Development of new systems for hydrogen production and carbon capture technologies, along with its potential implementation in the South American market

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Development of new systems for hydrogen production and carbon capture technologies, along with its potential implementation in the South American market

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Summary

Given the current climate crisis due to the anthropogenic CO_2 emissions, industry decarbonisation is key in the transition to climate neutrality. In particular, 7.2% and 0.6% of the total emissions came from steel and paper & pulp industries, respectively. The latter one accounts for approximately 6% of global industrial energy. In order to abate these sectors, Rouge H2 Engineering was found in 2015, after acquiring a patent from Graz University of Technology.

Rouge H2 Engineering has been developing Chemical Looping Technology which is considered as a next generation CO_2 capture technology. It can be used in a wide range of reducible gases as feedstock, in order to produce hydrogen along with carbon dioxide sequestration such as gasified biomass, landfill gas, biogas, and blast furnace gases. To do so, in a fixed bed reactor, metal oxide is reduced (usually hematite: Fe_2O_3) through those gases coming from the aforementioned industries, resulting in CO_2 sequestration. Afterwards, there is a reoxidation process of the oxygen carrier with steam, where hydrogen is produced as a product.

In this context, there are two main objectives set out for this master thesis:

From an academic perspective, the goal was to develop a strategy to decarbonize the paper and paper industry using Rouge H2 Engineering Technology, which consisted in the replacement of the boiler of the paper and pulp process for a gasifier. The results were obtained using Aspen Plus, to do so a model was validated thermodynamically, concluding that $Fe_{0.947}O$ is a good intermediate oxidation state of the oxygen carrier. Additionally, the fixed bed reactor was modelled with a finite number of reactors in counter current. It was also determined that the optimal number of reactors are 14 reactors per step (14 reactors for reduction, 14 for oxidation and 14 for air oxidation).

The simulations showed that the carbon capture is over 99.9% for all case studies, with an energy efficiency between 25.26% and 44.47% depending on the case, therefore allowing the conclusion that Rouge H2 Engineering technology overcomes the current implemented process, Namely, carbon capture using amine-scrubbing is 90% while the energy efficiency with the boiler is 12%. Additional simulation showed that as the operation temperature increases during the oxidations steps, so the energy efficiency using this novel technology also increases, due to a potential reuse of the heat released.

The second main objective of this work was to perform a research market in Latin America, in order to implement Rouge H2 Engineering technology. By applying methodological research to this objective, different stakeholders were contacted which resulted, in particular, in an important agreement with a multinational steelmaking company.

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1. Introduction

1.1. State of the art

The world is currently facing global warming due to the anthropogenic CO_2 emissions. According to the Climate Watch in 2020, 16.2%, 7.2% and 0.6% of the total emissions came from transportation, steel and paper & pulp industries, respectively (Climate Watch, https://ourworldindata.org/emissions-by-sector). Therefore, in order to achieve zero net emissions, the use of renewable energies, alternative fuels and carbon captures technologies must be deployed in the short and middle term to avoid climate consequences.

With regards to the transportation sector, hydrogen could be a potential candidate to decarbonize it, since its whole value chain, i.e., the production (from water or biomass), transportation, storage, and its combustion, might be carbon neutral (Holladay et al., 2009). In fact, H_2 is already produced in large scale, however more than 98% of the hydrogen production comes from fossil resources, mainly through natural gas steam reforming (accounting for 76% of the global production), and coal gasification (22%). The latter process is a thermochemical conversion, and it can use any biomass as a feedstock, being considered as one of the most advanced technologies for hydrogen production due to its high biomass conversion efficiency. This process must be carried out at approximately 1000 ºC, requiring an oxidising agent, like oxygen, air or steam, to produce syngas (a synthesised gas composed of H_2, CH_4, CO, N_2, and CO_2) (Lepage et al., 2021).

Currently, only 2% of the current H_2 production comes from renewable resources, mostly from water electrolysis. This means that these technologies are implemented in specific regions with solar and wind sources (Lepage et al., 2021). Nevertheless, in order to reach net zero emissions, it will be key that clean energy must be produced a decentralized way. This topic will be further discussed in section 1.1.3.2 Chemical Looping Technologies.

Concerning the steel and paper & pulp industries, they will be discussed in the following sections. Firstly, their processes production will be described, and then the potential decarbonization strategies.

1.1.1. Steel Industry

The steel and iron industry (SII) are responsible for the largest CO_2 emissions, accounting for 31% of all industrial emissions. These emissions come from the fact that this sector is high energy intensive, it is highly dependent on using coal, and also due to the significant volumes of steel being manufactured (Bui et al., 2018). China is the world's biggest crude steel supplier whose production represents 49.7% globally in 2017 with 8.317 billion tons of annual crude steel production (Zhang et al., 2019).

There are three routes to produce steel: Electric Arc Furnace (EAF), Direct Reduction Iron (DRI) and Blast Furnace – Basic Oxygen Furnace (BF-BOF). The latter is the most common one, representing 70% of the total steel produced (Quader et al., 2015). Moreover, in China, the route BF-BOF accounts for approximately 90% of the whole crude steel production (Zhang et al., 2019). Figure 1 shows the steel production process for the BF-BOF route for a Chinese company, including CO_2 emissions in the different steps. A detailed description is explained below:

I. Coking: The coal is firstly washed and then converted to coke by removing volatile substances in coke ovens. Some by-products are obtained such as coke oven gas (COG), benzene and tar, which are further recovered.

II. Sintering: In parallel to the coking step, iron ore agglomerates are sintered. In other words, the powder ores are mixed and heated over 1000 °C, to be compacted, forming a solid mass, but without melting it to the point of liquefaction.

III. Iron making (IM) process: Sinter and coke coming from the previous steps, as well as other substances as lump ore, fluxes, are fed in the BF (see Figure 1), to further perform the reduction of iron ore to iron. As a by-product, blast furnace gas (BFG) leaves the blast furnace at the top.

IV. Steel making (SM): After IM, the hot metal and the recovered scrap are fed to the basic oxygen furnace (BOF) to remove the remaining carbon oxygen. In this step, basic oxygen furnace gas (BOFG) is also recovered.

V. Continuous casting (CC): Once the steel is produced, it follows the casting step in which the liquid metal is poured into a mould, to obtain the desired shape, and then allowed to solidify. This is performed in hot-rolling mills which is a highly energetic demanding process. However, the energy contained in the mixed gases of COG, BFG and BOFG can be used as fuel (see Figure 1).

Table 1. Gas emission rates and energy consumption during steel production processes using blast furnace- basic oxygen furnace route (per ton of steel). Table extracted from Manzolini et al., 2020

Gas	Composition [mol %]							
	CH_4	CO	CO_2	C_2H_6	H_2	H_2O	N_2	O_2
BOFG	0.0	56.9	14.4	0.0	2.4	12.2	13.8	0.0
BFG	0.9	22.3	22.1	0.0	3.6	3.2	48.8	0.0
COG	23.0	3.8	0.96	2.7	59.5	4.0	5.8	0.2
Overall	0.1	25.3	21.4	0.0	3.8	3.6	45.7	0.0

The mixed gases of COG, BFG and BOFG can also be burned in the power plant (see Figure 1). Usually steelmaking process is energy self-sufficient, and production is often higher than required, so electricity is injected into the grid (Zhang et al., 2019). However, around 50%

of the overall carbon dioxide emissions of this process come from the power generation (Manzolini et al., 2020). The gas composition, regarding the emissions from the route BF-BOF, is shown in Table 1.

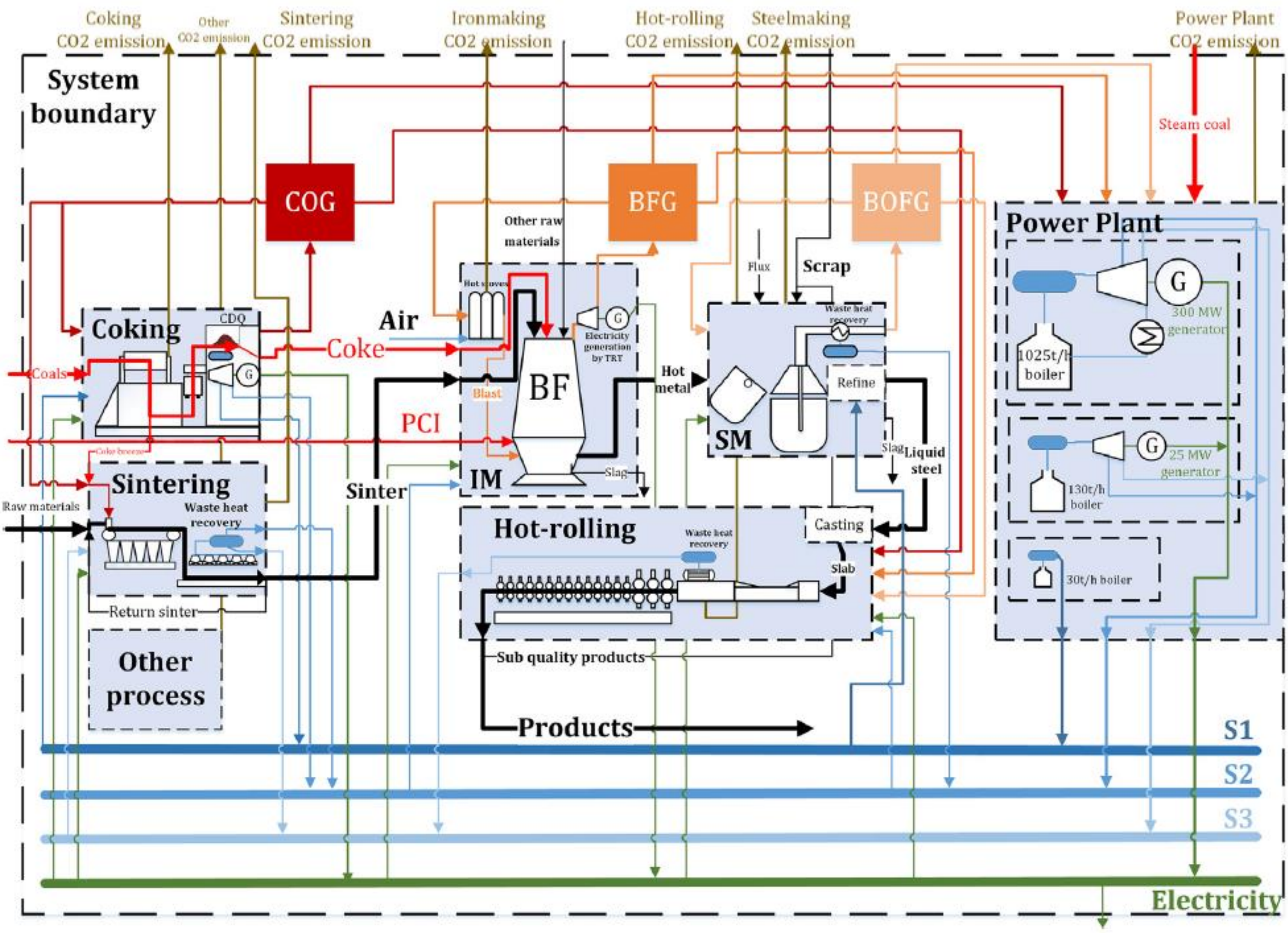

Figure 1. Schematic diagram of the material and energy flows, along with CO_2 emission from iron and steel making process. Reprinted from Zhang et al., 2019.

1.1.2. Paper and Pulp Industry

The pulp and paper industry (PPI) is between the top five most energy-intensive industries globally, accounting for approximately 6% of global industrial energy. In addition to this, it is responsible for 2% of the total industrial CO_2 emissions (Furszyfer Del Rio et al., 2022). Pulping is the process where the wood fibers are separated, and it can be achieved through two different mechanisms:

- Mechanical: This route separates the cellulose fibers via mechanical or physical procedures. Even though this mechanism can transform 95% of the wood into pulp, lignin causes that pulp becomes yellow. As a result, the product is mainly used for products with a short lifespan such as magazine paper and newsprints.
- Chemical: This route is also called Kraft process or sulfate process, since it separates cellulose fibers from lignin and other wood components through a hot mixture of water, sodium hydroxide (NaOH), and sodium sulfide (Na_2S). This solution (known as white liquor) breaks the bonds between lignin, hemicellulose, and cellulose. The final product is high-quality, stronger and brighter paper.

The papermaking process is shown in Figure 2. The first step is chipping the raw material in order to improve the efficiency of the following treatment, which consists mainly in five steps, detailed below (Furszyfer Del Rio et al., 2022; Naqvi et al., 2010):

I. Pulp digester: This corresponds to the aforementioned chemical treatment, supplying the so-called white liquor into wood chips. This process is performed between 150 and 170 ºC under highly alkaline conditions. For this reason, it is necessary to use NaOH.

II. Screening and washing: Water, lignin dissolved, and chemicals are removed through gravitational forces and then vacuumed. The mixture of the dissolved lignin and chemicals is called black liquor.

III. Bleaching: The separated pulp is bleached (removal of natural color from a fiber) with chlorine dioxide and hydrogen peroxide. The pulp will contain remaining water.

IV. Stock preparation and paper making: the water remaining in the bleaching step is thermally removed, to be further conditioned to the final product specifications. For example, paper is further treated with a sizing step.

V. Papers driers: This second dry step is performed if the remaining moisture is between 5 and 9%.

Most of PPIs using Kraft processes are self-sufficient from the energetic point of view. Namely, these industries can meet all internal steam and electricity demands for the processes. This energy comes from combustion of black liquor in the recovery boiler. During this process, there is not only a recovery energy from the black liquor, but also a recovery of the cooking chemicals. After the boiling process, these remaining chemicals are processed with water and CaO to obtain again the so-called white liquor, closing the loop, as it is shown in Figure 3 (Naqvi et al., 2010).

Even though there is a recovery of energy and chemicals in the PPI, this industry contributes to about 40% of industrial wastewater globally. In particular, the combustion of black liquor in the recovery boiler represents 74% of the CO_2 emissions (Furszyfer Del Rio et al., 2022).

1.1.3. Carbon capture technologies

So far, it has been discussed the processes of two industries which are high CO_2 emitters globally, i.e., steelmaking (SII) and pulp & paper industries (PPI). Conversely, in this section, two technologies related to carbon capture will be described, and further how to apply them in order to decarbonize SII and PPI.

1.1.3.1. Amine-scrubbing

Amine scrubbing is a technology already deployed in large scale and has been operating for over 60 years in the chemical and oil industries. It was originally designed to remove H_2S and CO from gas streams (Thambinuthu et al., 2002). However, it has been adapted to remove CO_2 from mixtures of gases, and it has been highly developed; as a result, it is considered to have the highest Technology Readiness Level (TRL, where 1 is basic technology research and 9 is the commercial operation in a large-scale). For instance, this technology has been utilized in two commercial-scale facilities in coal-fired power plants: Boundary Dam and Petra Nova (Bui et al., 2018).

The principle behind, it is a liquid-phase chemisorption, using a chemical absorbent for CO_2 aqueous monoethanolamine (MEA) at 20–30 wt%. MEA reacts with CO_2 to form carbamate or bicarbonate as products. The reactions are shown below in (1) and (2), respectively (where R_3 could be -H or -$CR_aR_bR_c$). The kinetics of these reactions, along with the viscosity of the absorbent, determine the mass transfer and the absorption capacity (Bui et al., 2018).

$$CO_2 + 2R_1R_2NH \leftrightarrow R_1R_2NCOO^- + R_1R_2NH_2^+ \quad (1)$$

$$CO_2 + R_1R_2NR_3 \leftrightarrow HCO_3^- + R_1R_2NHR_3^+ \quad (2)$$

This is an end-of-pipe technology, meaning that it is applied only on the flue gas and therefore does not directly affect the manufacturing process itself. For example, in a power plant, post-combustion is implemented as it is shown in Figure 4.a). Nevertheless, it requires energy management strategies as well as start-up and shut-down procedures.

In addition to the energy requirements, there are important concerns regarding the use of MEA and other amine solvents. For instance, they can cause corrosion in the presence of oxygen and suffer high degradation rates from reaction with SO, and NO. This means there is an extra and big energy consumption to regenerate them, and a pre-treatment stage is necessary. As a consequence, this technology requires large equipment and high feed of solvent, which means high capital and operating costs (Chow et al., 2003). Moreover, water use is necessary to minimize these losses of amine, and when they are not avoided, it can cause environmental hazards, since amines can participate in atmospheric reactions to produce ozone and other toxic compounds (Nguyen et al., 2010).

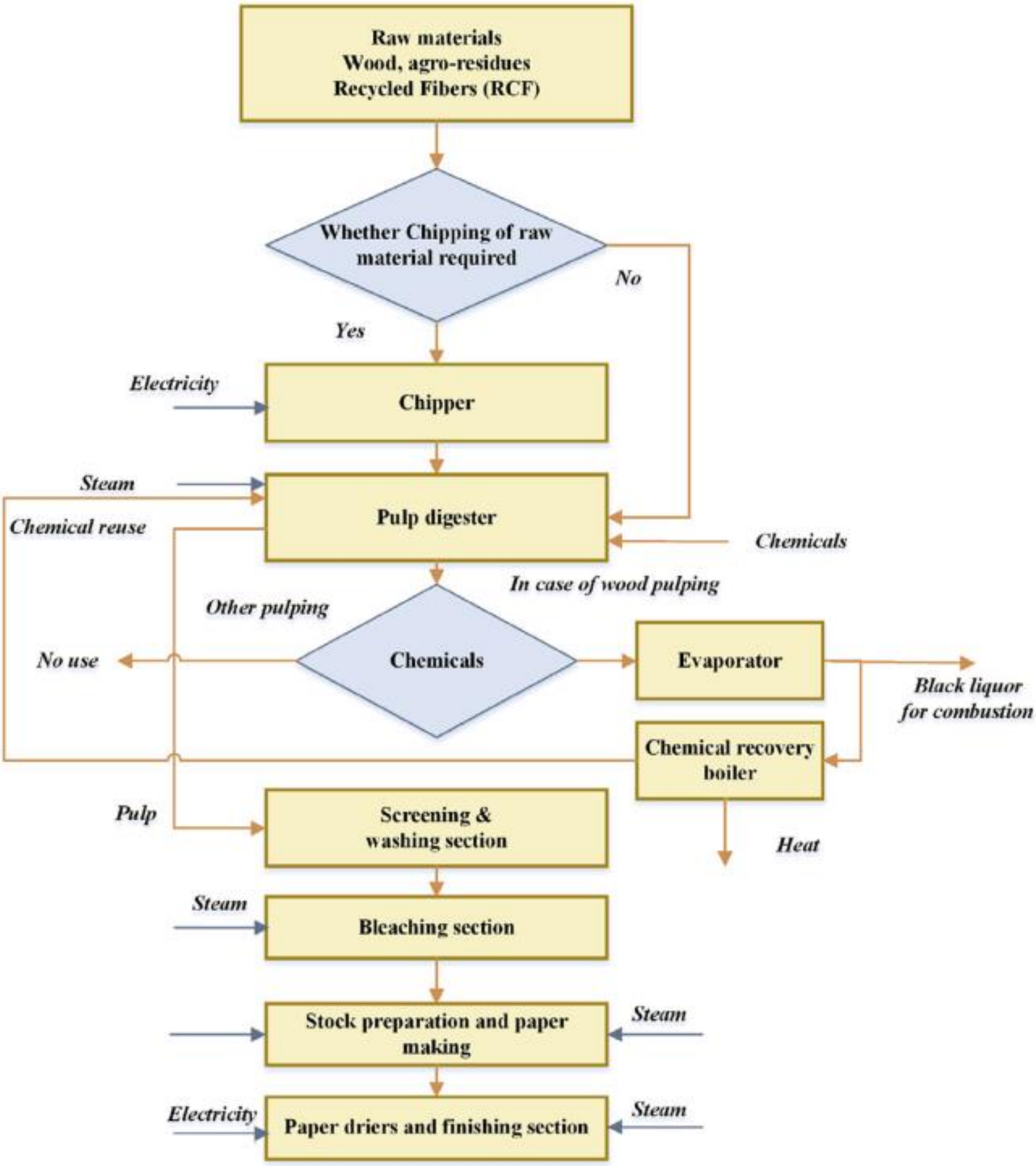

Figure 2. Kraft papermaking process. Reprinted from Furszyfer Del Rio et al., 2022.

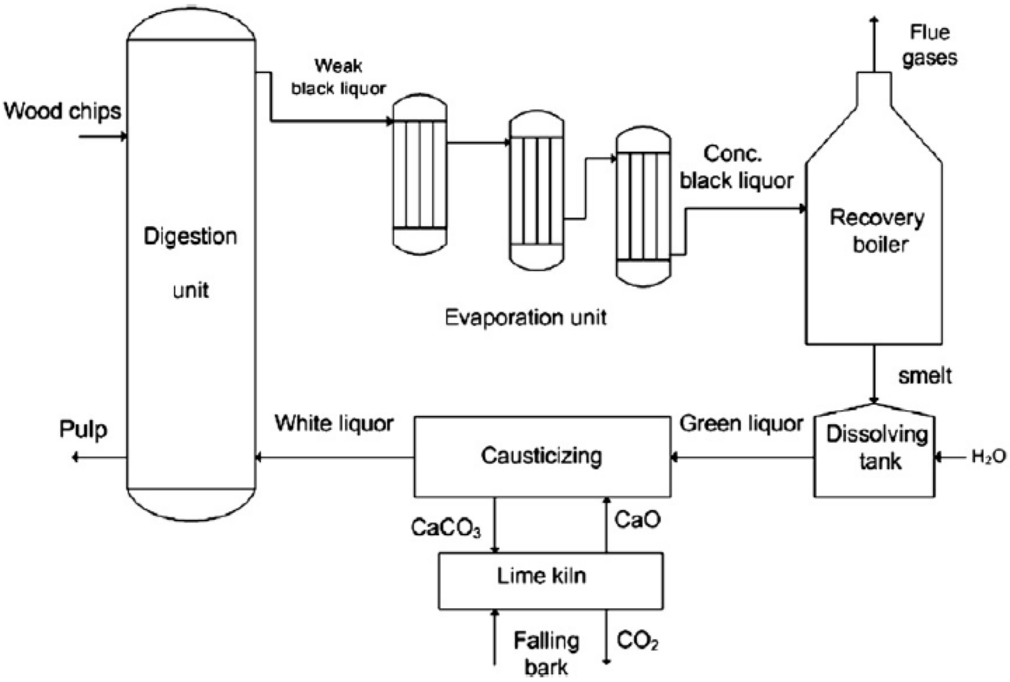

Figure 3. Energy and chemical recovery cycle in Kraft process. Reprinted from Naqvi et al., 2010.

1.1.3.2. Chemical Looping Technologies

According to Bui et al., 2018, Chemical Looping Technologies (CLT) is considered as a next generation CO_2 capture technology. However, the idea behind it is not new since its research started in the early 20th century, manufacturing gas phase oxygen was one of the first uses of CLT (Brin process). Currently, this technology can use a wide range of reducible gases as feedstock, in order to produce hydrogen along with carbon dioxide sequestration (Bock et al., 2018). For instance, it can utilize gasified biomass, landfill gas, biogas, and recently studied BFG.

Given this wide range of feedstock, CLT has the potential to be an efficient technology to produce on-site hydrogen, in a decentralized way (Zacharias et al., 2019). The principle behind chemical looping refers to the process in which a metal oxide (MeO) is used as chemical intermediate, being an oxygen carrier, to separate the fuel from the gaseous oxidation media in combustion reactions.

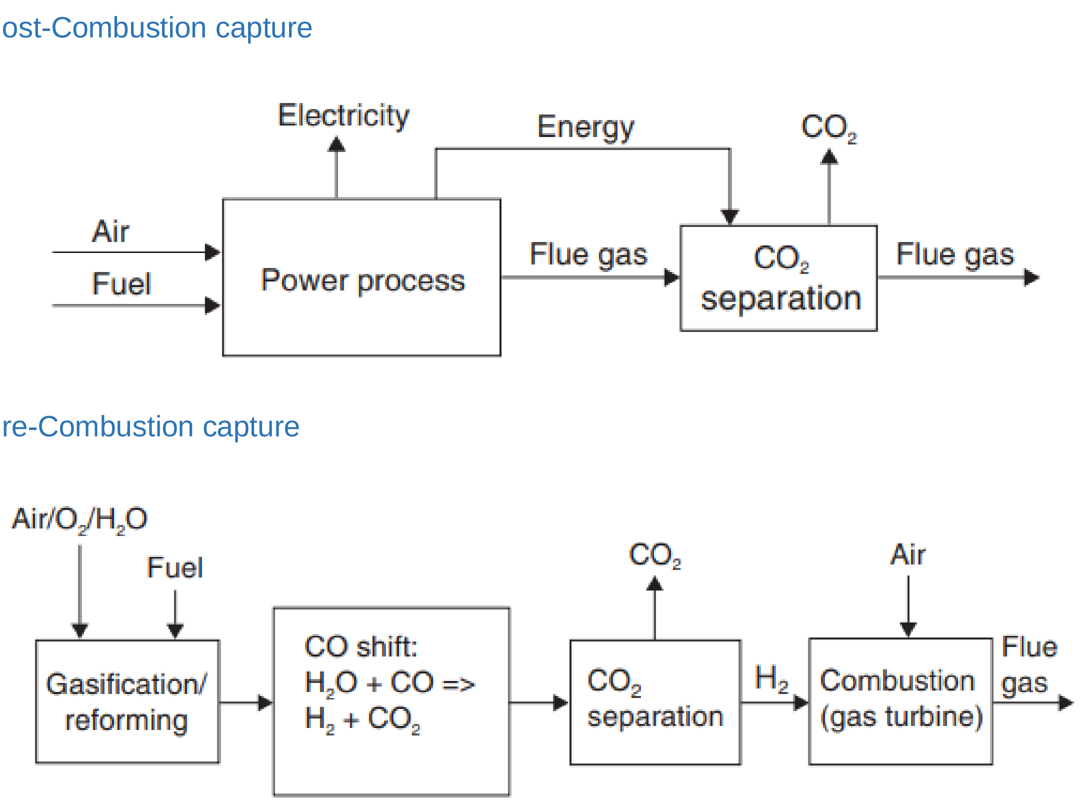

Figure 4. Strategies for carbon capture. a) Post-combustion. b) Pre-combustion. Reprinted from Thambinuthu et al., 2002.

In the particular case of H_2 production, so-called chemical looping hydrogen processes (CLH) are based, firstly, on the reduction of the MeO (usually hematite: Fe_2O_3) by the input gases which enables CO_2-sequestration after water condensation (see Reactions (3) to (8) for more details). Secondly, there is a reoxidation process of the oxygen carrier with steam, where hydrogen is produced as a product (Bock et al., 2021). The reactions of this last process correspond to the inverse ones shown in (3), (4) and (5), without CO_2 injection, this means the reactions (6), (7) and (8) are not performed, since there is only water steam feed. Otherwise, carbon monoxide would be also obtained, reducing the purity of the hydrogen produced.

Reduction reaction with hydrogen:

$$3Fe_2O_3 + 2H_2 \rightarrow 2F_3O_4 + 3H_2O \qquad \Delta H_{R,1073K} = -7 \left[\frac{kJ}{mol}\right] \qquad (3)$$

$$Fe_3O_4 + H_2 \rightarrow FeO + H_2O \qquad \Delta H_{R,1073K} = 47 \left[\frac{kJ}{mol}\right] \qquad (4)$$

$$FeO + H_2 \rightarrow Fe + H_2O \qquad \Delta H_{R,1073K} = 17 \left[\frac{kJ}{mol}\right] \qquad (5)$$

Reduction reaction with carbon monoxide:

$$3Fe_2O_3 + CO \rightarrow 2F_3O_4 + CO_2 \qquad \Delta H_{R,1073K} = -41 \left[\frac{kJ}{mol}\right] \tag{6}$$

$$Fe_3O_4 + CO \rightarrow FeO + CO_2 \qquad \Delta H_{R,1073K} = 13 \left[\frac{kJ}{mol}\right] \tag{7}$$

$$FeO + CO \rightarrow Fe + CO_2 \qquad \Delta H_{R,1073K} = -17 \left[\frac{kJ}{mol}\right] \tag{8}$$

Air oxidation reaction:

$$4Fe_3O_4 + O_2 \rightarrow 2Fe_2O_3 \qquad \Delta H_{R,1073K} = -242 \left[\frac{kJ}{mol}\right] \tag{9}$$

Reaction (9), or also called air oxidation, is used to reach the full oxidation state of iron (III), taking back the oxygen carrier to the initial state and completing the loop. This process is performed for thermodynamics reasons, since steam oxidation is not able to obtain the highest oxidation state Fe_2O_3 again (Bock et al., 2021).

CLH can potentially be applied in the steel industry since blast furnace top gas (BFG) includes reducible gases (see Table 1), so this technology can be implemented as pre-combustion carbon capture technology (see Figure 4.b). This topic will be deeper discussed in the next section 1.2.

1.2. Rouge H2 Engineering

Rouge H2 Engineering (RGH2) is the start-up in which this master thesis is performed. It is based in Graz, Austria and it was founded in 2015. After the acquisition of a patent from Graz University of Technology, which consists in the adaptation of the CLH in a fixed-bed reactor. In 2016, RGH2 scaled-up the system up to 10 kW and in 2018 a prototype of 60 kW was validated, with a production capacity of 42 kg of hydrogen per day.

In 2022, a pilot scale prototype started to operate in a landfill located in Lindlar, Germany. So far, the system has reached over 4,000 hours of continuous operation. As from this year, the company intensifies its research efforts towards carbon capture with hydrogen production from industrial feed gases.

The process flowsheet of RGH2's Chemical Looping technology is shown in Figure 5, where biogas is used as a feedstock. It is important to highlight that the media supply is pre-treated water and desulphurized biogas (processes not shown in Figure 5). From the process engineering point of view, the system also requires pumps (for water, noted as PP), compressors (for biogas and air, noted as CP) and a steam reboiler (heat exchangers, noted as HX) (Bock et al., 2021).

Regarding to the system operation, the gases are introduced either to the reduction-oxidation reactors while using a counter current heat exchanger (noted as HX Red, HX Ox in Figure 5), with the respective outlet gas streams as heat sources. The gases obtained from the reduction step (lean gas) are cooled through a heat exchanger (HU #3), therefore, the removed heat from this process is used to supply heat to the local heating lines and for the downstream recirculation compressor (CP recirculation). The burner shown in Figure 5 provides the energy requirements for the reforming (used to transform methane into carbon monoxide and hydrogen, which are endothermic reactions) and reduction reactions (Bock et al., 2021).

The furnace outlet gases, shown in Figure 5, are released at 950 ºC, and they are used for the steam vaporization which is necessary in the oxidation reactions. The hydrogen product gas from the latter process is cooled up to 20 ºC through heat exchangers (noted as HX subcool) in order to freeze out excess water vapor. In this way, pure hydrogen is obtained, reaching concentrations up to 99.99% (Bock et al., 2021).

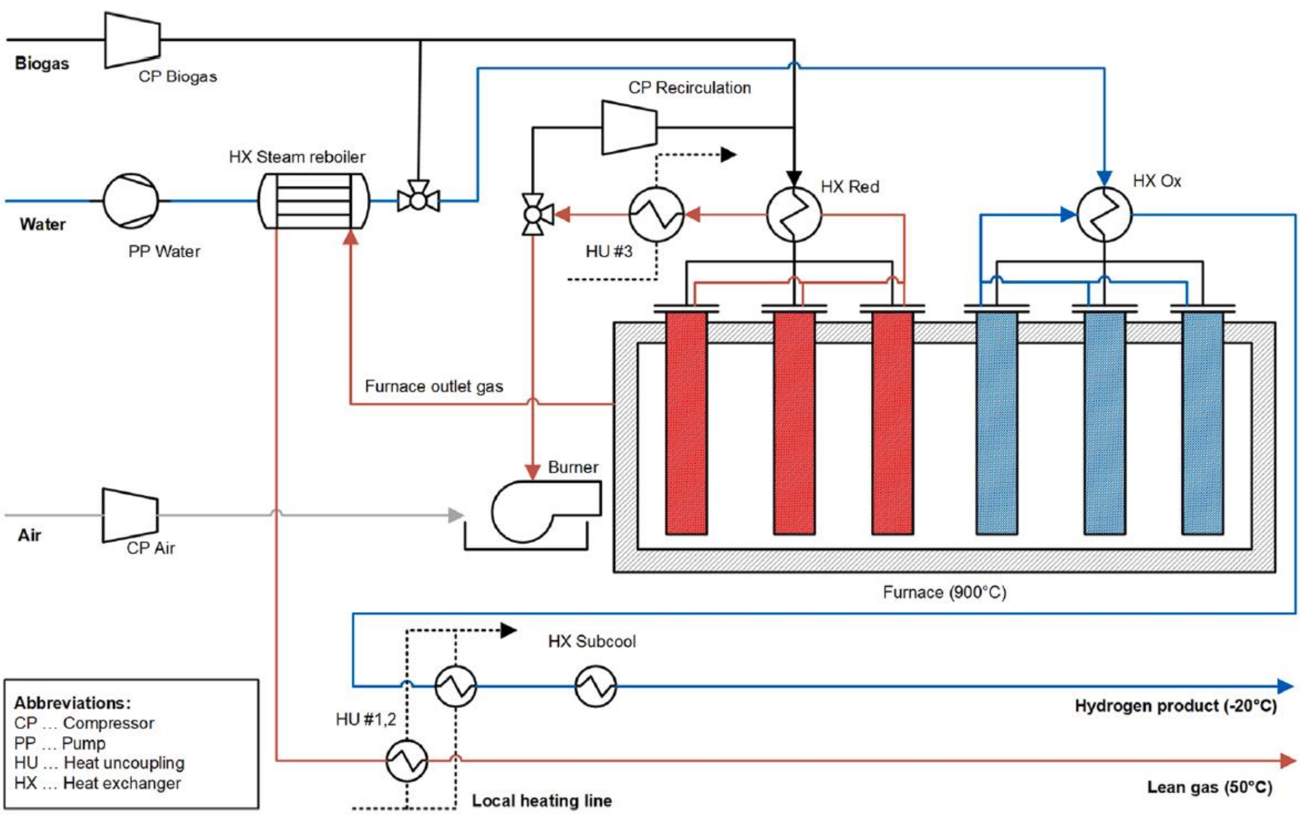

Figure 5. Process flowsheet of Rouge H2 Engineering technology. Reprinted from Bock et al., 2021.

After validating the prototype in 2020 using biogas as a feedstock, RGH2 concluded that its technology has the following competitive advantages:

- The direct production of high-purity hydrogen, eliminating the necessity of a downstream purification process.
- The system has no moving parts in the high temperature section. In addition to this, all the instrumentation operates below 200 ºC. This means that it is possible to use conventional components with long lifetime.
- As it is a fixed-bed reactor, it implies an easy operation in comparison with a permanent fluidization in fluidized-reactors.
- The system not only produces high-purity hydrogen, but it is also able to obtain up to 100 bars through liquid water compression, avoiding further compression processes.
- With the integration of an air oxidation step, CO_2 sequestration and N_2 production are inherent capabilities of the technology.

1.3. Objectives

Given the importance of decarbonizing the SMI and PPI along with producing hydrogen in a decentralized way, the goals of this master thesis are sub-divided in academic and commercial objectives. Regarding the first one, a process model will be implemented. With this model, thermodynamic process simulations will be performed for applications in SMI and PPI. On the other hand, the commercial objectives are focused on the sectors where the company has already know-how about it, and they are listed below:

1.3.1. General Objective

1.3.1.1. Academic General Objective

Developing a strategy to decarbonize the paper and paper industry using Rouge H2 Engineering Technology.

1.3.1.2. Commercial General Objective

Performing a research market in Latin America, in order to implement Rouge H2 Engineering technology in that region, focused on Chile and Brazil.

1.3.2. Specific Objectives

1.3.2.1. Specific Academic Objectives

I. Analysing the feasibility of replacement of boilers by gasifiers in the pulp and paper industry.

II. Modelling the Rouge H2 Engineering technology in Aspen Plus.

III. Performing simulations in Aspen Plus, to determine the hydrogen yield and carbon capture efficiency, through Rouge H2 Engineering technology, using the syngas coming from the gasification of the black liquor as feedstock, in the pulp and paper industry.

IV. Comparing efficiencies obtained using Rouge H2 Engineering technology and amine-scrubbing approach, applied in the pulp and paper industry.

1.3.2.2. Specific Commercial Objectives

I. Identifying key stakeholders from the steelmaking and biomass industry in Latin America.

II. Organizing meetings and performing presentation to the stakeholders on behalf of Rouge H2 Engineering.

III. Research for funding opportunities in the European Union and Latin America which are suitable for Rouge H2 Engineering current state of development.

IV. Supporting the application of Rouge H2 Engineering to different fundings in the European Union and Latin America.

2. Methodology

2.1. Academic Methodology

This section was developed following a logical and chronological step which are described below:

I. Literature study: Relevant information regarding the decarbonisation strategy for PPI is shown.

II. Model development and validation: Design of a suitable model for RGH2's hydrogen technology in ASPEN Plus. Thermodynamic validation of the model using the Baur-Glaessner diagram, along with the optimal configuration of the reactors are described. The scope of the model is not to represent the kinetics behind of the system, to appropriately replicate the occurring solid and gaseous reaction products in a thermodynamic process model.

III. Simulations: Once the decarbonization strategy is defined, and the model is fully validated, simulations are performed in order to predict the carbon capture and hydrogen production efficiency for a particular PPI. The scope of these simulations is limited to the correct prediction of the chemical looping technology, and not its inclusion into the whole PPI process.

2.2. Commercial Methodology

In order to perform systematic research of key stakeholders in Latin America, and avoiding arbitrary contacts, the following strategy was adopted: firstly, the existing associations in the biomass and steel industry were identified, then through LinkedIn, strategical people from these institutions were contacted, as these stakeholders could be a link to potential partners or clients. In addition to this, the initiative Low Carbon business action was considered significant, since this project funded by the European Union aims to transfer technology from Europe to Latin America (Low carbon business action, https://latam.lowcarbonbusinessaction.com/). A schema of this approach is shown in Figure 6.

Regarding the research on suitable funding opportunities, the corresponding investigation was performed through Google, pursuant to which the relevant fundings (i.e., focused on technologies in pilot scale stage or, in other words, with a Technology Readiness Level (TRL) equal or greater than 5) were identified.

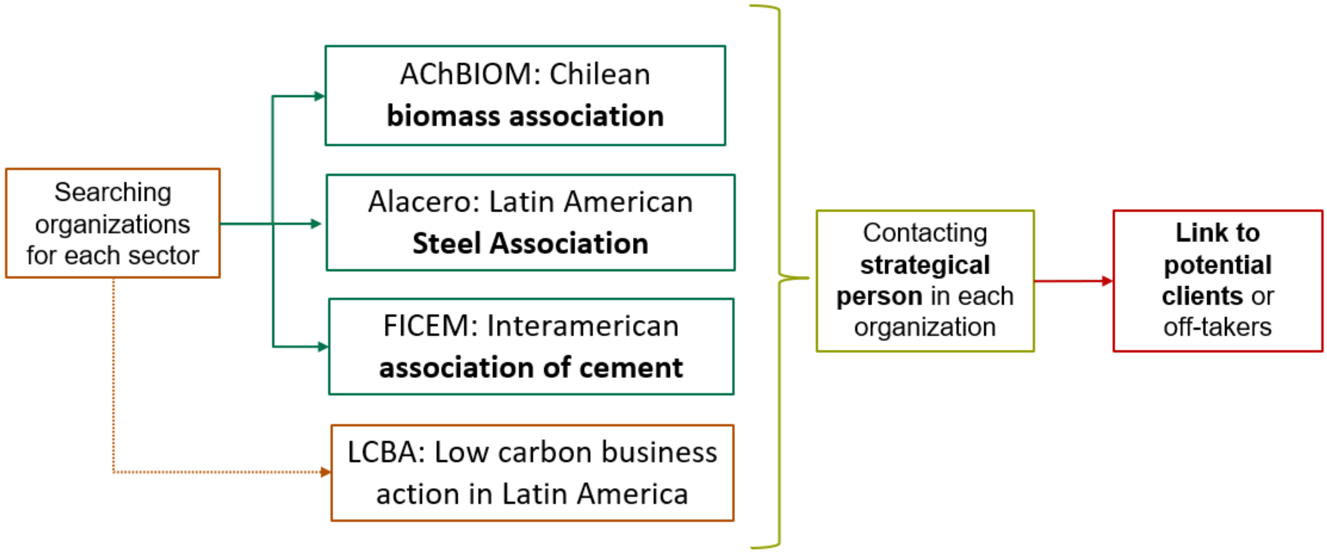

Figure 6. Strategy used to reach different stakeholders.

3. <u>Results and Discussions</u>

3.1. Academic Results and Discussions

3.1.1. <u>Literature study</u>

The strategy selected to reduce CO_2 emissions in the PPI was the replacement of the boiler for a gasifier since the combustion in this equipment represents 74% of the CO_2 emissions (Furszyfer Del Rio et al., 2022), as discussed in Section 1.1.2. Even though the traditional recovery process with the recovery boiler has proven to work well, this process has disadvantages such as low electricity generation efficiency (12%), smelt-water explosions, and reduced-sulfur gas emissions. While gasification has the potential to generate carbon-neutral energy products (for example, PPI is an electricity exporter), if black liquor is gasified instead of being combusted in the recovery boiler, a pulp mill could become an electricity exporter without release of CO_2 . Moreover, organic constituents of the black liquor can produce syngas for biofuel production such as hydrogen, methanol, DME, methane, etc. (Naqvi et al., 2010).

Black liquor gasification (BLG) is not a novel technique, it has been developing since the 1960s and has become a more recurrent trend in the PPI since many recovery boilers are or will become economically obsolete. Therefore, companies are looking for alternatives and BLG is one with better energy efficiency and a more sustainable concept. For instance, Chemrec is a Swedish company which used this strategy through pressurized oxygen-blown gasifier, which gasify black liquor at 32 bar and 950–1000ºC, using oxygen as oxidation agent. In Figure 7 is shown this configuration, and in Table 2 its syngas composition (Naqvi et al., 2010).

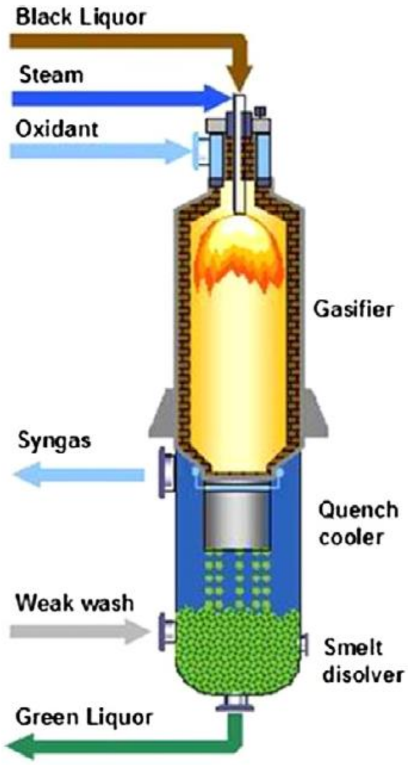

Figure 7. Black liquor gasification system deployed by Chemrec (Naqvi et al., 2010)

Hence, the system proposed to decarbonize the PPI consists in replacing the boiler with a gasifier, and the syngas obtained from this last step can be a potential feedstock for the application of RGH2 technology. Its gas composition was obtained from Naqvi et al., 2010 and Ferreira & Balestieri, 2015, along with a fully theoretical gas composition (50% CO and 50% hydrogen). See data shown in Table 2.

Table 2. Syngas composition from black liquor gasification. Data from (Naqvi et al., 2010)

Gasifier	Syngas composition [% molar fraction]					Reference
	CO	CO_2	H_2	H_2O	N_2	
Chemec: wet basis	29.70	14.93	30.55	22.05	0.23	Naqvi et al., 2010
Chemec: dry basis	38.10	19.15	39.19	0.00	0.30	Naqvi et al., 2010
Theoretical 1	26.61	8.05	14.29	6.95	43.42	Ferreira & Balestieri, 2015

Another important step, before developing a model, is properly understanding how a fixed bed reactor operates. This is a type of chemical reactor where reagents can be gases or liquids which flow through a solid bed of catalyst particles (in the case of RGH2 technology: the oxygen carrier). It is called "fixed bed" because the catalyst bed remains stationary during the reaction process. The reactants usually flow through the fixed bed reactor in either upward or downward directions, in this way the reaction takes place as a heterogeneously catalyzed gas reaction (Eigenberger, 1992.)

Fixed bed reactors are widely used in industrial processes, for instance in hydrogenation processes for the food and petrochemicals industries, as well as toxic substances treatment (nitrogen oxides removal from power station flue gases). They have important features such as high conversion rates, efficient heat and mass transfer, and scalability. Moreover, they can operate by controlling the temperature (isothermally) or without control (adiabatic). This is an important operating condition, since temperature is one of the most important variables to influence a chemical reaction (Eigenberger, 1992.).

3.1.2. Model development

As it was already discussed, RGH2's technology uses the Chemical Looping technology. An additional element to be highlighted is this process is performed in a fixed- bed reactor (see Figure 5) where the solid bed of catalyst particles is initially only composed of Fe_2O_3, while the gas flowing through depends on the step of the process. For the reduction step the reactants are the feedstock; hence it could be BFG, syngas, etc. While for the oxidation step the catalyst is reduced, so the gas feed is steam water in order to oxidize the oxygen carrier.

It is noteworthy that the reduction and oxidation reactions are being performed in the same reactor, using the same catalysts, but with a different state of oxidation. Taking this phenomenology into consideration, and since Aspen Plus V14 does not have dedicated fixed bed reactors for gas-solid reactions in its database. Hence, two approaches were considered to represent this type of reactor with the available tools this software can provide:

I. **Reaction step model**: Representation of the system through three equilibrium reactors (REQUIL). The idea behind the abstraction of the fixed-bed reactor consists in separate each step of the process in different reactors. In other words, the one-single step RGH2´s technology is modelled with three REQUIL in series, corresponding to the reduction, oxidation and air oxidation step, respectively.

II. **Cascade model**: Representation of the system through several "equilibrium stages" with Gibbs reactors (RGIBBS). The principle considered came from a theoretical point of view, which is that a fixed bed reactor can also be modelled as infinite reactors in counter current, each of them in a different equilibrium state. Therefore, a discretization of this system was considered using from one to 20 reactors per step (see the layout in Annex A.2). For example, for 3 RGIBBS per step, the output of gases of the first reduction-reactor (RED-1) will be the input for the second reactor (RED-2). Therefore, the outlet of the RED-2 will be the inlet of RED-3. While for the solids, the output of RED-1, will be the input of the third oxidation-reactor (OX-3), as well as the output of RED-3 reactor will be the inlet of OX-1. Finally, same configuration was taken for air oxidation-reactors (AOX-1, AOX-2, and AOX-3). The entire arrangement is shown in

Figure 8. The idea behind of this strategy is modelling a batch operation with changing equilibrium, in this way each reactor models a different equilibrium through the length of the bed.

3.1.3. Model implementation

The different model approaches were implemented using ASPEN Plus v14 with the Peng–Robinson equation of state. PR-EOS represents properly experimental volumetric, thermal, and phase behaviour data for syngas processing (Myint et al., 2016). The chosen convergence methods are shown in Table 3. The following components were included in the simulation: H_2, H_2O, CO, CO_2, N_2, O_2 and CH_4 as "Conventional" compounds, while Fe_2O_3, Fe_3O_4, $Fe_{0.947}O$, FeO, and Fe were included as "Solid" compounds. From the thermodynamic data were automatically included from the following database: APV140 Inorganic, APV140 Solids, APV Pure40, APV140 Aqueous, NISTV140 NIST-TRC and APESV140 AP-EOS. Solid carbon deposition was not considered in the model.

As aforementioned, two different modelling strategies were considered. The first one was through separate REQUIL reactors for the respective reaction steps. However, after running the model, ASPEN PLUS had convergence issues. It means, the software was not able to complete the mass balance of the system. There can be different explanations about it, and one of them could be numerical issues. For that reason, different combinations of methos were selected (see Table 3), always providing the same warnings (non-convergence) after executing the model.

The second approach was considered through minimization of the Gibbs free energy in a cascade of several RGIBBS, where the feed of metal oxide was considered in cross-current with the gas inlet, in order to represent the reduction-oxidation state gradient of the oxygen carrier (see Figure 8) in a fixed-bed reactor. The reactors operated isothermally and at constant pressure. For the sake of simplicity, the layout taking into consideration 9 reactors (3 for reduction, 3 for steam oxidation, and 3 for air oxidation) is shown in Figure 8, where syngas inlet (SYN-IN) was considered at 950ºC and 25 bars, as it was reported by (Ferreira & Balestieri, 2015). This modelling strategy did not provide convergence issues, so this was the approach selected in the following simulations. Therefore, a thermodynamical validation was first performed by comparing the simulation results with the Baur-Glaessner diagram. Then, the optimal number of reactors is determined taking the steadiest hydrogen production as a key parameter.

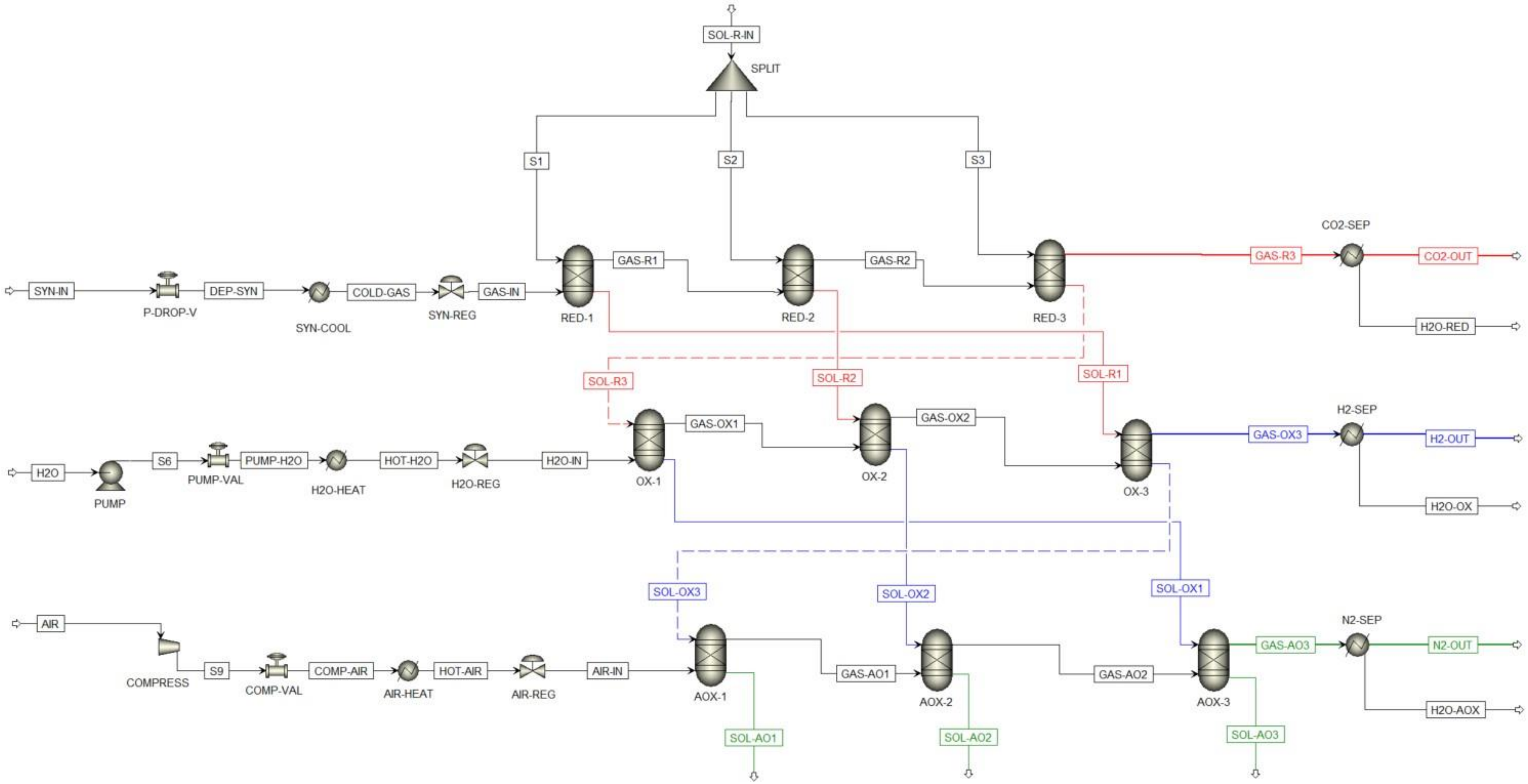

Figure 8. Layout of the system using Aspen Plus

Table 3. Default convergence methods in Aspen v14

Item	Method
Tears	Broyden
Single design spec	Newton
Multiple design spec	Broyden
Tears and design spec	Broyden
Optimization	SQP

Once the model obtained the expected data from the phenomenological point of view, the hydrogen yield and carbon capture efficiency were determined under different syngas composition. In order to make a quantitative comparison, the CO_2 sequestration for the amine-scrubbing approach was considered 90%, as previously reported by Bui et al., 2018.

3.1.4. Model validation

As mentioned before, the system was modelled by minimizing the Gibbs free energy for reactants in solid and gas phase (see Figure 8). In order to carry out this procedure, the gas-solid equilibrium was analysed for the oxidation states of the oxygen carrier (Fe_3O_4, FeO, Fe), as it is shown in Equation (10), to compare it's results with the Baur-Glaessner diagram (Hacker et al., 1998). This step is required, since setting a non-realistic gas-solid equilibrium in the model would induce non-accurate predictions.

Oxidation states of the oxygen carrier:

$$Hematite\ (Fe_2O_3) \leftrightarrow Magnetite\ (Fe_3O_4) \leftrightarrow Wuestite\ (Fe_{1-y}O_1) \leftrightarrow Iron\ (Fe) \qquad (10)$$

Therefore, the sensitivity analysis tool in ASPEN Plus was used to vary the hydrogen concentration and temperature, in order to reproduce the Baur-Glaessner diagram (Figure 9 (C)). The reaction conditions are shown in Table 4, taking into consideration one single RGibbs reactor. Figure 9 shows the corresponding results (graphs were obtained using Matlab R2021, in Annexes A.3.1. Thermodynamics validation, the codes to obtained them are shown, in which the oxidation states for Wuestite are: $y = 0$ and $y = 0.053$ in Equation (10). In other words, two different sensitivity analysis were carried out, one for FeO and another for $Fe_{0.947}O$, in Figure 9 (A) and (B), respectively.

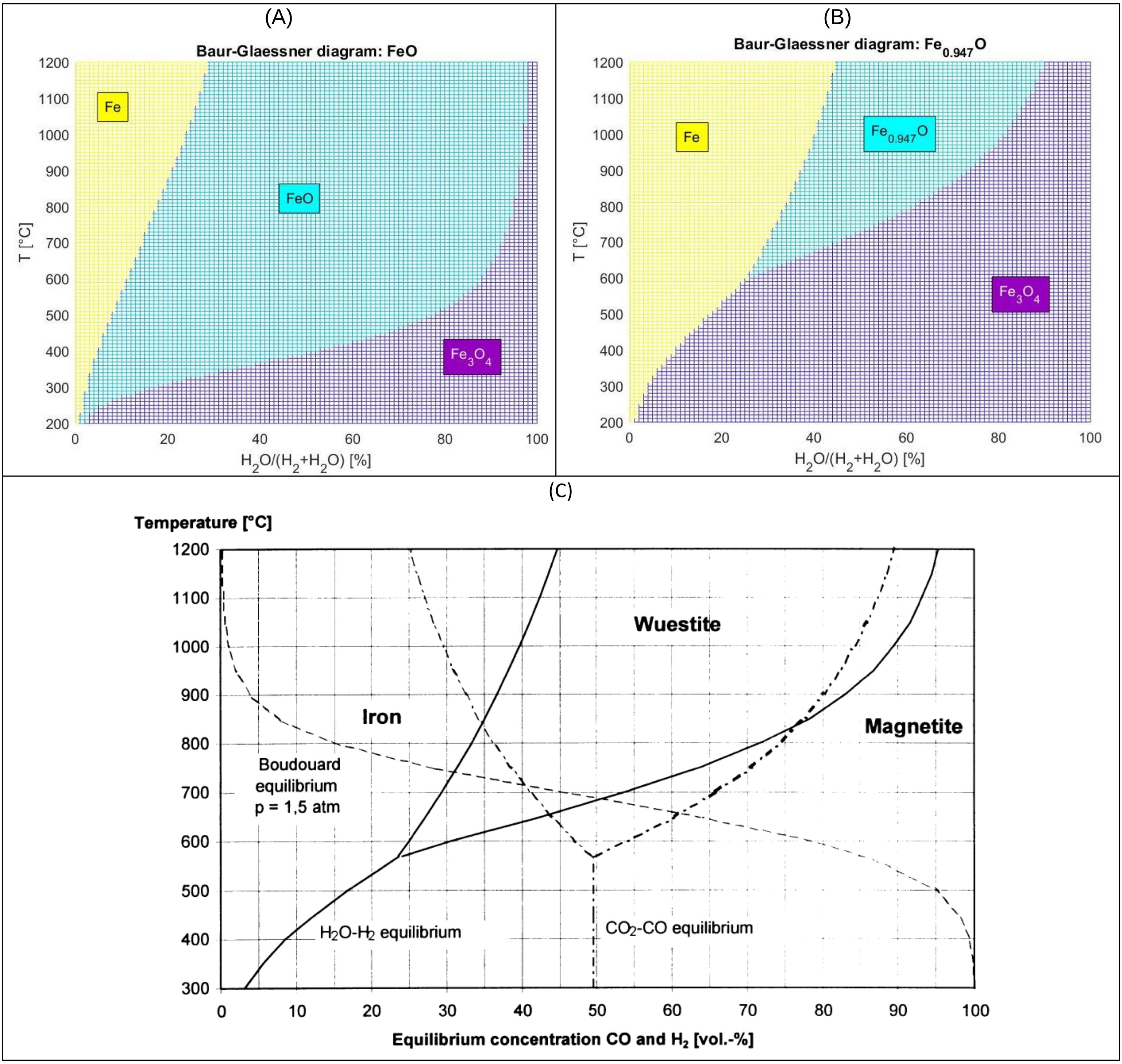

Figure 9. Thermodynamical validation results. (A) Using FeO as intermediate reduction state. (B) Using $Fe_{0.947}O$ as intermediate reduction state. (C) The original Baur-Glaessner diagram (Hacker et al., 1998)

Table 4. Operation conditions to perform the thermodynamical validation of the model.

Operating conditions	Value	Unit
H_2	0-999	kmol/h
Temperature	200-1200	ºC
Pressure	1.5	Bar
Steam H_2O	1	kmol/h
Oxygen carrier	10^{-5}	kmol/h

On the one hand, regarding the sensitivity analysis using FeO as intermediate oxidation state, Figure 9 (A) shows that not only the area covered is wider in comparison with the Baur-Glaessner diagram in Figure 9 (C), but also the values obtained are not consistent. Moreover, the results obtained are not plausible sense from a chemical perspective, since between 200 and 300ºC there is still presence of FeO, even though the hydrogen concentration is over 95%. Under the latter conditions, in a realistic system, the reductive capacity will be so high that the conversion from Fe_3O_4 to Fe would have a quick kinetics. Therefore, no intermediate oxidation state would be observed, as it is represented by the Baur-Glaessner diagram.

On the other hand, by using $Fe_{0.947}O$ as intermediate oxidation state, the results obtained in Figure 9 (B) show a good representation of the Baur-Glaessner diagram from a numerical point of view as well as phenomenological perspective. The reaction equilibrium is well represented, the equilibrium corresponds well with the Baur-Gleassner diagram, and $Fe_{0.947}O$ is not present below 600°C. Hence, from now on, all the following simulations will use Fe_2O_3, Fe_3O_4, $Fe_{0.947}O$ and Fe as chemical species.

The second step was to validate the RGIBBS-cascade approach, by determining the right amount of counter current reactors to be used. To do so, a feed gas inlet was 12.65 [kmol/h] whose composition was 50mol% CO and 50mol% hydrogen (that flow was taken in order to achieve 1 MW as input (see Table 4). As solid inlet, 39 [kmol/h] of Fe_2O_3 were chosen, to ensure a reduction of around 99% of the Fe_2O_3 to at least Fe_3O_4 at 850ºC and 5 bar. Finally, in order to ensure a complete steam reoxidation, 1000 [kmol/h] of steam water and 50 [kmol/h] of O_2 for the air oxidation were used.

The results are shown in Figure 10, where it is possible to see the different oxidation profile as a function of the number of reactors:

- For **one reactor** per reaction step, the amount of moles of iron in Fe_3O_4 is 98.6%, and there is no presence at all of $Fe_{0.947}O$.

It is important to highlight that a single RGIBBS reactor corresponds to a continuous stirred-tank reactor (CSTR), such as an ideally mixed, continuous fluidized bed reactor. With this kind of system, there is no hydrogen production since the thermodynamical equilibrium is favoured by the fully conversion of the inlet towards Fe_3O_4. As a consequence, $Fe_{0.947}O$ or Fe is not produced which means there are no further chemical species to be oxidized by the steam oxidation later on, and hence, no hydrogen production (see the inverse reaction (3), (4), and (5)). It is noteworthy again that, in order to close the loop of the oxygen carrier, that last oxidation step (from Fe_3O_4 to Fe_2O_3, see reaction (6)) does not produce H_2, since it does not require water, but oxygen. However, the reduction step can be carried out and carbon capture itself can be performed. Therefore, if the aim is to produce hydrogen, a reactor which is not always in a perfect equilibrium must be used.

- For **three reactors** per reaction step in counter current (it means in total 9 reactors: 3 for reduction, 3 for steam oxidation, and 3 for air oxidation), the layout is shown in Figure 8 and, accordingly, the results in Figure 10. The Fe_3O_4 moles concentration decreased due to an improved reduction to $Fe_{0.947}O$ and Fe_2O_3.
- With **more than 9 reactors** per step in counter current, there is only a small presence of Fe (0.6%). With this last configuration, the oxidation state profile is the one expected in a fixed bed reactor. If we imagine a gas stream with reductive capacity entering the reactor, it will fully reduce the oxygen carrier from Fe_2O_3 to Fe in its way. While the gas advances along the reactor, it will have less H_2 or CO available to keep reducing, so the main reaction will be from Fe_2O_3 to $Fe_{0.947}O$, and so on. In the last section of the fixed bed reactor, as it is expected, the completely oxidized gas cannot reduce the iron oxide anymore, and there is only Fe_2O_3. This general behaviour (i.e, one fixed-bed reactor where all the oxidation states are present) are well represented from 10 to 20 counter current reactors, as shown in Figure 10.

Therefore, at least 30 reactors in counter current (10 for reduction, 10 for steam oxidation and 10 for air oxidation) are needed to better represent the phenomenology behind this process. Figure 11 shows the hydrogen production as a function of the number of reactors. It should be noted that a big oscillation occurs with a small number of reactors, and while this number increases, the H_2 production becomes steadier, with a less pronounced oscillatory behavior. With the aim of quantifying this variation, Figure 11 also shows the relative error. This curve is composed by calculating the hydrogen average production from 10 to 20 reactors, which is 0.444 [MW], and then applying Equation (11).

Calculation of the relative error from 10 to 20 reactors:

$$Relative\ error_n\ [\%] = \left|\frac{H_{2,reactor=n} - 0.444}{0.444}\right| \cdot 100 \qquad (11)$$

Thanks to Equation (11), and therefore the results shown in Figure 11, it is possible to conclude that 14 reactors is a reasonable trade-off between reproducible data (Figure 11, red point) and calculation effort. Even though Figure 11 evidences that 16 reactors estimate a higher value for hydrogen production (black point), the goal of this model is to better represent and provide reliable data of the reality. Therefore, the model used to perform the simulations in 3.1.5 Simulation corresponds to use 14 reactors for reduction, 14 for steam oxidation and 14 for air oxidation.

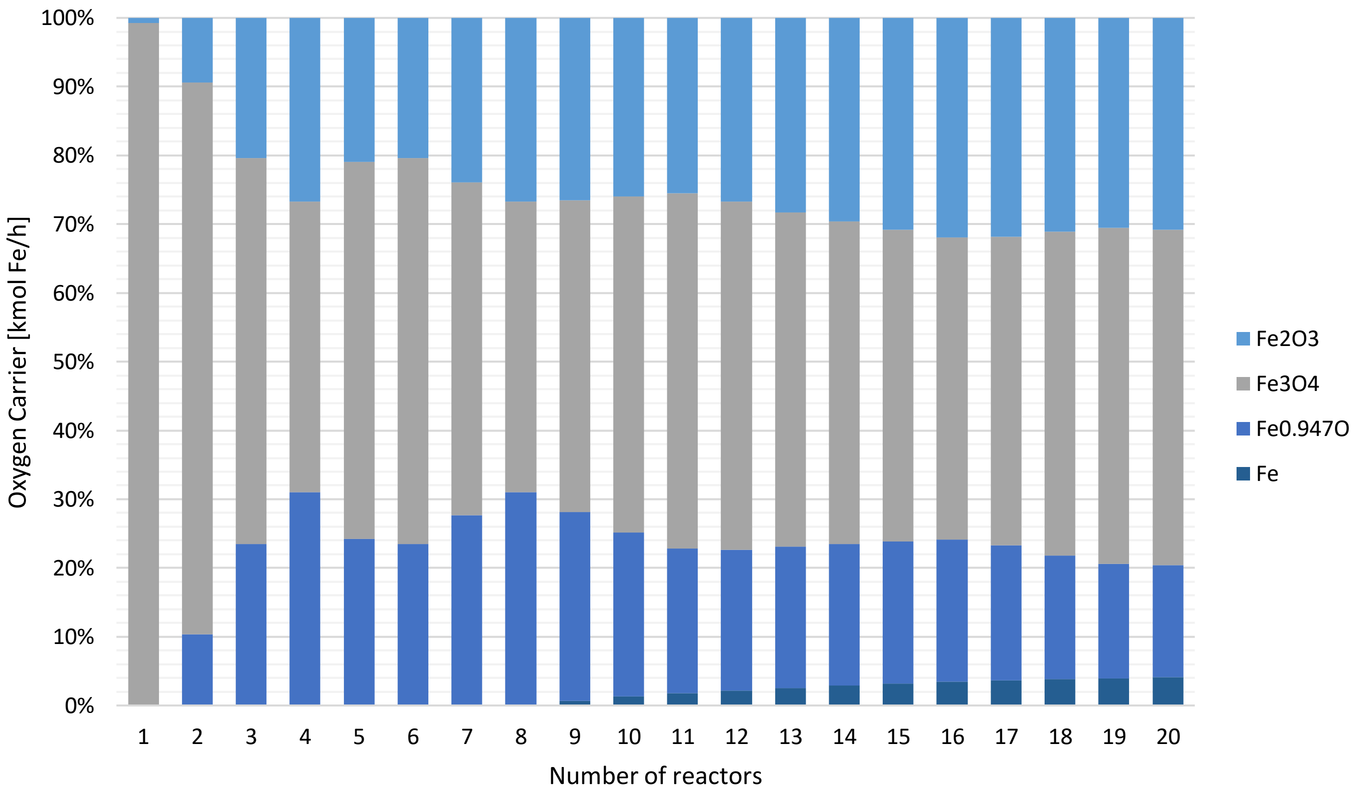

Figure 10. Summarized solid composition after the reduction step as a function of the number of reactors.

3.1.5. Simulations

The process simulation in Aspen Plus in Figure 8 shows 9 reactors: 3 for reduction, 3 for steam oxidation, and 3 for air oxidation, but the real configuration used was a cascade of 14 RGIBBS reactors for each step, as shown in Annex A.2. Firstly, the syngas pressure and temperature are reduced to 5 bars and 850ºC, respectively. These reductions are performed through a needle valve and a condenser. This step is necessary since those are the optimal operating conditions for the fixed-bed reactor (Stephan Nestl & Dipl-Ing Drtechn Viktor Hacker, 2015). For the same reasons, the inlet of water and air must reach those operating conditions, which are accomplished by a pump and a compressor, respectively, followed by a "heater" unit in both cases.

Figure 11. Hydrogen production as a function of the number of reactors in counter current, and the relative error in comparison with the average hydrogen production from 10 to 20 reactors.

The implementation of a compressor for the syngas input was not considered since this stream is already pressurized and at high temperature (25 bar and 950 ºC). Regarding the pump and the compressor, an efficiency of 70% was considered for both equipment.

It should be noted that in this layout (see Figure 8), there is always a regulator valve in each gas input. They are set in this way, in order to provide a more realistic approach, and it is justified from the simulation point view when a sensitivity analysis is performed. If, for example, flow or pressure are modified, which can be carried out by opening or closing these valves. Finally, a separator in the oxygen carrier input was implemented, to split in 14 equals flows for the respective reactors. It is important to highlight that several optimizations can be done to the design, such recycling water, oxygen carrier and oxygen. However, to avoid convergence issues in Aspen Plus, these streams were not re-connected.

Once the model was validated, the application of RGH2 for each case was simulated following these parameters: 14 reactors in counter current, Fe_2O_3=39 [kmol/h], O_2=50 [kmol/h], steam H_2O=1000 [kmol/h] (in order to ensure a complete reoxidation), 850ºC and 5 bar. Also, Table 5 shows the syngas inlet flow, which was determined considering 1 MW of energy in the input flow. The latter value is obtained through Equation (12) and the system efficiency is calculated according to Equation (13). These mathematical expressions are based on the energy contained in the gases, represented through the high heating value (HVV), and where

$X_{z,F}$ is the molar fraction of the compound "Z" (hydrogen or carbon monoxide in this case), in the stream "F" (inlet or outlet). In this scenario, as it mentioned above, the inlet flow (F_{in}) was adjusted to fix the input energy to 1 MW.

Formula to calculate the input energy of the syngas coming from the black liquor gasification:

$$Input\ energy = F_{in} \cdot \left(HHV_{H_2} \cdot X_{H_2,in} + HHV_{CO} \cdot X_{CO,in}\right) \tag{12}$$

Formula to calculate the efficiency of the process:

$$Efficiency = \frac{F_{out} \cdot HHV_{H_2} \cdot X_{H_2,in}}{Input\ energy} \tag{13}$$

Where $\Delta H^0_{f,H2} = HHV_{H_2} = 286\ [kJ/mol]$ and $\Delta H^0_{f,CO} = HHV_{CO} = 283\ [kJ/mol]$.

In Table 5, it should be highlighted that the case Theoretical 2 requires a lower flow in the syngas inlet in order to reach 1 MW, which is explained due to the high concentration of carbon monoxide and hydrogen in comparison to the other gases.

The simulations results are shown in Table 6, that describes the composition of the gas output, the amount of carbon captured and the hydrogen produced. Moreover, it also shows one of the most important values, which is the efficiency of each case. It provides information whether it is feasible to implement the RGH2 technology.

Regarding the composition of the gas output, it is noteworthy that the hydrogen molar fraction remains constant for all cases. Two reasons explain this result: firstly, in the oxidation step, there is no presence of contaminants since only steam water is fed, and it has been assumed that there is no carbon deposition (therefore, there is no reconversion into CO or CO_2, which might be additional contaminants). Secondly, since in the output of oxidation step there is only low presence of water and hydrogen and the cooler was set at 20ºC and 2 bar (H2-SEP in Figure 8), then the dew point of this mixture is fixed and, as a consequence, the water concentration for all outlet streams (H2-OUT and CO2-OUT, see Table 6) was 1.2%.

Table 5. Input energy in MW for each case, using 14 reactors in counter current, Fe_2O_3=39 [kmol/h], O_2=50 [kmol/h], steam H_2O=1000 [kmol/h], 850 °C and 5 bar.

Case	Syngas inlet [kmol/h]	Component	Molar Fraction	Inlet flow [mol/s]	Energy per component [kW]	Total input energy [MW]
Chemec: wet basis	21.0	H_2	0.306	1.782	509.7	1.0
		CO	0.297	1.732	490.3	
		H_2O	0.221	1.289	-	
		CO_2	0.149	0.869	-	
		N_2	0.002	0.012	-	
Chemec: dry basis	16.37	H_2	0.392	1.782	509.6	1.0
		CO	0.381	1.732	490.3	
		H_2O	0.000	0.000	-	
		CO_2	0.192	0.873	-	
		N_2	0.003	0.014	-	
Theoretical 1	30.96	H_2	0.143	1.228	351.4	1.0
		CO	0.266	2.288	647.6	
		H_2O	0.07	0.602	-	
		CO_2	0.08	0.688	-	
		N_2	0.434	3.732	-	
Theoretical 2: 50% CO, 50% H_2	12.65	H_2	0.500	6.327	502.6	1.0
		CO	0.500	6.327	497.3	

It is important to define the purposes of the produced hydrogen. For instance, if said purpose is fuel cell applications, the commonly recommended purity level is at least 99.9%, since impurities can adversely affect their performance (Murugan & Brown, 2015). In that scenario, in order to improve the purity of H_2, lower temperatures should be set in the cooler. However, the equipment would require higher energy consumption and, therefore, increase the OPEX of this process.

Concerning the purity of CO_2, the same argument used with the hydrogen can be applied for this stream, in order to explain its concentration (operating conditions of the cooler and the dew point). Nevertheless, an extra variable can be added by analysing the purity of this molecule for "Theoretical 1". In this case, the carbon dioxide purity is 43.9% since there is a significant presence of nitrogen (54.9%). Therefore, the aforementioned additional variable is the input gas composition, as shown in Table 2 (CO_2 and N_2 molar fractions are 8.05% and 43.42%, respectively). Given the intrinsic characteristics of RGH2 technology, i.e. carbon capture, the concentration in the output for both chemical species increase (CO_2 from 8.05% to 43.9%, and N_2 from 43.42% to 54.9%). In fact, although the quantity of carbon captured in kmol/h is comparable in the different cases, the purity is affected by the inlet gas composition. Finally, the outlet stream "N2-OUT" only contains oxygen due to the abovementioned reason (i.e, that the air oxidation is carried out with pure oxygen), so the remaining O_2 in this line corresponds to the one non-reacted, due to a full oxidation, according to Reaction (6).

Following the same argument of the last paragraph, i.e., the amount of hydrogen depends on the oxidation state of the oxygen carrier, and crossing the information between Table 5 and Table 6, it is noteworthy that the case Theoretical 2 has the highest energy efficiency (44.74%). This is once again explained due to the high concentration of carbon monoxide and hydrogen in comparison with the other cases. In fact, in Table 6 it is possible to ascertain that the case 2 (Chemec: dry basis) has the second highest efficiency (36.01%) which is consistent with the data in Table 5, where CO and H_2 have the second highest concentration in the input gas.

Aspen Plus has an important feature, which is providing the energy consumption of the whole equipment of the process. The breakdown of the energy consumption by the whole system per case, considering reactors, pumps, compressors, heaters and coolers, are shown in Annex A.1. It should be noted that the total energy balance shows that there is a release of energy, which makes sense since the oxidation reaction, especially air-oxidation, have a negative enthalpy. Therefore, they are exothermic, explaining this output of energy.

In all cases, the energy release for the reactor OX-1 is close to zero, since this reactor is being fed by RED-14 (data not shown), which has the least reduced species from the last process. In other words, in OX-1, as the reagents are mostly already oxidized, there are no reactions performed, and as a result, no release of energy. Conversely, reactors OX-13 and OX-14 are the ones releasing over 95% of the total energy corresponding to the oxidation step. Once again, it is explained by the state of oxidation of the feed since this3 equipment received the most reduced species by being in counter current with the reduction reactors.

It should also be highlighted that simulations show that RGH2 technology not only has higher efficiency associated with the hydrogen production, but there is also heat release, which can be used in the pulp and paper process. Therefore, this technology is significantly more energy efficient than the current process used by these industries.

It is remarkable that, in the four cases studied, current efficiency was overcome by using boilers (12%). Therefore, RGH2 is a convenient alternative for PPI not only from the energy point of view, but also from the sustainability perspective, since burning hydrogen to produce energy does not release CO_2 emissions. Moreover, the heat extracted by using RGH2 technology is coming from a process in which the CO_2 is leaving the system in a purified line, with enough purity to be directly stored (CCS) or utilized (CCU), except in case 3 (Theoretical 1), where there is a high nitrogen concentration in the output.

The most realistic case studied is considered to be the number 1 (wet basis), for the following reasons:

- Case 2: dry syngas does not contain water in the final mixture of gases. According to Naqvi et al., 2010, the equilibrium calculations and the results obtained from a pilot plant, showed presence of H_2O in the syngas.
- Case 3 was obtained theoretically.
- Case 4 was designed in order to develop the thermodynamic validation, with very low probability to find that gas composition in the pulp and paper industry.

Therefore, the following simulations are performed taking into consideration the case 1, wet basis. A sensitivity analysis was performed, modifying the pressure and temperature of the fixed-bed reactor carrying out the conversion process. The temperature was varied between 700ºC and 950ºC; the latter value, considered the upper limit, is the gasifier outlet temperature. In that case, no cooling is required in this stream which means less energy consumption. Following the same idea, the pressure was varied between 5 and 25 bars, in order to avoid energy losses during expansion. Results are shown in Figure 12 (A) and (B) for the CO_2 and hydrogen production, respectively.

Figure 12 (A) and (B) evidence that, in general, there is no dependence on the pressure for the H_2 and CO_2 production. Figure 12 (B) shows a flat surface, which means that carbon dioxide production is not influenced by temperature either.

The hydrogen production shows small variations as function of pressure at low temperatures (between 700ºC and 730ºC), but then its increase is only due to an increase in the temperature, and therefore it is invariant with respect to pressure. This last property can be explained by the fact there are no changes in the gas phase volume since the reaction is equimolar. In other words, according to Principle of Le-Chatelier, if reactants and products have the same number of moles of gas, then there will be no modifications in the equilibrium if the volume is constant.

Table 6. Simulation results using Aspen Plus, for different cases, for an input of 1 MW of syngas, 14 reactors in counter current, Fe_2O_3=39 [kmol/h], O_2=50 [kmol/h], steam H_2O=1000 [kmol/h], 850 ºC and 5 bar.

Case	Outlet Streams	Outlet Gas composition [% molar fraction]					Carbon capture [kmol/h]	Hydrogen production [kmol/h]	Efficiency [%]
		H_2	CO_2	N_2	H_2O	O_2			
Chemec: wet basis	H2-OUT	98.8	0.0	0.0	1.2	0.0	9.60	3.24	25.26
	CO2-OUT	0.0	98.1	0.7	1.2	0.0			
	N2-OUT	0.0	0.0	0.0	0.0	100			
Chemec: dry basis	H2-OUT	98.8	0.0	0.0	1.2	0.0	9.69	4.59	36.01
	CO2-OUT	0.0	98.3	0.7	1.2	0.0			
	N2-OUT	0.0	0.0	0.0	0.0	100			
Theoretical 1	H2-OUT	98.8	0.0	0.0	1.2	0.0	10.80	4.15	32.62
	CO2-OUT	0.0	43.9	54.9	1.2	0.0			
	N2-OUT	0.0	0.0	0.0	0.0	100			
Theoretical 2: 50% CO, 50% H_2	H2-OUT	98.8	0.0	0.0	1.2	0.0	6.33	5.70	44.74
	CO2-OUT	0.0	98.8	0.0	1.2	0.0			
	N2-OUT	0.0	0.0	0.0	0.0	100			

This non-pressure dependence can be an advantage for the downstream processes in the storage of H_2, since less energy would be required to reach 700 bar, the typical pressure at which this fuel is stored. Zacharias et al., 2019 carried out a laboratory study of hydrogen production using chemical loop, obtaining high product gas pressures ranging from 22.1 to 30.1 bar, and reaching a hydrogen purity of up to 99.3%. This study has concluded that pressurized hydrogen production of up to 95 bars with fixed bed chemical looping is possible, however one drawback was found: some zones were not accessible for the oxygen stream during air oxidation due to sintered structures. Moreover, higher pressures required equipment with highly pressure resistant materials, which meant a higher CAPEX. Therefore, an economic analysis should also be performed to determine whether the operation of the system at high pressures is the best option.

The stairs-shape of the curve in Figure 12 (A), can be explained by the discretization of the system. With infinite reactors, increasingly continuous and smooth hydrogen production is expected as temperature increases. This is indicated by the fact that the stages of constant hydrogen production changes with the number of reactors, thus they seem to be dependent on the number of equilibrium stages.

To confirm this hypothesis, more reactors in counter current should be deployed in Aspen Plus. While the performance of that work is outside of this master thesis scope, it will be considered in the projections, as mentioned below in Section 4. (Conclusions and Projections).

A deeper analysis was carried out regarding the increase of efficiency as a function of the temperature. Figure 13 shows the different oxidation state between 700ºC and 950ºC, confirming that higher reduction states are reached by the oxygen carrier as temperature increases. This is consistent with the Baur-Glaessner diagram (see Figure 9 (C)), which evidences that at higher temperatures, less hydrogen or carbon monoxide is required to reach iron or wuestite.

Therefore, as shown in Figure 13, at higher temperatures, production of $Fe_{0.947}O$ increases for a fixed syngas flow and composition. As a consequence, more hydrogen is produced in the oxidation step. This feature might have important implications in the future reactor design: If H_2 production and input syngas are fixed, then less amount of oxygen carrier should be loaded as temperature increases, which means smaller reactors can be built. Although this implies a reduction in the CAPEX, an increase in the OPEX is expected due to the higher energy consumption. The performance of an economic analysis to assess the viability of this conclusion, along with a Life Cycle Assessment (LCA) regarding the CO_2 emissions by injecting more energy to the system, is recommended as Projections of this master thesis.

Moreover, one of the assumptions considered is that reactors operate isothermally. This is an idealized assumption for a preliminary analysis and should be considered based on the actual reactor design in future.

3.1.6. Comparative analysis with amine-scrubbing technology

By comparing the results with amine-scrubbing carbon capture, the advantages of the RGH2 technology are evident. A comparative table, regarding the steelmaking industry, is shown in Table 7. The items where the exact figure is not known is due to the lack of industrial scale data, preliminary estimates can be obtained through simulations, which project lower energy demand and costs of the chemical loop approach over amine scrubbing as baseline technology.

As comparison for PPI, some publications reported that the cost of retrofitting a pulp plant with post-combustion amine capture using MEA is 122.5–131 €/tCO_2, while for BLG, the implementation of CCS yields CO_2 avoidance costs of 29 and 61 €/tCO_2 for pulp mills and integrated mills, respectively (Furszyfer Del Rio et al., 2022). Even under the worst-case scenarios, almost all options remain under 100 €/t CO_2 avoided. (Al-Kaabi et al., 2017). Using the mathematical transitivity relation and the data in Table 7, (i.e., whenever x>y and y>z, then also x>z), it is possible to infer that using RGH2 technology could result in an even more reduced cost.

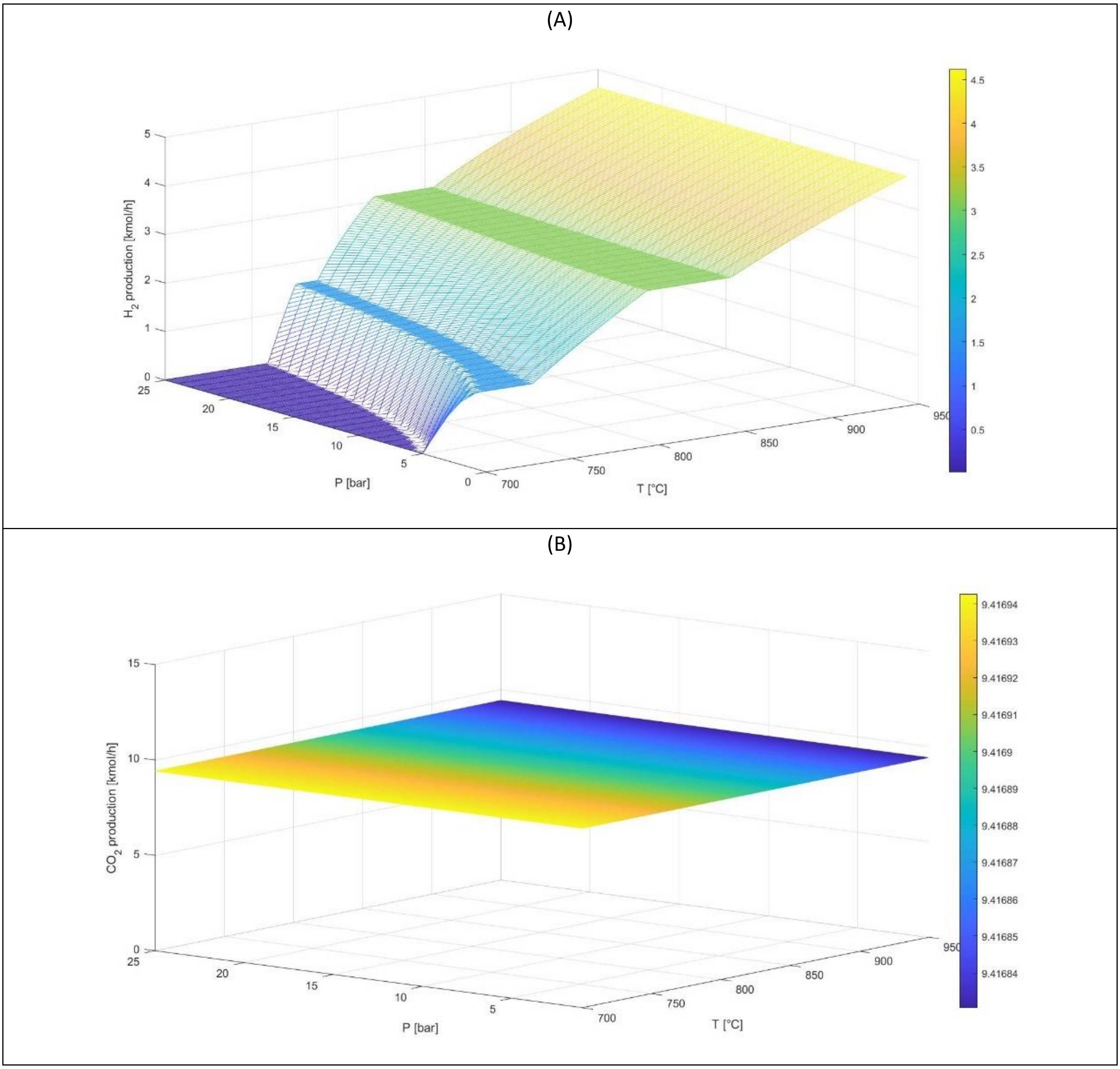

Figure 12. Sensitivity analysis varying temperature and pressure for wet syngas with 14 reactors. (A) Results for hydrogen production and (B) for CO_2 production

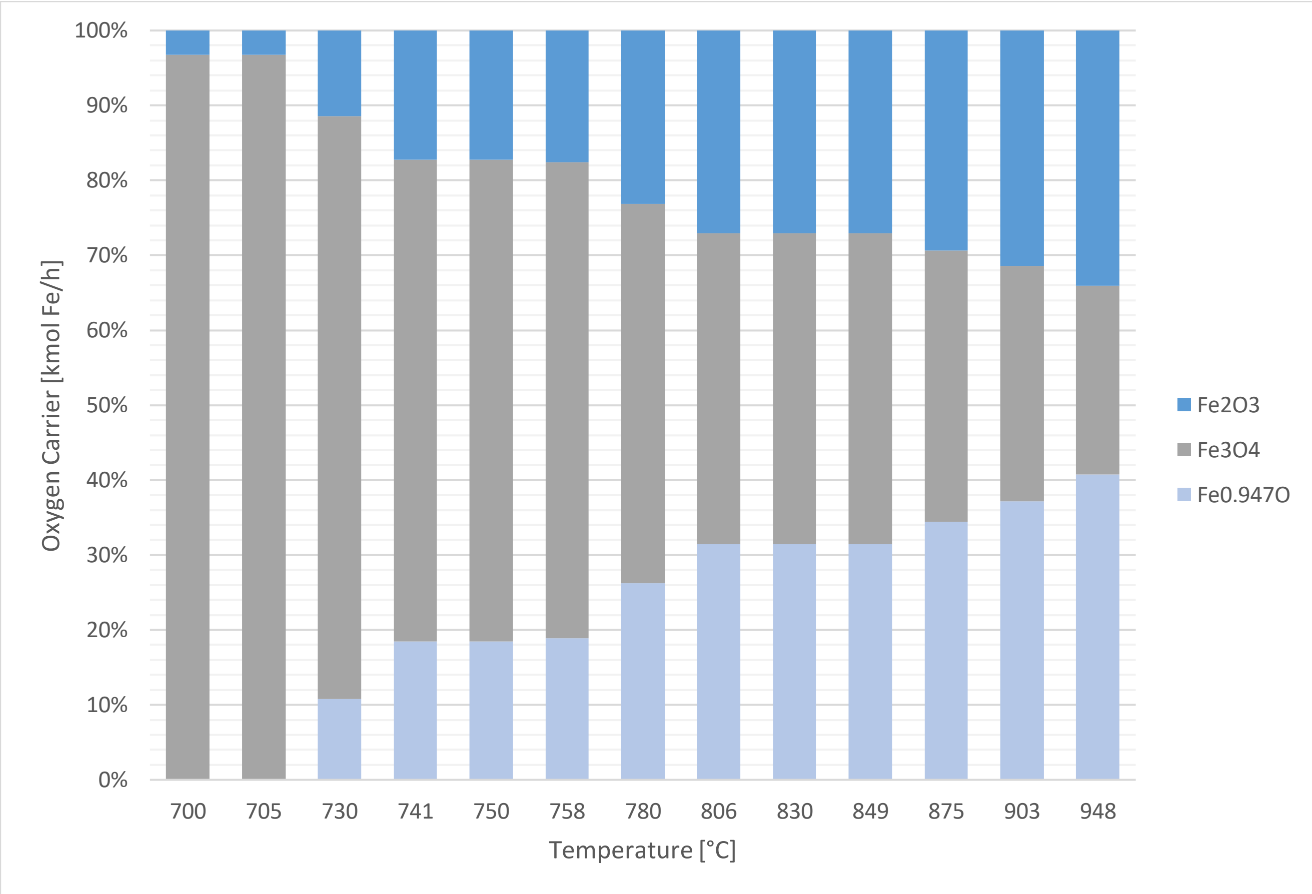

Figure 13. Oxygen carrier oxidation state profile as a function of the temperature, for 14 reactors per step in counter current.

Table 7. Comparative table between amine-scrubbing and RGH2 technology for the steelmaking industry

Item	Amine-scrubbing	RGH2 Technology
Process step	Post-combustion	Pre-combustion
CO_2 Capture rate	90%	99.5%
Outputs	CO_2	CO_2, H_2, N_2 and heat
Energy demand	2.5 MJ/kgCO_2	Less
Cost of CO_2 avoided	38 euros/tCO_2	Less
Others	Big structure	Less land and water use

The reasons why RGH2 should be less energetic demanding than amine-scrubbing is based on process itself. A conventional wet scrubbing technology requires a high amount of externally provided heat for the desorber. Furthermore, the CO_2 capture rate depends strongly on a high CO conversion in the water-gas shift reaction (see Figure 4.b) and the shifted gas needs to be cooled prior to entering the wet scrubbing separation section, which requires energy (Manzolini et al., 2020).

On the other hand, carrying out a high temperature cyclic process, like the one performed by RGH2 technology, has several advantages. Firstly, the heat rejected from the cyclic chemical looping process is at a temperature (typically around 700-900°C) above the turbine inlet temperature, which means that all the heat released can be recovered back into a steam power cycle. In other words, the global energy balance is more efficient. Secondly, in the chemical looping combustion, the fuel is in direct contact with the metal oxide, so the loss associated with the combustion reaction is partially avoided. (Bui et al., 2018)

From the operational point of view, and according to the RGH2 experts (confidential data), CO_2 fluctuations are are no issue for RGH2 technology.

Finally, regarding the carbon capture itself, simulations showed a higher efficiency for RGH2 technology in comparison with amine-scrubbing. Table 6 shows purities of up to 98% when there is no nitrogen in the input gas composition. When N_2 increases, the CO_2 purity decreases, but the carbon capture remains over 99.99% since the other streams do not have presence of carbon dioxide. Therefore, an important conclusion of this master thesis is that RGH2 technology is not only more efficient than amine-scrubbing regarding the carbon capture, but also from an economic, energy and environment (no losses of amine) point of view.

3.2. Commercial Results and Discussions

3.2.1. Stakeholders research

According to the strategy adopted in Figure 6, different stakeholders of those institutions were contacted through LinkedIn. In the following paragraphs a brief description of each association will be provided, then the results obtained by contacting the respective stakeholders are presented. It is important to highlight that the contact with Interamerican Association of Cement (FICEM) was not developed, since the gases emissions coming from this industry do not have reductive capacity, which means they do not contain CO or H_2, but mostly CO_2. Therefore, they are no suitable for Rouge H2 Engineering technology (Bosoaga et al., 2009).

I. **Chilean Biomass Association** (AChBIOM, https://www.achbiom.cl/web2/)

AChBIOM serves as the unifying body for producers of biomass raw materials such as pellets, wood chips, and firewood, as well as representatives of equipment manufacturers, transporters, project development companies, certifying and academic institutions. In this way, AChBIOM drives the advancement of Biomass (Bioenergy) in Chile.

Its mission is to enlighten the population about the benefits that stem from the responsible utilization of biomass as biofuels for sustainable bioenergy. In pursuit of this objective, AChBIOM collaborates closely with the government to establish enduring regulatory frameworks that offer long-term stability, transparency, and minimize investment risks within the sector.

Moreover, AChBIOM actively foster business opportunities for the associates. By promoting the proper utilization of this resource and maintaining constant engagement with all stakeholders (between them national and international research centers), in order to build a progressive path forward and embrace a future-oriented approach.

AChBIOM understands that biomass, as a cornerstone of Bioenergy, serves as a catalyst for Chile's comprehensive development, with due consideration for its three fundamental pillars: societal, environmental, and economic aspects.

The energetic valorisation of biomass lies at the heart of the circular economy, effectively reshaping the linear production model. It is seamlessly integrated into a broader bioeconomy, finding synergy with higher-level sectors such as agriculture, the forestry industry, and even urban organic waste management, culminating in a harmonious and sustainable progression.

The motivation to contact AChBIOM is that they connect RGH2 with any pulp and paper industry which could be interested in applying the decarbonisation strategy described in the Academic Results.

II. **Low carbon business action in Latin America** (LCBA, https://latam.lowcarbonbusinessaction.com/)

Platform for Business, an initiative funded and supported by the European Union, emerges as a tool of progress and collaboration. Its main goal is to foster enduring and value-added B2B relationships between low-carbon technology providers from the EU and visionary companies seeking sustainable solutions in Argentina, Brazil, Chile, Colombia, Mexico, and Canada.

The primary objectives are the promotion of a sustainable transition for businesses, fostering them towards a future circularity and a low-carbon economy. Through the internationalization of European small and medium-sized enterprises (SME), the platform acts as a catalyst for innovation and sustainability, empowering local counterparts to not only adapt but thrive in an increasingly interconnected and dynamic world. By facilitating knowledge exchange and fostering strategic partnerships, the platform contributes to the development and implementation of innovative technologies for a sustainable future.

Another vital facet of the LCBA lies in its commitment to support strategies for carbon emissions reduction. Recognizing the urgent need to address the pressing challenges posed by climate change, the platform provides a collaborative space where stakeholders can collectively work towards reducing their environmental footprint. In order to foster sustainable practices, the platform promotes businesses to embrace environmentally conscious approaches.

In addition, the platform dedicates itself to enhance resource efficiency and promote circularity in production and consumption models. By encouraging the adoption of circular economy principles, such as recycling, waste reduction, and resource optimization, the LCBA paves the way for more sustainable and responsible business practices. This holistic approach drives positive change throughout the entire value chain, ensuring that resources are used efficiently, waste is minimized, and the economic, social, and environmental aspects of sustainability are intricately woven together.

The LCBA welcomes the active participation of European companies operating within sectors closely aligned with the circular or low-carbon economy. These enterprises must have a maximum workforce of 499 employees, and the majority ownership (≥ 51%) must be held in the European Union. By being duly constituted in an EU member state, these suppliers underscore their dedication to upholding the highest standards of quality, ethics, and sustainability.

The motivation to be part of the LCBA is clear, RGH2 not only fits with all the requirements, i.e. being a SME, ownership over 51% in the EU, and promoting decarbonization technologies, but also it could be an "open-door" into the Latin American market.

III. **Latin American Steel Association** (Alacero, https://alacero.org/)

Alacero's mission is to promote the use of steel as the optimal material for a growing number of applications. They aim to raise awareness about the industry's commitment to environmental conservation and highlight steel as the most recyclable material. Alacero strives to foster strong connections within the steel industry's value chain and advocate for fair competition conditions in the region. Additionally, they aim to disseminate best practices in industrial safety and actively participate in international industry forums.

Regarding to its vision, Alacero envisions itself as the regional institution representing the steel industry in Latin America, working towards the promotion and sustainability of steel based on its significance for the region's development.

The main Alacero's objective aims to gather and represent the value chain of the steel industry in Latin America, promoting integration among its various components. They seek to foster values and promote and disseminate the industry's contributions in areas such as innovation, quality, human resource development, and sustainable regional development. Furthermore, Alacero strives to strengthen the bonds among its partners to collectively face the common challenges ahead. They communicate the distinctive values of the industry and the benefits of steel as a material in a clear and efficient manner.

There are two main reasons to reach out to Alacero:

- They have a vast network, alliance of over 60 prominent producing and related companies, collectively contributing to an annual steel production of 65 million tons. This remarkable output represents 95% of the steel manufactured in Latin America, underscoring the influential role Alacero plays in the region's steel industry.

- This organization is commitment to fostering collaboration, driving innovation, and promoting the decarbonization of the steel industry. Therefore, they are open to assess technologies like the one of Rouge H2 Engineering. In fact, according to their sustainability report, they made an agreement with the Interamerican development bank in order to fund innovations which can contribute to reduce the CO_2 emissions of this industry. The funding is oriented to fund the scale-up of technologies from pilot to industrial scale. Therefore, it totally matches with the current status of RGH2.

3.2.2. Contacting Stakeholders Results

I. Chilean Biomass Association

The general manager of AChBIOM was contacted. The first contacts were through LinkedIn, afterwards by e-mail, and finally it was possible to organize a videocall. In that meeting I could explain to him the potential of the technology and its comparative advantages, as it was already described in Academic Results. The stakeholder saw a big potential of RGH2 technology, but he was not sure if in Chile the boilers used in the PPI are about to be changed. In other words, perhaps now it is not the right moment to try to enter in the market. However, he provided me the e-mail of one potential client, after writing them I just received a reply some weeks after, and when I tried to organize a meeting, I never got an answer.

II. Low carbon business action in Latin America

The first contact with LCBA team was though e-mail and afterwards it was possible to set a videocall. The purpose of this meeting was to establish a mutual understanding, introduce ourselves, and foster collaboration. During the meeting, we had the opportunity to exchange valuable insights and address pertinent questions and concerns regarding our application to join the association.

Following the meeting, the application process to the platform was completed. After a couple of days, we received the confirmation that RGH2 had successfully become an official member of the LCBA. This represents a potential opportunity for RGH2, since LCBA's platform database signifies that any company in the region seeking cutting-edge technologies to decarbonize their processes can readily access and explore the solutions offered by us. In other words, it provides the opportunity to connect with potential clients and foster meaningful collaborations to decarbonize their processes.

A second meeting was carried out with LCBA, they explained to us that unfortunately the funding from EU is about to finish. However, they are optimistic that the initiative will be extended for at least another year. If that is the case, in 2024 RGH2 could be part of matchmaking initiatives, in order to meet different stakeholders in the region.

III. Latin American Steel Association

The most successful contact was the Latino American Steel association (ALACERO), in this case the Head of Sustainability was contacted, and Figure 14 shows the network created after having a meeting with her. Firstly, she made the link with the CEO of Sustainability of an important steelmaking industry located in a country in South America. This is a multinational steelmaking manufacturing corporation is currently one of the most innovative companies in terms of decarbonizing their processes.

Since I was the first link with ALACERO, I introduced RGH2 to this company. A presentation was prepared the week before, and to further receive feedback from our CTO, after introducing his comments, the presentation was also shown to the CEO of RGH2 and once again his comments were included. The presentation took place in 15th March 2023, and it was a success, since the CEO of Sustainability connected us with the global CTO of Decarbonization of said multinational steelmaking company. For that meeting, a customized presentation was designed, and it was performed by the whole RGH2 team: CEO, chairwoman, Head of Research, an external expert and me. The meeting took place on 3rd April, and once again it was a success. The parties agreed to sign a non-disclosure agreement to keep working together.

The scope of this part of the master thesis was defined in consultation with the CEO and chairwoman of RGH2, aimed to establish initial contacts with potential clients or partners. The objective was achieved upon delivering our presentation to the CEO of Sustainability. As a result, the commercial objectives were over-accomplished. The positive response by the CEO of Sustainability and other stakeholders affirmed that RGH2 technology has a big potential, and also the effectiveness of our presentation. The commercial success achieved through these meetings could be a milestone in the future of RGH2, in order to scale-up the technology.

As a conclusion of this stakeholder research, in Latin America there is still no motivation to innovate in terms of decarbonisation technologies, due to there is not a regulatory framework which motivates the development of them. For example, most of the countries do not have in their agenda to deploy carbon taxes like Europe is doing. Therefore, RGH2 should wait a couple of years to deploy its technology in those latitudes, but not leave for two main reasons:

I. The potential market of the Latin America is promising thanks to the huge amount of biomass available, and the big steel making factories present in this region.

II. The big positive impact on the environment. Currently, in terms of sustainability the industries in Latin America are one step behind in comparison with the European ones. Therefore, any innovation implemented in that region could imply an important reduce in the CO_2 emissions. For example, if the steelmaking processes, the coal (reducing agent) is replaced by syngas (which can come from the gasification of waste biomass), then overall emissions could be even negative. This is due to the biomass uses CO_2 to grow, afterwards the process would not emit this gas thanks to RGH2 technology. Therefore, by producing steel, the global emissions of CO2 would decrease.

3.2.3. Funding Opportunities Results

In parallel, the Head of Sustainability of ALACERO also connected us with the Inter-American Bank Development (IDB), since this institution is funding decarbonizing technologies, in pilot scale, to be deployed in steelmaking (Inter-American Development Bank, https://www.iadb.org/en). The meeting was set on 29th March 2023, and I carried out the presentation. The meeting was positive, the Lead Energy Specialist at IDB said RGH2 technology has a lot of potential, but in order to move forward we would have to present a cost analysis. Therefore, we agreed to meet in three months to update him on this matter.

Regarding the funding opportunities available in Chile, I attended some webinars to obtain further information, as per Table 8. However, given the current state of development of RGH2 technology, this company is not yet eligible for such funds, since it does not yet have any turnover, as well as no presence in the Chilean market and therefore no end-users. Having reached out to the commercial area of RGH2, the information provided was that the company could apply to these fundings in the following years.

Concerning the opportunities in Europe, RGH2 considers to apply this year to the European Innovation Council (EIC) Accelerator which provides funding worth over €1.13 billion for start-ups and small and medium-sized enterprises (SMEs) to develop and scale up high impact innovations having the potential to create new markets (EIC 2023 work programme, https://eic.ec.europa.eu/eic-2023-work-programme_en).

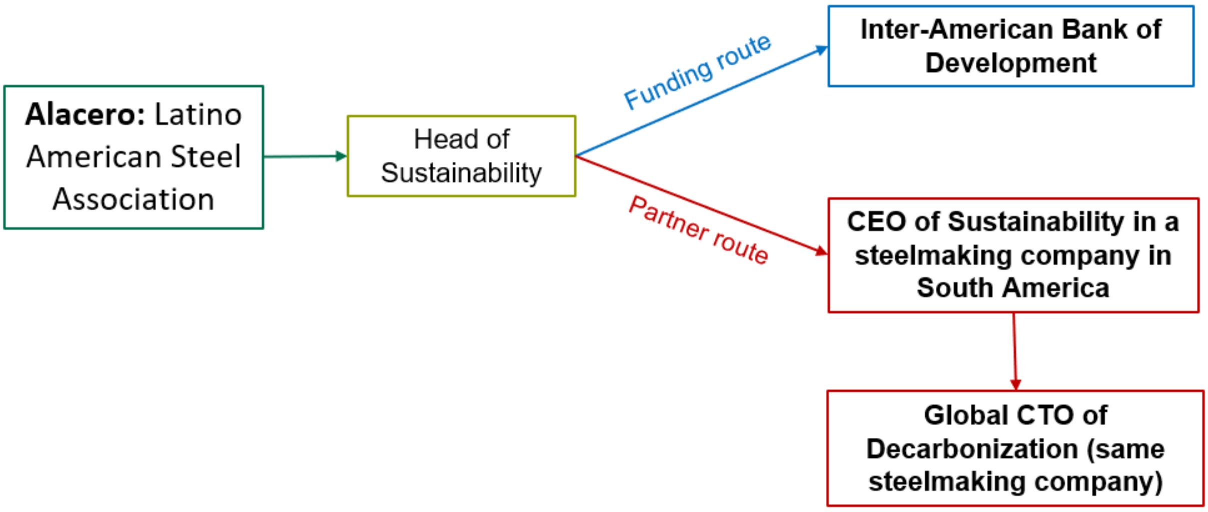

Figure 14. Network developed in order to find a partner for Rouge H2 Engineering.

Table 8. Funding opportunities in Chile

Program	Benefits	Requirements
Green Hydrogen Accelerator Programme[1]	First stage: Funding up to **35,000 euros**, corresponding the 70% of the consulting company services: **Basic engineering.** Second stage: Funding up to **930,000 euros to implement the technology.**	It requires a **final user of the hydrogen.** Coordination with a Chilean consulting company.
International Hydrogen Ramp-Up Program: Public-Private Partnership[2]	Networking and project scouting. **Assistance to implement pilot projects** in green hydrogen and power-to-X. Support of the various project ideas with in-depth studies and **technical trainings.** Minimum volume of **public contribution: 100,000 euros**; minimum volume of overall PPP measure: 200,000 euros.	It requires a turnover of 800,000 euros/year. **It could be in partnership with another company.**

[1] Agencia de Sostenibilidad Energética, https://www.agenciase.org/aceleradora-h2v/
[2] Bundesministerium für Wirtschaft und Klimaschutz, https://www.german-energy-solutions.de

Another important funding which may be of interest for RGH2 is the financial instrument for the environment or "L'Instrument Financier pour l'Environnement" (LIFE, https://cinea.ec.europa.eu/programmes/life/life-calls-proposals_en#type-of-grants) started thanks to European Parliament support in May 1992, aimed to co-finance projects related to the management of Special Protection Areas dedicated to birdlife preservation. From that moment, the budget was increased including more sectors. The overall budget for the implementation of the LIFE programme 2021-2027 will be EUR 5.432 billion. Currently, this funding has the following sub-programmes:

I. **Nature and biodiversity:** aiming at the protection and restoration of Europe's nature and halting and reversing biodiversity loss.

II. **Circular economy and quality of life:** aiming at facilitating the transition toward a sustainable, circular, toxic-free, energy-efficient and climate-resilient economy and at protecting, restoring and improving the quality of the environment.

III. **Climate change mitigation and adaptation:** aiming at contributing to the shift towards a sustainable, energy-efficient, renewable energy-based, climate-neutral and resilient economy.

IV. **Clean energy transition:** aiming at facilitating the transition towards an energy-efficient, renewable energy-based, climate-neutral and resilient economy by funding coordination and support actions across Europe, through supporting the delivery of EU policies and attracting private finance in the field of sustainable energy.

The sub-programmes most related to RGH2 technology are number II and III. Regarding to Climate change mitigation and adaptation, even though this sub-programme looks having a different focus in comparison with RGH2 goals, I quote "co-finances projects in the areas of urban adaptation and land-use planning, resilience of infrastructure, sustainable management of water in drought-prone areas, flood and coastal management, resilience of the agricultural, forestry and tourism sectors". By digging deeper, it also provides support for pilot projects that contribute to the reduction of greenhouse gas emissions.

The Circular economy and quality life sub-program co-finances projects in the environmental sector, in particular in the area of the circular economy, including recovery of resources from waste, water, air, noise, soil and chemical management as well as environmental governance. If we consider the blast furnace gases as a waste and hydrogen as a resource, RGH2 technology fits to this sub-program. It provides mostly action grants for projects implementing innovative through the so-called Standard Action Projects (SAP).

For these 2 sub-programmes, the submission dates are from mid-April to September 2023. Interesting is also the approach of LIFE funding in close-to-market projects, i.e., projects that have a high level of technical and business readiness at industrial or commercial scale. They ways LIFE supports are through: Business plan development advice, presentation guidance -

training on how to communicate with potential investors and connecting projects with intellectual property rights specialists.

4. Conclusions and Projections

Two main objectives were raised for this master thesis. The academic one was to develop a strategy to decarbonize the paper and paper industry using Rouge H2 Engineering Technology (RGH2). This consisted in replacing the boiler of the paper and pulp process with a gasifier to further use RGH2 technology to capture the CO_2 emissions as well as producing hydrogen. The results were obtained using Aspen Plus simulations; in order to do so, a model was validated thermodynamically, concluding that Fe-$Fe_{0.947}O$-Fe_3O_4-Fe_2O_3 represent the oxygen carrier thermodynamics properly. Moreover, it was determined that the optimal modelling of the fixed bed reactor is using 14 reactors per step in counter current (14 reactors for reduction, 14 for oxidation and 14 for air oxidation).

The simulations showed that the carbon capture is over 99.9% for four different cases, with energy efficiency between 25.3% and 44.5% depending on the input gas composition. Therefore, RGH2 may outperform the current technologies: Carbon capture efficiency using amine-scrubbing is 90%, while the energy efficiency with the boiler is 12%. Furthermore, it was shown that the higher the operating temperature, the higher the energy efficiency of RGH2's technology, providing insights regarding the equipment design.

The second main objective was to perform a research market in Latin America, in order to implement Rouge H2 Engineering technology in that region. The results of the methodology applied fulfilled this objective, since collaboration agreements were reached with an important steelmaking company.

Regarding the projections of this master thesis, the extension of the model verification could be considered, by making simulations with more than 20 reactors per step and including solid carbon as potential product in the model. Finally, an economic analysis should be performed to assess the use of air instead of pure oxygen (as it was considered the simulations performed) during the oxidation step as well as operating at higher temperatures. This latter not only implies higher energy consumption of the system, but also higher CO_2 emissions depending on the source of the energy. Therefore, it is also advisable to carry out a life cycle assessment of this process.

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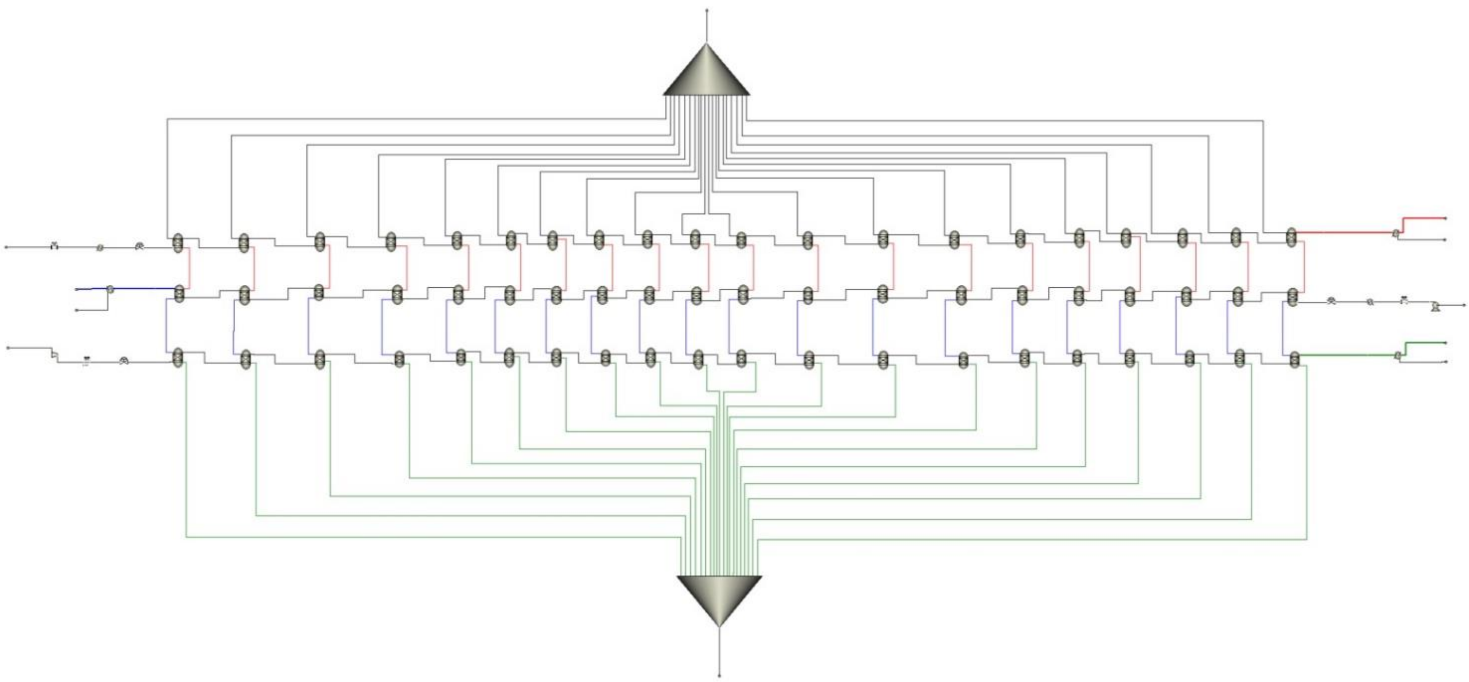
6. Annexes

A.1. Breakdown energy consumption per equipment

Table 9. Energy consumption per equipment for each case

	Case 1	Case 2	Case 3	Case 4
Reactors Net heat duty [kJ/sec]				
Reduction 1-14	-26,62	-3,90	-27,98	-2,88
Oxidation 1-14	-50,30	-71,23	-64,51	-68,34
Air Oxidation 1-14	-654,62	-571,35	-578,17	-467,90
Total [kW]	**-731,55**	**-646,48**	**-670,66**	**-539,12**
Impulsion Equipment: Net work required [kW]				
Compressor	136,59	136,59	136,59	136,59
Pump	3,20	3,20	3,20	3,20
Total [kW]	**139,79**	**139,79**	**139,79**	**139,79**
Heaters: Net heat duty [kJ/sec]				
AIR-HEAT	282,06	282,06	282,06	282,06
CO2-SEP	-344,59	-246,88	-353,30	-202,87
H2-SEP	-20928,77	-20909,59	-20928,77	-20893,71
H2O-HEAT	20152,17	20152,17	20152,17	20152,17
N2-SEP	-341,04	-345,72	-345,34	-351,53
SYN-COOL	-22,64	-17,08	-31,17	-11,56
Total [kW]	**-1202,81**	**-1085,04**	**-1224,35**	**-1025,44**
Energy Balance [MW]	**-1,79**	**-1,59**	**-1,76**	**-1,42**

A.2. Layout of the system with 20 reactors.



A.3. MATLAB codes to obtain sensitivity analysis results.

A.3.1. Thermodynamics validation

```
clc
clear all
close all

dataMeO0947 = xlsread('Sensivity analysis thermodynamics model
validation','Fe0947O','D2:I10202');
dataMeO = xlsread('Sensivity analysis thermodynamics model
validation','FeO','D2:I10202');

Fe2O3_data = dataMeO(:,6);
Fe3O4_data = dataMeO(:,5);
FeO_data = dataMeO(:,4);
Fe_data = dataMeO(:,3);

Fe2O3_data0947 = dataMeO0947(:,6);
Fe3O4_data0947 = dataMeO0947(:,5);
FeO_data0947 = dataMeO0947(:,4);
Fe_data0947 = dataMeO0947(:,3);

T = 200:10:1200;
```

```
H2_in = xlsread('Sensivity analysis thermodynamics model
validation','FeO','E2:E102');

Fe2O3_matrix = zeros(length(T),length(H2_in));
Fe3O4_matrix = zeros(length(T),length(H2_in));
FeO_matrix = zeros(length(T),length(H2_in));
Fe_matrix = zeros(length(T),length(H2_in));

Fe2O3_matrix0947 = zeros(length(T),length(H2_in));
Fe3O4_matrix0947 = zeros(length(T),length(H2_in));
FeO_matrix0947 = zeros(length(T),length(H2_in));
Fe_matrix0947 = zeros(length(T),length(H2_in));

for t=1:1:length(T)
    for h = 1:1:length(H2_in)
     Fe2O3_matrix(t,h) = Fe2O3_data(h+(t-1)*length(H2_in));
     Fe3O4_matrix(t,h) = Fe3O4_data(h+(t-1)*length(H2_in));
     FeO_matrix(t,h) = FeO_data(h+(t-1)*length(H2_in));
     Fe_matrix(t,h) = Fe_data(h+(t-1)*length(H2_in));

     Fe2O3_matrix0947(t,h) = Fe2O3_data0947(h+(t-1)*length(H2_in));
     Fe3O4_matrix0947(t,h) = Fe3O4_data0947(h+(t-1)*length(H2_in));
     FeO_matrix0947(t,h) = FeO_data0947(h+(t-1)*length(H2_in));
     Fe_matrix0947(t,h) = Fe_data0947(h+(t-1)*length(H2_in));
    end
end

H2O_frac = 100./(1+H2_in);

figure(1)
mesh(H2O_frac,T,Fe3O4_matrix)
hold on
mesh(H2O_frac,T,FeO_matrix*5.1e9)
mesh(H2O_frac,T,Fe_matrix*1.1e10)
ylabel('T [°C]');
xlabel('H_{2}O [%]');
zlabel('MeO [kmol/h]');
title('Baur-Glaessner diagram: FeO')


figure(2)
mesh(H2O_frac,T,Fe3O4_matrix0947)
hold on
mesh(H2O_frac,T,FeO_matrix0947*5.1e9)
mesh(H2O_frac,T,Fe_matrix0947*1.1e10)
ylabel('T [°C]');
xlabel('H_{2}O [%]');
zlabel('MeO [kmol/h]');
title('Baur-Glaessner diagram: Fe_{0.947}O')
```

A.3.2. Temperature and pressure sensitivity analysis regarding wet syngas

```
clc
clear all

dataMeO = xlsread('Sensivity analysis wet
syngas_points','Tabelle1','D2:G6276');

H2_data = dataMeO(:,3);
CO2_data = dataMeO(:,4);

T = 700:1:950;
P = 1:1:25;


H2_matrix = zeros(length(T),length(P));
CO2_matrix = zeros(length(T),length(P));

for t=1:1:length(T)
    for p = 1:1:length(P)
    H2_matrix(t,p) = H2_data(p+(t-1)*length(P));
    CO2_matrix(t,p) = CO2_data(p+(t-1)*length(P));
    end
end


figure(1)
mesh(T,P,H2_matrix')
xlabel('T [°C]');
ylabel('P [bar]');
zlabel('H_2 production [kmol/h]');

figure(2)
mesh(T,P,CO2_matrix')
xlabel('T [°C]');
ylabel('P [bar]');
zlabel('CO_2 production [kmol/h]');
axis([T(1) T(end) P(1) P(end) 0 15])
```