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EXECUTIVE SUMMARY OF THE THESIS

Hydrogen production exploiting biomass: An industrial case study

TESI MAGISTRALE IN ENERGY ENGINEERING – INGEGNERIA ENERGETICA

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ACADEMIC YEAR: 2021-2022

1. Introduction

The current structure of energy sources supply in Europe and the challenges related to climate change require to exploit the domestic low carbon emissions resources in the best way. Electricity production from renewables is not sufficient alone to reach the final goals of net-zero emissions, due to intermittent generation, difficulties in storing electricity and to guarantee grid resilience, as well as issues related to electrification of some sectors. Therefore, green hydrogen as an energy carrier may play a crucial role to carry out the decarbonization of hard-to-abate sectors, as well as it can work as energy storage of excess electricity helping to increase the grid resilience. This thesis aims at (i) analyzing the H_2 production routes exploiting biomass, as either energy source or feed, and (ii)at identifying the most promising processes to produce hydrogen in an industrial case study. Hence, the final purpose is to provide a techno-economic assessments of the most promising technologies in order to discuss their features, and to show, for the case study, for which markets conditions green hydrogen production could be feasible and through which technology.

2. State of the art

Biomass can be used to produced hydrogen directly or indirectly, via thermochemical, biological, and electrochemical processes. **Thermochemical processes,** like gasification, use heat to promote the chemical transformation of biomass into a syngas that afterwards undergoes upgrading and purification processes to obtain pure H_2. Gasification processes are flexible with respect to the input, since several biomasses can be utilized, and are typically distinguished according to the gasification agents. Air, steam, or pure oxygen can be adopted. They lead to profoundly different techno-economic results, since there are differences in costs, reactor types, as well as syngas yield and hydrogen content. Steam is the most indicated agent to produce H_2 from biomass since it is relatively cheap compared to pure oxygen, maintaining some positive features with respect to air, i.e., it produces a N_2-free syngas with also greater H_2 yield. However, steam gasification requires a more complex system since the heat required from the process must be supplied externally. Hence, the double fluidized bed (DFB) technology is adopted. **Biological processes** involve the use of microorganisms to break down the biodegradable material into biogas. Some biological processes directly produce a relevant quantity of H_2, but they are still far from commercialization. Instead, anerobic digestion is a commercial technology which produces biogas from which bio-methane can be separated and used for H_2 production via steam reforming. Biological processes require specific biomass as feed, such as animal manure, food waste or sewage sludge and they are typically operated in batch reactors with long residence time.

Electrochemical processes refer to electrolysis that leads to H_2 production using water and electricity, which can be generated by a power plant fed by biomasses. Compared to the previous technologies, electrolysis has a first step of electricity generation from biomass, but afterward it directly produces nearly pure hydrogen, while biological and thermochemical processes require additional processes to obtain purified hydrogen.

The most promising technologies for the case study are steam gasification and electrolysis.

Steam gasification is based on dual fluidized bed (DFB) technology that produces syngas. Then, to increase syngas H_2 content and to raffinate hydrogen, the syngas goes through water gas shift (WGS) reactor, tar removal section, CO_2 absorber and pressure swing adsorption (PSA) unit. Currently, syngas production from gasification may reach values around 70% of cold gas efficiency (CGE) if a proper heat recovery strategy is applied, while the final yield of H_2 varies in the range of 40-100 $g_{H_2}/kg_{biomass\_dry}$ according to process set up and biomass type. Although individual unit operations have good readiness (TRL 8-9), the overall process is less mature, in fact there are no commercial plants which produce hydrogen via gasification.

Low temperature electrolysis technologies with the highest readiness are the alkaline (ALK) and proton exchange membrane (PEM) electrolyzers. Nowadays, ALK electrolyzer is the most robust and mature technology, it can reach a specific consumption of 50 kWh_e/kg_{H2} and a stack lifetime in the range of 60,000-100,000 hours. Furthermore, it requires relatively inexpensive and non-critical material, as nickel and stainless steel, therefore the system cost about 600 €/kW_e for a 100 MW_e size. On the other side, PEM electrolyzer adopts more expensive materials, as titanium, iridium, and platinum. Hence, it costs about 900 €/kW_e for a 100 MW_e size, also due to a lower maturity status. Both technologies have strong economies of scale from the kW sizes to the 10 MW_e capacity, with limited impact afterwards. Nowadays, the PEM electrolyzer stack lifetime is in the range of 50,000-80,000 hours and the system operation may achieve 55 kWh_e/kg_{H2} of consumption. However, it presents some advantages compared to ALK electrolyzer: thanks to a higher power density it offers a lower footprint, a wider load range, faster dynamics, and a simpler balance of plant (BoP). Furthermore, it allows a higher stack operating pressure, with the possibility of differential pressure configurations where the two half-cells operate in different conditions [1], [2].

3. Case study

This thesis develops a techno-economic feasibility study regarding the installation of a hydrogen production process within an industrial facility. The industrial site is composed by nine firms within the Tampieri Financial Group. The main firm is one of the European leaders in vegetable oil production from sunflower, corn germ, and grape seeds. This represents the main energy-consuming factory, while the others feature relatively low-energy demands. Among them, one firm is devoted to managing power generation for the entire industrial site. The oil production processes require high- and low-pressure vapor, as well as electricity, while the other firms require electricity only. These demands are typically constant during a day, with little change during night. However, the load can change day by day according to operating processes and treated biomass types. The average consumption values are 5.46 MW_e (84% of which is related to oil production), 17.0 t/h of low-pressure (LP) vapor, and 1.4 t/h of high-pressure (HP) vapor. To satisfy these demands, the site currently feature two CHP plants fed by biomass, which is operated according to vapors demands. The surplus electricity currently receives the 'green certificates' incentive scheme. This study looks forward and aims at evaluating new ways to valorize this surplus, since the incentive are due to end in 2026. According to the company strategy for the next future, Figure 1 represents the load duration curve of electricity surplus, from which H_2 production of a possible plant will depend.

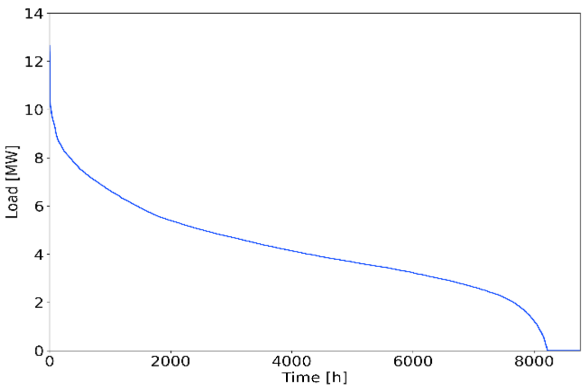

Figure 1: Load duration curve of electricity surplus

The mix of biomasses treated in 2021 are:

- 37% Meat and bone meal (M&B meal)
- 25% Grape pomace
- 17% Residual wood
- 14% Dried and not-dried grape skin

The remaining 7% are mostly vegetable wastes (6%) and sewage sludge (<1%). The corresponding total annual amount is 169,215 t. However, this study is not based on the current amount and mix of biomasses since, according to company view, there is a lot of uncertainty on their prices as well as their availability in the next years. Moreover, natural gas (NG) is also used in the industrial case for 58,310 MWh_{lhv}/y. The majority is used in the drying process of the oil production chain, while the remaining part is fed to the CHP plant. Nevertheless, the latter represents less than 5% of the total plant energy input, as to be compliant with incentive regulation. Finally, it must be underlined that electricity consumed in the industrial area is not charged for transmission and distribution costs, since a proprietary local grid is present, nor other indirect costs. Therefore, the firms pay electricity at the hourly price of day-ahead market.

4. Configurations modeling

According to the case study features (section 3) and available biomass-to-H_2 processes (section 2), the techno-economic assessments are performed on two configurations based on the most promising technologies. The first proposal is based on steam gasification, given its flexibility to biomass input and ability to process biomass amount like the one currently treated. The second configuration is based on electrolysis, since it is the easiest solution to exploit the electricity surplus in the industrial site, as well as the more compact and mature technology. Two models are developed that firstly evaluate technical performances considering year-long operation, and then perform an economic assessment assuming a 20 years perspective. The analysis is repeated for several sizes and for different prices of electricity, natural gas, and biomass. Simulations considering the previous four years (2018-2021) are performed, as well as a broader sensitivity analysis on electricity and NG prices. All the assumptions and input values are based on achievable target values in 2030, since it is the most likely year for the investment to start. Values from the current state-of-the-art are used for parameters with challenging goals, or whenever 2030 objectives are not available.

4.1. Gasification

Gasification plants as well as CHP plants are characterized by high thermal inertia, hence long times are required during transient. Due to this feature, it is assumed a target number of yearly operating hours, equal to 8,000 h/y, during which the plant works at nominal thermal power input. A simplified process flow diagram is reported in Figure 2 and each unit operation is modeled by literature data. **Gasification** section is modeled coupling company's biomasses with biomasses for which experimental data are available, according to CHNOS composition. Each biomass has associated operating parameters as temperature, steam-to-biomass ratio (SB), bed material, CGE, dry syngas composition and water conversion [3]. Additionally, it is assumed to gasify singularly each biomass. The syngas leaves the gasification section at 350°C, after a first heat recovery and filtering. Capex is evaluated considering economies of scales via an exponential factor of 0.65, with a reference Capex of 26.69 M€ for a 32 MW_{th} size. While variable costs as electricity, bed material, and water consumptions, as well as solid disposal are considered according to [4]. **WGS reactor** is modeled as one high temperature stage operated isothermally at 350°C. The molar steam-to-dry syngas ratio is taken equal to 1.4, while the CO conversion is assumed to be 85%. The Capex is assessed by a scaling factor of 0.7, and a reference value of 141.3 k€ for a daily H_2 production of 1500 kg/day. **Heat exchangers** are modeled to compute just the heat recoverable from the process. All of them are indirectly included in

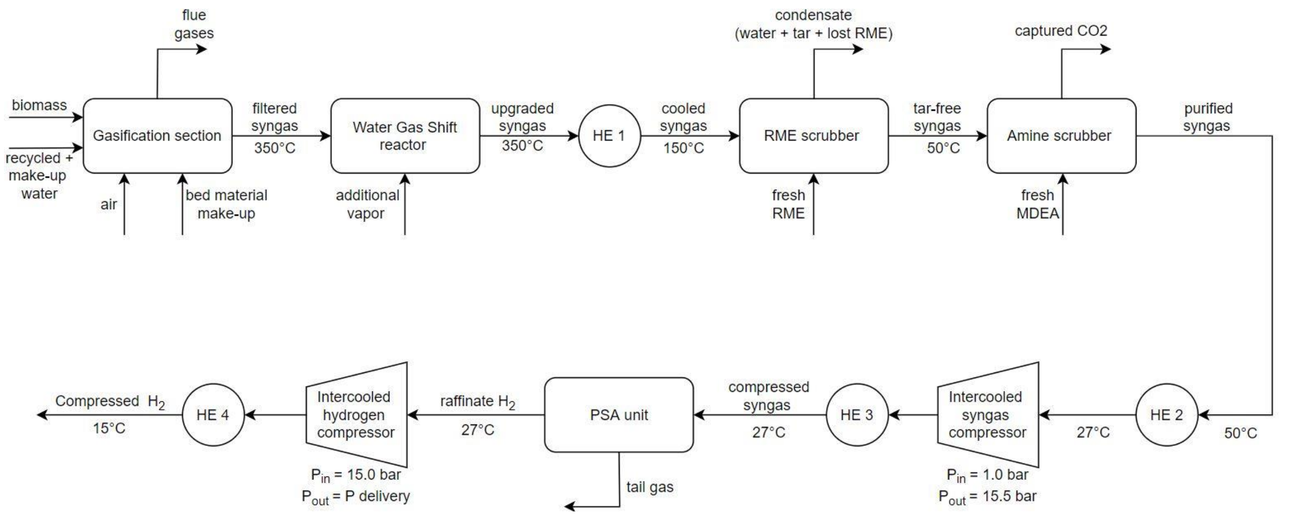

Figure 2: Gasification configuration process flow diagram

the sections of intercooled compressors, except for "HE 1" (Figure 2), that is not accounted in the assessment since its costs should not be relevant compared to other components. **Tar removal section** (RME scrubber) is considered only for the economic evaluation since tar is not modeled. Capex is computed according to inlet volumetric flow rate considering economies for scales. This approach is further used for amine scrubber and PSA unit. Besides, RME consumption is taken equal to 2 kg/MWh$_{th}$ for a price of 1.1 €/kg. The **amine scrubber** imposes a CO_2 separation via absorption of 90% that afterward is vented into the atmosphere. Electricity and heat consumptions are given according to the captured CO_2, respectively 0.4 MJ$_e$/kg$_{CO2}$ and 2.4 MJ$_{th}$/kg$_{CO2}$ [4]. **Syngas and hydrogen compressor** are modeled assuming an inlet temperature of 300 K and evaluating the ideal power consumption that is after scaled according to compressor and electric motor efficiencies. Number of intercooling stages is chosen according to the total required pressure difference. While parameters as molecular weight, specific heat ratio and compressibility factor depend on flow composition. The compressor Capex cost function varies according to intercooling stages, and it considers economies of scale through an exponential factor of 0.61. The **PSA unit** is modeled with an H_2 recovery of 90% to which corresponds a purity level higher that 99.997% [2]. In addition, valuable tail gas of PSA unit is used to firstly satisfy heat needs of H_2 production process and then to substitute the NG currently used in the industrial site. Finally, variable costs related to maintenance of all unit operations, assurance, labor cost, auxiliary consumption and plant overhead are considered as 9% of total Capex.

4.2. Electrolysis

Electrolyzer has a faster dynamic with respect to a gasifier and a boiler, hence an hourly production strategy can be adopted to optimize the investment. The willingness-to-pay (WTP) for electricity used to produce H_2 is defined in Eq. 1 [5]. The production logic compares the WTP with the electricity market price in the same hour: if WTP is higher than electricity price, H_2 is produced; otherwise, electricity is sold to the grid.

$$WTP\left[\frac{€}{MWh}\right] = \frac{P_{H_2} + C_{inc} - C_{H_2O} - C_{tr}}{e_{electrolyzer} + e_{compressors}} \quad \text{Eq. 1}$$

Where P_{H_2} [$€/kg_{H_2}$] hydrogen price, C_{inc} [$€/kg_{H_2}$] incentives on H_2 sale, C_{H_2O} and C_{tr} [$€/kg_{H_2}$] water consumption and H_2 transport costs. Finally, $e_{electr.}$ e $e_{compr.}$[MWh/kg_{H_2}] the electrolyzer and compressor efficiencies.
The input parameters for electrolysis model are:

- Hourly profile of available electricity (Figure 1)
- Hourly electricity prices on Italian market
- Parameters for electrolyzer and compressor

The electrolyzer is sized considering that part of the available electricity is consumed by the compressor. The electrolyzer is modeled according to data in Table 1 and considering for Capex strong economies of scale for sizes from 0.5 to 10 MW$_e$. Efficiency is assumed constant at partial load.
2030 targets are used for Capex and efficiency, while other parameters derive from current state of the art [1], [2].
ALK electrolyzer looks the best option for this case study since electricity is not generated from intermittent renewables that requires very fast dynamics and wide range load.

Table 1: Electrolyzer parameters

Technology	*ALK*	*PEM*
Efficiency [kWh/kg]	48	50
Minimum load [%]	30	10
Operating pressure [bar]	15	30
Opex [% of Capex]	3	3
Stack lifetime [hours]	75,000	60,000
Stack Capex [% of Capex]	45	45

4.3. Economic evaluation

Hydrogen price is evaluated according to three different end application.
H_2 injection in the natural gas grid: H_2 price is estimated via energy equivalence with NG. **Industrial use:** currently H_2 price is set by grey hydrogen production, hence it is computed by a correlation that links grey H_2 price with NG cost. **Transport use:** H_2 price is assessed through a cost for kilometer equivalence between diesel heavy-duty trucks and fuel cell ones, subtracting 36% at final price since it is considered for the H_2 refueling station (HRS). While transport cost is assumed null due to strategic position of the industrial site.
The average prices of energy sources are summarized in Table 2 and Table 3 as reference, despite hourly electricity price and daily NG prices are used.

Table 2: Electricity, NG, diesel, and biomass prices

Year	*E el [€/MWh]*	*NG [€/MWh]*	*Diesel [€/l]*	*Biomass [€/t]*
2018	60.71	24.24	1.49	69.33
2019	51.25	16.07	1.48	70.28
2020	37.80	10.42	1.32	63.18
2021	125.20	46.30	1.49	69.15

Table 3: Hydrogen prices

Year	*2018*	*2019*	*2020*	*2021*
$P_{H_2}[€/kg_{H_2}]$ *NG grid injection*	0.81	0.54	0.35	1.54
$P_{H_2}[€/kg_{H_2}]$ *Industrial*	1.92	1.52	1.24	3.02
$P_{H_2}[€/kg_{H_2}]$ *Transport*	3.73	3.71	3.31	3.73

The economic evaluation is mostly based on the following KPIs: levelized cost of hydrogen (**LCOH**), net present value (**NPV**), profitability index (**PI**), and payback period (**PBP**). The LCOH represents the cost of hydrogen production, assuming identical annual operation over the entire lifetime and considering financial factors. It is equivalent to the sale price of H_2 that would lead to reach an NPV equal to zero. The PI is the ratio between NPV and actualized Capex, hence it shows the return on investment. Finally, if the investment is profitable the PBP is underlined, i.e., the year during which the NPV becomes equal or greater than zero.

5. Results and discussion

5.1. Gasification

The results presented for H_2 production via gasification derive from biomasses mix equally distributed between grape pomace, residual wood, and grape skin. Finally, limestone is used as bed material for economic evaluation and delivery pressure of H_2 is set to 200 bar.
Set the model inputs, the H_2 production cost mainly depends on following parameters:

- Electricity, NG, H_2 and biomasses mix prices (Table 2)
- Avoided NG cost thanks to tail gas use
- Economies of scale

Sizes from 5 to 50 MW_{th} of biomass input are evaluated and the LCOH is reported in Figure 3.

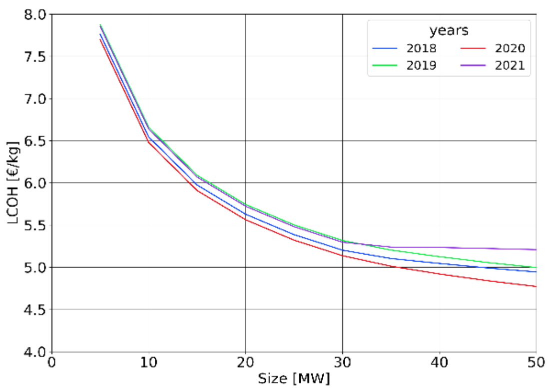

Figure 3: Gasification LCOH as a function of size

Selected a year, the main trend is given by the economies of scale that result very relevant from 5 to 25 MW_{th}. At the same time, increasing the size up to 32 MW_{th} the NG substitution increases until its fully replacement. This gives another relevant contribution to the LCOH decreases. However, for larger plant sizes the trend becomes flatter due to lower economies of scale and since part of the extra tail gas available cannot be valorized at NG price. Looking to the previous four year, the LCOH values stay in a very narrow range, even though energy sources' prices have significant variations. In fact, the increase in electricity cost and in NG avoided cost somehow balance according to current link between electricity and NG market. While the biomass mix cost remained quite constant in the considered years. This feature also explains the slight curves' divergence for size above 30 MW_{th}, given by the balance interruption because part of tail gas cannot be used for NG substitution. This aspect is clearly shown in Figure 4, where for a size of 30 MW_{th} the variable cost composition is depicted for the past four years.

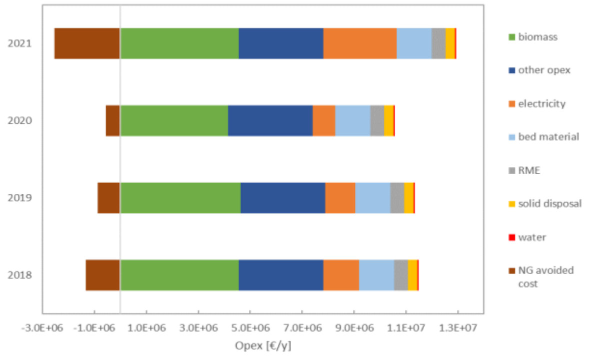

Figure 4: Opex composition for 30 MWth size

The main variable costs in order of relevance are biomass (39.7%), "other Opex" (28.3%) (mainly maintenance), electricity (12.0%) and fresh bed material (11.8%), to which correspond a 2018 total yearly Opex of 10.2 M€/y, while Capex for a 30 MW_{th} plant is 36.2 M€. H_2 production and electric power required to operate the process are reported in Table 4. The optimal size for the case study is between 20 and 30 MW_{th} since a larger plant would draw a relevant amount of electricity from national grid implying additional costs, according to Figure 1. For instance, the hours during which electric power is equal or above 1.89 and 2.83 MW_e are 7,727 and 6,726, respectively.

Table 4: H_2 production and P_{el} demand vs size

Size [MW_{th}]	*H_2 prod. [t/y]*	*P_{el} add [MW_e]*
10	852	0.94
20	1,705	1.89
30	2,558	2.83
40	3,410	3.78
50	4,263	4.72

Although 6,726 hours are far from the goal of 8,000, a 30 MW_{th} size might have sense thanks to: relevant economies of scale, substitution of almost all NG used in the industrial site, and because plant likely operates between 7,000 and 8,000 hours, hence electricity draw from the national grid is lower. The LCOH obtained via gasification varies between 5.2 to 5.8 for sizes in the optimal range (Figure 3), hence is still high compared to estimated H_2 prices (Table 3), therefore, considering the past four years, the investment is not feasible unless a proper incentive is designed. Opex composition and sensitivity analysis demonstrated as H_2 production via gasification does not strongly depend on electricity, while the use of cheap biomasses, and an optimized bed material could significantly decrease the LCOH. Nevertheless, cheap biomasses typically require further challenges since the consequences given by high N and S contents must be properly managed.

5.2. Electrolysis

The results of H_2 production via electrolysis refer to an ALK electrolyzer, H_2 price for transport application and a delivery pressure of 200 bar. In contrast to gasification, the operating hours (OH), and consequently the H_2 production and the LCOH, of the electrolysis configuration depend on the H_2 price, given the adopted production logic. The yearly OH are affected from daily H_2 price and hourly electricity price. The higher the electricity cost, the lower the operating hours. While the greater the H_2 price, the higher the OH. In addition, operating hours depend also on minimum load of the electrolyzer, hence increasing its size, the OH decrease although it is profitable to produce H_2, because the hours during which available electric power is below the minimum load become greater. This turns into a strong increase in H_2 production up to sizes of 4.0 MW_e, a maximum around 7.5 MW_e size, and a significant decrease for larger electrolyzer sizes. The H_2 production as function of electrolyzer size together with Capex cost function explain LCOH presented in Figure 5. Chosen a year, going from low to intermediate sizes, the trend shows a decrease in LCOH since H_2 production relevantly increases and the specific investment cost decreases thanks to economies of scale. The minimum LCOH is achieved for optimal size of about 4-4.5 MW_e. Moving toward larger sizes there is an increase of LCOH, because H_2

production reaches slowly the cited maximum and then decreases due to minimum load constraint, while absolute capex becomes higher.

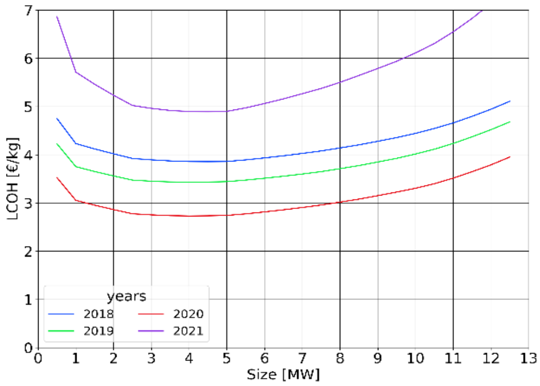

Figure 5: Electrolyzer LCOH as a function of size

Different LCOH values between considered years depend on hourly electricity and daily H_2 prices which averages are reported in Table 2 and Table 3. This specific case related to H_2 in transport application is the only end use for which the investment looks profitable since LCOH for the optimal size is lower than its price, expect for the 2021. The current link between electricity and H_2 prices, given by NG cost, disadvantages hydrogen production when both prices increase. This depends also on strong LCOH dependency on electricity cost, that accounts for about 92% of total Opex.

5.3. Technology comparison

The two configurations are compared in Table 5 choosing sizes in the optimal range. The H_2 production via gasification presents higher investment costs as well as operative costs, however it guarantees a greater hydrogen production compared to electrolysis. Although, biomasses are already managed in the industrial site, this configuration has a large land footprint since several unit operations are needed to carry out the H_2 production. On the other side, an additional section for H_2 production via electrolysis requires just an electrolyzer system and a compressor, hence it has a smaller footprint. Capex and variable costs are much lower, therefore it results the less risky solution, given the smaller maximum economic loss. Although electrolysis provides a significant lower H_2 production, it results the readiest technology since CHP plant fed by biomass is a commercial technology, as well as the alkaline electrolyzer. Furthermore, it allows to overcome possible problems related to the gasification of a biomasses mix composed by several types.

Table 5: Configuration comparison, *(max value)

Configuration	*Gasification*	*Electrolysis*
Size	30 MW_{th_input}	4.5 MW_e
Capex [M€]	36.16	3.97
H_2 prod. [t/y]	2,558	* 630
Land footprint	Big	Small
Current TRL	7-8	9

Results of the sensitivity analysis on electricity and NG prices for both configurations are summarized in Table 6. H_2 price also enter the analysis since it is set according to an industrial end user as described in section 4.3. Table 6 derives from a comparison of profitability indexes of the two configurations, hence it allows to underline in which markets conditions the investment in H_2 production is profitable and with which technology. When both technologies have PI greater than zero, the one with the highest PI is chosen. Hydrogen production via gasification is favored by high H_2 price because of the relatively high LCOH (see Figure 3). However, current Italian market link between electricity and NG turns into a quite constant LCOH even with relevant prices variations. Hence, the investment results feasible for high H_2 price even if electricity price is high as well. In fact, from H_2 price of 6.67 €/kg and NG cost of 120 €/MWh, gasification configuration turns to be profitable for any electricity price.
On the other side, H_2 production via electrolysis is extremely favored by low price electricity since it decreases significantly the LCOH, while its economic performance quickly gets worse with an electricity cost increase. In fact, even if hydrogen is sold at 10.64 €/kg, the electricity cost must be lower than 120 €/MWh to produce H_2 competitively. Low-price electricity makes advantageous the H_2 production instead of electricity sale, however, in the analyzed case study, if the electricity price is low, the power generation firm does not have reasons to produce that surplus electricity since it would be valorized to a price lower than LCOE of CHP plant (>120 €/MWh). Hence for low electricity price, although H_2 production looks better than selling surplus electricity (base case), both

Table 6: Gasification vs Electrolysis investment comparison
legend: pink area → PI<0 (-), blue area → electrolysis (E), green area → gasification (G)

P H2 [€/kg]	1.71	2.70	3.70	4.69	5.68	6.67	7.67	8.66	9.65	10.64
NG [€/MWh] / E_el [€/MWh]	20	40	60	80	100	120	140	160	180	200
50	-	-	E	E	E	E	E	E	E	E
100	-	-	-	G	G	G	E	E	E	E
150	-	-	-	-	G	G	G	G	G	G
200	-	-	-	-	G	G	G	G	G	G
250	-	-	-	-	G	G	G	G	G	G
300	-	-	-	-	-	G	G	G	G	G
350	-	-	-	-	-	G	G	G	G	G
400	-	-	-	-	-	G	G	G	G	G

solutions lead to an overall negative profit for the financial group, i.e., the best option would be not to produce the surplus electricity.

6. Conclusions

This thesis shows techno-economic performance of steam gasification and electrolysis according to the case study. Optimal sizes for both technologies are 20-30 MW_{th} of biomass input for gasification and 4.0-4.5 MW_e for electrolysis, corresponding to a maximum hydrogen production of 2,558 t/y and 630 t/y, respectively. The resulting LCOH is about 5.0 €/kg and 3.5 €/kg, respectively, according to size of 30 MW_{th} and 4.5 MW_e, and 2019 energy prices. Gasification turns to have a lower dependency on electricity price than electrolysis and it produces a valuable tail gas that is used to substitute NG in the industrial area, but LCOH is significantly affected by biomasses costs. Electrolysis LCOH strongly depends on the electricity price, since a high-price situation implies large missed revenues. However, it is a more mature technology, and it requires a significantly smaller investment. Nevertheless, there is not a single best solution since results vary according to electricity, NG, H_2 and biomass prices. The sensitivity analysis on energy markets (electricity, NG and H_2) shows that, for the case study, the only profitable solution is gasification if NG and H_2 prices are above 120 €/MWh and 6.67 €/kg as in 2022, however it is an uncertain condition, mostly in the long run. On the other side, electrolysis looks feasible only for electricity prices lower than CHP plant LCOE, hence it should not be considered. In fact, even if electrolysis results better than electricity sale, the best option would be not to produce surplus electricity. Consequently, according to technology features and H_2 end use, proper incentives are needed to invest in green hydrogen production, even to cover possible energy markets fluctuations.

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