

FACULDADE DE ENGENHARIA DA UNIVERSIDADE DO PORTO

A study on heating requirements and economic analysis of the low-temperature methane decomposition for clean hydrogen production

Inês Moreira Marques



Master's in Mechanical Engineering

Supervisor: Professor Abel Rouboa

Second Supervisor: Professor Adélio Mendes

Company Supervisor: Engineer Francisco Neto

September 26, 2022

A study on heating requirements and economic analysis of the low-temperature methane decomposition for clean hydrogen production

Inês Moreira Marques

Master's in Mechanical Engineering

September 26, 2022

Abstract

The worsening of climate change has been the greatest challenge of the 21st century at a global scale. The current economic and energy situation, which resulted from the coronavirus pandemic and the war in Ukraine, is accelerating Europe's energy transition towards independence from fossil fuels. An investment in alternative energy sources will be the solution for Europe's energy independence and its assertion in the fight against climate change. An energy economy centred on the use of hydrogen is shaping the future of the energy sector. However, hydrogen production currently relies heavily on fossil fuels and accounts for the emission of 830 Mt of CO₂ per year. Therefore, a variety of CO₂-free hydrogen production technologies have been developed, where methane decomposition is included.

The low-temperature methane decomposition process only produces hydrogen and solid carbon as final products, with no CO₂ emissions. It operates at temperatures *ca.* 500 °C and requires less energy than water electrolysis. This work focuses on the study and analysis of the heating requirements and economic viability of this process. This is done through a material and energy balance in terms of commodities for an annual production of 350 tonnes of hydrogen, considering the use of different heating equipment. The calculations for this study were performed in Engineering Equation Solver and Aspen Plus software. An economic analysis is then performed based on CAPEX and OPEX values. The purpose is to compare the levelised cost of hydrogen production from methane decomposition, methane steam reforming and water electrolysis.

Among the heating equipment that was considered, it is estimated that the use of a hydrogen furnace is more economical than a hydrogen engine, as it requires less hydrogen for the same operating conditions. Electric heating was found to be the most economically competitive solution, especially considering lower electricity prices resulting from an increasing use of renewable energy sources. The average LCOH of methane decomposition was estimated in a value of *ca.* 2 € kg⁻¹, which is economically competitive with methane steam reforming and water electrolysis.

Keywords: hydrogen, methane decomposition, energy transition, greenhouse gas emissions.

Resumo

O agravamento das alterações climáticas tem sido o maior desafio do século XXI a uma escala global. A atual situação económica e energética, resultante da pandemia de coronavírus e da guerra na Ucrânia, está a acelerar a transição energética na Europa no sentido de esta se tornar independente de combustíveis fósseis. Um investimento em fontes de energia alternativas será a solução para a independência energética da Europa e a sua afirmação na luta contra as alterações climáticas. Uma economia energética centrada no uso de hidrogénio está a moldar o futuro do setor energético. No entanto, atualmente a produção de hidrogénio depende grandemente do uso de combustíveis fósseis e é responsável pela emissão de 830 Mt de CO₂ por ano. Desta forma, uma variedade de tecnologias de produção de hidrogénio sem emissões de CO₂ têm vindo a ser desenvolvidas, onde se inclui a decomposição do metano.

O processo de decomposição do metano a baixa temperatura apenas produz hidrogénio e carbono sólido como produtos finais, sem emissões de CO₂. Este opera a *ca.* 500 °C e necessita de menos energia do que a eletrólise da água. Este trabalho foca-se no estudo e análise das necessidades caloríficas e na viabilidade económica do processo. Isto é feito através de um balanço material e energético em termos de produtos para uma produção anual de 350 toneladas de hidrogénio, considerando o uso de diferentes tecnologias de aquecimento. Os cálculos deste estudo foram realizados nos programas informáticos Engineering Equation Solver e Aspen Plus. A análise económica é, então, realizada e baseia-se em valores de CAPEX e OPEX. O objetivo é comparar os custos nivelados da produção de hidrogénio através da decomposição do metano, da reformação do metano e da eletrólise da água.

Entre os equipamentos de aquecimento considerados, foi estimado que o uso de uma fornalha a hidrogénio seja mais económica do que um motor a hidrogénio, visto que requer um menor caudal de combustível para as mesmas condições de operação. O aquecimento elétrico foi considerado a solução mais economicamente competitiva, especialmente tendo em conta um cenário de preços de eletricidade mais baixos, resultantes de um aumento no uso de fontes renováveis de energia. O custo nivelado de hidrogénio, em média, foi estimado num valor de *ca.* 2 € kg⁻¹, que é economicamente competitivo com a reformação de metano e a eletrólise da água.

Palavras-chave: hidrogénio, decomposição do metano, transição energética, emissões de gases de efeito de estufa.

Acknowledgements

The past five years of studying Mechanical Engineering have been the toughest and the greatest that I have experienced. The writing of my master thesis is the culmination of this significant period of my life, which has proportioned great learning opportunities, not only at an academic level but also on a personal level. My acknowledgements go to the people that have accompanied my growth and that have supported me through my highs and lows in this path, but also to the ones that have helped me and believed in me throughout this last semester.

Firstly, I direct my sincere gratitude to Professor Carlos Pinho, that overflows with a great knowledge of combustion processes and has aided me in this work. Even though his academic career is coming to an end, I will forever cherish and remember all his dedication, patience and wisdom. Thank you for all the conversations we held.

Secondly, I thank Tiago Lagarteira for guiding me and believing in my work. I have learned a lot about how to take on challenges and have broaden my view in a variety of subjects, even outside the academic range. Thank you for your constructive criticism and for supporting me from day one. Vítor and Luís have also been precious elements to this work, as they have always answered to any doubts I would have. Thank you for helping me whenever I asked. Finally, I thank Paula Dias for her kindness and dedication, specially in the days prior to my presentation.

I now address my lunch friends, who have accompanied me during this last semester. Thank you for always being punctual to our lunchtime and for waiting for everyone to arrive, so that none of us would eat alone. I would also like to thank you for all the fun moments away from responsibilities and for always going along with last-minute plans, usually related to quiz nights and beer/wine.

To Carolina and Joana, I thank you for showing me that I am capable of anything as long as I work hard and believe in myself. You are a true source of inspiration and have been a great example of hard-working women that also acknowledge the importance of having fun. To David, I thank you for always being there to listen, to dance and to support me no matter what.

To Alex, for never ceasing to believe in me and for always pushing me to go beyond my limits. Even though you were far away in the past years, you are the reason I am here today. Thank you for all the love and understanding.

To my family, that has always supported me through my toughest challenges. To my brother Miguel, for teaching me to not take life so seriously and for passing on his sense of humor. To my sister Joana, for all the advises and for teaching me to be patient. To my mother Judite, that always believes in our capabilities and holds an unconditional love for her children. To my father José, for teaching me to be resilient and for enabling us to pursue our dreams.

Inês Marques

The project 112CO2 has received funding from the European Union's Horizon 2020 programme, through a FET Proactive research and innovation action under grant agreement No. 952219.



Funded by the Horizon 2020
Framework Programme of the
European Union

“Mais vale burro vivo do que sábio morto.”

Ditado Popular

Contents

1	Introduction	1
1.1	Background and presentation of the project	1
1.2	Pixel Voltaic	2
1.3	Structure	2
2	The Energy Paradigm and State of the Art of Hydrogen Production	3
2.1	Environmental Policies	3
2.2	Greenhouse Gas Emissions	4
2.3	Energy Sources	5
2.4	Energy Storage	7
2.4.1	Hydrogen Storage and Distribution Infrastructures	9
2.5	Hydrogen Economy	11
2.6	Hydrogen Production Technologies	12
2.6.1	Water Electrolysis	13
2.6.2	Methane Steam Reforming	14
2.6.3	Methane Decomposition	16
2.7	Industrial Heating Solutions	18
2.7.1	Conventional Furnaces	18
2.7.2	Electric Furnaces	20
2.7.3	Hydrogen-fueled Furnaces	20
2.7.4	Combined Heat and Power Solutions	21
2.8	Economic Analysis	24
2.9	Low-Temperature Catalytic Methane Decomposition Model	26
2.9.1	Computer Simulation	26
2.9.2	Thermodynamic Model	26
2.9.3	Combustion Models	29
3	Model and Simulation	39
3.1	Components	39
3.2	Simulation Flowsheet	40
3.2.1	Methane Decomposition Reactor	40
3.2.2	Heating Needs	41
3.3	Economic Analysis	42
4	Results and Discussion	45
4.1	Methane Decomposition Process	45
4.2	Hydrogen Spark-Ignition Engine	46
4.3	Hydrogen Furnace	49
4.4	Engine vs Furnace	50

4.5	Economic Analysis	51
4.5.1	Sensitivity Analysis	56
4.6	Hydrogen as Combustion Fuel	59
5	Conclusions and Future Work	61
5.1	Future Work	62
	References	65
A	EES models	75
A.1	Hydrogen Engine	76
A.2	Hydrogen Furnace	80
B	Combustion Properties	83

List of Figures

Figure 2.1-	Annual CO ₂ emissions from fossil fuels, by world region [7].	4
Figure 2.2-	Global CO ₂ emissions by sector, from 1990 to 2018 [7].	5
Figure 2.3-	Electricity production by source, on a global perspective, from 1985 to 2021 [8].	6
Figure 2.4-	Installed renewable power capacity in GW from 2016 to 2021 and capacity added in 2021 [13].	7
Figure 2.5-	Specific energy plotted against stored energy for hydrogen fuel cells and battery systems [19].	8
Figure 2.6-	Hydrogen phase diagram as a function of pressure and temperature. Adapted from [25].	9
Figure 2.7-	Density and temperature plot for hydrogen storage at different pressure values [19].	10
Figure 2.8-	Global hydrogen demand by sector, from 2000 to 2020 [32].	11
Figure 2.9-	Estimations of global hydrogen demand by sector from 2020 to 2050 [32].	12
Figure 2.10-	Diagram of different hydrogen production methods [39].	13
Figure 2.11-	Linde process flow sheet of steam-reforming plant. Adapted from [49]. .	15
Figure 2.12-	Typical arrangements of tubular reformer furnaces: a) bottom fired, b) top fired, c) terrace wall, d) side fired [79].	19
Figure 2.13-	Schematic diagram of Linde's top-fired furnace for steam reforming. Adapted from [49].	19
Figure 2.14-	Operating principles of resistance heating technologies: a) Heating of catalyst support (adapted from [87]); b) Heating of conducting particles in catalytic medium (adapted from [83]).	20
Figure 2.15-	Schematic of Solid Oxide Fuel Cell operating on hydrogen [93].	21
Figure 2.16-	Schematic diagram of an engine cylinder operating in a four-stroke cycle [95].	23
Figure 2.17-	Hydrogen production costs from methane steam reforming, according to different regions of the world [26].	24
Figure 2.18-	Natural gas Dutch TTF price evolution from 2018-2022 in EUR MWh ⁻¹ [101].	25
Figure 2.19-	Property method selection assistant diagram from Aspen Plus.	28
Figure 2.20-	Pressure-volume diagram of ideal constant-volume combustion [95]. . .	30
Figure 2.21-	Schematic plot of internal energy (U) or enthalpy (H) as function of temperature (T) for combustion at constant volume (U on y-axis) or at constant pressure (H on y-axis) [95].	31
Figure 2.22-	Schematic plot of internal energy (U) or enthalpy (H) as function of temperature (T) for adiabatic combustion at constant volume (U on y-axis) or at constant pressure (H on y-axis) [95].	33

Figure 2.23-	Fuel conversion efficiency as a function of compression ratio and adiabatic constant of mixture, for an ideal gas constant-volume cycle [95].	36
Figure 2.24-	Schematic plot of internal energy (U) or enthalpy (H) as function of temperature (T) for non-adiabatic combustion at constant volume (U on y-axis) or at constant pressure (H on y-axis). Adapted from [95].	37
Figure 3.1-	Aspen Plus flowsheet with methane preheating and decomposition reactor operating conditions.	42
Figure 4.1-	Aspen Plus flowsheet of methane decomposition system with heating from engine exhaust gases.	48
Figure 4.2-	Aspen Plus flowsheet of methane decomposition system with furnace integration.	50
Figure 4.3-	Sensitivity analysis on hydrogen engine. The values presented account for resulting LCOH (H2 engine opex relates to the influence of higher hydrogen fuel costs (5 € kg _{H₂} ⁻¹) in LCOH and H2 engine is subject to a variation of -30 % and +40 % in LCOH).	56
Figure 4.4-	Sensitivity analysis on hydrogen furnace. The values presented account for resulting LCOH (H2 furnace opex relates to the influence of higher hydrogen fuel costs (5 € kg _{H₂} ⁻¹) in LCOH and H2 furnace is subject to a variation of -30 % and +40 % in LCOH).	57
Figure 4.5-	Sensitivity analysis on electrical heating. The values presented account for resulting LCOH (electric opex relates to the case where electricity costs vary between 15 € MWh ⁻¹ and 70 € MWh ⁻¹ , and electric CAPEX is subject to a variation of -30 % and +60 % in CAPEX).	57
Figure 4.6-	Sensitivity analysis on electrolysis. The values presented account for resulting LCOH (electrolysis opex relates to the case where electricity costs vary between 15 € MWh ⁻¹ and 70 € MWh ⁻¹ , and electrolysis capex is subject to a variation of -30 % and +60 % in CAPEX).	58
Figure 4.7-	Sensitivity analysis on the different scenarios.	58
Figure B.1-	Combustion properties of different fuels [95].	83

List of Tables

Table 2.1-	CO ₂ emissions and energy demand for different hydrogen production processes. Adapted from [57]	16
Table 2.2-	Thermodynamic assumptions for ideal model of spark-ignition engine. Adapted from [95]	29
Table 3.1-	Model components in Aspen Plus	40
Table 3.2-	Aspen Plus Unit Operation Models of Reactors	41
Table 3.3-	Decomposition Reactor Chemical Reaction Settings	41
Table 3.4-	Operating conditions of methane decomposition reactor and of methane stream	42
Table 3.5-	Values considered for the price of utilities and commodities	43
Table 4.1-	Operating conditions of methane decomposition reactor, including heating requirements and streams	45
Table 4.2-	Methane feed stream preheating conditions	46
Table 4.3-	Reactant and product mixture composition in mass fraction in spark-ignition engine	46
Table 4.4-	Values for compression ratio and specific thermodynamic properties of reactant mixture	47
Table 4.5-	Thermodynamic properties of the working fluid in the engine operating cycle (1-4) and in the heating processes (5-7)	47
Table 4.6-	Reactant and Product gas mixtures chemical composition in mass flow rate.	48
Table 4.7-	Mechanical power and indicated fuel conversion efficiency of spark-ignition engine	48
Table 4.8-	Reactant and product mixture composition in mass fraction of combustion process in furnace	49
Table 4.9-	Thermodynamic properties of the different stages in furnace combustion process	49
Table 4.10-	Reactant and product mass flow rate in hydrogen-fuelled furnace.	49
Table 4.11-	CAPEX and OPEX values for base low-temperature methane decomposition process, in [$\text{€ kg}_{\text{H}_2}^{-1}$]	51
Table 4.12-	LCOH of methane decomposition considering the use of a hydrogen engine	52
Table 4.13-	LCOH of methane decomposition considering the use of a hydrogen furnace	53
Table 4.14-	LCOH of using electric heating (considering electricity price of 45 € MWh^{-1})	53
Table 4.15-	LCOH according to production process	54
Table 4.16-	LCOH comparison of methane decomposition (MD) process using natural gas (NG) and biomethane (Bio), and the cost reduction from selling carbon by-product (C) and from CO ₂ allowances (CO ₂). Values presented in [$\text{€ kg}_{\text{H}_2}^{-1}$]	54

Nomenclature

Abbreviations

BC Bottom-center

CAPEX Capital Expenditures

CCUS Carbon Capture, Utilisation and Storage

CHP Combined Heat and Power

CMD Catalytic Methane Decomposition

CPA Cubic-Plus-Association

EES Engineering Equation Solver

EU European Union

GERG2008 Groupe Européen de Recherches Gazières 2008

GHG Greenhouse Gases

ICE Internal Combustion Engine

LCOH Levelised Cost of Hydrogen

Li-ion Lithium-ion

LK-PLOCK Lee-Kesler-Plocker

MIBEL Mercado Ibérico de Electricidade (Iberian ELectricty Market)

MSR Methane Steam Reforming

OPEX Operating Expenses

P2G Power-to-Gas

P2H Power-to-Heat

P2L Power-to-Liquid

PC-SAFT Perturbed-Chain Statistical Association Fluid Theory

PENG-ROB Peng-Robinson

SOFC Solid Oxide Fuel Cell

SRK Soave-Redlich-Kwong

TC Top-center

USD US Dollar

WGS Water Gas Shift

Symbols

$\tilde{\Delta h}_f^o$ Enthalpy of formation at reference conditions [J mol^{-1}]

ΔH^o Enthalpy of reaction at reference conditions [J mol^{-1}]

γ Adiabatic constant

ρ Molar density [mol m^{-3}]

$\tilde{R}$ Molar gas constant [$\text{J K}^{-1} \text{mol}^{-1}$]

$\dot{m}$ Mass flowrate [kg s^{-1}]

$\dot{Q}$ Calorific power [W]

$\dot{W}_{c,i}$ Indicated power [W]

$\dot{W}_c$ Compression power [W]

$\dot{W}_e$ Expansion power [W]

$\eta_{f,i}$ Indicated fuel conversion efficiency

a, b Constants

c_p Specific heat at constant pressure [$\text{J kg}^{-1} \text{K}^{-1}$]

c_v Specific heat at constant volume [$\text{J kg}^{-1} \text{K}^{-1}$]

h Specific enthalpy [J kg^{-1}]

K_P Equilibrium constant

M Molar mass [kg kmol^{-1}]

m Mass [kg]

n Number of moles [mol]

P Pressure [Pa]

p Partial pressure [Pa]

q_{HVp} Specific heat of reaction for the complete combustion of unit mass of fuel at constant pressure [J kg^{-1}]

q_{HVv} Specific heat of reaction for the complete combustion of unit mass of fuel at constant volume [J kg^{-1}]

r_c	Compression ratio
R	Universal gas constant [$\text{J mol}^{-1} \text{K}^{-1}$]
s	Specific entropy [$\text{J K}^{-1} \text{kg}^{-1}$]
T	Temperature [$^{\circ}\text{C}$]
u	Specific internal energy [J kg^{-1}]
V_c	Clearance volume [m^3]
v	Specific volume [$\text{m}^3 \text{kg}^{-1}$]
$W_{c,i}$	Indicated work per cycle [J]
W_c	Compression Work [J]
W_e	Expansion Work [J]
Z	Compressibility Factor

Chapter 1

Introduction

1.1 Background and presentation of the project

The current economic and energy situation, which resulted from the coronavirus pandemic and the war in Ukraine, made clear the need for getting access to more reliable sources of energy. The development of technologies that take advantage of renewable and endogenous sources gives Europe a twofold benefit: resilience against political instabilities in energy supplying countries and contribute for the urgent energy decarbonisation. The urgency to decrease and end the use of fossil fuels points out to the production and use of green-hydrogen as it is presently the best choice when large amounts of energy are considered. Even though hydrogen is emerging as a clean alternative to fossil fuels, its main source still relies heavily on fossil fuels, such as natural gas (methane steam reforming) and coal (coal gasification), which account presently for the emission of 830 Mt of CO₂ per year.

A variety of CO₂-free hydrogen production technologies have been developed through the past decades, namely water electrolysis and methane steam reforming with carbon capture, utilisation and storage (CCUS). However, these technologies are still too expensive or in an early stage of commercialization, which prevents its swift industrial implementation.

A novel process based on methane decomposition is currently being developed and is expected to tackle these economic and environmental constraints. It operates at low temperature, *ca.* 500 °C, and requires less energy than methane pyrolysis or water electrolysis. It only produces hydrogen and solid carbon as final products, with no CO₂ emissions and is estimated to be economically competitive with electrolysis and methane steam reforming with carbon capture.

The purpose of this work is to study and analyse the viability of the low-temperature catalytic methane decomposition process in relation to its energy requirements and economic feasibility. A material and energy balance is made in terms of commodities for an annual production of 350 tonnes of hydrogen, considering the use of different heating equipment. This work is developed under the guidance of University of Porto and Pixel Voltaic in the context of a Master thesis in Mechanical Engineering.

1.2 Pixel Voltaic

The low-temperature methane decomposition process that is addressed in this work is currently being developed under an European project named 112CO₂. This project is funded by the Horizon 2020 Framework Programme of the European Union and aims to provide a feasible and fast-deploying solution for a rapid and economically sustainable transition in the energy sector.

In this consortium are included the University of Porto, coordinator of the project and responsible for the reactor design and optimization, and Pixel Voltaic responsible for system integration, demonstration and commercial exploitation. Pixel Voltaic is a spin-off company from the University of Porto that was established in 2018 and operates in the field of energy related technologies. Additionally, there are seven project partners that comprise the 112CO₂ consortium and the project is organised in seven work packages, each under the remit of each partner.

1.3 Structure

The document is organised in five chapters and is complemented with additional information in appendixes at the end of the document. This first chapter presents an introduction and general insight into the work developed during this Master thesis.

The second chapter presents the current environmental and energy crisis, which have urged Europe to act upon its energy independence while fighting against climate change. To address part of these issues, a plan is being developed to transition the European energy paradigm into a hydrogen-focused economy. Therefore, it is presented the estimated increase in hydrogen demand and the current level of CO₂ emissions related to hydrogen production. Following this, it is reviewed the state of the art of hydrogen production technologies and heating solutions. Then, it is described the theoretical modelling, in a thermodynamic point of view, of the alternative heating technologies considered for the low-temperature catalytic methane decomposition.

The third chapter is dedicated to the mathematical modelling of the heating processes and to introduce the base parameters for the economic analysis. The fourth chapter provides the results for commodities requirements and associated economical expenditures. It is also conducted a technical discussion on the studied model and an analysis of the economic viability of this process. The final chapter presents the summarised conclusions of the project and provides insight into the future work that may be developed following this study.

Chapter 2

The Energy Paradigm and State of the Art of Hydrogen Production

2.1 Environmental Policies

The Paris agreement has been the global promoter for limiting temperature increase beyond 1.5 - 2 °C until 2050, compared to pre-industrial levels [1]. The European Union (EU) has set its own targets to accelerate and lead the way to climate neutrality through the European Green Deal. It aims to reduce greenhouse gases by at least 40 % towards 50 - 55 % until 2030 in comparison to the values of 1990, and to eliminate greenhouse gases (GHG) net emissions by 2050 [2]. It is also intended to increase renewable sources by 32 % in energy consumption and improve energy efficiency by 32.5 % [3].

The EU energy paradigm is also under extensive reformulation due to the war in Ukraine [4]. The REPower EU program was created to further speed up the process of the energy transition and to establish a plan to diversify the supply of energy sources to EU, and thus decrease energy dependence from Russia [4]. It is important to acknowledge that in 2020 the Russian Federation hold *ca.* 20 % of the global proved reserves of natural gas, and represented *ca.* 40 % of the total natural gas imports by pipeline in Europe [5]. This means that a great effort is being made to reform the energy system in due course, in an environmental and economically sustainable way, while also ensuring security and stability of supply.

2.2 Greenhouse Gas Emissions

It is important to analyse the data related to GHG emissions to further understand the scale and environmental impact of the energy transition. GHG account for all man-made gas emissions that contribute to global warming, namely carbon dioxide, methane, nitrogen trifluoride, nitrous oxide, sulfur hexafluoride, hydrofluorocarbons, perfluorinated compounds and fluorinated gases [6]. In the EU, it is observed that CO₂ emissions, in kilotonnes of CO₂ equivalent per gas type, are far greater than the remaining gases, accounting for 80 % of the total [6]. This data is crucial to set a focus point on the strategies to be put into place in order to prevent temperature increase in the near future, starting with phasing out CO₂ emissions.

Even though EU's efforts are making progress towards reducing emissions and reaching the values settled in the Paris Agreement, there are still increasing CO₂ emissions in a global perspective. According to Figure 2.1 Asian countries represent the larger and fastest growing portion of CO₂ emissions worldwide [7] which will compromise the 2050 targets.

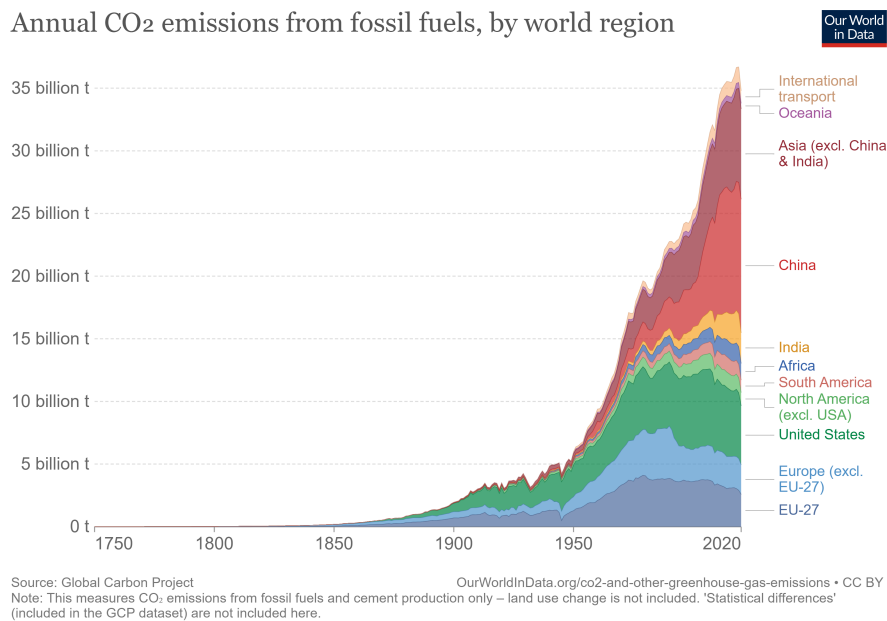


Figure 2.1 – Annual CO₂ emissions from fossil fuels, by world region [7].

With a focus set on reducing CO₂ emissions, it is now important to identify the sectors that contribute most to these levels. In 2018 more than 36 Gt of CO₂ were emitted globally, with electricity and heat production representing more than 15 Gt of CO₂ emissions, around 42 % of the total [7], followed by the transport sector with more than 8 Gt, with a share around 22 % of the total [7]. In Figure 2.2 it is depicted the evolution of worldwide CO₂ emissions by sector, from 1990 to 2018.

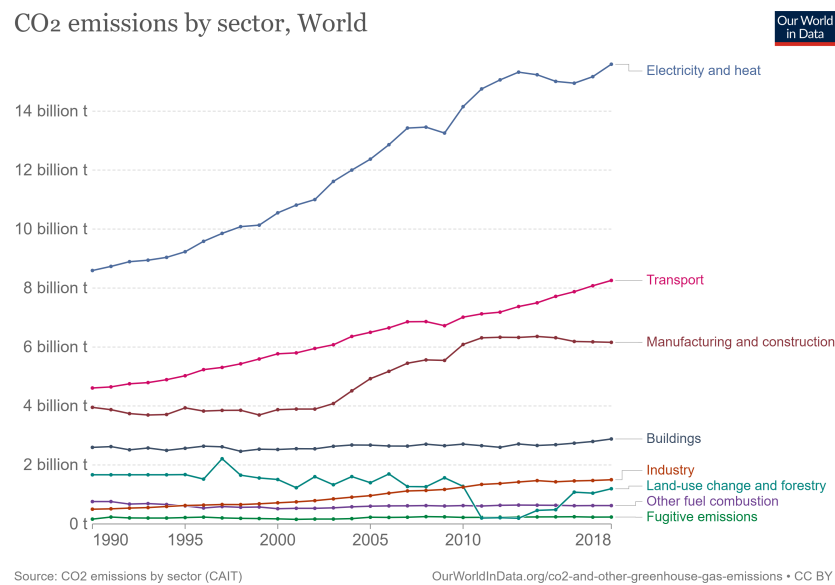


Figure 2.2 – Global CO₂ emissions by sector, from 1990 to 2018 [7].

2.3 Energy Sources

It is urgent to act upon curtailing CO₂ emissions across all sectors, but specially in electricity, heat production and transportation. Therefore, there has been an effort to increase the share of low-carbon energy sources in the energy mix [8]. Historically, there are two main energy sources that are considered carbon-free: renewables (including hydroelectricity) and nuclear power [8]. Since the 1970's, nuclear fission and hydroelectricity have been the two main sources of low-carbon electricity generation, together representing a share of around 35% of the total worldwide electricity production in 1985 [8, 9]. In Figure 2.3 it is shown the global electricity production by energy source in percentage, from 1985 to 2021 [8].

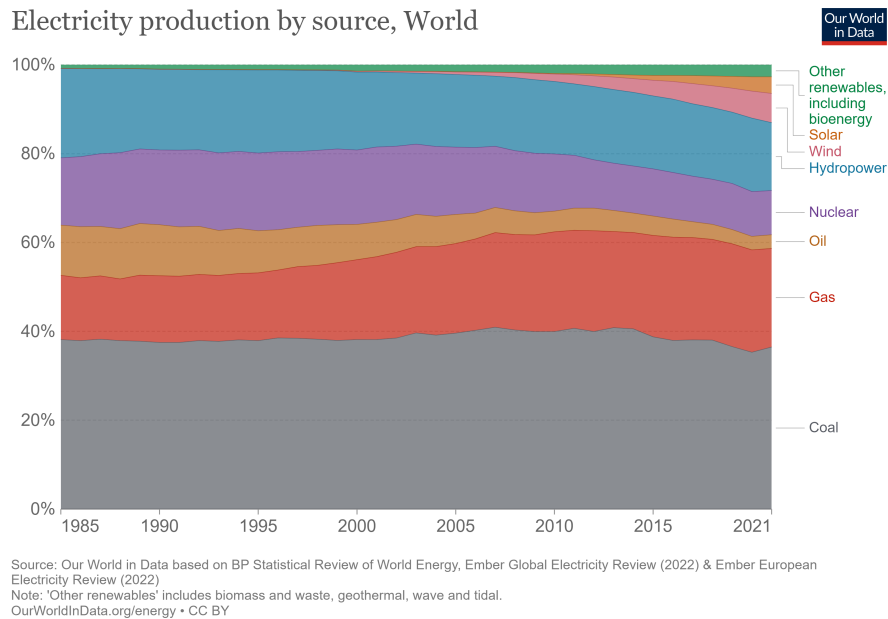


Figure 2.3 – Electricity production by source, on a global perspective, from 1985 to 2021 [8].

However, due to previous nuclear accidents at Three Mile Island, Chernobyl and Fukushima Daiichi there has been a rise in public concern regarding the safety and environmental benignity of nuclear power. Alongside radiation-related concerns, there has also been an increase in construction costs and lead time for nuclear reactors that has led to a lack of interest in this industry [9]. Nevertheless, the current political scenario in the EU is bringing up discussion on whether EU countries should invest, or reinvest, in nuclear power to respond to the current energy crisis and increase its energy independence from Russia [10]. It is a controversial topic of discussion as there are still doubts regarding the benefits of using nuclear energy and the European Commission has yet included a nuclear strategy to prepare for Russian supply cuts [11].

Renewable energy source technologies have been emerging as a solution to counteract climate change, while also providing for remote, broad and secured energy supply [12]. In the past decade, there has been an increase in installed renewable power capacity mainly due to technological improvements and affordable solutions. These were made possible by an increase in support policies and growing competition towards these technologies [12].

In Figure 2.4 there is a graphical representation of the growing renewable power capacity installed from 2016 to 2021 [13]. It is visible that hydropower technologies are reaching a saturation point and have been stabilising its installed capacity over the years. On the other hand, there has been a visible increase in solar and wind conversion technologies, where both energy sources have almost doubled their installed capacities from 2016 to 2021 (Solar: *ca.* 0.3 to 0.9 TW ; Wind: *ca.* 0.5 to 0.8 TW) [13]. In 2021 a total of *ca.* 3 TW of renewable installed capacity was reached at a global scale, with hydropower still representing the renewable source with largest generation capacity, 40 %, followed by solar, 28 % and wind, 27 % [13].

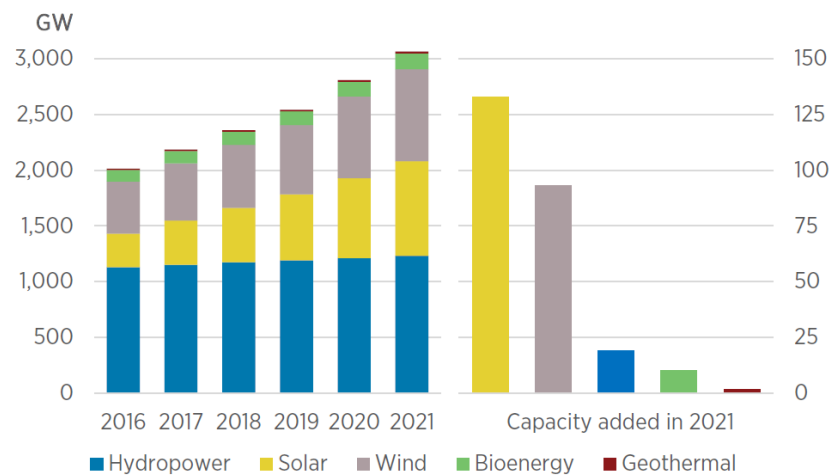


Figure 2.4 – Installed renewable power capacity in GW from 2016 to 2021 and capacity added in 2021 [13].

2.4 Energy Storage

Despite the increase in investment in renewable technologies, there are still some obstacles regarding resource variability in space and time. Another surging problem that has been holding off its growth is their low integration in heating and cooling systems and transport applications [12]. In order to overcome these drawbacks, energy storage systems will take on a major role on the energy transition and help lead the way to decarbonisation [14].

A variety of storage systems will be required to both integrate a higher share of renewable energy into the energy-mix and simultaneously satisfy the needs of the entire energy sector. Each energy field demands for specific performance characteristics, such as storage capacity, charging and discharge rates, charge/discharge cycles and, ultimately, costs [14–16]. This becomes clear when considering the full range of energy-demanding services and devices, - from mobile gadgets, to light-weight transportation, to industrial scale heating and heavy-duty transportation - as they operate on very different conditions [12, 14, 17].

In recent years, there has been an exponential growth in number of filled patents relating electricity storage, in comparison to other technological areas, mainly related to Lithium-ion (Li-ion) batteries [15]. Accordingly, Li-ion batteries have been dominating the market for portable electronic devices and light-weight electric vehicles, and have greatly improved their performance and cost in the past decade [15, 18]. Despite that, this technology is still far from reaching performance and cost targets for large-scale and stationary storage solutions [15, 18].

To fulfill this gap, hydrogen fuel cells have been emerging as a viable solution [19]. These electrochemical devices operate on hydrogen and oxygen to produce heat and electrical energy [19]. This technology has great environmental advantages in comparison to Li-ion batteries and is more appropriate for high energy requirements[20], as Figure 2.5 shows.

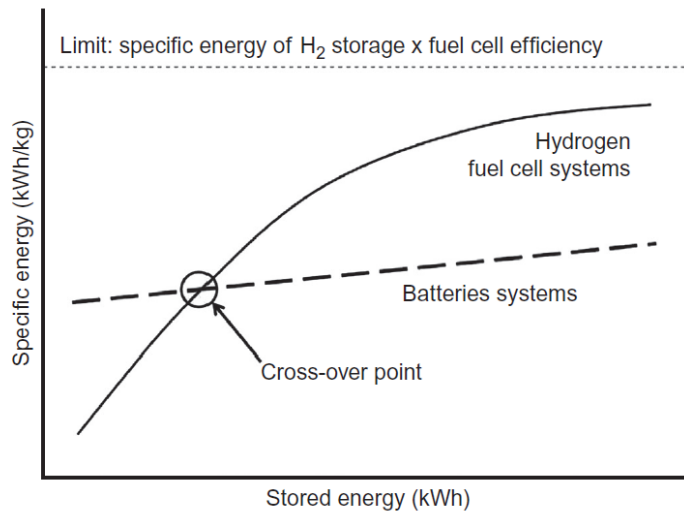


Figure 2.5 – Specific energy plotted against stored energy for hydrogen fuel cells and battery systems [19].

The use of fuel cells for high energy-demanding applications is mostly due to the fact that H_2 has the highest gravimetric energy density, around 39.4 kWh/kg, than any other fuel or battery device [19, 20]. Moreover, fuel cells are capable of working continuously whilst there is fuel being provided to the equipment, in contrast to conventional battery systems that have to be recharged from time to time and eventually wear out and need to be replaced [20].

However, fuel cells are not yet competitive in terms of cost and storage efficiency [20]. The latter is due to the very low volumetric density of hydrogen in comparison to other fossil fuels and the necessity to first process the gas to enable its storage [20]. Together with its low energy density by volume it requires the use of larger storage devices in comparison to conventional batteries [19].

In this view, sector coupling is becoming an important piece in the energy panorama [17]. This concept basically integrates power and end-use sectors in a co-dependent system by the indirect electrification of end-use applications such as transportation and heating [17, 21]. This is achieved with the use of excess electricity, usually generated from renewables at periods of surplus and at lower cost, to produce hydrogen, via electrolysis, or synthetic methane, via Sabatier reaction [17, 22]. Hydrogen and synthetic methane can now be used as energy vectors in a variety of pathways, such as Power-to-Gas (P2G), Power-to-Liquids (P2L) and Power-to-Heat (P2H) [17], also collectively known as Power-to-X [17, 22].

Power-to-Gas is one of the great focus points in the energy transition strategy due to the low-emission hydrogen production process from electricity [22]. The main goal is to distribute and store hydrogen feedstock in the same infrastructures that are currently used for natural gas, as this would allow for a rapid dissemination of hydrogen in industrial processes and heavy-duty transportation, that are still deeply associated with fossil fuels and significant levels of CO_2 emissions [21]. Accordingly, a plan is already being designed for a pan-European hydrogen distribution network for the upcoming 10 to 20 years [23], in an effort to accelerate the energy transition into a hydrogen economy [23, 24]. In fact, hydrogen is already being traded in dedicated pipelines and

trucks, on a local level, and it is predicted that these infrastructures will evolve from industrial clusters and local facilities into a vast pipeline network [24].

2.4.1 Hydrogen Storage and Distribution Infrastructures

Hydrogen has a density of 0.09 kg m^{-3} at ambient conditions ($P=1 \text{ bar}$ and $T=25^\circ\text{C}$), which is very low compared to the density of natural gas, 0.71 kg m^{-3} . This poses a great challenge to hydrogen storage because it is necessary to increase its density in order to reduce storage volume [25]. There are several ways to attain this, either by compressing hydrogen, decreasing temperature below the critical point or by interaction with another material, that allows reducing repulsion of hydrogen molecules [25]. In fact, this molecular behaviour determines the critical point, that in the case of hydrogen is located at -240.15°C (33 K) [25]. In Figure 2.6 is presented the phase diagram of hydrogen.

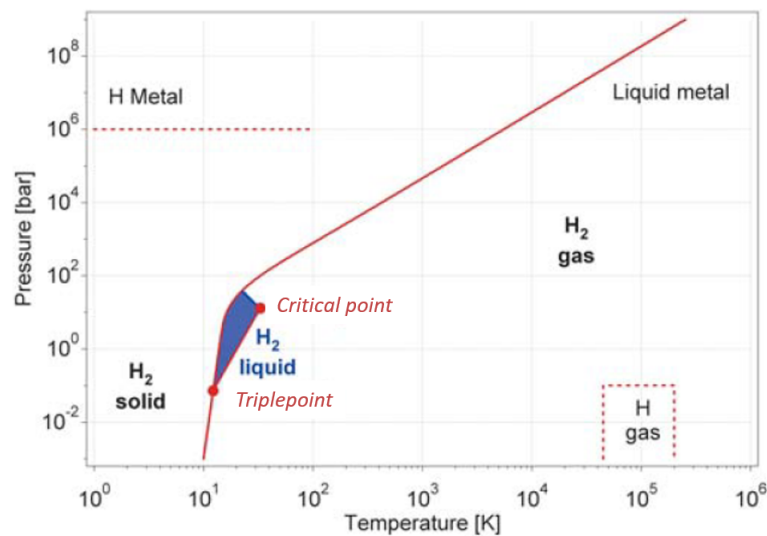


Figure 2.6 – Hydrogen phase diagram as a function of pressure and temperature. Adapted from [25].

In essence, H_2 can physically be stored inside a vessel by increasing its density through pressure or temperature change [19]. In Figure 2.7 there is a graphical representation of H_2 density values according to temperature and typical storage pressure values [19]. The common temperature conditions in these storage systems are designated cryo in the -273.15°C to -123.15°C (0 to 150 K) range, cold in the -123.15°C to -43.15°C (150 to 230 K) range and near ambient, above -43.15°C (230 K). Pressure values go from 0.5 MPa (5 bar) up to 70 MPa (700 bar) [19].

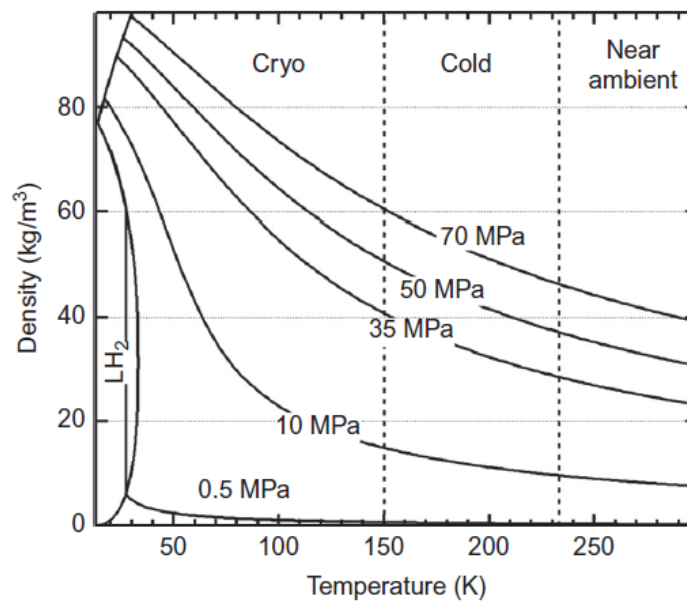


Figure 2.7 – Density and temperature plot for hydrogen storage at different pressure values [19].

Hydrogen storage solutions are defined by volume capacity, storage life, discharge speed, pressure conditions, and geological availability [26]. There are several ways to store hydrogen, so the configuration chosen must meet the requirements of each application [26]. Usually, vessels and small-scale reservoirs are used for low amounts of hydrogen that require reduced storage time or for mobile applications, whereas large-scale reservoirs are used for industrial-scale needs and long term storage [26].

In order to accomplish the hydrogen economy concept there is still one important factor to take into account: hydrogen distribution. There are already hydrogen pipeline infrastructures privately owned by chemical industry campuses, where they practise the called captive hydrogen production and use [27]. Local generation and consumption may be possible in a few situations, but to attain a global scale of hydrogen integration in the energy sector, it is crucial to extensively distribute hydrogen in a secure, economical and reliable manner to places far from production [28]. This includes all forms of distribution, from ground transportation to overseas [24].

An immediate solution to help accelerate energy transition is to integrate hydrogen into the existing natural gas network [29]. Naturally, some problems arise with this method that are currently being studied [29]. On one hand, there is pipeline embrittlement due to contact of steel with hydrogen that may lead to fissures and leakage [29]. However, this problem mainly occurs on steel pipes, particularly high quality steels. It is not as relevant in Europe as most grid networks are made from polyethylene, where this is not an issue. In the particular case of Portugal, the most used materials are polyethylene and API X57 steel, which do not fall within specifications of high quality steel [29]. Nevertheless, volume concentrations of blended hydrogen up to 20 % do not represent considerable threat to material embrittlement [29].

On the other hand, the existence of a gas mixture in the supply grid may be problematic to industrial consumers, specially in the chemical sector, where variations in the blended contents

may affect quality of production [29]. Additionally, most domestic and commercial equipment are not ready to operate with blended H_2 in natural gas supply [29]. Another matter that may arise with widespread network systems is difference in threshold levels of H_2 between borders [28].

In sum, there are several strategies to be put into place that, together, will allow to reach the stipulated targets, and there is an increasing consensus that a thorough reformulation of energy systems is needed and that sector coupling will likely be the answer [17]. In fact, energy requirements can be better satisfied, secured, cleaner and cheaper by improving efficiency of equipment, diversifying energetic sources and combining the different energetic infrastructures in an integrated way [30].

2.5 Hydrogen Economy

On the course of the past years, hydrogen has predominantly been used as feedstock in the sectors of iron and steel, refineries and chemical industries. Since the year 2000 demand for hydrogen has been increasing, reaching about 90 Mt of global hydrogen demand in 2020 [31, 32]. In order to further comprehend the proportion of hydrogen demand in each sector, Figure 2.8 shows that, in 2020, about 40 Mt of H_2 were used as feedstock for refinery processes, 45 Mt for the chemical industry (where 34 Mt are dedicated to ammonia production), and 5 Mt for iron and steel, mainly for the making of direct reduced iron (DRI) [32].

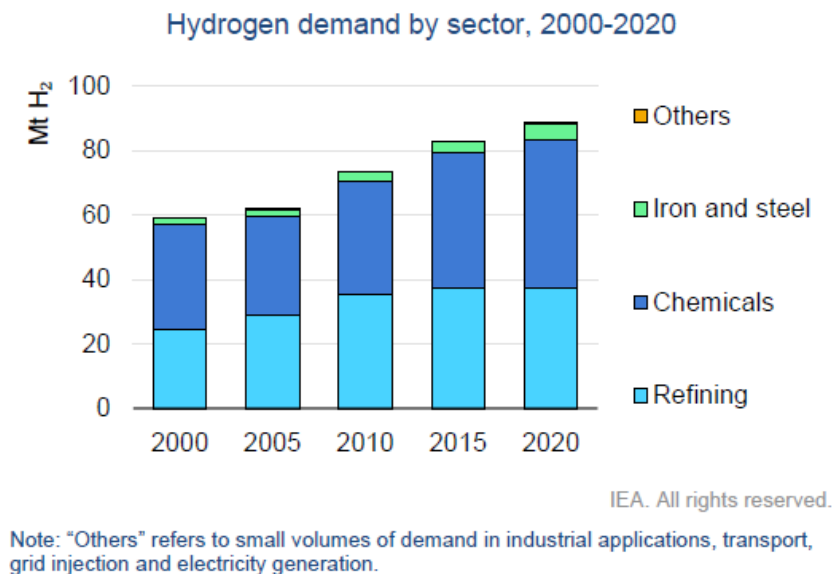


Figure 2.8 – Global hydrogen demand by sector, from 2000 to 2020 [32].

In recent years, H_2 has become increasingly popular as an energy carrier due to its versatility and emission-free potential [33, 34]. Therefore, there is a global focus on materializing the hydrogen economy concept [35] that includes heavily integrating H_2 in the current energy system [32]. However, current political measures are far from reaching the aimed H_2 utilisation requirements

that enable attaining the net zero emission targets by 2030 and beyond [32]. Despite this, it is predicted that H_2 demand will greatly increase and production levels will have to keep up with this growth. Figure 2.9 depicts expected H_2 demand in the near decades according to the announced pledges scenario and the net-zero emissions scenario by 2050.

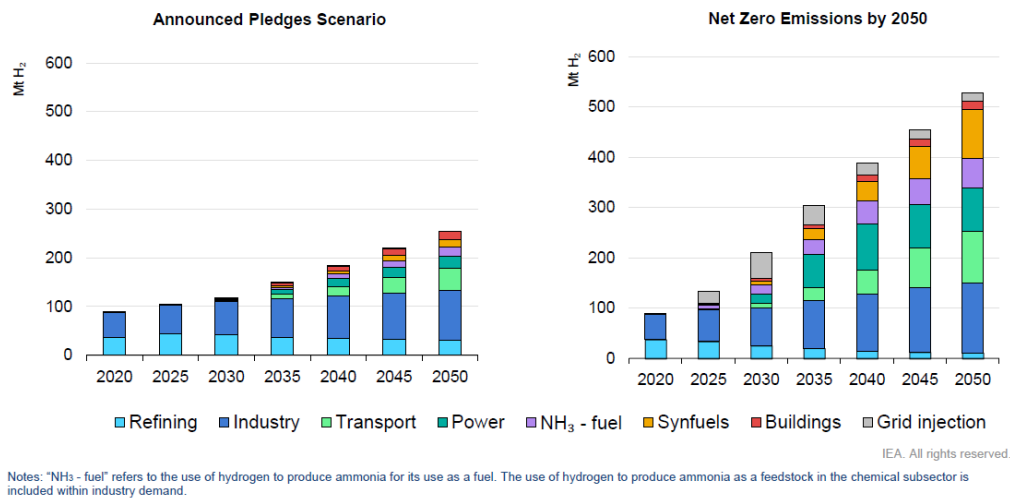


Figure 2.9 – Estimations of global hydrogen demand by sector from 2020 to 2050 [32].

2.6 Hydrogen Production Technologies

Hydrogen usually appears associated in compounds, such as water, biomass and hydrocarbons, and not in its pure form [34]. This means that it is not a primary source of energy, so in order to get pure hydrogen, it is required to extract it using processes that are currently associated with high energy demand and greenhouse gas emissions [36].

Hydrogen production currently depends greatly on fossil fuels with the aggravating factor that the technologies used account for the emission of 830 Mt CO₂ per year, which is comparable to the CO₂ emissions of the United Kingdom and Indonesia together [26]. The purpose is to find and develop hydrogen production technologies that emit less amounts of greenhouse gases [26]. Recently, efforts have been made to develop downstream treatments that result in carbon capture and storage (CCS) [37] or carbon capture and valorization (CCV) [38], but these processes result in an increase in cost of approximately 1 USD kg⁻¹ of H₂ [27]. They also allow to perpetuate the use of fossil fuels, instead of setting the focus on reducing its use [37].

There are two main sources of compounds that are transformed to get hydrogen and other products - fossil fuels and renewables [39] - and the nature of the process can either be thermal, electrolytic or biological [40]. Figure 2.10 depicts a flowchart with different methods of hydrogen production. The diversity of sources and processes to produce hydrogen can be seen as an advantage - it does not rely only on one method - however, it can be seen as a difficulty regarding the convergence to a single solution on the development of low-carbon hydrogen technologies [40].

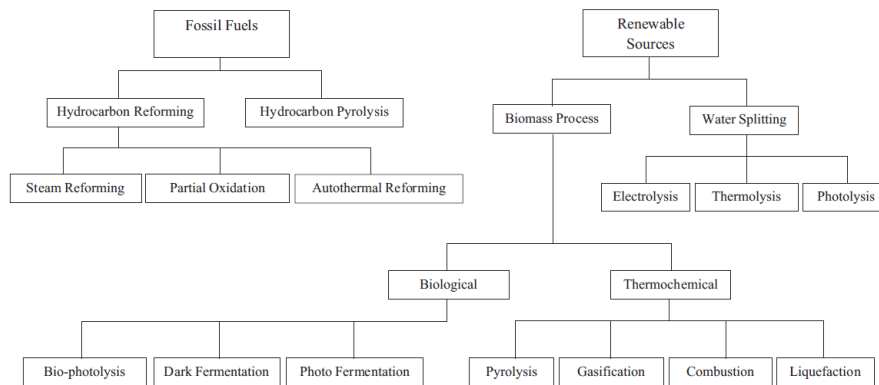
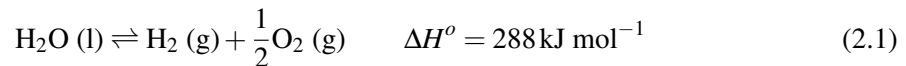


Figure 2.10 – Diagram of different hydrogen production methods [39].

2.6.1 Water Electrolysis

Renewable sources are currently the preferred route for hydrogen production due to their environmental advantages [41]. Considering the specific case of water electrolysis (equation 2.1) [42], it is an emission-free process that is very endothermic [39] and can be powered by electricity generated from renewable sources such as wind, solar and hydro [42, 43]. This is commonly categorized as green hydrogen production and is becoming the focus of many energy transition plans [26, 43]. Despite its increasing interest, this method has several drawbacks related to the low efficiency of conversion of water and required investment costs that impede it from competing with conventional technologies [41].



There is a wide variety of devices for water electrolysis, with three predominant technologies at current use and development [26]. Alkaline electrolyzers are matured and commercialised technologies that have been used since the 1920's mainly in countries with great hydropower resources, but since the 1970's have been decommissioned due to the rise of natural gas and its use in methane steam reforming [26]. These devices operate on cheaper materials hence being economically competitive in comparison to other electrolysis technologies [26].

Then are proton exchange membrane (PEM) electrolyzers that operate on pure water and are able to produce hydrogen at high pressure levels (30 to 60 bar, in comparison to 1-30 bar for alkaline electrolyzers) [26]. They have been developed in the 1960's to overcome operational issues of alkaline electrolyzers, but these devices lack economic competitiveness due to the use of expensive materials and have shorter lifetime in comparison to alkaline electrolyzers [26].

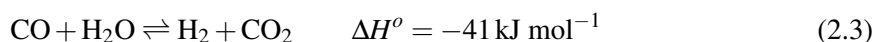
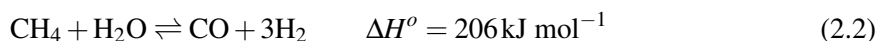
Solid oxide electrolysis cells (SOEC) are the least developed technologies as they have not yet been commercialised [26]. These devices use materials, such as ceramics for the electrolyte, that cheaper than PEM materials. SOEC operate at high temperatures (650 -1000 °C) and have high electrical efficiency. A great advantage of these devices is that they can operate reversibly - as a fuel cell - which is a topic that is addressed further ahead in this chapter. Nevertheless, the high

operating temperatures, in both cases, portray a big challenge in their development due to material degradation [26].

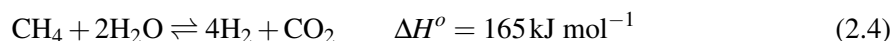
Natural gas is the current primary source of methane that is widely used for hydrogen production, accounting for approximately three quarters of the annual global dedicated hydrogen production [26]. The interest in the use of methane is based on several aspects, namely the high H/C ratio compared to other hydrocarbons [34] and great availability [41]. Methane molecules are very stable due to their strong C-H bond [34, 44], therefore its thermal decomposition only takes place at very high temperatures, above 1200 °C [44].

2.6.2 Methane Steam Reforming

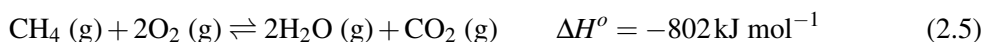
Methane steam reforming (MSR) [45] is the global predominant technology for hydrogen production [32] at an industrial scale for chemicals and refineries (for feedstock and energy) [26]. It is one of the cheapest methods to produce hydrogen reaching values around 0.9 to 1.8 USD kg⁻¹ H₂ (without carbon taxes) [27]. This process is based on the endothermic reaction of methane and water vapour to generate hydrogen and carbon monoxide, also called syngas (equation 2.2) [45]. It is followed by the water gas shift (WGS) reaction that further transforms the carbon monoxide products into hydrogen and carbon dioxide (equation 2.3) [46].



The overall reaction equation of this process is obtained by the sum of the previous:



This process occurs at temperatures around 450 - 850 °C and pressures of 3 to 25 bar [34], which demands for heavy energy supply to the process. The heating requirements are usually fulfilled by the combustion of part of the methane that is fed-in (equation 2.5) and from the use of exothermal heat from WGS [47, 48]. The combustion of methane means that not only the main reaction is responsible for the emission of CO₂, but also the means used to keep the MSR operating.



There are several companies that provide steam-reforming solutions, such as Linde [49] and Mahler AGS [50] and in Figure 2.11 there is a schematic representation of the steam-reforming plant developed by Linde. There are several steps involved in this hydrogen production process that are generally present in any steam reforming unit, and that are described below, with the figure serving as an example.

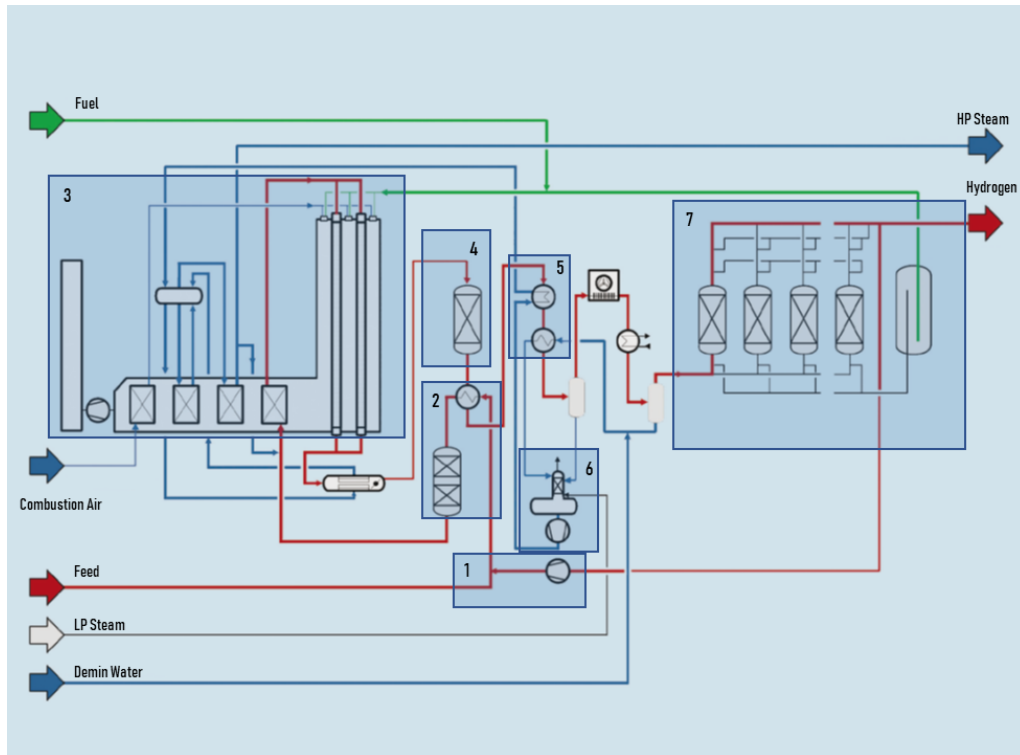


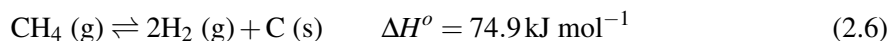
Figure 2.11 – Linde process flow sheet of steam-reforming plant. Adapted from [49].

Conventional MSR starts with the processing of CH_4 and H_2O to reach the operating conditions of the reformer [51]. Water is pumped (box 6), then is pre-heated (box 5) in a heat exchanger using energy from the exothermal WGS reaction (box 4) and then it evaporates into steam with the heat provided by flue gas from CH_4 combustion (box 3) [51]. Simultaneously, CH_4 is also compressed (box 1), pre-treated (box 2) and mixed with the water steam to make the feed stream, which is then heated to 900°C before entering the reformer (box 3) [51]. The reformer operates equivalently to a shell and tube reactor, where catalysts are placed inside the tubes, where the reforming reactions occur [34] and on the outside there is, usually, the combustion of CH_4 to provide heat to the reaction (equation 2.5) [52]. This is one of the most important and expensive equipment used in a steam reforming plant [53], and are usually known as steam-methane reformers or reformer furnaces [50, 53].

From there, the gas stream goes to a second reactor where the WGS (box 4) occurs at temperatures around 200°C [51]. At this point, the gas stream is predominantly composed of H_2 and is cooled down to 40°C in order to condensate the remaining water (boxes 2 and 5) [51]. Then, there is only a H_2 and CO_2 current that needs to be purified, usually in a Pressure Swing Adsorption (PSA) unit [49] (box 7) and CO_2 is captured to be further utilised or stored [51].

2.6.3 Methane Decomposition

Methane thermal decomposition [54], also known as methane pyrolysis, is the endothermic process for H₂ production where methane molecules are thermally dissociated into gaseous hydrogen and solid carbon (equation 2.6) at very high temperatures (above 1200 °C) [34, 44]. This method produces only pure hydrogen and carbon that are easily separated, thus eliminating conventional purification steps [44] and CO₂ sequestration requirements [55, 56].



In Table 2.1 there is summarised information regarding the three main processes addressed above, regarding chemical reactions, CO₂ emissions and energy demand by kg of H₂ produced. Even though methane decomposition occurs at high temperatures, it requires around one fifth of the energy necessary for the electrolysis process [57]. Nonetheless, it is possible to lower the temperature at which this reaction occurs through the use of catalysts [44].

Table 2.1 – CO₂ emissions and energy demand for different hydrogen production processes. Adapted from [57]

Process	Chemical Equation	CO ₂ Emissions (kg CO ₂ kg ⁻¹ H ₂)	Energy Demand* (kJ mol ⁻¹ H ₂)
Methane Reforming	$\text{CH}_4 + 2\text{H}_2\text{O} \rightleftharpoons 4\text{H}_2 + \text{CO}_2$	8.85	41.3
Water Electrolysis	$\text{H}_2\text{O} \rightleftharpoons \text{H}_2 + 1/2\text{O}_2$	0	288
Methane Decomposition	$\text{CH}_4 \rightleftharpoons 2\text{H}_2 + \text{C}$	0	37.5

*Minimal energy demand, according to standard enthalpy values.

Catalysts are chemical agents that promote and accelerate reactions between gases [58]. In this case, solid carbon or metal catalysts are used to reduce the temperature of methane decomposition to values around 500 - 600 °C, thus decreasing the energy required [44]. This process is called low-temperature catalytic methane decomposition (CMD).

The formation of solid carbon particles usually occurs in the surface of the catalyst which can be problematic because it starts covering the catalyst and blocks its contact with methane, deactivating the occurring reaction [41]. The carbon structures that are produced vary according to the catalyst and operating conditions [59]. Once this difficulty is surpassed, carbon can be used to either be stored or commercialised [59], even to locations far from production sight due to its easy handling and transportation.

Catalytic methane decomposition takes place inside a reactor and there is a wide variety of configurations available [59, 60]. The most used and studied reactors for CMD are fixed-bed reactor [61], fluidized bed reactor [62], plasma reactor [63], molten-metal reactor [64] and membrane reactor [65]. The choice of reactor is extremely important and can be decisive in the viability of the process at an industrial level [59, 60].

Fixed-bed reactors are usually associated with the use of carbon catalysts, but have also been studied with Iron, nickel and noble metal catalysts [60]. These were the first reactors to be used in

studies about the influence of experimental variables on methane conversion [60], however, complications due to clogging and pressure increase were the main reasons for the reducing interest in this design over time [59].

Fluidized bed reactors came up as a viable alternative, as they allow for a continuous removal of the solid carbon that is formed around the catalyst [66] and therefore widen the lifespan of the catalyst [59]. This also means that the reactor can work continuously in time, being a huge industrial advantage in comparison to the fixed-bed reactors where production has to be halted in order to remove the solid carbon particles [59]. Further research has been made regarding the use of a two-stage fluidized-bed reactor with the purpose of reaching an equilibrium between carbon production and carbon diffusion rates [67].

Plasma reactors have a wide variety of configurations that allow to obtain different degrees of methane conversion, operational costs and energy efficiency on hydrogen production [63]. They are based on the same operating principle - the use of an electric field to heat up electrons and generate reactive species that will trigger the chemical reactions, thus eliminating the need to heat the whole volume of gas [63]. However, energy efficiency [68] and generation of heavier hydrocarbons [63] are great drawbacks, comparing to other solutions, and represent the main challenges of this technology [59].

Molten metal reactors contain a catalytic molten metal bath that provides the heat transport requirements for CMD and allows for solid carbon removal [64]. In this case, carbon particles can either leave the reactor with exhaust gases and be collected in filters or be directly removed from the surface of the bath by density difference, similar to what happens with slag in iron foundry [64]. Nevertheless, this configuration requires high operating temperatures, similar to values of non-catalytic methane decomposition which leads to high energy demand and reactor wear [59].

Membrane reactors configuration is usually based on one of the previous reactor designs with the addition of a membrane that serves as a filter [59]. In essence, the membrane is made to only let through certain components of a gas mixture, so there are two streams with distinct chemical composition on each side of the membrane: the permeate stream with the permeable elements and the retentate stream with the remaining components [69]. In this case, this membrane is only permeable to hydrogen, resulting in a concentrated stream of this gas in the permeate side [65]. The main advantage of this configuration is that the chemical reaction is not thermodynamically limited [65], only depending on inlet concentration, resulting in higher conversion rates than of chemical equilibrium [70]. In the case of hydrogen permeability the preferred base element for membrane composition is palladium [71].

Methane Decomposition in the Industry

At present time, there are a few companies dedicated to the process of methane pyrolysis, where BASF Group, Hazer Group and Sakowin Green Energy are included. The BASF Group methane pyrolysis process occurs in a moving bed reactor with carbon particles and operates at temperatures around 1200-1400 °C [72]. The main goal is to obtain these high temperatures via an electric heater that is being developed by the company, using renewable source energy [72, 73]. However, without

the use of renewable sources, the electric heater does not portray a sustainable solution due to the high electricity demand of the process.

The Hazer Group is also developing a pilot plant for methane decomposition based on a system of fluidized-bed reactors with iron ore catalysts [74]. This process operates at around 900 °C, and may be powered with the combustion of natural gas mixed with part of the hydrogen that is produced or by electrical systems using renewable energy sources [75]. In order to obtain a fully sustainable system, it also intends to use bio-methane as feedstock of the process [75, 76].

Sakowin Green Energy are developing a process of low-temperature microwave plasma decomposition of methane, also called Plasmalysis, at atmospheric pressure [77]. This process offers the same environmental advantages as low-temperature catalytic decomposition of methane, but it still poses some challenges on understanding the carbon structures that are formed and if they will assure economical viability of the process [78].

2.7 Industrial Heating Solutions

The heating requirements of the process of methane decomposition will be a focus point on this work, and are very important to take into account either from an energetic and economical point of view, but also concerning GHG emissions. On a first approach, the heating technologies used for methane steam reforming were analysed in order to find the most suitable and economical solutions that are already present in the industry.

2.7.1 Conventional Furnaces

In typical industrial steam reforming units, a furnace is used to continuously provide calorific power to the reforming reaction [51, 79]. The steam methane reformer is composed of tubes filled with catalytic material that are placed inside the furnace [80]. Then, a combustion process outside the tubes triggers heat transfer phenomena to the catalytic material. According to the location of the burners relatively to the catalytic tubes, there are different arrangements of furnaces in the industry, that will provide different heat flux profiles and temperature control to the catalytic material [79]. In Figure 2.12 are presented four main varieties of furnaces, according to the mentioned arrangements [79].

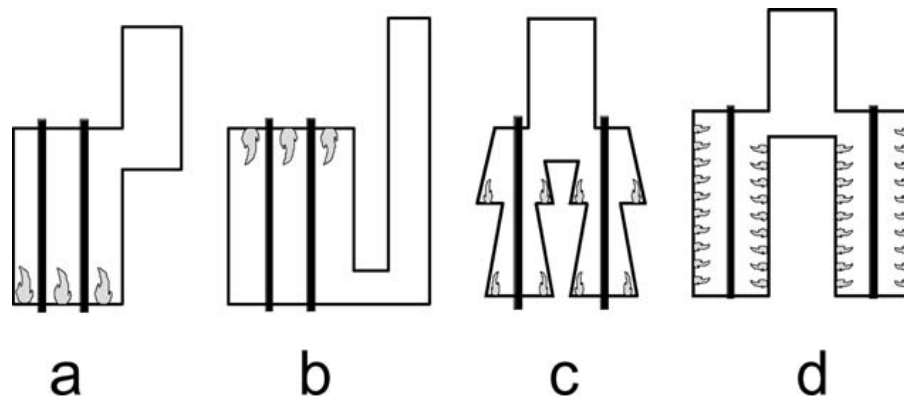


Figure 2.12 – Typical arrangements of tubular reformer furnaces: a) bottom fired, b) top fired, c) terrace wall, d) side fired [79].

Among these, one of the most common configurations used is the top-fired furnace, as it provides propitious heat transfer conditions to the SMR process. In Figure 2.13 is a schematic version of Linde's steam reforming unit that consists of a top-fired furnace. The heat from combustion is provided to the tubes, where the reaction occurs and flue gas is also used for pre-heating requirements.

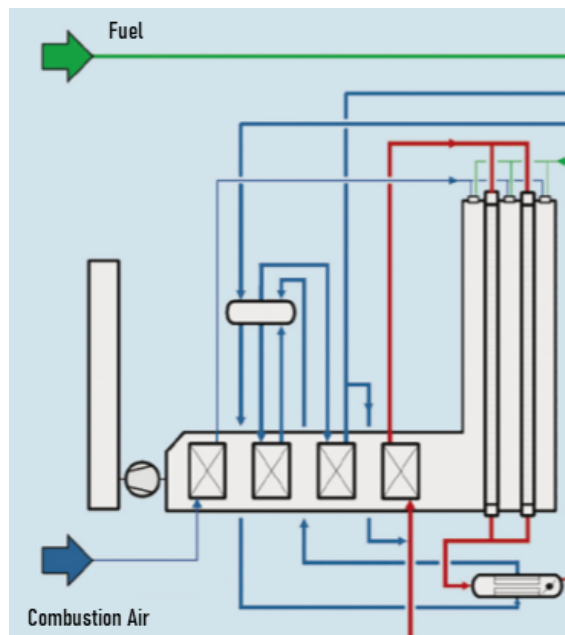


Figure 2.13 – Schematic diagram of Linde's top-fired furnace for steam reforming. Adapted from [49].

However, these reformer furnaces usually operate on natural gas, which means that the main source of calorific power to this process comes from the combustion of hydrocarbons and leads to CO₂ emissions. Even though there are carbon capture technologies that reduce the environmental impact of the process, there are still associated techno-economical difficulties that have been addressed previously in this chapter [51, 81].

2.7.2 Electric Furnaces

An alternative to combustion furnaces is achieved by electrifying the heating process of the reformer. At present time, there is a wide range of electrified reformer technologies that have been developed, from joule heating [82, 83], to plasma reactors [63, 78], to solar reactors [84], and induction heating [85]. These provide several advantages to the reforming process, regarding temperature control, methane conversion levels and energy efficiency [82, 86], and are environmentally benign solutions if renewable source electricity is used as power source [86, 87].

Electrically-assisted heating of reforming reactors is a technology that was first approached in the 1980's [82]. It was only a decade later that resistance heating was used directly on the catalyst support and gave way to the technologies that are being developed today [82, 86]. Resistance heating consists on providing a direct electrical current through a conductive material [83]. This material can act simultaneously as heating and catalytic agent [83], through the use of metallic particles as conductors [83, 88], or it can simply operate as heating equipment and be used as catalyst support [86, 87]. Figure 2.14 shows the different methods of using joule heating that are described.

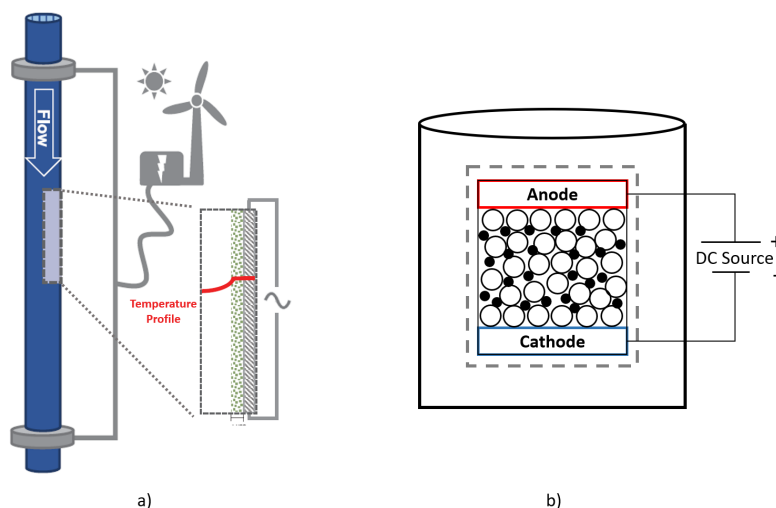


Figure 2.14 – Operating principles of resistance heating technologies: a) Heating of catalyst support (adapted from [87]); b) Heating of conducting particles in catalytic medium (adapted from [83]).

2.7.3 Hydrogen-fueled Furnaces

Another path to decarbonise the power supply can be with the use of hydrogen as combustion feedstock to the furnace. Similar to the reforming furnace, there can be hydrogen furnaces that provide the calorific needs to the process without CO_x emissions. If the combustion of hydrogen uses air as oxidising agent there will still be NO_x emissions, but on this work the focus will be set on the combustion of hydrogen with pure oxygen, which only generates water as flue product.

There has been an increase in use and development of hydrogen combustion technologies in a wide range of industries around the globe. One example of that is the Nero combustion furnace developed by Noritake Co., Limited, in partnership with the Tokyo Gas Group for the production

of electrode materials for li-ion batteries [89]. Another example is from Hydrogen Technologies Inc., that have also patented a novel method for hydrogen combustion with pure oxygen in vacuum conditions, with a technology that operates similar to a conventional steam boiler, called Dynamic Combustion Chamber TM[90].

2.7.4 Combined Heat and Power Solutions

An interesting solution would be one that involves a cogeneration system, also known as combined heat and power (CHP), that consists on the simultaneous generation of heat and electrical power [91]. Local generation of electrical power in CHP systems, in contrast to centralised production, has proven to increase overall energy efficiency by 50 % [92]. There are a variety of different devices that can be used for CHP, but in this work there are only considered two of them: internal combustion engine and solid oxide fuel cell.

Solid Oxide Fuel Cells (SOFC) are high-temperature devices that convert chemical energy directly into electrical energy and heat [93]. There is a wide variety of fuel cells, according to structural and operating conditions, but these devices are equally advantageous in comparison to conventional power generation units - high efficiency, no moving parts, low noise and near-zero or even zero emissions [94]. These devices can operate on a basic cell structure composed of an electrolyte, a cathode, an anode and interconnection wires [93]. In the case of SOFC, a ceramic material is used for the solid oxide electrolyte, and this component allows for the conduction of oxygen ions from the cathode to the anode, where it reacts with the fuel provided (e.g., hydrogen, natural gas, ...) and releases 2 electrons that flow through an external circuit [93]. In Figure 2.15 is depicted a schematic of a fuel cell, where the aforementioned components and chemical interactions are present.

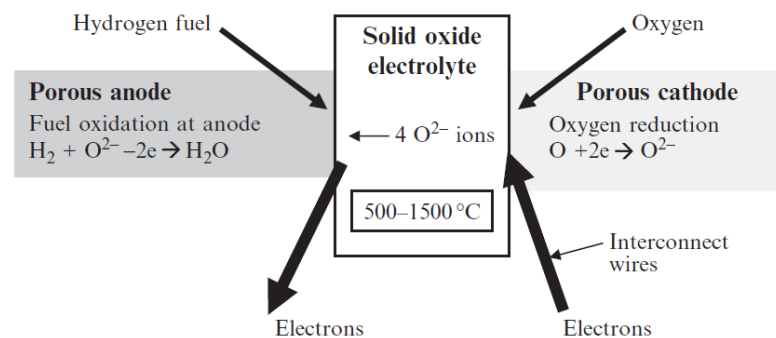
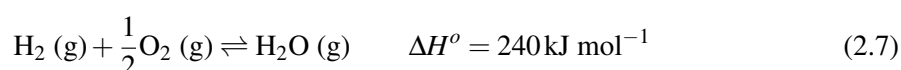


Figure 2.15 – Schematic of Solid Oxide Fuel Cell operating on hydrogen [93].

Internal combustion engines (ICE) are mechanical devices that use the chemical energy of a fuel to produce mechanical power [95]. There are two types of engines that are generally used: spark-ignition engines and compression-ignition engines [95]. Spark-ignition engines are commonly used with gasoline, but can also be used with other fuels such as hydrogen [95, 96]. In internal combustion engines it is the reactant and product mixtures that interact with the mechanical parts to produce work, and are considered the working fluids of the operating cycle [95]. The

use of hydrogen as fuel and oxygen as oxidising agent results in a zero-emission solution that only produces water vapour. If the high-temperature exhaust water is used for heating requirements, the engine can be considered a combined heat and power solution with no CO_x nor NO_x emissions.

Hydrogen combustion engines have been studied on a laboratory scale since the 19th century and have taken up special interest in the 1980's when concerns regarding automotive emissions and fuel shortage rose up [97, 98]. Hydrogen combustion with a pure stream of oxygen produces only water steam as flue gas, according to equation 2.7. If hydrogen is used to feed an internal combustion engine, it is possible to obtain calorific power from the exhaust flue gas and the mechanical power output that can be converted into electricity. This way, the heating requirements can be fulfilled and electrical power is generated in a sustainable way.



A spark-ignition engine, also known as a four-stroke engine [95], is considered for the internal combustion of hydrogen and it is based on the Otto cycle [96, 97]. This operating cycle comprises four main stages [95]:

1. Intake stroke - piston travels from top-dead-center (TC) crank position to bottom-dead-center (BC) crank position to let the fuel-air mixture into the cylinder.
2. Compression stroke - piston travels from BC to TC and the mixture is compressed at clearance volume, V_c . As the piston is reaching TC, a spark triggers combustion and there is a rapid increase in pressure inside the cylinder.
3. Expansion stroke - the pressurized and high-temperature combustion gases move the piston downwards, from TC to BC, and promote crank rotation. The exhaust valve opens as the piston is reaching BC.
4. Exhaust stroke - the remaining gases exit the cylinder due to pressure difference and to the movement of the piston from BC to TC. The inlet valve opens as piston reaches TC and the exhaust valve closes just as the piston starts descending to BC. The cycle is repeated.

These steps are depicted in Figure 2.16, including piston positions at each step and corresponding volume inside the cylinder.

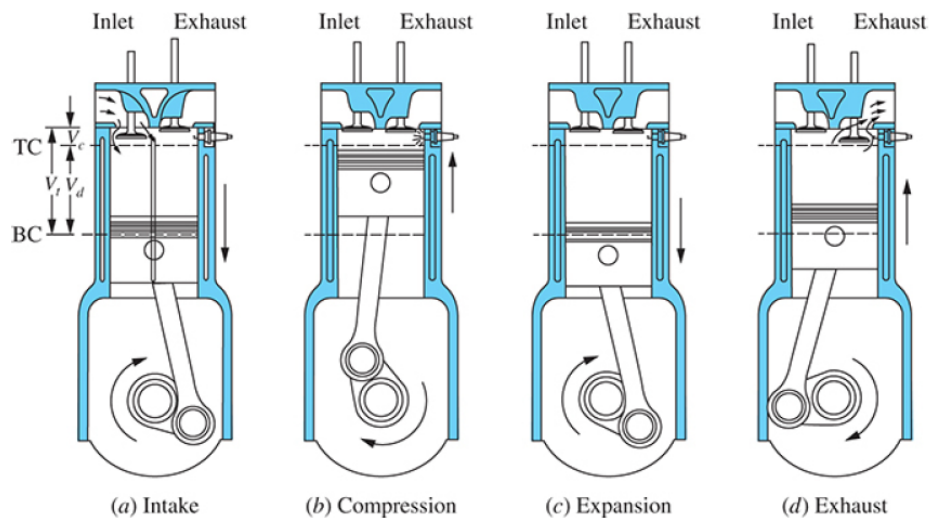


Figure 2.16 – Schematic diagram of an engine cylinder operating in a four-stroke cycle [95].

A theoretical approach is made in order to comprehend and analyse the thermodynamic properties of the working fluids at each stage of the internal combustion engine [95]. There are more complex models that are based on the theoretical cycle and were developed into more realistic approaches, but will not be addressed in this study. At this point, it is important to emphasize that the engine is not a closed system in a thermodynamic point of view, therefore the working fluid does not complete a full thermodynamic cycle [95]. Instead, it goes through a complete operating cycle, defined by a sequence of processes that comprehend the different thermodynamic states of the working fluid [95]. It consists of an ideal engine cycle that also considers the ideal gas model, composing the ideal gas standard cycles.

2.8 Economic Analysis

The commercial viability of a process not only depends on its technical feasibility, but also on the economic viability. The investment attractiveness is measured by predicting product sales, its selling price and a variety of costs that may arise in the time being [99]. In relation to forecasting it is important to acknowledge its variance over time and the uncertainties related to the data available [99]. In manufacturing processes, the cost of a product is greatly determined by engineering decisions, at approximately 85 %. The acquisition of equipment, also known as capital expenditure, is one of the first steps into making the manufacturing process economically viable [99].

Capital expenditures (CAPEX) are heavy purchases made by companies that are meant to be in use for a long period of time, and is usually related to physical assets [100]. Operating expenses (OPEX) are daily outlays that are necessary for the continuity of operational activities, such as labor-related expenses and rent [100].

Hydrogen production costs are greatly influenced by a diversity of economic factors, with CAPEX and feedstock being the predominant price-determining elements [26]. In this view, besides demonstrating the technical feasibility of the low-temperature catalytic methane decomposition process, it is also pivotal to compare the expected costs of the developing project to conventional technologies already in use.

Production costs of these different technologies also vary according to geographical location, due to availability of resources [26, 36] and to funding capacity for hydrogen-related projects [36]. Figure 2.17 depicts the variation in hydrogen production costs, from natural gas, in different regions of the globe [26].

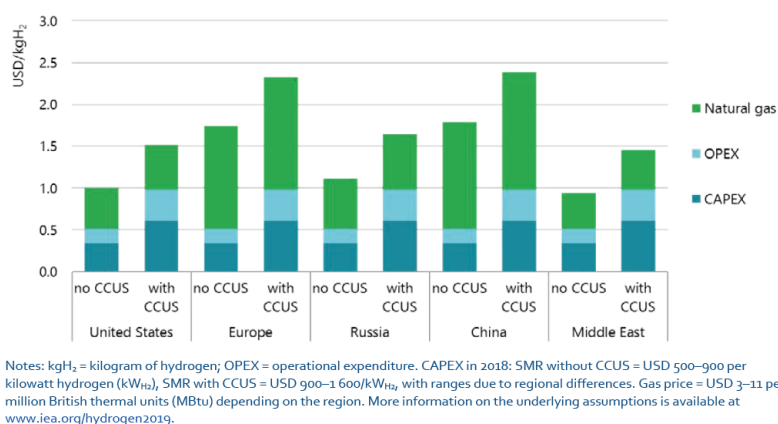


Figure 2.17 – Hydrogen production costs from methane steam reforming, according to different regions of the world [26].

In Figure 2.17 it is visible that the least expensive hydrogen production from natural gas is in regions such as the United States, Russia and Middle East. In fact, these correspond to the regions with greatest amount of proved natural gas reserves in the world, with the Middle East accounting for 40 %, the Commonwealth of Independent States (where Russia is included) accounting for 30 % and North America with 8 % [5].

The current economic and political situation surrounding the war in Ukraine has set off the prices of natural gas in the EU, as *ca.* 40 % of the natural gas imported by pipeline is from Russia [5]. Figure 2.18 shows the price evolution of natural gas from Dutch TTF throughout the past 5 years, and it is clear the influence of war on the price escalation and instability.



Figure 2.18 – Natural gas Dutch TTF price evolution from 2018-2022 in EUR MWh⁻¹ [101].

The current shortage in semiconductors is also a source of increasing expenses related to electric equipment, as this sector has suffered a huge setback with COVID-19 pandemic and is currently being affected by the war in Ukraine [102, 103].

It is then clear the importance of adequately analysing hydrogen production costs as processes rely greatly on these materials. Therefore, the reference costs are based on estimations previous to 2020, where price values were more stable. Additionally, a sensitivity analysis is performed for each process to visualise how these prices can vary with uncertainty level and to verify what may be the most economically competitive solutions.

2.9 Low-Temperature Catalytic Methane Decomposition Model

The present work aims to provide a techno-economic analysis of the low-temperature catalytic methane decomposition, based on numerical models of heating processes. A focus was set on studying heating equipment that can simultaneously be able to fulfill the energy requirements, be environmentally sustainable and be economically competitive in comparison to other technologies.

The low-temperature catalytic methane decomposition process developed by Pixel Voltaic occurs in a membrane reactor at temperatures from 500 to 650 °C. According to what was previously mentioned, the decomposition of methane originates gaseous hydrogen and solid carbon. In order to avoid carbon accumulation on the surface of the catalyst, a small portion of the produced hydrogen stream is also fed to the reactor, which bonds back to the carbon molecules forming methane particles, in a step called regeneration. The main purpose of this developing technology is to reach permanent state hydrogen production, with cyclic regeneration and efficient methane conversion for a long period of time [104].

This is a promising hydrogen production technology as it competes with methane steam reforming for being CO_x-free of emissions, with water electrolysis due to the lower CAPEX of the methane decomposition process and lower energy requirements, and with thermal methane decomposition processes due to lower operating temperatures. All these characteristics lead to a cost-competitive and clean technology that may take part in the energy transition towards the hydrogen economy.

2.9.1 Computer Simulation

The computer simulation software Aspen Plus V12 was used to develop a simplified model of an industrial system for the low-temperature catalytic methane decomposition process. This has proven to be a very useful tool for providing estimates on energy needs, associated costs and environmental impacts, without requiring large industrial facilities nor manpower. Therefore, the use of simulation software not only has great economic advantages, but is also a time-saving alternative to physically develop wide and complex industrial processes. These capabilities, from a business point of view, translate to the ability of providing a competitive solution in the market, which may determine the success and prosperity of one's company [105].

The Engineering Equation Solver (EES) software was also used on the development of the model, as an auxiliary tool for energy requirement calculations and to determine thermodynamic properties of the fluids involved in different stages of the processes. Even though major improvements have been made in the field of numerical simulation throughout the years, one must not forget of the technical and non-technical issues that may arise in the real world.

2.9.2 Thermodynamic Model

The selection of the thermodynamic model is a very important topic as it defines the equations of state that correlate Pressure (P), Volume (V) and Temperature (T). These properties are dependent

on the intermolecular interactions between the substances involved [106] and become very relevant when dealing with the processing of different chemical substances in order to achieve an accurate numerical model of the process.

The ideal gas equation of state is the fundamental and simplest form of representing gases thermodynamic behaviour [107]. A gas can be considered ideal when it is adequate to assume that its molecules have an infinite distance between them, so that intermolecular forces are approximately zero [108], which usually occurs at lower values of pressure [108].

The compressibility factor, Z (equation 2.8) [106], is used to compare actual fluid behaviour with ideal gas assumption - when the value of Z is one, the fluid behaves as an ideal gas, and as this value turns non-unitary, the fluid behaviour deviates from the ideal gas hypothesis [106]. This deviation is due to the presence of attractive and repulsive forces that occur due to molecular interaction, as stated by the van der Waals Equation (equation 2.9) [106]. Accordingly, in the presence of real gases, molecular interactions are non-negligible and an adequate model must be applied. Note that most equations of state currently used were developed based on van der Waals's model.

$$Z = \frac{PV}{RT} \quad (2.8)$$

$$Z = 1 + Z^{rep} + Z^{att} = 1 + \frac{b\rho}{1 - b\rho} + \frac{a\rho}{RT} \quad (2.9)$$

Aspen Plus software provides a methods selection assistant that eases this specification step. This tool is quite helpful as it sets oriented questions based on the components or process types that are involved in the simulation model. Then, it provides a number of suggested property methods according to the input given. In this view, one can either give input according to the components or the process type, as each path of questions will provide a variety of suggestions that may be adequate to the model. This tool is used to find the most suitable method considering the gaseous substances that are dealt with in this simulation model, namely methane and hydrogen.

In Figure 2.19 are represented two diagrams that display the logical path that the methods selection assistant enables via the specification according to component and process type involved in the simulation model. On one hand, there is methane that is a hydrocarbon component and the mixtures that are dealt with in the system do not contain petroleum assays nor pseudocomponents. Therefore, there are three suggested methods by the assistant tool: Peng-Robinson (PENG-ROB), Soave-Redlich-Kwong (SRK) and Lee-Kesler-Plocker (LK-PLOCK). On the other hand, the system of methane decomposition falls under the gas processing type and that specification provides three more methods to be considered: Perturbed-Chain Statistical Association Fluid Theory (PC-SAFT), Cubic-Plus-Association (CPA) and Groupe Européen de Recherches Gazières 2008 (GERG2008).

According to the information provided by Aspen Plus, PENG-ROB property method is adequate for nonpolar mixtures including hydrocarbons and light gases (carbon dioxide and hydrogen,

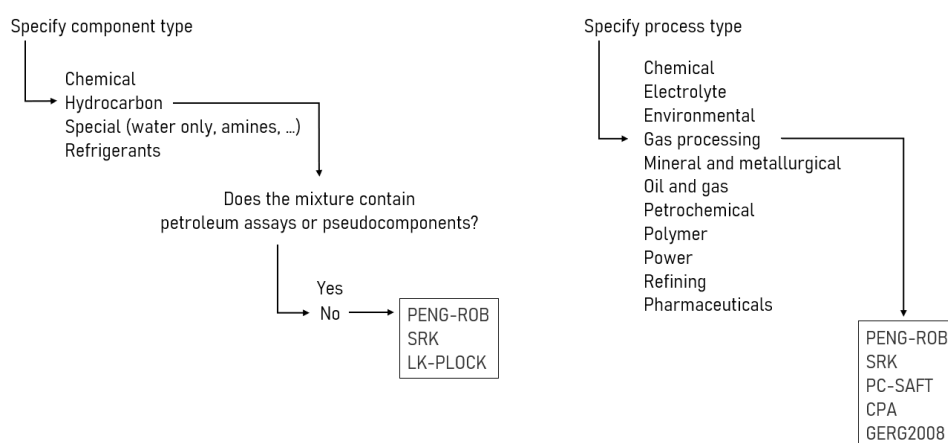


Figure 2.19 – Property method selection assistant diagram from Aspen Plus.

for example). It is also proper for high temperature and pressure regions, usually applied in hydrocarbon processing systems. The SRK characteristics are very similar to PENG-ROB, except it also enables accurate calculations for water-hydrocarbon immiscibility, which is not addressed in this process. About the LK-PLOCK, it is suggested that the PENG-ROB and SRK methods are more suitable for gas-processing systems, which is the case, so this method is not considered.

The use of PC-SAFT is adequate in the range from small to large molecules, which includes normal fluids, water, alcohols, and ketones, polymers and copolymers and their mixtures. Then, CPA provides a model that can be written on the basis of two terms - one representing the physical forces (attractive and repulsive) and another the association forces (hydrogen bonding), and CPA was developed as a combination of the SRK equation of state with an association term similar to that present in PC-SAFT.

Finally, the GERG2008 model is an extension of the previous GERG2004 model, used for natural gas and mixtures consisting of natural gas components. It has been adopted as the standard equation of state for natural gas applications, namely processing, transportation and storage, and is suitable for modelling thermodynamic properties and phase equilibrium of a total amount of 21 natural gas components and their mixtures, including methane, hydrogen, oxygen and water. Recent studies show that the GERG2008 equation of state may be applied for hydrogen-containing mixtures at temperatures from 722 to 930 K and pressures from 15.4 to 30.3 MPa [109]. However, the maximum range of temperature and pressure covered by the software is $60\text{ K} < T < 700\text{ K}$ and $P < 70\text{ MPa}$ which is outside the temperature operating conditions considered for this simulation model (around 723 K and higher). Although GERG2008 is the model that would be more suitable for this application, specially considering a scenario where natural gas is the feed stream of the system, it is best to opt for a model that can operate over the entire interval of temperature and pressure conditions.

2.9.3 Combustion Models

There are two heating technologies that are thermodynamically modelled in order to study the commodities required in this process - the hydrogen internal combustion engine and the hydrogen furnace.

The working fluids in each combustion device (furnace and internal combustion engine) will go through different operating conditions and hence different thermodynamic stages. While in the combustion furnace the only step that is considered is the hydrogen combustion itself, in the internal combustion engine the working fluids go under different thermodynamic stages throughout the operating cycle, as mentioned in the previous subsection and displayed in Figure 2.16.

Alongside the existence of an operating cycle, there is also another aspect that distinguishes both devices: the combustion process. The combustion inside the furnace occurs at constant pressure and the combustion in the spark-ignition engine occurs at constant volume [95]. This is very important to take into consideration as this affects the amount of energy that is involved in each process.

Spark-Ignition Engine

The different steps of the spark-ignition engine have been previously described and it is important to supplement that with the thermodynamic assumptions that are made in order to develop the mathematical and purely theoretical model of the engine's operating conditions.

Figure 2.20 represents a pressure-volume diagram concerning an ideal cycle under unthrottled operation with constant-volume combustion. The numbers shown in the figure are ordered in an equal manner to the cycle that was presented in Figure 2.16, and are now described in Table 2.2 according to the thermodynamic considerations that are made for each step of the cycle.

Table 2.2 – Thermodynamic assumptions for ideal model of spark-ignition engine. Adapted from [95]

Process	Assumptions
Compression (1-2)	1. Adiabatic and reversible (isentropic)
Combustion (2-3)	1. Adiabatic 2. Combustion at constant volume
Expansion (3-4)	1. Adiabatic and reversible (isentropic)
Exhaust (4-5-6) and Intake (6-7-1)	1. Adiabatic 2. Valve events occur at top- and bottom-center 3. No change in cylinder volume as pressure differences across open valves drop to zero 4. Inlet and exhaust pressures constant 5. Velocity effects negligible

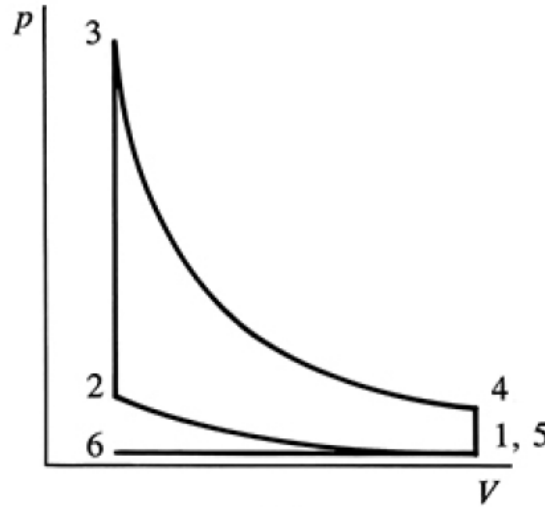


Figure 2.20 – Pressure-volume diagram of ideal constant-volume combustion [95].

In addition to the thermodynamic assumptions, the main operating parameters, defined by thermodynamics, are fundamental for the modelling of the spark-ignition engine. Starting from the compression stroke, and using the notation from Figure 2.20, the compression ratio, r_c is defined in equation 2.10 [95].

$$\frac{v_1}{v_2} = r_c \quad (2.10)$$

In spark-ignition engines the value of r_c is typically in the range of 8 to 12 [95]. This means, that the maximum cylinder volume is around 8 to 12 times higher than the minimum volume [95] (this is visible in Figure 2.16 in a) and b)).

Considering the process is adiabatic and reversible, comes equation 2.11 [95].

$$s_2 = s_1 \quad (2.11)$$

The compression work W_c is then given by equation 2.12 [95].

$$W_c = U_1 - U_2 = m(u_1 - u_2) \quad (2.12)$$

If the working fluid is considered to be an ideal gas, then equation 2.12 can be simplified into equation 2.13 [95].

$$W_c = mc_v(T_1 - T_2) \quad (2.13)$$

It follows the combustion process, that occurs at constant volume [95],

$$v_3 = v_2 \quad (2.14)$$

It is also considered to be adiabatic, therefore, from the first law of thermodynamics [95],

$${}_2Q_3 - {}_2W_3 = (U_3 - U_2) \quad (2.15)$$

$$U_3 - U_2 = 0 \quad (2.16)$$

However, the values of internal energy that are available in databases, are usually relative to the species at reference temperature, T_0 [95]. To facilitate the understanding of the following equations, the subscript 2 is replaced by R (reactants) and subscript 3 is replaced by P (products). The variation in internal energy from the combustion process is then given by

$$U_P(T_0) - U_R(T_0) = (\Delta U)_{V,T_0} \quad (2.17)$$

and considering equation 2.16,

$$[U_P(T) - U_P(T_0)] - [U_R(T) - U_R(T_0)] = -(\Delta U)_{V,T} \quad (2.18)$$

where T is the temperature at which the combustion reaction occurs, in this case, the adiabatic flame temperature [95]. It is relevant to point out that, during combustion, the internal energy of the system decreases an amount of $(\Delta U)_{V,T_0}$, as the reaction is exothermic [95]. At a given combustion temperature, T , $(\Delta U)_{V,T}$ is the heat of reaction at constant volume [95].

To further understand the energy flow during the combustion process, Figure 2.21 depicts a schematic plot of internal energy (U) as function of temperature, for reactants and products of a given constant-volume combustion reaction [95].

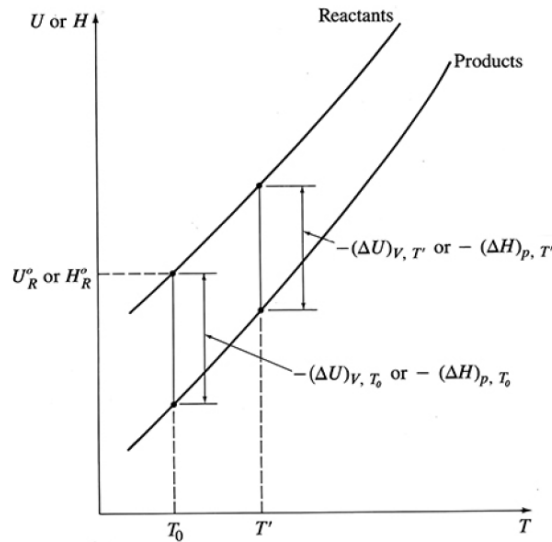


Figure 2.21 – Schematic plot of internal energy (U) or enthalpy (H) as function of temperature (T) for combustion at constant volume (U on y-axis) or at constant pressure (H on y-axis) [95].

Note that $(\Delta H)_{p,T}$ is the heat of reaction at constant pressure at temperature T [95]. Both $(\Delta U)_{V,T}$ and $(\Delta H)_{p,T}$ can be related, according to equation 2.19 [95].

$$(\Delta H)_{p,T} - (\Delta U)_{v,T} = p(V_P - V_R) \quad (2.19)$$

If all species involved in the reactant and product mixtures are ideal gases, then, according to the ideal gas law, comes equation 2.20,

$$(\Delta H)_{p,T} - (\Delta U)_{v,T} = \tilde{R}T(n_P - n_R) \quad (2.20)$$

where n_P and n_R are the number of kmol of gas products and reactants respectively, except for inert gases [95].

It is important to note that the internal energy of combustion products will depend on the proportion of water phases (gaseous and liquid) in the product mixture [95]. The same can be applied to the reactant mixture, according to the phase of the fuel used [95].

The values of enthalpy of both reactants and products can be obtained according to the enthalpies of formation, $\tilde{h}_f^o$, of the reactants and products [95], according to equations 2.21 and 2.22 [95].

$$H_R^o = \sum_{\text{reactants}} n_i \tilde{h}_{f,i}^o \quad (2.21)$$

$$H_P^o = \sum_{\text{products}} n_i \tilde{h}_{f,i}^o \quad (2.22)$$

The enthalpy of formation of a given species is associated to the enthalpy increase due to the formation of one mole of the given chemical compound from its elements [95]. The superscript ^{o} denotes standard state (1 atmosphere at given temperature) and most thermodynamic calculations are done relative to a reference state, usually defined at 298.15 K (25 °C) and 1 atmosphere [95]. Therefore, enthalpies of formation are tabulated for all species of common use according to temperature [95].

However, when fuel chemical composition is unknown, it is not possible to calculate the enthalpy of reactants through each enthalpy of formation [95]. In these cases, the heating value of the fuel is measured [95]. The heating value of a fuel is the absolute value of heat of reaction for the complete combustion of unit mass of fuel at constant volume (q_{HV_v}) or pressure (q_{HV_p}), at a standard temperature, usually 298.15 K (25 °C) [95]. The heating value relates to heat of reaction as follows in equations 2.23 and 2.24.

$$q_{HV_p} = -(\Delta h)_{p,T_0} \quad (2.23)$$

$$q_{HV_v} = -(\Delta u)_{v,T_0} \quad (2.24)$$

Furthermore, if the fuel contains hydrogen it means that water will be one of the products of combustion and, depending on its physical state, it is important to distinguish the higher heating value (water in liquid phase) from the lower heating value (water in vapour phase) [95]. These

values are most commonly tabulated for constant pressure combustion and the difference in the heating values between constant pressure and constant volume is small [95], but they can be calculated from equation 2.20.

As it was mentioned previously, the combustion process is theoretically adiabatic, therefore the final products are at the adiabatic flame temperature [95]. The values for adiabatic flame temperatures are usually tabulated as a function of atmospheric pressure and fuel-air ratio, for each known fuel. In this case, the adiabatic flame temperature has to be calculated, as the pressure and temperature conditions of the reactants are specific of this study.

In this view, the final temperature that products of combustion reach can be calculated from thermochemical data [110]. In order to achieve this, the combustion process at standard temperature is defined in two stages, the first considers the heat released upon combustion at standard temperature and the second considers the heating of the product mixture to a temperature value where its enthalpy, or internal energy, is equal to the magnitude of heat of reaction [110].

However, if reactant gases are at a different temperature from the standard value, then an additional stage has to be considered before the combustion reaction - the cooling (when temperature is higher than standard temperature) of the reactant gas mixture to standard temperature. This leads to an energy balance that is presented in equation 2.18 for constant volume combustion and that can be depicted in Figure 2.22.

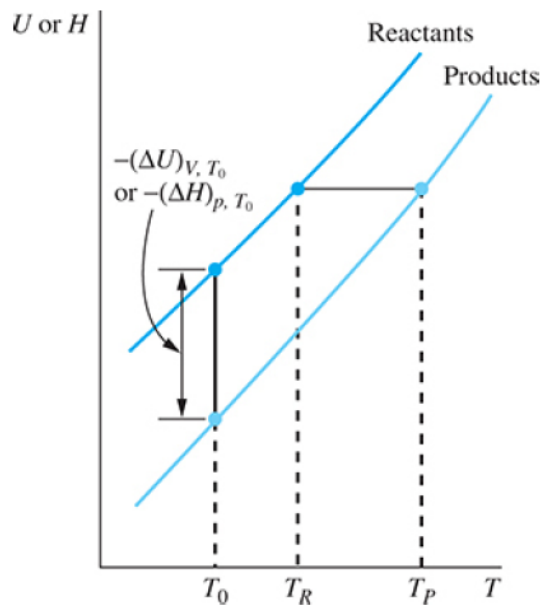


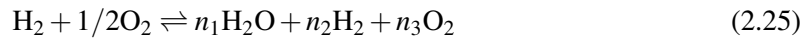
Figure 2.22 – Schematic plot of internal energy (U) or enthalpy (H) as function of temperature (T) for adiabatic combustion at constant volume (U on y-axis) or at constant pressure (H on y-axis) [95].

In this Figure, it is visible the constant U evolution on an adiabatic combustion process at constant volume, where reactants at temperature T_R go through a cooling process until T_0 , then combust into the product mixture at T_0 and these products are heated to T_P . Where T_P corresponds to adiabatic flame temperature.

Despite this, if the stoichiometric and complete combustion of hydrogen-oxygen is considered and accounting that the enthalpy value of the combustion product is equal to the enthalpy of reaction, then it should produce 1 mole of water vapour at *ca.* 5000 °C [110]. In reality, this level of temperature is never achieved due to dissociation, an endothermic process where the inverse chemical reactions occur thus limiting flame temperature [110].

In this process both dissociation and temperature are dependent on one another as temperature defines the extent of dissociation in the gas products and the final chemical composition influences flame temperature [110]. The presence of dissociation increases the complexity of calculations as it demands for iterative methods, which can be supported by a calculation software such as EES.

In order to include dissociation in the model it is important to establish the chemical equilibrium, considering the ideal gas model. In equation 2.25 is the chemical reaction of hydrogen combustion considering dissociation of water into hydrogen and oxygen compounds, the latter being solely depicted in equation 2.26.



The chemical balance is simple, as there are only hydrogen (equation 2.27) and oxygen (equation 2.28) compounds.

$$2 = 2n_1 + 2n_2 \quad (2.27)$$

$$1 = n_1 + 2n_3 \quad (2.28)$$

Then follows the establishment of chemical equilibrium constants that are only function of temperature for ideal gases and have their values tabulated [110]. This constants relate to the partial pressures of each component in the product mixture, as depicted in equation 2.29. The equilibrium constant, $K_{P,\text{H}_2\text{O}}$, is used for the dissociation of water.

$$K_{P,\text{H}_2\text{O}} = \frac{p_{\text{H}_2\text{O}}}{(p_{\text{H}_2})(p_{\text{O}_2})^{1/2}} \quad (2.29)$$

The combustion products at adiabatic flame temperature, stage 3, now go through the expansion stroke [95]. The volume ratio from 3 to 4 is defined by the compression ratio, according to equation 2.30 [95].

$$\frac{v_4}{v_3} = r_c \quad (2.30)$$

Similar to the compression stroke, this stage is also considered to be adiabatic and reversible, defined by equation 2.31 [95].

$$s_4 = s_3 \quad (2.31)$$

The expansion work is then determined by equation 2.32 [95].

$$W_e = U_3 - U_4 = m(u_3 - u_4) \quad (2.32)$$

If the working fluid is considered to be an ideal gas, then equation 2.32 can be simplified into equation 2.33 [95].

$$W_e = mc_v(T_3 - T_4) \quad (2.33)$$

The indicated work per cycle, $W_{c,i}$ is given by equation 2.34 and it is the sum of the expansion work and of the compression work in each cycle, the latter being a negative quantity [95].

$$W_{c,i} = W_e + W_c \quad (2.34)$$

The indicated fuel conversion efficiency, $\eta_{f,i}$, is now defined by equation 2.35 [95].

$$\eta_{f,i} = \frac{W_{c,i}}{m_f q_{LHV}} \quad (2.35)$$

Equation 2.35 can be rewritten according to equations 2.34, 2.32 and 2.12, giving equation 2.36 for the constant-volume cycle [95].

$$\eta_{f,i} = \frac{m[(u_3 - u_4) - (u_2 - u_1)]}{m_f q_{LHV}} \quad (2.36)$$

If the working fluid is considered an ideal gas, then the denominator in equation 2.36 can be directly related to temperature, according to equation 2.37 [95].

$$mc_v(T_3 - T_1) = m_f q_{LHV} \quad (2.37)$$

Then, the indicated fuel conversion efficiency can be defined as only function of temperature, according to equation 2.38 [95].

$$\eta_{f,i} = \frac{(T_3 - T_4) - (T_2 - T_1)}{T_3 - T_2} = 1 - \frac{T_4 - T_1}{T_3 - T_2} \quad (2.38)$$

If the isentropic processes of compression (1-2) and expansion (3-4) strokes are revisited considering the ideal gas model, the following temperature-volume relations are attained in equation 2.39 [95]. The adiabatic constant γ is defined in equation 2.40 and its value depends on mixture composition [95].

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1} = r_c^{\gamma-1} = \frac{T_3}{T_4} \quad (2.39)$$

$$\gamma = \frac{c_p}{c_v} \quad (2.40)$$

From equation 2.39, the indicated fuel conversion efficiency can be rewritten into a simpler form, in equation 2.41, that can be analysed according to mixture composition in Figure 2.23 [95].

$$\eta_{f,i} = 1 - \frac{1}{r_c^{\gamma-1}} \quad (2.41)$$

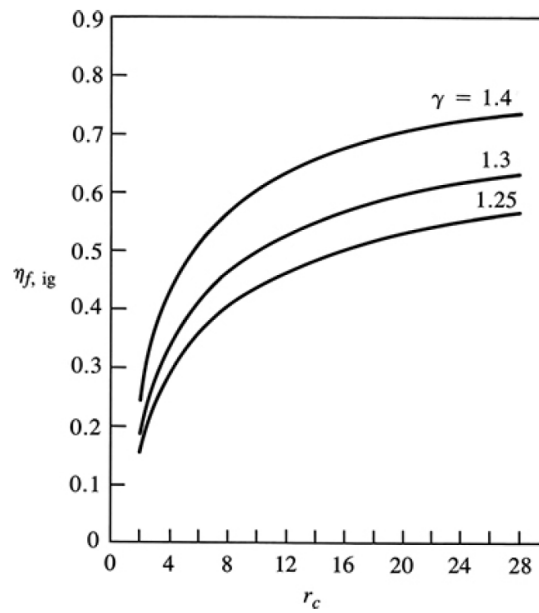


Figure 2.23 – Fuel conversion efficiency as a function of compression ratio and adiabatic constant of mixture, for an ideal gas constant-volume cycle [95].

Combustion Furnace

The combustion process in the furnace occurs at constant pressure and considers hydrogen as fuel and oxygen as oxidising agent. Therefore, the heat of reaction calculations are made in relation to enthalpy values, in contrast to the spark-ignition engine where internal energy was considered. This also means that in Figure 2.21, it is considered H in the y-axis, instead of U .

In this device the reactants are fed at ambient conditions (25 °C, 101.3 kPa) and even though dissociation might occur at the highest temperature levels, it is considered that throughout the furnace the dissociated compounds are continuously combusted. This is very important to take into consideration, as the heat released by a complete combustion is higher than one where dissociation occurs.

Another aspect that distinguishes the hydrogen furnace from the spark-ignition engine is that the combustion process is not modelled to be adiabatic, as it provides heat directly to the reactor, which is placed inside the furnace, instead of through its exhaust gases. This means that final products reach a lower level of temperature than adiabatic flame temperature, as depicted by the

dotted line in Figure 2.24, as $T_{P'}$ represents products final temperature of a given combustion process that is not adiabatic.

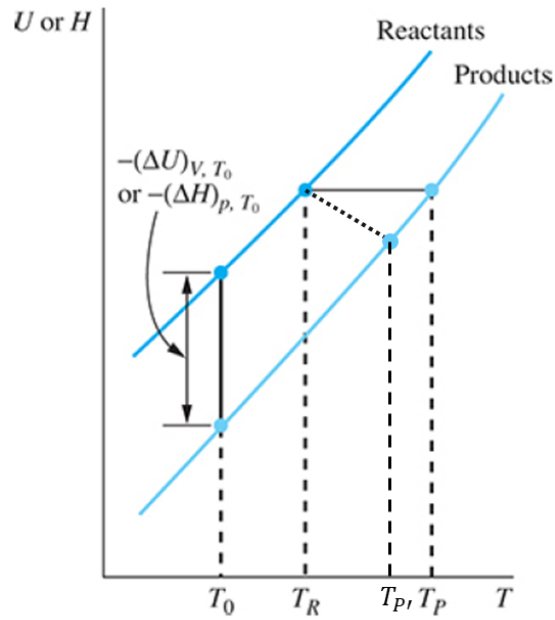


Figure 2.24 – Schematic plot of internal energy (U) or enthalpy (H) as function of temperature (T) for non-adiabatic combustion at constant volume (U on y-axis) or at constant pressure (H on y-axis). Adapted from [95].

Chapter 3

Model and Simulation

The aim of this work is to provide an economic and thermodynamic analysis of heating devices for the low-temperature catalytic methane decomposition process at an industrial scale. Aspen Plus V12 and EES software were used for the thermodynamic modelling of the processes. First, an Aspen model of the methane decomposition process was developed to calculate the heating requirements of the process. Then, calculations were made in EES software to determine commodities requirements for hydrogen combustion technologies. Finally, Aspen Plus was used to develop models of the methane decomposition process with the integration of the heating technologies considered. In the following subsections are presented the technical aspects required for the development of these simulation models.

3.1 Components

The first step in the Aspen Plus simulation model is to select the material components that will take part in the process configuration. In this case, the materials that will be considered in the system are provided in Table 3.1. The content of this table is the same that appears on the Aspen Plus software configuration window, where "Component ID" refers to the identification that the user provides for each component, the component type is specified in order to attribute the appropriate model for property calculation, in this case "Conventional" refers to typical components that may participate in vapor-liquid phase equilibrium and "Solid" provides models to accurately calculate conventional solid's properties. Then, the "Component Name" and "Alias" specify the name of the component in a long string and in a unique string based on its atomic formula. Finally, the "CAS Number" is the number assigned uniquely to each chemical substance by the Chemical Abstracts Service (CAS) of the American Chemical Society.

The models that are considered for analysis only consider the decomposition of methane, instead of the use of natural gas. This assumption simplifies the modelling process as the use of natural gas would require further gas separation techniques and a profound knowledge of the influence of residual gases in the chemical reaction inside the reactor, which are still underdeveloped and, therefore, not considered in this work.

Table 3.1 – Model components in Aspen Plus

Component ID	Type	Component Name	Alias	CAS number
CH4	Conventional	METHANE	CH4	74-82-8
C	Solid	CARBON-GRAPHITE	C	7440-44-0
H2	Conventional	HYDROGEN	H2	1333-74-0
H2O	Conventional	WATER	H2O	7732-18-5
O2	Conventional	OXYGEN	O2	7782-44-7

The next step is to define the global property methods and models that are adequate for the calculations involving thermodynamic and transport properties. This model will only consider pure gas streams and will neglect chemical interaction in multicomponent gaseous mixtures. The substances used do not deviate far from the ideal gas behaviour, even under the operating conditions of the process, therefore, in order to reduce computational effort and simplify the model, the ideal gas assumption will be considered.

3.2 Simulation Flowsheet

The simulation flowsheet was developed as a simple design, based on the main pieces of equipment required for the methane decomposition process and for a macro analysis of the operating conditions in the heating equipment. The first element to be taken into consideration was the reactor, which is regarded as the central piece that defines the operating conditions of the system. Then, the model was constructed based on the required upstream treatments from the reactor. The downstream treatments are mainly focused on gas-solid and gas separation processes that are closely related to the chemical sector and will not be addressed in a thorough manner in this work. The upstream treatment of the feed gas, however, will be taken into account regarding the heating requirements.

3.2.1 Methane Decomposition Reactor

In order to run a simulation on Aspen Plus software, it is required to build the Main Flowsheet with the Unit Operation Models that are necessary for the processes involved. These Unit Operation Models are items that represent real equipment parts, namely, reactors, heat exchangers, pressure changers and so on.

To begin this build-up, there is the central piece of the whole operation - the reactor. Aspen Plus has a variety of seven reactor configurations that are presented in Table 3.2.

Table 3.2 – Aspen Plus Unit Operation Models of Reactors

Model	Description
RStoic	Stoichiometric reactor based on known fractional conversions or extents of reaction
RYield	Nonstoichiometric reactor based on known yield distribution
REquil	Rigorous equilibrium reactor based on stoichiometric approach
RGibbs	Rigorous reaction and/or multiphase equilibrium based on Gibbs free energy minimization
RCSTR	Rigorous continuous stirred tank reactor with rate-controlled reactions based on known kinetics. Also allows for equilibrium reactions
RPlug	Rigorous plug flow reactor with rate-controlled reactions based on known kinetics
RBatch	Rigorous batch or semibatch reactor with rate-controlled reactions based on known kinetics

This process of methane decomposition is still under development, so there are several aspects related to the occurring chemical reaction that are unknown, therefore rigorous reactor models will not be considered. For the purpose of this work, an approximate solution is sufficient and RStoic was the chosen model. In order to use the RStoic it is required to set the operating conditions, specify the stoichiometry and level of conversion of the chemical reaction. These settings are specified in Table 3.3.

Table 3.3 – Decomposition Reactor Chemical Reaction Settings

Rxn no.	Specification type	Fractional conversion	Fractional Conversion of component	Stoichiometry
1	Frac. Conversion	1	CH ₄	CH ₄ ⇌ 2H ₂ +C

3.2.2 Heating Needs

The methane gas stream that enters the reactor needs to be preheated in order to lower the temperature difference and the heating needs inside the reactor. The reactor itself also requires calorific power in order to hold hydrogen production continuously at a temperature of 500 °C. A set of heat exchangers were used to simulate the heat transfer from the spark-ignition engine flue gas to the reactor and to the methane feed stream. In the case of the hydrogen furnace, it was considered the calorific power from the combustion reaction and similar heat exchangers for methane preheating.

In Table 3.4 it is specified the temperature and pressure conditions of the reactor and of the methane feed stream. For the methane stream, T_i is the inlet temperature and T_f is the final temperature that the stream reaches before entering the reactor. In Figure 3.1 it is visible part of the Aspen Plus flowsheet where the unit operation models of the reactor and heat exchanger are defined and the stream values are available.

Table 3.4 – Operating conditions of methane decomposition reactor and of methane stream

MD Reactor	
T [°C]	500
P [kPa]	101.3
Methane Stream	
T_i [°C]	25
T_f [°C]	500
P [kPa]	101.3

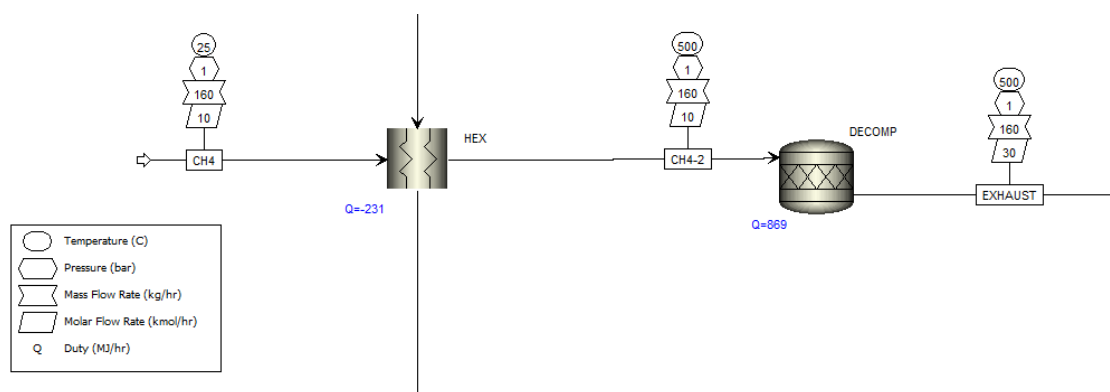


Figure 3.1 – Aspen Plus flowsheet with methane preheating and decomposition reactor operating conditions.

3.3 Economic Analysis

The economic analysis was based on available data and estimated prices for certain components, therefore it is provided with low accuracy, especially for the low temperature methane decomposition process, possibly varying in a range of -30 % to +60 % [111]. The comparative analysis was based on CAPEX and OPEX costs of each process, and also on the final LCOH [112].

This comparison was based on a time frame prior to the COVID-19 pandemic and the war in Ukraine, as these events have utterly destabilised the economy [113]. The EU was considered as reference location for price calculation, as price values vary according to geographical location, as mentioned in chapter 2. Even though the majority of data available presents price values in USD kg_{H₂}⁻¹, even when referring to EU context, a conversion factor of Euro to US Dollar of 1.15 was applied, based on the average values from 2018 to 2020 [114]. The calculations relating the economic analysis were performed on Microsoft Excel software.

Table 3.5 provides the price values of utilities and commodities that were considered for the calculations. Note that these values relate to a time period prior to 2020, to enable a coherent comparison with technology price, except for electricity, where it is considered the price established in the Portuguese national hydrogen program, based on the Iberian Electricity Market (MIBEL) [115]. Alternative price scenarios for both hydrogen and electricity were considered, as these are

usually more volatile according to source of production. In this sense, it was considered an alternative price of $5 \text{ € kg}_{\text{H}_2}^{-1}$, as the costs associated to electrolysis may be the double of methane reforming [116], and a decreased cost of electricity assuming the use of local production from solar photovoltaic, of 15 € MWh^{-1} [115].

Table 3.5 – Values considered for the price of utilities and commodities

Commodities	Price	Year	Ref.
NG TTF [$\text{€ kg}_{\text{NG}}^{-1}$]	0.30	2018	[101]
Biomethane [$\text{€ kg}_{\text{Bio}}^{-1}$]	0.76	2018	[117]
Hydrogen [$\text{€ kg}_{\text{H}_2}^{-1}$]	2.5	2019	[26]
Hydrogen (electrolysis) [$\text{€ kg}_{\text{H}_2}^{-1}$]	5	2019	[116]
Oxygen [$\text{€ kg}_{\text{O}_2}^{-1}$]	0.06	2021	[118]
Electricity [€ MWh^{-1}]	45	2020	[115]
Electricity (solar) [€ MWh^{-1}]	15	2040	[115]

Chapter 4

Results and Discussion

4.1 Methane Decomposition Process

The mathematical modelling of the heating devices is based on the operating conditions of the methane decomposition reactor and on the heating requirements of the methane stream. It is important to acknowledge that assumptions are made to simplify the construction and analysis of this model. It was not considered transient regimes of starting up or shutting down the production process, only permanent regime. Everything operates at atmospheric pressure, with no regards considering distance travelled by gas flows nor pressure losses in the system. The heating equipment do not account for external heat losses and downstream treatments from the reactor are not analysed. The combustion processes use oxygen as oxidising agent instead of air.

It is first presented the heating needs of the methane decomposition system. In Table 4.1 it is specified the operating conditions of the reactor, as well as heating requirements and mass flow rates on the inlet, $\dot{m}_{\text{CH}_4}$, and outlet, $\dot{m}_{\text{H}_2}$ and $\dot{m}_{\text{C}}$. In Table 4.2 there is information on the preheating conditions of the methane feed stream and the corresponding heating needs for the specified methane mass flow rate.

Table 4.1 – Operating conditions of methane decomposition reactor, including heating requirements and streams

Reactor	
T [°C]	500
P [kPa]	101.3
$\dot{Q}$ [kW]	241.5
$\dot{m}_{\text{CH}_4}$ [kg h ⁻¹]	160
$\dot{m}_{\text{H}_2}$ [kg h ⁻¹]	40
$\dot{m}_{\text{C}}$ [kg h ⁻¹]	120

Table 4.2 – Methane feed stream preheating conditions

Methane Stream	
T_i [°C]	25
T_f [°C]	500
P [kPa]	101.3
$\dot{Q}$ [kW]	64.1
$\dot{m}_{\text{CH}_4}$ [kg h ⁻¹]	160

4.2 Hydrogen Spark-Ignition Engine

In order to develop a mathematical model of the thermodynamic behaviour of a hydrogen spark-ignition internal combustion engine, EES software was used as an auxiliary tool to calculate the different thermodynamic states of the working fluids throughout the operating cycle. The full equation and results windows can be found in appendix A.

The exhaust gases, mainly composed of water vapour, are used to first heat the reactor and then to preheat the methane stream. It is important to note that there is an intermediate step in this process, as after the exhaust gases are used to heat the reactor, approximately 10 % of that mass flux is recirculated into the inlet stream of the engine in an operation called Exhaust Gas Recirculation (EGR) [95]. This technique is commonly used in some engines to reduce NO_x emissions [95], but in this case it was used to lower flame temperature. Usually, and according to operating conditions, spark ignition engines can have up to 30 % of the exhaust gases recycled [95].

As it was mentioned in chapter 2, the purpose of this device is to capitalise from the high-temperature exhaust gases for heating purposes and the mechanical power from crank rotation.

The combustion reaction of hydrogen with oxygen occurs between steps 2 and 3 of the operating cycle outlined in Figure 2.20 and according to equation 2.7. However, due to the high temperature that is achieved in this stage, dissociation occurs and hydrogen and oxygen molecules appear on the product gas mixture. In Table 4.3 there is the reactant and product mixture composition, in mass fraction, which was obtained after the calculations and for a product temperature of 3876°C.

Table 4.3 – Reactant and product mixture composition in mass fraction in spark-ignition engine

	Reactant Mixture [%]	Product Mixture [%]
H ₂	0.1007	0.033
O ₂	0.7993	0.2615
H ₂ O	0.1	0.7055

It is assumed that hydrogen and oxygen are provided at ambient conditions, and are mixed with the recirculated exhaust gases when entering the cylinder. The chemical composition of the

mixture in stages 1 and 2 is the one displayed in Table 4.3 under "Reactant Mixture". In knowing the mixture composition, it is possible to determine the value of the adiabatic constant, γ , from the values of constant pressure specific heat, c_p , and constant volume specific heat, c_v . Table 4.4 provides the values of this constants and the value for compression ratio that was applied, according to literature suggestions.

Table 4.4 – Values for compression ratio and specific thermodynamic properties of reactant mixture

Constants	
r_c	10
γ	1.376
c_p [kJ kg ⁻¹ K ⁻¹]	2.454
c_v [kJ kg ⁻¹ K ⁻¹]	1.778

The working fluids in the spark-ignition engine go through several thermodynamic stages included in the operating cycle depicted in the P-V diagram of Figure 2.20 and described in chapter 2.

The operating cycle starts with the mixture of reactants with recirculated gas, at stage 1, then follows the compression stroke to stage 2, adiabatic combustion occurs until stage 3, where the gas mixture composition now corresponds to the one displayed in Table 4.3 under "Product Mixture". It follows the expansion stroke to stage 4 and the exhaust stream leaves the engine cylinder under the thermodynamic conditions of stage 5. From there, the exhaust gas is used to heat the reactor and at stage 6 part of that stream is recirculated into the engine, while the remaining is used to preheat the methane stream until it reaches stage 7. Table 4.5 displays the thermodynamic properties results of the working fluids throughout this operating cycle and heating processes.

Table 4.5 – Thermodynamic properties of the working fluid in the engine operating cycle (1-4) and in the heating processes (5-7)

	1	2	3	4	5	6	7
T [°C]	61.21	519.8	3876	2364	2364	550	120
P [kPa]	101.3	2410	10288	654.2	101.3	101.3	101.3
h [kJ kg ⁻¹]	-1237	-130.7	1537	-3323	-3323	-8314	-9248
s [kJ kg ⁻¹ K ⁻¹]	12.88	12.87	15.47	15.47	16.48	13.36	11.77
v [m ³ kg ⁻¹]	2.131	0.2131	0.2131	2.131	13.8	4.306	2.057

The mass flow rate of hydrogen that is required was determined in order to fulfill the heating needs presented in Tables 4.1 and 4.2, and considered the thermodynamic conditions of the exhaust stream presented in Table 4.5, under stages 5, 6 and 7. Table 4.6 shows the resulting mass flow rates for the reactant and product gas mixtures. It is important to notice that the reactants flow rate is applied to stages 1 and 2, while the products flow rate is valid from stage 3 to 6. Then, the mass flow rate is separated due to recirculation, and its value is 247.2 kg h⁻¹ in stage 7.

4.3 Hydrogen Furnace

The mathematical modelling of the combustion furnace was first developed on EES software (appendix A) and then confirmed by Aspen Plus software. In this case, a furnace is set up with the reactor inside it, meaning that combustion heat is directly transferred into the reactor. Therefore, the combustion process is not adiabatic and it is expected that final products reach a lower than the adiabatic flame temperature. It is also considered that dissociation occurs in the zones at highest temperature and that throughout the length of the furnace dissociation products are continuously combusted [80]. The chemical composition of the exhaust products is water vapour, corresponding to a complete combustion process in a global view.

In Table 4.8 is the reactant and product mixture composition by mass fraction, which was obtained after the calculations and for a product temperature of 1377 °C. It was considered the stoichiometric combustion of hydrogen with oxygen into water vapour.

Table 4.8 – Reactant and product mixture composition in mass fraction of combustion process in furnace

	Reactant Mixture [%]	Product Mixture [%]
H ₂	0.1119	0
O ₂	0.8881	0
H ₂ O	0	1

The hydrogen furnace operates on the principles described in chapter 2. It considers hydrogen combustion at constant pressure and the heat of reaction is partly transferred directly to the methane decomposition reactor. Then, the exhaust flow is used to preheat the methane stream. The results from the thermodynamic model of the hydrogen furnace are displayed in Table 4.9.

Table 4.9 – Thermodynamic properties of the different stages in furnace combustion process

	1	2	3
<i>T</i> [°C]	25	1377	200
<i>P</i> [kPa]	101.3	101.3	101.3
<i>h</i> [kJ kg ⁻¹]	0	-10345	-13090

The resulting mass flow streams are presented in Table 4.10.

Table 4.10 – Reactant and product mass flow rate in hydrogen-fuelled furnace.

	Reactants	Products
H ₂ [kg h ⁻¹]	9.40	0
O ₂ [kg h ⁻¹]	74.64	0
H ₂ O [kg h ⁻¹]	0	84.04
Total [kg h ⁻¹]	84.04	84.04

In Figure 4.2 is depicted the Aspen Plus flowsheet that was developed to simulate the heat transfer to the reactor and to preheat the methane stream. The combustion process was modelled in the unit named "furnace", where the exothermic heat corresponds to the heating requirements of the reactor. Then, the methane preheating was modelled similar to the spark-ignition engine case, resorting to a multistream heat exchanger unit.

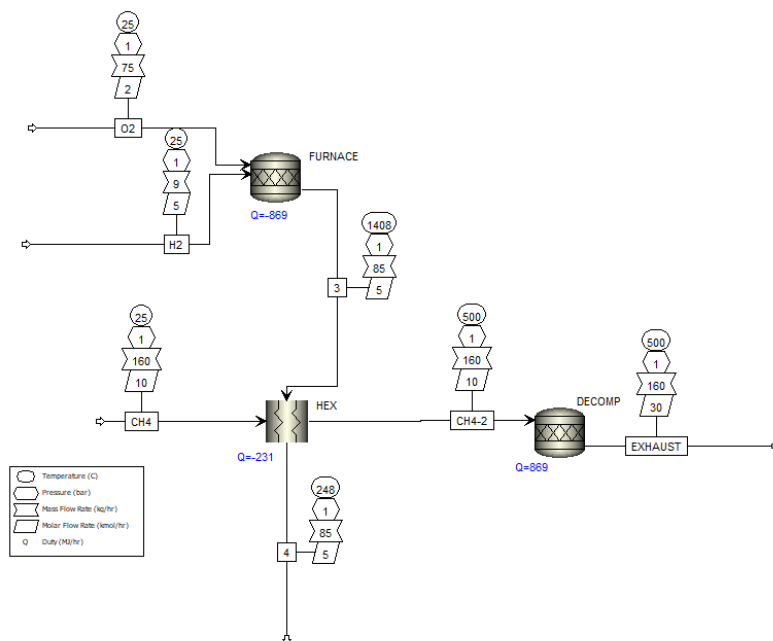


Figure 4.2 – Aspen Plus flowsheet of methane decomposition system with furnace integration.

4.4 Engine vs Furnace

The results from the use of a hydrogen engine and a hydrogen furnace to fulfill the heating requirements are very different from one another. The hydrogen engine demands for a mass flowrate of 29 kg h^{-1} of hydrogen and 230 kg h^{-1} of oxygen in order to produce enough water vapour to both provide heat to the reactor, at temperatures above 500°C , and to preheat the methane stream. In contrast, the hydrogen furnace only requires a stream of 9.4 kg h^{-1} of hydrogen and 74.6 kg h^{-1} of oxygen. This is mainly due to the fact that in the furnace, heat from combustion is directly provided to the reactor, instead of going through different thermodynamic stages where such high temperatures are not achieved at the end. The matter with hydrogen and oxygen demand is that it translates to economic expenditures in terms of OPEX, as it is presented later in this chapter.

It is important to note that hydrogen consumption is lower than the amount hydrogen being produced (40 kg h^{-1}), which means that part of this could be used to feed the heating equipment. This scenario is not considered for economic analysis, as it is only considered the use of external hydrogen and oxygen for operation costs, but it means that this process can be self-sustained if needed.

The engine provides mechanical power that can be used to power other stages of the process, or be used by external consumers. A more detailed economic analysis should be done to fully understand the cost-effectiveness of the engine in comparison to the furnace.

4.5 Economic Analysis

The economic analysis is carried out to allow an economic comparison between the various heating systems and, subsequently, between the methane decomposition process and other hydrogen production processes. It is first presented the price estimates for the low-temperature methane decomposition, based on literature data and on the different heating solutions developed in this work. Then, it is compared to conventional and upcoming hydrogen production technologies.

The CAPEX values for the base methane decomposition process consider the value of the catalytic reactor, heat exchangers and Pressure Swing Adsorption (PSA) units and are based on the values from methane steam reforming [119]. It was considered that all this equipment has a lifetime of 20 years.

The OPEX values are based on the price of commodities for a methane stream of 160 kg h^{-1} . Two scenarios are considered for these calculations, as methane can either come from natural gas or from biomethane sources. These values are presented in Table 4.11 and do not account for heating-related costs.

Table 4.11 – CAPEX and OPEX values for base low-temperature methane decomposition process, in [$\text{€ kg}_{\text{H}_2}^{-1}$]

	Value	Unit	Ref.
CAPEX			
Reactor	0.236	[$\text{€ kg}_{\text{H}_2}^{-1}$]	[119]
Heat Exchangers	0.002	[$\text{€ kg}_{\text{H}_2}^{-1}$]	[119]
PSA	0.008	[$\text{€ kg}_{\text{H}_2}^{-1}$]	[119]
OPEX			
Natural Gas	0.717	[$\text{€ kg}_{\text{H}_2}^{-1}$]	
Biomethane	1.83	[$\text{€ kg}_{\text{H}_2}^{-1}$]	
Total CAPEX	0.246	[$\text{€ kg}_{\text{H}_2}^{-1}$]	
LCOH NG	0.963	[$\text{€ kg}_{\text{H}_2}^{-1}$]	
LCOH Bio	2.08	[$\text{€ kg}_{\text{H}_2}^{-1}$]	

A first observation of these results allows to conclude that the OPEX costs are much more predominant than CAPEX costs for the base LCOH for methane decomposition. It is also visible that the use of biomethane duplicates the base cost of production (without considering heating equipments). Nevertheless, biomethane is becoming increasingly popular due to its environmental benefits and to the prospect of becoming more economical than natural gas in the near future [117, 120].

The price values of the heating technologies studied are analysed, in order to provide the overall LCOH for the methane decomposition process. It is first presented the economic results relating to the hydrogen engine, and then the results for the hydrogen furnace. Note that LCOH values account for the cost of methane decomposition and for the integration of each heating solution.

The hydrogen spark-ignition engine has a power value equivalent to high power capacity automotive engines, *ca.* 300 HP. In this sense, the cost of this solution can be estimated by the price of converting a conventional spark-ignition engine to operate on hydrogen instead of gasoline [121, 122]. Besides, hydrogen engines are already being studied as a carbon-free alternative in the shipping sector [123, 124], where its CAPEX is also compared to the value of conventional ship engines [123].

In Table 4.12 are presented the CAPEX and OPEX estimated values for a hydrogen engine with the same power characteristics as the one modelled in this process. The CAPEX value was obtained from the average value between the conversion process of a Shelby Engine 427CI STAGE I, which includes the cost of the hydrogen tank, and estimated values from the shipping sector. It was considered that the engine lifetime is 20 years and the OPEX value was only based on commodities cost, namely hydrogen and oxygen.

Table 4.12 – LCOH of methane decomposition considering the use of a hydrogen engine

	Value	Unit	Ref.
CAPEX			
Engine	0.036	[€ kg _{H₂} ⁻¹]	[121, 122]
OPEX			
Hydrogen	1.81	[€ kg _{H₂} ⁻¹]	
Oxygen	0.331	[€ kg _{H₂} ⁻¹]	
Total CAPEX	0.036	[€ kg _{H₂} ⁻¹]	
Total OPEX	2.14	[€ kg _{H₂} ⁻¹]	
LCOH	3.14	[€ kg _{H₂} ⁻¹]	

The CAPEX for the hydrogen furnace is based on reformer furnaces literature estimations based on the heating power of the furnace [125]. Its lifetime was considered 20 years and the OPEX costs are only based on commodities.

Table 4.13 – LCOH of methane decomposition considering the use of a hydrogen furnace

	Value	Unit	Ref.
CAPEX			
Furnace	0.010	[€ kg _{H₂} ⁻¹]	[125]
OPEX			
Hydrogen	0.588	[€ kg _{H₂} ⁻¹]	
Oxygen	0.107	[€ kg _{H₂} ⁻¹]	
Total CAPEX	0.010	[€ kg _{H₂} ⁻¹]	
Total OPEX	0.695	[€ kg _{H₂} ⁻¹]	
LCOH	1.67	[€ kg _{H₂} ⁻¹]	

The values presented in Tables 4.12 and 4.13 demonstrate that the hydrogen furnace is more economical in comparison to the hydrogen engine. In fact, it was found that *ca.* 70 % of LCOH with the use of a hydrogen engine comes from OPEX of the heating equipment, whereas for the furnace the OPEX only represents *ca.* 40 %.

An additional source of heating was considered to enable a cost comparison of these technologies with electric heating. Electric energy demand was calculated based on the total heating power required by the process, *ca.* 0.3 MW, and assuming the use of joule heating. This results in an energy demand of 27.5 MJ kg⁻¹ of hydrogen that is fulfilled with electric heating. The CAPEX was considered to be included in the base costs of methane decomposition and OPEX costs are only related to electricity requirements, based on the calculations described. Table 4.14 provides the OPEX and LCOH values of this solution.

Table 4.14 – LCOH of using electric heating (considering electricity price of 45 € MWh⁻¹)

	Value	Unit	Ref.
OPEX			
Electricity	0.344	[€ kg _{H₂} ⁻¹]	
LCOH	1.31	[€ kg _{H₂} ⁻¹]	

In contrast to the other heating devices, OPEX costs for electric heating only account for 25 % of LCOH. Therefore, electric heating presents two economic advantages in comparison to the others - it is more economical and depends less on OPEX prices.

In fact, this electricity demand could be fulfilled by the internal combustion engine, if its resulting mechanical power were converted to electrical power. However, considering equipment efficiencies and the amount of hydrogen required for this level of power, it would still not portray an economical solution as heating device.

Table 4.15 provides an overview of LCOH values according to production method. It includes methane steam reforming with and without carbon capture (CCUS), electrolysis and methane decomposition, where an average value of LCOH was considered.

Table 4.15 – LCOH according to production process

	LCOH	Unit	Ref.
SMR without CCUS	2.30	[€ kg _{H₂} ⁻¹]	[26]
SMR with CCUS	2.76	[€ kg _{H₂} ⁻¹]	[26]
Electrolysis	3.01	[€ kg _{H₂} ⁻¹]	[126]
Methane Decomposition	2.04	[€ kg _{H₂} ⁻¹]	-

The values presented in Table 4.15 are promising for the methane decomposition process, as it can be economically competitive with MSR, with and without CCUS, and electrolysis. It is important to highlight that it was not considered the commercialisation of the solid carbon by-product of methane decomposition nor the cost reduction from CO₂ allowances from the use of biomethane. On one hand, both methane steam reforming and methane decomposition can benefit from the use of biomethane instead of natural gas, as it is considered a method for capturing atmospheric CO₂. This results in negative emissions and is economically benefited from CO₂ allowances. On the other hand, only methane decomposition presents a by-product that has high commercial value. In fact, the price of solid carbon varies according to its structure ranging from 100 € t⁻¹ to 1000 € t⁻¹, according to its crystalline properties [59]. Many markets for solid carbon materials are emerging both for amorphous carbon structures (doping concrete, asphalts, rubber, steel, etc.) and for ordered structures (components for fuel cells, batteries, sensors, etc.).

In a scenario where it is considered the cost reduction from selling carbon by-product and from CO₂ allowances, it is estimated an average hydrogen cost decrease of ca. 15 %. For these calculations, it was considered a price of 100 € t⁻¹ of carbon [59] and 25 € t⁻¹ of CO₂ [127], when biomethane is used. In Table 4.16 it is presented the estimated values for the different methane decomposition scenarios, from the use of natural gas, biomethane and the estimated reduction on LCOH.

Table 4.16 – LCOH comparison of methane decomposition (MD) process using natural gas (NG) and biomethane (Bio), and the cost reduction from selling carbon by-product (C) and from CO₂ allowances (CO₂). Values presented in [€ kg_{H₂}⁻¹]

	Engine	Furnace	Electric
MD NG	3.14	1.67	1.31
MD Bio	4.26	2.78	2.42
MD NG+C	2.84	1.37	1.00
MD Bio+C+CO ₂	3.76	2.28	1.92

Even with the use of biomethane, which is more than the double price of natural gas, methane decomposition is economically competitive with methane steam reforming, especially when considering the economic benefits from carbon by-product and CO₂ allowances. According to what was previously mentioned, electric heating has a huge economic advantage in comparison to the other heating devices, as it portrays the most economically competitive solution in every aspect.

It is important to note that hydrogen production cost from water electrolysis is greatly dependent on the price and availability of renewable source electricity. As it was mentioned in chapter 2, the strategy of using renewable sources is not homogeneously beneficial for all European countries. Time and spatial variability of sources, such as wind and solar, results in different hydrogen prices according to country of production. Additionally, an enormous investment is required in electrolysis because the infrastructures for hydrogen storage and distribution are scarce. In its turn, methane decomposition will benefit from the already existing natural gas infrastructures and supply chains. Combining these reasons, the price of green hydrogen from water electrolysis varies ($3 - 8 \text{ € kg}^{-1}$) a lot as often referred in technology reports [128].

Even though methane decomposition appears to be economically competitive with the remaining technologies, it is important to consider the uncertainty level related to the low maturity of the technology and the current excessive price of natural gas caused by coronavirus pandemic and the geopolitical issues between the EU and Russia. Nevertheless, and after the expected stabilisation in terms of natural gas supply, the hydrogen market will return to a scenario of 2019. The reforming of natural gas and mainly methane decomposition are expected to be more competitive than water electrolysis because they will require less technological changes in production, distribution, and storage.

A sensitivity analysis is conducted to better comprehend the range of prices that can be reached, considering uncertainties in the calculated values. The analysis is performed for each methane decomposition scenario, without considering the economic benefits from selling carbon by-product and CO₂ allowances. It is also performed for electrolysis, as this process still has a high level of uncertainty relating its production costs.

4.5.1 Sensitivity Analysis

The difficulty in accurately predicting hydrogen production costs lies not only on the current economic instability but also on the lack of available data from producers. Nevertheless, a cost was estimated for the methane decomposition process and compared to other available technologies, and is now subject to a sensitivity analysis. In this section, the purpose is to understand the range of values that each hydrogen production scenario may reach. Therefore, stacked bar charts were used to provide visual results. In these charts, the y-axis presents the technology under analysis and the x-axis presents the range of price values. The middle of the bars indicates the LCOH value calculated in the previous section, and each bar ranges from the lower to the upper bound of the price interval, between the estimated minimum and maximum values, respectively.

The sensitivity analysis performed accounts for different factors according to each technology. Figures 4.3 and 4.4 present, respectively, the sensitivity analysis applied to the hydrogen engine case and to the hydrogen furnace case. It was considered a standard variation of -30 % and +40 % for the calculated values of LCOH. An additional scenario considers the same lower bound of -30 % and an upper bound that considers a more expensive value for hydrogen fuel ($5 \text{ € kg}_{\text{H}_2}^{-1}$), which results in a variation of LCOH due to OPEX. This allows to understand how the overall cost of the methane decomposition process may vary for each case.

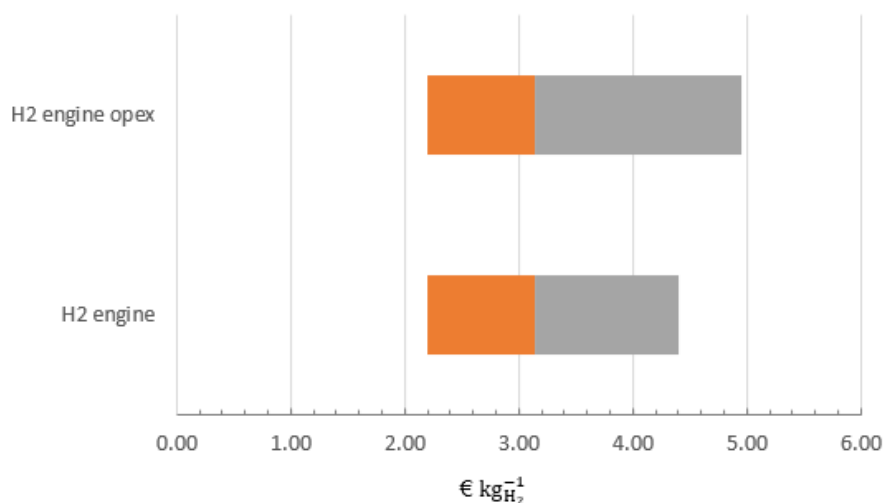


Figure 4.3 – Sensitivity analysis on hydrogen engine. The values presented account for resulting LCOH (H2 engine opex relates to the influence of higher hydrogen fuel costs ($5 \text{ € kg}_{\text{H}_2}^{-1}$) in LCOH and H2 engine is subject to a variation of -30 % and +40 % in LCOH).

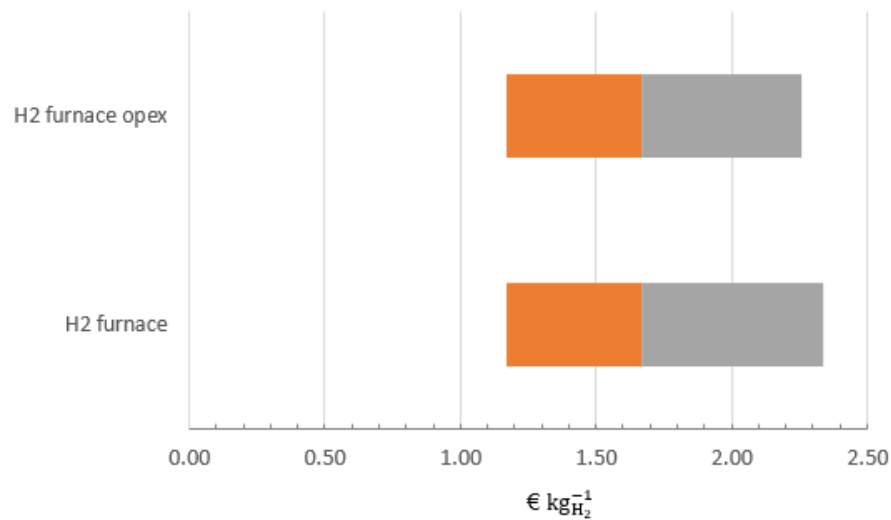


Figure 4.4 – Sensitivity analysis on hydrogen furnace. The values presented account for resulting LCOH (H2 furnace opex relates to the influence of higher hydrogen fuel costs (5 € kg_{H₂}⁻¹) in LCOH and H2 furnace is subject to a variation of -30 % and +40 % in LCOH).

A sensitivity analysis was also performed on the electric heating scenario and on electrolysis, as these share the same uncertainty parameters - variation in CAPEX due to materials price fluctuation and variation in OPEX due to electricity prices. For the variation in CAPEX it was considered a range from -30 % to +60 % over the estimated CAPEX price. For the variation in OPEX, the lower value considered the use of only solar sourced electricity, at 15 € MWh⁻¹, and the upper value considered a rise in +60 % over the base OPEX price. The resulting LCOH values are presented in Figures 4.5 and 4.6.

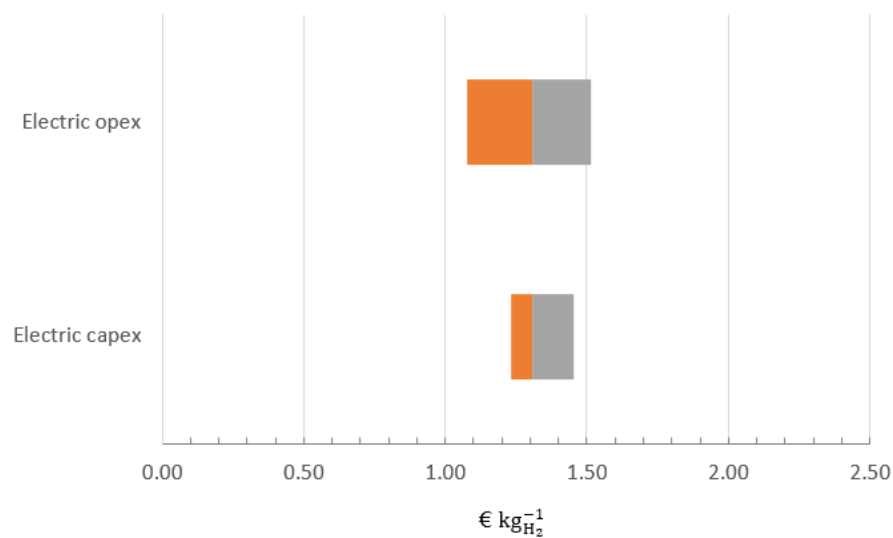


Figure 4.5 – Sensitivity analysis on electrical heating. The values presented account for resulting LCOH (electric opex relates to the case where electricity costs vary between 15 € MWh⁻¹ and 70 € MWh⁻¹, and electric CAPEX is subject to a variation of -30 % and +60 % in CAPEX).

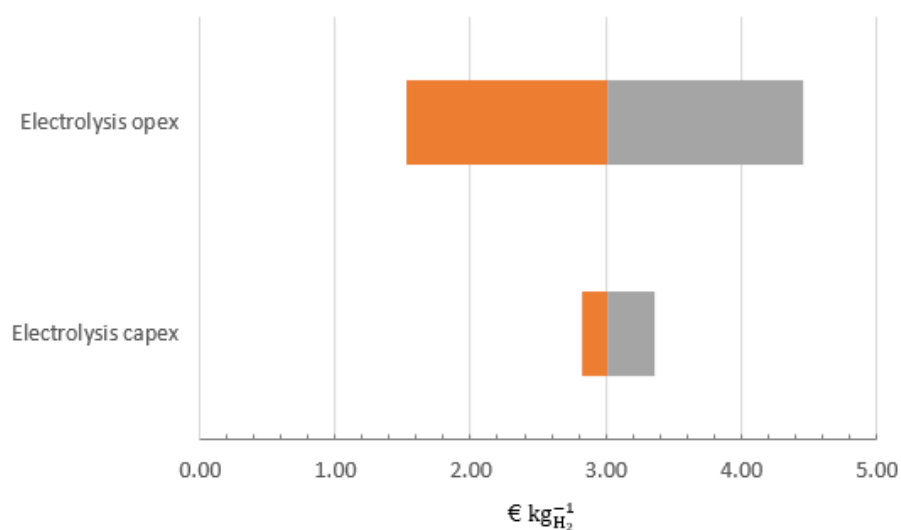


Figure 4.6 – Sensitivity analysis on electrolysis. The values presented account for resulting LCOH (electrolysis opex relates to the case where electricity costs vary between 15 € MWh⁻¹ and 70 € MWh⁻¹, and electrolysis capex is subject to a variation of -30 % and +60 % in CAPEX).

Figure 4.7 gathers the previous sensitivity analysis scenarios in a single chart to better comprehend the different magnitudes of price values that are reached in each case.

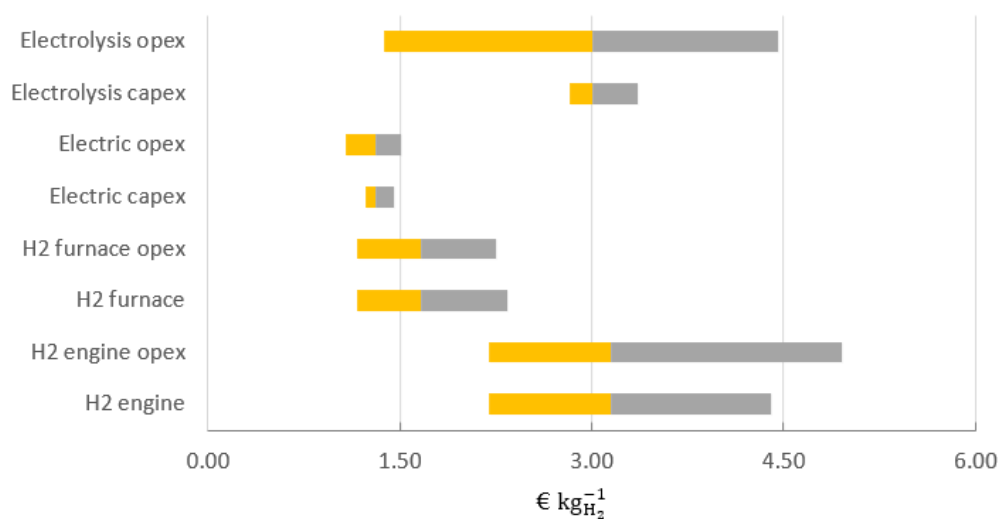


Figure 4.7 – Sensitivity analysis on the different scenarios.

From the sensitivity analysis performed, methane decomposition process costs may vary from 1.08 to 4.96 € kg_{H₂}⁻¹. The lower bound corresponds to the lowest price that was achieved with the use of electric heating and the upper bound to the highest price achieved with the use of a hydrogen engine. The electric heating is the most economical solution, but the hydrogen furnace can also be a promising heating device, especially considering that methane decomposition can become a self-sustained process in that scenario.

Even when considering an electricity cost of 70 € MWh^{-1} , electric heating remains more economical than the use of a furnace. Additionally, electric heating also presents a lower LCOH than electrolysis when the price of electricity from renewable sources is considered 15 € MWh^{-1} . In fact, electrolysis only becomes competitive with methane decomposition on the lower range of electricity prices and if electric heating is not considered.

The values presented in Table 4.15, and considering the sensitivity analysis performed, it is possible to conclude that methane decomposition is economically competitive with remaining technologies.

4.6 Hydrogen as Combustion Fuel

In this work a study is made on the use of hydrogen as fuel. It considered the stoichiometric combustion of hydrogen with oxygen as a means to achieve a zero emission heating solution, while also resorting to common technologies. The analysis of fuel properties values, included in appendix B, allows to compare, on a thermodynamic level, the advantages of using hydrogen in fuel compositions, instead of methane or gasoline. On one hand, the lower heating value of hydrogen is 120 MJ kg^{-1} , which is *ca.* 2.5 times higher than the lower heating value of methane and almost 3 times higher than that of gasoline. This means that less mass is required from hydrogen than from methane or gasoline to obtain the same level of energy. However, the mass density of hydrogen is *ca.* 10 times lower than methane and gasoline, consequently requiring a larger storage volume than these.

In what comes to hydrogen use in internal combustion engines, an interesting aspect is that the relation between c_v and c_p values of hydrogen is higher than those of methane or gasoline, which results in a γ value that is higher when hydrogen is used and, therefore, increases indicated fuel conversion efficiency of spark-ignition engines.

Nevertheless, there are combustion properties that pose technical and safety issues with the use of hydrogen in spark-ignition engines, in comparison to gasoline. The wide range of flammability of hydrogen can bring concerns regarding its safe handling, but it also enables to operate on a wide range of fuel-air mixtures, leading to a greater fuel economy [96]. There are reported issues with backfiring problems due to small quenching distance of hydrogen flames, in relation to gasoline, and pre-ignition problems due to low minimum ignition energy [96]. However, these issues can be avoided by an adequate design of the injection system and by the establishment of appropriate engine control parameters [96, 121].

Chapter 5

Conclusions and Future Work

The aim of this work was to provide a thermodynamic and economic analysis of the low temperature methane decomposition process at an industrial scale, resorting to different heating technologies. The results were achieved and the main conclusions from this work are now summarised.

Among the heating equipment studied in this work, the hydrogen furnace is the one that requires a less amount of commodities to operate in the set of conditions established. Consequently, it presents the most economical solution ($1.67 \text{ € kg}_{\text{H}_2}^{-1}$) in comparison to the hydrogen spark-ignition engine ($3.14 \text{ € kg}_{\text{H}_2}^{-1}$). An advantage of using the hydrogen furnace is that the methane decomposition process can become self-sustained if part of the hydrogen that is produced is used for heating requirements. Despite this, the use of electric heating is economically competitive, with a LCOH of $1.31 \text{ € kg}_{\text{H}_2}^{-1}$ and can reach values of $1.08 \text{ € kg}_{\text{H}_2}^{-1}$, due to estimates of a decrease in electricity prices, which will result from an extensive use of renewable sources.

The low-temperature methane decomposition process is a CO_2 -free technology that can help decarbonise the hydrogen production industry. It competes with methane steam reforming due to its environmental benignity and due to its economic potential. Even though electrolysis presents the same environmental advantages as methane decomposition, it is less likely to compete on economic terms. On one hand, the electricity requirements of electrolysis are quite elevated in comparison to methane decomposition. On the other hand, methane decomposition can additionally benefit from the selling of solid carbon by-product.

The use of biomethane can be another key element for an increasing interest in methane decomposition. The increasing price of natural gas in Europe, as presented in chapter 2, is paving the way for its replacement with biomethane, as it presents an economical alternative and is not dependent on geopolitical issues. Its environmental role relating carbon capture is also a great advantage to its use and may represent an extra source of income. Overall, the LCOH from methane decomposition ($2.04 \text{ € kg}_{\text{H}_2}^{-1}$) shows its competitiveness compared to the state-of-the-art hydrogen production and great potential for further price decrease if biomethane is used as feedstock and solid carbon by-product is valorised in the future.

5.1 Future Work

There is a wide range of future work that could be developed following this project and that was presented to Pixel Voltaic. There is a number of different topics that can be addressed from the methane decomposition process itself to the projection of a complex industrial plant for hydrogen production. Some of these topics are addressed below.

The use of natural gas instead of pure methane as feed stream of the process. It is common to directly use natural gas instead of pure streams of methane due to its lower cost. Even though natural gas is mainly composed of methane (*ca.* 75 %) the presence of other compounds may affect hydrogen production. Therefore, it is important to consider two aspects: the treatment of natural gas to have a stream with high purity level of methane and the influence of other natural gas compounds on hydrogen production in the methane decomposition process.

The use of air in combustion processes instead of oxygen and accounting for fuel/air mixtures. Combustion processes usually use air instead of oxygen due to its lower cost. This increases the complexity of combustion modelling as air is made from a mixture of different compounds, which results in a variety of combustion products at the outlet. Usually, it is related with NO_x emissions that are undesirable. Another important aspect to consider is the quality of the fuel-air mixture, as it influences the combustion process. An improper mixture of reactants frequently leads to the presence unburnt fuel in the exhaust gas.

Methane decomposition costs and sensitivity analysis considering the commercialisation of solid carbon and CO₂ capture benefits. In Table 4.16 it is presented the estimated values of LCOH from methane decomposition considering the commercialisation of solid carbon and CO₂ capture benefits. However, these values were not compared to scenarios where biomethane is also used in methane steam reforming, nor was provided a detailed sensitivity analysis regarding these price reductions. Subsequent economic studies should be conducted to confirm the economic competitiveness of methane decomposition and should consider the current extreme energy and economic scenarios.

Heat transfer studies. It was not considered heat losses in the heating equipment nor the homogeneity of heating inside the reactor or of the methane stream. A lower energy efficiency of the heating devices will contribute to an increase in the required input energy of the system, which results in a higher demand for commodities and increase in production costs. As for the temperature homogeneity inside the reactor, it is a crucial parameter as it can greatly influence production levels. A poor heat distribution inside the methane decomposition reactor can lead to low conversion efficiency, which can result in higher demand for methane and, consequently, higher costs.

Pressure losses in the system. In a real scale industrial plant it is important to account for pressure losses along the tubes to assure appropriate material flows throughout the system. It is important to define flow velocity and pressure, as well as pipe dimensions in order to control the flowing conditions of each material.

Analysis of separation processes. In this work it was defined that methane conversion efficiency in the reactor was 100 % and solid-gas (carbon-hydrogen) separation processes were not considered. Part of the methane that is not decomposed may flow in the outlet stream, requiring a posterior separation process. This is usually done by PSA which is an energy consuming process, but can also be done by catalytic membranes inside the reactor. It is also necessary to separate the solid carbon particles from the gaseous stream, but this is still under development.

Thermodynamic model. It is considered the ideal gas model for simplification of analysis. To consider a real scale industrial plant, the methane decomposition process has to be studied with greater detail in terms of thermodynamics. Aspen Plus software is a powerful tool that can compute a variety of thermodynamic models. The GERG2008 may be a realistic model to consider for this task, but it is not adequate to use for temperatures above 430 °C in the Aspen Plus software. Therefore, it could be useful to improve the GERG2008 model to be appropriate to use for this process.

References

- [1] UNFCCC . Paris agreement. 2015.
- [2] Secretariat-General European Commission . Communication from the commission to the european parliament, the european council, the council, the european economic and social committee and the committee of the regions the european green deal. 2015.
- [3] European Commission . Clean energy for all europeans. 2019.
- [4] European Commission . REPowerEU: affordable, secure and sustainable energy for Europe. 2022. URL: https://ec.europa.eu/info/strategy/priorities-2019-2024/european-green-deal/repowereu-affordable-secure-and-sustainable-energy-europe_pt.
- [5] BP . bp Statistical Review of World Energy 2021 2021;URL: <https://www.bp.com/content/dam/bp/business-sites/en/global/corporate/pdfs/energy-economics/statistical-review/bp-stats-review-2021-full-report.pdf>.
- [6] EEA . EEA greenhouse gases - data viewer 2021;URL: <https://www.eea.europa.eu/data-and-maps/data/data-viewers/greenhouse-gases-viewer>.
- [7] Ritchie H, Roser M, Rosado P. CO₂ and Greenhouse Gas Emissions. Our World in Data 2020;URL: <https://ourworldindata.org/co2-and-other-greenhouse-gas-emissions>.
- [8] Ritchie H, Roser M, Rosado P. Energy. Our World in Data 2020;URL: <https://ourworldindata.org/energy>.
- [9] IEA . Nuclear Power and Secure Energy Transitions. Report; IEA; 2022. URL: <https://www.iea.org/reports/nuclear-power-and-secure-energy-transitions>.
- [10] Campbell C. As Putin Threatens Nuclear Disaster, Europe Learns to Embrace Nuclear Energy Again. TIME 2022;URL: <https://time.com/6169164/ukraine-nuclear-energy-europe/>.
- [11] European Commission . Save Gas for a Safe Winter: Commission proposes gas demand reduction plan to prepare EU for supply cuts. 2022. URL: https://ec.europa.eu/commission/presscorner/detail/en/ip_22_4608.
- [12] IRENA , IEA , REN21 . Renewable Energy Policies in a Time of Transition. Report; IRENA, OECD/IEA and REN21; 2018. URL: <https://www.irena.org/publications/2018/apr/renewable-energy-policies-in-a-time-of-transition>.

- [13] IRENA . Renewable capacity highlights. International Renewable Energy Agency, Abu Dhabi 2022;URL: https://irena.org/-/media/Files/IRENA/Agency/Publication/2022/Apr/IRENA_RE_Capacity_Highlights_2022.pdf.
- [14] IRENA . Electricity storage and renewables: Costs and markets to 2030. International Renewable Energy Agency, Abu Dhabi 2017;URL: <https://www.irena.org/publications/2017/oct/electricity-storage-and-renewables-costs-and-markets>.
- [15] IEA . Innovation in Batteries and Electricity Storage. IEA, Paris 2020;URL: <https://www.iea.org/reports/innovation-in-batteries-and-electricity-storage>.
- [16] Deng D. Li-ion batteries: basics, progress, and challenges. Energy Science Engineering 2015;3(5):385–418.
- [17] Olczak M, Piebalgs A. Sector coupling: the new eu climate and energy paradigm? 2018;URL: <https://fsr.eui.eu/wp-content/uploads/QM-AX-18-017-EN-N.pdf>.
- [18] Tian Y, Zeng G, Rutt A, Shi T, Kim H, Wang J, Koettgen J, Sun Y, Ouyang B, Chen T. Promises and challenges of next-generation “beyond li-ion” batteries for electric vehicles and grid decarbonization. Chemical reviews 2020;121(3):1623–69.
- [19] Stetson NT, McWhorter S, Ahn CC. 1 - Introduction to hydrogen storage. Woodhead Publishing. ISBN 978-1-78242-362-1; 2016, p. 3–25.
- [20] Manoharan Y, Hosseini SE, Butler B, Alzahrani H, Senior BTF, Ashuri T, Krohn J. Hydrogen fuel cell vehicles; current status and future prospect. Applied Sciences 2019;9(11):2296.
- [21] IRENA . World Energy Transitions Outlook: 1.5°C Pathway. International Renewable Energy Agency, Abu Dhabi 2022;URL: <https://irena.org/publications/2022/mar/world-energy-transitions-outlook-2022>.
- [22] Maroufmashat A, Fowler M. Transition of future energy system infrastructure; through power-to-gas pathways. Energies 2017;10(8):1089.
- [23] European Hydrogen Backbone . European Hydrogen Backbone - A European hydrogen infrastructure vision covering 28 countries 2022;URL: <https://ehb.eu/files/downloads/ehb-report-220428-17h00-interactive-1.pdf>.
- [24] Pawelec G, Muron M, Bracht J, Bonnet-Cantalloube B. Clean Hydrogen - Monitor 2020. Report; Hydrogen Europe; 2020. URL: <https://hydrogeneurope.eu/wp-content/uploads/2021/11/Clean-Hydrogen-Monitor-2020.pdf>.
- [25] Züttel A. Hydrogen storage methods. Naturwissenschaften 2004;91(4):157–72.
- [26] IEA . The Future of Hydrogen. Report; 2019. URL: <https://www.iea.org/reports/the-future-of-hydrogen>.
- [27] Wijk Av. Hydrogen - a carbon-free energy carrier and commodity. Report; 2021. URL: https://hydrogeneurope.eu/wp-content/uploads/2021/11/2021.11_Hydrogen-as-a-carbon-free-energy-carrier-and-commodity-clean.pdf.

- [28] Kanellopoulos K, Busch S, De Felice M, Giaccaria S, Costescu A. Blending hydrogen from electrolysis into the european gas grid. Publications Office of the European Union 2022;URL: <https://publications.jrc.ec.europa.eu/repository/handle/JRC126763>. doi:10.2760/908387.
- [29] Simoes S, Amorim F. Using natural gas grids for transport and distribution of H₂. LNEG-Resource Economics Unit 2020;URL: https://www.lneg.pt/wp-content/uploads/2021/01/H2_redes_gas_v4_EN2.pdf.
- [30] Guelpa E, Bischi A, Verda V, Chertkov M, Lund H. Towards future infrastructures for sustainable multi-energy systems: A review. Energy 2019;184:2–21.
- [31] de BRUYN S, Jongsma C, Kampman B, Görlach B, Thie JE. Energy-intensive industries: Challenges and opportunities in energy transition. Policy Department for Economic, Scientific and Quality of Life Policies 2020;URL: [https://www.europarl.europa.eu/RegData/etudes/STUD/2020/652717/IPOL_STU\(2020\)652717_EN.pdf](https://www.europarl.europa.eu/RegData/etudes/STUD/2020/652717/IPOL_STU(2020)652717_EN.pdf).
- [32] IEA . Global Hydrogen Review 2021. Report; 2021. URL: <https://www.iea.org/reports/global-hydrogen-review-2021>.
- [33] Directorate-General for Energy , European Commission . Communication from the commission to the european parliament, the council, the european economic and social committee and the committee of the regions - a hydrogen strategy for a climate-neutral europe 2020;URL: <https://op.europa.eu/en/publication-detail/-/publication/n/5602f358-c136-11ea-b3a4-01aa75ed71a1/language-en>.
- [34] Navarro RM, Pena M, Fierro J. Hydrogen production reactions from carbon feedstocks: fossil fuels and biomass. Chemical reviews 2007;107(10):3952–91.
- [35] Muradov N, Veziroğlu T. From hydrocarbon to hydrogen–carbon to hydrogen economy. International journal of hydrogen energy 2005;30(3):225–37.
- [36] IRENA . Geopolitics of the energy transformation: The hydrogen factor. Report; 2022.
- [37] Gunderson R, Stuart D, Petersen B. The fossil fuel industry’s framing of carbon capture and storage: Faith in innovation, value instrumentalization, and status quo maintenance. Journal of Cleaner Production 2020;252:119767.
- [38] Olajire AA. Valorization of greenhouse carbon dioxide emissions into value-added products by catalytic processes. Journal of CO₂ Utilization 2013;3:74–92.
- [39] Nikolaidis P, Poullikkas A. A comparative overview of hydrogen production processes. Renewable and sustainable energy reviews 2017;67:597–611.
- [40] da Silva Veras T, Mozer TS, da Silva César A. Hydrogen: trends, production and characterization of the main process worldwide. International journal of hydrogen energy 2017;42(4):2018–33.
- [41] Zhang J, Li X, Chen H, Qi M, Zhang G, Hu H, Ma X. Hydrogen production by catalytic methane decomposition: carbon materials as catalysts or catalyst supports. International Journal of Hydrogen Energy 2017;42(31):19755–75.
- [42] Holladay JD, Hu J, King DL, Wang Y. An overview of hydrogen production technologies. Catalysis today 2009;139(4):244–60.

- [43] Ajanovic A, Sayer M, Haas R. The economics and the environmental benignity of different colors of hydrogen. *International Journal of Hydrogen Energy* 2022;47(57):24136–54.
- [44] Ashik U, Daud WW, Abbas HF. Production of greenhouse gas free hydrogen by thermocatalytic decomposition of methane—a review. *Renewable and Sustainable Energy Reviews* 2015;44:221–56.
- [45] Xu J, Froment GF. Methane steam reforming, methanation and water-gas shift: I. intrinsic kinetics. *AIChE Journal* 1989;35(1):88–96.
- [46] Gallucci F, Comite A, Capannelli G, Basile A. Steam reforming of methane in a membrane reactor: an industrial case study. *Industrial engineering chemistry research* 2006;45(9):2994–3000.
- [47] Lee JH, Trimm DL. Catalytic combustion of methane. *Fuel Processing Technology* 1995;42(2):339–59.
- [48] IEA . Hydrogen Production and Storage. Report; 2006. URL: <https://www.iea.org/reports/hydrogen-production-and-storage>.
- [49] Linde Engineering . Hydrogen (Accessed 15/07/2022) 2017;URL: https://www.linde-engineering.com/en/images/H2_1_1_e_12_150dpi_NB_tcm19-4258.pdf.
- [50] Mahler AGS . Hydrogen Generation by Steam Reforming | Mahler AGS (Accessed 15/07/2022). 2021. URL: <https://www.mahler-ags.com/en/plants/hydrogen-plant-c/>.
- [51] Zhu L, Li L, Fan J. A modified process for overcoming the drawbacks of conventional steam methane reforming for hydrogen production: Thermodynamic investigation. *Chemical Engineering Research and Design* 2015;104:792–806.
- [52] Rahimpour MR, Hesami M, Saidi M, Jahanmiri A, Farniaei M, Abbasi M. Methane steam reforming thermally coupled with fuel combustion: Application of chemical looping concept as a novel technology. *Energy Fuels* 2013;27(4):2351–62.
- [53] Linde Engineering . Steam-methane reformer (SMR) for hydrogen production (Accessed 15/07/2022). 2022. URL: https://www.linde-engineering.com/en/process-plants/furnaces_fired_heaters_incinerators_and_t-thermal/steam_reformer_furnaces/steam_reformer_for_hydrogen_production/index.html.
- [54] Pring JN, Fairlie DM. X.—the methane equilibrium. *Journal of the Chemical Society, Transactions* 1912;101:91–103.
- [55] Lau HC, Ramakrishna S, Zhang K, Radhamani AV. The role of carbon capture and storage in the energy transition. *Energy Fuels* 2021;35(9):7364–86.
- [56] Abbas HF, Daud WW. Hydrogen production by methane decomposition: a review. *International journal of hydrogen energy* 2010;35(3):1160–90.
- [57] Bode A. New process for clean hydrogen. BASF Research Press Conference 2019;URL: <https://www.basf.com/global/en/media/events/2019/basf-research-press-conference.html>.

- [58] Twigg MV. Catalyst Handbook. 2nd ed.; Routledge; 1996. ISBN 9781315138862.
- [59] Alves L, Pereira V, Lagarteira T, Mendes A. Catalytic methane decomposition to boost the energy transition: Scientific and technological advancements. *Renewable and Sustainable Energy Reviews* 2021;137:110465.
- [60] Qian JX, Chen TW, Enakonda LR, Liu DB, Basset JM, Zhou L. Methane decomposition to pure hydrogen and carbon nano materials: State-of-the-art and future perspectives. *International Journal of Hydrogen Energy* 2020;45(32):15721–43.
- [61] Suelves I, Pinilla J, Lázaro M, Moliner R, Palacios J. Effects of reaction conditions on hydrogen production and carbon nanofiber properties generated by methane decomposition in a fixed bed reactor using a nickel catalyst. *Journal of Power Sources* 2009;192(1):35–42.
- [62] Dunker AM, Kumar S, Mulawa PA. Production of hydrogen by thermal decomposition of methane in a fluidized-bed reactor—effects of catalyst, temperature, and residence time. *International journal of hydrogen energy* 2006;31(4):473–84.
- [63] Kheirollahivash M, Rashidi F, Moshrefi MM. Hydrogen production from methane decomposition using a mobile and elongating arc plasma reactor. *Plasma Chemistry and Plasma Processing* 2019;39(2):445–59.
- [64] Steinberg M. Fossil fuel decarbonization technology for mitigating global warming. *International Journal of Hydrogen Energy* 1999;24(8):771–7.
- [65] Iulianelli A, Basile A. Chapter 12 - Development of membrane reactor technology for H₂ production in reforming process for low-temperature fuel cells. Elsevier. ISBN 978-0-12-817807-2; 2020, p. 287–305.
- [66] Qian JX, Chen TW, Enakonda LR, Liu DB, Mignani G, Basset JM, Zhou L. Methane decomposition to produce CO_x-free hydrogen and nano-carbon over metal catalysts: A review. *International Journal of Hydrogen Energy* 2020;45(15):7981–8001.
- [67] Weizhong Q, Tang L, Zhanwen W, Fei W, Zhifei L, Guohua L, Yongdan L. Production of hydrogen and carbon nanotubes from methane decomposition in a two-stage fluidized bed reactor. *Applied Catalysis A: General* 2004;260(2):223–8.
- [68] Moshrefi MM, Rashidi F. Hydrogen production from methane decomposition in cold plasma reactor with rotating electrodes. *Plasma Chemistry and Plasma Processing* 2018;38(3):503–15.
- [69] Gallucci F, Fernandez E, Corengia P, van Sint Annaland M. Recent advances on membranes and membrane reactors for hydrogen production. *Chemical Engineering Science* 2013;92:40–66.
- [70] Ishihara T, Miyashita Y, Iseda H, Takita Y. Decomposition of methane over Ni/SiO₂ catalysts with membrane reactor for the production of hydrogen. *Chemistry letters* 1995;24(2):93–4.
- [71] Yun S, Oyama ST. Correlations in palladium membranes for hydrogen separation: A review. *Journal of membrane science* 2011;375(1-2):28–45.

- [72] BASF . New Technologies (Accessed 20/07/2022). 2022. URL: <https://www.basf.com/global/en/who-we-are/sustainability/we-produce-safely-and-efficiently/energy-and-climate-protection/carbon-management/innovations-for-a-climate-friendly-chemical-production.html>.
- [73] Kochendörfer K. New technology for clean high-temperature reactions (Accessed 02/08/2022) 2019;URL: <https://www.basf.com/global/en/media/events/s/2019/basf-research-press-conference.html>.
- [74] Cornejo A, Chua HT. A Process for Producing Hydrogen and Graphitic Carbon from Hydrocarbons. 20180065850 15/563,430 . 2018.
- [75] Hazer Group . Preliminary Conceptual Modelling Economic Analysis. 2018. URL: <http://hazergroup.com.au/wp-content/uploads/2018/02/43s02ddygyy15.pdf>.
- [76] CSIRO HyResource . Hazer Commercial Demonstration Plant (Accessed 28/07/2022). 2022. URL: <https://research.csiro.au/hyresource/hazer-commercial-demonstration-plant/>.
- [77] Sakowin S, Fréjus F. Microwave plasma conversion of methane for hydrogen production. AMPERE 2021 2021;:214–8.
- [78] Vander Wal R, Sengupta A, Musselman E, Skoptsov G. Microwave-driven plasma-mediated methane cracking: Product carbon characterization. C 2018;4(4):61.
- [79] Ferreira-Aparicio P, Benito MJ, Sanz JL. New trends in reforming technologies: from hydrogen industrial plants to multifuel microreformers. Catalysis Reviews 2005;47(4):491–588. Doi: 10.1080/01614940500364958.
- [80] Tran A, Aguirre A, Durand H, Crose M, Christofides PD. Cfd modeling of a industrial-scale steam methane reforming furnace. Chemical Engineering Science 2017;171:576–98.
- [81] Wilberforce T, Olabi A, Sayed ET, Elsaid K, Abdelkareem MA. Progress in carbon capture technologies. Science of The Total Environment 2021;761:143203.
- [82] Spagnolo D, Cornett L, Chuang K. Direct electro-steam reforming: a novel catalytic approach. International journal of hydrogen energy 1992;17(11):839–46.
- [83] Lu YR, Nikrityuk PA. Scale-up studies on electrically driven steam methane reforming. Fuel 2022;319:123596.
- [84] Rodat S, Abanades S, Sans JL, Flamant G. A pilot-scale solar reactor for the production of hydrogen and carbon black from methane splitting. International Journal of Hydrogen Energy 2010;35(15):7748–58.
- [85] Ma J, Jiang B, Gao Y, Yu K, Lv Z, Si-ma W, Yuan D, Tang D. A compact and high-efficiency electrified reactor for hydrogen production by methane steam reforming. International Journal of Hydrogen Energy 2022;doi:<https://doi.org/10.1016/j.ijhydene.2022.04.281>.
- [86] Rieks M, Bellinghausen R, Kockmann N, Mleczko L. Experimental study of methane dry reforming in an electrically heated reactor. International Journal of Hydrogen Energy 2015;40(46):15940–51.

- [87] Wismann ST, Engbæk JS, Vendelbo SB, Bendixen FB, Eriksen WL, Aasberg-Petersen K, Frandsen C, Chorkendorff I, Mortensen PM. Electrified methane reforming: A compact approach to greener industrial hydrogen production. *Science* 2019;364(6442):756–9.
- [88] Labrecque R, Lavoie JM. Dry reforming of methane with co₂ on an electron-activated iron catalytic bed. *Bioresource technology* 2011;102(24):11244–8.
- [89] Noritake . Hydrogen combustion technology carves out carbon neutral society (Accessed 13/08/2022) 2021;URL: https://www.noritake.co.jp/eng/noritake_dift/.
- [90] Jericho Energy Ventures . Hydrogen technologies - corporate presentation 2022;URL: https://hydrogentechnologiesinc.com/wp-content/uploads/sites/2/2022/02/Hydrogen-Technologies-Corporate-Presentation_Final-03.2022.pdf.
- [91] Montazerinejad H, Eicker U. Recent development of heat and power generation using renewable fuels: A comprehensive review. *Renewable and Sustainable Energy Reviews* 2022;165:112578.
- [92] Martinez S, Michaux G, Salagnac P, Bouvier JL. Micro-combined heat and power systems (micro-chp) based on renewable energy sources. *Energy Conversion and Management* 2017;154:262–85.
- [93] Kendall K, Kendall M. High-temperature solid oxide fuel cells for the 21st century: fundamentals, design and applications. Elsevier; 2015. ISBN 0124104835.
- [94] Hawkes A, Staffell I, Brett D, Brandon N. Fuel cells for micro-combined heat and power generation. *Energy Environmental Science* 2009;2(7):729–44.
- [95] Heywood JB. Internal combustion engine fundamentals. McGraw-Hill Education; 2018. ISBN 1260116107.
- [96] Ciniviz M, Köse H. Hydrogen use in internal combustion engine: a review. *International Journal of Automotive Engineering and Technologies* 2012;1(1):1–15.
- [97] Allan AB. Hydrogen as the fuel for a spark ignition otto cycle engine. Report; Department of Mechanical Engineering University of Toronto; 1982.
- [98] Das L. Hydrogen engines: a view of the past and a look into the future. *International Journal of Hydrogen Energy* 1990;15(6):425–43.
- [99] Park CS. Fundamentals of Engineering Economics. 4th ed.; Pearson Education; 2020. ISBN 978-1-292-26479-0.
- [100] Ross S. CapEx vs. OpEx: What’s the Difference? (Accessed 02/09/2022). Investopedia 2022;URL: <https://www.investopedia.com/ask/answers/112814/whats-the-difference-between-capital-expenditures-capex-and-operational-expenditures-opex.asp>.
- [101] Trading Economics . EU Natural Gas 2022;URL: <https://tradingeconomics.com/commodity/eu-natural-gas>.

- [102] Bhatti U. Global manufacturers signal record increase in prices paid for energy and semiconductors in February (Accessed 19/09/2022). S&P Global Market Intelligence 2022;URL: <https://ihsmarkit.com/research-analysis/global-manufacturers-signal-record-increase-in-prices-paid-for-energy-and-semiconductors-in-february-mar22.html>.
- [103] J.P.Morgan . Supply Chain Issues and Autos: When Will the Chip Shortage End? (Accessed 19/09/2022). 2022. URL: <https://www.jpmorgan.com/insights/research/supply-chain-chip-shortage>.
- [104] Mendes A, Pedrero C, Catarino M. Catalytic Methane Decomposition and Catalyst Regeneration, Methods and Uses Thereof. PCT/IB2019/060868. 2020.
- [105] McHaney R. Understanding computer simulation. Bookboon; 2009.
- [106] Elliott JR, Lira CT, Lira CT. Introductory chemical engineering thermodynamics; vol. 668. Prentice Hall Upper Saddle River, NJ; 2012.
- [107] Perry R, Green D, Maloney J. Perry's Chemical Engineers' Handbook. McGraw-Hill; 1999. ISBN 9780071355407.
- [108] Smith JM, Ness HCV, Abbott MM, Swihart MT. Introduction to Chemical Engineering Thermodynamics. Eighth ed.; 2 Perm Plaza, New York, NY 10121: McGraw-Hill Education; 2018. ISBN 978-1-259-69652-7.
- [109] Cheng S, Li F, Shang F, Ma W, Jin H, Sakoda N, Zhang X, Guo L. A review of experimental researches on the thermophysical properties of hydrogen-containing mixtures at high temperatures and high pressures. Journal of Chemical Engineering Data 2021;66(9):3361–85.
- [110] Gaydon AG, Wolfhard HG. Flames, Their Structure, Radiation, and Temperature. 4th ed.; Chapman Hall; 1979. ISBN 978-0470264812.
- [111] Newnan DG, Eschenbach TG, Lavelle JP. ENGINEERING ECONOMIC ANALYSIS. 11th ed.; Oxford University Press, Inc.; 2012. ISBN 978-0-19-977804-1.
- [112] Song H, Liu Y, Bian H, Shen M, Lin X. Energy, environment, and economic analyses on a novel hydrogen production method by electrified steam methane reforming with renewable energy accommodation. Energy Conversion and Management 2022;258:115513.
- [113] UN . Fragile economic recovery from COVID-19 pandemic upended by war in Ukraine (Accessed 14/09/2022) 2022;URL: <https://www.un.org/en/desa/fragile-economic-recovery-covid-19-pandemic-upended-war-ukraine>.
- [114] Trading Economics . Euro Dollar Exchange Rate - EUR/USD 2022;URL: <https://tradingeconomics.com/euro-area/currency>.
- [115] Direção-Geral de Energia e Geologia . Roteiro e Plano de Ação para o Hidrogénio em Portugal. 2019. ISBN 978-972-8268-51-0. URL: <https://www.dgeg.gov.pt/media/d14dduhz/p3-roteiro-e-plano-de-a%C3%A7%C3%A3o-para-o-hidrog%C3%A9nio-em-portugal.pdf>.

- [116] S&P Global . GASTECH 2021: European gas industry calls for political support on hydrogen (Accessed 18/09/2022) 2021;URL: <https://www.spglobal.com/commodityinsights/en/market-insights/latest-news/energy-transition/092321-gastech-2021-european-gas-industry-calls-for-political-support-on-hydrogen>.
- [117] EBA . A way out of the EU gas price crisis with biomethane (Accessed 25/09/2022). 2022. URL: https://www.europeanbiogas.eu/a-way-out-of-the-eu-gas-price-crisis-with-biomethane/#_ftn1.
- [118] Micari M, Agrawal KV. Oxygen enrichment of air: Performance guidelines for membranes based on techno-economic assessment. *Journal of Membrane Science* 2022;641:119883.
- [119] Tiijonen T. Techno-economic analysis of methane decomposition process a scale-up study of three reactor types. Thesis; 2021. URL: <https://trepo.tuni.fi/bitstream/handle/10024/133575/TiijonenTuomas.pdf?sequence=2>.
- [120] Cappannelli M, McGlade C, Zeniewski P, Feuvre PL, Gould T. Outlook for biogas and biomethane: Prospects for organic growth. Report; IEA; 2020. URL: <https://www.iea.org/reports/outlook-for-biogas-and-biomethane-prospects-for-organic-growth>.
- [121] Sopena C, Diéguez P, Sainz D, Urroz J, Guelbenzu E, Gandía L. Conversion of a commercial spark ignition engine to run on hydrogen: Performance comparison using hydrogen and gasoline. *international journal of hydrogen energy* 2010;35(3):1420–9.
- [122] Llanos M. Hydrogen cars ready to roll — for a price (Accessed 06/09/2022) 2004;URL: <https://www.nbcnews.com/id/wbna4563676>.
- [123] Taljegard M, Brynolf S, Grahn M, Andersson K, Johnson H. Cost-effective choices of marine fuels in a carbon-constrained world: results from a global energy model. *Environmental science technology* 2014;48(21):12986–93.
- [124] Horvath S, Fasihi M, Breyer C. Techno-economic analysis of a decarbonized shipping sector: Technology suggestions for a fleet in 2030 and 2040. *Energy Conversion and Management* 2018;164:230–41.
- [125] Turton R, Bailie RC, Whiting WB, Shaeiwitz JA. Analysis, synthesis and design of chemical processes. Pearson Education; 2008. ISBN 0132459183.
- [126] Keipi T, Tolvanen H, Kontinen J. Economic analysis of hydrogen production by methane thermal decomposition: Comparison to competing technologies. *Energy Conversion and Management* 2018;159:264–73.
- [127] Trading Economics . EU Carbon Permits. 2022. URL: <https://tradingeconomics.com/commodity/carbon>.
- [128] IRENA . Green Hydrogen Cost Reduction: scaling up electrolyzers to meet the 1.5°C climate goal 2020;URL: https://www.irena.org/-/media/Files/IRENA/Agency/Publication/2020/Dec/IRENA_Green_hydrogen_cost_2020.pdf.

Appendix A

EES models

A.1 Hydrogen Engine

```

M_h2=molar mass(H2)
M_o2=molar mass(O2)
M_h2o=molar mass(H2O)
M_mix=x_h2_r*M_h2+x_o2_r*M_o2+x_h2o_r*M_h2o

R_mix=R#/M_mix

n_h2_r=1
n_o2_r=1/2
n_h2o_r=a
n_r=n_h2_r+n_o2_r+n_h2o_r

m_h2_r=n_h2_r*M_h2
m_o2_r=n_o2_r*M_o2
m_h2o_r=n_h2o_r*M_h2o
m_r=m_h2_r+m_o2_r+m_h2o_r

x_h2_r=n_h2_r/n_r
x_o2_r=n_o2_r/n_r
x_h2o_r=n_h2o_r/n_r

z_h2_r=m_h2_r/m_r
z_o2_r=m_o2_r/m_r
z_h2o_r=m_h2o_r/m_r
z_h2o_r=0,1

T_e_h2=25
P_e_h2=101,3
T_e_o2=25
P_e_o2=101,3
T_e_h2o=550
P_e_h2o=101,3

"Mix H2,O2,H2O-----"
m_h2_r*h_0_h2+m_o2_r*h_0_o2+m_h2o_r*h_0_h2o=m_r*h_1
m_h2_r*v_0_h2+m_o2_r*v_0_o2+m_h2o_r*v_0_h2o=m_r*v_1

h_0_h2=enthalpy(H2;T=T_e_h2)
h_0_o2=enthalpy(O2;T=T_e_o2)
h_0_h2o=enthalpy(H2O;T=T_e_h2o)
v_0_h2=volume(H2;T=T_e_h2;P=P_e_h2)
v_0_o2=volume(O2;T=T_e_o2;P=P_e_o2)
v_0_h2o=volume(H2O;T=T_e_h2o;P=P_e_h2o)

P_1=101,3
T_1+273,15=P_1*v_1/R_mix

"2-----"
r_c=10
v_2=v_1/r_c
P_2=P_e_h2*(r_c)^gamma
(T_2+273,15)=P_2*v_2/(R_mix)

c_p=z_h2_r*cp(H2;T=(T_1+T_2)/2)+z_o2_r*cp(O2;T=(T_1+T_2)/2)+z_h2o_r*cp(H2O;T=(T_1+T_2)/2)
c_v=z_h2_r*cv(H2;T=(T_1+T_2)/2)+z_o2_r*cv(O2;T=(T_1+T_2)/2)+z_h2o_r*cv(H2O;T=(T_1+T_2)/2)
gamma=c_p/c_v

s_1=z_h2_r*entropy(H2;T=T_1;P=P_1)+z_o2_r*entropy(O2;T=T_1;P=P_1)+z_h2o_r*entropy(H2O;T=T_1;P=P_1)
s_2=z_h2_r*entropy(H2;T=T_2;P=P_2)+z_o2_r*entropy(O2;T=T_2;P=P_2)+z_h2o_r*entropy(H2O;T=T_2;P=P_2)
h_2=(m_h2o_r*enthalpy(H2O;T=T_2)+m_h2_r*enthalpy(H2;T=T_2)+m_o2_r*enthalpy(O2;T=T_2))/m_r

W_dot_c=m_r*c_v*(T_1-T_2)

```

```

"Combustion+Dissociation-----"

"H-----"
2+2*a=2*n_h2o_p+2*n_h2_p

"O-----"
1+a=n_h2o_p+2*n_o2_p

n_p=n_h2o_p+n_h2_p+n_o2_p

"Kp-dissociation-----"
K_P_2=((n_h2o_p^2)*(n_p))/((n_h2_p^2)*n_o2_p*(P_2*10^(-2)))
K_P_2=K_P^2

K_P=interpolate('T-K_P';T';K_P';T=(T_3+273,15);19;22)

"products-----"
m_p=n_h2_p*M_h2+n_o2_p*M_o2+n_h2o_p*M_h2o

z_h2o_p=(n_h2o_p*M_h2o)/m_p
z_h2_p=(n_h2_p*M_h2)/m_p
z_o2_p=(n_o2_p*M_o2)/m_p

m_h2o_p=(n_h2o_p*M_h2o)
m_h2_p=(n_h2_p*M_h2)
m_o2_p=(n_o2_p*M_o2)

DELTA_U=DELTA_U_p+DELTA_U_reacao+DELTA_U_r
DELTA_U_p=m_h2o_p*intenergy(H2O;T=T_3)+m_h2_p*intenergy(H2;T=T_3)+m_o2_p*intenergy(O2;T=T_3)-m_h2o_p*
intenergy(H2O;T=25)-m_h2_p*intenergy(H2;T=25)-m_o2_p*intenergy(O2;T=25)
DELTA_U_reacao=-lowerheatingvalue(H2)*(m_h2_r-m_h2_p)-R#*(298,15)*(n_p-n_r)
DELTA_U_r=(m_h2_r*intenergy(H2;T=25)+m_o2_r*intenergy(O2;T=25)+m_h2o_r*intenergy(H2O;T=25))-(m_h2_r*
intenergy(H2;T=T_2)+m_o2_r*intenergy(O2;T=T_2)+m_h2o_r*intenergy(H2O;T=T_2))
DELTA_U=0

"3-----"
x_h2o_p=n_h2o_p/n_p
x_h2_p=n_h2_p/n_p
x_o2_p=n_o2_p/n_p

M_pr=x_h2_p*M_h2+x_o2_p*M_o2+x_h2o_p*M_h2o
R_p=R#/M_pr

v_3=v_2
P_3=(R_p*(T_3+273,15))/v_3
h_3=(m_h2o_p*enthalpy(H2O;T=T_3)+m_h2_p*enthalpy(H2;T=T_3)+m_o2_p*enthalpy(O2;T=T_3))/m_p
s_3=(m_h2o_p*entropy(H2O;T=T_3;P=P_3)+m_h2_p*entropy(H2;T=T_3;P=P_3)+m_o2_p*entropy(O2;T=T_3;P=P_3))/m_p

DELTA_h=h_3-h_2
DELTA_h_flow=m_p*h_3-m_r*h_2

"Estado 4-----"
v_4=v_1
s_4=s_3

r_c_34=v_3/v_4
P_4=P_3*(r_c_34)^gamma_34
(T_4+273,15)=P_4*v_4/(R_p)
h_4=(m_h2o_p*enthalpy(H2O;T=T_4)+m_h2_p*enthalpy(H2;T=T_4)+m_o2_p*enthalpy(O2;T=T_4))/m_p

c_p_34=z_h2_p*cp(H2;T=(T_3+T_4)/2)+z_o2_p*cp(O2;T=(T_3+T_4)/2)+z_h2o_p*cp(H2O;T=(T_3+T_4)/2)
c_v_34=z_h2_p*cv(H2;T=(T_3+T_4)/2)+z_o2_p*cv(O2;T=(T_3+T_4)/2)+z_h2o_p*cv(H2O;T=(T_3+T_4)/2)
gamma_34=c_p_34/c_v_34

```

```

W_dot_e=m_p*c_v_34*(T_3-T_4)
W_dot_c_i=W_dot_e+W_dot_c
eta_f_i=1-(1/r_c^(gama-1))

"5 -----"
P_5=P_e_h2
h_5=h_4
h_5=(m_h2o_p*enthalpy(H2O;T=T_5)+m_h2_p*enthalpy(H2;T=T_5)+m_o2_p*enthalpy(O2;T=T_5))/m_p
v_5=(m_h2o_p*volume(H2O;T=T_5;P=P_5)+m_h2_p*volume(H2;T=T_5;P=P_5)+m_o2_p*volume(O2;T=T_5;P=P_5))/m_p
s_5=(m_h2o_p*entropy(H2O;T=T_5;P=P_5)+m_h2_p*entropy(H2;T=T_5;P=P_5)+m_o2_p*entropy(O2;T=T_5;P=P_5))/m_p

"Reactor heating-----"
T_6=550
h_6=(m_h2o_p*enthalpy(H2O;T=T_6)+m_h2_p*enthalpy(H2;T=T_6)+m_o2_p*enthalpy(O2;T=T_6))/m_p
v_6=(m_h2o_p*volume(H2O;T=T_6;P=P_5)+m_h2_p*volume(H2;T=T_6;P=P_5)+m_o2_p*volume(O2;T=T_6;P=P_5))/m_p
s_6=(m_h2o_p*entropy(H2O;T=T_6;P=P_5)+m_h2_p*entropy(H2;T=T_6;P=P_5)+m_o2_p*entropy(O2;T=T_6;P=P_5))/m_p

Q_dot_reator=m_p*alpha*eta_reator*(h_5-h_6)
Q_dot_reator=355376+514044
eta_reator=1
m_r*alpha*z_h2_r/M_h2=n_dot_h2_reator
Q_dot_reator=m_dot_6*(h_5-h_6)

"Methane pre-heating-----"
T_7=120
h_7=(m_h2o_p*enthalpy(H2O;T=T_7)+m_h2_p*enthalpy(H2;T=T_7)+m_o2_p*enthalpy(O2;T=T_7))/m_p
v_7=(m_h2o_p*volume(H2O;T=T_7;P=P_5)+m_h2_p*volume(H2;T=T_7;P=P_5)+m_o2_p*volume(O2;T=T_7;P=P_5))/m_p
s_7=(m_h2o_p*entropy(H2O;T=T_7;P=P_5)+m_h2_p*entropy(H2;T=T_7;P=P_5)+m_o2_p*entropy(O2;T=T_7;P=P_5))/m_p

Q_dot_ch4=((m_dot_6+m_7)*(1-0.142))*(h_6-h_7)
Q_dot_ch4=m_ch4*(enthalpy(Methane;T=500;P=P_5)-enthalpy(Methane;T=25;P=P_5))
eta_ch4=1
m_ch4=160
m_dot_total=(m_dot_6+m_7)

W_dot_c180=m_dot_total*c_v*(T_1-T_2)
W_dot_e180=m_dot_total*c_v_34*(T_3-T_4)
W_dot_c_i180=W_dot_e180+W_dot_c180
eta_f_i180=1-(1/r_c^(gama-1))

```

SOLUTION

Unit Settings: SI C kPa kJ mass deg

a = 0.1111 [kmol]	$\alpha = 8,701$ [1/h]
$c_p = 2,454$ [kJ/(kg*k)]	$c_{p,34} = 3,223$ [kJ/(kg*k)]
$c_v = 1,784$ [kJ/(kg*k)]	$c_{v,34} = 2,693$ [kJ/(kg*k)]
$\Delta h = 1668$ [kJ/kg]	$\Delta h_{flow} = 33389$ [kJ]
$\Delta U = 0$ [kJ]	$\Delta U_p = 178928$ [kJ]
$\Delta U_r = -17623$ [kJ]	$\Delta U_{reacao} = -161305$ [kJ]
$\eta_{ch4} = 1$ [dim]	$\eta_U = 0,5783$ [dim]
$\eta_{f180} = 0,5783$ [dim]	$\eta_{reator} = 1$ [dim]
$\text{gama} = 1,375$ [dim]	$\text{gama}_{34} = 1,197$ [dim]
$h_{0,h2} = 0$ [kJ/kg]	$h_{0,h2o} = -12374$ [kJ/kg]
$h_{0,o2} = 0$ [kJ/kg]	$h_1 = -1237$ [kJ/kg]
$h_2 = -130,7$ [kJ/kg]	$h_3 = 1537$ [kJ/kg]
$h_4 = -3323$ [kJ/kg]	$h_5 = -3323$ [kJ/kg]
$h_6 = -8314$ [kJ/kg]	$h_7 = -9248$ [kJ/kg]
$K_P = 1,347$	$K_{P,2} = 1,814$
$m_7 = 113,9$ [kg/h]	$m_{ch4} = 160$ [kg/h]

$\dot{m}_6 = 174,2 \text{ [kg/h]}$
 $M_{H_2} = 2,016 \text{ [kg/kmol]}$
 $m_{H_2O,p} = 14,08 \text{ [kg]}$
 $m_{H_2,p} = 0,6643 \text{ [kg]}$
 $M_{mix} = 12,42 \text{ [kg/kmol]}$
 $m_{O_2,p} = 5,272 \text{ [kg]}$
 $m_p = 20,02 \text{ [kg]}$
 $m_r = 20,02 \text{ [kg]}$
 $n_{H_2O,p} = 0,7816 \text{ [kmol]}$
 $n_{H_2,p} = 0,3295 \text{ [kmol]}$
 $n_{O_2,p} = 0,1647 \text{ [kmol]}$
 $n_p = 1,276 \text{ [kmol]}$
 $P_1 = 101,3 \text{ [kPa]}$
 $P_3 = 9954 \text{ [kPa]}$
 $P_5 = 101,3 \text{ [kPa]}$
 $P_{e,H_2O} = 101,3 \text{ [kPa]}$
 $\dot{Q}_{ch4} = 230656 \text{ [kJ/h]}$
 $r_c = 10$
 $R_{mix} = 0,6892 \text{ [kJ/(kg}\cdot\text{K)]}$
 $s_1 = 12,96 \text{ [kJ/(kg}\cdot\text{K)]}$
 $s_3 = 15,5 \text{ [kJ/(kg}\cdot\text{K)]}$
 $s_5 = 16,48 \text{ [kJ/(kg}\cdot\text{K)]}$
 $s_7 = 11,77 \text{ [kJ/(kg}\cdot\text{K)]}$
 $T_2 = 519,8 \text{ [C]}$
 $T_4 = 2364 \text{ [C]}$
 $T_6 = 550$
 $T_{e,H_2} = 25 \text{ [C]}$
 $T_{e,O_2} = 25 \text{ [C]}$
 $v_{O,H_2O} = 3,75 \text{ [m}^3\text{/kg]}$
 $v_1 = 2,209 \text{ [m}^3\text{/kg]}$
 $v_3 = 0,2209 \text{ [m}^3\text{/kg]}$
 $v_5 = 13,8 \text{ [m}^3\text{/kg]}$
 $v_7 = 2,057 \text{ [m}^3\text{/kg]}$
 $\dot{W}_{c180} = -235750 \text{ [kJ/h]}$
 $\dot{W}_{c1180} = 937106 \text{ [kJ/h]}$
 $\dot{W}_{e180} = 1172856,84 \text{ [kJ/h]}$
 $x_{H_2O,r} = 0,06896$
 $x_{H_2,r} = 0,6207$
 $x_{O_2,r} = 0,3103$
 $z_{H_2O,r} = 0,1$
 $z_{H_2,r} = 0,1007$
 $z_{O_2,r} = 0,7993$

$\dot{m}_{total} = 288,1 \text{ [kg/h]}$
 $M_{H_2O} = 18,02 \text{ [kg/kmol]}$
 $m_{H_2O,r} = 2,002 \text{ [kg]}$
 $m_{H_2,r} = 2,016 \text{ [kg]}$
 $M_{O_2} = 32 \text{ [kg/kmol]}$
 $m_{O_2,r} = 16 \text{ [kg]}$
 $M_{pr} = 15,69 \text{ [kg/kmol]}$
 $\dot{n}_{H_2,restor} = 8,701 \text{ [kmol/h]}$
 $n_{H_2O,r} = 0,1111 \text{ [kmol]}$
 $n_{H_2,r} = 1 \text{ [kmol]}$
 $n_{O_2,r} = 0,5 \text{ [kmol]}$
 $n_r = 1,611 \text{ [kmol]}$
 $P_2 = 2402 \text{ [kPa]}$
 $P_4 = 632,8 \text{ [kPa]}$
 $P_{e,H_2} = 101,3 \text{ [kPa]}$
 $P_{e,O_2} = 101,3 \text{ [kPa]}$
 $\dot{Q}_{restor} = 869420 \text{ [kJ/h]}$
 $r_{c,34} = 0,1$
 $R_p = 0,5299 \text{ [kJ/(kg}\cdot\text{K)]}$
 $s_2 = 12,95 \text{ [kJ/(kg}\cdot\text{K)]}$
 $s_4 = 15,5 \text{ [kJ/(kg}\cdot\text{K)]}$
 $s_6 = 13,36 \text{ [kJ/(kg}\cdot\text{K)]}$
 $T_1 = 61,21 \text{ [C]}$
 $T_3 = 3876 \text{ [C]}$
 $T_5 = 2364 \text{ [C]}$
 $T_7 = 120$
 $T_{e,H_2O} = 550 \text{ [C]}$
 $v_{O,H_2} = 12,14 \text{ [m}^3\text{/kg]}$
 $v_{O,O_2} = 0,7647 \text{ [m}^3\text{/kg]}$
 $v_2 = 0,2209 \text{ [m}^3\text{/kg]}$
 $v_4 = 2,209 \text{ [m}^3\text{/kg]}$
 $v_6 = 4,306 \text{ [m}^3\text{/kg]}$
 $\dot{W}_c = -16380 \text{ [kJ]}$
 $\dot{W}_{c,1} = 65111 \text{ [kJ]}$
 $\dot{W}_e = 81491 \text{ [kJ]}$
 $x_{H_2O,p} = 0,6126$
 $x_{H_2,p} = 0,2583$
 $x_{O_2,p} = 0,1291$
 $z_{H_2O,p} = 0,7035$
 $z_{H_2,p} = 0,03318$
 $z_{O_2,p} = 0,2634$

A.2 Hydrogen Furnace

```

M_h2=molarmass(H2)
M_o2=molarmass(O2)
M_h2o=molarmass(H2O)
M_mix=x_h2_r*M_h2+x_o2_r*M_o2

R_mix=R#/M_mix

n_h2_r=1
n_o2_r=1/2
n_r=n_h2_r+n_o2_r

m_h2_r=n_h2_r*M_h2
m_o2_r=n_o2_r*M_o2
m_r=m_h2_r+m_o2_r

x_h2_r=n_h2_r/n_r
x_o2_r=n_o2_r/n_r

z_h2_r=m_h2_r/m_r
z_o2_r=m_o2_r/m_r

n_h2o_p=1
m_h2o_p=n_h2o_p*M_h2o

"combustion-----"
DELTA_H=DELTA_H_p+DELTA_H_reacao+DELTA_H_r

DELTA_H_p=(m_dot_total)*(enthalpy(H2O;T=T_2)-enthalpy(H2O;T=25))
DELTA_H_reacao=-lowerheatingvalue(H2)*(m_dot_total)*z_h2_r
DELTA_H_r=-((m_dot_total)*z_h2_r*enthalpy(H2;T=T_1)+(m_dot_total)*z_o2_r*enthalpy(O2;T=T_1))
DELTA_H=-Q_dot_reactor

T_1=25
h_1=-DELTA_H_r/m_r
H_11=-DELTA_H_r
h_2=enthalpy(H2O;T=T_2)

Q_dot_reactor=355376+514044

"methane pre-heating-----"
T_3=200
P_3=101,3
h_3=enthalpy(H2O;T=T_3)

Q_dot_ch4=m_dot_total*(h_2-h_3)
Q_dot_ch4=m_ch4*(enthalpy(Methane;T=500;P=P_3)-enthalpy(Methane;T=25;P=P_3))
eta_ch4=1
m_ch4=160

m_dot_h2_total=(m_dot_total)*z_h2_r
m_dot_o2_total=(m_dot_total)*z_o2_r

n_dot_h2_total=m_dot_h2_total/M_h2
n_dot_o2_total=m_dot_o2_total/M_o2

SOLUTION
Unit Settings: SI C kPa kJ mass deg
ΔH = -869420 [kJ/h]
ΔH_r = 0 [kJ/h]
η_ch4 = 1
ΔH_p = 258544 [kJ/h]
ΔH_reacao = -1,128E+06 [kJ/h]
h1 = 4,517E+15 [kJ/kg]

```

$H_{11} = 0$ [kJ/h]
 $h_3 = -13090$ [kJ/kg]
 $\dot{m}_{H_2, total} = 9,404$ [kg/h]
 $\dot{m}_{total} = 84,04$ [kg/h]
 $M_{H_2O} = 18,02$ [kg/kmol]
 $\dot{m}_{H_2, r} = 2,016$ [kg/h]
 $M_{O_2} = 32$ [kg/kmol]
 $\dot{m}_r = 18,02$ [kg/h]
 $\dot{n}_{O_2, total} = 2,332$ [kmol/h]
 $\dot{n}_{H_2, r} = 1$ [kmol/h]
 $\dot{n}_r = 1,5$ [kmol/h]
 $\dot{Q}_{CH_4} = 230656$ [kJ/h]
 $R_{mix} = 0,6923$ [kJ/(kg*K)]
 $T_2 = 1377$ [C]
 $x_{H_2, r} = 0,6667$
 $z_{H_2, r} = 0,1119$

$h_2 = -10345$ [kJ/kg]
 $\dot{m}_{CH_4} = 160$ [kg/h]
 $\dot{m}_{O_2, total} = 74,632$ [kg/h]
 $M_{H_2} = 2,016$ [kg/kmol]
 $\dot{m}_{H_2O, p} = 18,02$ [kg/h]
 $M_{mix} = 12,01$ [kg/kmol]
 $\dot{m}_{O_2, r} = 16$ [kg/h]
 $\dot{n}_{H_2, total} = 4,665$ [kmol/h]
 $\dot{n}_{H_2O, p} = 1$ [kmol/h]
 $\dot{n}_{O_2, r} = 0,5$ [kmol/h]
 $P_3 = 101,3$ [kPa]
 $\dot{Q}_{reactor} = 869420$
 $T_1 = 25$ [C]
 $T_3 = 200$ [C]
 $x_{O_2, r} = 0,3333$
 $z_{O_2, r} = 0,8881$

Appendix B

Combustion Properties

Fuel	Formula (phase) ^a	Molecular weight	Specific gravity (density, ^b kg/dm ³)	Heat of vaporization, kJ/kg ^c	Specific heat		Higher heating value, MJ/kg	Lower heating value, MJ/kg	LHV of stoich. mixture, MJ/kg ^d	(A/F) _s	(F/A) _s	Fuel octane rating	
					Liquid, kJ/kg · K	Vapor c _p , kJ/kg · K						RON	MON
<i>Practical fuels^e</i>													
Gasoline	C ₈ H _{18.29} (l)	~100	0.72–0.78	350	2.4	~1.7	46.3	43.0	2.76	14.6	0.0685	91–99	82–89
E10 gasoline	C ₈ H _{18.46} O _{0.6430} (l)	~100	~0.75	400	2.4	~1.7	44.5	41.5	2.82	13.7	0.0730	96 ^f	85 ^f
Light diesel	C ₁₂ H ₂₆ (l)	~170	0.78–0.84	270	2.2	~1.7	46.1	43.2	2.79	14.5	0.0690	—	—
Heavy diesel	C ₁₆ H ₃₄ (l)	~200	0.82–0.88	230	1.9	~1.7	45.5	42.8	2.85	14.4	0.0697	—	—
Natural gas	C ₄ H _{9.88} N _{0.16} (g)	~18	(~0.79)	—	—	~2	50	45	2.9	15.7 ^f	0.0637	—	—
<i>Pure hydrocarbons</i>													
Methane	CH ₄ (g)	16.04	(0.72)	509	0.63	2.2	55.5	50.0	2.72	17.23	0.0580	120	120
Propane	C ₃ H ₈ (g)	44.10	0.51 (2.0)	426	2.5	1.6	50.4	46.4	2.75	15.67	0.0638	112	97
Isooctane	C ₈ H ₁₈ (l)	114.23	0.692	308	2.1	1.63	47.8	44.3	2.75	15.13	0.0661	100	100
Cetane	C ₁₆ H ₃₄ (l)	226.44	0.773	358	2.2	1.6	47.3	44.0	2.78	14.82	0.0675	—	—
Benzene	C ₆ H ₆ (l)	78.11	0.879	433	1.72	1.1	41.9	40.2	2.82	13.27	0.0753	125	115
Toluene	C ₇ H ₈ (l)	92.14	0.867	412	1.68	1.1	42.5	40.6	2.79	13.50	0.0741	120	109
<i>Alcohols</i>													
Methanol	CH ₃ O(l)	32.04	0.792	1100	2.6	1.72	22.7	20.0	2.68	6.47	0.155	109	89
Ethanol	C ₂ H ₅ O(l)	46.07	0.785	900	2.5	1.93	29.7	26.9	2.69	9.00	0.111	109	90
<i>Other fuels</i>													
Carbon	C(s)	12.01	~2	—	—	—	33.8	33.8	2.70	11.51	0.0869	—	—
Carbon monoxide	CO(g)	28.01	(1.25)	—	—	1.05	10.1	10.1	2.91	2.467	0.405	106	—
Hydrogen	H ₂ (g)	2.015	(0.090)	—	—	1.44	142.0	120.0	3.40	34.3	0.0292	120–140	—

^a(l) liquid phase; (g) gaseous phase; (s) solid phase.

^bDensity in kg/m³ at 0°C and 1 atm.

^cAt 1 atm and 25°C for liquid fuels; at 1 atm and boiling temperature for gaseous fuels.

^dBetween 3.5 and 3.7 MJ/m³.

^e10% ethanol adds some 2–5 octane numbers: so RON and MON depend on rating of base gasoline.

^f(A/F)_s influenced by N₂ and CO₂ content.

RON, research octane number; MON, motor octane number.

Figure B.1 – Combustion properties of different fuels [95].