



MASTER SEMESTER PROJECT

Optimization of the Hydrogen Network in an Oil Refinery

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Abstract

The stricter environmental and product quality regulations are pushing oil refineries to increase hydrotreatment and hydrocracking capacities to lower the sulfur contents in the products, thus leading to a higher demand for hydrogen. The efficient use of hydrogen becomes a necessity. This project used two different approaches, which are Pinch Technology (PT) and mathematical modeling using mixed integer nonlinear programming (MINLP), to obtain optimal Hydrogen network designs in a refinery. The hydrogen consuming and producing processes of an oil refinery were analyzed and identified. Computation of the missing information in the current scenario was conducted and then a reference case was established. With the focus on various purities, pressures and flowrates for the hydro-processing units, a pinch analysis was realized in order to set a target for the minimum hydrogen requirement of the system. A MINLP method was further created to optimize the hydrogen network with the objective functions to minimize the hydrogen consumption and the total annualized cost. A number of scenarios were analyzed considering different hydrogen production technologies and electricity suppliers. The results show that the scenario with the best economical performance is the one with hydrogen production from Steam Methane Reforming without Carbon and Capture and electricity supplied by a wind farm with a Total Annualized Cost of 142 [$M CHF/year$]. However, the one with hydrogen production from Steam Methane Reforming with Carbon Capture and electricity from a wind farm has the best overall performance with a total annualized Cost of 222 [$M CHF/year$]. The technologies using electrolysis for the production of hydrogen have the lowest CO_2 emissions but are 98 [$M CHF/year$] more expensive than the previous scenario. However, with the evolution of green hydrogen technologies, this cost gap is expected to decrease.

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1 Introduction

Achieving net-zero emissions requires a radical change in the way energy is supplied, transformed and used. The rapid growth of wind, solar and hydrogen technologies has shown the potential of new clean energy technologies to reduce emissions. However, these technologies need to be deployed on a far greater scale, especially in the industry field, in order to achieve net-zero emissions.

An oil refinery or petroleum refinery is an industrial process plant where crude oil is transformed and refined into more useful products such as naphtha, gasoline, diesel fuel and fuel oils. A refinery may use about 1.5% up to 8% of feed as fuel, depending on the complexity of the refinery. A typical world-scale refinery transforms 300,000 barrel crude oils per day, which will lead to CO_2 emissions ranging from 0.8 to 4.2 million tons per year [1]. Greenhouse gases (GHGs) emissions from the refining industry are responsible for 6% of all industrial GHG emissions as both the consumer and the provider of energy, making it the third-largest stationary emitter of greenhouse gases (GHGs) in the world [2]. Therefore, a central pillar of the net-zero target is the acceleration of refinery decarbonization.

The stricter environmental and product quality regulations are pushing oil refineries to increase hydrotreatment and hydrocracking capacities to lower the sulfur contents in the products, thus leading to a higher demand for hydrogen. Therefore, the efficient use of hydrogen has been given particular emphasis in recent years. This project investigates the role of hydrogen in the refinery transition. The production and consumption of hydrogen in different qualities in an oil refinery are studied and a mathematical programming model is built to analyze and optimize the hydrogen network flow. The integration of different hydrogen production technologies are specifically stressed with electricity from various sources.

The main questions that this project aims to answer are:

- Where is hydrogen used in an oil refinery and why it is needed? What are the qualities and quantities of hydrogen in different processes?
- What are the main technologies for hydrogen production? What are their costs and environmental impacts?
- How to optimize the hydrogen network based on the data that is given? How to integrate hydrogen production of external resources into an oil refinery?
- Are the results convincing and reasonable? How to improve the work?

2 Literature Review

The two most popular approaches to optimal Hydrogen network designs are Pinch Technology (PT) and mathematical modeling using mathematical programming (MP). A very first representation using this technique with the analogy heat load/flow rate (quantity) and temperature/purity (quality) was proposed by Towler et al.[3] and then it was improved by Alves et al.[4] in the form of hydrogen surplus in order to analyze the hydrogen distribution system. In Figure 1a, the purity profile and the hydrogen excess and deficit are represented. This allows to define the minimum hydrogen requirement of the system.

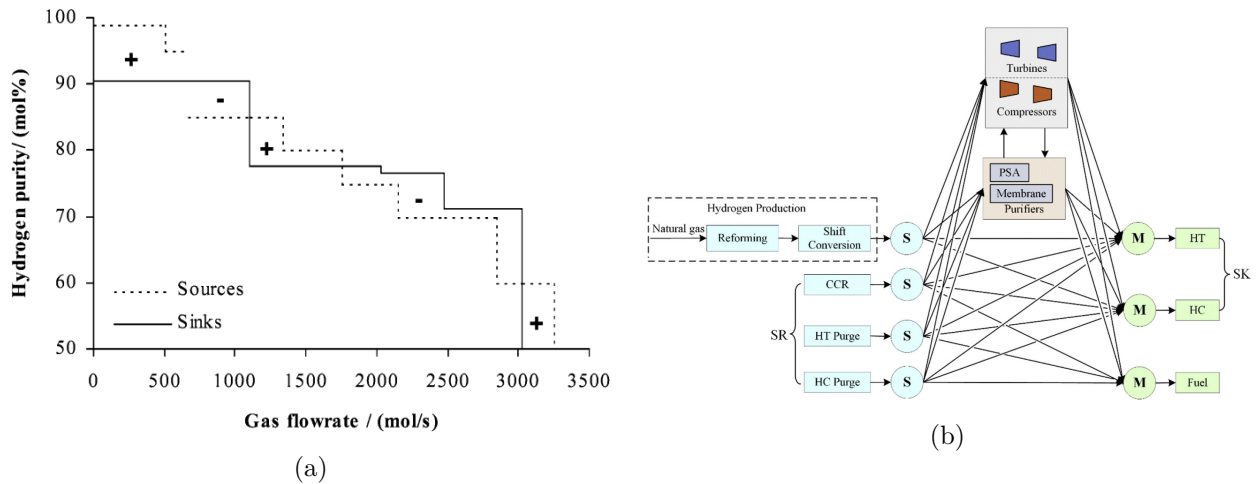


Figure 1: (a) Purity profile highlighting the pockets between the source and sink curves with hydrogen excess (+) and deficit (-) [4], (b) Superstructure of refinery hydrogen network integrated with hydrogen compressors and turbines [5].

The use of mathematical programming techniques seems more appropriate in order to consider simultaneously pressure constraints and contaminants restrictions. Girardin et al.[6], Chang et al.[7], Yang et al. [8] and Liu et al. [5] developed mathematical programming methods for hydrogen network superstructure optimization in an oil refinery. In the work of Girardin et al.[6], the combination of an evolutionary algorithm and mixed integer linear programming (MILP) network design models allowed to develop a multi-objective optimization methodology to solve the hydrogen recovery network design problems. In the work of Chang et al. [7], a superstructure for the hydrogen network is formulated as a new MINL model whose non-linearities do not come from the constraint of compression power which is expressed by using a linear equation which eliminates the need to have the pressures of compressors as variables. The results show a 3.1% to 4.5% reduction in the total annualized cost compared with those of literature ones. A hydrogen network superstructure with light hydrocarbon recovery is developed by Yang et al.[8]. Several solvers are combined to determine the optimal hydrogen network design. The results show that the hydrogen consumption decreases by 13% and the total annualized cost is reduced of 28% because of light hydrocarbon recovery. Liu et al [5] proposed a new superstructure of refinery hydrogen network that uses hydrogen turbines to recover the expansion work. Several objective functions were used to analyse sequential mathematical models such as minimization of hydrogen consumption, compression work, total power consumption and total annualized cost. In Figure 1b, such a superstructure

is presented. The results show that the total annualized cost can be reduced by 3.9% by using hydrogen turbines for power recovery.

3 Refinery Processes

Crude oil is a complex mixture of hydrocarbons ranging from methane to asphalt, with varying proportions of paraffins, naphthenes, and aromatics. The objective of crude distillation is to fractionate crude oil into light-end hydrocarbons (C_1-C_4), naphtha, gasoline, kerosene, diesel, and atmospheric residue. Some of these broad cuts can be marketed directly, while others require further processing in order to make them saleable. The Refineries have three basic steps:

1. Separation
2. Conversion
3. Treatment

In Figure 2, a block flow diagram of an oil refinery is presented.

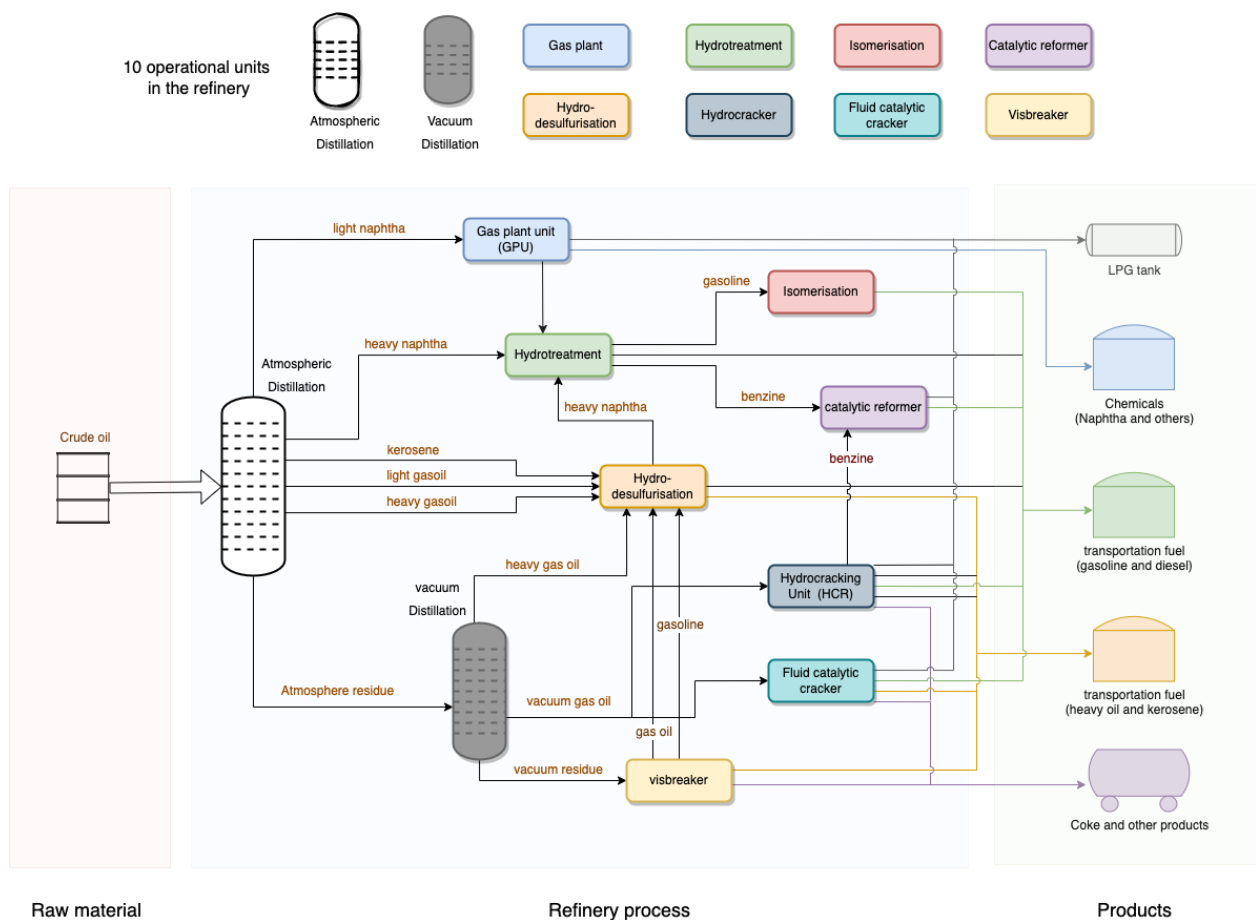


Figure 2: Block Flow diagram of an oil refinery.

The first processing step in the refinery, after desalting the crude, is the separation of crude into a number of fractions by distillation. The liquids and vapors are separated inside the distillation units into different components according to their boiling points. The heavy components are condensed on the bottom and the light ones are evaporated to the top. This can be seen in Figure 3.

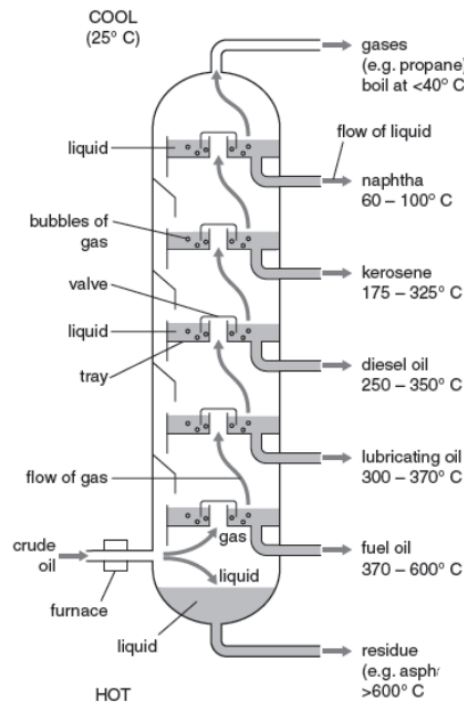


Figure 3: Distillation of crude oil.

The light components such as gasoline and liquefied refinery gases vaporise and rise to the top of the distillation tower, where they condense back to liquids. With the same reasoning the medium weight liquids such as kerosene and distillates stay in the middle of the distillation tower. The heavier liquids such as the gas oils are separated on the bottom part of the distillation tower, these are the ones with the highest boiling points.

After distillation, lower value distillation components can be processed into lighter and higher value products such as gasoline. The most used conversion method is called the cracking because it uses heat, pressure, catalysts or hydrogen to transform heavy hydrocarbon molecules into lighter ones. There are other processes of crude oil conversion that instead of splitting molecules as in cracking, they rearrange the molecules such as in the catalytic reforming process.

3.1 Catalytic Reforming Process

The catalytic reforming process uses heat, moderate pressure and catalysts to transform low octane naphtha (particularly heavy naphtha that is rich in naphthenes) into high-octane and low-sulfur reformat. The block flow diagram of the catalytic reforming process is presented in Figure 4.

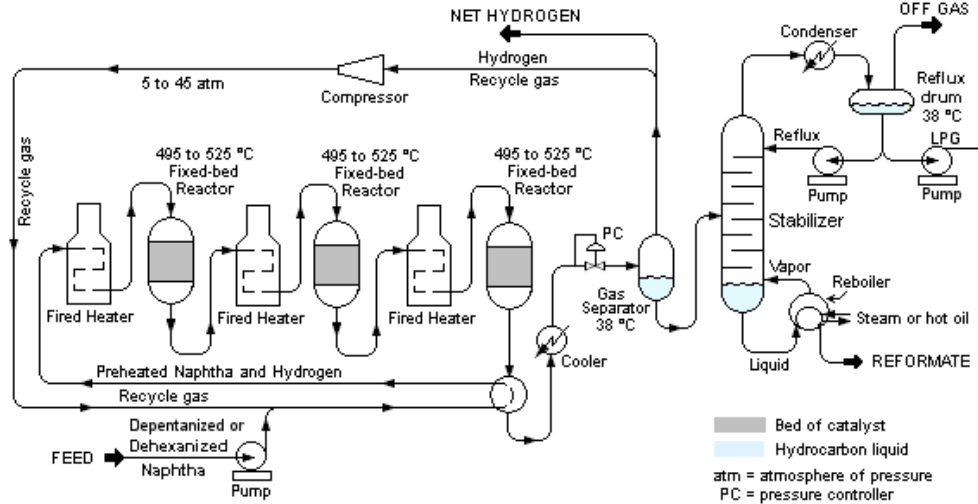


Figure 4: Block flow diagram of the catalytic reforming process in an oil refinery.

As can be seen on Section A.1 which explains in detail the main reactions of this process, the most valuable byproduct from catalytic reforming is hydrogen. This hydrogen might be used to satisfy its increasing demand in the hydrotreating and hydrocracking processes. In most cases, the naphtha feedstock needs to be hydrotreated before the catalytic reforming process in order to protect the platinum catalyst from being poisoned by the sulfur or nitrogen species.

The main focus of this project is the hydrogen network and therefore the hydrogen production on the catalytic reforming process and how much energy is used are important informations. The following data presented in Table 1 was found in reference [9].

Table 1: Data for Catalytic Reforming Process

Variable	Quantity
Inlet Reactor Temperature SOR [°C]	501.11
Inlet Reactor Temperature EOR [°C]	545
Separator Pressure [bar]	12.76
Separator Temperature [°C]	54.44
Recycle Ratio [mol_{H_2}/mol_{feed}]	4.5
Liquid Hourly Space Velocity on Weight basis (WHSV) [1/hour]	2.75
Hydrogen yield weight percentage of feed [weight%] 96 RON	1.93
Hydrogen yield weight percentage of feed [weight%] 100 RON	3.1
Hydrogen yield weight percentage of feed [weight%] 102 RON	3.2
Fuel Gas consumption [MJ/ton_{feed}]	153954.94
Steam consumption [MJ/ton_{feed}]	31189.15
Power consumption [MJ/ton_{feed}]	19.08
Cooling water consumption [ton_{water}/ton_{feed}]	31850

3.2 Hydrotreatment Processes

Crude oil contains several contaminants. These impurities can damage the equipment, the catalysts and the quality of products when going through the refinery processing units. There are also legal limits on the contents of some impurities such as for sulphur. The mission of hydrotreating processes is the removal of these impurities (mainly sulfur and nitrogen but also oxygen, olefins and metals) from the distillation components as naphtha, kerosene, gas oils and atmospheric residues. The operating conditions of treatment depend on the type of feed and the desired desulfurization levels in the treated product. The hydrotreating process consists of mixing hydrogen with the feedstock and heating this mix to 300-380 [°C]. This mix then enters a reactor loaded with a catalyst which promotes the reactions presented in Figure 5.

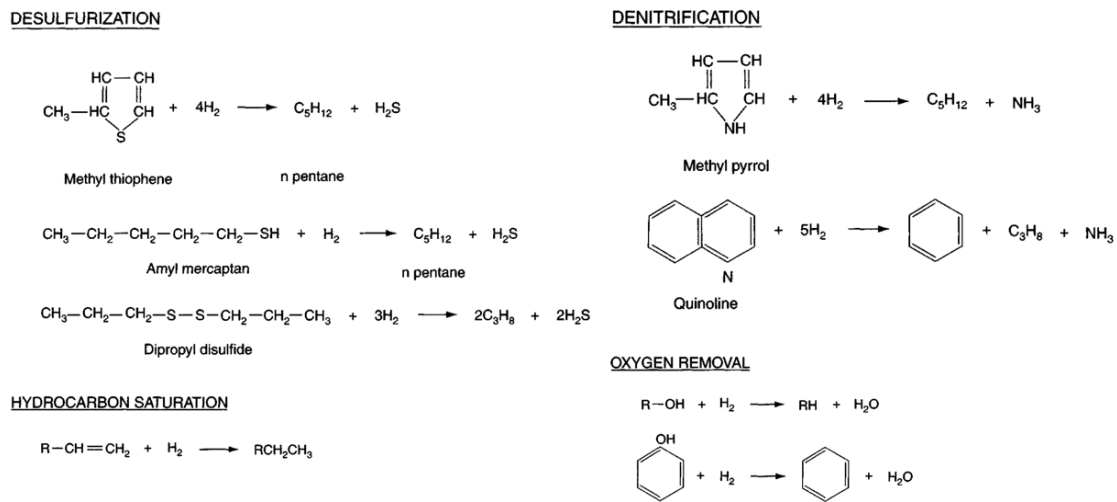


Figure 5: Basic hydrotreating processes reactions [9].

In order to make the feed suitable for further treatment on the catalytic reforming process to improve the octane number, the distillation component naphtha needs to be hydrodesulfurized before. As mentioned before, the main focus of this project is the hydrogen network. Therefore, the hydrogen consumption on the hydrotreating processes and the energy demand are important information. The following data presented in Table 2 was found in reference [9].

Table 2: Data for Naphtha Hydrotreating Process.

Variable	Quantity
Inlet Reactor Temperature SOR [°C]	320
Inlet Reactor Temperature EOR [°C]	370
Hydrogen Partial Pressure at Reactor Outlet [bar]	11.03
Liquid Hourly Space Velocity on Weight basis (LHSV) [1/hour]	4
Hydrogen Consumption [kgH ₂ /ton _{feed}]	0.67
Hydrogen yield weight percentage of feed [weight%]	0.8
Fuel Gas consumption [MJ/ton _{feed}]	28733.831
Steam consumption [MJ/ton _{feed}]	24420.439
Power consumption [MJ/ton _{feed}]	36
Cooling water consumption [ton _{water} /ton _{feed}]	48230
Distilled water consumption [ton _{water} /ton _{feed}]	113.75

The aim of the kerosene hydrotreating process is to upgrade raw kerosene into jet fuel by removing the sulfur content. The sulfur in the raw kerosene can cause corrosion problems in aircraft engines and fuel handling and storage facilities. The nitrogen present on the raw kerosene can cause color stability problems. For aviation turbine fuels (ATF), the flash point and freeze point of the hydrotreated kerosene cut has to be rigorously controlled to meet the stringent requirements. This hydrotreated kerosene cut is achieved with the introduction of hydrogen and a presence of a catalyst in the reactor where the sulfur and nitrogen compounds are converted into hydrogen sulfide and ammonia. The data for the kerosene hydrotreating is presented in Table 3 and was found in reference [9].

Table 3: Data for Kerosene Hydrotreating Process.

Variable	Quantity
Inlet Reactor Temperature SOR [$^{\circ}C$]	315.56
Inlet Reactor Temperature EOR [$^{\circ}C$]	370
Hydrogen Partial Pressure at Reactor Outlet [bar]	76.19
Recycle ratio [kg_{H_2}/ton_{feed}]	45.66
Hydrogen Consumption [kg_{H_2}/ton_{feed}]	8.25
Hydrogen yield weight percentage of feed [$weight\%$]	1.37
Fuel Gas consumption [MJ/ton_{feed}]	112811.81
Steam consumption [MJ/ton_{feed}]	1990.8
Power consumption [MJ/ton_{feed}]	54
Cooling water consumption [ton_{water}/ton_{feed}]	21840
Distilled water consumption [ton_{water}/ton_{feed}]	154.7

As for the previous process, the gas oil hydrotreating process is designed to reduce sulfur and other impurities that are present in the raw gas oil cut. The data for the gas oil hydrotreating is presented in Table 4 and was found in reference [9].

Table 4: Data for Gas Oil Hydrotreating Process.

Variable	Quantity
Inlet Reactor Temperature [$^{\circ}C$]	340.56
Hydrogen Partial Pressure at Reactor Outlet [bar]	119.14
Liquid Hourly Space Velocity on Weight basis (LHSV) [$1/hour$]	1.72
Hydrogen Consumption [kg_{H_2}/ton_{feed}]	6.28
Hydrogen yield weight percentage of feed [$weight\%$]	0.71
Fuel Gas consumption [MJ/ton_{feed}]	15926.37
Steam consumption [MJ/ton_{feed}]	7299.59
Power consumption [MJ/ton_{feed}]	22.5
Cooling water consumption [ton_{water}/ton_{feed}]	15925

3.3 Hydrocracking Process

The hydrocracker upgrades VGO (vacuum gas oil) through cracking while injecting hydrogen into a high volume of high-quality diesel and kerosene products. The process consists of causing feed to react with hydrogen in the presence of a catalyst under specified operating conditions: temperature, pressure, and space velocity. The principal hydrocracking reactions are presented on Figure 6.

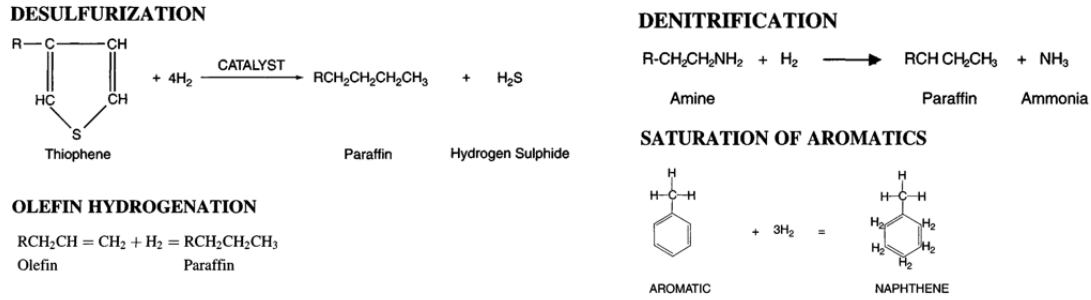


Figure 6: Basic hydrocracking process reactions [9].

As mentioned before, the main focus of this project is the hydrogen network and therefore the hydrogen consumption on the hydrocracking process and how much energy is used are important informations. The following data presented in Table 5 was found in reference [9].

Table 5: Data for Vacuum Gas Oil (VGO) Hydrocracking Process.

Variable	Quantity
Catalyst Average Temperature [°C]	412.78
Hydrogen Partial Pressure at Reactor Inlet [bar]	137.9
Liquid Hourly Space Velocity on Weight basis (LHSV) [1/hour]	1.72
Hydrogen Consumption [kgH ₂ /ton _{feed}]	17.09
Hydrogen yield weight percentage of feed [weight%]	2.25
Makeup plus Recycle at Reactor Inlet [kg/ton _{feed}]	74.313
Makeup Hydrogen Purity [vol.%]	95
HP Separator Temperature [°C]	60
HP Separator Pressure [bar]	166.51
Bleed Rate (100 [% H ₂]) [kgH ₂ /ton _{feed}]	2.973
Recycle Compressor Suction Pressure [bar]	164.78
Recycle Compressor Discharge Pressure [bar]	187.19
Fuel Gas consumption [MJ/ton _{feed}]	39815.932
Steam consumption [MJ/ton _{feed}]	7693.186
Power consumption [MJ/ton _{feed}]	64.8
Cooling water consumption [ton _{water} /ton _{feed}]	15015
Distilled water consumption [ton _{water} /ton _{feed}]	728

3.4 Isomerization Process

The isomerization process converts light naphtha into a higher value gasoline blendstock by changing its molecular shape and raising its octane number. The resulting isomerate is not high octane (typically 82-87 RON), however it is much better than light naphtha which is around 70 RON. The isomerization process is conducted in an atmosphere of hydrogen over a fixed bed of catalyst and at operating conditions that promote isomerization and minimize hydrocracking. In Figure 7 one can see the typical process flow of the isomerization process. As mentioned before, the main focus of this project is the hydrogen network and therefore the particular emphasis is put on the hydrogen consumption of isomerisation unit. The following data presented in Table 6 was found in reference [9].

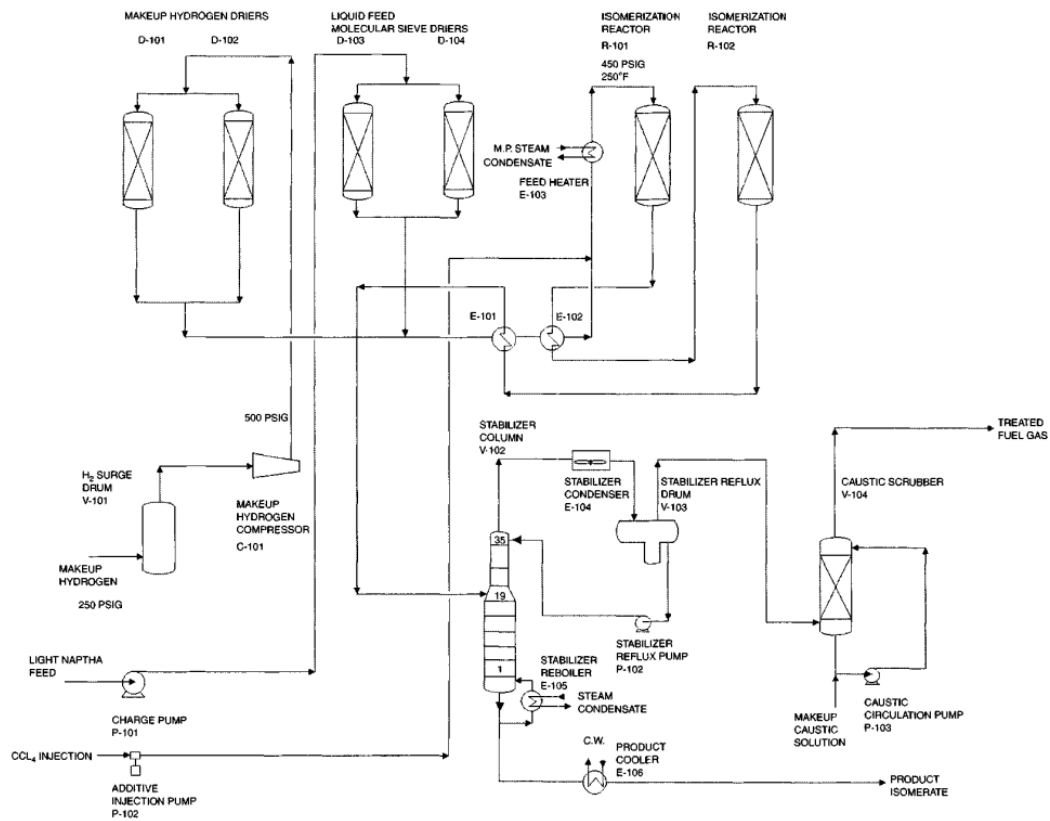


Figure 7: Process flow diagram of Isomerization Process [9].

Table 6: Data for Isomerization Process.

Variable	Quantity
Reactor Inlet Temperature [$^{\circ}\text{C}$]	160
Reactor Pressure [bar]	31.03
H_2/HC mole ratio [$\text{mol}_{\text{H}_2\text{Recycle}}/\text{mol}_{\text{feed}}$]	0.05
Liquid Hourly Space Velocity on Weight basis (LHSV) [1/hour]	2
Hydrogen yield weight percentage of feed [weight%]	0.4
Steam consumption [$\text{MJ}/\text{ton}_{\text{feed}}$]	35568.9
Power consumption [$\text{MJ}/\text{ton}_{\text{feed}}$]	25.99
Cooling water consumption [$\text{ton}_{\text{water}}/\text{ton}_{\text{feed}}$]	279825

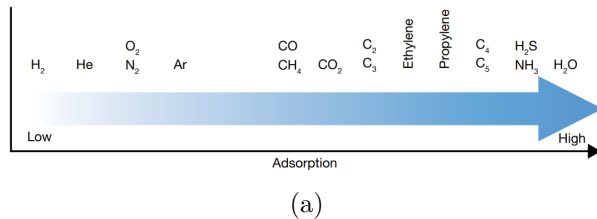
4 Hydrogen Purification Processes

In refineries, part of the makeup hydrogen is supplied by the catalytic reforming process detailed in Section 3.1. However, the other part of the hydrogen used for the processes mentioned above comes from a hydrogen production unit (Steam Methane Reforming in most cases). Hydrogen gas is not found in nature in its pure form, therefore the investment in hydrogen production units is necessary. Since hydrogen has become highly demanded in refineries, its recovery and purification can reduce the hydrogen consumption from production units and can also reduce CO_2 emissions as a result of reducing the capacity of steam methane reforming hydrogen production units [10].

To maximize their value, hydrogen-rich offgas streams must first be removed of process related impurities. The three predominant technologies available to clean off-gas hydrogen streams are:

- Membrane separation
- Pressure swing adsorption (PSA)
- Cryogenic distillation

The pressure swing adsorption (PSA) system works on the principle of physical adsorption that, at elevated partial pressure, the adsorbents can retain a larger volume of gaseous components, some stronger than others. Adsorption strength typically increases with the molecular weight of each component, and hydrogen has the weakest strength of adsorption of these components as can be seen in Figure 8a. Thus, most impurities contained in the hydrogen-containing feed stream are selectively adsorbed and a high-purity hydrogen product obtained. PSA systems can produce ultra-high purity (up to 99.999% pure) hydrogen. They can operate at high or low pressure, but they require complex control schemes and have higher capital and operational costs than membrane separation.



Parameter	Membrane Separation	Pressure-Swing Adsorption	Cryogenic Distillation
H ₂ Purity	90%–98%	99.9+%	95%–99%
H ₂ Recovery	85%–95%	75%–92%	90%–98%
H ₂ Product Pressure	< Feed pressure	Feed pressure	Feed/Low pressure
Feed Pressure	300–2,300 psig	150–600 psig	>75–1,100 psig
H ₂ Feed Content	>25–50%	>40%	>10%
Byproduct Capability	Poor	Poor	Excellent
H ₂ Capacity	1–50+ MM scfd	1–200 MM scfd	10–75+ MM scfd
Pretreatment Requirements	Minimum	None	CO ₂ , H ₂ O removal
Capital Cost	Low	Medium	Higher
Scale Economics	Modular	Moderate	Good
Startup Time	Minutes	Minutes	Hours

(b)

Figure 8: (a) PSA adsorption strength [11], (b) Hydrogen purification Processes. [11].

According to [10], the total cost of the Pressure swing adsorption (PSA) process was lower than the other processes for the Tehran Refinery. However the amount of recovered hydrogen in the PSA process is lower than in the membrane separation and cryogenic distillation processes as can be seen in Figure 8b.

The following data presented in Table 7 was found in reference [9].

Table 7: Data for Pressure Swing Adsorption (PSA) Process.

Variable	Quantity
Hydrogen Inlet PSA Purity [<i>vol.</i> %]	78.46
Hydrogen Recovery [<i>weight</i> %]	83
Adsorption Pressure [<i>bar</i>]	18.96
Adsorption Temperature [$^{\circ}C$]	40.56
Dessorption Pressure [<i>bar</i>]	0.14
Dessorption Temperature [$^{\circ}C$]	40.56
Steam consumption [<i>MJ/ton_{feed}</i>]	149309.75
Power consumption [<i>MJ/ton_{feed}</i>]	3.88
Cooling water consumption [<i>ton_{water}/ton_{feed}</i>]	602420

5 Current Osmose Scenario

This section aims to detail the current scenario extrated from the Osmose model, which is a model of an actual refinery validated by experts in the domain. However the hydrogen network flow is missing in this model and needs to be implemented. In Figure 9, the current scenario is presented. The hydrogen consumption, the purge gas, the catalytic reforming unit hydrogen production and the makeup gas of each process are already known in the current hydrogen network flow. With this information the reference case of the hydrogen network flow presented in Figure 10 was built.

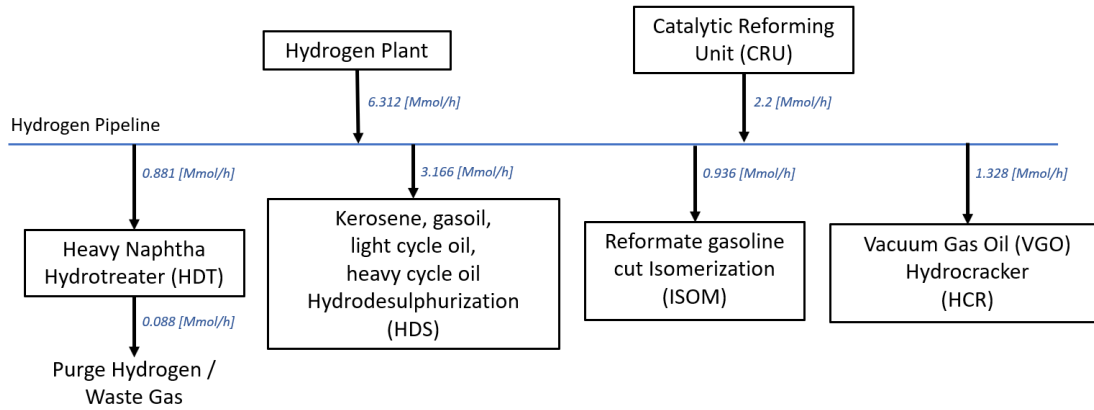


Figure 9: Block flow diagram of current hydrogen network flow.

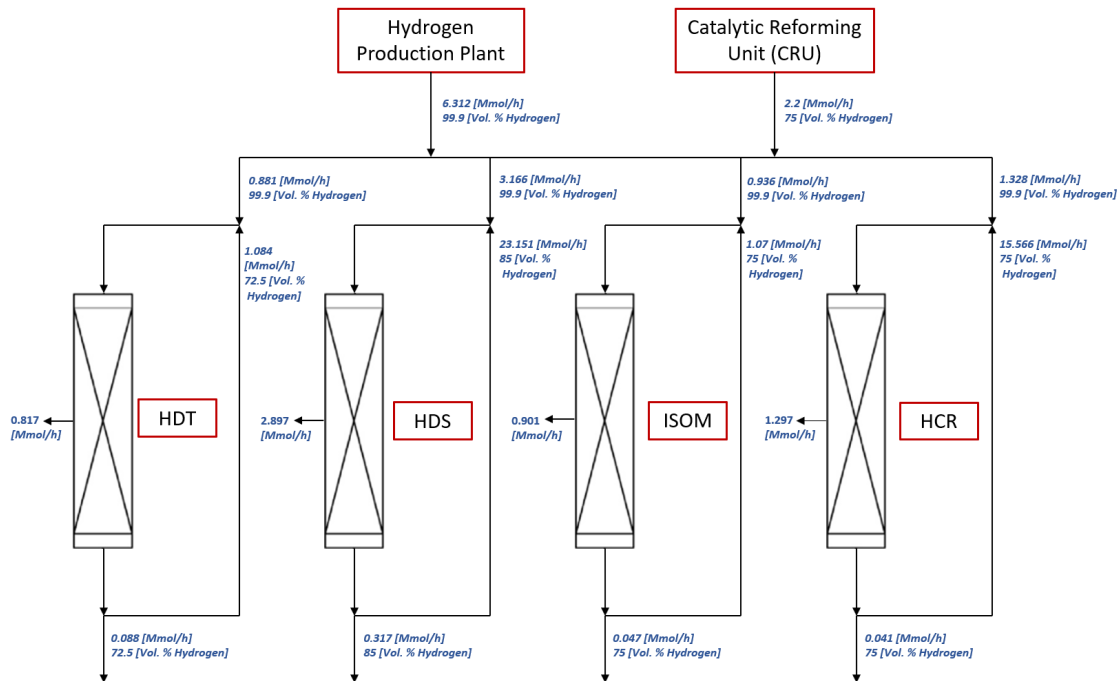


Figure 10: Block flow diagram of reference case with data from current Osmose scenario.

In order to obtain all the data presented in Figure 10, several assumptions were made. It was assumed that the recycle gas and purge gas exist. A simplified diagram mentioned in [12] which can be seen in Figure 11 was used to represent each process.

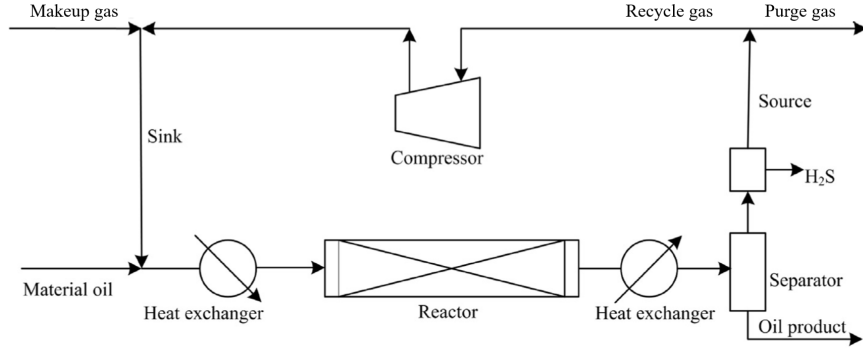


Figure 11: Coupled Sink and Source. [12]

The first step was to compute the hydrogen balance which is presented in Equations 1 and 2. $\dot{M}_{H_2_i}$ corresponds to the hydrogen molar flow rate of the stream i in $[Mmol H_2/h]$ and \dot{M}_i corresponds to the molar flow rate of the stream i in $[Mmol/h]$. The relationship between these two is presented in Equation 3 where Φ^i is the purity of hydrogen in the stream i .

$$\dot{M}_{H_2_{Consumption}} = \dot{M}_{H_2_{Makeup}} - \dot{M}_{H_2_{Purge}} \quad [Mmol H_2/h] \quad (1)$$

$$\dot{M}_{H_2_{Reactor Outlet}} = \dot{M}_{H_2_{Recycle}} + \dot{M}_{H_2_{Purge}} \quad [Mmol H_2/h] \quad (2)$$

$$\dot{M}_{H_2_i} = \Phi^i \cdot \dot{M}_i \quad (3)$$

The data presented on Table 8 is the initial known and assumed data and the spaces that aren't filled are the data that can be computed with the known one.

Table 8: Initial data from Osmose model for Hydrotreating Process.

Variable	Quantity
Feedstock	Heavy Naphtha
Feedstock Flow rate $[Mmol/h]$	1.56
Makeup Gas Flow rate $[Mmol/h]$	0.88
Makeup Gas Purity $[vol.\%]$	99.9
Purge Gas Flow rate $[Mmol/h]$	0.088
Purge Gas Purity $[vol.\%]$	72.5
Recycle Gas Flow rate $[Mmol/h]$	
Recycle Gas Purity $[vol.\%]$	72.5
Hydrogen Consumption $[Mmol/h]$	
Hydrogen Reactor Inlet Purity $[vol.\%]$	
Hydrogen Reactor Outlet Purity $[vol.\%]$	
Hydrogen Partial Pressure on Reactor Inlet $[bar]$	
Hydrogen Partial Pressure on Reactor Outlet $[bar]$	11.0316

In order to find the missing data several relations were established and are presented in Equations 4 to 8.

$$\Phi_{Reactor Outlet} = \frac{PP_{H_2, Reactor Outlet}}{P_{Reactor Outlet}} \quad (4)$$

$$\frac{P_{Reactor Inlet}}{P_{Reactor Outlet}} = \frac{\dot{M}_{Reactor Inlet}}{\dot{M}_{Reactor Outlet}} \quad (5)$$

$$\frac{PP_{H_2,Reactor Outlet}}{P_{Reactor Outlet}} = \frac{\dot{M}_{H_2,Reactor Outlet}}{\dot{M}_{Reactor Outlet}} \quad (6)$$

$$\dot{M}_{Reactor Inlet} = \dot{M}_{Recycle} + \dot{M}_{Makeup} \quad (7)$$

$$\dot{M}_{H_2,Reactor Outlet} = \frac{\dot{M}_{Reactor Inlet} \cdot PP_{H_2,Reactor Outlet}}{P_{Reactor Inlet}} \quad (8)$$

With all of these relations and with the previous mass balances equations, the unknowns such as the recycle gas molar flowrate and the reactor inlet purity can be computed with equations 9 and 10.

$$\dot{M}_{Recycle} = \frac{(\dot{M}_{Makeup}) \cdot \frac{PP_{H_2,Reactor Outlet}}{P_{Reactor Inlet}} - \dot{M}_{H_2,Purge}}{\Phi^{Recycle} - \frac{PP_{H_2,Reactor Outlet}}{P_{Reactor Inlet}}} \quad (9)$$

$$\Phi^{Reactor Inlet} = \frac{PP_{H_2,Reactor Inlet}}{P_{Reactor Inlet}} = \frac{\Phi^{Makeup} \cdot \dot{M}_{Makeup} + \Phi^{Recycle} \cdot \dot{M}_{Recycle}}{\dot{M}_{Makeup} + \dot{M}_{Recycle}} \quad (10)$$

Thus, the following Table 9 can be completed. The same reasoning was applied for the other three processes and their corresponding data are presented in Tables 9 and 10.

Table 9: Reference case data computed for HDT process on the left and HDS process on the right.

Variable	Quantity	Variable	Quantity
Feedstock	Heavy Naphtha	Feedstock	Kerosene, Gasoil, Light and Heavy Cycle Oil
Feedstock Flow rate [Mmol/h]	1.56	Feedstock Flow rate [Mmol/h]	2.55
Makeup Gas Flow rate [Mmol/h]	0.88	Makeup Gas Flow rate [Mmol/h]	3.17
Makeup Gas Purity [vol.%]	100	Makeup Gas Purity [vol.%]	100
Purge Gas Flow rate [Mmol/h]	0.088	Purge Gas Flow rate [Mmol/h]	-
Purge Gas Purity [vol.%]	72.5	Purge Gas Purity [vol.%]	-
Recycle Gas Flow rate [Mmol/h]	3.39	Recycle Gas Flow rate [Mmol/h]	47.10
Recycle Gas Purity [vol.%]	72.5	Recycle Gas Purity [vol.%]	85
Hydrogen Consumption [Mmol/h]	0.82	Hydrogen Consumption [Mmol/h]	3.17
Hydrogen Reactor Inlet Purity [vol.%]	57.27	Hydrogen Reactor Inlet Purity [vol.%]	81.79
Hydrogen Reactor Outlet Purity [vol.%]	48.93	Hydrogen Reactor Outlet Purity [vol.%]	36.39
Hydrogen Partial Pressure on Reactor Inlet [bar]	14.61	Hydrogen Partial Pressure on Reactor Inlet [bar]	128.41
Hydrogen Partial Pressure on Reactor Outlet [bar]	11.0316	Hydrogen Partial Pressure on Reactor Outlet [bar]	119

Table 10: Reference case data computed for ISOM process on the left and HCR process on the right.

Variable	Quantity	Variable	Quantity
Feedstock	Reformat Gasoline Cut	Feedstock	Vaccum Gas Oil (VGO)
Feedstock Flow rate [Mmol/h]	0.31	Feedstock Flow rate [Mmol/h]	0.19
Makeup Gas Flow rate [Mmol/h]	0.94	Makeup Gas Flow rate [Mmol/h]	1.33
Makeup Gas Purity [vol.%]	100	Makeup Gas Purity [vol.%]	100
Purge Gas Flow rate [Mmol/h]	-	Purge Gas Flow rate [Mmol/h]	-
Purge Gas Purity [vol.%]	-	Purge Gas Purity [vol.%]	-
Recycle Gas Flow rate [Mmol/h]	1.09	Recycle Gas Flow rate [Mmol/h]	8.5
Recycle Gas Purity [vol.%]	75	Recycle Gas Purity [vol.%]	75
Hydrogen Consumption [Mmol/h]	0.94	Hydrogen Consumption [Mmol/h]	1.33
Hydrogen Reactor Inlet Purity [vol.%]	74.92	Hydrogen Reactor Inlet Purity [vol.%]	76.92
Hydrogen Reactor Outlet Purity [vol.%]	34.96	Hydrogen Reactor Outlet Purity [vol.%]	63.66
Hydrogen Partial Pressure on Reactor Inlet [bar]	23.251	Hydrogen Partial Pressure on Reactor Inlet [bar]	137.9
Hydrogen Partial Pressure on Reactor Outlet [bar]	10.85	Hydrogen Partial Pressure on Reactor Outlet [bar]	111.92

6 Pinch Analysis

Considering the analogy between heat load and flow rate (quantity) and between temperature and purity (quality), the minimum hydrogen requirement can be defined by applying pinch based techniques. A hydrogen network has been analysed on [4], where a systematic method for the analysis of hydrogen distribution systems based on the concept of hydrogen surplus is proposed. The pinch techniques set the target for the minimum flow rate of fresh hydrogen required by the refinery. Once this minimum flow rate of hydrogen is known one can start working on the hydrogen network design with the goal of approaching to this minimum flow rate of hydrogen. The closer a system is to the minimum supply of hydrogen, the higher is the efficiency at which the network is operating.

The first step to establish the minimum hydrogen requirement is to identify the sinks and sources of hydrogen in the system. A sink is a stream that uses hydrogen from the hydrogen network, whereas a source is a stream that provides hydrogen to the network [6]. According to the data known from the current Osmose scenario the Table 11 summarizes all the sources and sinks for this particular system which was explained in detail in Section 5.

Table 11: Sources and Sinks Table.

	Process	Purity [Vol.%H ₂]	Flow rate [Mmol/h]
Makeup	HDT	99.9	0.881
	HDS	99.9	3.166
	ISOM	99.9	0.936
	HCR	99.9	1.328
Recycle	HDT	72.5	1.084
	HDS	85	23.151
	ISOM	75	1.070
	HCR	75	15.566
Purge	HDT	72.5	0.088
	HDS	85	0.317
	ISOM	75	0.047
	HCR	75	0.041
Sources	CRU	75	2.2
	HDT	72.5	1.172
	HDS	85	23.468
	ISOM	75	1.117
	HCR	75	15.607
	FRESH	99.9	6.312
Sinks	HDT	84.93	1.965
	HDS	86.805	26.317
	ISOM	86.666	2.007
	HCR	76.923	16.894

With the information found on Table 11 and the analogy with the hot and cold composite curves one can compute the composite curves of sources and sinks and the minimum hydrogen requirement using hydrogen flow rate and purity which are presented in Figure 12. Combining these two curves, one can define the hydrogen Grand composite curve which is a limiting curve which is presented in Figure 13. Hydrogen of purity below the pinch point which is 86.67 [vol.%] will feed a purification

unit to produce high quality hydrogen above the pinch point and low purity hydrogen. This high quality hydrogen will be reused by mixing. The modification of the hydrogen pinch point resulting from the integration of a purification unit allows the reduction of the fresh hydrogen flowrate according to [6].

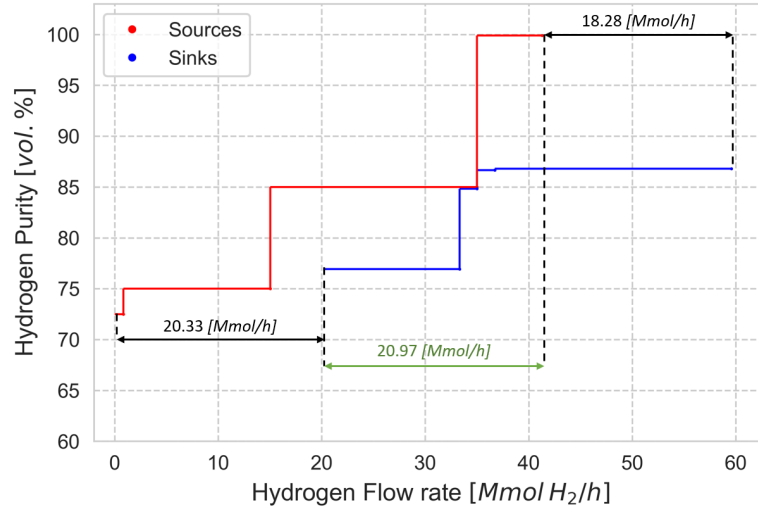


Figure 12: Composite curves of hydrogen purity and quantity.

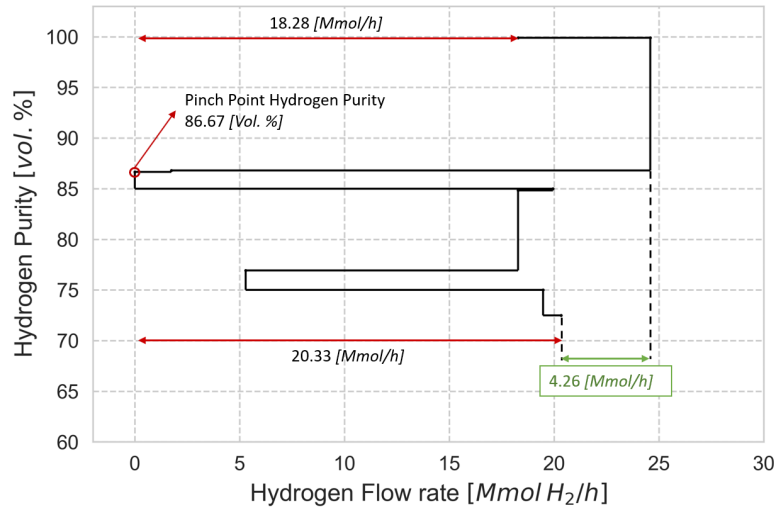


Figure 13: Grand composite curve of hydrogen purity and quantity.

One can see on Figures 12 and 13 that the maximum hydrogen recovery is $20.97 [Mmol_{H_2}/h]$ and that the minimum hydrogen requirement is equal to $4.26 [Mmol_{H_2}/h]$. This last value is important for the next step which the design of the hydrogen network. These graphical methods however have some disadvantages such as the fact they didn't consider purity and other constraints such as pressure and contaminant simultaneously.

7 Hydrogen Network Superstructure

7.1 Problem Statement

In an oil refinery there is a set of hydrogen sources which is named in this project $SR = \{i \mid i = 1, 2, \dots, I\}$ and a set of hydrogen sinks $SK = \{j \mid j = 1, 2, \dots, J\}$. A set of units that combines both these sets was also defined as $U = SR \cup SK = \{u \mid u = 1, 2, \dots, U\}$. A set of utilities such as the different hydrogen production power plants, the purification unit and the use of off-gas hydrogen as fuel is defined as $Ut = \{m \mid m = 1, 2, \dots, M\}$. A set of different electricity suppliers is defined as $E = \{e \mid e = 1, 2, \dots, E\}$ and a set of the hydrogen consumption processes related to the reactors is also defined as $C = \{k \mid k = 1, 2, \dots, K\}$.

The set of utilities, $Ut = \{m \mid m = 1, 2, \dots, M\}$, provides hydrogen with a constant purity ϕ_m^{out} . The set of hydrogen sources, $SR = \{i \mid i = 1, 2, \dots, I\}$, provides hydrogen at a constant outlet pressure P_i^{out} . The set of hydrogen consumption processes related to the reactors, $C = \{k \mid k = 1, 2, \dots, K\}$, have fixed hydrogen flowrates $C_k^{H_2}$ and minimum hydrogen purity constraints brought by the minimum hydrogen partial pressure requirement at the outlet $\Phi_k^{out, min}$. Each unit on the hydrogen sinks set, $SK = \{j \mid j = 1, 2, \dots, J\}$, has a constant pressure defined at the inlet P_j^{in} . The off gases can be reused between other units or go directly to the purifier for hydrogen purification or disposed to the fuel gas sink. The aim is to have the optimised hydrogen network flow design (the molar mass flowrates $F_{i,k}$ from sources to sinks, the outlet hydrogen purities Φ_k^{out} as well as the positioning of compressors) depending on different objective functions such as the minimum fresh hydrogen consumption, the minimum total annualized cost including operational and investment costs and the minimum CO_2 emissions. Several assumptions were made in order to simplify the problem similarly done in [7]:

- All gas streams are mixtures of only hydrogen and methane since the other components are in much smaller proportions [7].
- The ideal gas law is used since the hydrogen a very close behaviour to ideal.
- The known input data of the hydrogen sources and sinks and utilities such as inlet and outlet pressures and the hydrogen consumption on the reactors are constants.
- The compression processes are single-stage and adiabatic with fixed index γ and efficiency η .
- The suction temperature of the compressor is set to $\hat{T} = 298.15 [K]$.
- There are no phase changes in the network.

7.2 Mathematical Model

In this section the NLP formulation of the problem is explained. It is divided into several paragraphs that detail the hydrogen balances on several units, the connection constraints, molar mass flowrate constraints, compression constraints along with the cost calculation and objective function. The complete list of indices, sets, variables and parameters is in the Appendix.

Hydrogen Consumption in Reactors

With the data computed in Section 5 for the hydrogen consumption on the reactors of the different processes the following constraints can be made. The parameter $C_k^{H_2}$ corresponds to the hydrogen

consumption on the reactors of the refinery processes and are imposed constants in order to maintain the same amount of refined products. The variable $F_{i,k}^{H_2}$ corresponds to the amount of pure hydrogen that travels from a certain source $i \in SR$ to a hydrogen consuming process $k \in C$ which is a subset of the hydrogen sinks SK . The constraint presented in Equation 16 guarantees the hydrogen mass balance on the hydrogen consuming process $k \in C$. The purity at the outlet of these hydrogen consuming processes ϕ_k^{out} which is a variable of the problem is defined in Equation 17 in function of the variables and parameters mentioned above.

$$C_k^{H_2} = 0.817 [Mmol_{H_2}/h] \quad k = \text{HDT} \quad (11)$$

$$C_k^{H_2} = 2.987 [Mmol_{H_2}/h] \quad k = \text{HDS} \quad (12)$$

$$C_k^{H_2} = 0.901 [Mmol_{H_2}/h] \quad k = \text{ISOM} \quad (13)$$

$$C_k^{H_2} = 1.297 [Mmol_{H_2}/h] \quad k = \text{HCR} \quad (14)$$

$$\sum_{i=1}^I F_{i,k}^{H_2} - C_k^{H_2} \geq 0 \quad \forall i \in SR, \forall k \in C \quad (15)$$

$$\sum_{i=1}^I F_{i,k}^{H_2} = \sum_{j=1}^J F_{k,j}^{H_2} + C_k^{H_2} \quad \forall i \in SR, \forall k \in C, \forall j \in SK \quad (16)$$

$$\frac{\sum_{i=1}^I F_{i,k}^{H_2} - C_k^{H_2}}{\sum_{i=1}^I F_{i,k} - C_k^{H_2}} = \phi_k^{out} \quad \forall i \in SR, \forall k \in C \quad (17)$$

Set of Flow rate constraints

In this paragraph the constraints applied to the mass flow rates of particular units are presented. The constraint presented on Equation 21 imposes the total molar mass flowrate of traveling from the catalytic ceforming unit (CRU) to all the other sinks $j \in SK$. This value is given by the current Osmose data presented on Section 5. The constraint presented on Equation 22 imposes that a certain amount of hydrogen ($r_{m,u}$) produced in the steam methane reforming units (SMR1 and SMR2) needs to travel to the purifier if one of these hydrogen production units is used or not with the parameter y_m .

$$F_{i,j} \geq F_{i,j}^{H_2} \quad \forall i \in SR, j \in SK \quad (18)$$

$$F_{i,j}^{H_2} = F_{i,j} \cdot \phi_i^{out} \quad \forall i \in SR \setminus \{\text{PSA}\}, \forall j \in SK \setminus \{\text{FUEL}\} \quad (19)$$

$$F_{i,j}^{H_2} \geq 0 \quad i = \text{PSA}, j = \text{FUEL} \quad (20)$$

$$\sum_{j=1}^J F_{u,j} = 2.2 [Mmol/h] \quad u = \text{CRU}, \forall j \in SK \quad (21)$$

$$F_{m,u} \geq y_m \cdot r_{m,u} \cdot \sum_{j=1}^J F_{m,j} \quad m = \text{SMR1}, u = \text{PSA}, \forall j \in SK \quad (22)$$

$$F_{i,j} = 0 \quad i = \text{SMR1}, \forall j \in SK \quad (23)$$

$$F_{i,j} = 0 \quad i = \text{PEM}, \forall j \in SK \quad (24)$$

Constraints on Purification Unit (PSA)

This paragraph is dedicated to the purification unit (PSA). The first two constraints presented on Equations 25 and 26 are the hydrogen molar mass flow rate balance and the molar mass flow rate balance on the purification unit respectively. The last constraint presented on Equation 27 imposes that the 17% of hydrogen (recovery rate of PSA system is 83% as mentioned in [9]) that it is not recovered on the purification unit will go directly to the fuel gas sink unit.

$$\sum_{i=1}^I F_{i,u}^{H_2} = \sum_{j=1}^J F_{u,j}^{H_2} \quad \forall i \in SR, u = \text{PSA}, \forall j \in SK \quad (25)$$

$$\sum_{i=1}^I F_{i,u} = \sum_{j=1}^J F_{u,j} \quad \forall i \in SR, u = \text{PSA}, \forall j \in SK \quad (26)$$

$$0.17 \cdot \sum_{i=1}^I F_{i,u}^{H_2} = F_{u,j}^{H_2} \quad \forall i \in SR, u = \text{PSA}, j = \text{FUEL} \quad (27)$$

Purity constraints

In this paragraph the constraints applied on the hydrogen purities of several utilities and hydrogen consumption units are explicitly detailed. The first four constraints from Equations 28 to 31 were computed according to the current Osmose scenario and were presented in Section 5. The constraint on Equation 32 imposes that the purities at the outlet of each consuming unit must be greater than the minimum purity established in order for a connection to exist. The last four constraints presented on Equations 33 to 37 are the hydrogen purities of the hydrogen production plants, the catalytic reforming unit (CRU) and the purification unit (PSA) found in literature.

$$\Phi_k^{out,min} = 0.8483 \quad k = \text{HDT} \quad (28)$$

$$\Phi_k^{out,min} = 0.86805 \quad k = \text{HDS} \quad (29)$$

$$\Phi_k^{out,min} = 0.86666 \quad k = \text{ISOM} \quad (30)$$

$$\Phi_k^{out,min} = 0.7692 \quad k = \text{HCR} \quad (31)$$

$$\Phi_k^{out} \geq \Phi_k^{out,min} \quad \forall k \in C \quad (32)$$

$$\Phi_m^{out} = 0.75 \quad m = \text{SMR1} \quad (33)$$

$$\Phi_m^{out} = 0.75 \quad m = \text{SMR2} \quad (34)$$

$$\Phi_m^{out} = 0.999 \quad m = \text{PEM} \quad (35)$$

$$\Phi_i^{out} = 0.999 \quad m = \text{PSA} \quad (36)$$

$$\Phi_i^{out} = 0.75 \quad i = \text{CRU} \quad (37)$$

Compressor equations

In this paragraph the compressor related constraints and variables are detailed. The constraints from Equation 38 to 52 impose constant pressures for both inlet and outlet of the all units of the problem. Several of these pressures were computed according to the current Osmose scenario and are presented in Section 5 and others were taken from literature. The parameter $z_{i,j}$ presented in Equation 53 verifies if there is the need of a compressor for the connection from a certain source $i \in SR$ to a certain sink $j \in SK$. The power of the different compressors $pw_{i,j}$ is defined in Equation 54 with $F_{i,j}$ the molar mass flowrate that travels from a source $i \in SR$ to a sink $j \in SK$, η the compressor's efficiency, γ the adiabatic index, \hat{R} and \hat{T} the gas constant and the suction temperature of the compressor respectively. The constraints on Equations 55 and 56 impose minimum and maximum compression ratios as it is done mentioned [7].

$$P_j^{in} = 21.641 [bar] \quad j = \text{HDT} \quad (38)$$

$$P_j^{in} = 136.283 [bar] \quad j = \text{HDS} \quad (39)$$

$$P_j^{in} = 25.893 [bar] \quad j = \text{ISOM} \quad (40)$$

$$P_j^{in} = 137.895 [bar] \quad j = \text{HCR} \quad (41)$$

$$P_j^{in} = 18.961 [bar] \quad j = \text{PSA} \quad (42)$$

$$P_j^{in} = 17.926 [bar] \quad j = \text{FUEL} \quad (43)$$

$$P_i^{out} = 29 [bar] \quad j = \text{SMR1} \quad (44)$$

$$P_i^{out} = 12.755 [bar] \quad j = \text{CRU} \quad (45)$$

$$P_i^{out} = 11.032 [bar] \quad j = \text{HDT} \quad (46)$$

$$P_i^{out} = 119 [bar] \quad j = \text{HDS} \quad (47)$$

$$P_i^{out} = 12.731 [bar] \quad j = \text{ISOM} \quad (48)$$

$$P_i^{out} = 122.038 [bar] \quad j = \text{HCR} \quad (49)$$

$$P_i^{out} = 18.961 [bar] \quad j = \text{PSA} \quad (50)$$

$$P_i^{out} = 29 [bar] \quad j = \text{SMR2} \quad (51)$$

$$P_i^{out} = 29 [bar] \quad j = \text{PEM} \quad (52)$$

$$\text{If } P_j^{in} \geq P_i^{out} \longrightarrow z_{i,j} = 1, \quad \text{else } 0, \quad \forall i \in SR, j \in SK \quad (53)$$

$$pw_{i,j} = z_{i,j} \cdot \frac{F_{i,j} \cdot \hat{R} \cdot \hat{T}}{\eta} \cdot \frac{\gamma}{\gamma - 1} \left[\left(\frac{P_j^{in}}{P_i^{out}} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right] \quad \forall i \in SR, j \in SK \quad (54)$$

$$P_j^{in} \geq \text{Ratio}^{\min} \cdot z_{i,j} \cdot P_i^{out} \quad \forall i \in SR, j \in SK \quad (55)$$

$$P_j^{in} \leq \text{Ratio}^{\max} \cdot z_{i,j} \cdot P_i^{out} \quad \forall i \in SR, j \in SK \quad (56)$$

Objective Functions

Three different objective functions were considered. The first one being the minimum hydrogen consumption of the system (presented in Equation 57) in order to validate the mathematical model if the value found for the minimum hydrogen requirement is equal to the one found with Pinch Analysis presented in Section 6.

$$\begin{aligned} \text{Min Fresh hydrogen} = y_{SMR1} \cdot \sum_{i=SMR1, j \in SK} F_{i,j}^{H_2} + y_{SMR2} \cdot \sum_{i=SMR2, j \in SK} F_{i,j}^{H_2} \\ + y_{PEM} \cdot \sum_{i=PEM, j \in SK} F_{i,j}^{H_2} \end{aligned} \quad (57)$$

The second objective function considered is the minimum total annualized cost of the system and it is presented in Equation 58.

$$\begin{aligned} \text{Min Total Annualized Cost} = \text{Cost}^{NG} + \text{OPEX}^{SMR} + \text{Cost}^{elec} + \text{CAPEX}^{PSA} + \\ \text{CAPEX}^{Compressor} + \text{CAPEX}^{SMR} + \text{CAPEX}^{PEM} - \text{Profit}^{Fuel} \end{aligned} \quad (58)$$

The operational and investment cost of the different utilities and resources are presented in the equations below. There are several cost terms that are considered. The units of the objective function for the total annualized cost are $[CHF/year]$

Cost^{NG} is the cost of natural gas when the hydrogen is produced in steam methane reforming plants (SMR1 and SMR2) considered in this project and it's formula is presented in Equation 59.

$$\text{Cost}^{NG} = \sum_{i=SMR1, j \in SK} F_{i,j}^{H_2} \cdot c_{SMR1}^{NG} \cdot \text{top} \cdot y_{SMR1} + \sum_{i=SMR2, j \in SK} F_{i,j}^{H_2} \cdot c_{SMR2}^{NG} \cdot \text{top} \cdot y_{SMR2} \quad (59)$$

OPEX^{SMR} is the operational cost related to the Steam Methane Reforming unit plants and it is proportional to the hydrogen molar mass flowrate $F_{i,j}^{H_2}$ that is consumed and it's formula is presented in Equation 60.

$$\begin{aligned} \text{OPEX}^{SMR} = \sum_{i=SMR1, j \in SK} F_{i,j}^{H_2} \cdot \text{OPEX}^{SMR1} \cdot \text{top} \cdot y_{SMR1} \\ + \sum_{i=SMR2, j \in SK} F_{i,j}^{H_2} \cdot \text{OPEX}^{SMR2} \cdot \text{top} \cdot y_{SMR2} \end{aligned} \quad (60)$$

Cost^{elec} corresponds to the electricity cost associated to the power of the compressors and also if the electrolyzer is used to produce hydrogen. y_e is the parameter associated to the use of a certain electricity supplier. The formula to compute this cost is presented in Equation 61.

$$\text{Cost}^{elec} = \sum_{i \in SR, j \in SK} pw_{i,j} \cdot c_e^{elec} \cdot \text{top} + \sum_{i=PEM, j \in SK} F_{i,j}^{H_2} \cdot \text{coef}_{PEM} \cdot \text{top} \cdot y_{PEM} \quad (61)$$

For the off-gases that are not used as a source, they can travel to the FUEL unit and be converted into heat. The equivalent profit of this fuel can be computed as in Equation 62. HV_{H_2} and HV_{CH_4}

are respectively the standard heat of burning hydrogen and methane and c^{Fuel} is the cost coefficient of fuel value.

$$\text{Profit}^{Fuel} = \text{top} \cdot c^{Fuel} \sum_{i \in SR, j = \text{FUEL}} (F_{i,j}^{H_2} \cdot \text{HV}_{H_2} + (F_{i,j} - F_{i,j}^{H_2}) \cdot \text{HV}_{CH_4}) \quad (62)$$

The investment cost of the purification unit (PSA) can be computed as shown in Equation 63. According to [7], the investment cost of the purifier is proportional to the sum of molar mass flowrates at the inlet which is $F_{i,j=\text{PSA}}$. af corresponds to the annualization factor and can be computed as in Equation 64 where i denotes the interest rate and n the life in years of the equipment. The coefficients α^{PSA} and β^{PSA} denote the cost coefficients of the purifier.

$$\text{CAPEX}^{PSA} = af \cdot \sum_{i \in SR, j = \text{PSA}} (\alpha^{PSA} \cdot y_j + \beta^{PSA} \cdot F_{i,j}) \quad (63)$$

$$af = \frac{i(1+i)^n}{(1+i)^n - 1} \quad (64)$$

The cost of the compressors corresponds to $\text{CAPEX}^{Compressor}$ and can be computed using Equation 65 according to [7]. The coefficients a , b and c are the cost coefficients of the compressors.

$$\text{CAPEX}^{Compressor} = af \cdot \sum_{i \in SR, j \in SK} (a \cdot z_{i,j} + b \cdot pw_{i,j}^c) \quad (65)$$

CAPEX^{SMR} is the investment cost related to the Steam Methane Reforming unit plants and it is proportional to the hydrogen molar mass flowrate $F_{i,j}^{H_2}$ that is consumed and it's formula is presented in Equation 66.

$$\begin{aligned} \text{CAPEX}^{SMR} = & \sum_{i=\text{SMR1}, j \in SK} F_{i,j}^{H_2} \cdot \text{CAPEX}^{SMR1} \cdot \text{top} \cdot y_{SMR1} \\ & + \sum_{i=\text{SMR2}, j \in SK} F_{i,j}^{H_2} \cdot \text{CAPEX}^{SMR2} \cdot \text{top} \cdot y_{SMR2} \end{aligned} \quad (66)$$

CAPEX^{PEM} corresponds to the investment cost of the electrolyzer. It is also proportional to the hydrogen molar mass flowrate that it produces and it is decomposed as follows in Equations 67 to 70. w_{PEM} and x_{PEM} are cost coefficients and y_{PEM} is the parameter that defines if the electrolyzer is used or not.

$$C_{system} = w_{PEM} + x_{PEM} \cdot \sum_{i=\text{PEM}, j \in SK} F_{i,j}^{H_2} \quad (67)$$

$$C_{markup} = 0.5 \cdot C_{system} \quad (68)$$

$$C_{installation} = 0.5 \cdot (C_{markup} + C_{system}) \quad (69)$$

$$\text{CAPEX}^{PEM} = af \cdot 1.5 \cdot 1.5 \cdot C_{system} = af \cdot 1.5 \cdot 1.5 \cdot (w_{PEM} + x_{PEM} \cdot \sum_{i=\text{PEM}, j \in SK} F_{i,j}^{H_2}) \cdot y_{PEM} \quad (70)$$

The third objective function considered is the minimum CO_2 emissions of the system and it is presented in Equation 71.

$$\text{Min } \mathbf{CO2}_{emissions} = \text{CO2}_{em}^{SMR} + \text{CO2}_{em}^{Elec} \quad (71)$$

The $\text{CO2}_{\text{em}}^{\text{SMR}}$ corresponds to the CO_2 emissions of the Steam Methane Reforming plant for the production of hydrogen and its formula is presented in Equation 73. The parameters $c_{\text{SMR1}}^{\text{CO2}}$ and $c_{\text{SMR2}}^{\text{CO2}}$ correspond to the carbon dioxide emissions associated to the production of hydrogen.

$$\text{CO2}_{\text{em}}^{\text{SMR}} = \sum_{i=\text{SMR1}, j \in \text{SK}} F_{i,j}^{\text{H}_2} \cdot c_{\text{SMR1}}^{\text{CO2}} \cdot y_{\text{SMR1}} + \sum_{i=\text{SMR2}, j \in \text{SK}} F_{i,j}^{\text{H}_2} \cdot c_{\text{SMR2}}^{\text{CO2}} \cdot y_{\text{SMR2}} \quad (72)$$

The $\text{CO2}_{\text{em}}^{\text{Elec}}$ corresponds to the CO_2 emissions of the different electricity suppliers and its formula is presented in Equation 73. The parameter c_e^{CO2} corresponds to the carbon dioxide emissions associated to the electricity supplier.

$$\text{CO2}_{\text{em}}^{\text{Elec}} = \sum_{i \in \text{SR}, j \in \text{SK}} pw_{i,j} \cdot c_e^{\text{CO2}} + \sum_{i=\text{PEM}, j \in \text{SK}} F_{i,j}^{\text{H}_2} \cdot \text{coef}_{\text{PEM}} \cdot c_e^{\text{CO2}} \cdot y_{\text{PEM}} \quad (73)$$

8 Scenarios

Several scenarios were implemented on the model in order to have a better understanding of the hydrogen network and also to find the best solutions. The most usual hydrogen production plant used in oil refineries is the Steam Methane Reforming [9] and therefore two types of these plants were considered. The third hydrogen production plant chosen was an electrolyzer. Since the electrolyzer uses electricity to produce hydrogen, this method if used with electricity from renewable sources might be a better option both from an economic and environmental point of view. Three hydrogen production plants were chosen to be compared and implemented on the model and are as follows:























































- Steam Methane Reforming without Carbon Capture (SMR1).
- Steam Methane Reforming with Carbon Capture (SMR2).
- Polymer electrolyte membrane electrolysis (PEM)

Three electricity suppliers were chosen to be compared and implemented on the model and are as follows:

- Electricity from the grid.
- Electricity from Onshore Wind farm.
- Electricity from Solar Photovoltaic (PV).

The studied scenarios are summarized in Table 12.

Table 12: Testing scenarios.

	Scenario 1	Scenario 2	Scenario 3	Scenario 4	Scenario 5	Scenario 6	Scenario 7	Scenario 8	Scenario 9
SMR without CC (SMR1)									
SMR with CC (SMR2)									
PEM Electrolyzer									
Electricity Grid									
Onshore Wind Farm									
Solar PV									

9 Results

9.1 First Objective function: Minimum Hydrogen Requirement

In order to verify if the mathematical model presented in Section 7.2 is coherent with the pinch analysis realized in Section 6 the mathematical model was tested with the same conditions the pinch analysis was realized. The resulting hydrogen network flow is presented in Figure 14 (the compressors are not included in the figure). The minimum hydrogen requirement given by the model is $4.27 [Mmol H_2/h]$ which is the same result found with the pinch analysis in Section 6. This validates the base layer of the mathematical model.

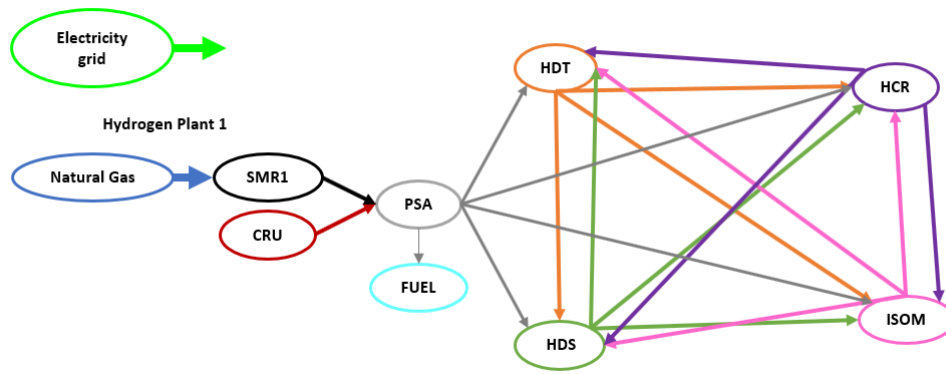


Figure 14: Network representation for minimum hydrogen requirement.

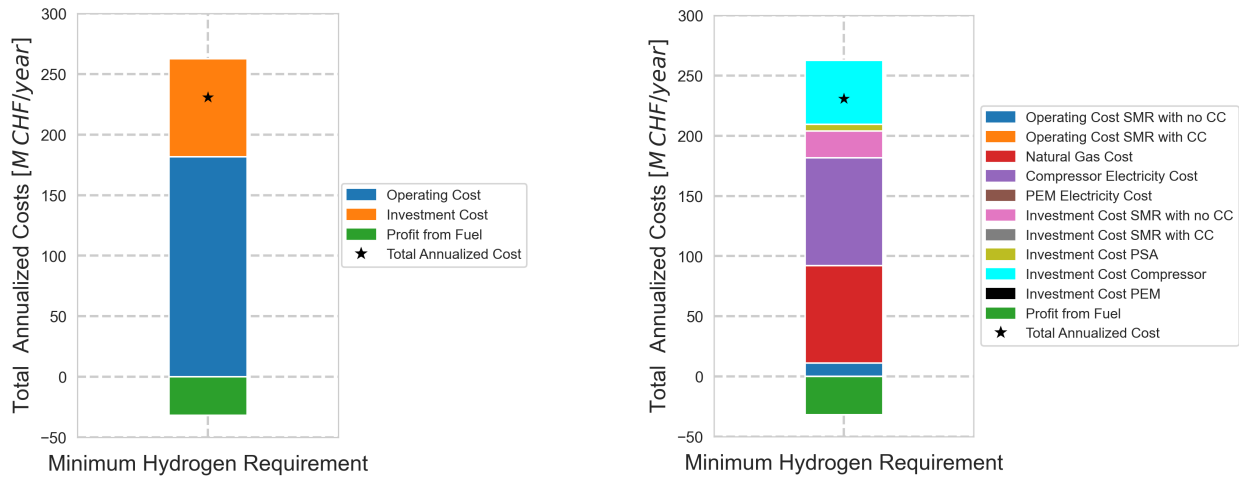


Figure 15: Total Annualized Costs for the MHR Optimization.

One can see on Figure 15 the Total Annualized Costs for the scenario where the objective function minimizes the hydrogen consumption with the utilities of Scenario 1. The Total Annualized Cost is $231 [M CHF/year]$, where the highest contributions are from the electricity cost due to the compressors ($90 [M CHF/year]$), the natural gas cost ($81 [M CHF/year]$) and the compressor's investment cost ($53 [M CHF/year]$). The high cost from the compressors is expected since the

model minimizes the hydrogen consumption and therefore connections between the processes with high power compressors might be preferred even though they are more expensive than other possible connections. The detailed annualized costs presented on Figure 15 are presented in Table 13.

Table 13: Results for minimum hydrogen requirement.

Variable	Quantity
Fresh Hydrogen Consumption [$Mmol_{H_2}/h$]	4.27
Operating Cost SMR1 [$M CHF/year$]	11.23
Operating Cost SMR2 [$M CHF/year$]	-
Operating Cost Natural Gas [$M CHF/year$]	80.68
Compressors Electricity Cost [$M CHF/year$]	89.63
Number of Compressors	18
PEM Electricity Cost [$M CHF/year$]	-
Investment Cost SMR1 [$M CHF/year$]	22.48
Investment Cost SMR2 [$M CHF/year$]	-
Investment Cost Purifier PSA [$M CHF/year$]	5.45
Investment Cost Compressors [$M CHF/year$]	53.18
Investment Cost PEM [$M CHF/year$]	-
Profit from Fuel [$M CHF/year$]	31.94
Total Annualized Operating Cost [$M CHF/year$]	181.54
Total Annualized Investment Cost [$M CHF/year$]	81.116
Annualized CO ₂ Emissions [$tonsCO_{2eq}/year$]	790'278
Environmental Tax Annualized Cost [$M CHF/year$]	75.87
Total Annualized Cost without CO ₂ Emissions Cost [$M CHF/year$]	230.71
Total Annualized Cost with CO ₂ Emissions Cost [$M CHF/year$]	306.58

9.2 Second Objective function: Minimum Total Annualized Cost

In this section, the objective function is the Total Annualized Cost which does not implies that the hydrogen requirements are the same as the ones found on the previous section. The Superstructure of Scenario 1 which is the SMR with no Carbon and Capture and electricity supplied from the electricity grid is shown in Figure 16 (the compressors are not included in the figure). For each scenario there is a different network flow. For the one presented here in Figure 16 there are also recycling flows that re-enter the same process but are not represented in the Figure due to its complexity.

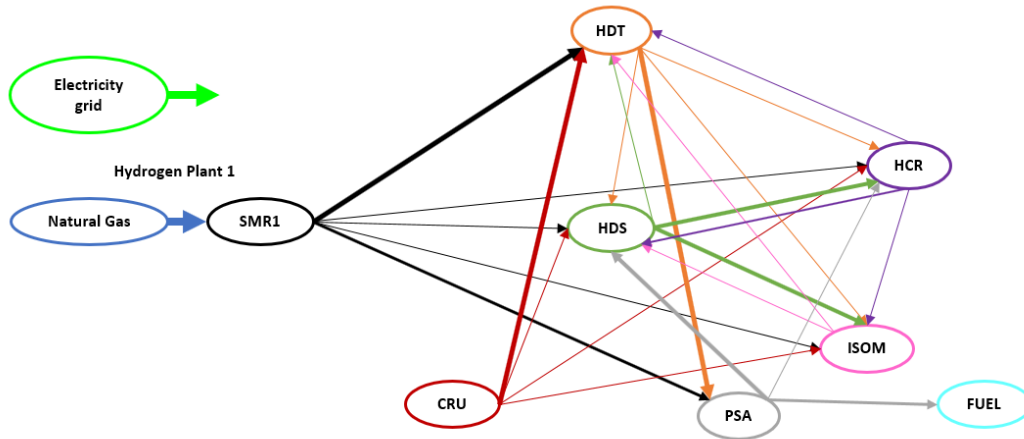


Figure 16: Network representation of Scenario 1.

It can be seen in Table 14 that the hydrogen consumption for all the scenarios is higher than the value found for the minimum hydrogen requirement presented in Section 9.1. This is due to the fact that in order to have the minimum hydrogen requirement found on the previous section a lot of compressor power and high power compressors need to be used and that can be quite expensive. One can see on Figure 17 the Total Annualized Costs for the all the scenarios presented in section 8 and the scenario with the minimum hydrogen requirement presented in the previous section. The scenario with the lowest Total Annualized Cost is scenario 2 with a Total annualized Cost of 142 $[M CHF/year]$. It is followed by scenario 3 with a Total annualized Cost of 146 $[M CHF/year]$ and the scenario with the highest Total Annualized Cost is scenario 7 costing 903 $[M CHF/year]$.

Table 14: Results Total Annualized Cost optimization for all scenarios.

Variable	MHR	Scenario 1	Scenario 2	Scenario 3	Scenario 4	Scenario 5	Scenario 6	Scenario 7	Scenario 8	Scenario 9
Fresh Hydrogen Consumption $[M mol H_2/h]$	4.27	5.34	5.34	5.34	5.34	5.34	5.34	5.31	5.31	5.31
Operating Cost SMR1 $[M CHF/year]$	11.23	14.06	14.06	14.06	-	-	-	-	-	-
Operating Cost SMR2 $[M CHF/year]$	-	-	-	-	30.63	30.63	30.63	-	-	-
Operating Cost Natural Gas $[M CHF/year]$	80.68	100.98	100.98	100.98	110.92	110.92	110.92	-	-	-
Compressors Electricity Cost $[M CHF/year]$	89.63	38.38	13.32	16.78	33.03	11.47	14.44	49.78	16.37	21.76
Number of Compressors	18	20	20	20	19	19	19	14	14	14
PEM Electricity Cost $[M CHF/year]$	-	-	-	-	-	-	-	838.54	291.06	366.52
Investment Cost SMR1 $[M CHF/year]$	22.48	28.14	28.14	28.14	-	-	-	-	-	-
Investment Cost SMR2 $[M CHF/year]$	-	-	-	-	50.49	50.49	50.49	-	-	-
Investment Cost Purifier PSA $[M CHF/year]$	5.45	5.95	5.95	5.95	5.95	5.95	5.95	58.34	58.34	58.33
Investment Cost Compressors $[M CHF/year]$	53.18	22.98	22.98	22.98	19.8	19.8	19.8	29.6	28.06	29.6
Investment Cost PEM $[M CHF/year]$	-	-	-	-	-	-	-	22.38	22.38	22.38
Profit from Fuel $[M CHF/year]$	31.94	43.32	43.32	43.32	41.68	43.32	43.32	43.03	43.03	43.03
Total Annualized Operating Cost $[M CHF/year]$	181.54	153.42	128.36	131.82	174.57	153.01	155.98	888.33	307.44	388.28
Total Annualized Investment Cost $[M CHF/year]$	81.116	57.06	57.06	57.06	76.24	76.24	76.24	57.82	56.27	57.82
Annualized CO ₂ Emissions $[tons CO_2-eq/year]$	790'278	905'657	863'252	863'766	416'756	380'263	380'705	1'005'205	23'722	35'6687
Environmental Tax Annualized Cost $[M CHF/year]$	75.87	86.94	82.87	82.92	40.01	36.51	36.55	96.5	2.28	3.43
Total Annualized Cost without CO ₂ Emissions Cost $[M CHF/year]$	230.71	167.17	142.11	145.56	207.5	185.93	188.9	903.11	320.68	403.07
Total Annualized Cost with CO ₂ Emissions Cost $[M CHF/year]$	306.58	254.11	224.98	228.49	247.51	222.44	225.45	999.61	322.95	406.49

The detailed distribution of each the Total Annualized Cost is presented in Figure 18 for all scenarios and without scenario 7 in Figure 19. One can see that for scenarios 1 to 6 the majority of the costs are due to the natural gas cost (50% to 70% depending on the scenario) and then the investment costs of the Steam Methane Reforming plants (16% to 27% depending on the scenario). The high cost of the electricity used for the electrolyzer in scenarios 7,8 and 9 is expected since the amount of hydrogen needed is quite high. scenarios 8 and 9 are more expensive than all the others but are quite far away from the others (scenario 8 is 113 $[M CHF/year]$ from scenario 2). The detailed annualized costs presented on Figures 17, 18 and 19 are presented in Table 14.

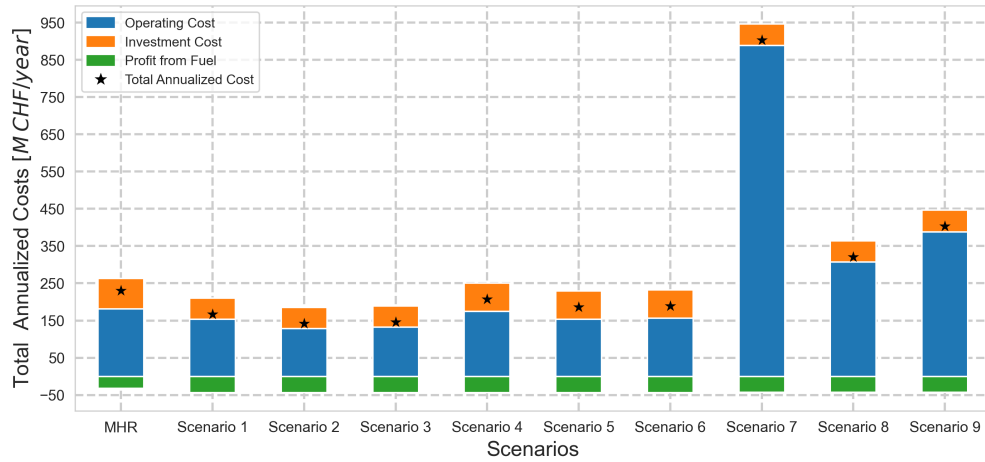


Figure 17: Total Annualized Costs Breakdown.

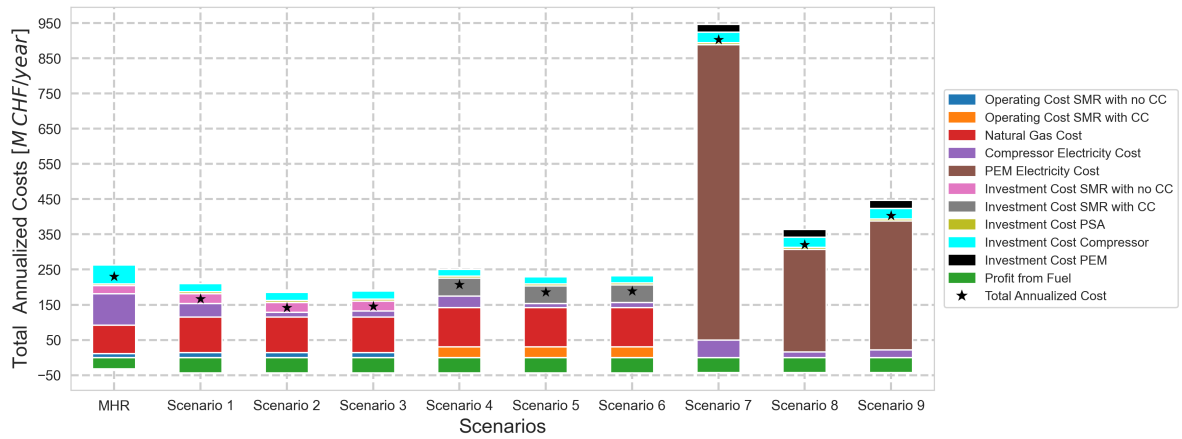


Figure 18: Total Annualized Costs Breakdown in detail.

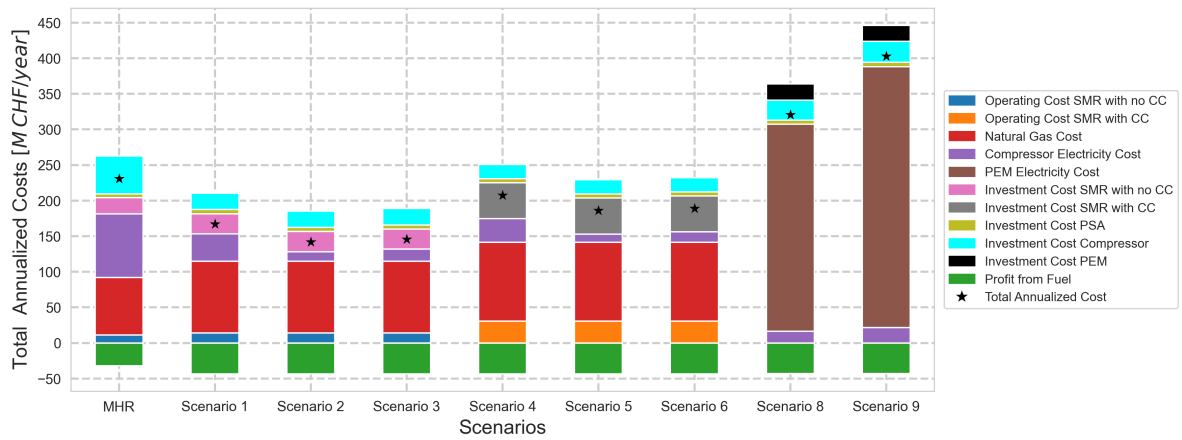


Figure 19: Total Annualized Costs Breakdown in detail without Scenario 7.

9.2.1 Implementation of CO_2 emissions

The CO_2 emissions associated with the utilities and electricity suppliers for all the scenarios were computed. One can see in Figures 20, 21 and 22 the impact of the CO_2 emissions tax in the Total Annualized Costs knowing that the carbon levy for a ton of CO_2 emitted in Switzerland was 96 CHF in 2018. In Figure 20, it can be seen that the Total Annualized Costs for scenarios 4 to 6 become much more competitive with scenarios 1,2 and 3. This was expected because scenarios 1 to 3 use a Steam Methane Reforming plant without Carbon Capture to produce hydrogen. With the CO_2 emissions considered the best scenario is scenario 5 costing 222 [M CHF/year] instead of scenario 2 that now costs 225 [M CHF/year].

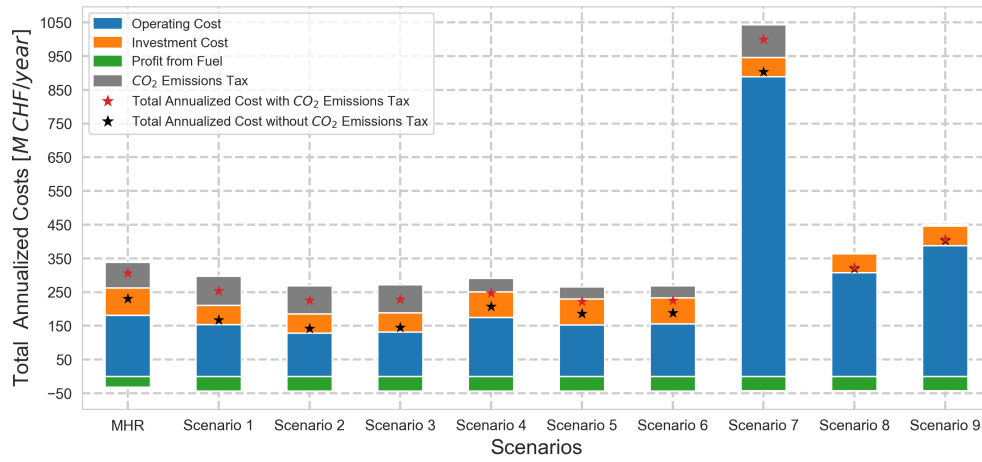


Figure 20: Total Annualized Costs Breakdown with CO_2 emissions tax.

The implementation of the CO_2 emissions tax brings scenarios 8 and 9 which have small CO_2 emissions compared to the others closer to the others. Scenario 8 has a Total Annualized Cost of 323 [M CHF/year] which is now 98 [M CHF/year] more expensive than scenario 2. The results containing the CO_2 emissions are presented in Table 14.

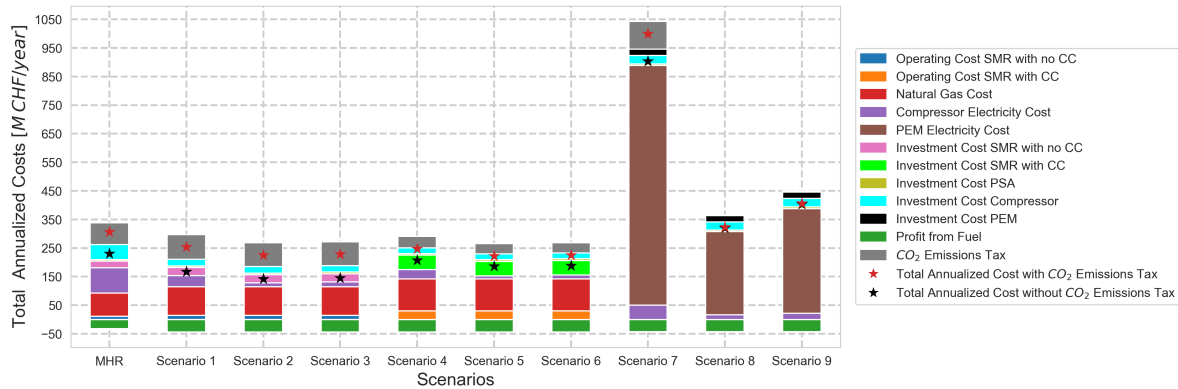


Figure 21: Total Annualized Costs Breakdown in detail with CO_2 emissions tax.

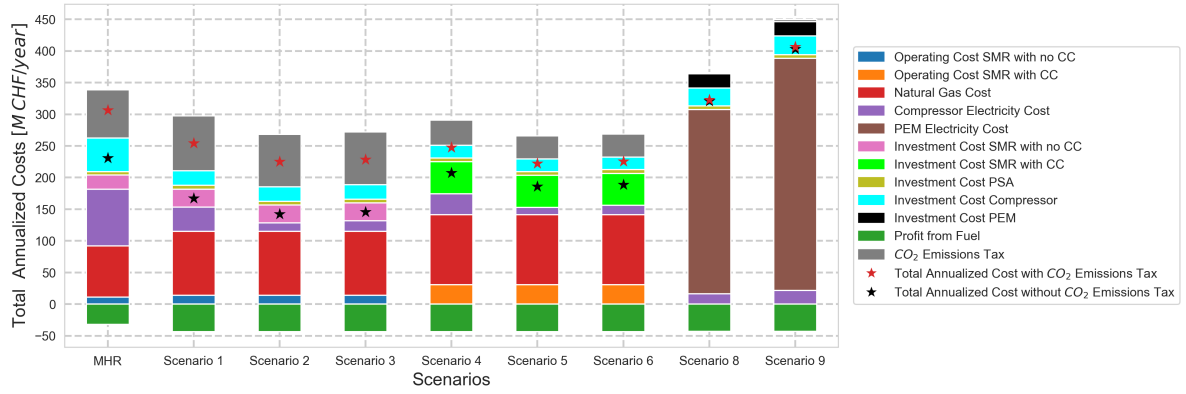


Figure 22: Total Annualized Costs Breakdown in detail without Scenario 7 with CO_2 emissions tax.

In Figure 22, the Total Annualized Cost of the scenario with the Minimum Hydrogen Requirement which is 307 [M CHF/year] is only 16 [M CHF/year] of the Total Annualized Cost of Scenario 8 which has much lower CO_2 emissions, precisely 767'000 [ton CO_{2eq}] less.

10 Conclusion and Improvements

In this project a superstructure of refinery hydrogen network with the implementation of compressors is developed. A non-linear mathematical programming model with the minimum hydrogen consumption and minimum total annualized cost as the optimization objectives is formulated. A reference case with the data known from the current scenario was created and therefore multiple scenarios considering different hydrogen production technologies and different electricity suppliers were analyzed and compared.

The results show that the scenarios using the electricity from renewable sources are very promising and have better results both economically and environmentally than the scenarios that use the electricity from the grid. The best scenario when minimizing the Total Annualized Cost is the scenario 2 with a Steam Methane Reforming plant for hydrogen production and electricity provided from an onshore wind farm costing 142 [$M CHF/year$] if CO_2 emissions are not considered. It was shown that the minimum hydrogen requirement might not be the target if one wants to minimize the Total Annualized Cost. With the CO_2 emissions implemented, the results show that the scenario with the lowest Total Annualized Cost is the scenario 5 with Carbon Capture on the Steam Methane Reforming plant and electricity supplied from a wind farm costing 222 [$M CHF/year$] with 380'000 [$ton CO_{2eq}/year$]. The scenario with the lowest CO_2 emissions is scenarios 8 using the PEM electrolyzer and the electricity supplied from a wind farm with 24'000 [$ton CO_{2eq}/year$] but costing 323 [$M CHF/year$] with the difference from scenario 2 being 44% of its cost which is significant. The Total Annualized Cost using the PEM is high thus impeding its application on the refinery today. However, in the future with the low cost electricity from renewable sources, other types of electrolyzers more efficient and with more stricter environmental policies there will be great opportunities for this type of technology.

Some improvements that can be made are presented below:

- Implement other types of electrolyzers that might be more efficient.
- Implement on the model in more detail other sources of CO_2 emissions.
- Realize a sensitivity analysis of some parameters such as natural gas and electricity costs.
- Realize Multi optimisation results – Pareto Curves (method explained in Section A.3).
- Heat Integration of different processes.

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A Appendix

A.1 Catalytic Reforming Process detailed description

The first main family of reactions that takes place in the the catalytic reforming process is the dehydrogenation of naphtenes to aromatics. The main characteristics of these reactions are:

- Fast reaction
- Preference to high temperature and low pressure
- Increases of the octane number
- Highly endothermic reaction
- Hydrogen production
- Volume reduction

Since they are very rapid and highly endothermic reactions, they occur in the first reactor, with a large temperature drop. The Total Average Free Gibbs Energy Change for these reactions is represented on Figure 23.

				ΔG (Btu/lbmole)	Proportion Variable
Dehydrogenation of alkylcyclohexane to aromatic					
	Methylcyclohexane \rightarrow Methylbenzene + 3H ₂				
Gibbs Free Energy (Btu/lbmole)	11,736	52,704		40,968	20%
	Methylcyclopentane \rightarrow Cyclohexane \rightarrow Benzene + 3H ₂				
Gibbs Free Energy (Btu/lbmole)	15,390	13,662	55,780	40,390	20%

Figure 23: Dehydrogenation of naphthenes to aromatics [13].

The second family of reactions is the dehydrocyclization of paraffins to aromatics. The main characteristics of these reactions are:

- Slow Reaction and needs severe conditions
- Enhanced at high temperatures and low pressures
- Increases the Octane number
- Highly endothermic
- Produces hydrogen
- Reduces volume

Since they are slow reactions with low temperatures, they occur in the third reactor. The Total Average Free Gibbs Energy Change for these reactions is represented in Figure 24.

Dehydrocyclization of paraffins to aromatics				
	n-Heptane \rightarrow Methylbenzene + 4H ₂			
Gibbs Free Energy (Btu/lbmole)	3,762	52,704	56,466	17%

Figure 24: Dehydrocyclization of paraffins to aromatics [13].

The third family of reactions is the isomerization of paraffins to isoparaffins. The main characteristics of these reactions are:

- Moderate Reaction
- Does not consume hydrogen
- the Octane number
- Athermic
- Contributes to increase
- Increases volume

Since these reactions are quicker than the previous ones, they occur in the second reactor. The Total Average Free Gibbs Energy Change for these reactions is represented in Figure 25.

Isomerization of paraffins to isoparaffins				
n-Hexane → Isohexane				
Gibbs Free Energy (Btu/lbmole)	90	-1,728	-1,818	17%
Methylcyclopentane → Cyclohexane				
Gibbs Free Energy (Btu/lbmole)	15,390	13,662	-1,728	17%

Figure 25: Isomerization of paraffins to isoparaffins [13].

The fourth family of reactions is the hydrocracking of paraffins. The main characteristics of these reactions are:

- Slow reaction
- Enhanced at high temperatures and pressures
- Increase the Octane number
- Exothermic
- Consumes hydrogen
- Decreases volume

Since these reactions are the slowest and give low temperatures they occur in the third reactor with the dehydrocyclization of paraffins to aromatics. The Total Average Free Gibbs Energy Change for these reactions is represented in Figure 26.

Hydrocracking – saturation of olefins and cracking of paraffins					
n-Decane → Isohexane + n-Butane					
Gibbs Free Energy (Btu/lbmole)	14,814	-1,728	-28,272	-44,814	9%

Figure 26: Hydrocracking – saturation of olefins and cracking of paraffins [13].

A.2 Parameters used in AMPL model

The majority of the parameters presented in Table 15 are the same used in [7]. The electricity prices were taken from the International Renewable Energy Agency (IRENA) website and from Eurostat which has the European Statistics. The PEM electrolyzer cost parameters were given by Shengyue Lu which is currently doing her Master thesis on this subject. The parameters cost for the Steam Methane Reforming plants and natural gas were found in "The Future of Hydrogen" technology report published in 2019 from the International Energy agency (IEA).

Table 15: AMPL code Parameters

Symbol	Parameter	Value
$r_{m=SMR1,SMR2,u=PSA}$	Flowrate ratio from SMR1 or SMR2 to PSA	0.25
γ	Adiabatic index	1.4
η	Compression efficiency	0.75
\hat{T}	Suction temperature of compressor [K]	298.1
\hat{R}	Gas Constant [$J \cdot mol^{-1} \cdot K^{-1}$]	8.314
R_t	Hydrogen recovery ratio of purifier	0.83
$Ratio^{min}$	Low bound of the compression ratio given to compressors	1.1
$Ratio^{max}$	High bound of the compression ratio given to compressors	8
c_{SMR1}^{NG}	Natural Gas Cost for SMR1 [CHF/Mmol _{H₂}]	2365.824
c_{SMR2}^{NG}	Natural Gas Cost for SMR2 [CHF/Mmol _{H₂}]	2598.528
$OPEX^{SMR1}$	Operating Cost for SMR1 [CHF/Mmol _{H₂}]	329.28
$OPEX^{SMR2}$	Operating Cost for SMR2 [CHF/Mmol _{H₂}]	717.504
$CAPEX^{SMR1}$	Investment Cost for SMR1 [CHF/Mmol _{H₂}]	659.328
$CAPEX^{SMR2}$	Investment Cost for SMR2 [CHF/Mmol _{H₂}]	1182.9124
top	Time of operation [hours/year]	8000
c_{Grid}^{elec}	Average Electricity Cost from grid in Europe [CHF/MJ]	0.0414
c_{Wind}^{elec}	Electricity Cost from Onshore Wind farm [CHF/MJ]	0.0144
c_{PV}^{elec}	Average Electricity Cost from solar PV [CHF/MJ]	0.0181
$coef_{PEM}$	PEM electrolyzer hydrogen production coefficient [MJ/Mmol _{H₂}]	26049600
HV_{H_2}	Standard heat of hydrogen [MJ/Mmol _{H₂}]	285830
HV_{H_4}	Standard heat of Methane [MJ/Mmol _{H₂}]	890350
af	Annualized factor of capital expenses	0.1
i	Interest Rate	0.08
n	Lifetime [years]	20
α^{PSA}	Installation cost of purifier [CHF]	483648
β^{PSA}	Purchase cost of purifier [CHF/Mmol/h]	6695522.88
a	Installation cost of compressor [CHF]	161424.9744
b	Purchase cost of compressor [CHF/kW]	1922.54976
c	Exponent coefficient of compressor's capital cost	0.8
w_{PEM}	Installation cost of PEM [CHF]	26049600
x_{PEM}	Purchase cost of PEM [CHF/Mmol _{H₂}]	13488960
$c_{SMR1}^{CO_2}$	CO ₂ Emissions for SMR1 [kg CO _{2eq} /Mmol _{H₂}]	20200
$c_{SMR2}^{CO_2}$	CO ₂ Emissions for SMR2 (90%) [kg CO _{2eq} /Mmol _{H₂}]	8888
$c_{Grid}^{CO_2}$	CO ₂ Emissions for Electricity from Grid Switzerland [kg CO _{2eq} /Mmol _{H₂}]	0.04694
$c_{Wind}^{CO_2}$	CO ₂ Emissions for Electricity from Onshore Wind Farm [kg CO _{2eq} /Mmol _{H₂}]	0.0011
$c_{PV}^{CO_2}$	CO ₂ Emissions for Electricity from Solar PV [kg CO _{2eq} /Mmol _{H₂}]	0.00167
-	Conversion USD to CHF	0.96
-	Carbon levy in Switzerland [CHF/ton CO _{2e}]	96

A.3 Multi-objective Optimization

Section 9 allowed to analyse different scenarios with single objective optimization. In this section, a multi-objective optimization is made to combine different criteria in order to take a decision. The decision making is based on the trade-off between the two objective functions. The process to solve this optimization is to find a so called "Pareto Frontier" where none of the objectives functions can be improved in value without degrading the other objective values. An example of Pareto frontier can be shown below:

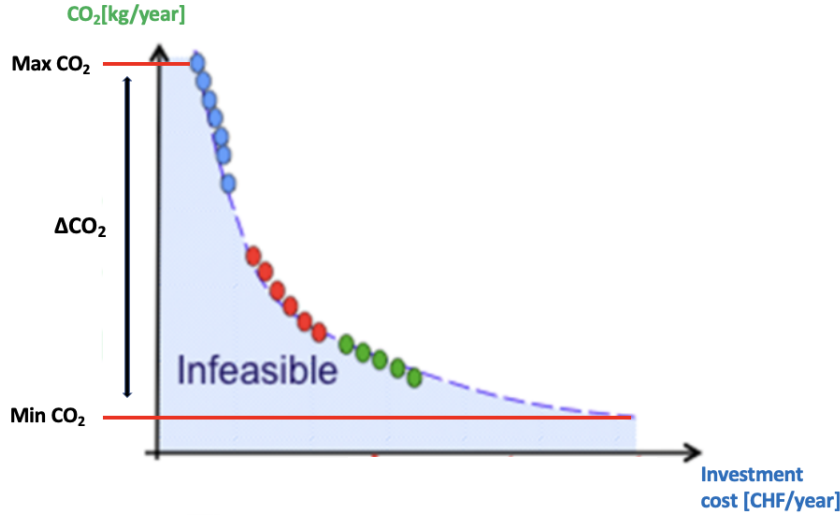


Figure 27: Pareto Front Model

In this analysis, the objective functions chosen for the multi-objective optimization are the Total Annualized Costs in Swiss Francs per year and the CO_2 emissions per year. The boundaries of the Pareto Frontier can be found by a single objective optimization as previously done in Section 9.2.1. The following points are found by computing a single objective minimization on the investment cost with an additional constraint for the CO_2 as:

$$\begin{aligned}
 &\text{minimize} && \text{Total Annualized Cost [M CHF/year]} \\
 &\text{subject to} && CO_2 \leq \min CO_2 + \frac{i}{N} \cdot \Delta CO_2 \\
 &&& N = \text{total number of points computed on the frontier} \\
 &&& i = \text{iteration}
 \end{aligned} \tag{74}$$