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TESI DI LAUREA

ASSESSMENT OF HYDROGEN PRODUCTION FROM SOLID WASTE PYROGASIFICATION: TECHNICAL FEASIBILITY, ENVIRONMENTAL IMPACT, AND COST-BENEFIT ANALYSIS

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SMR: Steam methane reforming

WGS: Water gas shift

USA: United States of America

EU: European Union

GHG: Greenhouse gas

CCS: Carbon capture storage

SEWGS: Sorption-Enhanced Water Gas Shift

RDF: Refuse-derived fuel

AEC: Alkaline electrolysis cell

AEM: Anion exchange membrane

PEM: Proton exchange membrane

PEMEC: Polymer electrolyte membrane

SOEC: Solid oxide electrolysis cell

LHV: Lower heating value

HTS: High temperature shift

MTS: Medium temperature shift

LTS: Low temperature shift

HER: Hydrogen evolution reaction

OER: Oxygen evolution reaction

MEA: Membrane electrode assemblies

PSA: Pressure swing adsorption

BFD: Block flow diagram

PFD: Process flow diagram

ABSTRACT

The global accumulation of plastic waste, particularly non-recyclable types, has become an escalating environmental issue, contributing to pollution in landfills and industrial sectors. The durability of plastics, combined with the inefficiency of current recycling technologies, creates significant challenges for waste management systems and increases the pressure on industrial infrastructures to develop more sustainable solutions. The growing accumulation of non-recyclable plastic waste and the increasing demand for sustainable energy sources present significant environmental and societal challenges. This thesis investigates the technical and economic feasibility of hydrogen production through the pyrolysis of plastic waste, with a detailed cost-benefit analysis of process configurations. Advanced technologies such as Steam Methane Reforming (SMR) and Water-Gas Shift (WGS) reactors were implemented, with simulations conducted using the COCO Simulator, coupled with hydrogen separation via polystyrene membranes. The primary objective was to assess whether sufficient hydrogen can be produced and efficiently separated to support commercial applications.

Simulation results revealed that the integration of SMR and WGS led to a significant enhancement in hydrogen yield. Additionally, the economic analysis demonstrated the potential for improved sustainability by incorporating liquid CO_2 recovery as an additional revenue stream. These findings indicate that retrofitting existing pyrolysis plants with hydrogen production capabilities could offer a viable solution to plastic waste management while contributing to a cleaner energy future.

Chapter 1

OVERVIEW OF PLASTIC WASTE STATE OF ART AND HYDROGEN PRODUCTION TECHNOLOGIES

Not all plastic can be recycled. Not all plastic is the same. There are lands, sea sides and island covered in plastic and what can be done is to reuse or recycle the most common material nowadays. Global plastics production was 200 million tons in the last year and most of it is not recycled. In the USA, the world's biggest plastics polluter, in 2021 only 5% of over 50 million of domestic plastic waste produced was recycled (DW, 2023).

1.1 State of art of the current plastic waste situation

The problem of non-recyclable plastics is a critical challenge for the environment and society. Most of the plastic produced globally is not recyclable, contributing to the accumulation of waste in oceans and landfills. Non-recyclable plastics can persist for centuries, releasing microplastics that contaminate marine and terrestrial ecosystems (Geyer et al., 2017). In Europe, the management of plastic waste presents significant challenges, particularly in terms of environmental sustainability and resource efficiency. The predominant method for disposing of plastic waste is incineration, which, while effective in reducing the volume of waste, also contributes to greenhouse gas emissions. Recycling is the second most common method, but it remains limited in its scope and effectiveness. Approximately 25% of plastic waste still ends up in landfills, where it can persist for centuries, contributing to long-term environmental degradation.

One of the key issues in European plastic waste management is the reliance on exporting plastic waste for recycling. Currently, half of the plastic collected for recycling in Europe is sent to non-EU countries, primarily due to the lack of adequate facilities, advanced technology, and financial resources within the EU to handle the waste locally. In 2020, the EU exported 32.7 million tons of waste, including not only plastic but also ferrous and non-ferrous metal scraps, paper, textiles, and glass (European Parliament, 2018). The primary destinations for these exports are Turkey, India, and Egypt. Historically, a significant portion of Europe's plastic waste exports were sent to China. However, China's recent ban on plastic waste imports has forced Europe to reconsider its waste management strategies.

1.1.1 Plastic recycling rates

The low recycling rates in Europe are particularly concerning, as they result in substantial economic and environmental losses. It is estimated that 95% of the value of plastic packaging materials is lost after a very short first-use cycle. Moreover, the production and incineration of plastic are major contributors to greenhouse gas emissions. In 2019, over 850 million tons of greenhouse gases were emitted globally due to these processes. If current trends continue, these emissions could rise to 2.8 billion tons by 2050 (European Parliament, 2018). The major problem hindering plastic recycling concerns the quality and cost of recycled products compared to brand-new ones. Companies that process plastic require a large amount of recycled plastic, production must meet very stringent quality standards, and the price must remain competitive.

1.2 Energy crisis: problem and possible solutions

In addition to the issue of plastic waste, currently the world is in a global energy crisis that keeps getting worse. Europe is having the major implications for markets, policies, and economies worldwide. Fossil fuels are the main suppliers of the primary energy demand. Their prices are still rising and the concern about greenhouse gas emissions coming from burning fossil fuels started to alarm the future of the energy sector. CO_2 emissions from global fossil fuel combustion saw a record rise in 2021 [fig 1] and high fossil fuel prices and record levels of emissions offer strong reasons to move away from reliance on these fuels.

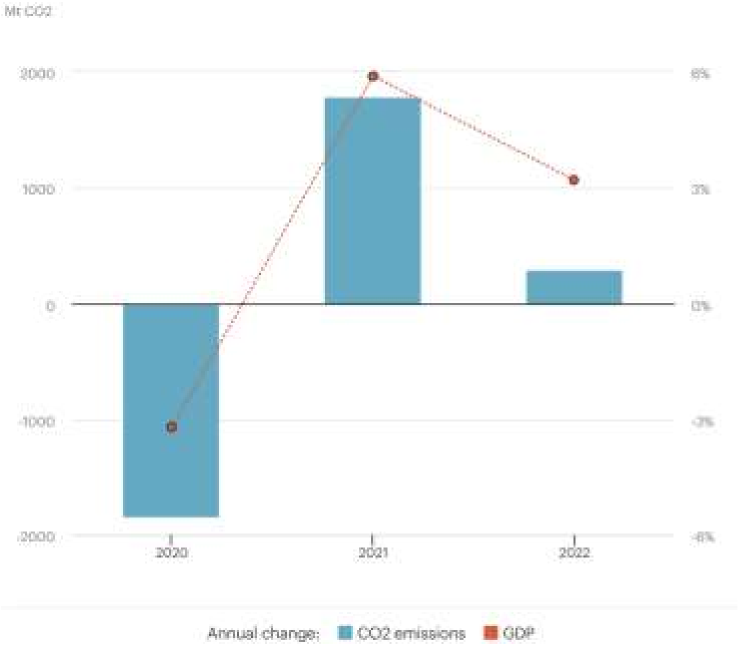

Figure 1.1: CO_2 emissions in recent years (IEA, 2022)

1.1.2 Hydrogen from Plastic: Tackling Waste and CO2

The production of hydrogen presents a promising solution to both plastic waste and CO_2 emissions. One emerging approach is the pyrolysis or gasification of non-recyclable plastics, which can convert these materials into hydrogen and other valuable by-products. By turning plastic waste into hydrogen, this method addresses the mounting issue of plastic pollution, especially the 200 million tons of plastic produced globally each year, most of which is not recycled (DW, 2023). This process also significantly reduces the environmental impact of plastic waste accumulation in oceans and landfills, where plastic can persist for centuries.

When hydrogen is produced from renewable sources, such as biomass or through electrolysis powered by renewable energy, it can be used as a clean fuel, replacing fossil fuels that are responsible for over 850 million tons of CO_2 emissions annually (European Parliament, 2018). Hydrogen production from plastic waste could reduce these emissions, while simultaneously preventing harmful greenhouse gases from the incineration of plastic waste. Studies suggest that plastic-derived hydrogen could cut CO_2 emissions by 30% compared to traditional hydrogen production methods using natural gas.

The European Union and other countries are beginning to invest in this technology to create a circular economy model, where plastic waste is converted into hydrogen energy, addressing both waste management and clean energy production. If widely adopted, these technologies could play a key role in reducing global CO_2 emissions, which are projected to rise to 2.8 billion tons by 2050 unless alternative solutions are implemented (European Parliament, 2018).

1.1.3 Hydrogen as energy source

An alternative source of energy is hydrogen, a promising energy carrier and the most abundant chemical element in the universe. Compared to conventional fuels, it has a high energy content (Giuseppe Zollino 2021). Hydrogen is not directly the source of energy. It is a vector able to store energy that permits the transport, distribution, and usage of energy. Based on the raw materials and the primary energy source used for its production, hydrogen can be:

- Grey: hydrogen produced by fossil fuel;
- Blue: hydrogen produced from fossil fuels with carbon capture and storage;
- Green: hydrogen produced from water electrolysis powered entirely by renewable sources;
- Purple: hydrogen produced from water electrolysis powered by nuclear energy.

Grey hydrogen is the most produced and it is the one that pollutes more CO_2 than every other type. It is the 95% of the total hydrogen produced. To be more precised, the main feedstocks used for hydrogen production are natural gas, oil, coal, and electrolysis. Natural gas contributes to the 48% of hydrogen production. Via carbon gasification the direct emissions due to hydrogen are around 20 kg_{CO2}/kg_{H2}. Via steam reforming of natural gas the direct emissions lower at around 9 kg_{CO2}/kg_{H2}. Blue hydrogen comes from the use of fossil fuels followed by carbon capture and sequestration. Green hydrogen has the smallest environmental impact. It is produced by water electrolysis that uses energy or renewable sources to function. In this case, GHG emissions are zero. The downside comes from the gained energy of this process. With the actual technologies, to produce 1 kg of H_2 via electrolysis 55-58 kWh/kg_{H2} are needed (Energy Transitions Commission, 2023) and the low heating value of H_2 is 33.3 kWh/kg_{H2}. This means that green hydrogen needs more energy to be produced than the one it gains. Purple hydrogen has zero CO_2 emissions.

Hydrogen is mainly used as raw material in petrochemical companies to produce ammonia and methanol and for manufacturing metals from their oxides. Purified hydrogen can be utilized to help downstream processes to enhance performances while converting raw materials into higher value products.

Through processes such as gasification or pyrolysis, non-recyclable plastic waste can be transformed into syngas, which is then used to produce hydrogen. This method not only helps reduce the massive accumulation of plastic waste, but also offers a low-carbon alternative to conventional hydrogen production methods that rely on fossil fuels. According to recent studies, gasification of waste materials can generate high-purity hydrogen (up to 99.5%), while simultaneously capturing CO_2 with a purity of 99.9%, making it suitable for Carbon Capture and Storage (CCS) applications (Fuel Processing Technology, 2024). This approach effectively turns a significant environmental issue into a renewable energy resource, promoting both waste reduction and clean energy production.

In one specific pilot study, a 5-column Sorption-Enhanced Water Gas Shift (SEWGS) unit recovered 88.6% of hydrogen from syngas derived from refuse-derived fuel (RDF), a mix of plastic and other waste materials. Additionally, it achieved 95% carbon capture efficiency, while using steam at 350°C during the process (Fuel Processing Technology, 2024). These results highlight the economic and environmental potential of combining plastic waste management with hydrogen production for energy and industrial applications.

1.3 Main technologies used for green hydrogen production

The current technologies used for green hydrogen production are: Alkaline electrolysis cell (AEC), Anion exchange membrane (AEM), Polymer electrolyte membrane/Proton exchange membrane (PEM/PEMEC) and Solid oxide electrolysis cell (SOEC) [Figure 1.2].

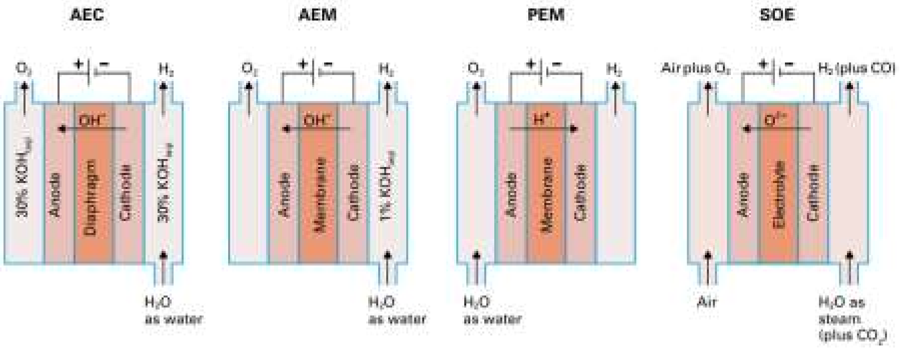

Figure 1.2: Main technologies for hydrogen production (sbh4GmbH, 2021)

For the AEC technology, an aqueous solution of potassium hydroxide is used. It has a good efficiency, it is a well know technology and it does not need expensive materials. PEM has a polymeric membrane; it is costly mainly due to the cathode made of platinum/palladium. AEM is an AE plus a polymeric membrane. It is innovative, but not used at big scale. SOEC utilizes as electrolyte solid ceramics; it is the most efficient technology (80-90% on LHV) and it can work with different kinds of fluids, but it operates at 600-900°C, it is expensive, and it is only studied at small scale for now. Here a table describing these technologies, and their characteristics is presented.

	Alkaline Electrolysis Cell (AEC)	**Anion Exchange Membrane/Alkaline Electrolyte Membrane (AEM)**	**Polymer Electrolyte Membrane/Proton Exchange Membrane PEM/PEMEC**	**Solid Oxide Electrolysis Cell (SOEC)**
Electrode material	-Cathode: Ni, Co or Fe -Anode: Ni	-Cathode: Ni or Ni alloys -Anode: Fe, Ni or Co oxides	-Cathode: Pt/Pd -Anode: IrO2/RuO2	-Cathode: Ni -Anode: La/Sr/MnO (LSM) or La/Sr/Co/FeO (LSCF)
Electrolyte	Lye: 25-30% Potassium Hydroxide solution in water	Anion Exchange ionomer (e.g. AS-4)	Fluoropolymer ionomer (eg Nafion, a DuPont brand)	Zirconium Oxide with ~8% Yttrium Oxide
Energy source	100% electrical power	100% electrical power	100% electrical power	~25% heat from steam, ~75% electrical power

Current density (A/cm2)	Up to 0.5 A/cm^2	0.2 – 1 A/cm^2	Up to 3 A/cm^2	Up to 0.5 A/ cm^2
Hydrogen or syngas product	Hydrogen	Hydrogen	Hydrogen	Hydrogen (or syngas if fed with steam and CO2)
Gas outlet pressure (bar)	Up to 40 bar	Up to 35 bar H2, 1 bar O2	Up to 40 bar	Close to atmospheric
Cell temperature (°C)	~80 °C	~60 °C	~60 °C	~750 to 850 °C

Table 1.1: Characteristics of Hydrogen Technologies (sbh4 GmbH, 2021)

	Alkaline Electrolysis Cell (AEC)	**Anion Exchange Membrane/Alkaline Electrolyte Membrane (AEM)**	**Polymer Electrolyte Membrane/Proton Exchange Membrane PEM/PEMEC**	**Solid Oxide Electrolysis Cell (SOEC/SOEC)**
Efficiency (% LHV)	55-65	50-70	60-70	80-90
Advantages	-Cheaper cost production and electrolyser cost (noble metals not needed) -Cheap materials -High lifetime -Consolidated and reliable technology	-Less corrosive electrolyte than the Alkaline -Cheaper cost production and electrolyser cost (noble metals not needed) -Lower acidity in the electrolytic solution -Possibility to work at partial loads (20%-100%) -High pressures -Good purity	-Good mass transfer -Higher efficiency thanks to the solid electrolyte -High current density -Higher H2 production at the same surface used -No gas crossover due to the membrane -Possibility to work at partial loads (20%-100%) -Can work with renewable sources -High pressures	-Can work also as fuel cell -Can work also with other fluids
Disadvantages	-Low current density with bigger plan dimensions compared to other technologies -No membrane, gas crossover -Limited Hydrogen purity -Limited partial load (40%-100%) -Not valuable with renewable sources -Limited operative pressures (higher the pressure, higher the chances of gas crossover)	-Low current density with bigger plan dimensions compared to other technologies -Not many applications at large scale -High cell degradation coefficient	-Moderate degradation coefficient -High initial cost -Rare metals are needed -Low recycling percentage	High Temperature (600-900°C) -Small ranges of load -Small lifetime -Academic level, only few commercial applications -High costs

Table 1.2: Advantages and Disadvantages of Hydrogen Technologies

1.3.1 Steam methane reforming

Steam Methane Reforming (SMR) is a crucial industrial process for producing hydrogen (H_2), predominantly from natural gas. SMR involves the reaction of methane (CH_4) with steam (H_2O) over a nickel-based catalyst at high temperatures (700-1000°C) and moderate pressures (3-25 bar) (Carbon Capture Science & Technology, 2021). The primary reaction is endothermic:

$$CH_4 + H_2O \rightleftarrows CO + 3H_2O$$

This is usually followed by the Water-Gas Shift (WGS) reaction. The SMR process starts with the desulfurization of methane to protect the catalyst. The desulfurized methane is mixed with steam and heated before entering the reformer. Inside the reformer, methane and steam react over the catalyst to produce syngas (H_2, CO, and CO_2). Integrating pyrolysis with SMR leverages the high H_2 potential of the syngas while addressing waste plastic disposal challenges. Integrating syngas from the pyrolysis of non-recyclable plastic waste into SMR processes offers a promising pathway for sustainable hydrogen production.

1.3.2 Water gas shift technology

CO and water react reversibly and slightly exothermically to produce additional hydrogen moles, increasing the hydrogen yield. This process is called a water gas shift reaction. The amount of CO in the stream is decreased by the WGS reaction, however large amounts of CO produced during reforming processes can poison downstream catalysts and lower hydrogen output. Equation (1) describes the WGS reaction, which takes place at a low temperature, and it does not depend on pressure:

$$CO + H_2O \rightleftarrows H_2 + CO_2 \ \ \Delta H = -41.15\frac{kJ}{mol} \ (1)$$

WGS reduces the CO content of the product by converting 1mol of CO into 1mol of CO_2, while generating an additional mole of H_2. Given that the WGS equilibrium constant drops with increasing temperature, operating at lower temperatures improves conversion. High temperatures cause the reaction to shift toward the production of CO, lowering the hydrogen yield. To address this issue, WGS is carried out in two stages: high-temperature shift (HTS) and low-temperature shift (LTS). In the first stage, CO content is reduced from roughly 10% to 2% using HTS catalysts, typically iron catalysts, at an intake temperature of 350-550°C and pressure of 20-30 bar. Although the reaction is quick in HTS, thermodynamics restricts the quantity of carbon monoxide that may be transferred. As a result, the CO content is reduced to 0.2%-0.4% in the LTS stage at an adiabatic temperature of 50°C, often utilizing copper catalysts. Before proceeding with the LTS stage, a cooling system must be used. HTS and LTS reactions could be integrated in the same microreactor. Another way for purifying hydrogen is to use a CO selective methanation reactor.

1.3.3 Proton exchange membrane

In terms of sustainability and environmental impact, PEM water electrolysis is one of the favourable methods for the conversion of renewable energy to high pure hydrogen. The simplicity of PEM electrolysis plant makes it more appealing for industrial applications. The most advanced electrocatalysts for PEM electrolysis are more costly than alkaline water electrolysis because they have high activity noble metals like Pt/Pd for the hydrogen evolution reaction (HER) at the cathode and $IrO2/RuO2$ for the oxygen evolution reaction (OER) at the anode (Materials Science for Energy Technologies, 2019).

Therefore, maintaining high efficiency while lowering production costs is one of the primary problems in PEM water electrolysis. Water is electrochemically split into hydrogen and oxygen at their respective electrodes, such as the cathode for hydrogen and the anode for oxygen, in PEM water electrolysis. PEM water electrolysis is obtained by pumping of water to the anode where it is split into oxygen ($O2$), protons ($H+$) and electrons ($e-$). These protons are exchanged via proton conducting membrane to the cathode side. The external power circuit, which supplies the reaction's driving force (cell voltage), is where the electrons leave the anode. Protons and electrons recombine to form hydrogen at the cathode side.

Membrane electrode assemblies (MEAs), current collectors (gas diffusion layers), and separator plates are the main parts of a PEM water electrolysis cell. The membrane is the structural core of the PEM cell. Perfluorosulfonic acid polymer membranes, such as those found in Nafion, Fumapem, Flemion, and Aciplex, are the most widely utilized membranes. These membranes have special qualities like excellent durability, high proton conductivity, dimensional stability with temperature changes, high strength, high efficiency, and high oxidative stability. The water electrolysis method's activation energy is reduced by using electrocatalysts to accelerate charge transfer kinetics.

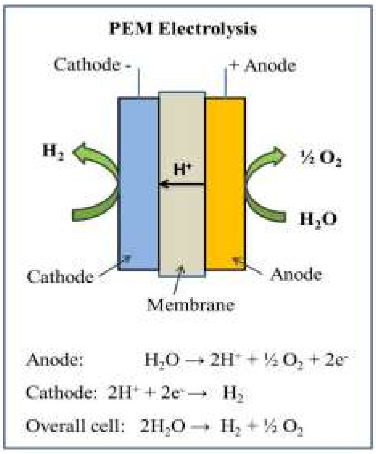

Figure 1.3: PEM electrolysis (Materials Science for Energy Technologies, 2019).

Equation (2) of the hydrogen production rate clearly demonstrates that the bigger the current density (i) and the higher the efficiency (η), the smaller the active area (A) and proportionately lower the capital cost, considering the daily hydrogen production mass and the number of electrolytic cells to be the same number. Regarding the effect of voltage, in general, lower voltages result in lower electricity usage, which lowers the PEM electrolyzer's electricity cost. Eqs. (3) and (4) illustrate how much electricity is needed for water electrolysis to produce 1 mol hydrogen. Therefore, to discover the appropriate voltage and current, one must locate the polarization curve's optimal point.

$$V_{H_2} = 0.000418 \times m \times i \times A \times \eta \ \ (2)$$

$$w = Q \times EOP = n * N_a \times e \times EOP = 2 * 6.023 * 10^{23} \times 1.6 \times 10^{-19} \times EOP \ (3)$$

$$EOP = 1.229 + \eta_a + \eta_c + \eta_{other} \ (4)$$

V_{H_2}: hydrogen production rate (Nm3/h)

m: number of cells in electrolyzer

i: current of cell in electrolyzer (A/cm2)

A: active area of single cell in electrolyzer (cm2)

η: current efficiency (%)

w: electricity required to generate 1 mol of hydrogen by water electrolysis (J)

Q: electric quantity (C)

EOP: actual operating voltage of electrolyzer (V)

n: absolute value of the total number of positive or negative valence in a compound

Na: Avogadro’s number

e: charge carried by a single electron

ηa: anode overpotential (V)

ηc: catode overpotential (V)

ηother: other overpotential (V)

1.3. 4 Hydrogen from biomass

Biomass gasification is the process of thermochemically converting biomass into a gaseous fuel (syngas) using a gasification medium such as air, oxygen, or steam. It occurs at temperatures ranging from 500 to 1400 °C, operating pressures ranging from atmospheric to 33 bar depending on the plant scale and the final application of the produced syngas, and reactor types are classified based on the flow and velocity of the gasification agent. It is estimated that a typical route of biomass gasification-steam reforming-PSA requires 2.4 TJ of primary energy input per TJ of hydrogen, and for a plant with an expected hydrogen output of 139,700 kg/day and biomass costs ranging from 46 to 80 $/dry-ton, the hydrogen production cost is expected to be 1.77 to 2.05 $/kg (Renewable and Sustainable, 2017).

1.4 Parameters affecting H2 yield in steam gasification

- Small granulometry provides a larger contact surface and a better heat transfer during gasification, improving the homogeneous reaction (Steam reforming, WGS). Decreasing granulometry increases H_2 yield and decreases tar and char content.
- Increasing the temperature produces a higher H_2 yield due to complete homogenous reactions. Increasing the temperature decreases the tar content in the gas produced.
- Increasing S/B (Steam to biomass ratio) exhibits a higher H_2 yield. Low S/B promotes CH_4 and carbon formation (reformed at higher S/B). Need to be optimised for each process.
- Catalysts Increase H_2 and CO production by shifting reforming reactions and the WGS reaction. Decrease tar content by promoting the conversion reaction (increase H_2 yield). The most suitable catalysts for gasification reaction are Ni-based catalysts, alkaline metal oxides, olivine, and dolomites. Nickel and cerium catalysts prevent carbon deposition and coking.
- Longer residence time increases biomass conversion to gas. (Fuel, 2001)

1.5 Hydrogen purification methods

The Pressure-Swing Adsorption (PSA) process has gained popularity in recent decades for its ability to recover and purify hydrogen, methane, and carbon dioxide for industrial purposes.

1.5.1 PSA process

The PSA process is used in refining, petrochemicals, ammonia production, and steel manufacture. More than 85% of hydrogen production units now use the PSA method to purify hydrogen. This notice is notable for both its cost-effectiveness and its simplicity. PSA technology allows for the production of pure hydrogen from a gas containing 60-90mol% hydrogen. The PSA phase normally follows the SMR and WGS steps. The PSA method involves contacting hydrogen-containing gas with a solid adsorbent in a packed column under high pressure. Non-hydrogen species are adsorbed onto adsorbent pores, such as silica gel, activated carbon, or zeolite. After desorbing the adsorbed species, the pressure is reduced to regenerate the adsorbent. CO, CH_4 and CO_2 are then released into the burner to create heat for further hydrogen synthesis. Desorption can be accomplished through either depressurization or purging with free hydrogen steam. PSA, despite its basic principle, is a complex technology due to its multi stage adsorption process and cyclic structure. The PSA process maintains constant temperature while changing pressure throughout adsorption and desorption phases. At constant temperature, the adsorption isotherm demonstrates the link between partial pressure and equilibrium loading of the adsorbent material (Advances in Synthesis Gas: Methods, Technologies and Applications, Hydrogen Purification Methods).

1.5.2 Gas permeation with membranes

Another technology for hydrogen purification is gas permeation with membranes. The membrane has a crucial role in producing hydrogen from traditional resources, as shown in several chemical industries. A membrane is permeable and allows materials to pass through depending on a driving factor, such as pressure, temperature, or concentration gradient. Membrane-assisted separation allows for many continuous flow patterns, including cocurrent, countercurrent, mixed, cross, and dead-end flows. Membrane technology requires constant conditions, little moving parts, low energy use, and compact design. The hydrogen membrane system is a simple and effective way to separate hydrogen from syngas. Membrane purification technology relies on a partial pressure gradient to drive the process.

The size of the hydrogen purification plant dictates whether to use membrane-based or PSA technology. PSA is preferable in larger plants, but membrane technology is superior in smaller scales. Hydrogen separation via membrane is also desirable in moving platforms or in situations where a shock may alter the PSA adsorbent bed. However, the membrane separation approach is continuous, whereas PSA is a cyclical process.

Membrane-assisted technology allows for more control over processes, including membrane temperature, feed, and permeate pressure. There are four types of membranes utilized or suggested for hydrogen production based on separation regime: polymeric, porous, dense, and ion-exchange membranes (Shiraz University, Hydrogen Purification Methods). A good membrane for hydrogen production requires strong selectivity, stability, and permeability to operate at high streams and constrained surfaces.

Polymeric membranes are better suited for hydrogen generation than ion-conductive membranes. Polymeric membranes are categorized into two types: asymmetric and composite. The first type has a single polymer composition and a thin, dense permselective layer. The second type has a thick, porous layer covered by a thin, dense permselective layer made of a distinct polymer composition. Porous membranes, including ceramic, metal, and carbon, are being developed for this purpose. A diagram of the hydrogen-selective membrane process is shown in Figure 1.4.

The membrane-assisted approach produces high purity hydrogen (85-95 vol%). This process for isolating hydrogen from syngas is simple, adaptable, reliable, and user-friendly. This approach offers numerous benefits, including a long-lasting membrane. Membrane technology can be simply added into exciting plants without significant changes to the unit. The membrane approach provides modest utility.

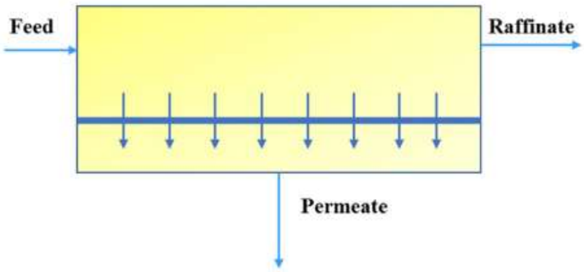

Figure 1.4: Hydrogen separation membrane (Advances in Synthesis Gas : Methods, Technologies and Applications, Hydrogen Purification Methods)

1.6 Aim of the thesis

The issue of non-recyclable plastic waste presents a significant environmental challenge due to its persistence in landfills and potential for pollution. Traditional recycling methods are often ineffective for certain types of plastics, which contributes to their accumulation and environmental impact. As global production of plastic continues to rise, finding alternative solutions for managing non-recyclable waste becomes increasingly urgent.

One possible solution is the use of pyrolysis and gasification technology to convert non-recyclable plastics into hydrogen. This approach not only addresses waste management concerns but also contributes to the growing demand for sustainable energy sources like hydrogen. This thesis focuses on the study of an alternative outcome for the plastic waste, carried out in collaboration with Ethan S.p.a., by making a cost-benefit analysis on the addition of hydrogen recovery units in their pyrogasification plant. In particular, different upgrades to the plant are analyzed to find the most convenient one. COCO simulator together with Excel data analyzer have been used to simulate the chosen option and to achieve some practical results. An energy balance is calculated as an important input of the economic analysis. At last, this thesis' goal is to investigate the possibility of upgrading the pyrolysis plant to the production of secondary products rather than energy and show its validity for the current environmental challenging period.

Chapter 2

CURRENT PROCESS DESCRIPTION AND ALTERNATIVE CONFIGURATIONS

2.1 Description of the current pyrogasification process

The thesis is focused on the pyrolysis plant of Ethan S.p.a.. It is a complete pilot-scale plant, which can be modified and adapted to improve its performances. The plant is interesting because it utilizes mixed waste collected from private companies by Ethan, that doesn't have much validity in the recycling sector and its main destination would be landfill. Its current output is electric energy, that is already a valuable upgrade but has some slight NO_2 emission issues and energy is its one and only output. After a detailed explanation of the whole process, some possible changes will be analysed.

2.1.1 Starting plant configuration

Pyrolysis process involves feeding plastic waste, approximately 962 tons per year, into a gasification chamber. The chamber [figure 2.1], made of AISI 304 steel, is divided into four sections: a loading zone, an ash collection area, an intermediate zone for gasification, and an upper zone for thermocatalytic cracking. The loading zone ensures airtight containment, while the ash collection area collects residue. The intermediate zone facilitates the gasification reaction, converting the waste into gas, and the upper zone enables thermocatalytic cracking to break down primary substances.

Figure 2. 1: Gasification Chamber

Initially, the waste enters the gasification zone and quickly reaches optimal reaction conditions, with a temperature of around 800°C in the presence of air, maintained at a sub-stoichiometric level to prevent complete combustion of the waste. The resulting syngas is discharged from the top of the chamber, where the breakdown of heavy hydrocarbon vapours such as tar and char occurs, transforming them into syngas components like CO, H_2, and CH_4. A total of 19,240 tons per year of residual ashes are conveyed outside to a container through an extraction screw. It flows at a rate of 700 m^3/h and has a heating value of 32.6 MJ/kg (the energy intensity is 9 $kWh/kg_{product}$). (Veneto Green Cluster, 2020)

As the syngas leaves the thermocatalytic cracking zone, it carries fine solid particulates consisting of ash and traces of non-gasified activated carbon. These particulates enter two parallel cylindrical filters [figure 2.2], each 2 cm thick and with a diameter of 250 mm. This section is dedicated to the filtering of the syngas from the gasifier. The filters consist of 18+18 high-density filtration candles, providing a removal efficiency of 99.5%. Inside these filters, the particulates are separated and precipitated at the bottom. A system called Pulsejet, which uses high-pressure nitrogen insufflation, is employed to clean the candles.

Figure 2. 2: Cylindrical filters

Further purification of the syngas takes place in a pair of Venturi scrubber and washing towers [figure 2.3]. In the first scrubber, the syngas is mixed with a solution of sulfuric acid (H_2SO_4) to remove ammonia. It then enters the first washing tower from the bottom, where it moves counter-currently to a descending flow of the reagent solution. This process eliminates residual particulate matter and neutralises salts, which settle at the tower's bottom. The water used in this process is purified and cooled in a closed-loop system, which allows for its reuse in the washing tower.

Figure 2. 3: Venturi Scrubbers

This absorption and cleaning process is repeated in a second scrubber Venturi, where the syngas is mixed with a caustic soda (NaOH) solution to break down hydrogen sulphide, and a larger washing tower for further syngas purification. The syngas is finally discharged at a temperature of 60°C after undergoing purification, cooling, and water recovery processes.

Figure 2. 4: Overview of the pyrogasification plant

To prevent clogging, a pair of coalescence filters [figure 2.5] is utilised to remove liquid particles like water and oil from the gas. These filters also serve as safety devices, detecting pressure differences caused by particulate matter and triggering an alarm to alert operators of any anomalies. Overall, this gas cleaning system effectively eliminates particulate matter, neutralises salts, and breaks down harmful gases, ensuring the purified syngas meets the required standards.

Figure 2. 5: Coalescence filters

The final flowrate of syngas entering the engine amounts to 5820 tons per year. The engine used in this system is a Perkins Engines model, with a power capacity of 242 kW. Approximately 10% of the generated electricity powers the plant itself. The emissions flow rate from the engine are equal to 18.379 tons per year. In the event of any anomalies, the syngas is automatically redirected to an external safety torch, where it is temporarily combusted until the optimal conditions of the plant are restored. Under normal circumstances, the gas proceeds to fuel the combustion engine, which drives the generator to produce electricity and heat.

The Block-Flow Diagram referred to a hourly basis and to a yearly basis is reported below [figures 2.6 and 2.7]. It is important to highlight the peculiarity of the pyrolysis process, which transforms a solid input into a syngas and finally into electricity. Solid wastes are mainly ashes from the combustion chamber, wastewater derives from scrubbers while gas emissions originate from the engine.

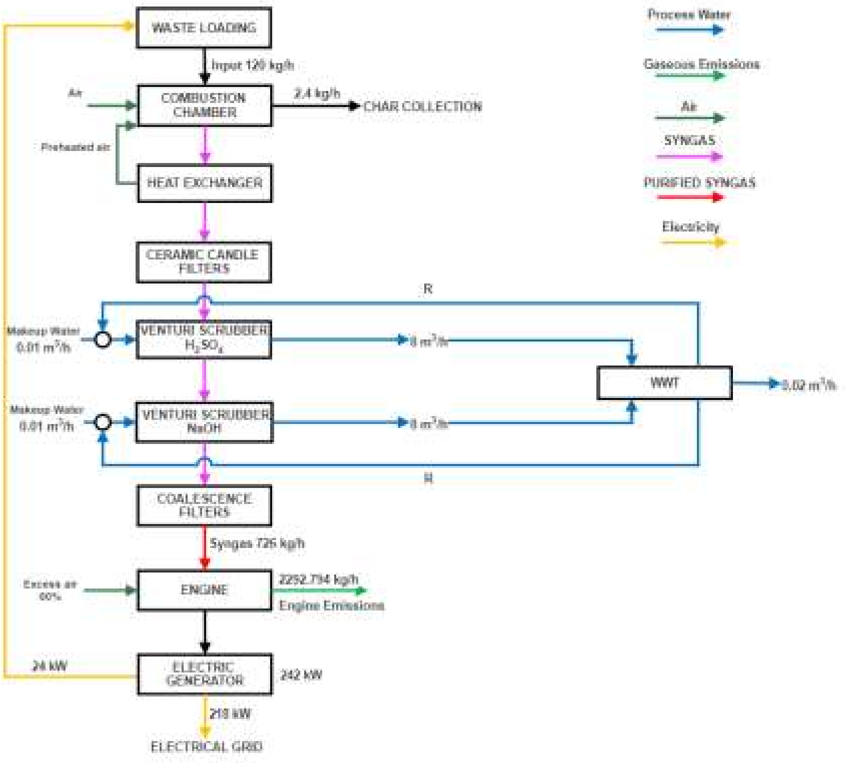

Figure 2. 6: Block flow diagram of the plant configuration, hourly basis

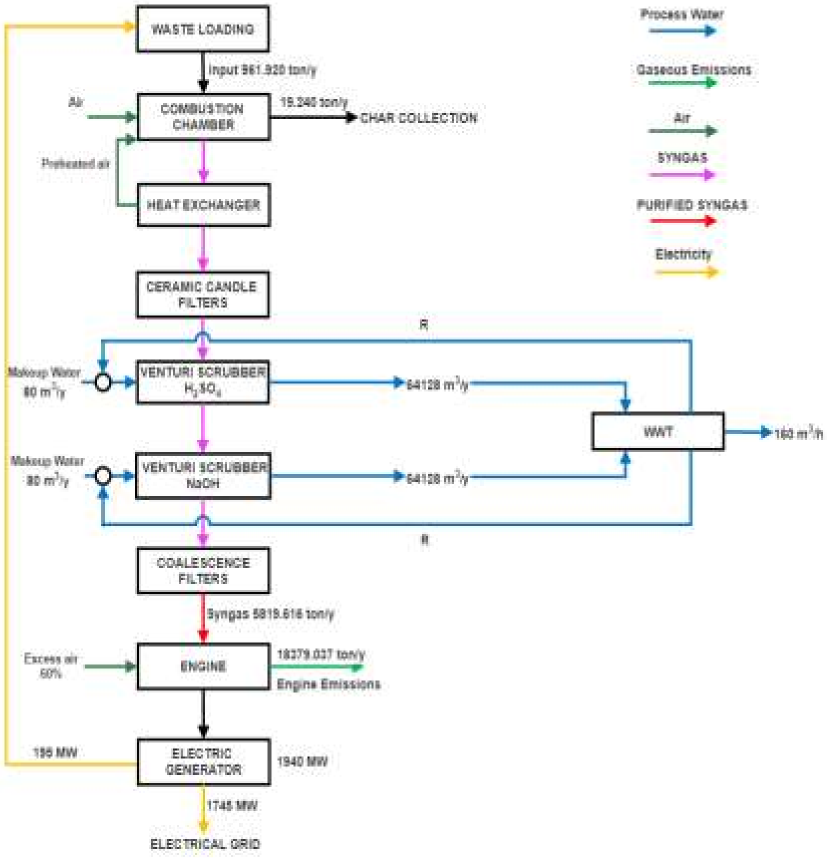

Figure 2. 7: Block flow diagram of the plant configuration, yearly basis

2.1.2 New plant configuration

Lately the plant has been modified by adding a pyrolysis unit [figure 2.8] before the gasification chamber, right after the loading zone. This new configuration makes the cracking of mixed waste easier and mixes it in order to acquire a more homogeneous output. The plant works at around 400°C at ambient pressure. It decreases the concentration of unwanted compounds such as carbon dioxide since the pyrolysis process does not rely at all to injecting oxygen to increase the temperature in the rectangular chamber.

Figure 2. 8: New configuration with the addition of the pyrolysis unit

2.2-Alternative process configurations

The process goal is to generate electricity from non-recyclable plastic waste. It is a fully automated plant with some minor checks to do now and then. It has achieved a fully defined purpose, and it can be considered completed the way it is. But this plant has still room for improvement. Many different compounds can be recovered by adding some other process units. The carbon footprint can be improved and compounds like H_2 and liquid CO_2 can be separated to recover important and valuable products that can be sold to achieve a better cost-benefit balance.

Four options were studied, and simulations were made to understand which one was the best. These options are:

- Addition of a membrane for hydrogen separation before the cogenerator

- Addition of a WGS reactor right after the combustion chamber
- Addition of a WGS reactor and a PSA right after the combustion chamber
- Addition of a WGS and a PSA right after the combustion chamber and a PEM electrolyzer after the cogenerator.

2.2.1 Option 1: Polystyrene membrane

A polystyrene membrane for hydrogen separation can be a promising option due to its chemical stability and ease of manufacturing. It is lightweight and relatively inexpensive, making it suitable for large-scale applications. Polystyrene has good gas permeability, which can allow selective hydrogen transport. However, its effectiveness depends on the purity of the hydrogen required.

It is advantageous for separating hydrogen from gases like N_2, O_2, CH_4, and CO_2 due to its specific gas permeability properties. It shows higher permeability for smaller, lighter molecules like hydrogen compared to larger gases such as methane and CO_2 [table 2.1]. This makes it a more selective and efficient choice for separating hydrogen in mixtures with these gases. Additionally, polystyrene membranes are more affordable and easier to produce than metal membranes like palladium, offering a cost-effective solution for hydrogen separation in industrial applications. However, its performance may still be limited for achieving ultra-high purity hydrogen.

Permeability	**Value**	**Unit**
H_2	56.00	barrer
CO_2	23.30	barrer
O_2	7.47	barrer
CH_4	2.72	barrer
N_2	2.55	barrer
CO	20.00	barrer
H_2S	2.72	barrer

Table 2. 1: Permeability values for selected polystyrene membrane (Geankoplis, 2018)

It may not be the best option for ultra-pure hydrogen applications, as its selectivity can be lower compared to other materials like palladium (Cerone, 2024). Additionally, its performance may degrade at higher temperatures, limiting its use in more demanding environments.

It has been chosen to add the membrane after the cleaning process was completed, to avoid the issue of dealing with high concentrations of H_2S and other compounds. In [figure 2.9] it has been highlighted the added unit.

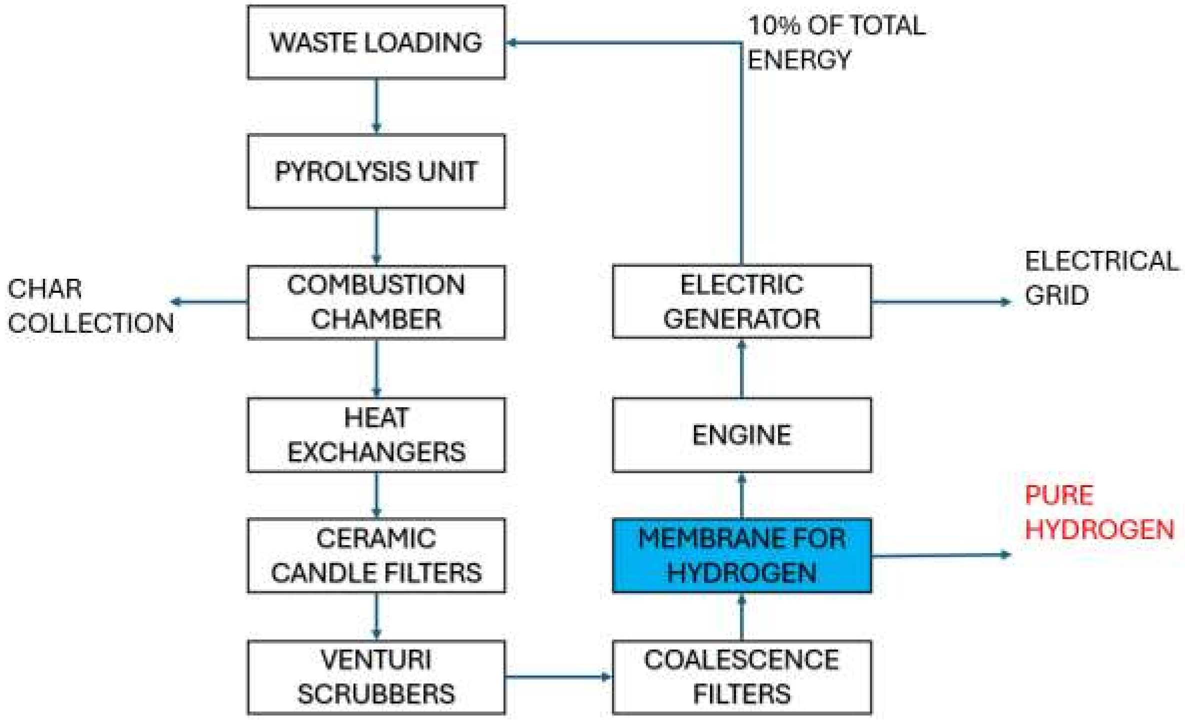

Figure 2. 9: Block flow diagram, Option 1

2.2.2 Option 2: Water-gas shift

A WGS unit in this pyro-gasifier processing plastic waste can enhance hydrogen production by converting carbon monoxide CO and steam into additional H_2 and CO_2. This increases the overall hydrogen yield, making the process more efficient for energy recovery. The addition of a WGS unit [figure 2.10] also optimizes the syngas composition, improving its suitability for downstream processes like fuel cells or chemical synthesis.

However, there are challenges to consider. The WGS reaction requires specific temperature control and catalysts, which can add complexity and cost to the system. Additionally, managing the CO_2 produced may require further treatment or capture systems. While the WGS unit can improve hydrogen output, the increased equipment and operational requirements must be carefully balanced against the benefits.

Adding this WGS is beneficial since a goal is to increase hydrogen production, which has a growing market value. By converting steam in the syngas into hydrogen, the facility could diversify its output and tap into the hydrogen market, potentially increasing profitability. Additionally, hydrogen can be sold for higher-value applications such as fuel cells, offering a premium over electricity alone.

However, the capital and operational costs of installing and maintaining a WGS unit, along with the necessary CO_2 management, might offset the gains from hydrogen production. Since the current setup already operates efficiently for electricity, the return on investment could be slower. The decision depends on market demand for hydrogen and the potential cost savings or revenue increase from selling hydrogen alongside electricity.

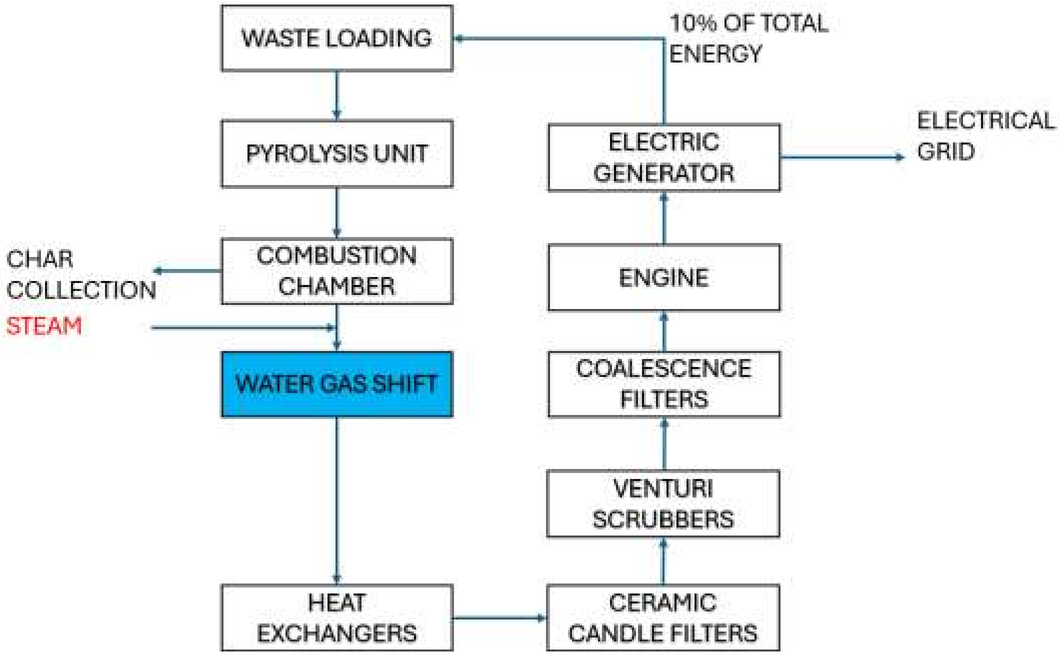

Figure 2. 10: Block flow diagram, Option 2

2.2.3 Option 3: WGS and PSA

PSA efficiently purifies hydrogen, adding value to the overall output compared to generating only electricity. Hydrogen has a higher market price, which could offset the costs of installing and operating the PSA unit. This option [figure 2.11] has two main outputs that generate profits. Although the electricity generated will be lower due to the separation of hydrogen beforehand, it acquires pure hydrogen as second product for further revenues.

The economic value that the plant achieves from adding a PSA unit to produce hydrogen depend largely on the price of hydrogen in the market compared to electricity. Pure hydrogen, especially in regions where clean energy policies are being promoted, is sold at a higher price per unit than electricity generated from syngas because of its high energy demand. More importantly, hydrogen can be stored or placed in other chemically feasible compounds ready to be used. This could significantly boost revenue, particularly if the hydrogen is sold to industries like transportation, chemical manufacturing, or energy storage, which have growing demand for clean hydrogen.

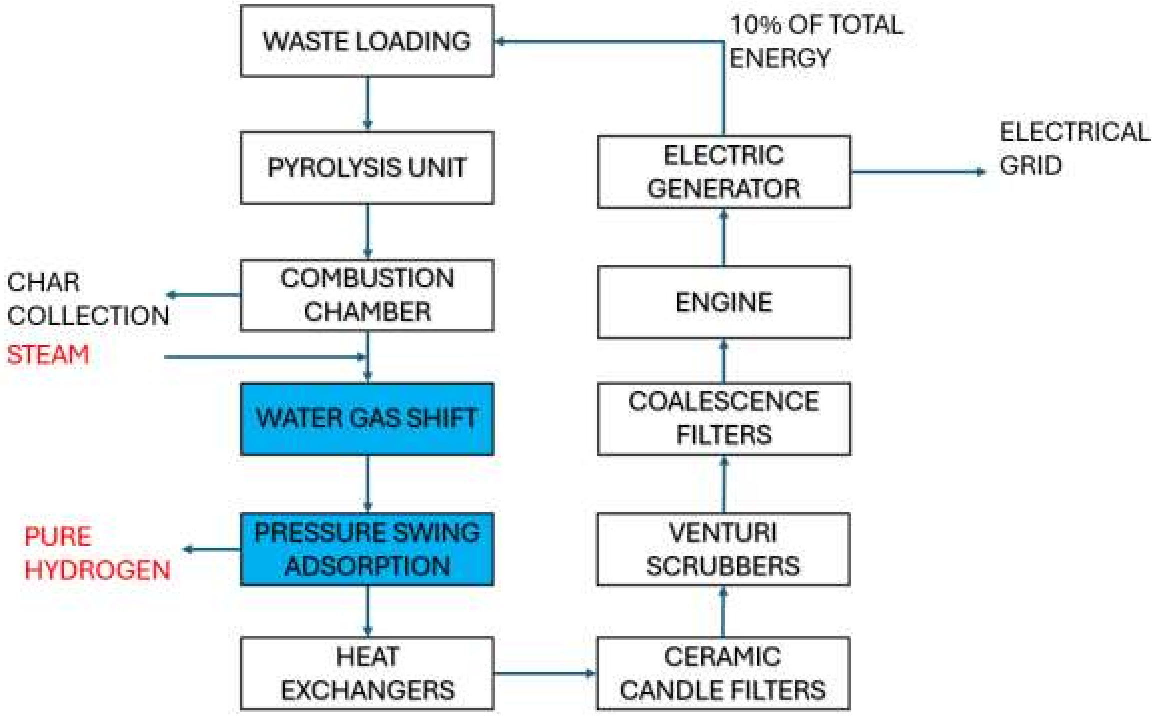

Figure 2. 11: Block flow diagram, Option 3

2.2.4 Option 4: PEM electrolyzer

In this configuration, all the energy generated from syngas is directed to power a PEM electrolyzer, so the system [figure 2.12] is fully transitioned from primarily electricity generation to hydrogen production. This allows the facility to produce pure hydrogen for high-demand markets such as transportation, industrial processes, or hydrogen fuel cells. Given the higher market value of hydrogen compared to electricity, this could substantially increase revenue, especially if the demand for clean hydrogen continues to grow. Furthermore, this new plant would descrease to zero the greenhouse gas emissions, since everything is used to power the hydrogen production unit.

Generally, a PEM electrolyzer needs 53 kWh to produce 1 kg of Hydrogen, which means that 242 kW produce 4.57 kg/h of Hydrogen (Ayers, May 20, 2020).

However, shifting all energy towards hydrogen production means that no electricity would be available for grid export, eliminating that revenue stream. Additionally, the efficiency of converting syngas to electricity, then to hydrogen, may result in some energy losses compared to direct syngas-based hydrogen production methods. The decision would hinge on local market dynamics: if hydrogen prices and demand are high, it could be profitable to focus entirely on hydrogen. Otherwise, a balanced approach with some electricity generation might still be more economically viable.

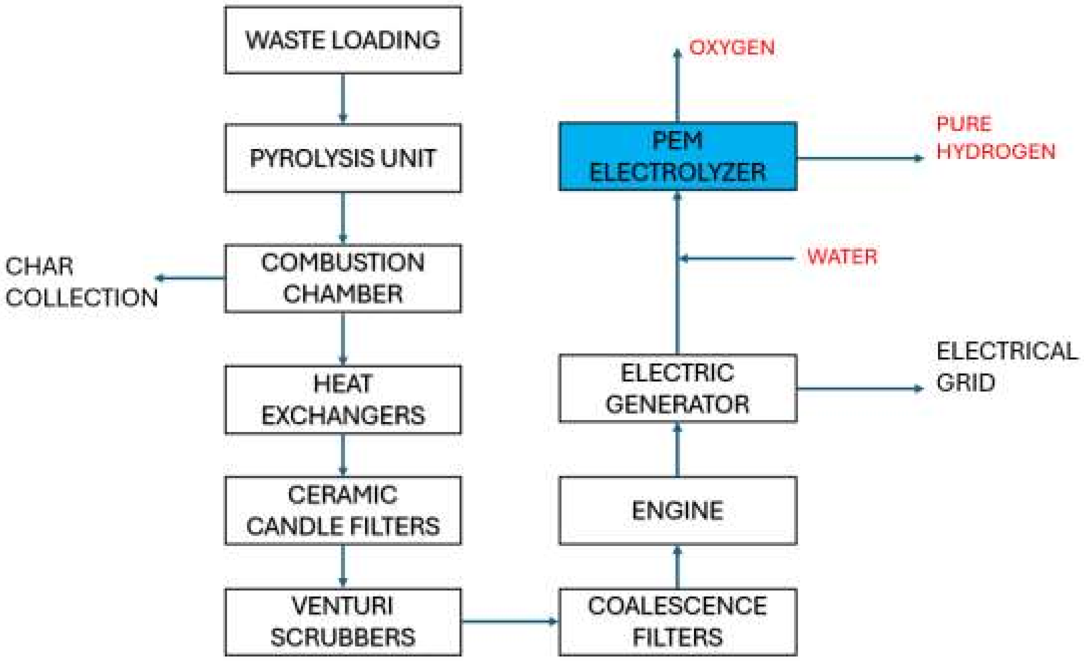

Figure 2. 12: Block flow diagram, Option 4

2.2.4 Option 5: Hydrogen and liquid CO_2 recovery

The last studied option is a hybrid between the first and second options, plus an addition: the recovery of liquid CO_2. This was the chosen option to be further studied via simulations that are described in detail in the next paragraph. In order to prove the validity of a SMR unit, two simulations were made: one with just a WGS system and one with a SMR+WGS system. These systems have been chosen to maximize H_2 concentration, while pure CO_2 is obtained after passing from gas to liquid phase thanks to compression and cooling devices. Then, a membrane is utilized to separate the hydrogen from all the other compounds that are sent to the Perkins engine to produce electricity.

These setups [figures 2.13, 2.14] have many outputs, and they are very flexible. From non-recyclable plastic waste, usually destined to landfill, these systems can produce:

- Pure hydrogen
- Liquid CO_2
- Electric energy

Before the electric generator, a polystyrene membrane like that described in option 1 has been chosen to separate the flow of pure hydrogen for its simplicity and low cost compared to PSA, for example.

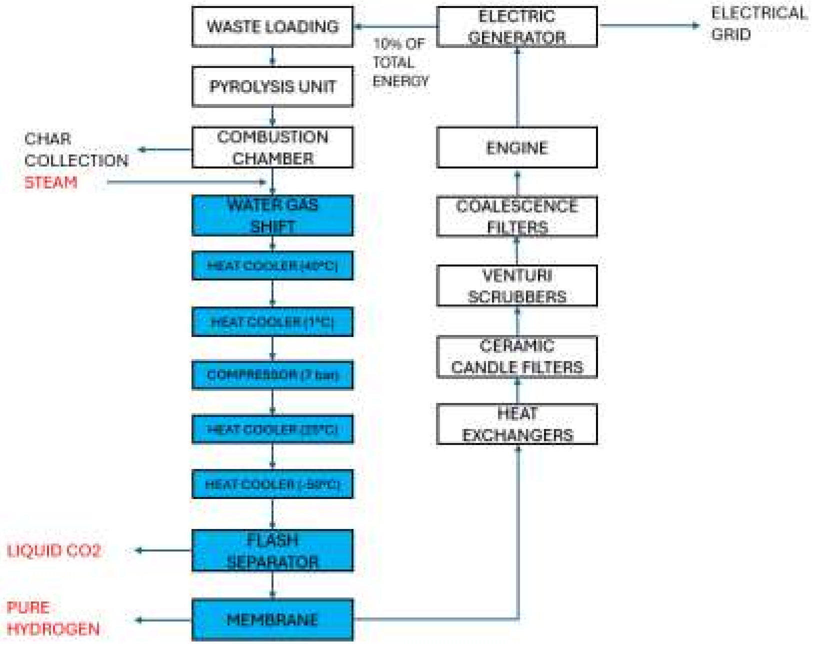

Figure 2. 13: Block flow diagram, option 5.1

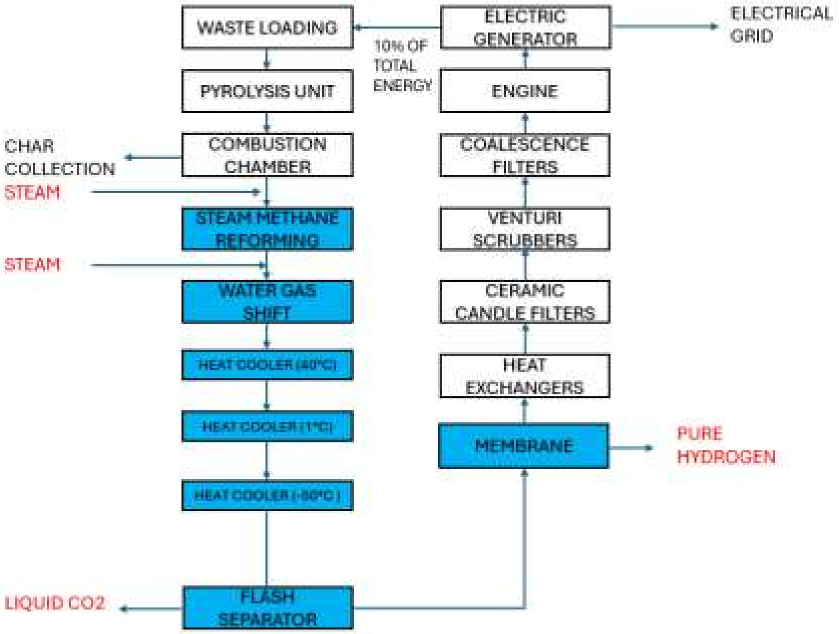

Figure 2. 14: Block flow diagram, option 5.2

2.3 Process simulations

The last option has been chosen by the company to be the one to further study. COCO simulator has been used to acquire more realistic data about the output concentrations of the interested compounds, being hydrogen and carbon dioxide. Every unit needed to liquefy CO2 was simulated in order to acquire information on the operating conditions that must be used, and the corresponding energy duties. The steam input entering the WGS reactor has a 0.55:1 molar ratio with the total syngas flow (Iacono, 2018).

2.3.1 COCO Simulator

The COCO Simulator is a tool used for chemical process simulation, allowing users to model and analyze various chemical systems. It supports different scenarios by integrating mathematical models and algorithms to evaluate the effects of various process configurations. It is employed to compare and analyze the implications of various options, aiding in decision-making for environmental planning and research.

The COCO Simulator utilizes a graphical interface known as the Process Flow Diagram (PFD) to define the processes for simulation. Users can click on a unit operation to modify its parameters using the CAPE-OPEN standard or access the unit operation's specific user interface, if available.

This capability is made possible by the CAPE-OPEN standard, which facilitates interoperability between process modeling software. The COCO thermodynamic library, named "TEA," and its chemical compound database are derived from ChemSep LITE, a free simulator for distillation columns and liquid-liquid extractors. COCO's library includes over 100 property calculation methods along with their analytical or numerical derivatives. Additionally, COCO features a LITE version of COSMOtherm, an activity coefficient model based on *Ab initio* quantum chemistry methods. The simulator supports various unit operations, including stream splitters, mixers, heat exchangers, compressors, pumps, and reactors. It also includes a reaction numerics package that provides models for simple conversion, equilibrium, CSTR, Gibbs minimization, and plug flow reactors.

2.3.2 Simulation configuration of Option WGS

The diagram below shows the configuration of the plant from the WGS unit to the flash separator. The output of this last unit goes to the polystyrene membrane that is able to get a clean H_2 flow. Describing this PFD [figure 2.15] from the start, a steam flow is mixed with the syngas to heighten the production of H_2 due to the favourable reaction consisting in a reversible reaction with CO and steam as reagents and CO_2 and H_2 as products.

Following the WGS reactor, the gas mixture undergoes pressure and temperature adjustments to facilitate CO_2 separation. The first step is to decrease the temperature from 443°C to 1°C via a three-step cooling system. The first one cools down the stream to 80°C by a heat-exchanger fed by air; the second one cools it down to 40°C by water cooling and then to 1°C via a chiller. Subsequently, a flash separator is used to get rid of the liquid water in the flow. Then, in order to lower significantly the CO_2, it was decided to liquify it. This process involves:

- Increasing the pressure to 7 bar.
- Cooling the gas mixture to -50°C to liquefy CO_2.
- Separating the liquid CO_2 via a flash separator.

At these conditions, CO_2 condenses into a liquid phase, which can then be easily separated from the gas stream. This step effectively reduces the CO_2 content in the gas mixture, simplifying subsequent hydrogen purification steps. The temperature and pressure of each stream, with reference to figure 2.15, are summarized in Table 2.2

FLOW	**TEMPERATURE °C**	**PRESSURE bar**
WGS Input	400	1.2
2	443	1.2
3	40	1.2
4	1	1.2
6	0.6	1
7	244	7
8	25	7
9	-50	7
Output Gas	-50	7

Table 2. 2: Configuration of each flow in Water gas shift Block flow diagram

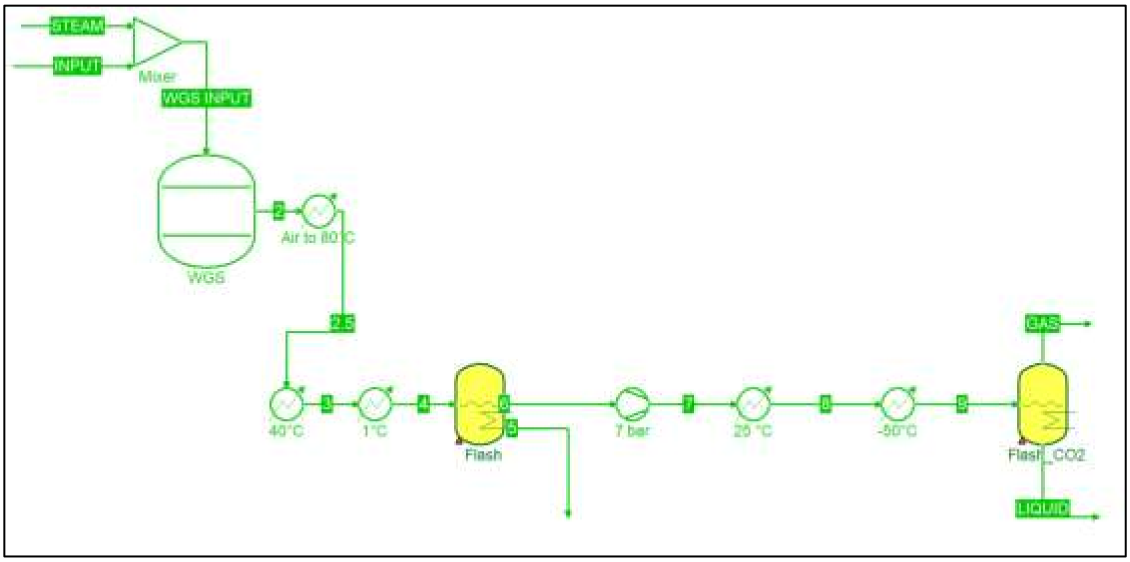

Figure 2. 15: WGS to Flash separator section

2.3.3 Simulation configuration of Option SMR+WGS

In this configuration [figure 2.16] [table 2.3], the SMR was implemented to convert the CH_4 into H_2 thanks to the favourable stoichiometric ratio 1:3 of the reaction:

$$CH_4 + H_2O \rightleftarrows CO + 3H_2$$

The syngas enters directly into the SMR reactor and subsequently to the WGS reactor in order to maximize the hydrogen percentage in the flow. Then, the separation units take place, similarly to the first configuration:

- Temperature is decreased to 1°C via a heat cooler.
- A flash separator is used to obtain a liquid water free flow.
- Temperature is decreased to -50°C via another heat cooler.
- At last, a flash separator is implemented to obtain liquid CO_2 flow and an only gas flow.

The operating conditions of the different streams are summarized in Table 2.3.

FLOW	**TEMPERATURE °C**	**PRESSURE bar**
Input	**550**	**20**
Input_SMR	**550**	**20**
1	**371**	**20**
Input_WGS	**371**	**20**
2	**416**	**20**
3	**1**	**20**
4	**1**	**20**
5	**1**	**20**
6	**1**	**20**
Output Gas	**-50**	**20**

Table 2. 3: Configuration of each flow in SMR+WGS Bfd

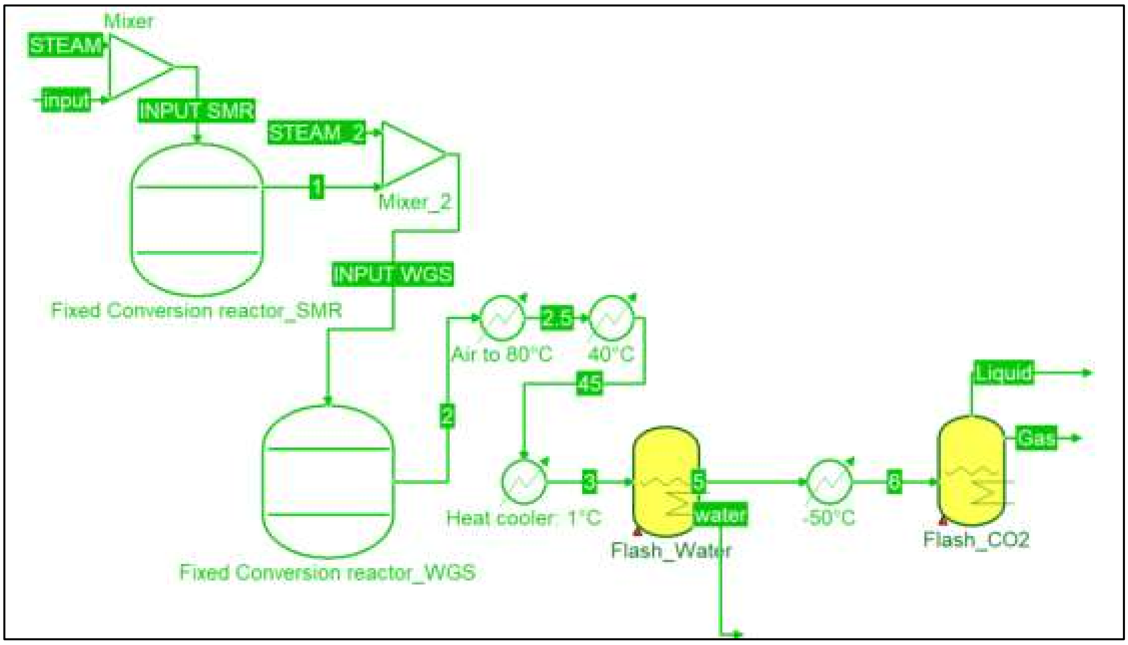

Figure 2. 16: SMR+WGS to Flash separator section

2.4 Simulation of the membrane purification stage

The final stage of the process employs a polystyrene membrane to separate hydrogen (H_2) from the remaining gas. Membrane separation leverages the difference in permeation rates of gases through a selective barrier. Polystyrene membranes are chosen for their specific permeability characteristics, which favor the passage of hydrogen over the other compounds (particularly nitrogen).

The membrane separation process operates under the following principles:

- Differential partial pressure across the membrane drives the separation.
- Hydrogen permeates through the membrane at a faster rate than nitrogen, resulting in a hydrogen-rich permeate stream and a nitrogen-rich retentate stream.

Membrane area, width and pressures were chosen based on an iterative calculation via Excel in order to obtain the best possible H_2 purity. Using two membranes instead of one can reduce costs by decreasing the total required surface area for separation. Each membrane can handle a portion of the separation duty, leading to lower flux rates per membrane, thus minimizing material and operational expenses. This configuration also allows better optimization of the process, improving cost efficiency without compromising performance. The results come from a system of 16 equations with 16 unknowns. The Solver, from Excel, works in this way:

- The unknowns are placed in a column, with a starting guess value (1 was chosen)
- The data must be placed in another column (also Area, width and pressures)

- The 16 equations must be written all in the same column, each one must be equal to 0
- Last, the squared sum of all the equation cells is calculated

The equations correspond to the mass balances between the inlet syngas and the permeate and retentate, the two outputs of the membrane. In membrane separation processes, the permeate flow refers to the stream that passes through the membrane, while the retentate flow refers to the stream that is retained on the feed side of the membrane. For this polystyrene membrane with high hydrogen (H_2) permeability, the permeate flow is expected to be richer in hydrogen, as H_2 can easily pass through the membrane. On the other hand, the retentate flow will contain a higher concentration of gases like nitrogen (N_2), methane (CH_4), or carbon dioxide (CO_2), as these gases have lower permeability compared to hydrogen.

The formulas are the ones as follows:

$$F_F \times y_{H_{2},F} = F_R \times y_{H_{2},R} + F_P \times y_{H_{2},P}$$

(2.1)

$$F_F \times y_{CO_{2},F} = F_R \times y_{CO_{2},R} + F_P \times y_{CO_{2},P}$$

(2.2)

$$F_F \times y_{O_{2},F} = F_R \times y_{O_{2},R} + F_P \times y_{O_{2},P}$$

(2.3)

$$F_F \times y_{CH_{4},F} = F_R \times y_{CH_{4},R} + F_P \times y_{CH_{4},P}$$

(2.4)

$$F_F \times y_{N_{2},F} = F_R \times y_{N_{2},R} + F_P \times y_{N_{2},P}$$

(2.5)

$$F_F \times y_{CO\ F} = F_R \times y_{CO\ R} + F_P \times y_{CO\ P}$$

(2.6)

$$F_F = F_R + F_P$$

(2.7)

$$y_{H_2S_R} = 1 - \sum_{i=1}^{NC} y_{i,R}$$

(2.8)

$$y_{H_2S_P} = 1 - \sum_{i=1}^{NC} y_{i,P}$$

(2. 9)

$$F_P \times y_{H_2,P} = \frac{P_{H_2} \times A}{\delta} \times (P_{R,H_2,R} - P_{R,H_2,P})$$

(2. 10)

$$F_P \times y_{CO_2,P} = \frac{P_{CO_2} \times A}{\delta} \times (P_{R,CO_2,R} - P_{R,CO_2,P})$$

(2. 11)

$$F_P \times y_{O_2,P} = \frac{P_{O_2} \times A}{\delta} \times \left(P_{R,O_2,R} - P_{R,O_2,P}\right)$$

(2. 12)

$$F_P \times y_{CH_4,P} = \frac{P_{CH_4} \times A}{\delta} \times \left(P_{R,CH_4,R} - P_{R,CH_4,P}\right)$$

(2. 13)

$$F_P \times y_{N_2,P} = \frac{P_{N_2} \times A}{\delta} \times \left(P_{R,N_2,R} - P_{R,N_2,P}\right)$$

(2. 14)

$$F_P \times y_{CO_P} = \frac{P_{CO} \times A}{\delta} \times \left(P_{R,CO_R} - P_{R,CO_P}\right)$$

(2. 15)

$$F_P \times y_{H_2S_P} = \frac{P_{H_2} \times A}{\delta} \times (P_{R,H_2\,S_R} - P_{R,H_2\,S_P})$$

(2. 16)

Where F indicates the feed flow rate (kmol/h); $y_{i,j}$ indicates the molar concentration of the specific compound i in the flow j that is either feed (F), retentate (R) or permeate (P); P_i is the permeability of the compound i, A is the area of the membrane and δ is the width of the membrane.

The results are satisfying when the squared sum is equal or close to 0. Area, width and pressures were manually changed to optimize the results. The flow rate and composition of the membrane inlet in the case of WGS and SMR+WGS configurations are shown in Figure 2.17 and 2.18.

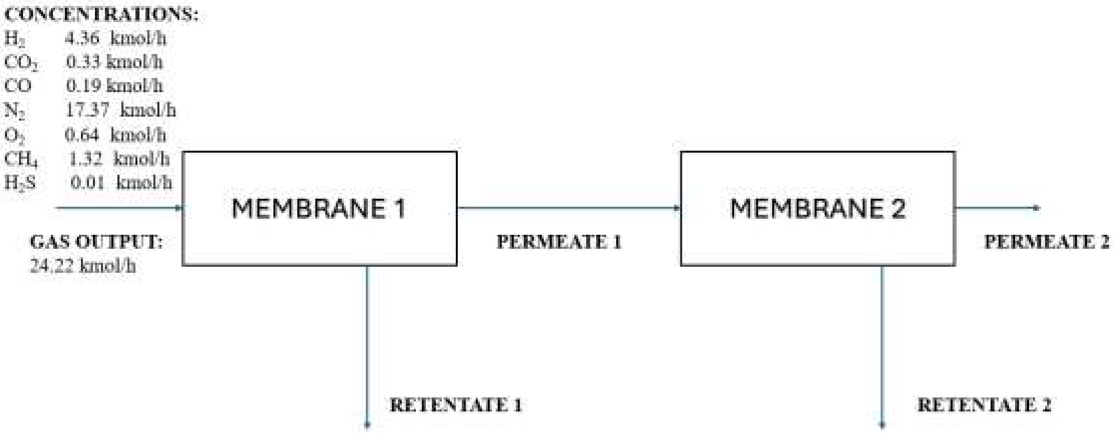

Figure 2. 17: Polystyrene membrane configuration in the Water gas shift option

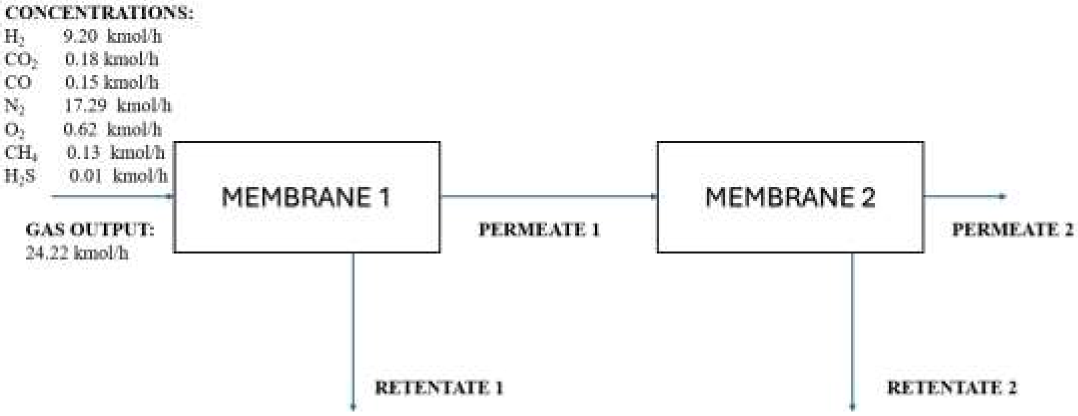

Figure 2. 18: Polystyrene membrane configuration in the Steam methane reforming plus Water gas shift option

Chapter 3

SIMULATION RESULTS

The simulation results provide valuable insights into the implementation of the WGS only option and the SMR+WGS option for this pyrolysis plant treating plastic waste. Using the COCO simulator, the performance of the WGS and SMR processes were evaluated, focusing on the efficiency of hydrogen production from the syngas generated during pyrolysis. Additionally, Excel Solver was employed to model the separation process utilizing the polystyrene membrane. These simulations aimed to determine whether the processes can generate and effectively separate sufficient hydrogen to support potential applications and economic viability. The findings will be discussed in detail, highlighting the operational parameters and the expected yield of hydrogen under the given conditions.

3.1 Simulation results

3.1.1 WGS configuration

The input flow coming from the pyrolysis of the plastic waste, is mixed with steam to enhance the hydrogen production. It was chosen to inject steam with a S/DG (Dry gas) ratio of 0.55, considered the optimal one (Iacono, 2018). In the mixed flow entering the Water gas shift reactor, steam is 35 mol% of the total [table 3.1].

STREAM NAME	**INPUT WGS**	**2**	**6**	**GAS OUTPUT**
TEMPERATURE (°C)	400	443	0.6	-50
PRESSURE (bar)	1.2	1.2	1.0	7
Total molar flow (kmol/h)	41.49	41.49	28.57	24.22
H_2O molar fraction (%)	35.00	31.42	0.42	0
CO_2 molar fraction (%)	6.45	10.52	15.27	1.37
CO molar fraction (%)	4.52	0.45	0.66	0.77
H_2 molar fraction (%)	6.45	10.51	15.26	18.00
N_2 molar fraction (%)	41.94	41.94	60.89	71.71
O_2 molar fraction (%)	1.52	1.52	2.25	2.63
CH_4 molar fraction (%)	3.22	3.22	4.68	5.47
H_2S molar fraction (%)	0.39	0.39	0.56	0.05

Table 3. 1: Temperature, pressure and molar fractions in % and kmol/h of the main flows in the Water gas shift configuration.

The WGS reactor is modelled as a Conversion reactor, with a fixed CO conversion of 95%. At the WGS outlet (stream 2), H_2 and CO_2 moles almost double than the initial values and the CO molar fraction drops from 4.52% to 0.45% [table 3.2]. As previously anticipated, now the goal is to remove water and CO_2 to heighten the H_2 concentration.

The temperature is then dropped to 1°C to simulate the removal of compounds that are present in the stream and that can only be removed at this low temperature. The H_2O present in the flow is hence separated by means of a flash separator. Afterwards, the aim is to separate the CO_2 changing its phase to liquid making it easier to move to a separate stream. In flow 6 [figure 3.1] the temperature drops to 0.6°C after water exits the syngas. Then, parameters for the CO_2 liquefaction must be met.

The flow enters a compressor that increases the pressure up to 7 bar, but as a consequence also temperature increases to 244°C. CO_2 liquefies at around 7 bar and at a temperature of -50°C (Kim, 2024). It has been chosen to cool down the gas in two steps, with two heat exchangers. First, temperature goes down to 25°C and then to -50°C. This low temperature is challenging, and it could potentially cost a lot.

Due to the liquefaction and the liquid and gas flows separation due to the second flash separator, CO_2 drops to 1.37%, reaching a great result for the carbon footprint side and hydrogen goes to 18% of the total flow.

Considering H_2 concentration was 10% in the initial flow, it has almost doubled. This result is in line with what was expected, and it is considered discrete. Mainly in the flow there are three compounds: nitrogen, hydrogen and methane. The highest concentration is still N_2, at 71.71% of the total amount, and CH_4 goes to 5.47%.

Now, the flow needs to undergo some other separation system to achieve a stream with hydrogen as the main compound. The system in question is the polystyrene membrane with which the H_2 concentration will be risen to hopefully around 90%, taking into account to loose the least amount of this compound.

3.1.2 SMR+WGS configuration

As in the WGS configuration, the input flow coming from the pyrolysis of the plastic waste, is mixed with steam to enhance the hydrogen production and the S/DG ratio is 0.55 (Iacono, 2018). The SMR reactor is modelled as Conversion reaction and the conversion of CH_4 was set equal to 90%. In the mixed flow exiting the SMR reactor, steam is 30.79% of the total [table 3.2].

	1	**2**	**5**	**GAS OUTPUT**
TEMPERATURE (°C)	550	416	1	-50
PRESSURE (bar)	20	20	20	20
Total molar flow (kmol/h)	43.90	68.04	33.31	27.58
H_2O molar fraction (%)	30.79	51.05	0.03	0
CO_2 molar fraction (%)	6.10	8.23	16.80	0.66
CO molar fraction (%)	7.01	0.23	0.46	0.55
H_2 molar fraction (%)	14.32	13.54	27.66	33.37
N_2 molar fraction (%)	39.64	25.57	52.24	62.67
O_2 molar fraction (%)	1.46	0.94	1.93	2.26
CH_4 molar fraction (%)	0.30	0.20	0.40	0.47
H_2S molar fraction (%)	0.37	0.24	0.47	0.02

Table 3. 2: Temperature, pressure and molar fractions in % and kmol/h of the main flows in the Steam methane reforming and Water gas shift configuration.

Exiting the SMR reactor, the flow is mixed with another steam flow, again with a S/DG ratio of 0.55 to further enhance the WGS reaction that is going to take place, with the same assumptions explained previously. H_2O rises from 13.52 kmol/h to 34.74 kmol/h [table 3.2]. The noticeable difference from the previous configuration is the CH_4 concentration: due to the steam methane reforming reaction, it drops from 1.34 kmol/h to 0.13 kmol/h.

Another different result is in the H_2 and the CO_2 mole values. When with only WGS they go up to 4.36 kmol/h each, adding the SMR reactor at the start of the system, they rise to 9.21 kmol/h and 5.60 kmol/h respectively. Hydrogen is more than double; this means that the room for the configuration of the membrane is bigger and it is easier to achieve a flow with H_2 as main compound without loosing too much of it and parameter compositions in the process. As for the previous configuration, two heating coolers that lower the temperature to 40°C first and then 1°C are implemented to liquefy water and separate it via a flash separator [table 3.2].

Since the starting pressure is already over 7 bar, there is no need for a compressor. Thanks to this, temperature remains the same, so only one heat cooler to get the gas flow to -50°C is needed. The final flow concentrations are described in the following table. A great difference of hydrogen concentration can be seen. Starting from around 10%, the WGS configuration rises it to 18%; instead, this SMR+WGS configuration brings it up even higher to 33.37% [table 3.2]. Adding this reactor shows that the best option is the latter one, at least in terms of rising H_2 concentration. Triplicating the percentage by adding common reactors and the right amount of steam can be considered a great result, knowing that the flow comes from plastic waste, a non-recyclable solid waste that has low value.

3.2 Membrane separation results

3.2.1 Water gas shift membrane results

The simulation for the membrane configuration is focused on balancing two important aspects of the hydrogen recovery goal: achieving a high purity of H_2 in the permeate and not losing much of it in the process. This task is done by many simulations, with a goal and a recovery factor of at least 50% and getting as close as possible to 90% purity in the permeate flow. All of this was done keeping in mind not to increase parameters such as Area, width and pressures too high, to keep them reasonable and realistic in the studied pilot plant, keeping as low as possible the costs.

After each simulation, Area, pressures and width of the membrane has been changed one by one to find an optimal value.

First observation was that rising the Area value, the efficiency of the membrane rises, in other words, the % of hydrogen passed to the permeate rises. The chosen value is 50 m^2.

Fixing this value of the Area, now the permeate and retentate pressures were changed after each iteration. It has been found that the bigger is the difference between those two pressures, the higher the efficiency. Keeping in mind that the values must remain realistic and feasible, a range of 28-33 atm for the retentate pressure and 1-5 atm for the permeate pressure have been chosen. More specifically, 30 atm and 1 atm respectively. If the retentate pressure value is higher, the efficiency rises, but the H_2 purity starts to decrease drastically. Choosing a value of 35 atm, for example, purity drops of 5%. Then, the value of the permeate pressure is low for the opposite reason: rising it, purity starts to decline.

As last, for the width value, 0.00001 m has been chosen. Simulating with a higher or lower value, either efficiency drops drastically, or Hydrogen purity goes to 25%, after just the first membrane.

In table 3.3 the final values are summarized.

Parameter	**Value**	**Unit**
Area	**50**	**m^2**
Retentate pressure	**30**	**atm**
Permeate pressure	**1**	**atm**
Width	**0.00001**	**m**

Table 3. 3: Final parameters for Membrane 1 of Water gas shift only system

As for the first membrane stage, the same considerations have been applied to carefully choose the value of the parameters. Since the flow is smaller than the gas output entering the first membrane, smaller values were chosen to keep the costs lower and still efficiency and H_2 purity at a reasonably high level. Smaller values are mandatory because a bigger membrane in area size and width, would have a much lower efficiency.

The parameters for the Membrane 2 are written in table 3.4.

Parameter	**Value**	**Unit**
Area	**10**	**m^2**
Retentate pressure	**12**	**atm**
Permeate pressure	**1**	**atm**
Width	**0.00001**	**m**

Table 3. 4: Final parameters for Membrane 2 of Water gas shift only system

In *figure 3.1* the completed Block flow diagram is represented.

The final results were discrete, with a great reduction of the N_2 flow rate that drops from 17.37 kmol/h to 0.22 kmol/h (98.73% reduction) in the hydrogen flow. Unfortunately, lowering nitrogen concentration, lowers slightly the H_2 one, so if a higher efficiency is achievable, the purity would drop respectively.

Final recovery obtained is 41.72% for a flow with 83.47% H_2 concentration. The two retentate flows are sent to the engine to produce energy. The combined flows have a total amount of 22.04 kmol/h.

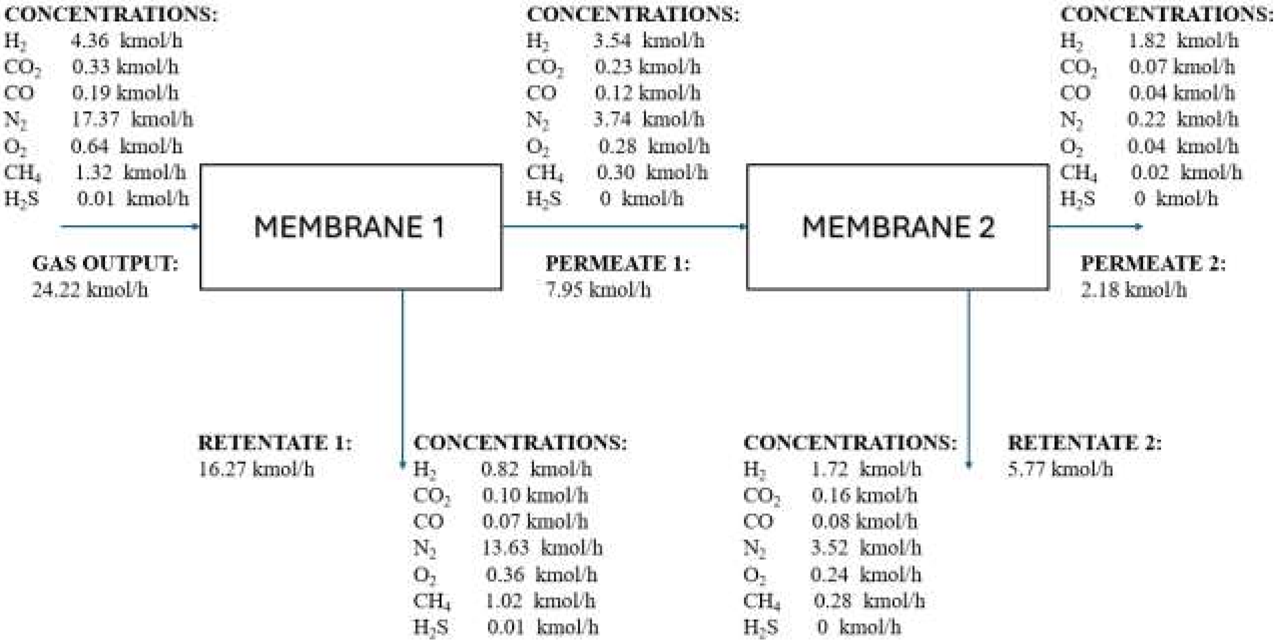

Figure 3. 1: Block flow diagram of the two membranes for the only Water gas shift option

3.2.2 Steam methane reforming + Water gas shift membrane results

Similarly to the configuration of the Water gas shift only, the membrane for the one with the addition of the Steam methane reforming has the same range of value for the parameters.

The simulation is done in the same way, trying to obtain a stream flow with a H_2 concentration of around 90% and the hydrogen recovery around 50%.

In this configuration, changing even just by a little percentage the parameters, efficiency and purity varied a lot. Possibly for the reason why the hydrogen starting value and purity were higher than the only WGS configuration, smaller Area and retentate pressure got better results than the ones used previously. The optimal ranges are 30-35 m^2 for the Area and 23-25 atm for the retentate. It has been chosen to use 35 m^2 and 24 atm. Trying to lower these values would result in losing H_2 recovery, rising just by a small amount the H_2 purity in the stream. Width and permeate pressure were kept the same [table 3.5].

Parameter	**Value**	**Unit**
Area	**35**	**m^2**
Retentate pressure	**24**	**atm**
Permeate pressure	**1**	**atm**
Width	**0.00001**	**m**

Table 3. 5: Final parameters for Membrane 1 of the Steam methane reforming and Water gas shift system

As for the last membrane, for the same reason as the previous configuration, the smaller the flow, the lower the values can be. In comparison, this membrane is slightly bigger than the last one for the WGS configuration, simply because the flow is 12% bigger. The membrane area is 50% bigger and pressure is slightly less, from 12 atm to 10 atm [table 3.6].

Retentate pressure and membrane width remain the same for each membrane configuration.

Parameter	**Value**	**Unit**
Area	**15**	**m^2**
Retentate pressure	**10**	**atm**
Permeate pressure	**1**	**atm**
Width	**0.00001**	**m**

Table 3. 6: Final parameters for Membrane 2 of the Steam methane reforming and Water gas shift system

The final results are as follows:

- Hydrogen purity: 93.16%
- Overall hydrogen recovery: 45.97%

Compared to the WGS only ones, these results are better, having a much higher purity while still keeping a decent hydrogen recovery ratio. The flow entering the membrane had 9.20 kmol/h of hydrogen and the one remaining in the last permeate flow is 4.23 kmol/h. The two retentate flows are sent to the engine to produce energy. The combined flows have a total amount of 23.04 kmol/h.

In *figure 3.2* the Block flow diagram of the two membranes is shown.

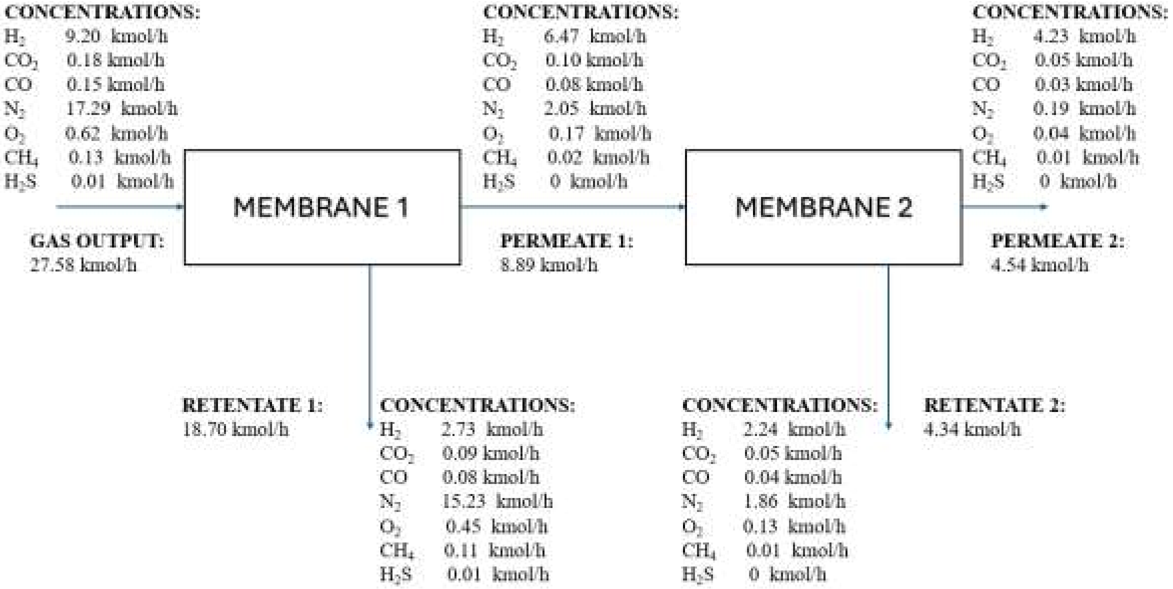

Figure 3. 2: Block flow diagram of the two membranes for the Steam methane reforming and Water gas shift option

3.3 Energy balance

In this section, the energy balance of the different process configurations are presented, accounting for the energy produced by the engine in the new proposed plant for the WGS only option and the SMR+WGS option as well as the energy consumed by the auxiliary units added to separate the different components. The flows that are used to generate the energy are the two retentate streams exiting the two membranes, full of nitrogen and with some hydrogen still present.

It is important to calculate this to have an idea of the loss in energy production, comparing these new plants to the current one.

3.3.1 Energy produced

Flows exiting the membranes are respectively 22.04 kmol/h and 23.03 kmol/h. To calculate how much energy is produced by the Perkins engine, these flows are transformed in kg/h, knowing the molecular weight of the flows that are 24.60 kg/kmol and 22.57 kg/kmol.

WGS option:

$$21.97\ \frac{kmol}{h} \times 24.60\frac{kg}{kmol} = 540.46\ \frac{kg}{h} \tag{3. 1}$$

SMR+WGS option:

$$23.11\ \frac{kmol}{h} \times 22.57\ \frac{kg}{kmol} = 521.59\ \frac{kg}{h} \tag{3. 2}$$

Whilst the second option is better in terms of hydrogen recovery and flow purity, the first option is slightly better for the energy production since it has more hydrogen in the stream.

Knowing the Lower Heating Values (LHV) of each compound, the produced energy for this new system has been calculated by finding the LHV of the total syngas and multiplying it by the syngas mass flow (3.4):

$$LHV_{TOT} = \sum_{i}^{n} m_i \times LHV_i$$

(3. 3)

$$Power\ produced = LHV_{TOT} \times Total\ mass\ flow$$

(3. 4)

m_i is the mass fraction of the single compound and LHV_i is its lower heating value. Knowing the molecular weight (MW) of each compound it was possible to find each m_i , by multiplying MW with its respective molar flow and then dividing it by the total mass flow:

$$m_i = \frac{(MW_i \times n_i)}{m_{TOT}}$$

(3. 5)

The mass flows for the WGS configuration are:

$$m_{H_2} = \frac{5.10\ \frac{kg}{h}}{540.46\frac{kg}{h}} = 0.94\%$$

$$m_{CO_2} = \frac{10.99\frac{kg}{h}}{540.46\frac{kg}{h}} = 2.03\%$$

$$m_{CO} = \frac{4.02\frac{kg}{h}}{540.46\frac{kg}{h}} = 0.74\%$$

$$m_{N_2} = \frac{480.29\frac{kg}{h}}{540.46\frac{kg}{h}} = 88.87\%$$

$$m_{O_2} = \frac{18.45\frac{kg}{h}}{540.46\frac{kg}{h}} = 3.41\%$$

$$m_{CH_4} = \frac{20.87\frac{kg}{h}}{540.46\frac{kg}{h}} = 3.86\%$$

$$m_{H_2S} = \frac{0.34\frac{kg}{h}}{540.46\frac{kg}{h}} = 0.06\%$$

The mass flows for the SMR+WGS configuration are:

$$m_{H_2} = \frac{10.02\frac{kg}{h}}{521.59\frac{kg}{h}} = 1.92\%$$

$$m_{CO_2} = \frac{6.03\frac{kg}{h}}{521.59\frac{kg}{h}} = 1.16\%$$

$$m_{CO} = \frac{3.40\frac{kg}{h}}{521.59\frac{kg}{h}} = 0.64\%$$

$$m_{N_2} = \frac{478.75\frac{kg}{h}}{521.59\frac{kg}{h}} = 91.79\%$$

$$m_{O_2} = \frac{18.63\frac{kg}{h}}{521.59\frac{kg}{h}} = 3.57\%$$

$$m_{CH_4} = \frac{2.05\frac{kg}{h}}{521.59\frac{kg}{h}} = 0.39\%$$

$$m_{H_2S} = \frac{2.73\frac{kg}{h}}{521.59\frac{kg}{h}} = 0.52\%$$

Here, the LHV for each compound:

$LHV_{H_2} = 33.32\ kWh/kg$

$LHV_{CO_2} = 0\ kWh/kg$

$LHV_{CO} = 2.81\ kWh/kg$

$LHV_{N_2} = 0\ kWh/kg$

$LHV_{O_2} = 0\ kWh/kg$

$LHV_{CH_4} = 13.89\ kWh/kg$

$LHV_{H_2S} = 4.25\ kWh/kg$

The total LHV for each configuration have been calculated using the equation *3.3* and then the energy embodied in the gas by equation *3.4*.

$$LHV_{WGS} \times m_{TOT_{WGS}} = 0.87\frac{kWh}{kg} \times 540.46\frac{kg}{h} = 470.20\ kWh/h$$

$$LHV_{SMR+WGS} \times m_{TOT_{SMR+WGS}} = 0.74\frac{kWh}{kg} \times 521.59\frac{kg}{h} = 383.50\ kWh/h$$

Via the same calculations, the energy contained in the gas in the current plant is 962.11 kW. Knowing that in truth, the engine is able to produce 242 kW, there is an efficiency to take into account. It has been calculated it by the ratio 242/962.11, obtaining an efficiency of 25.15%. Due to this, the actual powers produced from the proposed plants are 118.27 kW and 96.46 kW for the WGS and SMR+WGS, respectively. The results suggest that the produced energy using either one of those two configurations will achieve less than half the produced power than the current one. It was predictable, since CH_4, CO and H_2 are key compounds to rise the energy, and the proposed reactors consume the first two and the membrane separates from the main flow the hydrogen, leaving only some traces of what was before.

3.3.2 Energy balance for WGS configuration

The additional units counting for the energy balance in this configuration are the 2 heat coolers, the compressor to achieve 7 bar and the two compressors needed by the membrane (one with a pressure increase from 7 to 30 bar and the second one from 1 to 12 bar). From the COCO simulator, the electrical energy in kW is directly calculated for the heat coolers and the compressors.

In *table 3.7* the calculation results and the cooling and compressor data are written.

UNIT	ELECTRICAL ENERGY (kW)
Heat cooler 1°C	-39.05
Compressor 7 bar	-61.07
Heat cooler -50°C	-19.83
Compressor of membrane 1	-20.15
Compressor of membrane 2	-35.85
TOTAL	-175.95

Table 3. 7: Energy required for each unit in the Water gas shift option

3.3.3 Energy balance for SMR+WGS configuration

The additional units counting for the energy balance in this configuration are the the 2 heat coolers, and the two compressors needed by the membrane (one with a pressure increase from 20 to 24 bar and the second one from 1 to 10 bar). From the COCO simulator, the electrical energy consumption in kW is directly calculated for the heat coolers and the compressors.

UNIT	ELECTRICAL ENERGY (kW)
Heat cooler 1°C	-45.32
Heat cooler -50°C	-15.35
Compressor of Membrane 1	-2.30
Compressor of Membrane 2	-23.69
TOTAL	-86.66

Table 3. 8: Energy required for each unit in the Steam methane reforming + Water gas shift option

The net energy has been calculated subtracting, from the total energy produced, the energy needed to run the new units and the current energy needed to run the plant.

Net power for WGS configuration: 118.27-175.95-24.20 = -79.88 kW

Net power for SMR+WGS configuration: 96.46-86.66-24.20= -14.40 kW

As it can be seen, in both cases the energy consumption is higher than that produced by the engine, so a power input is required.

3.4 Preliminary economic considerations

In this paragraph the economic performances of the current plant system will be briefly analysed and compared to the alternative solutions for hydrogen co-production.

3.4.1 Economic analysis for the current plant

The current pyrolysis plant, which processes 120 kg/h of non-recyclable plastic waste, operates primarily as an electricity-generating facility. Through the pyrolysis of plastic, it produces a gross energy output of 1212 kWh over a 5-hour period, equating to 242.4 kWh/h. After accounting for the plant's internal energy needs (10% of the gross production), the net energy output stands at 218.2 kWh/h, which is sold as electricity. Over the course of 333 days per year, the plant generates an annual output of 1.74 GWh.

The financial model of this plant relies entirely on the sale of electricity. In the Italian industrial energy market, where prices typically range between €0.06 and €0.10 per kWh, the plant generates an annual revenue of €104,631 to €174,385. Since there are no additional processes, such as hydrogen or CO_2 separation, the operating costs are relatively low, limited primarily to maintenance and routine operations. With an estimated €10,000 to €20,000 in maintenance costs per year, the net annual profit for the current plant is approximately €94,631 to €154,385.

While this system is simple and relatively cost-effective to operate, its profit margins are limited by the fluctuations in electricity prices and its singular revenue stream. Additionally, the reliance on selling energy alone constrains the plant's potential profitability, especially in a market where renewable energy sources, like solar and wind, are becoming more competitive. As such, the current system, although stable, lacks the diversified revenue streams and potential for higher returns that could be realized with the integration of hydrogen production and CO_2 capture technologies.

3.4.2 Economic analysis for PEM

The production of hydrogen in this context provides a sustainable solution, reducing reliance on fossil fuels and promoting circular economy principles. In terms of economics, the pyrolysis process in this setup generates 242 kWh/h of electricity from non-recyclable plastic waste. This energy can either be sold directly or used to produce hydrogen via a PEM electrolyzer, as studied. The key comparison here is between the value of selling electricity directly and using it to produce hydrogen. Using 218 kWh/h of electricity corresponds to producing 4.57 kg/h of hydrogen. If we consider current hydrogen generation costs via PEM electrolysis, it ranges between $5.57/kg and $7.50/kg depending on the capacity utilization and electricity costs (Felgenhauer, 2015) (Krishnan, 2023). The PEM cost would range between 20.62 €/h and 27.76 €/h, that annualyis 164,795.04 €/y and 221,879.90 €/y. Selling hydrogen at a price range of 3 €/kg and 5 €/kg (Hydrogen cost and sales prices, 2024) it would generate a revenue of 109,570.32 €/y and 182,617.20 €/y. With Hydrogen incentives, set at 5 €/kg, it would generate a revenue up to 365,234.40 €/y. Net profits are between 143,354.50 €/y and 200,439.36 €/y.

Now, comparing this to the value of selling electricity: if the electricity is sold at an industrial rate of about €0.06 to €0.10 per kWh (Krishnan, 2023), 218 kWh/h would generate between €104,631 and €174,385. In conclusion, producing hydrogen via PEM electrolysis could be more economically viable if hydrogen prices remain high, particularly above $7/kg, or €6.32. However, if hydrogen prices drop below $6/kg, selling electricity might become the more profitable option. More importantly, PEM revenue is highly dependent on hydrogen incentives and price value. Without incentives, there would not be a profit, but a cost. Therefore, the economic feasibility will depend on market conditions for hydrogen and electricity, as well as future advancements in PEM electrolyzer efficiency and cost reduction.

In Europe, the price of blue hydrogen, which is produced from natural gas with carbon capture and storage (CCS), generally ranges from €3 to €5 per kilogram. This pricing is influenced by natural gas prices, carbon allowances, and the cost of CCS technology. For instance, the production cost of blue hydrogen in Europe has been impacted by rising natural gas prices, with some estimates pushing the cost close to €11.53/kg during high market fluctuations.

Some incentives will possibly be given to produce "renewable hydrogen" (NonsoloAmbiente, 2024). Since January 2024, the Government is thinking about the possibility to switch to greener fuels and hydrogen is one of them. It would contribute to the reduction of greenhouse gas emissions, especially compared to the more common fossil fuels. Thanks to this incentive, a company that produces hydrogen via an electrolyzer gains 5€/kg of hydrogen produced if the production comes from plants with a capacity smaller than 10 MW, the case in question.

Obviously, this does not come so easily, there are some other requirements:

- Hydrogen must be produced through an electrolytic process using renewable energy sources, in accordance with the methodologies established for renewable liquid and gaseous fuels of non-biological origin for transport, as outlined in Commission Delegated Regulation (EU) 2023/1184 of 10 February 2023.
- Furthermore, the hydrogen must meet the greenhouse gas emission reduction requirement, achieving a 73.4% reduction in lifecycle emissions compared to a reference fossil fuel with 94 gCO_2e/MJ, meaning hydrogen that results in less than 3 tCO_2eq per ton of hydrogen (tH_2). (IPCEI Idrogeno 1 (H2 Technology), 2024)

3.5 Cost-benefit analysis of the proposed configuration

3.5.1 Economic analysis for the WGS plant

In this analysis, it has been examined the economic implications of integrating hydrogen production technologies, cooling systems and polystyrene membranes into the pyrolysis plant. These components are essential for improving the efficiency of hydrogen and CO_2 separation, which can impact both production and profitability. Below is a detailed breakdown of the system's cost and revenue structure after the inclusion of these technologies. This analysis considers the incentives that EU provides for the hydrogen production technologies (IPCEI Idrogeno 1 (H_2 Technology), 2024).

3.5.1.1 Cost of WGS and Cooling Systems

The proposed system introduces several enhancements, including Steam Methane Reforming and Water-Gas Shift reactors to facilitate hydrogen production, along with a cooling system for CO_2 separation. These additions enable the production of 1.82 kmol/h of hydrogen (approximately 3.67 kg/h), translating to 29,302.67 kg of hydrogen per year. The new system also produces 4.03 kmol/h of CO_2, equating to 1,417.62 tonnes of CO_2 per year. In terms of energy, the new system needs power to work, since the energy balance is negative. 24.2 kW plus 55.68 kW are used to power the plant. This results in an annual cost of 210,672.32 €/y for the 638,400.96 kWh/y at 0.33 €/kW (EliteAmbiente). In terms of CAPEX value for the reactors, an estimation has been made based on (Madeira, 2021). Using scale economy estimates described in equation 3.6, the capital investment cost for this case has been found.

$$C_2 = C_1 \times (\frac{Q_2}{Q_1})^n = 446{,}305€ \tag{3.6}$$

Where:

C_2 = capital investment cost for the studied plant

C_1 = reference capital investment cost = 47.26 M€

Q_2 = flow rate of the studied plant in kg/d = 210.96 kg/day

Q_1 = reference flow rate in kg/d = 500,000 kg/day

n= scale factor = 0.6

3.5.1.2 Polystyrene Membrane Costs

Two polystyrene membranes are required for hydrogen and CO_2 separation:

- The first membrane has an area of 50 m^2, with a pressure difference of 30 atm → 1 atm.
- The second membrane has an area of 10 m^2, with a pressure difference of 12 atm → 1 atm.

These membranes are estimated to cost between 45 €/m^2 and 180 €/m^2 (BAKER, 2012). The assumed cost for this analysis is 100 €/m^2.

These membranes would have a total cost of 5000€+1000€.

3.5.1.3 Storage Costs

Based on U.S. storage estimates, which are like those in Europe, the cost of pressurized hydrogen storage ranges from €0.16 to €0.32 per kg. For 29,302.67 kg of hydrogen per year, storage costs are €4688 to €9376 per year.

3.5.1.4 Consumption of water

The water needed for the reaction is 265.24 L/h, that is 0.27 m^3/h. EliteAmbiente pays 3.28 €/m^3 for water consumption, so this addition would cost 7077.71 €/y.

The water used to cool down the stream before the cooling system, is 9,364.59 kg/h, calculated by using *equation 3.7* knowing that the temperature increase is 15°C, the power consumption is 163.10 kW, and the heat capacity of water is 4.18 kJ/kg.

$$m_{H_2} = \frac{Q}{c_p \times \Delta T} \tag{3.7}$$

This 9.36 m^3/h results in an annual cost of 245,481.20 €/y. Summing this with the steam water, the total cost of water is 252,558.91 €/y.

3.5.1.5 Air cooling system

Similarly to the previous calculation, the air needed to cool down the stream to 80°C is calculated. The temperature increase is 30°C, the power consumption is 142.09 kW, and the heat capacity of air is 1.05 kJ/kg.

$$m_{air} = \frac{Q}{c_p \times \Delta T} \tag{3.8}$$

These 16.24 m3/h results in an annual cost of 811.94 €/y, at a cost of 0.05 €/m^3 of air (Lourinho, 2023).

3.5.1.6 Annual Operating Costs

In summary, the total operating costs for the new system with WGS include

- Maintenance of the reactor, assuming 5% per year of the total CAPEX: 22,315.25 €/y
- Maintenance of the membrane, assuming 10% per year of the total cost: 600 €/y
- Electrical Energy costs: 210,672.32 €/y
- Water consumption: 7077.71 €/y +252,558.91 €/y = 259,636.62 €/y
- Air cooling system: 811.94 €/y
- Storage costs: 9376 €/y.

Total annual operating costs are therefore 503,412.13 €/y.

3.5.1.7 Hydrogen and CO2 Sales

Hydrogen is sold at a price of €3 to €5 per kg, resulting in an annual revenue of €87,908 to €146,513.35 without incentives. With the €5/kg hydrogen incentive, revenue increases to €234,421.36 to €293,026. CO_2 is sold at around 200€ per tonne (CHEMAnalyst, 2024), generating an additional €283,597.88 annually from 1417.99 tonne/y.

3.5.1.8 Total Revenues for the New System

- Without Hydrogen Incentives: Combined revenue from hydrogen and CO_2 is 429,111.23 €/y.
- With Hydrogen Incentives: Revenue increases to 576,623.88 €/y.

3.5.1.9 Net Profit for the New System

- Without Hydrogen Incentives: The net is -74,300.90 €/y.
- With Hydrogen Incentives: The net profit increases 73,211.75 €/y.

3.5.2 Economic analysis for the SMR+ WGS plant

3.5.2.1 Cost of SMR, WGS, and Cooling Systems

The proposed system introduces several enhancements, including Steam Methane Reforming and Water-Gas Shift reactors to facilitate hydrogen production, along with a cooling system for CO_2 separation. These additions enable the production of 4.23 kmol/h of hydrogen (approximately 8.52 kg/h), translating to 67,478 kg of hydrogen per year. The new system also produces 5.417 kmol/h of CO_2, equating to 1905 tonnes of CO_2 per year. In terms of energy, the new system needs 14.40 kW to run and for compressor and cooler units. This results in a cost of 37,977.98€ per year. In terms of CAPEX value of the SMR+WGS reactors, an estimation has been made based on (Madeira, 2021). Using scale economy estimates described in equation 3.9, the capital investment cost for this case has been found.

$$C_2 = C_1 \times (\frac{Q_2}{Q_1})^n = 698{,}852€ \tag{3. 9}$$

Where:

C_2 = capital investment cost for the studied plant

C_1 = reference capital investment cost = 47.26 M€

Q_2 = flow rate of the studied plant in kg/d = 445.44 kg/day

Q_1 = reference flow rate in kg/d = 500,000 kg/day

n= scale factor = 0,6

3.5.2.2 Polystyrene Membrane Costs

Two polystyrene membranes are required for hydrogen and CO_2 separation:

- The first membrane has an area of 35 m^2, with a pressure difference of 24 atm → 1 atm.
- The second membrane has an area of 15 m^2, with a pressure difference of 10 atm → 1 atm.

These membranes are estimated to cost between 45 €/m^2 and 180 €/m^2 (BAKER, 2012). The assumed cost for this analysis is 100 €/m^2.

These membranes would have a total cost of 3500€+1500€.

3.5.2.3 Storage Costs

Based on U.S. storage estimates, which are like those in Europe, the cost of pressurized hydrogen storage ranges from €0.16 to €0.32 per kg. For 67478 kg of hydrogen per year, storage costs are €10,796 to €21,593 per year.

3.5.2.4 Consumption of water

The water needed for these two reactions is 700.21 L/h, that is 0.70 m^3/h. The cost of water is 3.28 €/m^3 (Ethan spa), resulting in 18,349.63 €/y of 5,594.40 m^3/y.
The water used to cool down the stream before the fridge cooling system, is 3053.74 kg/h, calculated by using *equation 3.10* knowing that the temperature increase is 15°C, the power consumption is 53.19 kW, and the heat capacity of water is 4.18 kJ/kg.

$$m_{water} = \frac{Q}{c_p \times \Delta T} \tag{3.10}$$

These 24,405.50 m^3/y results in an annual cost of 80,050.05 €/y. Summing up with the steam water, the total cost is 98,399.68 €/y.

3.5.2.5 Air cooler system

The air used to cool down the stream before the water-cooling system, is 71,768 kg/h, calculated by using *equation 3.10* knowing that the temperature increase is 30°C, the power consumption is 627.97 kW, and the heat capacity of air is 1.05 kJ/kg.

$$m_{air} = \frac{Q}{c_p \times \Delta T} \tag{3.11}$$

These 573,569.86 m^3/y results in an annual cost of 28,678.49 €/y, knowing that the cost is 0.05 €/m^3 of air (Lourinho, 2023).

3.5.2.6 Annual Operating Costs

The operating costs for the new system include

- Maintenance of the reactors, assuming 5% per year of the total CAPEX: 34,942.60 €/y
- Maintenance of the membrane, assuming 10% per year of the total cost: 500 €/y
- Electrical energy cost: 37,977.98 €/y
- Storage costs: 21,593 €/y
- Air cooling system cost: 28,678.49 €/y
- Water consumption: 98,399.68 €/y.

Total annual operating costs are 222,091.75 €/y.

3.5.2.7 Hydrogen and CO2 Sales

Hydrogen is sold at a price of €3 to €5 per kg, resulting in an annual revenue of €202,434 to €337,390 without incentives. With the €5/kg hydrogen incentive, revenue increases to €544,512 to €674,780. CO_2 is sold at around 200€ per tonne (CHEMAnalyst, 2024), generating an additional €381,000 annually.

3.5.2.8 Total Revenues for the New System

- Without Hydrogen Incentives: Combined revenue from hydrogen, CO_2, and electricity is between 583,434 €/y and 718,390 €/y.
- With Hydrogen Incentives: Revenue increases to 1,055,780€.

3.5.2.9 Net Profit for the New System

- Without Hydrogen Incentives: The net profit is 496,298.25 €/y.
- With Hydrogen Incentives: The net profit increases to 833,688.25 €/y.

This analysis represents a preliminary and non-exhaustive economic evaluation, aimed at providing an indicative assessment of the feasibility of the proposed solutions. Key considerations such as capital expenditures (CAPEX) for various heat exchangers and coolers, the CAPEX of compressors (which can be significant), and the costs of catalysts in reactors have not been included. Therefore, no comprehensive return on investment analysis has been conducted, as the capital costs have not been fully accounted for in this preliminary assessment.

CONCLUSIONS

This thesis aims to find a profitable option to the current pyrolysis plant producing hydrogen instead of just electrical energy. While some options, like PEM, were discarded straight away due to the low profits and efficiencies, some others were studied more for their high potential. The main configurations consider the addition of one or two reactors to increase the H_2 yield (namely water-gas shift and steam methane reforming), a cooling system and a compressor for the liquefaction of CO_2, and membranes for hydrogen purification. Several simulations were conducted, achieving noticeable increases in the hydrogen concentration in the stream.

The first option showed an increase from 2.67 kmol/h of H_2 to 4.36 kmol/h. Using two polystyrene membranes having 50 m^2 and 10 m^2, a flow of 1.82 kmol/h and a 84 mol% concentration of hydrogen is achieved. The second option showed an increase from 2.67 kmol/h of H_2 to 9.20 kmol/h. Using two polystyrene membranes having 35 m^2 and 15 m^2, a flow of 4.23 kmol/h and a 93.16 mol% concentration of hydrogen is obtained. It can immediately be seen that the Steam methane reforming helps strongly the goal of achieving a rich flow of hydrogen, getting more than double the moles compared to using only the Water gas shift reactor.

Whilst the first configuration is easy to add to the current plant and the CAPEX cost is contained, it is still complicated to relocate CO_2 and N_2 in another stream. The syngas composition starts with the disadvantage of having a great concentration of nitrogen, a difficult compound to separate with high efficiencies. The annual costs depend mostly on the water and electricity price. With the current value, changing from electricity production from plastic waste to hydrogen production does not seem convenient from an economic point of view.

The second configuration is of more interest. A big change is in the energy balance: while in the first one, energy is required to be bought to run the new plant, here the net energy produced is still positive, keeping it as an active revenue. The liquid CO_2 obtained does not differ much in between configurations, but in the second one CH_4 is considerably less, rising the hydrogen production. Water consumption is another key factor, which in the second configuration is only 40% with respect to the previous case.

Due to these results, adding a SMR reactor may be convenient to start seriously switching the revenues from electricity to hydrogen and liquid CO_2. The membrane lacks on efficiency, and it may be not the best solution to achieve the highest possible H_2 production from plastic waste, but it is cheaper than other options such as the Pressure Swing Adsorption. The storage system of Hydrogen can be a difficult task to accomplish, since there is still no certain path to follow for this and it can result in a big loss of efficiency in the hydrogen recovery. Economically speaking, the net profitability of this new plant is on another level respect to just selling electricity, passing from around 154,000 €/y to 833,688.25 €/y net, or 134,835.25 € the first year due to the cost of the reactors. But from the second year, the profit difference would already be around 679,688.25 €/y more than the current plant. Hydrogen incentives are a key factor in achieving these numbers.

In conclusion, the goal of achieving a flow of 90% H_2 purity has been obtained. While the economic analysis shows that there are still some parameters to be studied more in depth, such as the PSA instead of the polystyrene membrane to achieve higher yield of hydrogen, making the revenues higher. Finally, it can be said that the production of hydrogen from a non-recyclable plastic waste, destined to landfill, shows a good potential.

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