 tonnes of green safe hydrogen per day, which will be added to the existing natural gas network and industry offtake.
<u>CAES</u> Zuidwending	Corre Energy BV	Netherlan ds	2024-NA	Project	CAES Zuidwending will implement a further design step that will allow green hydrogen to fully replace methane, providing a 100% renewable-CAES solution.
<u>Cavendish</u>	NG/ SGN / CADENT	United Kingdom	2019-2020	Project (Pilot)	Determine the viability of utilising existing infrastructure to enable the Isle of Grain region to supply decarbonised hydrogen to London and the South East. Ascertain what additional infrastructure would be required if the Isle of Grain was to supply all of London's hydrogen, including the identification of critical environmental issues and ecosystem mapping of stakeholders.
<u>CEN/GERG PNR</u> <u>H2NG and H2 in</u> <u>NG systems</u>	European Commission CEN / GERG / industry	Belgium	2020-2021	Project (R&D)	Prenormative study 'Removing the technical barriers to use of hydrogen in natural gas networks and for (natural) gas end users". Eight priority areas for study. These are safety, gas quality, underground storage, power generation, industrial use, steel pipes, network equipment and appliances.
Centurion/P2G	Storengy UK	United Kingdom	2018-2020	Project	A project exploring the electrolytic production, pipeline transmission, salt cavern storage and gas grid injection of hydrogen. The feasibility of placing a 100MW electrolyser at the INOVYN Runcorn site will be assessed.
Certification of the H2-ready network	Snam, RINA	Italy	NA-NA	Project (R&D)	Certification of the H2-ready network, Snam and RINA, will assess and certify the compatibility of each natural gas pipeline of Snam's network to transport up to 100% hydrogen, and study and test the compatibility of industrial burners. Further experiments, analysis and technology scouting in various areas of hydrogen production, storage and distribution are planned
<u>Chateauneuf</u>	BDR Thermea group	France	NA-NA	Project (Pilot)	Installation of a 28kW pure hydrogen boiler and a backup boiler (90kW) running with blends fluctuating from 0 to 10% H2, to supply heating for a complex of buildings in Chateauneuf. This demo is a complete ecosystem, producing, storing, and using our own hydrogen, as part of Ilot@ge project: since 2014, an electrolyser produces green H2 from local PV and wind electricity.
<u>CleanExport</u>	Equinor, Total E&P Norge, Gassco, Agder Energi, Air Liquide, SINTEF Industyr, NTNU	Norway	2020-2024	Project (R&D)	The project will develop a holistic, integrated energy- system model of electric power, hydrogen and natural gas with CCS, specifically designed for analysing clean Norwegian energy export. This holistic approach will enable the CleanExport project to explore new investments and alternative utilization of existing energy export infrastructure from Norway to Europe.

Cooperation between OGE, NIKOLA and IVECO	oge, Nikola, Iveco	Germany	2021-NA	Project	Joint project for the identification and development of hydrogen fueling stations for heavy duty trucks in Germany, in order to stimulate Fuel Cell Electric Vehicle (FCEV) truck sales and hydrogen demand, as well as support infrastructure partnerships
Damasławek	GAZ-SYSTEM	Poland	2024-2036	Project	The project calls for the first hydrogen cavern to be operational around 2030. The location and geological conditions allow for the creation of a storage facility of key importance to the energy security of Poland and the construction of the entire hydrogen economy. The storage facility can ideally fit into hydrogen clusters that will be created around industrial centers as well as offshore and renewable energy storage facilities.
<u>DIVINA project</u>	Snam, RINA e Bormioli	Italy	2022-NA	Project (R&D)	The main objective of the project is the concrete, experimental and industrial-scale evaluation of the effects of H2 combustion on the QUANTITY and QUALITY (seed count, control of the REDOX state and color) of the obtainable glass, as well as on NOx and SOx emissions, which must at least remain within the values and limits currently in place.
<u>Djewels</u>	Nouryon; N.V. Nederlandse Gasunie	Netherlan ds	2020-NA	Project	McPhy supplies innovative alkaline electrolysers to convert renewable electricity into 3000 tons of green hydrogen per year; BioMCN combines this hydrogen with CO 2 from other processes to produce renewable methanol. This results in a CO 2 reduction of 27,000 tons per year. DeNora also supplies electrodes – an important part of electrolysis technology – and Hinicio is involved as a consultant with a specialty in hydrogen. Nouryon and Gasunie plan to take a final investment decision for the factory in 2020.
<u>doing hydrogen</u>	GASCADE, ONTRAS	Germany	2022-2026	Project	The project 'doing hydrogen' aims to establish a Eastern German starting grid in cooperation with the German TSO ONTRAS as well as with potential producers and customers of clean hydrogen. It is embedded in the German hydrogen network and the European hydrogen backbone. Together with other German projects a connection to western neighboring countries (NL, BE, FR) is planned. The project will link the energy port of Rostock at the Baltic Sea with the central German industrial region and important industrial sites. For this network, 335 km of existing natural gas pipelines will be repurposed and some 140 km of new hydrogen pipelines will be built.
<u>Dolphyn</u>	ERM	United Kingdom	NA-NA	Project	The project looks to utilise the vast UK offshore wind potential to power electrolysers to produce hydrogen from the water the turbines float on. Large 10MW turbines consisting of desalinisation technology and PEM electrolysers will feed hydrogen at pressure via a single flexible riser to a sub-sea manifold with other turbines' lines. The gas is then exported back to shore via a single trunkline.
<u>Dolphyn ERM</u> <u>Project</u>	led by a partnership between Environmental Resource Management (ERM), the Tractebel unit of French energy company Engie, and the offshore specialist Offshore Design Engineering Limited (ODE).	United Kingdom	2020-2030	Project	The project aims to use the considerable resource of UK offshore wind to operate electrolysers in order to generate hydrogen from the seawater surrounding the wind turbines. Sizeable 10MW turbines comprising of desalinization capabilities and PEM electrolysers can inject pressurised hydrogen to a subsea manifold with other turbines' lines via a single flexible riser.

APPENDIX C: REGULATIONS AND LAWS

A variety of rules and standards govern the design, building, and operation of hydrogen systems in the general industry. Changes to current codes such as ASME B31.3, ASME B31.8, and the U.S. Department of Transportation's rules governing the transportation of natural and other gases through pipelines, as well as minimum safety criteria affecting the construction of natural gas pipelines. Additionally, the installation of hydrogen handling systems is controlled by a variety of laws, standards, and regulations. The following table provides codes for gaseous hydrogen systems and rules of conduct for handling hydrogen. However, the standards lack guidance addressing the materials and design of hydrogen-compatible systems, particularly high-pressure transmission pipes.

Table 27. Codes and Good practices.			
Code	Description		
NFPA Standard 50A	Gaseous hydrogen systems at consumer		
	sites		
NFPA Standard #30	Standard for tank vehicles for flammable		
	and combustible liquids		
NFPA Standard #386	Standard for portable shipping tanks for		
	flammable and combustible liquids		
NFPA Standard #68	Guide for explosion venting		
Code for good practice			
C-10	Recommendations for changes of service		
	for compressed gas cylinders		
C-11	Recommended practices for inspection of		
	compressed gas cylinders at time of		
	manufacture		
C-14	Procedures for fire testing of DOT cylinder		
	safety relief device systems		
C-15	Procedures for cylinder design proof and		
	service performance test		
G-5	Compressed gas association		
G-5.1	CGA Standard of gaseous hydrogen at		
	consumer sites		
G-5.3	CGA Commodity specification for		
	hydrogen		
P-1	Safe handling of compressed gas in		
	containers		
P-6	Standard density data atmospheric gases in		
	hydrogen		
P-12	Safe handling of cryogenic liquids		
L'Air Liquide	Guide de securite hydrogen		
ICG Code of Prectice	Gaseous hydrogen stations		

APPENDIX D: PHYSICAL LAWS

Gas Velocity

The pace of an incompressible fluid, which is characterized by the rate at which molecules travel from one location to another, differs from the velocity of pipeline gas. Since gas velocity is dependent on pressure, which fluctuates over the length of the pipeline, the flow is constant but non-uniform. Therefore, the greatest pressure is downstream, resulting in the greatest velocity, whereas the least velocity is upstream. For a pipeline length stretching from point 1 upstream to point 2 with no gas injection or delivery in between, the steady flow mass flow rate is computed as follows (Gondial, 2016).

$$M = Q_1 \rho_1 = Q_2 \rho_2$$

= $Q_b \rho_b \left(\frac{kg}{s}\right)$ (29)

Where Qb= gas flow rate at standard condition (m³/s) and ρ b= gas density (kg/m³) Equation can be written as:

$$Q_1 = \frac{Q_b \rho_b}{\rho_1} \left(\frac{m^3}{s}\right) \tag{30}$$

Applying the gas law equation

$$\rho_1 = \frac{P_1}{Z_1 R T_1} (\frac{kg}{m^3}) \tag{31}$$

Where T1 and P1 are temperature and pressure at point 1 of the section, while at standard conditions (IEA, 2019):

$$\rho_b = \frac{P_b}{Z_b R T_b} \left(\frac{kg}{m^3}\right) \tag{32}$$

Replacing the above values in Equation Q1:

$$Q_1 = Q_b \left(\frac{P_b}{T_b}\right) \left(\frac{T_1}{P_1}\right) Z_1\left(\frac{m^3}{s}\right)$$
(33)

For finding the velocity, we can use the below relation:

$$u_1 = \frac{Q_1}{A} \left(\frac{m}{s}\right) \tag{34}$$

Thus:

$$u_1 = \frac{Q_b Z_1}{A} \left(\frac{P_b}{T_b}\right) \left(\frac{T_1}{P_1}\right) \left(\frac{m}{s}\right)$$
(35)

Where A = area of cross section (m²)Elevation effects

Elevation has an effect on gas flow, but incompressible fluid flow is different. Because the density or specific weight of incompressible fluids, also known as liquids, is significantly higher than that of gases, the gravitational force exerted on the liquids when the fluid is ascending is quite high. In the case of gas, these elevation effects are significantly reduced. The following modifications can be made to the general flow equation to account for the gas pipeline's elevation difference (Gondial, 2016):

$$Q = 5.747 * 10^{-4} F\left(\frac{T_b}{P_b}\right) \left[\frac{P_1^2 - e^s P_2^2}{GT_f L_e Z}\right]^{0.5} D^{2.5}\left(\frac{m^3}{s}\right)$$
(36)

Where,

$$L_e = \frac{L(e^s - 1)}{s} \ (m) \tag{37}$$

The terms L_e and e^s account for the difference in elevation between upstream and downstream pipe ends. S is a parameter depending upon the elevation difference, flow temperature, gas gravity and compressibility factor Z and is expressed as (IEA, 2019):

$$s = \frac{0.0684G(H_2 - H_1)}{T_f Z} \tag{38}$$

Where

 $H_1 = elevation at upstream point 1 (m) and$ $<math>H_2 = elevation at downstream point 2 (m).$

REFERENCES

Adler, T. A., Flitton, M. A., Agawala, V. S. & Andryushchenko, T. N., 2003. *ASM Handbook, Volume 13A, Corrosion: Fundamentals, Testing, and Protection.* 9 ed. s.l.:ASM International.

Alcock, J., 2001. *Compilation of existing safety data on hydrogen and comparative fuels*, s.l.: European Integrated Hydrogen PRoject Phase 2 (EIHP2).

Altfeld, K. & Pinchbeck, D., 2013. *Admissible hydrogen concentrations in natural gas systems*, s.l.: Gas Energy.

Amaro, R. L. & et al, 2018. Development of a model for hydrogen-assisted fatigue crack growth in pipeline steel. *ASME Journal of Pressure Vessel Technology*, 140(2), pp. 1-13.

Ambriz, R. & Jaramillo, D., 2014. Mechanical Behavior of Precipitation Harderned Aluminum Alloys Welds. *Light Metal Alloys Applications*.

Anthony, W. T. & Neville, R. M., 1994. *The Role of Hydrogen in Enhancing Plastic Instability and Degrading Fracture Toughness in Steels*. s.l.:Wiley.

Association, A. G., 2006. *Plastic Pipe Manual for Gas service*. 8 ed. Washington DC 20001 USA: American Gas Association.

Association, E. I. G., 2004. Hydrogen Transportation Pipelines, Brussels: EIGA.

Bard, J. et al., 2022. *The limitations of hydrogen blending in the European Gas Grid*, Berlin: European Climate Foundation.

Barthelemy, H., 2011. Effects of pressure and purity on the hydrogen embrittlement of steels. *International Journal of Hydrogen Energy 36*, Volume 3, pp. 2750-2758.

Basile, A., Dalena, F., Tong, J. & Veziroglu, T. N., 2017. *Hydrogen Prodution, Separation and Purification for Energy*. First ed. London: The Institution of Engineering and Technology.

Beachem, C. D., 1972. A new model for hydrogen-assisted cracking (hydrogen "embrittlement"). *Metallurgical and Materials Transactions B*, Volume 3, pp. 441-455.

Brower, M. & al, e., 2012. Ignition delay time and laminar flame speed calculations for natural gas/hydrogen blends at elevated pressures. *ASME Paper GT2012-69310*, 11-15 June, Volume 2, pp. 1005-1016.

Cammarota, F. & al, e., 2009. Combined effects of initial pressure and turbulence on explosions of hydrogen-enriched methane/air mixtures. *Journal of Loss Prevention in the Process Industries*, September, 22(5), pp. 607-613.

Castello, P., Tzimas, E., Moretto, P. & Peteves, S. D., 2005. *Techno-economic assessment of hydrogen transmission and distribution systems in Europe in the medium and long term*, Netherlands: ECN.

Che, Z., 2018. Fatigue crack growth in hydrogen pipelines steels, Illinois: s.n.

13 July 2023

Christoph, K., Cartellieri, W. & Pfeifer, U., 1972. Bewertung der. Klopffestigkeit von Kraftgasen mittels der Methan- zahl und deren praktische. Anwendung bei Gasmotoren. 33(10), pp. 389-429.

Cialone, J. & Holbrook, J., 1988. Sensitivity of steels to degradation in gaseous hydrogen. In: L. Raymond, ed. *Hydrogen embrittlement: Prevention and control*. Ann Arbor, MI: ASTM STP 962, pp. 134-152.

De Vries, H., 2009. NaturalHy Project Final presentation. s.l., s.n.

De Vries, H., Florisson, O. & Thiekstra, G., 2007. SAFE OPERATION OF NATURAL GAS APPLIANCES FUELED WITH HYDROGEN/NATURAL GAS MIXTURES. San Sebastian Spain, s.n.

DEPA, 2019. *depa*. [Online] Available at: <u>https://depa.gr/</u> [Accessed 2023].

desfa, 2022. *www.desfa.gr*. [Online] Available at: <u>https://www.desfa.gr/national-natural-gas-system/transmission</u> [Accessed 2023].

Di Bella, F. A., 2015. Development of a centrifual Hydrogen Pipeline Gas Compressor. Volume 1785, pp. 596-622.

Dodds, P. E. & Demoullin, S., 2013. Conversion of the UK gas system to transport hydrogen. *International Journal of Hydrogen Energy*, Volume 38, pp. 7189-7200.

Drexler, S., Amaro, L., Slifka, J. & Bradley, E., 2018. Operating Hydrogen Gas Transmission Pipelines at Pressures Above 21 MPa. *Journal of Pressure Vessel Technology, Transactions of the ASME*, 140(6), pp. 061702 1-6.

EIGA, 2004. Hydrogen Transportation Pipelines, A document on design, construction, and operational requirements for hydrogen transportation pipelines, Brussels: European Industrial Gases Association.

EIGA, 2014. Hydrogen Pipeline Systems, Brussels: EIGA.

ENTSOG, GIE & Europe, H., 2021. *How to transport and store hydrogen, facts and figures,* Brussels: ENTSOG AISBL, GIE, Hydrogen Europe.

Escalante Soberanis, M. & Fernandez, A., 2010. A review on the technical adaptations for internal combustion engines to operate with gas/hydrogen mixtures. *International Journal of Hydrogen Energy*, 35(21), pp. 12134-12140.

Fekete, J. & al, e., 2015. Economic impact of applying high strength steels in hydrogen gas pipelines. *International Journal of Hydrogen Energy*, Volume 40, pp. 10547-10558.

Florisson, O., 2009. *NATURALHY an overview NATURALHY Final Public Presentation*. Groningen Netherlands, s.n.

Florisson, O., 2012. *NaturalHy Website*. [Online] Available at: <u>http://www.naturalhy.net</u> [Accessed 14 October 2014].

Gahr, S., Grossbech, M. L. & Birnbaum, H. K., 1977. Acta Metall. *Corrosion in Petrochemical industry*, Volume 25, p. 125.

Gavrilyuk, A., 2013. *Hydrogen Energy for Beginners*. Boca Raton: Taylor & Francis Group, LLC.

Gerboni, R., 2016. Introduction to hydrogen transportation. *Compendium of Hydrogen Energy*, Volume 2, pp. 283-299.

Gondal, A. I. & Sahir, H. M., 2012. Prospects of natural gas pipeline infrastructure in hydrogen transportation. *International Journal of Energy Research*, Volume 36, pp. 1338-1345.

Gondial, I., 2016. Hydrogen transportation by pipelines. *Compendium of Hydrogen Energy*, Volume 2, pp. 301-322.

Gonzalez, D. N., Van der Meer, S., Bonetto, J. & Herwijn, A., 2020. *Technical assessment of Hydrogen transport, compression, processing offshore, s.l.*: North Sea Energy.

GPA, 2019. Hydrogen in the gas distribution networks, s.l.: Government of South Australia.

GRTgaz & al, e., 2019. Technical and economic conditions for injecting hydrogen into natural gas networks - Final report. 51(4).

Gueugnaut, D. & al, e., 2008. *Evaluation of the Permeability to CH4 and CH*\$+*H2 of PE currently based in Gas distribution networks*, France: GAZ de France.

Hagen, A. B. & Alvaro, A., 2020. *Hydrogen Influence on Mechanical properties in pipeline steel*, NORWAY: Sintef report 2020:00130.

Haines, M. R., Polman, W. & De laat, J. C., 2004. *Reduction of CO2 emissions by addition of hydrogen to natural gas*. Vancouver Canada, Greenhouse Gas Control Technologies Conference.

Hirth, J., 2013. The Role of Hydrogen in Enhancing Plastic Instability and Degrading Fracture Toughness in Steels. In: W. T. Anthony & R. M. Neville, eds. *Hydrogen Effects in Materials.* s.l.:Wiley, pp. 505-522.

Holbrook, J., Cialone, H. J., Mayfield, M. E. & Scott, P. M., 1982. *Effect of Hydrogen on Low-Cycle-Fatigue Life and Subcritical Crack Growth in Pipeline Steels*, s.l.: NTRL.

Huang, Z. et al., 2006. Measurements of laminar burning velocites for natural gas-hydrogenair mixtures. *Combustion and Flame*, 146(1-2), pp. 302-311.

Hu, E. et al., 2009. Experimental and numerical study on laminar burning characteristics of premixed methane-hydrogen air flames. *International Journal of Hydrogen Energy*, 34(11), pp. 4876-4888.

IEA, 2019. The Future of Hydrogen, Japan: IEA.

13 July 2023

IEA, 2020. *International Energy Agency*. [Online] Available at: <u>https://www.iea.org/</u> [Accessed 2023].

IEA, CEM & HI, 2022. Global Hydrogen Review, s.l.: IEA.

IEA, G., 2003. *Reduction of CO2 emissions by adding hydrogen to natural gas*, Apeldoorn: Gastec NV.

Ilbas, M. et al., 2007. Laminar Burning velocities of Methane-hydrogen-air mixtures. *International Journal of Hydrogen Energy*, 31(12), pp. 1768-1779.

Knott, J. F., 1996. Fracture Toughness and Hydrogen Assisted Crack Growth in Engineering Alloys. In: W. T. Anthony & R. M. Neville, eds. *Hydrogen Effects in Materials*. s.l.:Wiley, p. 387.

Larfeidt, J., Anderson, M., Larsson, A. & Moell, D., 2017. *Hydrogen Co-Firing in Siemens Low NOX industrial Gas Turbines*, s.l.: Power-Gen Eur..

Lee, A. J. & Stephen, W., 2016. Hydrogen Embrittlement, s.l.: NASA TM-218602.

Leighty, W. C. & al, e., 2006. *Compressorless hydrogen transmission pipelines deliver large-scale stranded renewable energy at competitive cost*. Amsterdam, 23rd World Gas Conference.

Liquide, A., 2013. *Hydrogen Delivery Technologies and Systems; Pipeline Transmission of Hydrogen*. Arlington, VA. May, United States Department of Energy.

Lowesmith, B., Hankinson, G., spataru, C. & Stobbart, M., 2009. Gas build-up in a domestic property following realases of methane/hydrogen mixtures. *International Journal of Hydrogen Energy*, 34(14), pp. 5932-5939.

Melaina, W. M., Antonia, O. & Penev, M., 2013. *Blending Hydrogen into Natural Gas Pipeline Networks: A review of key issues (NREL/TP-5600-51995)*, Colorado 80401: National Renewable Energy Laboratory.

Melaina, W. M., Penev, M. & Zubov, Z., 2015. Hydrogen blending in Natural gas Pipelines. In: Y. Jinyue, ed. *Handbook of Clean Energy systems*. s.l.:John Wiley & Sons.

Miao, H., Jiao, Q., Huang, Z. & Jiang, D., 2008. Effect of initial pressure on laminar combustion characteristics of hydrogen-enriched natural gas. *International Journal of Hydrogen Energy*, 33(14), pp. 3876-3885.

Mohitpour, M., Golshan, H. & Murray, A., 2007. *Pipeline design & Construction A practical Approach*. 3 ed. New York: ASME Press.

Murakami, Y. & Ritchie, R., 2012. Effects of hydrogen on fatigue-crack propagation in steels. *Gaseous Hydrogen Embrittlement of Materials in Energy Technologies*, Volume 2, pp. 379-417.

Nanninga, N. E., Slifka, A., Levy, Y. & White, C., 2010. A review of Fatigue crack growth for pipeline steels exposed to hydrogen. *Journal of Research of the National Institute of Standards and Technology*, 1 December, 115(6), pp. 437-452.

Oriani, R. A., 1972. A mechanistic theory of hydrogen embrittlement of steels. *Berichte der Bunsengesellschaft für physikalische Chemie*, 76(8), pp. 848-857.

Petch, N. J. & Stables, P., 1952. Delayed fracture of metals under static load. *Nature*, Volume 169, pp. 842-843.

Polman, E. & Walters, M., 2002. *Pathways to a hydrogen society*. Orlando, Proceedings Natural Gas Technologies.

Pressouvre, G. M. & Bernstein, I. M., 1978. A quantitative analysis of hydrogen trapping. *Metallurgical transactions,* Volume 9, pp. 1571-1580.

RAE, 2022. *Requiatory Authority for Energy*. [Online] Available at: <u>https://www.rae.gr/</u> [Accessed MAY 2023].

Ronevich, J. & San Marchi, C., 2019. *Hydrogen effects on pipelibe steels and blending into natural gas*. Livermore CA: American Gas Associtation Sustainable growth Commitee.

Ruthven, D., Farooq, S. & Knaebel, K., 1994. *Pressure Swing Adsorption*, New York: Wiley-VCH.

Schmura, E. & Klingenberg, M., 2005. *Existing Natural Gas Pipeline Materials and Associated Operational*, Johnstown, PA 15904: DOE Hydrogen Program.

Scholten, F. & Walters, M., 2002. *Hydrogen diffusion through plastic pipes*. San Francisco, California, USA, s.n., pp. 280-284.

Slifka, A. J. et al., 2018. Fatigue measurement of pipeline steels for the application of transporting gaseous hydrogen. *ASME Journal of Pressure Vessel Technology*, 140(1), pp. 011407 1-12.

Smith, N. et al., 2017. *Identifying the commercial, technical and regulatory issues for injecting renewables gas in Australian distribution gas networks*, s.l.: Energy Pipelines CRC.

Speight, G., 2020. Handbook of Gasification Technology. s.l.:Wiley.

Steiner, K., 2018. Metering errors of residential meters and uncertainties of meter readings in case of injection of hydrogen into the natural gas network. *gwf Gas+Energie*, June, pp. 40-46.

Stetson, N., McWhorter, S. & Ahn, C., 2016. Introduction to hydrogen storage. In: *Compendium of hydrogen energy*. s.l.:Woodhead, pp. 3-25.

Stolten, D. & Emonts, B., 2016. *Hydrogen Science and Engineering : Materials, Processes, Systems and Technology*. Weinheim: Wiley-VCH.

Szummer, A., Jezierska, E. & Lublinska, K., 1999. Hydrogen surface effects in ferritic stainless steels. *Journal of Alloys and Compounds,* Volume 293-295, pp. 356-360.

Taamaliah, S. et al., 2018. Erratum to Fuel flexibility, stability and emissions in premixed hydrogen-rich gas turbine combustion: Technology, fundamentals, and numerical simulations. *Applied Energy*, January, 154(2015), pp. 1020-1047.

Terenzi, A., 2022. *Flow analysis for hydrocarbon pipeline engineering*. 1 ed. s.l.:Gulf Professional Publishing.

Troiano, A. R., 1960. The role of Hydrogen and other interstitials in the mechanical behavior of metals. *Transactions of the American Society of Metals*, Volume 52, pp. 54-80.

Troiano, A. R., 2016. The role of hydrogen and other interstitials in the mechanical behavior of metals. *Metallography, Microstructure and Analysis,* Volume 5, pp. 557-569.

Van den Noort, A., 2017. Verkenning waterstofinfrastructuur, 9704 CA Groningen: DNV-GL.

Vitovec, F. H., 1982. Modeling of hydrogen attack of steel in relation to material and environmental variables. *Current Solutions to Hydrogen Problems in Steels*, pp. 236-241.

Vosikovsky, O., 1981. Fatigue crack closure in an X70 steel. *International Journal of Fracture*, 17(3), pp. 301-309.

Wachob, H. F. & Nelson, H., 1980. *Influence of microstructure on the fatigue crack growth of A516 in hydrogen.* s.l., Proceedings of the Third International Conference on Effect of Hydrogen on Behavior of Materials, pp. 703-711.

Walter, R. & Chandler, W., 1976. *Cyclic-load crack growth in ASME SA-105 GRADE II steel in high-pressure hydrogen at ambient temperature*. USA, s.n., pp. 273-286.

Wang, A., Van der Leun, K., Peters, D. & Buseman, M., 2020. *European Hydrogen Backbone, How a dedicated hydrogen infrastructure can be created*, Utrecht: EHB.

Wei, R. P. & Shim, G., 1983. Fracture Mechanics and Corrosion Fatigue. In: T. W. Crooker & B. N. Leis, eds. *Corrosion Fatigue, Mechanics, Metallurgy, Electrochemistry & Engineering.* s.l.:American Society for Testing and Materials, pp. 5-25.

Yoshioka, S., Kumasawa, M. & Demizu, M., 1983. Fatigue crack growth behavior in hydrogen gas environment. *Journal of the Society of Materials Science Japan*, 32(355), pp. 435-440.

Zachariah-Wolf, J., Egyedi, T. M. & Hemmes, K., 2007. From natural gas to hydrogen via the wobbe index: the role of standardized gateways in sustainable infrastructure transitions. *International Journal of Hydrogen Energy*, 32(9), pp. 1235-1245.

Zapffe, C. & Sims, c., 1941. Hydrogen Embrittlement, Internal Stress and Defects in Steel. *Transactions of American Institue of Mining and Metallurgical Engineers*, Volume 145, p. 225.

Zohuri, B., 2019. *Hydrogen Energy, Challenges and Solutions for a Cleaner Future*. Albuquerque: Springler International Publishing AG.