

Enhance Hydrogen Recovery

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Abstract: Hydrogen plays a crucial role in refineries, to meet product specifications. Additionally, due to the current global socio-economic situation, the rationalization of natural gas and the reduction of greenhouse gas emissions has a direct impact on the achievement of profits and the development of companies. The aim of this work was recovering and purify the hydrogen from off gas streams being disposed to the fuel gas network at the Sines refinery, allowing for a reduction in CO₂ emissions and the consumption of raw materials associated with the on-purpose production of hydrogen at the Steam Methane Reformer unit. Two approaches were developed: the analysis of different technologies for hydrogen recovery; the development of a business case in partnership with a petrochemical complex to take better advantage of olefin offgases composition that are outside the limits of applicability of these technologies. By redirecting the identified streams to a hydrogen purification unit (ROG PSA), it is possible to recover 0.8 ton/h of hydrogen and a reduction of CO₂ emissions and natural gas consumption of 38 kton/yr and 13kton/yr, respectively. A total capital investment of around 14 M€ is needed. A model was also created to support decision-making on the most appropriate technology for future projects streams, whose conditions are within the applicability limit of hydrogen recovery technologies.

Keywords: Hydrogen Network; Fuel Gas Network; Hydrogen Recovery; Carbon Dioxide; Refinery

1. Introduction

Hydrogen plays a key role in refineries, being crucial for the proper functioning of their units, preventing catalyst poisoning, for example, and for meeting the specifications of finished products. Due to the growing environmental concern felt in today's society, not only have these specifications become more stringent but demanding targets have also been imposed to reduce greenhouse gas emissions. As a result of the Paris Agreement in 2015 and the Green New Deal in 2020, Europa accepted the challenge of becoming the first continent with a Net-Zero Emissions Economy by 2050 [1][2]. On the other hand, the global socio-economic situation, caused by the war between Russian and Ukraine, led to inflation in the commodity market, leading to an exorbitant increase in the price of commodities, namely natural gas. Until the beginning of the war, Russian was the main exporting country of natural gas. Thus, it became imperative to develop strategies to reduce CO₂ emissions and rationalization of hydrogen and natural gas

consumption to ensure that companies stabilize their position in the market.

In the Galp refinery, the main production units of hydrogen are the platforming unit and the steam methane reforming (SMR) unit. The platforming unit is a catalytic reforming unit that converts heavy naphtha SR into a gasoline blending component, the reform, which has a high economic interest due to its high-octane number. The hydrogen produced as a by-product in this unit has a purity of about 80%. The SMR unit is an on-purpose hydrogen production unit. In this unit, through the reaction of methane with steam is produced a high purity hydrogen up to 99,5%. SMR feedstock is typically Natural Gas, being able to process as an alternative light desulfurized naphtha. In the refinery the main consumers are the hydrotreatment units and hydrocracking unit. Hydrotreatment units are responsible for removing sulphur, oxygen, nitrogen and metals from crude oil and non-fossil feedstocks for co-processing, in order to treat intermediate products that can be incorporated into the

finished product pool, to achieve the quality specification of a commercial grade, or to be able to be reprocessed in a downstream unit. Hydrocracking is a catalytic hydrogenation process, which converts molecules with higher molecular weight into lighter molecules and, consequently, with greater commercial value. The main products of the hydrocracking unit are LPG, stabilized light and heavy naphtha, jet and diesel.

The hydrogen produced is integrated to the hydrogen network. Sines' refinery hydrogen network is in fact, composed by two different hydrogen networks: low and high purity. The first network is based on the Platforming hydrogen production, and it is connected to the following consumer: hydrodesulfurization/hydrotreating (HD and HN) and mild hydrocracker unit (HV). The second hydrogen network producers are the SMR units (HI and HR) and refinery off gas PSA (ROG PSA). On the consumers side of this network are other refinery hydrodesulfurization units (HG and HT) and at the hydrocracker unit (HC). In addition to the existing consumers, Sines' refinery will develop its green fuels conversion strategy by installing a HVO unit. This will increase the pure hydrogen consumption at site.

The fuel gas network is made up of fuel gas producers and consumers from the different plants of Sines's refinery. It is also necessary that there is a make-up of natural gas and/or propane, to keep the enthalpy of the network constant so that fuel gas consumers are not affected by variations in the composition and flow of offgas streams.

There is currently a unit at the Sines refinery responsible for purifying less pure hydrogen and integrating it into the pure hydrogen network, the ROG PSA. However, there are many other streams that are routed to the fuel gas network. Integration in the fuel gas network of these streams leads to the existence of a hydrogen composition in the fuel gas network of the Sines refinery, around 20% up to 50% vol.. This wide range of hydrogen content makes the choice of recovery technology critical for hydrogen recovery to be economically attractive.

The work focused on the development of strategies for the recovery and purification of hydrogen from the fuel gas network at the Galp Energia company's Sines refinery and adding it to pure hydrogen network, allowing for reduction in CO₂ emissions and the consumption of feedstock associated with the production of on-purpose hydrogen at the Steam Methane Reformer unit (SMR). With this goal, after analyzing the existing technologies in the market, the hydrogen and fuel gas refinery network, and the management strategies to those networks, we developed two approaches: the analysis of alternatives for hydrogen recovery and the creation of a model to support the decision-making of the most appropriate technology for each stream or set of streams, whose conditions are within the applicability limit of hydrogen recovery technologies; and the development of a business case in partnership with a petrochemical company. Finally, a proposal for the integration of the refinery's hydrogen network and fuel gas network was presented, with the respective savings in CO₂ emissions and natural gas consumption.

2. Separation Technologies

The three main hydrogen purification technologies used in refineries are Pressure Swing Adsorption (PSA), selective permeation membranes and cryogenic or cold-box separation [4]. Each of these options is based on a different separation principle, namely relative diffusivity, relative permeability and relative volatility, and consequently the characteristics of these processes differ significantly. Appropriate selection of hydrogen purification technology depends on economics, but also on efficiency and flexibility (e.g. stream composition), reliability and ease of future process expansion.

2.1. Pressure Swing Adsorption

The separation process using PSA is based on adsorption and is commonly used in refineries to purify gases like hydrogen. In PSA beds, adsorbents such as molecular sieve, active

carbon and silica gel are used. The PSA process requires a relatively high and superior purity feed, and it produces nearly pure hydrogen, up to 99,5%vol. Since this is a discontinuous process, to obtain continuous operation, we need two beds while one is adsorbing, the other is regenerating. At the Sines refinery, there are two types of PSA's: one associated with the operation of the SMRs, responsible for purifying the hydrogen produced; and a ROG PSA, responsible for the recovery of hydrogen from refinery off gases.

2.2. Membranes

Membranes may be polymeric or dense metallic membranes and have the pressure and concentration gradient as the driving force of separation. The gas transport mechanism in polymeric membranes and dense metallic membranes consists of the solution-diffusion mechanism. In the solution-diffusion mechanism, the permeation and selectivity of molecules is dependent on the solubility and diffusivity of the membrane-penetrating species. Components with higher membrane permeability cross the membrane at a higher rate compared to components with lower affinity.

When using membrane processes it is necessary to make a compromise between pressure loss and permeation area, and between purity and hydrogen recovery, since the greater the membrane area, the greater the amount recovered hydrogen, but the lower its purity.

Membrane systems are produced in relatively small modules, so more modules need to be added to obtain greater capacity. Thus, the cost of this system is linear to its capacity, making it economically more competitive the smaller its capacity.

2.3. Cryogenic Separation

Cryogenic separation consists of the separation of hydrogen from the remaining gases at cryogenic temperatures. This technology is based on the volatility of

components at low temperature. Hydrogen has a higher volatility than the other components present in offgas streams. These units require a high cost of pre-treatment to remove components that can solidify due to low temperature, such as water and CO₂. This technology is applied in large-scale units or when it is intended to recover a variety of products from a single feed stream, such as the recovery of light olefins from FCC offgas.

The table 1 resumes the compaction between the different separation technologies.

Table 1- Comparison between PSA, Membranes and Cryogenic Separation [3]

	PSA	Membranes	Cryogenic Separation
Minimum H2 composition (%vol.)	>40 or >75 (optimum)	>30	>20
Product purity (%vol.)	>99	85-95	90-98
H2 recovery (%vol.)	75-90	80-90	98-99
Turndown (%vol.)	30	30-50	10
Inlet Pressure (barg)	20-60	< 160	Design
Outlet Pressure (barg)	0.7 bar lower than inlet pressure	15-95 bar lower than inlet pressure	Design
Pre-treatments need	liquid removal	liquid removal	H ₂ O, H ₂ S, CO ₂ removal

2.4. Hydrogen and Fuel Gas Network Management Strategies

The management of the refinery's hydrogen network is a key element for the operation of the refineries, to minimize the hydrogen that is incorporated in the fuel gas network, allowing to increase flexibility and profitability refineries, without increasing the capacity of hydrogen production units. The good management of hydrogen and fuel gas networks allows direct benefits such as greater operational flexibility, optimized supply of hydrogen, and reduction of consumption of fossil fuels and greenhouse gas emissions associated with their production.

The analysis developed by Praxair [5] summarizes the main approaches used by refineries to extract value from offgases containing hydrogen in the composition. The incorporation of hydrogen-rich off gases in the fuel gas network, and its consequent recovery through calorific power, is the approach that adds the least value to the stream, and

alternatives to this approach must be sought. Three approaches to extract value from these streams are highlighted: integration of recovery technologies with hydrogen production, recovery of hydrogen and hydrocarbons in a cryogenic system, and processing of fuel gas in SMR.

3. Results

To minimize the loss of value of hydrogen-rich offgas streams when they are integrated into the fuel network and to respond to the refinery's internal demand for hydrogen, hydrogen recovery from these streams plays a key role, thus leading to the reduction of on-purpose production of hydrogen, without limiting the availability of hydrogen to consumers, and, consequently, reducing the CO₂ emissions associated with this process.

The recovery of hydrogen from the fuel gas network requires the following decisions, (1) choose which streams to treat, (2) which recovery strategy to apply, and (3) analyze the compromise to be made between product purity, recovery, and cost of capital.

Thus, the offgas streams that would be studied were first characterized. The result of this analysis is summarized in table 2. For a more detailed analysis of the impact of removing these streams from the fuel gas network to recover hydrogen and reduce a load of natural gas in on-purpose production in the HR, the average lower heating value and average emission factor of each stream were calculated (table 2).

Table 2- Stream characterization.

Classification	Stream	Pressure (barg)	Average Flow (Nm ³ /h)	Average H ₂ composition (%vol)	Average LHV (kcal/kg)	Average Emission Factor (ton CO ₂ /ton)
B	Sponge Absorber Offgas	49	3552	57%	11820	2,76
A	HD H ₂ Purge	40	839	89%	12884	2,50
D	HG Offgas	5	545	82%	19979	1,44
A	HG H ₂ Purge	49	824	98%	16093	2,11
B	Platforming OffGas	17	275	45%	24925	0,62
E	FCC OffGas	11	15495	26%	11950	2,83
C	Hydrocracker OffGas	7	4575	58%	11750	2,85
A	VO H ₂ Purge	25	3948	94%	12307	2,78
E	ROG PSA Tail Gas	0,45	6886	50%	19162	1,30

Since not all streams are within the operational limits of hydrogen separation and purification technologies, two different approaches have been developed for the treatment of these streams:

1. Analysis of alternatives for hydrogen recovery and creation of a model to support decision-making on the most appropriate technology for each stream or set of streams, whose conditions are within the applicability limit of hydrogen recovery technologies.
2. Development of a business case in partnership with a petrochemical complex to take better advantage of streams whose conditions are outside the limits of applicability of technologies, namely the FCC offgas and ROG PSA tail gas.

3.1. Analysis of alternatives for hydrogen recovery

The following study aims, firstly, to define the strategy to be applied to each of the streams to carry out the recovery of hydrogen, and then, to build a tool to support decision-making in choosing the purification process applicable to any stream. This tool aims to guide the company in a first analysis in choosing the best strategy to apply to a given stream to minimize project costs, without affecting the hydrogen or fuel gas consumer units, not replacing, therefore, the need to carry out a detailed analysis of the stream under study.

To achieve those aims, some assumptions, in particular were defined:

1. It was considered one year of production of 8400h.
2. Each scenario must guarantee the production of 7 ton/h of hydrogen with a purity of 99.5%. This production corresponds to the maximum production capacity of the SMR. In this sense, in scenarios where it is not possible to recover 7 ton/h of the stream under study, the SMR must ensure the remaining production of H₂ through natural gas. This assessment is a differential assessment compared to the base scenario of production of 7 ton/h of hydrogen in the SMR using natural gas (21 ton/h) as raw material and CO₂ emission of 57.96 ton/h. It

was assumed that the current hydrogen network is optimized.

3. The mass flow rate and pressure of each of types of streams (A, B, C or D) were considered constant.
4. Three possible strategies for hydrogen recovery were evaluated, namely, the incorporation of the stream to be treated in a new ROG PSA, in a combined membrane system with a new ROG PSA, or in the existing SMR, the HR. The product composition (pure hydrogen) at the exit of the membranes and ROG PSA and the respective physical properties of these streams were considered constant.
5. By removing these streams from the fuel gas network, so that their consumers are not affected, the compensation of the fuel gas network with natural gas was considered in the same proportion of calorific value (equivalent natural gas).
6. For the creation of the decision support tool, the variation of the hydrogen composition of each stream was obtained by normalizing the composition for increments of 2%vol. in hydrogen between 0 and 100% vol., thus assuming a variation of the remaining components proportional to the real composition of the current to be treated.
7. The decision on the strategy to apply to each stream must be taken based on the calculation of the project's margin, which corresponds to the difference between revenues, operating costs (OPEX), and the cost of equipment annualized for 10 years (annualization of CAPEX).

Only membranes were not considered since the membranes studied do not allow obtaining the minimum hydrogen purity (99.5%) necessary for the stream obtained to be inserted into the pure hydrogen network, on the other hand, the output pressure of the product stream of the membranes is the ideal pressure for feeding the ROG PSA, so this configuration allows you to minimize compression costs. It should be noted that when an SMR is fed with a stream with hydrogen in its composition, this fraction enters and leaves the reactor without changes, is then purified in the PSA (or other purification technology) associated with this unit with the remaining hydrogen produced in the reactor.

As a first analysis it was considered the prices of natural gas, CO₂, power, and cooling water in 2021. Table 3 resumes the main results obtained by the application of these assumptions to the selected streams. From the analysis of this table it is possible to conclude that the strategy that allows obtaining a greater annual margin to produce 7 ton/h of hydrogen is, for all streams under study, the ROG PSA, allowing for recovery 0.8 ton/h of hydrogen. ROG PSA is the strategy that allows for greater savings in CO₂ and natural gas.

Table 3- Main results for each stream.

Stream/ Stream Mixture	Mixture A	Mixture B	Hydrocracker Offgas	HG Offgas	
ROG PSA	Margin(M€/yr)	4,72	0,63	0,99	0,82
	H ₂ Recovered (ton/h)	0,42	0,13	0,21	0,04
	Balance of CO ₂ emissions (ton/ton H ₂ recovered)	-5,4	-5,2	-5,4	-4,8
	Balance of consumption of natural gas (ton/ton H ₂ recovered)	-1,9	-1,8	-1,9	-1,8
Membranes + ROG PSA	Margin(M€/yr)	-	0,52	0,57	-0,03
	H ₂ Recovered (ton/h)	-	0,11	0,19	0,03
	Balance of CO ₂ emissions (ton/ton H ₂ recovered)	-	-5,5	-5,3	-5,7
	Balance of consumption of natural gas (ton/ton H ₂ recovered)	-	-1,9	-1,8	-2,0
SMR	Margin(M€/yr)	2,52	0,28	-2,08	0,05
	H ₂ Recovered (ton/h)	0,54	0,56	1,32	0,07
	Balance of CO ₂ emissions (ton/ton H ₂ recovered)	-0,8	-0,5	0,2	-1,7
	Balance of consumption of natural gas (ton/ton H ₂ recovered)	-2,3	-0,2	0,1	-0,6
Selected Strategy	ROG PSA	ROG PSA	ROG PSA	ROG PSA	

It is also observed that between the ROG PSA and the hybrid Membranes-PSA system, the technology that allows a greater recovery of hydrogen is the ROG PSA, since in the membranes-PSA system to obtain the desired purity occurs a greater loss of hydrogen to the tail gas and tail gas from the membranes and PSA, respectively, than with ROG PSA alone. On the other hand, the hydrogen entering the SMR unit is recovered directly in the PSA associated with the unit, so in practice, considering that this PSA has the same recovery rate as the ROG PSA, the amount of hydrogen recovered in the two scenarios would be the same, however, from the same stream, the scenario that consists of including the stream as a charge to the SMR allows us to obtain a greater flow of purified product since part of the hydrocarbons in the feed is also converted into hydrogen.

When analyzing the costs of each technology, it is observed that, as expected, the technology with the greatest associated capital is the PSA membrane system, as it not only involves the investment of two technologies but also has a high cost of compression, since it is necessary to increase the pressure from the current to the high operating pressure of the membranes (71 barg). SMR as also high compression costs. The technology with the lowest associated costs is PSA.

For the construction of the decision model, the hydrogen composition of each was varied in increments of 2% vol. in hydrogen between 0 and 100% vol., and the previous assumptions were applied again for the whole range of hydrogen concentration, in order to obtain four analyses, one for each stream class. As an example, figure 1 represents the variation of the annual margin as a function of the hydrogen composition to produce 7 ton/h of hydrogen.

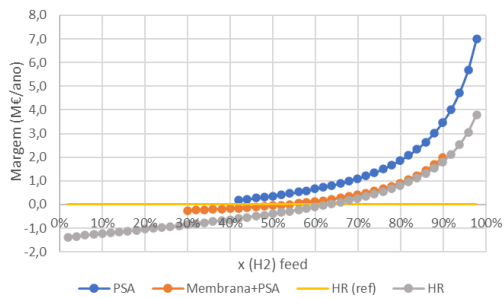


Figure 1- Annual margin to produce 7 ton/h of H₂ depending on the variation in hydrogen composition for each technology (Class A).

From the analysis performed on each stream individually, from variation of the margin as a function of the hydrogen composition and from the application of “dummy” streams do the model, it was possible to obtain the following decision model, applicable to any stream (figure 2). The first decision line represents the hydrogen composition of the stream to be treated. If the stream has a hydrogen composition of less than 30% vol. H₂ should be routed or maintained in the fuel gas network, as none of the technologies has the capacity to recover hydrogen with such a low purity. On the other hand, adding this current to the SMR load would not be advantageous either, since the amount of emitted CO₂ and natural gas consumption would either be higher or similar to the base case, so there would be no incentive. Between 30-40% vol. H₂ is a range outside the operating range of ROG PSA, but membrane technology can be applied. The third interval, between 40-74%vol., according to the literature, belongs to the operational range of all technologies under analysis, with 40%vol. corresponds to the minimum hydrogen composition recommended for PSA recovery. The last range corresponds to the range of optimal hydrogen compositions for PSA applicability.

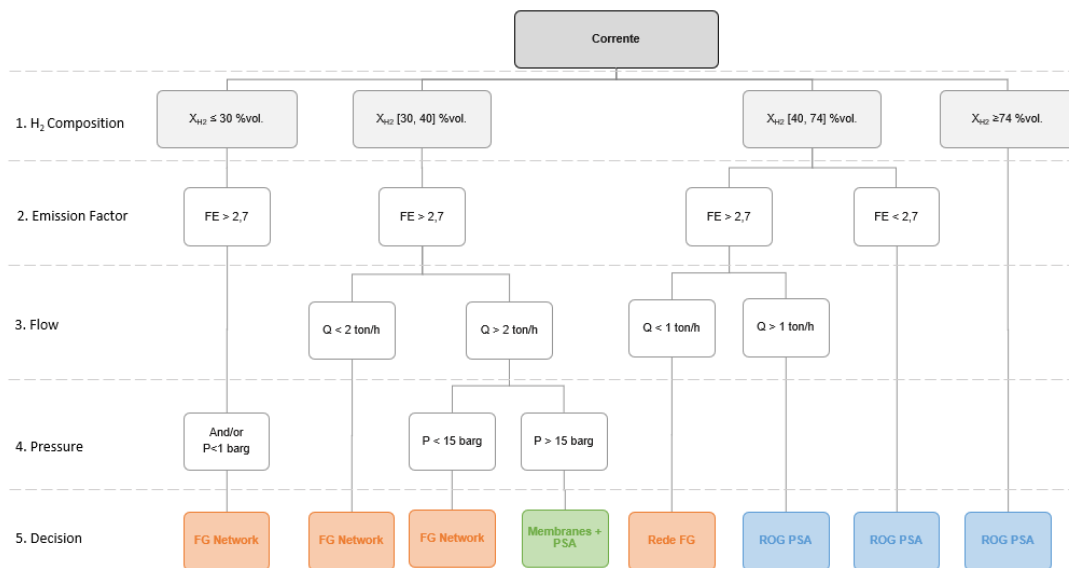


Figure 2- Support decision-making tool on selection the most appropriate technology for streams.

The hydrogen composition correlates decision-making with the light fraction of the stream (hydrogen), while the emission factor correlates with the heavy fraction (hydrocarbons) and, the flow and pressure link with the investment in capital for hydrogen recovery, as well as the amount of hydrogen that can be recovered.

If, when applying this tool, it indicates that the stream under study is routed or maintained in the fuel gas network, it should be considered to mix this stream with another, with a higher hydrogen composition, into obtain a new mixture with a higher hydrogen content.

The fact that all the parameters studied are not present in all branches does not imply that they are not relevant to the technology decision process. This is just a support tool to guide the user in the decision process and does not block a more exhaustive study for decision-making. The limited values are only indicative. For example, in general, it was observed that increasing the pressure of the stream increases the recovery interval of membranes-PSA and PSA, to the intervals of 30-40 %vol. H₂ and 40-74 %vol. H₂, respectively, disfavoring its inclusion in the fuel gas network. Additionally, the lower the emission factor compared to the emission factor of natural gas, the greater the reduction in CO₂ emissions observed, favoring the recovery of hydrogen.

The effect of the variation in the price of natural gas, CO₂, and electric power on the annual margin of the project was also analyzed, concluding that the increase in the price of CO₂ and natural gas favors the recovery of hydrogen from the fuel gas network since this process leads to a reduction in CO₂ emissions and consumption of natural gas. The increase in power price, disfavours the recovery of H₂ since the three approaches require the use of compression systems. The lower the stream pressure, the higher the compression ratio required to apply either approach, and consequently, the higher the energy consumption. The approach most affected by this increase is the membrane-PSA system, as it operates at higher pressure (71 barg).

4. Conclusion

The following table summarizes the approach that should be adopted for each current study in comparison with the forecast through the application of the decision-maker tool. It is possible to observe that the results are in agreement: the streams classified as A, B, C, and D must be recovered in a ROG PSA unit and the streams classified as E must be inserted or maintained in the fuel gas network except for the FCC offgas stream, whose composition of low hydrogen content and high olefin content does not allow it to be treated with any of the technologies studied nor to be included in the load to the SMR. It should be noted that according to this model, the tail gas streams from ROG PSA and Offgas and Return Gas from the petrochemical complex should be routed to the fuel gas network, this conclusion was corroborated by carrying out the profitability analysis of Hypothesis 1 and 2 and 3.

The diagram (figure 6) represents the proposed integration of the hydrogen and fuel gas networks resulting from this analysis. The implementation of this alternative has a capital investment of approximately of 14 M€.

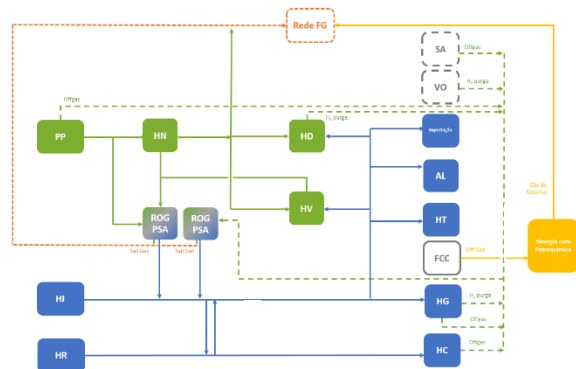


Figure 6- Proposal for integration between the hydrogen and the fuel gas networks.

On the other hand, if we analyze the stream that results from the mixture of all streams under analysis (streams that make up the A and B mixture, hydrocracker offgas, HG offgas, ROG PSA tail gas, and return gas that results from the business case) a flow rate equal to 20 ton/h is obtained, with a composition of 50% vol. in hydrogen and an emission factor of 2.53. If we apply the decision tool to this mixture, it is verified that this stream should be inserted into the ROG PSA and, performing the mass balance

to this system, it is concluded that it would be possible to recover 1.63 ton/h of hydrogen, from which would result in a reduction of 8.83 ton/h or 74 kton/year of CO₂ and 3.13 ton/h of natural gas.

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