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Chair of Petroleum and Geothermal Energy Recovery

Master's Thesis

Economic and Technical Evaluation of Hydrogen Production from Sour Gas Petroleum Reservoirs

Volker Pavalec, BSc

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Economic and Technical Evaluation of Hydrogen Production from Sour Gas Petroleum Reservoirs

In Cooperation with PM Lucas

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Kurzfassung

Schwefelwasserstoffproduktion aus Erdöllagerstätten ist mit immensen Kosten für die erdölproduzierende Industrie verbunden um die potentiellen Risiken für Mensch und Umwelt dieser toxischen Substanz auszugleichen.

Heutzutage wird ein Großteil des Schwefelwasserstoffs zu elementarem Schwefel reduziert, um den regolatorischen Anforderungen zu entsprechen und jedoch nicht um Profitabilität zu erhöhen. Diese Arbeit untersucht die ökonomischen und technischen Möglichkeiten um aus eben diesem Schwefelwasserstoff einen zukunftssicheren und wertvollen Rohstoff, elementaren Wasserstoff, zu erzeugen.

Im Laufe dieser Arbeit wurde eine Literaturrecherche durchgeführt, um den aktuellen Status der Forschung abzufragen und um einen potentiellen Prozess zu finden. Daraufhin wurde ein Pyrolysis Prozess mit Hilfe einer prozesstechnischen Software modelliert, um den thermalen Zerfall von Schwefelwasserstoff zu simulieren. Dieses Modell wurde darauffolgend entsprechend mit experimentellen Daten verifiziert, auf Feld-Daten hochskaliert und optimiert. Diese Simulationsergebnisse bildeten den Grundstein für die weitere ökonomische Analyse, angelehnt an einen Prozesskosten-Ansatz, basierend auf 9 szenarien mit unterschiedlichen Kosten- & Verkaufsperspektiven.

Je nach Kostenszenario wurden die Produktionskosten auf 4.1 [\$/tH_2] bis 37.9 [\$/tH_2] geschätzt, mit den Energiekosten als größten Teil der Produktionskosten. Die ökonomische Analyse hat gezeigt, dass nur zwei von den aufgestellten 9 Szenarien ein positives ökonomisches Potential aufweisen können, im Bereich von 5.5 [\$/tH_2] zu – 34.7 [\$/tH_2], und somit dieses Unterfangen ein wirtschaftlich nicht Positives zu sein scheint.

Darüberhinaus wurde eine Risikoanalyse durchgeführt, da Wasserstoff ein potentiell risikobehafteter Rohstoff ist. Basieren auf den Daten der NASA und dem U.S. Dpt. Of Energy wurden Risiken identifiziert und gereiht. Die Analyse hat gezeigt, dass 80% der Unfälle auf Materialversagen, Konstruktionsfehler und Fehler in/beim Beachten von Arbeitsanweisungen zurückzuführen sind. Um diese Risiken zu mitigieren sind zweckgeeignete Konstruktion für Wasserstoffanwendungen, spezialisiertes Training von Personal und dem Stand der Technik entsprechenden Arbeitsanweisungen maßgebend.

Abstract

Hydrogen sulfide from petroleum reservoirs presents major difficulties for oil companies. This harmful and toxic substance to human life and the environment poses a major risk for oil and gas operations worldwide and causes substantial costs in order to render harmless.

Nowadays, most H_2S is converted to elemental sulfur to meet regulatory requirements – not to achieve economic profitability. This study investigates the economic and technical feasibility of converting this sour gas to hydrogen, a potential invaluable resource for the future. Today, most of the hydrogen is produced by reforming processes with a substantial amount of carbon dioxide generation.

During this work, a literature review was conducted in order to review current research progress and to choose a potential economic and technical feasible process. Afterwards, a direct-thermal decomposition process of hydrogen sulphide was modelled via the use of state-of-the-art process modelling software with subsequent validation of the model on experimental data from research, upscaling to field data and further process optimization. This process model then served as baseline for an economic analysis with the application of a process-costing approach, based on 9 business case scenarios, each with different sales & cost perspectives in mind.

Depending on the cost scenario, production costs were estimated ranging from 4.1 [$/tH$_2$] to 37.9 [$/tH$_2$], with utility cost being the main factor during cost distribution. Economic analysis has shown that in only two out of all 9 scenarios a positive economic potential, ranging from 5.5 [$/tH$_2$] to – 34.7 [$/tH$_2$], making this a very unfavourable investment at the imposed assumptions.

On top of that, hydrogen handling and production is a risky business and a risk analysis, based on data from the U.S. Dpt. Of Energy and NASA, was conducted to identify and rank risks in accordance to international risk-management methods. This analysis has shown, that 80% of hydrogen-related incidents are caused by either equipment failure, design flaws or flaws in operating procedures. These flaws could be mitigated by fit-for-purpose design, specialized training of personnel and updating technical and operational procedures according to latest standards.

Table of Content

1 Introduction

Today, the world is witnessing a substantial increase in the installed capacity of renewable energy. Combined with wind and solar technologies, hydrogen will play a major part to facilitate a significant reduction of CO_2 emissions and increasing overall project profitability. hydrogen is widely used in the chemical industry, mainly for synthesizing ammonia and in the petroleum industry for refining operations.

Nowadays, most industrial hydrogen is still produced by methane reforming – a heat intensive process that produces tremendous amounts of off-gas, mainly carbon dioxide. The goal of thesis is to explore the possibility of producing this valuable, future proof resource from toxic and harmful waste gases in petroleum production processes. Huge amounts of sour gas, mainly hydrogen sulfide (H_2S) and carbon dioxide (CO_2), are contained in petroleum reservoirs worldwide, which could potentially serve as feedstock for generating a product of value to businesses and society alike. *Global proven and probable sour gas resources have an estimated potential of 4 trillion m^3 of net hydrocarbon gas. (Burgers et al. (2011))*

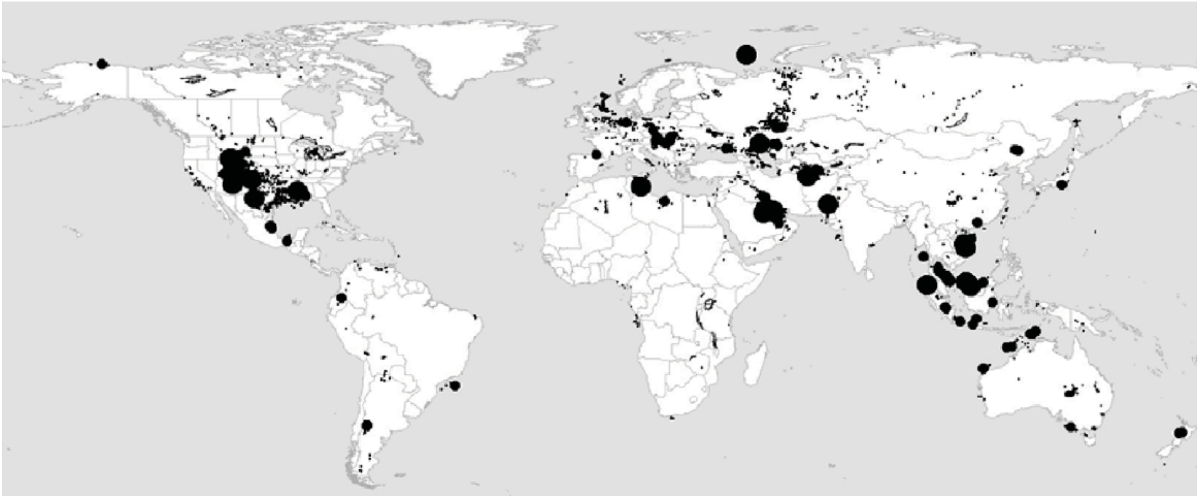

Figure 1: Worldwide Sour Gas Reservoirs with substantial H_2S/CO_2 content[1]

Usually, this sour gas is processed in a Claus plant and partially oxidized to elemental sulfur, which is rather a matter of environmental protection management than business decision focused on generating value. This work consists of three major parts: The introduction into the topic plus a review of literature about research already conducted, the process selection and modelling step, utilizing state of the art process simulation software, and subsequently linking the process simulation output to an economic model including sensitivity analysis and risk assessment when dealing with hydrogen production processes. Finally, a conclusion plus comparison to current standard processes will be given and further recommendations and ideas for research activities are provided.

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[1] Burgers et al. (2011): p. 2178

2 An Introduction to Hydrogen: Use and Production

In this chapter, the resource hydrogen and its complete value chain is explained and articulated to motivate this work and its objectives.

2.1 The Vision of a Hydrogen Economy

Over many centuries, hydrogen has attracted many scientists and visionaries. The compelling idea of automobiles and vehicles with built-in power plants that produce nothing more than water from their exhausts. This idea was a major point why research in hydrogen technology is still strongly pursued. Even the great novelist Jules Verne predicted the exciting hypothesis in his novel „L'Île mystérieuse" in 1987.[2]

The first concept for the idea of a hydrogen economy was made by an engineer named Lawaceck in 1968. His idea was to transfer energy through pipes using hydrogen.[3] Consequently, the first paper concerning this idea was published in 1972 by Appleby. In 1982 the National Science Foundation sponsored Texas A&M University a 5-year support for research in hydrogen as a fuel source and focused on the decomposition of water by light in an electrochemical cell. [26] By discovering this new field called "photo-electrochemistry" a conversion of light to hydrogen and electricity with efficiencies around 10 percent was made possible.[4]

Although hydrogen seemed to be the fuel of the future, there were notable considerations which hampered the development of this technology – overall cost.

When using sporadic sources such as wind and solar to produce hydrogen from water through electrolysis, one must consider storage. The cost for storage may be considerable, because of special materials and high pressures needed. Another consideration is transport, where pipelines can be used to send the hydrogen over long distances. These pipes need special steels to not diminish in function because of hydrogen embrittlement problems over long distances, which raises costs dramatically. Also, during conversion of hydrogen back to electricity, efficiency losses in fuel cells of about 50% are detrimental to economic viability. [5]

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[2] Sobyanin, V. (2006): On the Eve of Hydrogen Era; https://scfh.ru/en/papers/on-the-eve-of-hydrogen-era/; Accessed on 24.07.2019

[3] Bockris, J. (2013): p. 2579

[4] Bockris, J. (2013): p. 2583

[5] Bockris, J. (2013): p. 2584

2.2 Clean Opportunities

During the G20 summit in Japan (June 2019), the International Energy Agency (IEA) prepared an extensive report on why hydrogen has the potential to play a key role in energy supply and storage for the future. One of the many advantages over other energy sources are:[6]

1. **Potential of a zero-carbon impact**: Hydrogen can offer ways to decarbonize entire sectors (i.e. transportation, energy generation and industry)

2. **Versatility**: Hydrogen can be used in various ways, even with technologies available today. It can produce, store and move energy.

3. **Speeding up the transition to renewable energy sources:** Hydrogen has the potential to be the medium of choice for energy storage coming from sporadic sources of electricity (i.e. wind, solar, hydro)

4. **Untapped market potential of hydrogen:** Nowadays, the only markets that mostly use hydrogen is the refining and chemical industry – with huge untapped potential markets comprising transport, power generation and buildings.

Although it seems that hydrogen has many advantages over other energy sources, many challenges to make hydrogen the fuel of the future are still to be overcome.

2.3 Challenges for Hydrogen

Following the potential of hydrogen as an energy source, carrier and storage medium, the industry is still faced with many challenges:[7]

1. **Cost of hydrogen production from low-carbon energy:** Renewable energy is still not cost effective when producing hydrogen. According to latest research, with electricity prices from renewable sources falling rapidly, this could scale up clean hydrogen production.

2. **Lack of infrastructure:** Consumer prices are still high, which is highly dependent on infrastructure availability and consumer demand thereof. This challenge needs to be tackled not by single entities, but by a consortium of governments, industry partners and investors.

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[6] International Energy Agency (IEA) (2019): “The Future of Hydrogen”, p. 13

[7] International Energy Agency (IEA) (2019): “The Future of Hydrogen”, p. 14

3. **Governmental regulations on development of hydrogen technology:** Unnecessary barriers between industry and governmental bodies prevent expansion and investment in the hydrogen sector. International safety and regulatory standards need to be revised to benefit world-wide interaction in the global hydrogen economy.

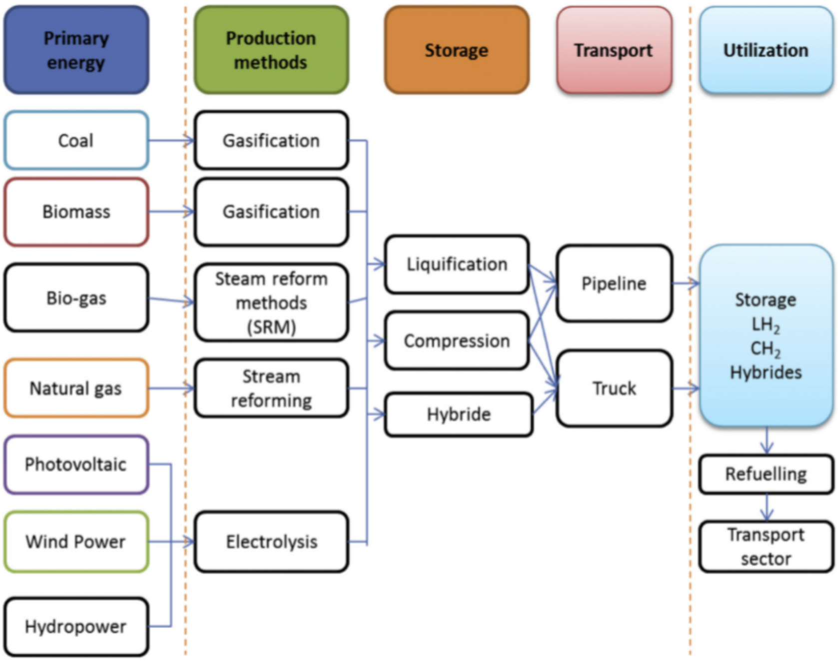

Figure 2:Hydrogen Production-to-Use Value Chain[8]

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[8] Source: Sinigaglia,T. et. al. (2017) : p. 24599

3 Literature Review

In this chapter, current practices and research activity in the field of hydrogen production from sour gas will be explored and some results of said research will act as a base for comparisons and assumptions during the remainder of this thesis. During this review, a short technical summary of every process will be given and its advantages or disadvantages from a technical and economic standpoint will be demonstrated.

The main processes of producing hydrogen from sour gas, which have been subjects of recent research activities, are:

- Hydrogen-Steam Methane Reforming (H_2SMR)
- Thermal Decomposition of Hydrogen Sulfide by Oxygen
- Superadiabatic Combustion (SAC)
- Direct thermal Decomposition of H_2S (Pyrolysis)

In the following chapter, these methods will be discussed in detail and a review on their suitability for modelling the desired process will be given.

3.1 Hydrogen-Sulfide Methane Reforming (H_2SMR)

The Hydrogen-Sulfide Methane Reforming process is a modification of the standard Steam Methane Reforming (SMR) method, which has been the benchmark process for hydrogen production during the last decades.[9] It incorporates the reformation of natural gas (methane) by steam (water) in a catalytic process where the two major products are carbon monoxide and hydrogen. During research it was found, that up to this point in time, no commercial application for H_2 production from H_2SMR was established.[10]

The overall reaction of the original SMR process is depicted in reaction (1):

$$2H_2O + CH_4 \rightarrow \ CO_2 + 4H_2 \ \Delta H^0{}_{298\,K} = 165.2\ kJ/mol \tag{1}$$

This process has one major disadvantage, as it produces (unwanted) 1 mole of CO_2 for every 4 moles of hydrogen created and builds the foundation of the H_2SMR process.

In this potentially viable process, the natural gas (methane) is reformed with hydrogen sulfide (H_2S) instead of steam according to reaction (2). [11]

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[9] Speight, J. (2011): p. 293

[10] Martinez-Salazar, A.L. et al. (2019): p. 12302

[11] Huang, C.; T-Raissi, A. (2008): p. 464

$$2H_2S + CH_4 \rightarrow CS_2 + 4H_2 \ \Delta H^0{}_{298\,K} = 232.4\ kJ/mol \tag{2}$$

The major advantages of this process compared to the SMR process are:

- Removal of unwanted hydrogen sulfide from upstream operations
- Producing carbon disulfide (CS_2) instead of unwanted carbon dioxide
- No prior removal of H_2S from the natural gas needed
- No production of greenhouse gases.

Carbon disulfide is used extensively in the petrochemical industry as a product for the agricultural and pharmaceutical market. [12]

The disadvantages of this process are:

- The highly endothermic nature of the H_2SMR process requiring tremendous energy input
- Methane decomposition forming carbon deposits and deactivating the catalysts.[13]

As discussed, the competing reaction for hydrogen sulfide methane reformation (Reaction (2)) is the thermal decomposition (pyrolysis) of methane to carbon and additional hydrogen (Reaction (3))

$$CH_4(g) \rightarrow C\ (s) + 2H_2\ (g)\ \Delta H^0{}_{298\,K} = 74.9\ kJ/mol \tag{3}$$

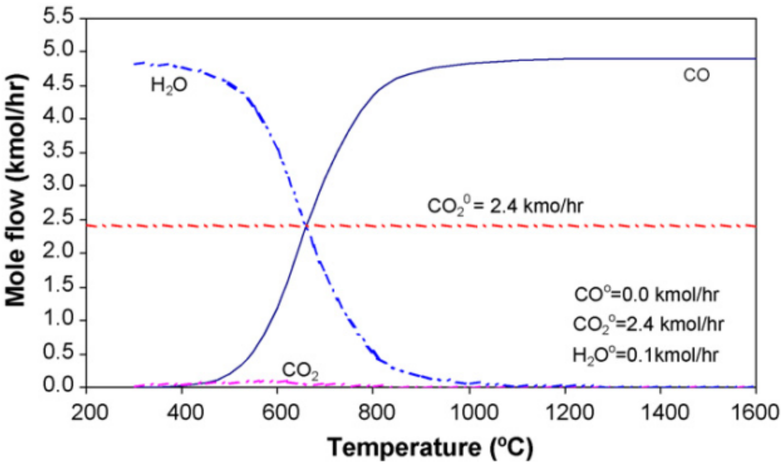

Figure 3: Temperature dependence of methane decomposition reaction equilibrium flow rates for pyrolysis at P= 1.0 atm [14]

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[12] Martinez-Salazar, A.L. et al. (2019): p. 12298

[13] Huang, C.; T-Raissi, A. (2007): p. 647

As seen in Figure 3, when the temperature exceeds 500 °C the reaction favors the decomposition of methane to solid carbon and hydrogen, thereby deactivating the catalyst surface. Therefore, to carry out H2SMR requires reaction conditions such that no carbon lay down occurs. (Huang, T-Raissi (2008))

These conditions were simulated, and pinch-point temperatures identified to minimize energy required and carbon lay down during reaction.

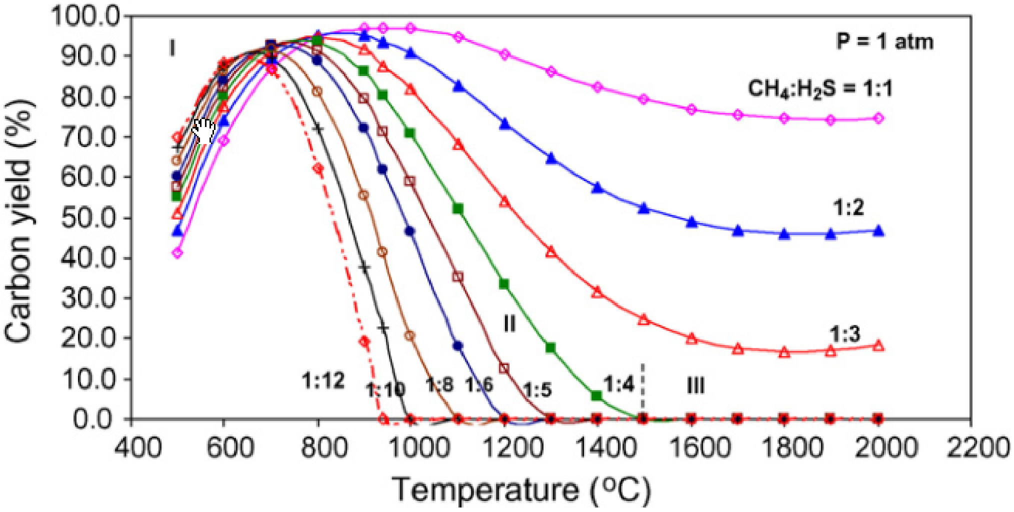

Figure 4: Carbon yield as a function of temperature and feed ratios (CH_4:H_2S) at P= 1.0 atm[15]

From this experiment, optimal process conditions for H_2SMR can be identified to avoid carbon laydown and maximize the conversion rate. Furthermore, three regions (I-III) can be identified were reactions (2) and (3) are competing with each other. In area (I) methane pyrolysis (reaction (3)) is prevalent, whereas in area (III) H_2SMR occurs with no carbon yield above 1500°C and a feed ratio of 1:4 (CH_4:H_2S). Furthermore, the calculations show that with decreasing feed ratio, the maximum carbon lay down temperature decreases as well. The simulation also showed that carbon laydown cannot be avoided at any temperature if the feed ratio

$$x = \frac{[CH_4]_0}{[H_2S]_0} > 0.25 \tag{4}$$

hereby making this process only viable at very high H_2S concentration.[16]

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[14] Source: Huang, C.; T-Raissi, A. (2007): p. 648

[15] Source: Huang, C.; T-Raissi, A. (2007): p. 466

The second competing reaction to the main H_2SMR reaction (2) is the thermal decomposition reaction of hydrogen sulfide to elemental sulfur and hydrogen according to reaction (5).

$$H_2S \rightarrow 0.5\, S_2\ + H_2\ \ \Delta H^0{}_{298\,K} = 79.9\ kJ/mol \tag{5}$$

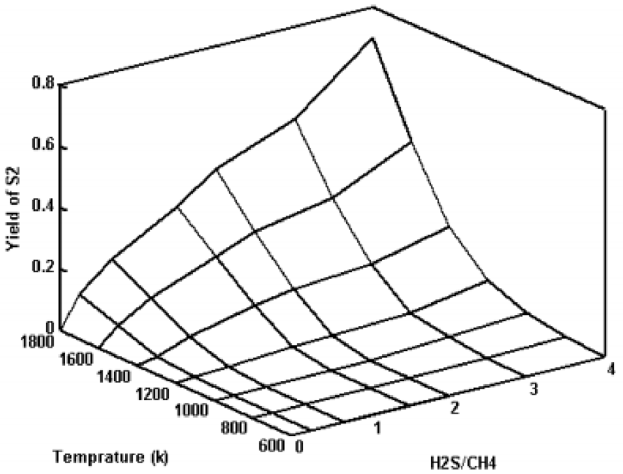

Figure 5: S_2 yield as function of H_2S:CH_4 and Temperature[17]

This decomposition step is the limiting reaction for the overall H_2SMR process, as it involves the production of sulfur in gaseous form (S_2) from thermal decomposition of H_2S.

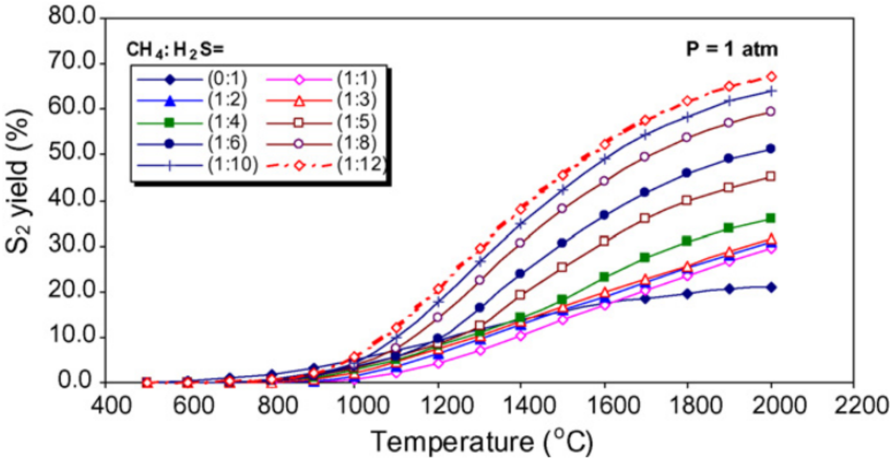

Figure 6: Diatomic sulfur gas (S_2) yield as a function of CH_4:H_2S and temperature at p = 1.0 atm[18]

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[16] Huang, C.; T-Raissi, A. (2007): p. 466

[17] Source: Hosseini, H. et al. (2010): p. 200

As seen in Figure 6, sulfur production and carbon lay down (Figure 4) cannot be avoided at the same time, as there is no temperature point where both are zero.[19]
This process is then sequentially followed by reaction of the produced S_2 and CH_4 from the feed stream to produce carbon disulfide and hydrogen. [20]

$$S_2 + CH_4 \rightarrow CS_2 + 2H_2 \tag{6}$$

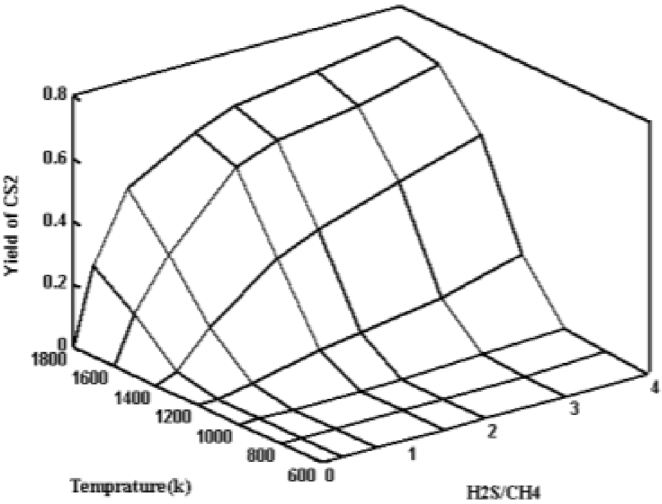

Figure 7: Carbon disulfide yield as a function of H_2S:CH_4 ratio and temperature [21]

3.1.1 H_2SMR Economic Review and Outlook

According to latest research (Martinez-Salzahar 2019)

> *"To date there are no commercial application for hydrogen production via hydrogen sulphide methane reformation however, results demonstrate it could be a competitive and financially viable option".*

Based on recent economic analysis the total energy cost is bigger than a comparable conventional Steam Methane Reforming process due to the heat of the reaction involved. In contrary to that, the total production cost in the H_2SMR process is lower because of much higher amount of hydrogen produced, according to the simultaneous competing reactions explained in Chapter 3.1, most of them producing hydrogen. Furthermore, H_2SMR does not produce a pollutant to the atmosphere. Instead it creates a valuable by-product in the form of carbon disulfide with much

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[18] Source: Huang, C.; T-Raissi, A. (2007): p. 467

[19] Huang, C.; T-Raissi, A. (2007): p. 468

[20] Hosseini, H. et al. (2010): p. 198

[21] Source: Hosseini, H. et al. (2010): p. 200

higher market value in comparison to elemental sulfur and therefore makes the use of a claus plant redundant. [22]

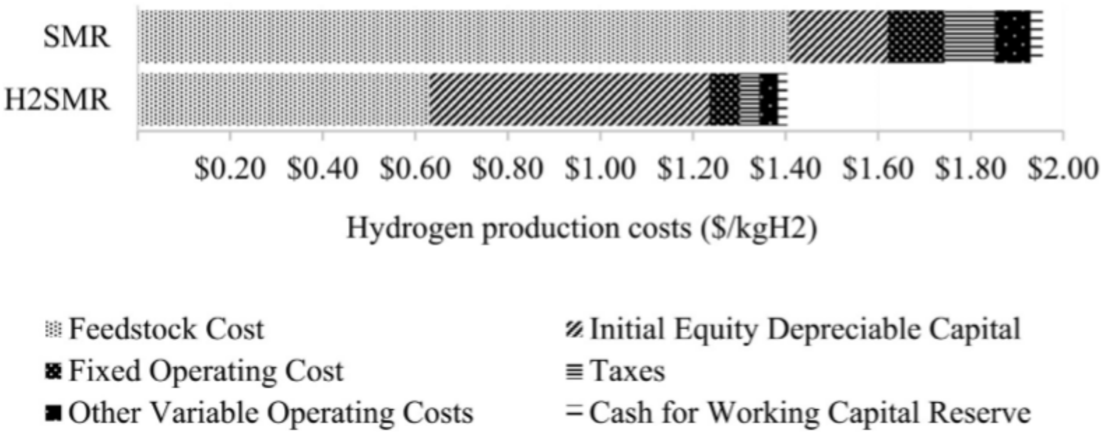

Figure 8: Total production cost comparison between conventional SMR and H_2SMR[23]

In this study, a previous model of conventional SMR[24] was compared to the newly proposed H_2SMR model. As seen in Figure 8, the economic analysis showed that the H_2SMR process had a total cost of 1.4 $ per kg hydrogen produced, whereas the conventional SMR process showed a total cost of 2 $/ kg hydrogen produced.

Huang and T-Raissi (2007) proposed a cryogenic H_2SMR process for producing liquid hydrogen, with efficiencies exceeding 80%, shown in Figure 9, making this process a potential valuable prospect for further research. [25]

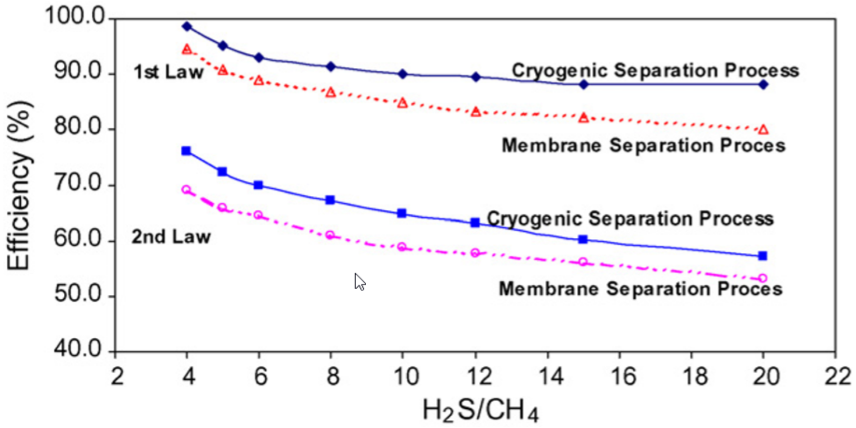

Figure 9: Efficiencies for the H_2SMR process as a function of $H_2S:CH_4$ ratio[26]

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[22] Martinez-Salazar A.L. et. al. (2019): p. 12301

[23] Martinez-Salazar A.L. et. al. (2019): p. 12301

[24] Rutkowsi, M. (2012)

[25] Huang, C.; T-Raissi, A. (2007): p. 471

3.1.2 Hydrogen Sulfide Methane Reformation (H_2SMR): Process Flow Diagram Sketch

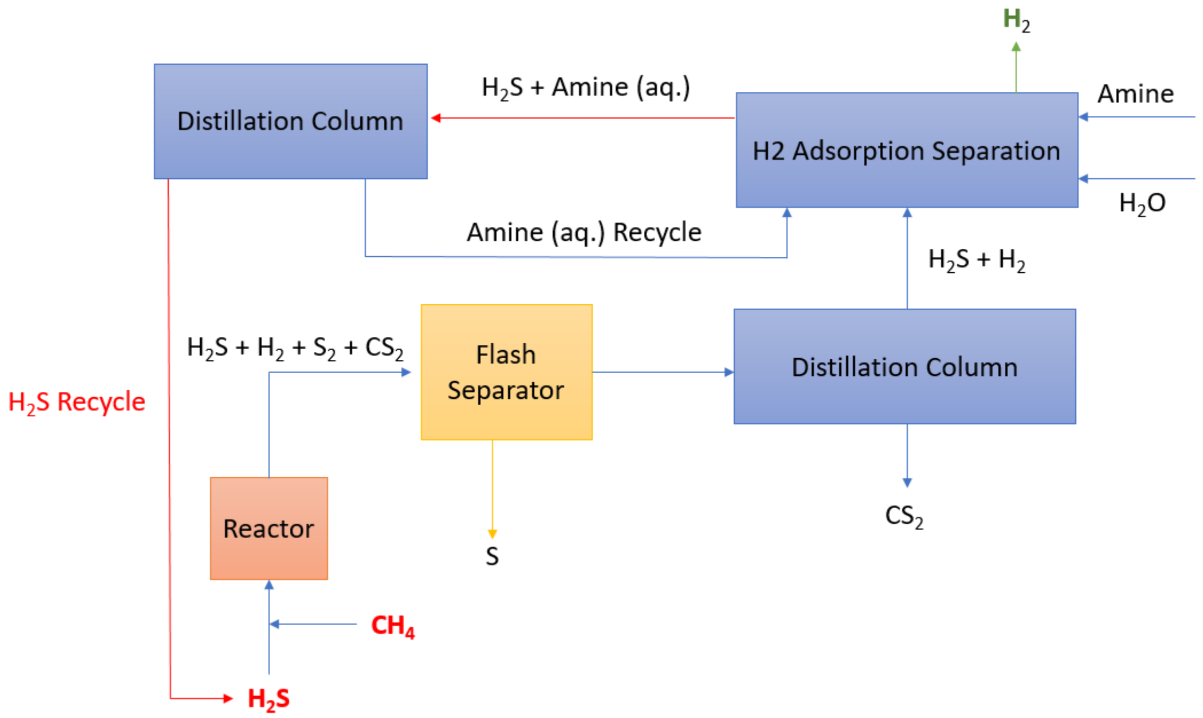

Figure 10: Proposed PFD design concept for the H_2SMR process[27]

The H_2S and CH_4 are mixed and send to a reactor, where hydrogen sulfide (H_2S), hydrogen (H_2), diatomic sulfur gas (S_2) and carbon disulfide (CS_2) are formed. In a subsequent step, the sulfur is condensed in a flash separator and CS_2 is knocked out in a distillation column. The hydrogen and hydrogen sulfide mixture are then separated via a generic chemical adsorption with an aqueous amine solution as solvent. In the last step, the loaded amine solution with hydrogen sulfide is regenerated and both the regenerated amine and the unreacted H_2S is recycled to the adsorption column and the reactor, respectively.

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[26] Source: Huang, C.; T-Raissi, A. (2007): p. 471

[27] Cf. Martinez-Salazar et. al. (2019)

3.2 Thermal Decomposition of Hydrogen Sulfide by Oxygen

As an alternative, the thermal decomposition of H_2S by oxygen could be a viable application for hydrogen production from sour gas. The main idea is to promote the competing thermal decomposition reactions, depicted in reactions (7) - (10) , by injecting oxygen (O_2) into the feed stream. [28]

$$H_2S + 1.5\,O_2 \rightarrow\ SO_2\ + H_2O \tag{7}$$

$$H_2S + 0.5\,SO_2 \rightarrow\ SO_2\ + H_2O \tag{8}$$

$$H_2S + O_2 \rightarrow\ H_2\ + SO_2 \tag{9}$$

$$H_2S + 0.5\,O_2 \rightarrow\ H_2O\ + 0.5\,S_2 \tag{10}$$

The oxygen feed input serves as feedstock to favor above decomposition reactions in comparison to the unwanted, reverse reaction and synthesis of hydrogen and sulfur products to hydrogen sulfide. (Reaction (11))

$$H_2 + 0.5\,S_2 \rightarrow\ H_2S \tag{11}$$

The experimental results (Palma et al. (2015)) have shown that H_2 yield and therefore H_2S conversion rate increased with temperature.[29]

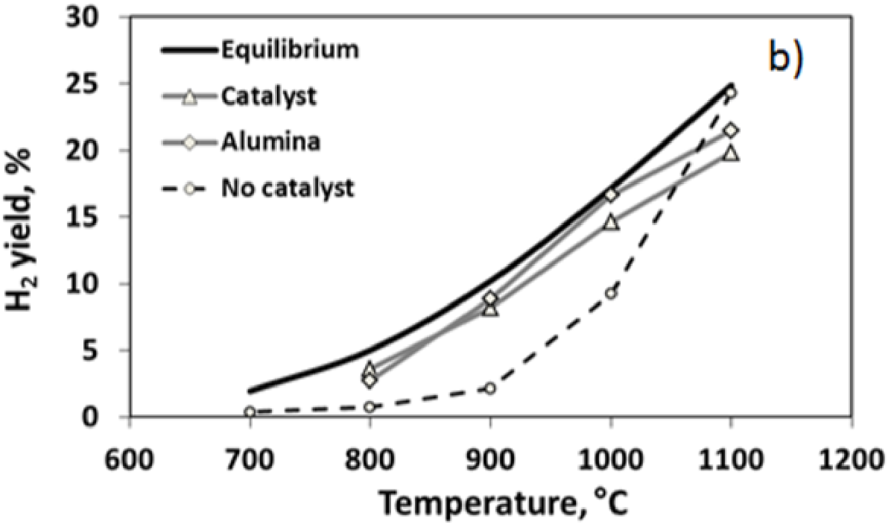

Figure 11: H_2 yield as a function of Temperature for thermal decomposition of H_2S[30]

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[28] Palma, V. et al. (2015): p. 107 ff.

[29] Palma, V. et al. (2015): p. 109

Figure 11 shows the increase of hydrogen yield and H_2S conversion rate with temperature, peaking at 1100°C with 20% yield and starts to decrease after that point.

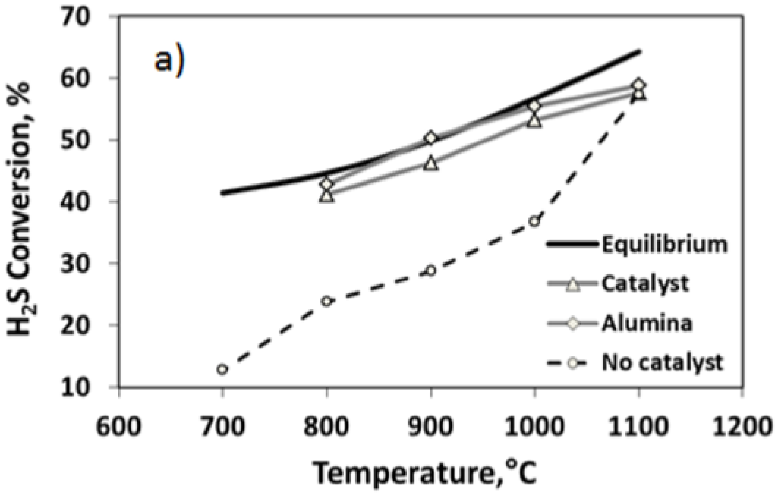

Figure 12: H_2S conversion rate as a function of temperature[31]

As seen in Figure 12, H_2S conversion rate correlates with H_2 yield as expected, peaking at 1100°C and 60% conversion.

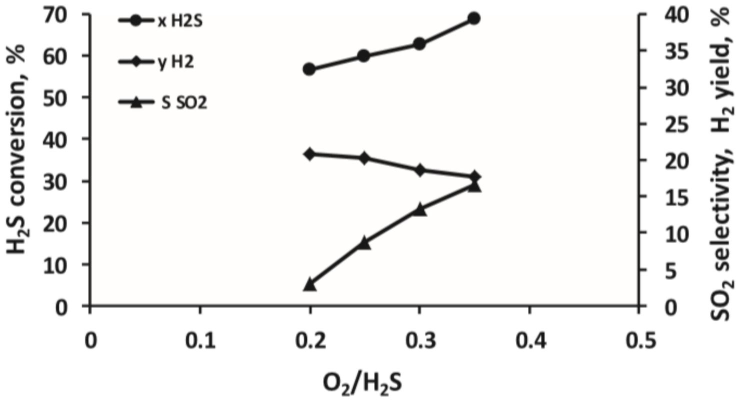

Figure 13: Effect of O_2:H_2S ratio on H_2 conversion rate, yield and SO_2 selectivity[32]

With these experimental results in mind, optimal process conditions are identified as follows:

1. 1100°C to maximize H_2 conversion rate and H_2 yield
2. O_2:H_2S ratio of 0.2 and
3. Usage of a molybdenum-based catalyst supported on Al_2O_3 to minimize SO_2 selectivity and production of undesired by-products.

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[30] Source: Palma, V. et al. (2018): p. 328

[31] Source: Palma, V. et al. (2018): p. 328

[32] Source: Palma, V. et al. (2015): p. 110

3.2.1 Thermal Decomposition of Hydrogen Sulfide by Oxygen – Economic Review and Outlook

During literature review, no current large-scale and commercial application of this process were found and only the small-scale experimental data as described and cited in the earlier pages of this document was present at the current date and time.

Nevertheless, his method can be a potential alternative to produce hydrogen from sour gas. In contrary to H_2SMR, this process does not produce carbon disulfide as by-product but rather elemental sulfur and sulfur dioxide, depending on operating conditions. Production of elemental sulfur itself is uneconomic and Sulfur dioxide needs to be cleaned from the tail-gas stream and therefore puts this process at an economic disadvantage and poses environmental threats without any further cleaning stages. Furthermore, the sour gas needs to be separated from hydrocarbons in this process in advance, which also imposes further cost.

The advantages of this potential process are:[33]

1. No methane needed, which decreases feedstock cost
2. Only oxygen as additional feedstock needed which is abundantly available at practically no cost
3. No specific H_2S feed ratio needed for process to favor products, only dependent on additional O_2 feed.
4. Less expensive in terms of energy, because the oxidation reaction provides heat for endothermic reactions.

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[33] Palma, V. et al. (2015): p. 112

3.3 Superadiabatic Combustion (SAC)

This process is an innovative, non-catalytic process for the production of hydrogen and sulfur from sour gas feedstock.[34] In 2000, the Institute of Gas Technology (IGT) in Illinois in cooperation with the University of Chicago (UIC) and BP Amoco have developed the idea of SAC, where thermal composition of a H_2S-rich waste stream is supported by the superadiabatic combustion of H_2S with oxygen. [35]

The thermal composition reaction of H_2S was already subject of major research and was already mentioned in Section 3.1 as a competing reaction in the H_2SMR process.

$$H_2S \rightarrow 0.5\, S_2 \; + H_2 \;\; \Delta {H^0}_{298\,K} = 79.9\; kJ/mol \tag{12}$$

Where this novel approach comes in is the generation of the thermal energy provided for this decomposition reaction to go underway. The idea is to use part of the H_2S waste gas for a partial oxidization reaction, depicted in Equation (13).

$$H_2S \; + \; 0.5\, O_2 \rightarrow 0.5\, S_2 \; + H_2O \;\; \Delta {H^0}_{298\,K} = -220.5\; kJ/mol \tag{13}$$

According to the stoichiometry of Equation (12) and Equation (13), the partial oxidization of one mole of the H_2S fuel gas can supply energy for the direct thermal composition of two moles of H_2S. To achieve high enough temperatures and provide economic feasibility to this production process, the principle of superadiabatic combustion (SAC), or filtration combustion, is utilized.

> *"The principle consists of the combustion of a gas-oxidant mixture in a porous ceramic medium with a high thermal capacity. The intense heat exchange between the burning gas mixture and the porous medium permits the accumulation of combustion energy in the porous matrix. As a result, the flame temperatures developed can be much higher than the adiabatic temperature for the mixture in free air." (Slimane, R. et. al. (2000))*

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[34] Slimane, R. et. al (2002): p. 1

[35] Slimane, R.; Lau, F.; Abbasian, J. (2000) : p. iv

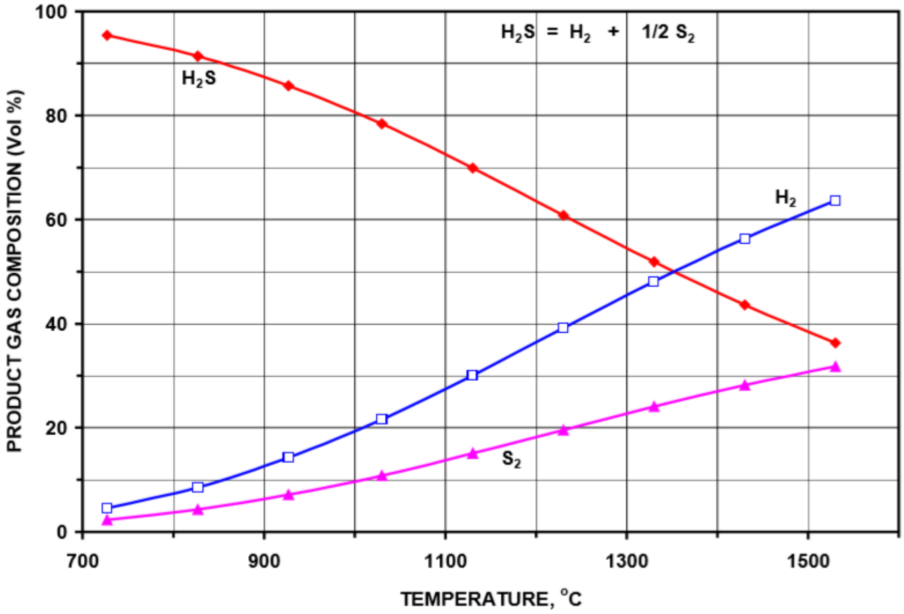

Figure 14: Product Gas Compositions during Thermal Decomposition of H_2S vs Temperature[36]

As seen in Figure 14, high temperatures at and above 1100°C are needed to achieve hydrogen product compositions of more than 20%. This means that the highly endothermic thermal decomposition reaction of H_2S needs massive amount of energy input, which would be provided by the partial oxidization of hydrogen sulfide with oxygen.

Key Process Parameter	**Recommended Range**	**Unit**
H_2S Fuel Gas Content	10 - 50	[vol%]
O_2 Oxidant Content	21 - 100	[vol%]
Equivalence Ratio	5 - 20	
Type of Inert Pellets	2 - 4	
Pellet Porosity	20 - 60	[%]
Inert Pellet Diameter	1 - 5	[mm]
Filtration Velocity	75 - 150	[cm/s]
SAC Reactor Temperature	1300 - 1500	[°C]

Table 1: Key Process Parameters and Ranges for the SAC process[37]

Figure 15 shows the difference in adiabatic and superadiabatic combustion temperature with respect to equivalence ratio. It can be seen, that the filtration

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[36] Source: Slimane, B et. al. (2002): p. 3

[37] Source : Slimane, B. et. al. (2000) : p.21

combustion process is working at a much higher temperature, favoring the thermal decomposition. Furthermore, the recommended range of equivalence ratio is 5 - 20, which would drastically decrease the adiabatic gas temperature even more. [38]

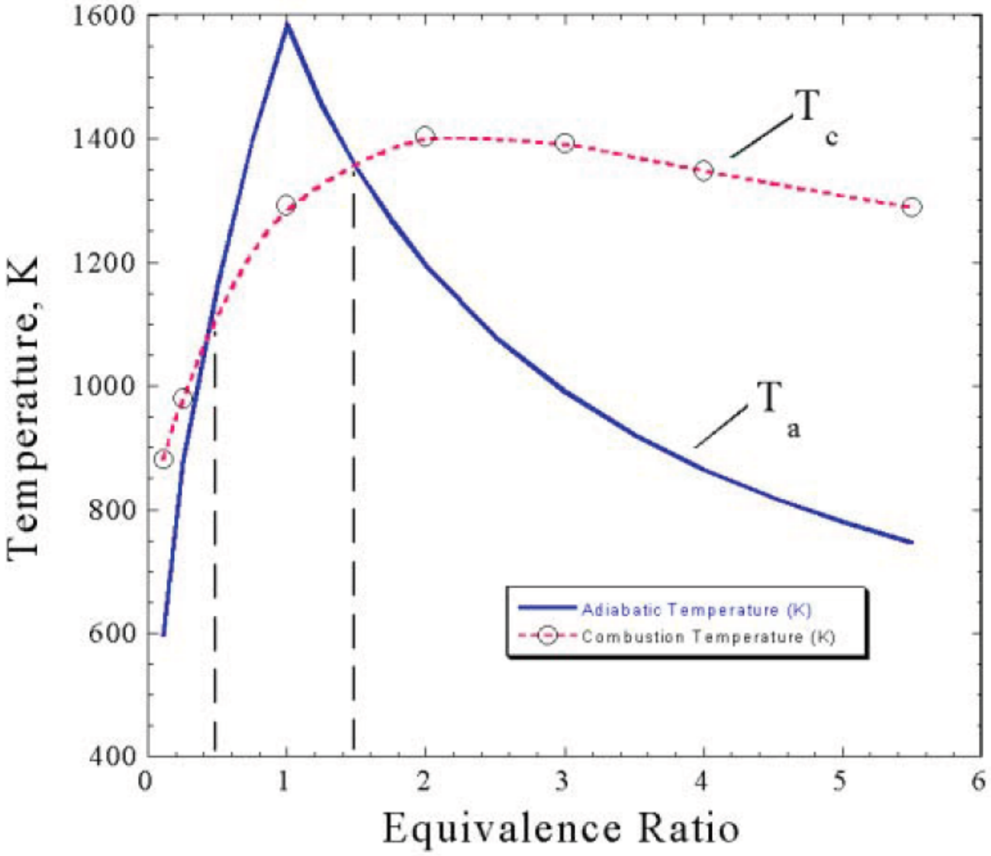

Figure 15: Comparison of Adiabatic Temperature and filtration combustion temperature of the H_2S as a function of Equivalence Ratio (v = 12 cm/s)[39]

The Equivalence Ratio is defined as the ratio of the fuel-to-oxidizer ratio ratio to the stochiometric fuel-to-oxidizer relation, shown in Equation (14). [40]

$$\varphi = \frac{fuel - to - oxidizer\ ratio}{(fuel - to - oxidizer\ ratio)_{st}} = \frac{m_{fuel}/m_{ox}}{(m_{fuel}/m_{ox})_{st}} = \frac{n_{fuel}/n_{ox}}{(n_{fuel}/n_{ox})_{st}} \qquad (14)$$

, where a ratio > 1 expresses excess fuel than it would be required for complete combustion stated by the stoichiometry. This means in the case of SAC, according to Table 1, excess fuel of five to ten times are favorable for filtration combustion.

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[38] Slimane, B. et. al. (2000) : p. 21

[39] Source : Bingue, J.P. et. al. (2000)

[40] Speight, J. G. (2011): p. 374

3.3.1 SAC: Process Flow Diagram Sketch

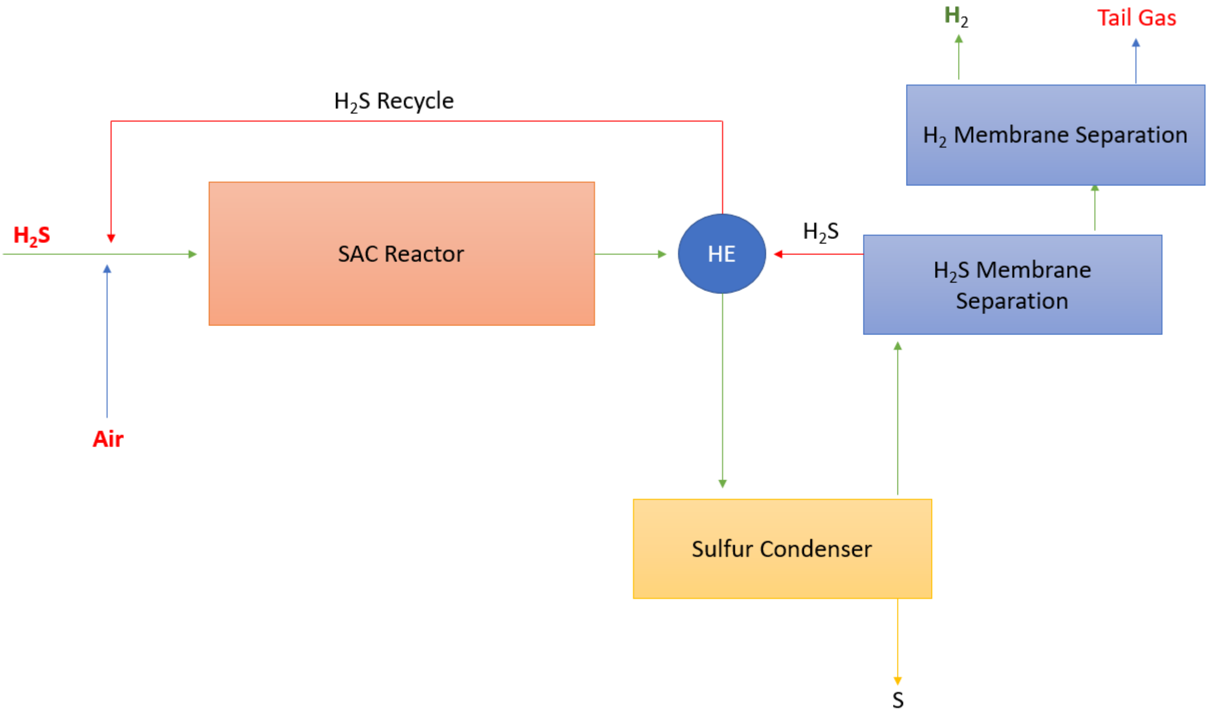

Figure 16: Proposed PFD design concept of the SAC process [41]

The H_2S saturated gas stream and air are mixed and undergo filtration combustion in the SAC Reactor. After the products from thermal decomposition pass through a heat exchanger (HE) they reach the Sulfur Condenser (similar to sulfur condensation and recovery in the Claus recovery process). After quenching of sulfur, the unreacted hydrogen sulfide must be separated and recycled, through a heat exchanger to the reactor. Membrane technologies (i.e. polyamide membranes, ceramic membranes or other high-temperature hydrogen separation systems) are being developed for similar applications. [32] After hydrogen sulfide separation, the H_2 is separated from the tail gas, which is treated afterwards.

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[41] Source: Simane, R. et. al. (2002) : p. 5

3.3.2 Superadiabatic Combustion : Economic Review and Outlook

According to research funded by the US. Department of Energy (DOE) this process is *„potentially suitable for treating gases containing H_2S at levels as low as 10%"*. [42] On the other hand, it is also stated that there was no meaningful assessment of the production cost of hydrogen during such early stages of development, so no economic estimation of these costs was done.

The advantages of this process are:[43]

1. Recovery of Hydrogen in addition to elemental sulfur
2. Noncatalytic process (no replacement of catalysts required)
3. No rigorous feed gas processing needed (compared to Claus)
4. Potential for eliminating costly tail gas processing (minimal SO_2 dropout due to high S_2/SO_2 selectivity)
5. Replaces CLAUS processes
6. Revenue of hydrogen product can offset costs

O_2 mole percent	**Temperature [°C]**					
	927	**1027**	**1127**	**1227**	**1327**	**1427**
0.99	15.9	23.2	31.8	40.9	49.9	58.3
1.96	18.5	25.6	33.9	42.8	51.6	59.7
2.91	21.0	27.9	36.0	44.7	53.2	61.0
3.85	20.7	27.7	35.9	44.5	53.1	61.0
4.76	23.2	30.0	38.0	46.4	54.7	62.4

Table 2: Estimated percentage of H_2S converted in the SAC reactor (not self-sustainable burner conditions with orange backdrop)[44]

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[42] U.S. DOE Hydrogen Program Review 2002: p. 12; NREL/CP-610-32405

[43] U.S. DOE Hydrogen Program Review 2002: p. 11; NREL/CP-610-32405

[44] Hanamura, K.; Echigo, R.; Zhdanok, S. A. (1993)

3.4 Direct Thermal Decomposition of H_2S (Pyrolysis)

Starting in 1986, Reed Robert from Houston Texas first filed a patent under No. 4575453 for a “Modified Claus Furnace” where he postulated a *“Modified Claus Furnace…containing a secondary chamber in heat exchange…wherein H2S is cracked to supply hydrogen…” (Reed, R. (1986))*

The main process idea was to use the heat in the furnace from an already existing Claus sulfur recovery process to crack open the hydrogen sulfide molecules into diatomic sulfur gas and elemental hydrogen, according to reaction (15).[45]

$$H_2S \rightarrow H_2 + \frac{1}{x} S_x \qquad \Delta H_{298\,K} = 79.9\ kJ/mol \tag{15}$$

, where x = 2.

This reaction is a highly endothermic process and equilibrium yields are poor below 1500°C [46] and is unfavorable for hydrogen formation without a catalyst. Fortunately, with the use of catalysts (i.e. Pt-Co, disulfides of molybdenum/tungsten or other transitional metal sulfides supported by alumina)[47] decomposition can be accelerated rapidly at 1000°C. Adewale, R. et. al (2015) have simulated a retro-fit Claus-plant for hydrogen-generation based on the research of Reed, R. L. (1986) and have identified that up to 24.5% of the initial hydrogen sulfide can be cracked in the retro-fit process to elemental hydrogen.[48]

Temperature [°C]	**Conversion [%]**
627	1.9
727	3.4
927	13.1
1127	**25.6**
1327	37.7
1527	47

Table 3: Equilibrium conversion rate [%] as a function of burner temperature[49] (Claus furnace temperature with orange backdrop)

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[45] Speight, J. G. (2011): p. 299

[46] Speight, J. G. (2011): p. 298

[47] Reed, R. L. (1986): p. 5

[48] Adewale, R. et. al. (2016): p.4825

[49] Source: Reed, R. L. (1986): p.6

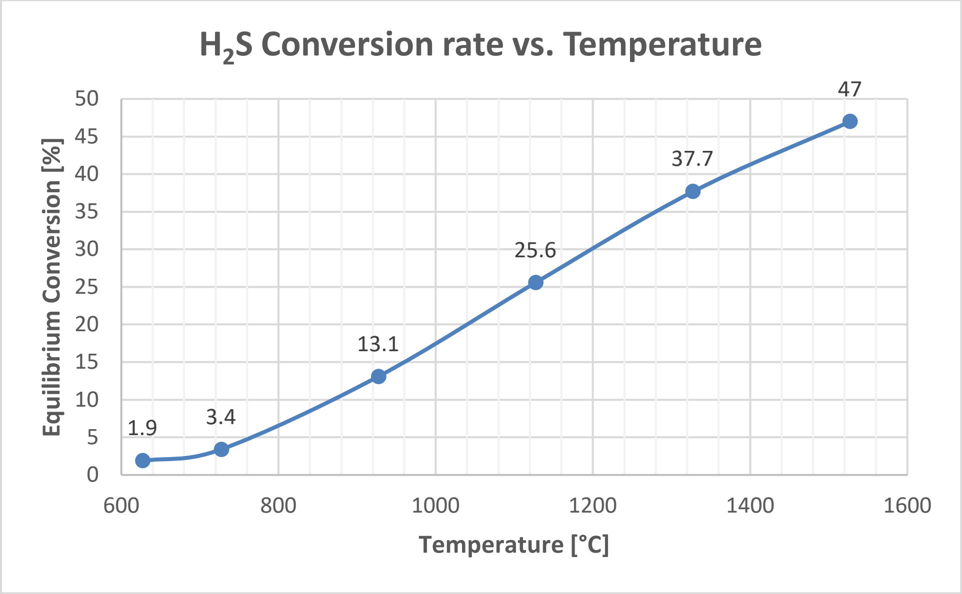

Figure 17: H_2S pyrolysis conversion rate vs. temperature[50]

As seen in Figure 17, there is a strong correlation between reactionary temperature setting and conversion rate. Typical Claus furnace adiabatic burner temperature is between 1000-1200°C so using the Claus burner as a heat source yields approx. 25% conversion.

3.4.1 Direct Thermal Decomposition (Pyrolysis): Process Flow Diagram Sketch

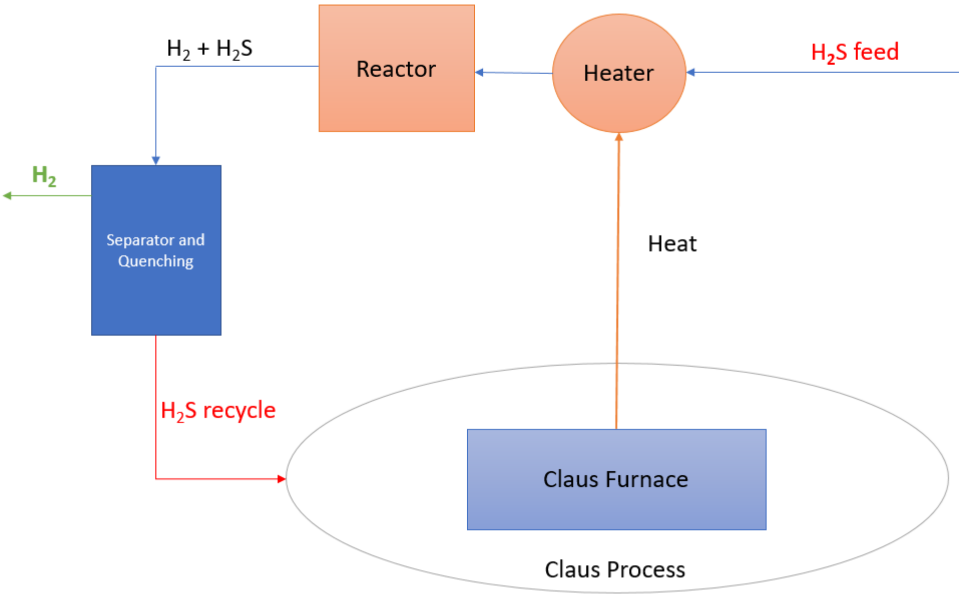

Figure 18: Proposed Process Flow Diagram Direct Thermal Decomposition[51]

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[50] Cf. Reed (1986)

4 Thesis Methodology

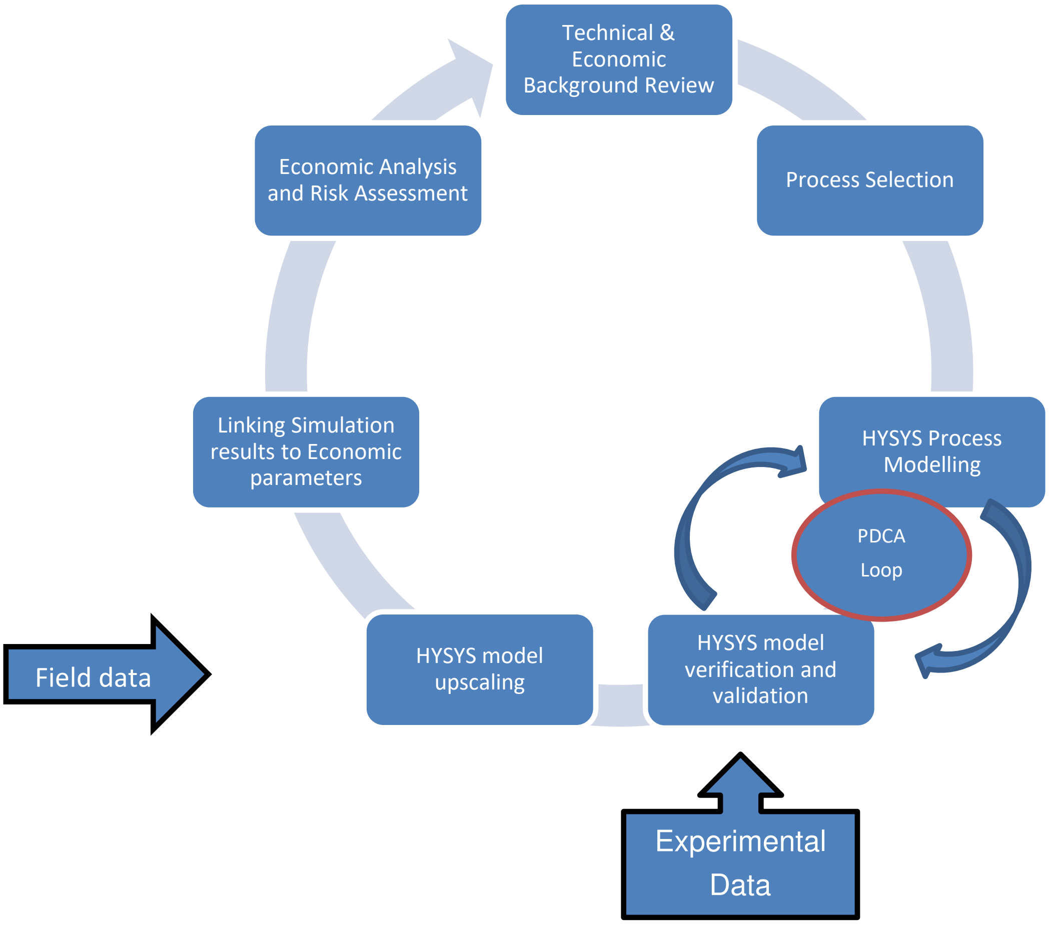

Figure 19: Thesis Workflow

Figure 19 above shows the proposed workflow of this thesis. At first, a literature review is conducted to determine the level of research this topic was already subject to and where it is currently at. After consideration of all available process suitable for conducting the proposed work, a process which fulfills the most criteria is chosen for further analysis. Subsequently this process will be modelled with a process simulation software suit and in the next step, preliminary results will be validated on the base of experimental data from literature. After this successful verification step, the process model is upscaled using commercial field data to generate the output parameters needed for further investigation. These parameters are linked to economic parameters and on that base, the final economic analysis is conducted and, based on the results, recommendations are given. On top of that, given the nature of hazardous compounds and chemicals involved, a risk assessment in accordance to the norm ISO 31000 is utilized to inform of, not only the monetary, but also the HSEQ perspective.

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[51] Cf. Adewale et al. (2016)

During process modelling, which was a substantial part of this thesis work, a PDCA Loop cf. ISO 9001 was utilized to ensure the correct verification of the proposed model, as it is mandatory for the subsequent steps of this workflow.

5 Process Selection

In this chapter, the process selection for hydrogen production is explained. All considerations and criteria for subsequent modelling in HYSYS are given and finally the selected process is presented.

5.1 Consideration Critera

For selecting the appropriate process, numerous criteria concerning the process applicability where identified, such as:

- Current status of process research…R
- Software Compatibility…SW
- Predicted Conversion rates…C
- Energy requirements…E
- Working Temperatures and Pressures…T, p
- Process feed Input…I
- Process products…P
- Experimental data availability…X

TC…Technical Challenge

- Current status of commerciality…M
- Availability of Industrial application…A
- Availability of Industrial data…AD
- Sustainability Considerations…S
- Risk Considerations…H

EF…Economic Feasibility

These criteria where accumulated to two super-criteria labeled “Technical Challenge” and “Economic Feasibility”, both being functions of their respective variables and are explicitly stated via Equations (16) and (17). These criteria were ranked based on the objective literature review conducted with additional expert consultation.

$$TC = f\,(R, SW, C, E, T, p, I, P, X) \tag{16}$$

and

$$EF = f\,(M, A, AD, S, H) \tag{17}$$

5.2 Selected Process

Based on the Criteria established in above in Section 5.1, the four processes in consideration were ranked and according to this ranking, chosen for the following process modelling step and economic analysis. As discussed in the technical literature review in Chapter 3, with both economic and technical aspects in mind, this feasibility-matrix was established.

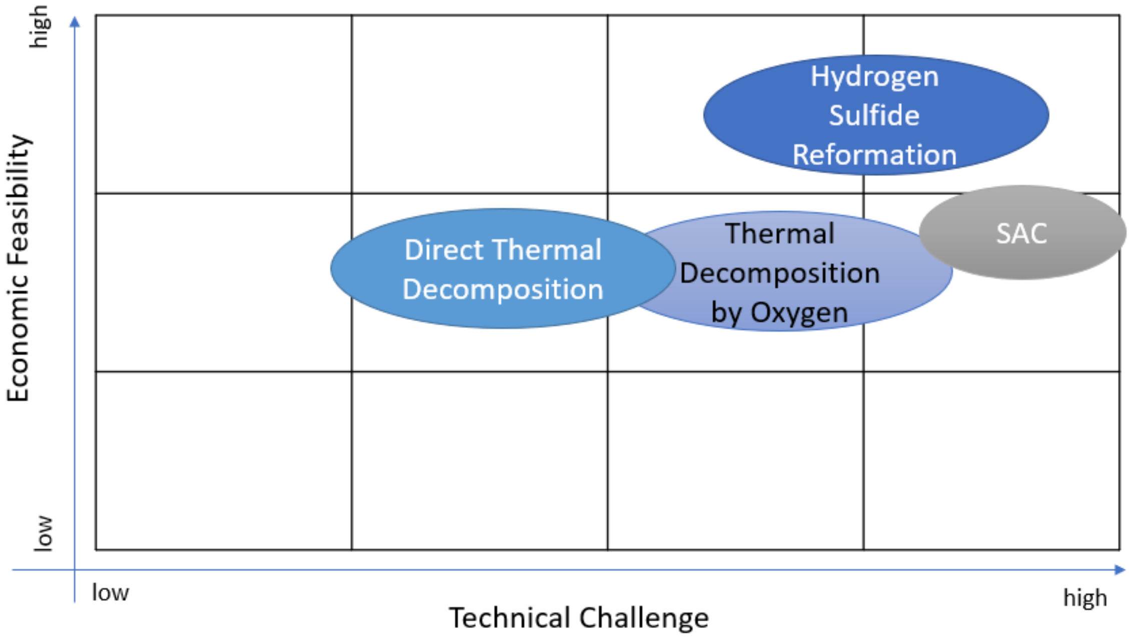

Figure 20: Feasibility-Matrix for Process Selection

Superadiabatic Decomposition (SAC) proved to be incompatible with the modelling software and, considering the high technical challenges (very high Temperatures), this process was dropped from the potential selection. Furthermore, no recent advancements or research was conducted since the early 2000's, which is indicative of its highly experimental nature and limited economic feasibility.

Hydrogen Sulfide Reformation on the other hand has shown to be a promising candidate for process modelling, as very recent research has shown favorable economics and technical challenges that can be overcome with todays resources. This is why the process was selected for further investigation and as a potential candidate for further analysis.

Thermal Decomposition by Oxygen and Direct Thermal Decomposition both have indications of medium to medium-low on both the technical challenge and the economic feasibility. Both have shown similar conversion rates, with direct thermal decomposition being the subject to more recent research of its seeming process simplicity. That being the case, with both processes being at a similar level, the simpler one with more available experimental data, being ***Direct Thermal Decomposition***, was chosen.

Once the processes were selected, the technical modelling step started which will be explained in the following chapter.

6 Process Modelling

In the following sections the technical process modelling steps, starting from a software overview until the complete modelling process is done, will be explained in detail. This step is a major part of this thesis and forms the technical prerequisite for all economic evaluations. The overarching process overview is depicted in Figure 21 below.

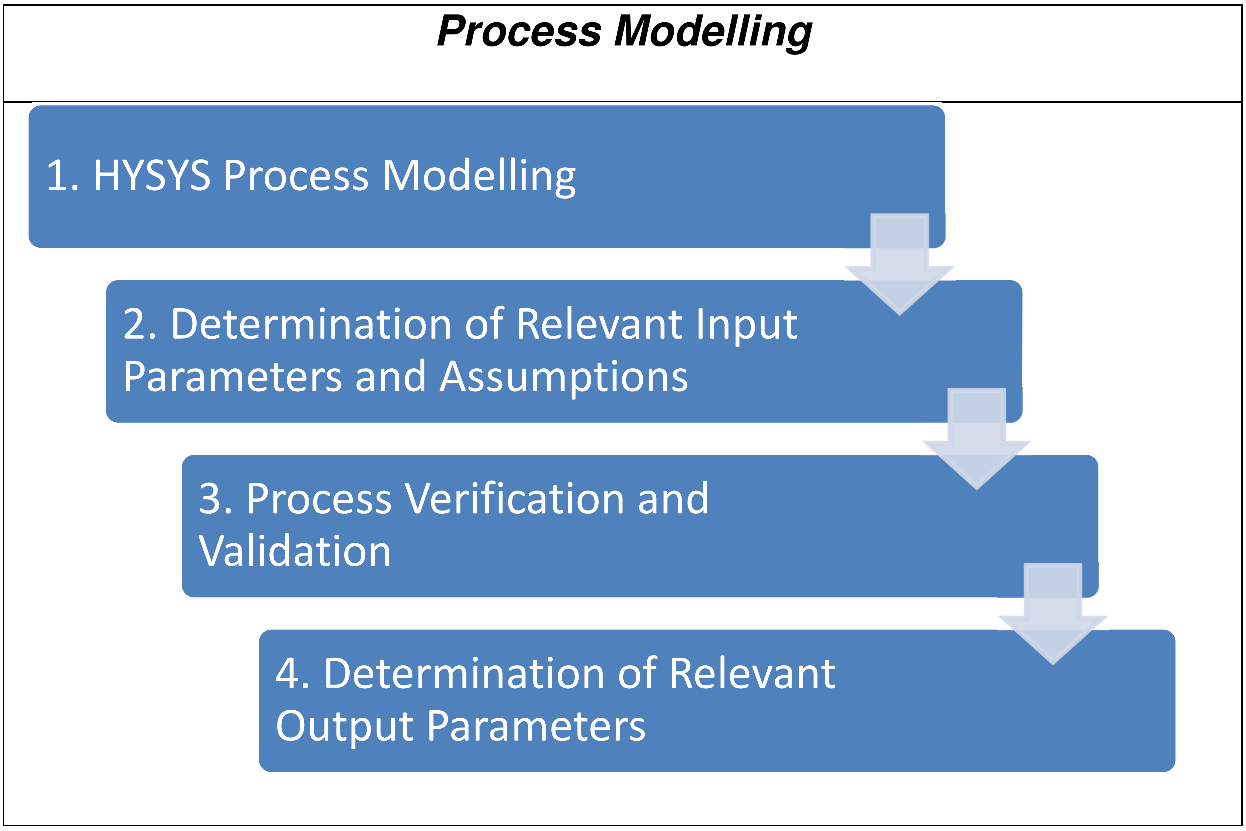

Figure 21: Process Modelling Staggered Process Overview

6.1 Software Overview

The software used for conducting the process modelling step is Aspen HYSYS v.10, which is an industry leading process simulation software. [52] The license was kindly provided the Chair of Petroleum and Geothermal Energy Recovery and sponsored by the cooperating company PM Lucas and has many potential applications, ranging over the whole value chain of chemical products from the downstream industry up to technical upstream applications.

Heat exchanger design, distillation columns, acid gas removal design and sulfur recovery optimization and full plant design are one of the many application possibilities HYSYS can offer.

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[52] Aspentech homepage: https://www.aspentech.com/en/products/engineering/aspen-hysys (Accessed 17.12.2019)

6.2 HYSYS Process Modelling

In this step, the two processes selected for further investigation explained in Chapter 5 are taken from a process concept phase (including black boxes) and transferred to a fully working HYSYS process simulation model.

6.3 HYSYS Modelling: Direct Thermal Decomposition

The first stage of the process modelling step is comprised of transferring a schematic proposed flow sheet black-box model to a working Process Flow Diagram (PFD) in Aspen HYSYS. The ideas and thoughts of previous research, discussed during the Technical Literature Review in chapter 3, furthermore fueled by the experts advising from the cooperating company side, were used as a basis for building these models.

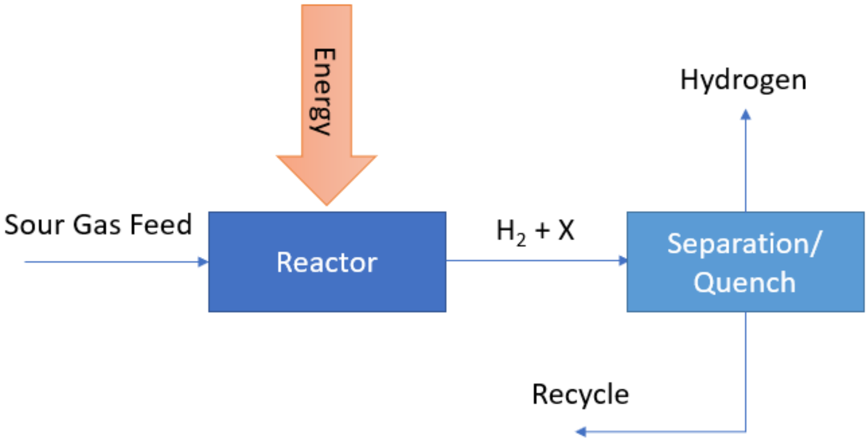

Figure 22: Direct Thermal Decomposition Process Sketch[53]

In Figure 22 above, the basic process design idea for the direct thermal decomposition process is shown. The feed, consisting of mainly hydrogen sulfide is decomposed to hydrogen and other components by energy input. This energy can come from different sources but needs to be substantial to drive the main thermal dissociation reaction. After the reaction occurs, the hydrogen is separated from the overall stream and collected. The residual stream is recycled to either a successive Claus process for further processing of the tail-gas or the hydrogen sulfide is separated from the other components (gas treating with high H_2S selectivity, i.e. chemical adsorption with MDEA solvent[54]) and recycled back to the reactor to increase efficiency of hydrogen production.

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[53] Source: Self (2019)

[54] Mokhatab S., Poe W. A., Speight J. G. (2006): p. 272

6.3.1 Reactor Design and Assumptions

A crucial part in defining the process model for simulation purposes is the design of the reactor, where all chemical reactions under investigation take place. Before choosing a reactor type and conducting the actual modelling, the assumptions and boundary conditions of the process model need to be defined.

Fluid Package (Equation of State)	Soave-Redlich-Kwong (SRK), Sulsim Fluid Package
Reactor Type	Plug Flow Reactor (PFR)
Reaction Type	Kinetic Rate Expression

Table 4: Direct Thermal Decomposition Assumptions and Pre-modelling design choices

6.3.1.1 Equation of State (Fluid Package)

In Table 4 above you can see the choice of fluid package and reactor type for the direct thermal decomposition reaction modelling process. The Soave-Redlich-Kwong, a modification on the Redlich-Kwong EOS, is a cubic equation of state, which empirically relates temperature, pressure and volumes of gases and is mainly used to predict properties of hydrocarbon gas systems of non-polar to slightly-polar components and was chosen via the built-in Aspen HYSYSv10 Property Package Selection Assistant and expert consultation.[55,56]

The SRK EOS is defined by:[57]

$$P = \frac{RT}{V-b} - \frac{a}{V*(V+b)} \tag{18}$$

where

$$b = 0.08664\frac{RTc}{Pc}, a = 0.042748\frac{(RTc)^2}{Pc}\left(1 + m\left(1-\sqrt{Tr}\right)\right)^2$$

and

$$Tr = \frac{T}{Tc}, m = 0.480 + 1.574\omega - 0.176\omega^2$$

---

[55] G. Soave (1972): p. 1197

[56] Assareh, M. (PVT Expert of PM LUCAS), personal communication, September 2019

[57] J. M. Prausnitz, R.N. Lichtenthaler, E.G. de Azevedo (1999)

Unfortunately, the SRK Fluid Package coming with Aspen HYSYS v10 is not capable of modelling the fluid phase of sulfur, which is why a Fluid-Package Transition is needed to correctly estimate liquid sulfur production in the simulation model. After consultation with process engineering experts of the cooperating company PM LUCAS, it was suggested that a Sulfur Recovery Unit model should be used to adequately describe this process in its entirety and to achieve liquid sulfur output. [58]

6.3.1.2 Reactor Type

For the type of reactor, a Plug Flow Reactor was chosen to model this thermal decomposition process, after consultation with a chemical expert, as most experimental results were based on this type of reactor and are subsequently used to verify the integrity of this process.[59] A PFR is also known as a “Tubular Reactor”, and generally consist of a bank of cylindrical pipes or tubes. Furthermore, the flow field is modelled as plug flow, implying that the stream is radially isotopic, meaning no mass or energy gradients. That also means that axial mixing is negligible. [60] During the simulation, all reactants flow through the reactor and are consumed by the reactor, establishing an axial variation in concentration, since the reaction is a function of concentration. To obtain this solution (axial profile of compositions, temperature, etc.), the plug flow reactor is split up into sub-volumes, where the reaction rate is considered uniform. Subsequently a molar balance is calculated in each of these sub-volumes according to Equation:[51]

$$F_{j0} - F_j \int_v rjdV = \frac{dN_j}{dt} = 0 \ (at\ steady\ state) \tag{19}$$

with the assumption of spatially uniformity reduces to

$$F_{j0} - F_j * r_j V = 0 \tag{21}$$

and therefore

$$F_j = F_{j0} + r_j V \tag{20}$$

where

F_j = inlet flowrate

$F_{j,0}$ = outlet flowrate

---

[58] Grubac, B. (Process Engineer of PM LUCAS), personal communication, 28.10.2019

[59] Monnery, W. personal communication, 5.10.2019

[60] Aspen HYSYS v10 Technical Description: Term “Plug Flow Reactor”, Accessed 7.1.2020

$r_j V$ = reaction rate times segment volume

For solving these equations, HYSYS uses Newton's Method as default and uses the outlet fluid composition for an assumed starting value. In this solution method, following equation is utilized:[51]

$$F_{k,j} = F_{k,0} - V \sum_{N}^{0} r_{k,n} \quad for\ all\ k \tag{22}$$

where:

$F_{k,j}$ = kth component's inlet flowrate

$F_{k,0}$ = kth component's outlet flowrate

$r_{k,n}$ = reaction rate of kth component in nth reaction

V = volume containing the reaction, i.e. reactor segment volume

As convergence criteria, the inner loop uses a fixed tolerance of 1.0E-6 on the sum of residuals of the equations, and the outer loop converges on the enthalpy of the outlet fluid using a line search strategy. This strategy calculates the new outlet fluid temperature by Equation (23) :[51]

$$T_{new} = \frac{H_{T1}}{H_{T1} + H_{T2}} (T1 - T2) + T1 \tag{23}$$

where:

H_{T1} = calculated enthalpy of outlet fluid at Temperature 1

H_{T2} = calculated enthalpy of outlet fluid at Temperature 2

T_i = bracketed Temperature points for convergence

After reaching a convergence criterion or after reaching a maximum of convergence set by the user, the loop calculation is stopped.

6.3.1.3 Reaction Design

The reaction that takes place in the PFR was modelled in accordance to Equation (24) stated below and already discussed in section 3.4 as part of the technical literature review:

$$H_2S \rightarrow H_2 + \frac{1}{x} S_x \qquad \Delta H_{298\,K} = 79.9\ kJ/mol \tag{24}$$

where x = 2.

To simulate the decomposition of hydrogen sulfide, a kinetic rate expression needs to be added in order to correctly model decomposition rate based on activation energy and temperature. This rate of reaction is used in the reactor calculation loops described in section 6.3.1.2 during reactor design. To determine rate of reaction, HYSYS uses forward Arrhenius parameters and stochiometric coefficients for each component. Based on these parameters and Equation, HYSYS calculates the rate expression for chosen reaction.[61][62]

$$r_A = k * f(BASIS) - k' * f'(BASIS) \tag{25}$$

,with

$$k = A * exp\left(-\frac{E}{RT}\right) * T^{\beta} \tag{26}$$

and

$$k' = A' * exp\left(-\frac{E}{RT}\right) * T^{\beta'} \tag{27}$$

where:

k = forward reaction rate constant

A = forward reaction Frequency Factor

E = forward reaction Activation Energy Factor

R = ideal gas constant

T = absolute temperature

β = forward extended reaction rate constant

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[61] Aspen HYSYS v10 Technical Description: Term “Kinetic Reactions”, Accessed 7.1.2020

[62] Aspen HYSYS v10 Technical Description: Term “About the Kinetic Reaction”, Accessed 7.1.2020

Based on experiments conducted on H_2S thermal decomposition (C.f. Hawboldt, Monnery, Svrcek (1999) [63], Dowling et. al (1990) and Kaloidas and Papayannakos (1989)), these input parameters where chosen in a fashion that should represent a conservative result concerning overall conversion rates. The values are stated in Table 5 below:

Parameter	**Value**	**Unit**
A	5260	Mol/cm^3 s/$atm^{1.5}$
E	45000	Cal/mol
A’	14.40	Mol/cm^3 s/atm^2
E’	23400	Cal/mol
Basis	Partial Pressure	atm

Table 5: Kinetic Reaction Parameters

6.3.2 Process Model Overview

With the considerations and assumptions explained in sections 6.2 to 6.3.1.3, a preliminary Process Simulation Model was build.

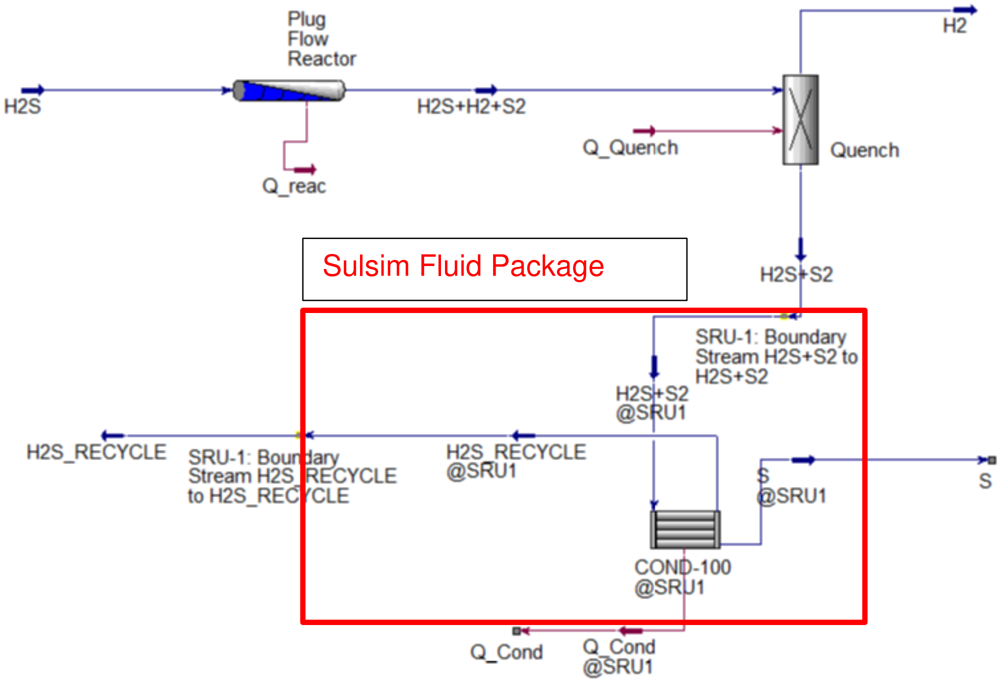

Figure 23: Preliminary PFD Direct Thermal Decomposition

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[63] Hawboldt, K.A.; Monnery, W.D.; Svrcek, W.Y. (1999): p. 957

6.3.3 Process Description

The sour gas feed enters the plug flow reactor, where it is heated to 1000°C+ and thermally decomposed to hydrogen gas (H_2) and diatomic sulfur gas (S_2). The unreacted H_2S is transported with the product gases to a cooling/quenching operation, where the hydrogen gas is separated from the stream. Subsequently the unreacted hydrogen sulfide and the sulfur (in gaseous form) is transported to the sulfur condensation, where it is cooled to liquid sulfur and separated from the unreacted H_2S. Finally, this unreacted sour gas is recycled to another decomposition reactor or to a claus plant for further treatment. The red rectangle in Figure 23 signifies the fluid package transition discussed in Section 6.3.1.1 during the equation of state explanation.

6.3.4 Reactor Design Verification and Validation

To verify the operation of the simulation model, build in HYSYS it is crucial to evaluate the simulation output to experimental data to make sure, HYSYS is operating correctly. This is common procedure in a process engineering environment and is done regularly to ensure correct modelling and simulation behavior. [64]

For this goal, the process in Figure 23 was changed according to an experimental research setup. (C.f. Hawboldt, Monnery, Svrcek (1999) [65] with following parameters:

Parameter	**Value**	**Unit**
Molar Flow Feed	1.015E-2	Kgmole/h
Mole fraction H2S feed	0.025	[-]
Reactor Temperature	950	°C
Reactor Length	1-20 (variable)	m
Reactor Diameter	5	mm

Table 6: Process Verification Parameters

The remainder of the feed mole fraction was filled with nitrogen (nfrac = 0.975) and during this step, only the functionality of the reactor itself was tested, as it is the most crucial design criterion overall.

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[64] Monnery, W. personal communication, 8.10.2019

[65] Hawboldt, K.A.; Monnery, W.D.; Svrcek, W.Y. (1999): p. 958 - 959

During this verification step, reactor temperature was set to 950°C and a sensitivity study (reactor length) was conducted to plot H_2S conversion rate over residence time and reactor length. These simulation results were then compared with the experimental results discussed in section 6.3.1.3. during reaction design. Comparison is done via H_2S conversion rate, which is defined by Equation (28) below:

$$H_2S\ Conversion\ \% = \frac{[H_2S]_0 - [H_2S]_1}{[H_2S]_0} * 100\ \% \tag{28}$$

, where

$[H_2S]_0$ = concentration of H2S in feed stream

$[H_2S]_1$ = concentration of H2S in outlet stream

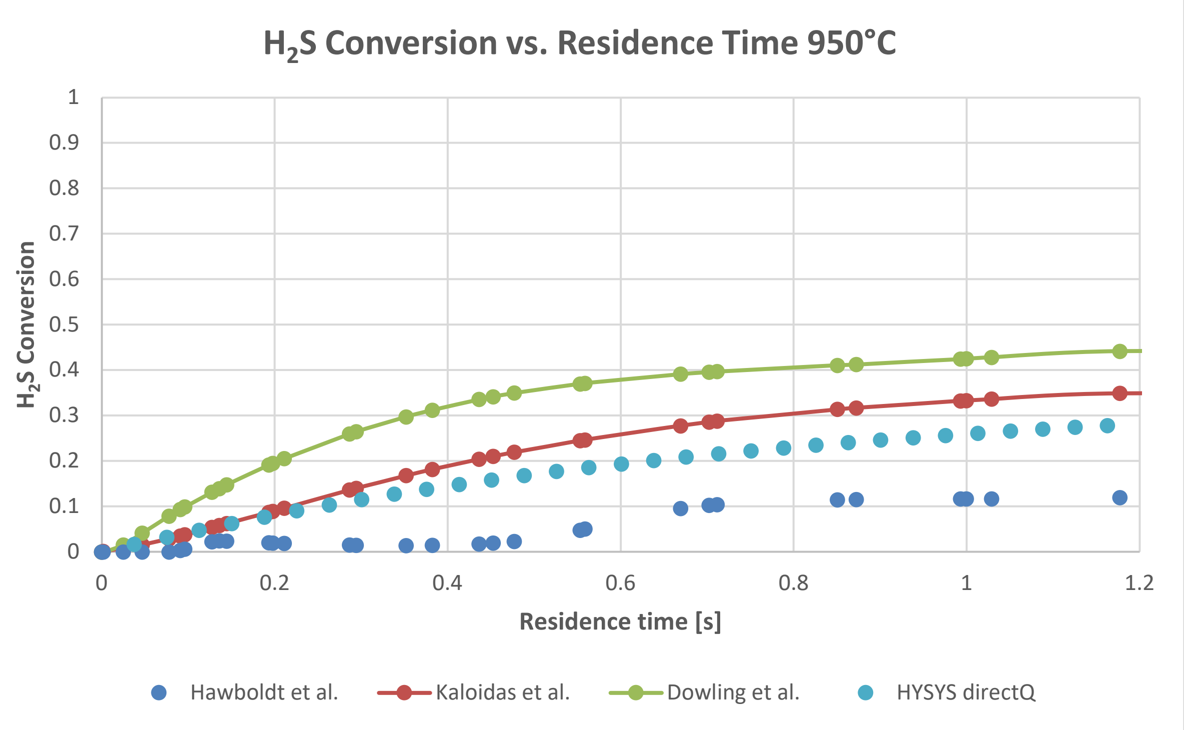

Figure 24: H_2S Conversion vs. Residence Time at 950°C

As seen in Figure 24, conversion rates are in ~10% range of experimental research at a low temperature of 950°C and comparing all experimental research, is approached conservatively as discussed in section 6.3.1.3 in reaction design, ensuring that the process is not over-specified for economic modelling.

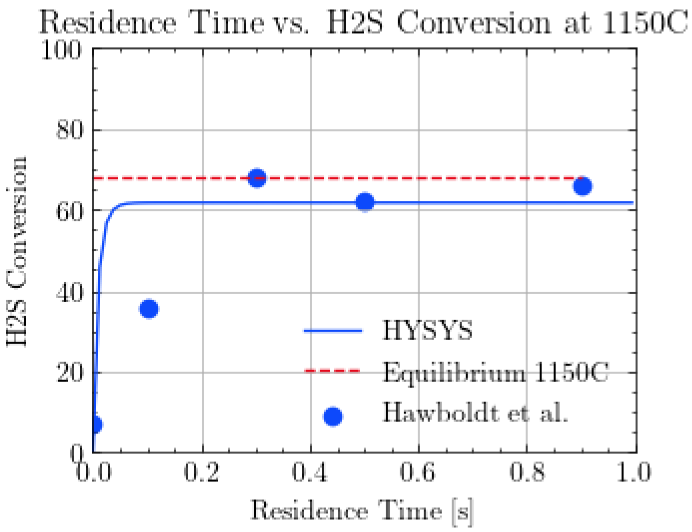

Figure 25: Residence Time vs. H2S Conversion at 1150 °C

Figure 25 shows the hydrogen sulfide conversion rate at 1150°C of the simulation model and compares it to equilibrium conditions of the thermal decomposition reaction and the experimental results of Hawboldt, Monnery, and Svrcek (1999). After a short amount of time, conversion rates are in ranges of ~5% to each other, which is a satisfying result going into upscaling.

6.3.5 Upscaling and Model Optimization

For upscaling purposes, the preliminary verified and tested process model is taken and upscaled for economic purposes. In this step, a industry standard sour-gas feed-stream is used as input. Following this procedure, the model is optimized to minimize heat losses and improve overall process efficiency. A typical sour-gas feed, coming from gas sweetening plants is shown in below:

Component	Flow Rate[kg/h]	Mass percent
Nitrogen	6.98E-02	0.01
CO2	597.2037	81.43
H2S	124.9975	17.04
Methane	4.117885	0.56
Ethane	3.352065	0.46
Propane	1.547004	0.21
i-Butane	0.14459	0.02
n-Butane	0.373937	0.05
i-Pentane	0.484202	0.07
n-Pentane	0.532575	0.07
n-Hexane	0.616878	0.08

Table 7: Typical sour gas feed stream

As seen in Table 7, not only hydrogen sulfide (H_2S) but also a significant amount of carbon dioxide (CO_2) are present in the feed stream. All other components, as their mass fraction is a lot less than 1% most of the time, are ignored and not taken into account during reaction modelling. Although a lot of CO_2 is present, research has shown that at temperature between 1000°C and 1300°C practically no decomposition is taken place and is thereby no accounted for as a competing reaction during thermal reaction modelling. (Cf. Nernst, Wartenberg (1906) and Langmuir (1906))

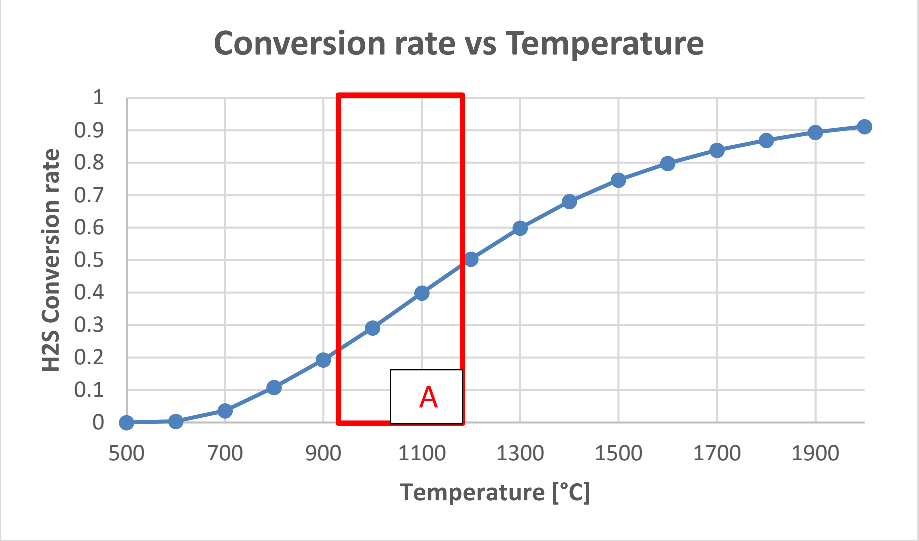

Figure 26: H_2S Conversion rate vs Temperature

In Figure 26 above, a sensitivity analysis was conducted to show how hydrogen sulfide conversion behaves while changing reactor temperature. Therefore, we can estimate the most favorable conditions for thermal decomposition, where the change in conversion rate to change is maximized, which is where the curves slope is at a maximum, signified by the red area A. (950°C – 1200°C)

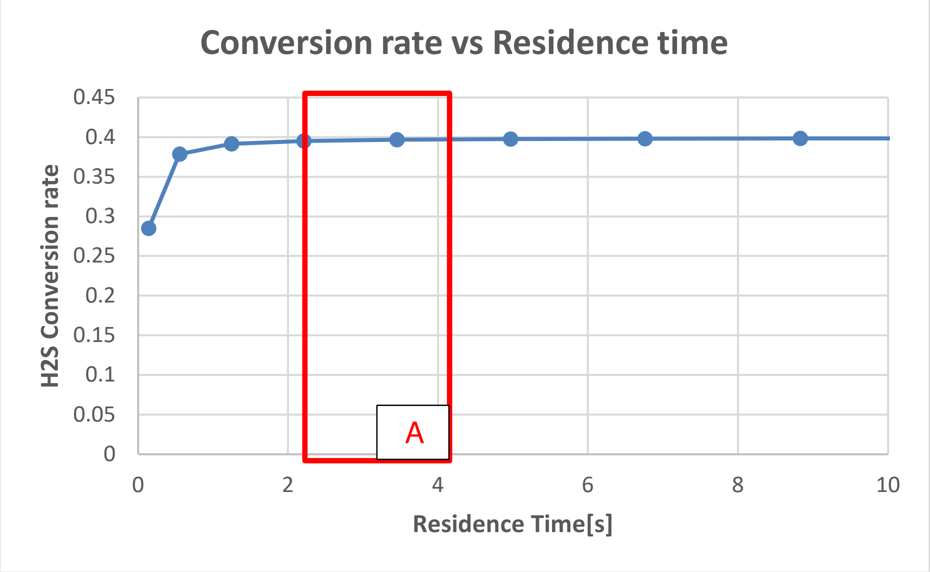

Figure 27: H_2S Conversion rate vs Residence time

Figure 27 shows a sensitivity case study while varying reactor length (for d = 1m) and thereby residence time. Optimum conversion rates can be identified when residence times of 2-4 seconds are achieved, marked by the red area A. Above 4 seconds residence time, no increase in conversion rates can be achieved.

Optimized Model

After all the considerations during upscaling operations, the model was optimized according to these findings. The final model, which serves as a base for economic analysis is shown in Figure 28 below.

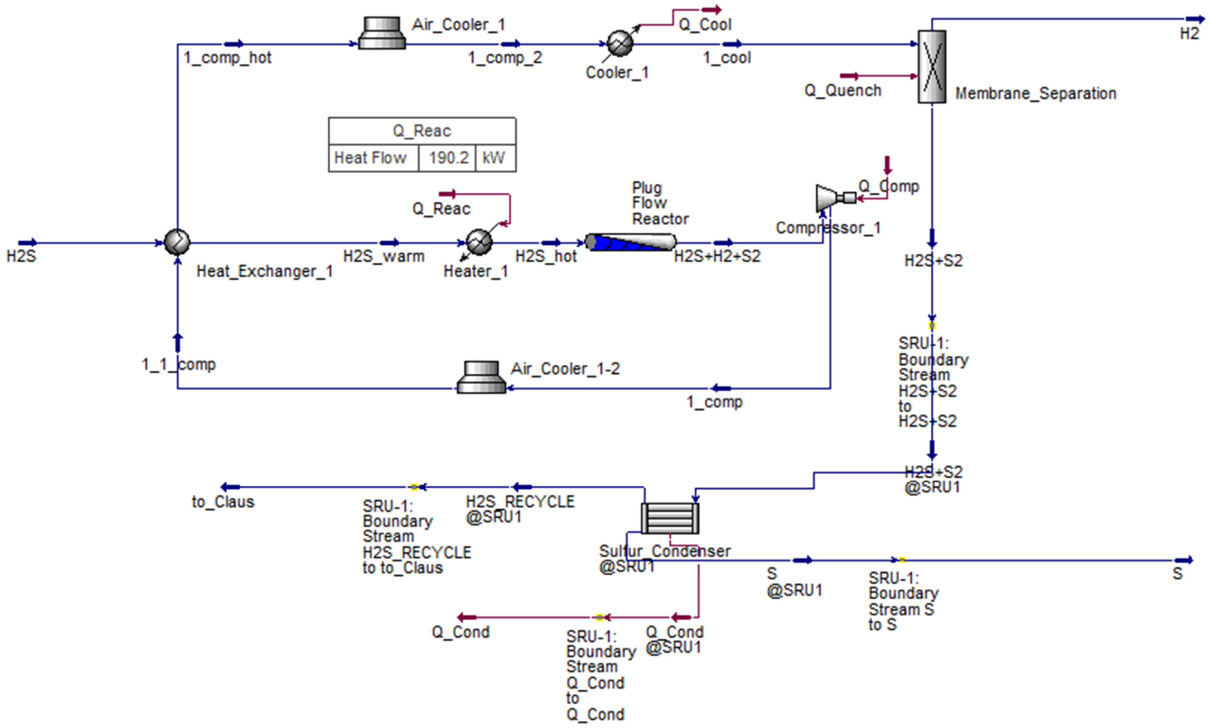

Figure 28: PFD Direct Thermal Decomposition of Hydrogen Sulfide

The optimized model is working with the same principles discussed in the process model overview section 6.3.2, but a few operators have been added to the PFD. A Heat Exchanger was added to warm the feed stream H_2S by utilizing the reactor outlet stream's heat and reducing the reactor's power consumption by 30%. Furthermore, a compressor was added downstream of the reactor and two air coolers and a cooler were added after compression to ensure a pressure/temperature that is required for membrane separation of hydrogen. Membrane separation efficiency is assumed to be 100%.[66]In Table 8 the pressure and temperatures of all material streams are presented.

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[66] Honeywell :UOP Polysep Membrane Systems: https://www.uop.com/?document=polysep-membrane-for-gas-extraction-purification&download=1

Stream	Temperature [°C]	Pressure [bar]
H2S	35	1.1
H2S_warm	350	1.05
H2S_hot	1100	1
H2S+H2+S2	1020	1
1_comp	1761	11.95
1_1_comp	1500	11.85
1_comp_hot	1265	11.8
1_comp_2	1000	11.7
1_cool	900	11.6
H2	100	11.6
H2S+S2	100	11.6
S	100	1.05
to_Claus	100	1.05

Table 8: Material Streams PFD

In Appendix A, the complete HYSYS report, containing all energy and material streams, is added. Based on this optimized model, the economic analysis is conducted in the following chapters.

6.4 HYSYS Modelling: Hydrogen Sulfide Methane Reformation

6.4.1 Process Model Overview

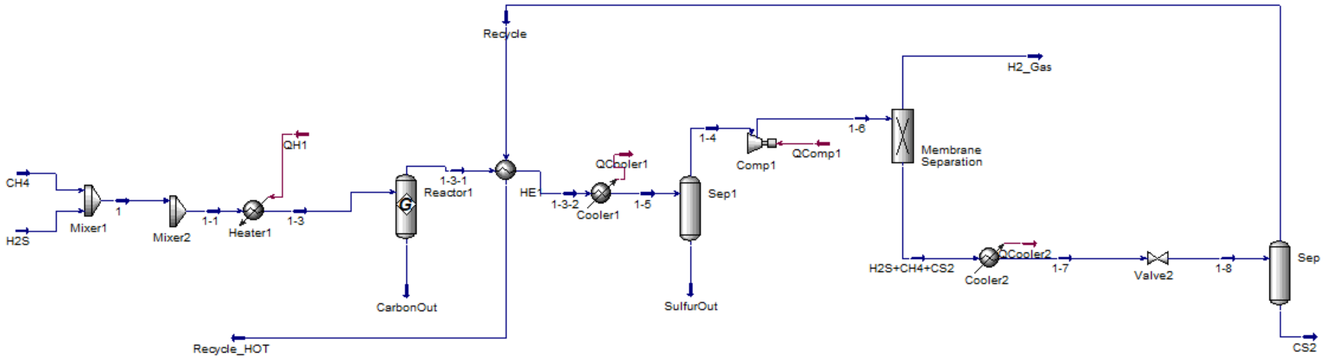

Figure 29: Preliminary PFD H_2SMR

Unfortunately, during modelling, no fit to experimental data was achieved during reactor design and following verification. Due to the massive nature of discrepancies in conversion rates, the model was not used for further analysis because of major uncertainties arising because of this fact concerning economics. Results from the verification can be seen in Appendix A.

7 Economic Analysis

This chapter will establish an integrated, top-down approach for an economic analysis, based on the simulation outputs from the following chapters.

7.1 Methodology

To successfully set up a profitable business idea, it is of pinnacle importance to set up organization and the willingness to develop through risk-taking and innovation. In economics, leadership combined with land, labour, resources and capital can equal profit. [67] Therefore, it is paramount to understand and set up a functioning organizational structure in order to achieve these goals. [68]

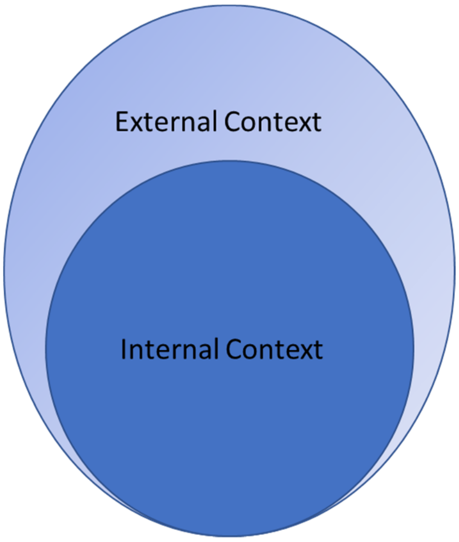

Figure 30: Organizational context cf. ISO 9001:2015

As stated above, the methodology used in this analysis is based on a number of perspectives, starting from the external context, which includes:

- Market Outlook of produced products and commodities

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[67] Business Dictionary: Definition of Entrepreneurship, http://www.businessdictionary.com/definition/entrepreneurship.html#ixzz3Emczs9AQ< Accessed 20.1.2020

[68] Cf. ISO 9001:2015 (2015): Clause 4, p. 1

From these conclusions, the internal context of organization is analysed by:

- Strategic Management considerations, based on the external context and company organization on a visionary and normative level and
- Operational Management considerations, which includes a Costing Analysis

Looking at a functioning organizational structure with profitable operations, it has to be aligned with all building blocks of the organizational structure, depicted in Figure 31 .

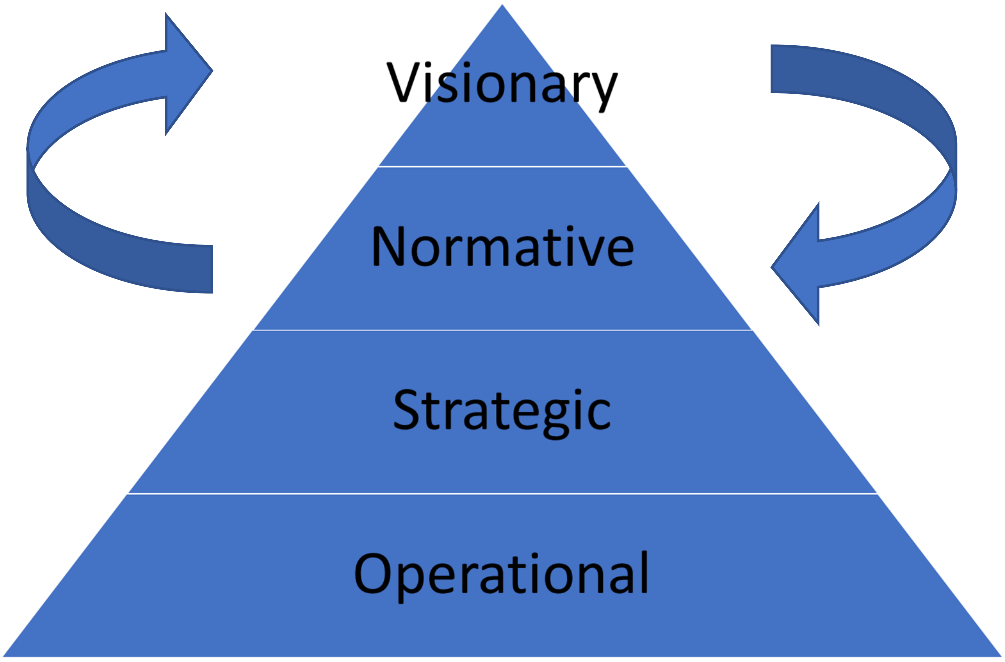

Figure 31: Organizational Structure[69]

According to “The Harvard Business Review”[70], it is imperative for managers throughout the entire company in order to understand the interest of the company as a unit in order to be successful, and not only focus on business units. Therefore, it is important to not only analyze operational costs, but also look at sustainability, governmental regulations and market aspects to see the bigger picture in order focus on long-term growth and profitability.

With these considerations in mind, the next chapter will focus on a market outlook of the produced goods.

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[69] Bundesverband Deutscher Unternehmensberater e.V. (2018): „Unternehmerische Kompetenz in der Unternehmensnachfolge“;https://www.bdu.de/fachthemenportal/gruendung-und-nachfolge/unternehmerische-kompetenz-in-der-unternehmensnachfolge/; Accessed 20.1.2020

[70] Harvard Business Review (2019): “Why Visionary Leadership Fails”; https://hbr.org/2019/02/why-visionary-leadership-fails; Accessed 20.1.2020

7.2 Market Outlook and Analysis

In order make important business decisions and implement strategic and operational plans, it is important to analyze market conditions of produced products and commodities by the company in mind.

Product	Input/Output
Hydrogen	Output
Sulfur	Output
Hydrogen Sulfide	Input

Figure 32: Products in this study subject to market research

To perform an analysis of a market, five categories where evaluated, consisting of:[71]

- Market size
- Target Costumers
- Competition
- Market Growth
- Potential Disruptors

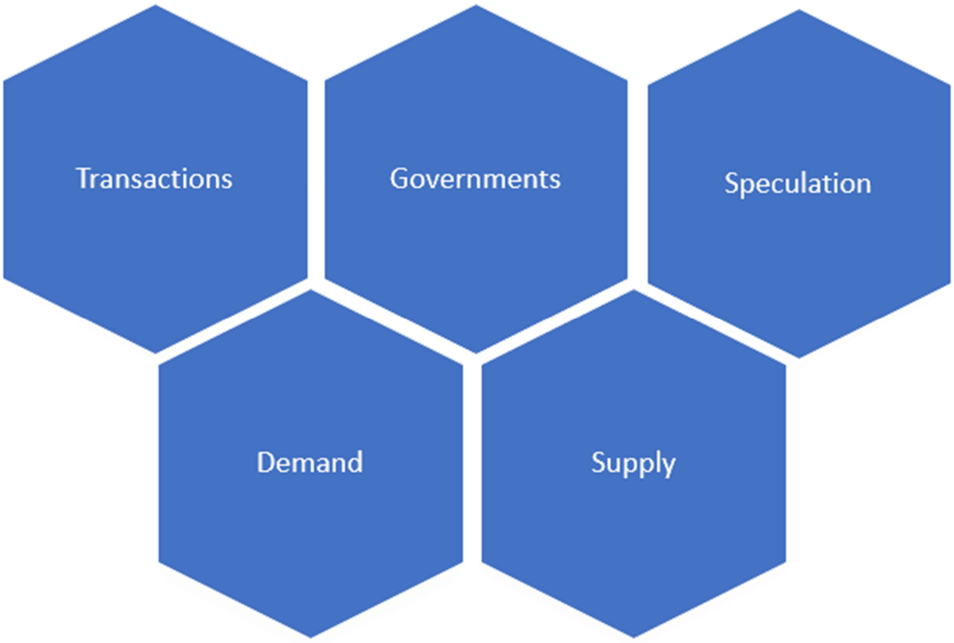

Figure 33: Five Factors for Market Movements

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[71] MarketResearch.com (2019): “What is a Market Analysis?”; https://blog.marketresearch.com/what-is-a-market-analysis; Accessed 20.1.2020

Prices of commodities and products alike are subject to the global market, which allow a company to capture profits. These markets are subject to fluctuations and over time, these fluctuations can change profitability. There are five major factors that can cause both long-term and short-term price movement:[72] This study aims to focus mainly on the side of Governments and Supply/Demand, as to include every consideration would enlarge the scope of this work. This market analysis directly influences the assumptions made during cost calculation following in the final chapters of this thesis.

7.2.1 Hydrogen

7.2.1.1 Hydrogen Market

Figure 34: Hydrogen Import Values (2017)[73]

Hydrogen is mainly used for refining petroleum, treating metals, producing fertilizers and processing foods.[74] With a total import volume of 11.7 Billion $ worldwide, China is by far the biggest importer of hydrogen, followed by Japan, as seen in Figure 34.

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[72] Investopedia (2019): „4 Factors That Shape Market Trends"; https://www.investopedia.com/articles/trading/09/what-factors-create-trends.asp; Accessed 20.1.2020

[73] Source: Observatory of Economic Complexity, oec.world; dataset: HS92

[74] U.S. Dept. Of Energy: https://afdc.energy.gov/fuels/hydrogen_basics.html; Accesed 20.1.2020

Looking at the change of trade volume for hydrogen, we can observe a sharp increase in imports during the early 2000's, mainly due to Asian markets, depicted in Figure 35 below.

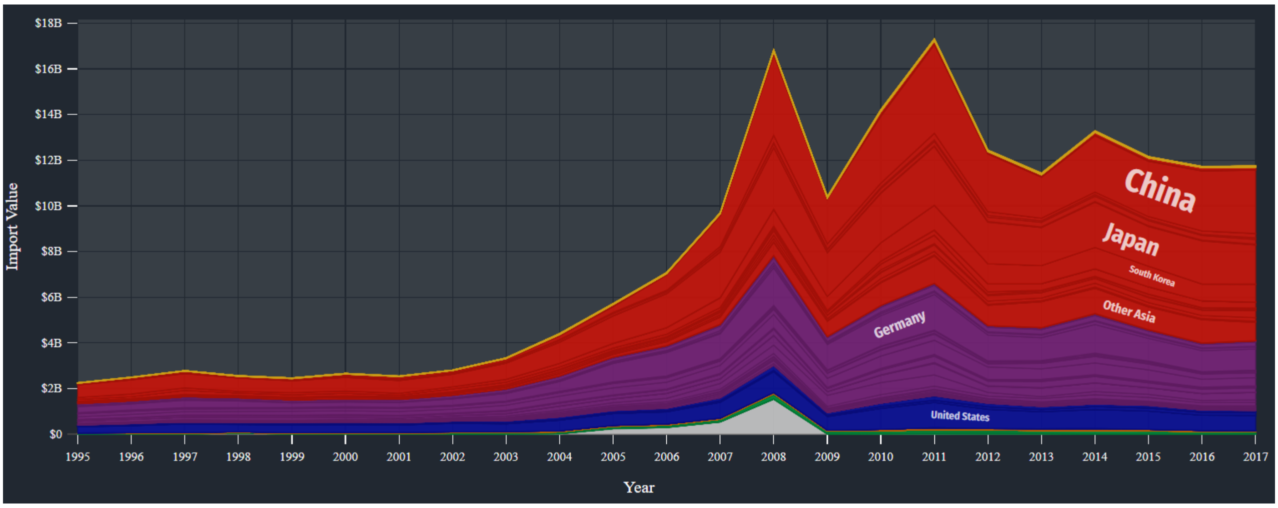

Figure 35: Hydrogen Imports 1995 - 2017[75] (Asian markets in red)

According to market research data[76] and business intelligence companies[77], the hydrogen market is expected to have a Compound Annual Growth Rate (CAGR) of more than 5%, with most of the growth happening in Asia and Africa during the next 5 years.

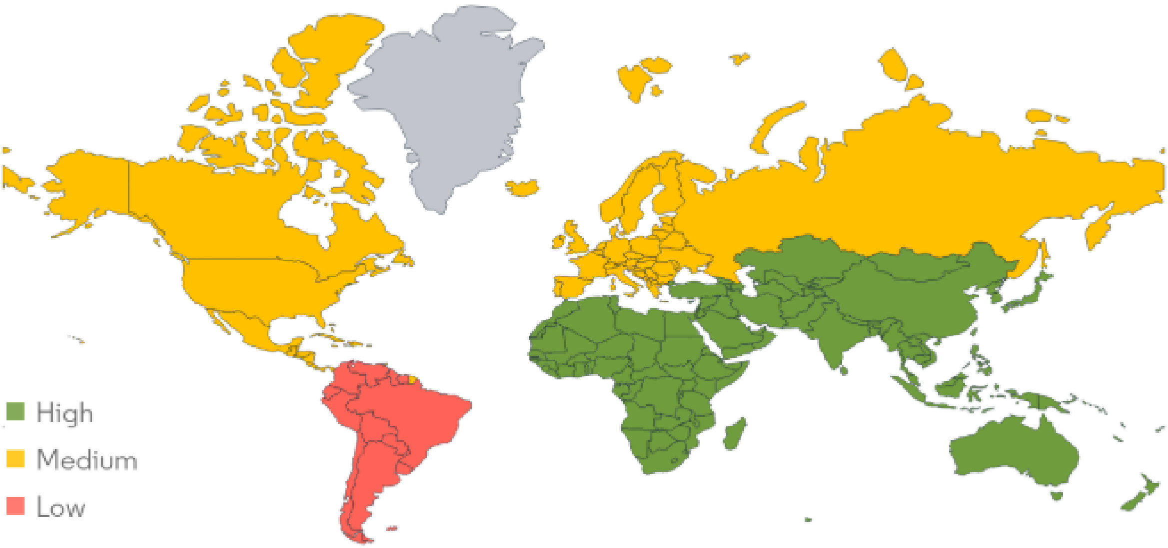

Figure 36: Hydrogen gas market's growth rate – by region 2019-2024[76]

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[75] Source: Observatory of Economic Complexity, oec.world; dataset: HS92

[76]Source: Mordor Intelligence (2019): Hydrogen Gas Market Industry Report; https://www.mordorintelligence.com/industry-reports/hydrogen-gas-market; Accessed 20.1.2019

7.2.2 Sulfur

7.2.2.1 Sulfur Market

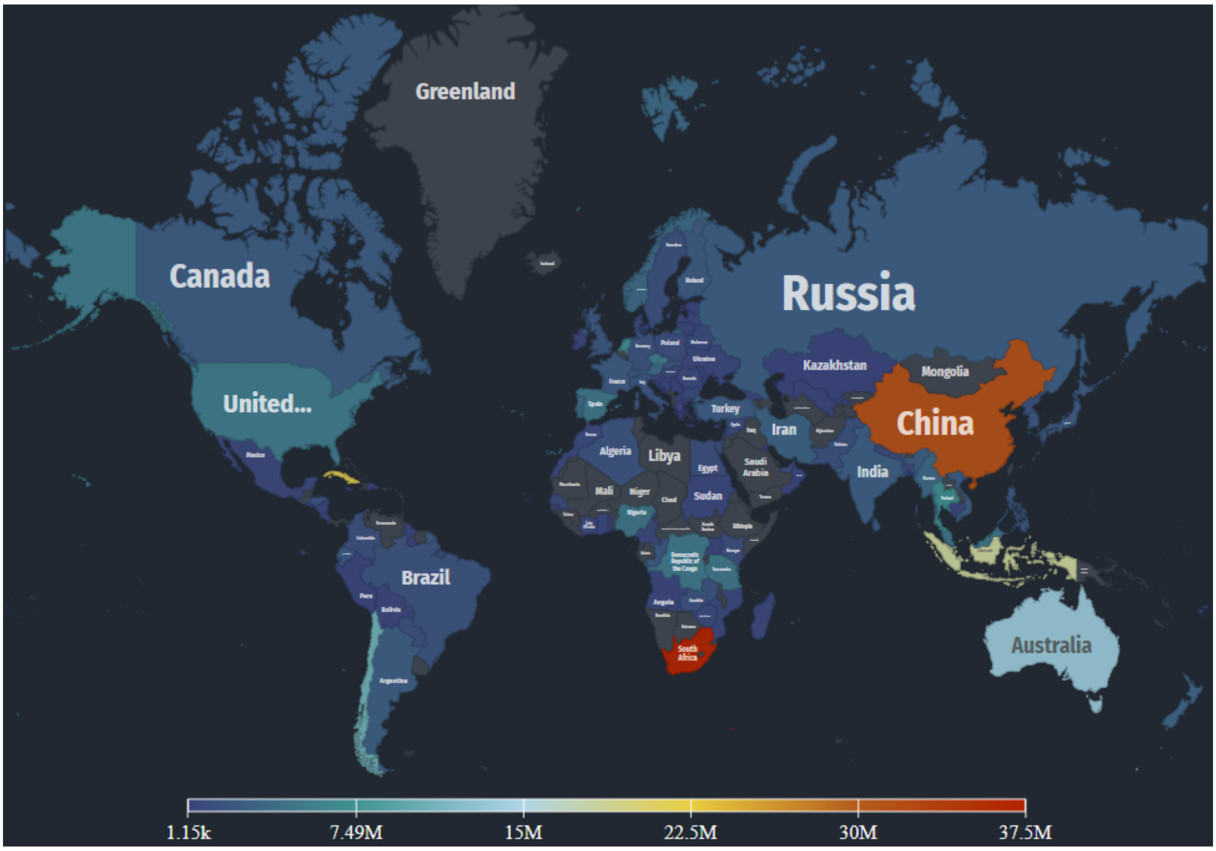

Figure 37: Sulfur Import Values (2017)[77]

Approximately, 6/7th of sulfur in used to produce sulfuric acid, which is largely used to manufacture fertilizers. Other important uses include the production of detergents, fibres, petroleum products, sheet metal, batteries and explosives.[78]

As seen in Figure 37, a total of 195 Million $ of sulfur was imported worldwide, with the biggest importers being South Africa and China. Sulfur imports have dropped significantly during the last few years, reaching a decade low-point in 2017, shown in Figure 38. Sulfur is mostly produced as a by-product of metallurgy and petroleum production.[79]

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[77] Source: Observatory of Economic Complexity, oec.world; dataset: HS92

[78] Encyclopaedia Britannica: „Uses of sulfur"; https://www.britannica.com/science/sulfur/Commercial-production#ref279410; Accessed 20.1.2020

[79] Australian Dpt. Of Energy and Mining:"Sulfur"; http://energymining.sa.gov.au/minerals/mineral_commodities/sulphur; Accessed 20.1.2019

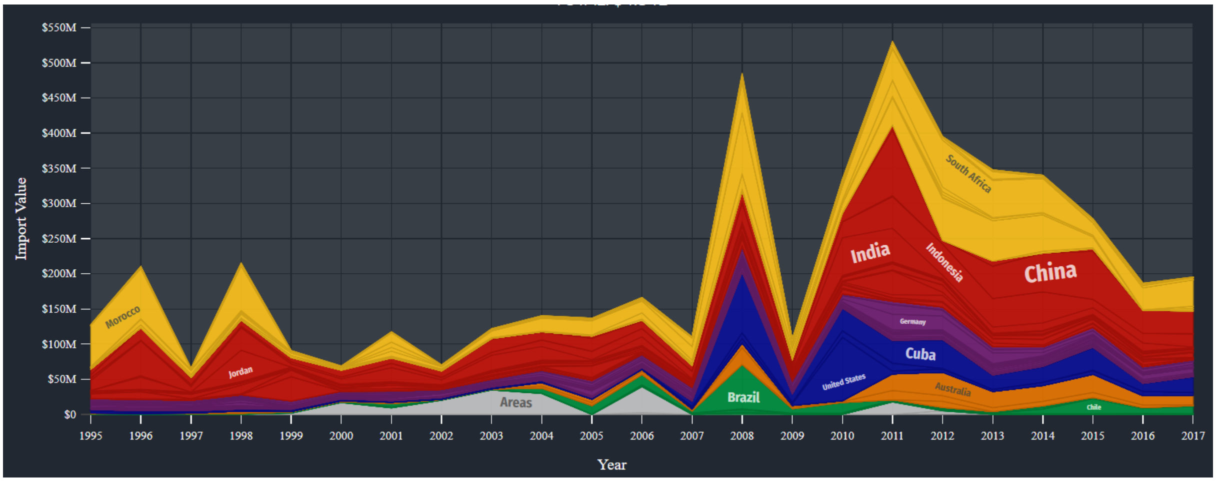

Figure 38: Sulfur Imports 1995 - 2017[80]

According to reports of Mordor Intelligence [81], Sulfur is expected to reach a CAGR of about 3%, mainly because of an increase in demand of fertilizing products worldwide. Arguably, the IMO's (International Maritime Organization) decision to reduce sulfur content in heavy fuel oil from 3.5% to 0.5% (mass/mass) by 2020 will spike sulfur supply even higher and drop prices subsequently, harming the market prospects.[82]

7.2.3 Hydrogen Sulfide

7.2.3.1 Hydrogen Sulfide Market

Hydrogen Sulfide is mainly used in the production of sulfuric acid and elemental sulfur mainly as a reagent and intermediate, because it can prepare other types of sulfur compounds. [83] During research, no hydrogen sulfide market per-se could be identified (only on a laboratory scale) as it is mainly produced as a by-product of petroleum production during Hydrodesulfurization (HDS) and subsequently neutralized because of environmental and safety reasons. Therefore, it can be seen as a pollutant, which can cause substantial cost, and not a resource.[84]

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[80] Source: Observatory of Economic Complexity, oec.world; dataset: HS92

[81] Mordor Intelligence: Sulfur Market – Growth, Trends, and Forecast (2020-2025); https://www.mordorintelligence.com/industry-reports/sulfur-market; Accessed 20.1.2020

[82] International Maritime Organization (2020): "Sulphur 2020"; http://www.imo.org/en/MediaCentre/HotTopics/Pages/Sulphur-2020.aspx; Accessed 20.1.2019

[83] Sciencing (2017): „Uses for Hydrogen Sulfide"; https://sciencing.com/bacteria-respire-4565280.html; Accessed 20.1.2020

[84] Khan, R.; Sayed, E. (2011): "Advances in Clean Hydrocarbon Fuel Processing", pp. 243-261

7.2.4 Market Research Summary

To signify the feasibility of the economics of this study, focusing on a market-based view, the two products are now compared.

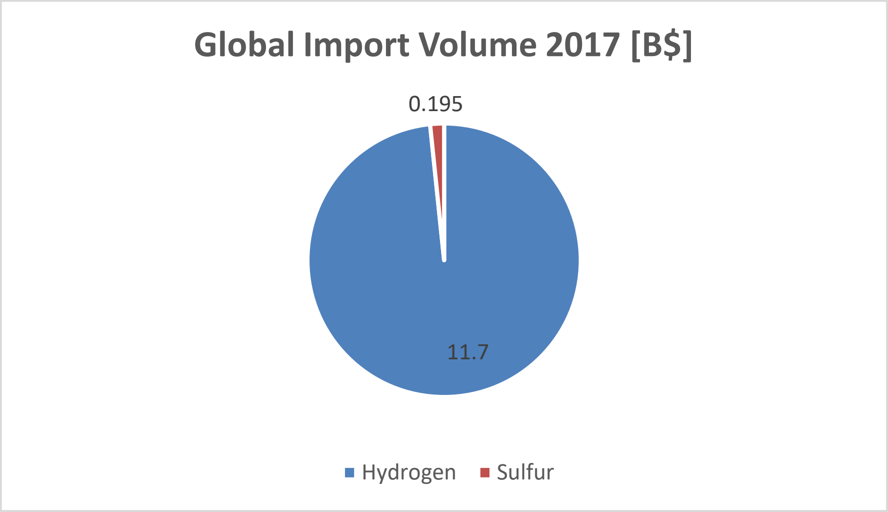

Figure 39: Global Import Volume Comparison

As seen in Figure 39 above, a massive difference in import volumes can be observed. Compared to sulfur, hydrogen imports have achieved more than 50 times the import volume of sulfur in recent years.

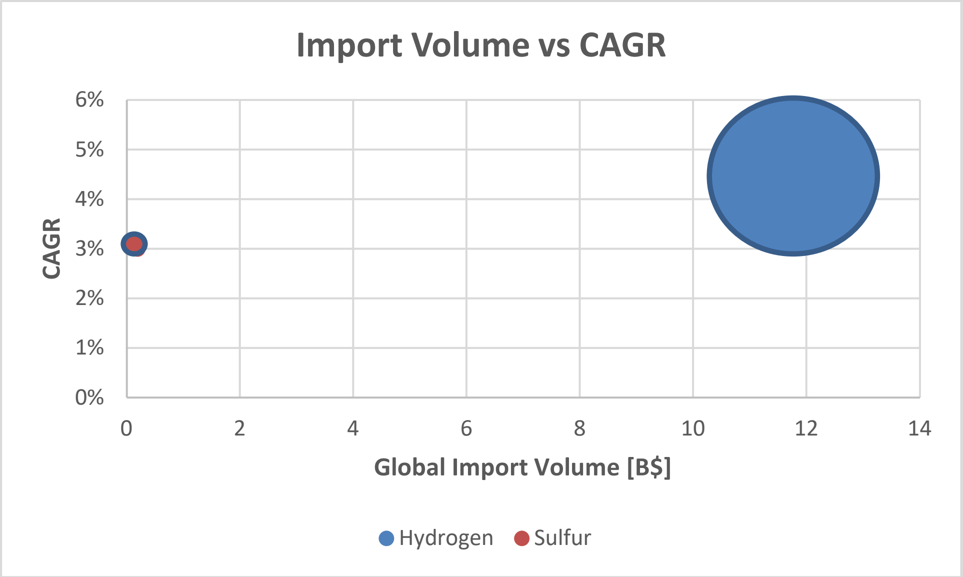

Figure 40: Import Volume vs CAGR Comparison

Figure 40 shows the comparison of hydrogen vs sulfur in both a market-volume and growth context. Comparing both outlooks, it can be seen that from a market point of view, that the hydrogen market poses more favorable conditions overall, with exceeding the sulfur market in both CAGR and volume. Below in Figure 41 a summary of the findings during market research are depicted.

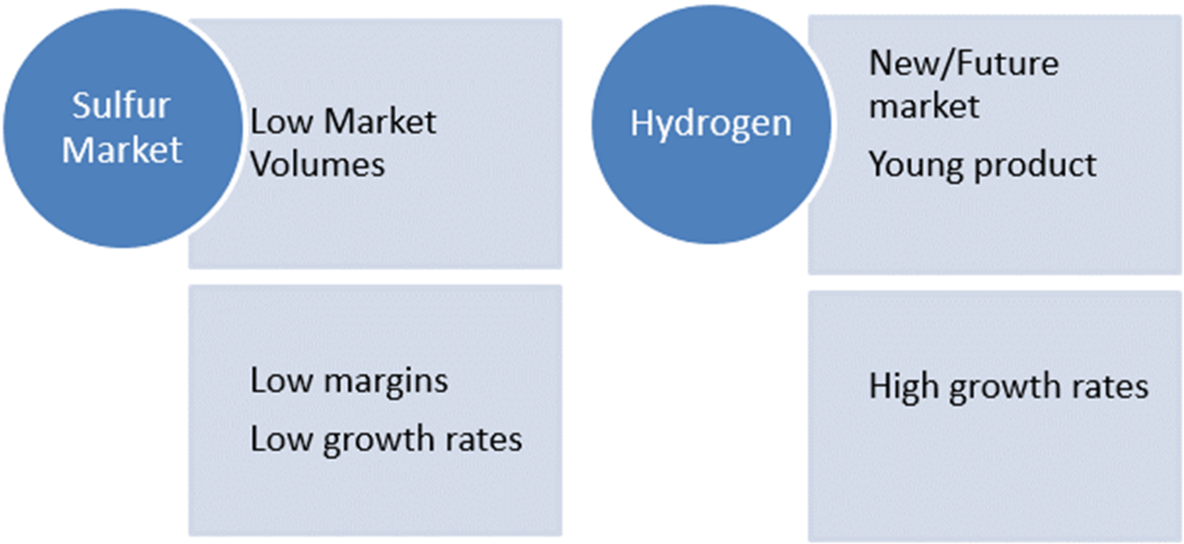

Figure 41: Market/Product Summary Comparison

Overall, production of hydrogen from hydrogen sulfide instead of sulfur can be seen as a good opportunity to ensure future growth and sustainability of operations and could add to the value of the company and furthermore act as a diversifying agent in the turbulent and highly cyclic energy business environment. On top of that, according to the International Energy Agency and its council members is currently investing 1.4 Billion € per year and is expected to grow to 1.9 Billion € during the next five years. [85]

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[85] IEA hydrogen (2017): Global Trends and Outlook for Hydrogen; p.16

7.3 Costing Analysis

In this chapter, a cost model is built on top of the market-based assumptions from the previous chapter and the output from the simulation model in Chapter 6.3.5.

7.3.1 Theory

Modern Cost Management and Accounting is trying to capture and analyze the techniques employed by the organization to drive success. *It is not solely focused on cost cutting, but must also be mindful of measuring and instituting control that drive an efficiently produced product.* [86] For this purpose, a type of Direct Costing approach is utilized, which is defined as a *plan for providing management with more information about cost-volume-profit relationships and for presenting this information in a form more readily understandable by management at all levels. (Cf. Walther, Skousen (2009))*

In this analysis, the Process Costing Method is used and acts as a performance controlling system. This approach is often employed when the system under investigation is a continuous flow of raw materials through various processes. [87] To create business value, good management decisions are mandatory and according to research, this method is fit for purpose of this work.[88]

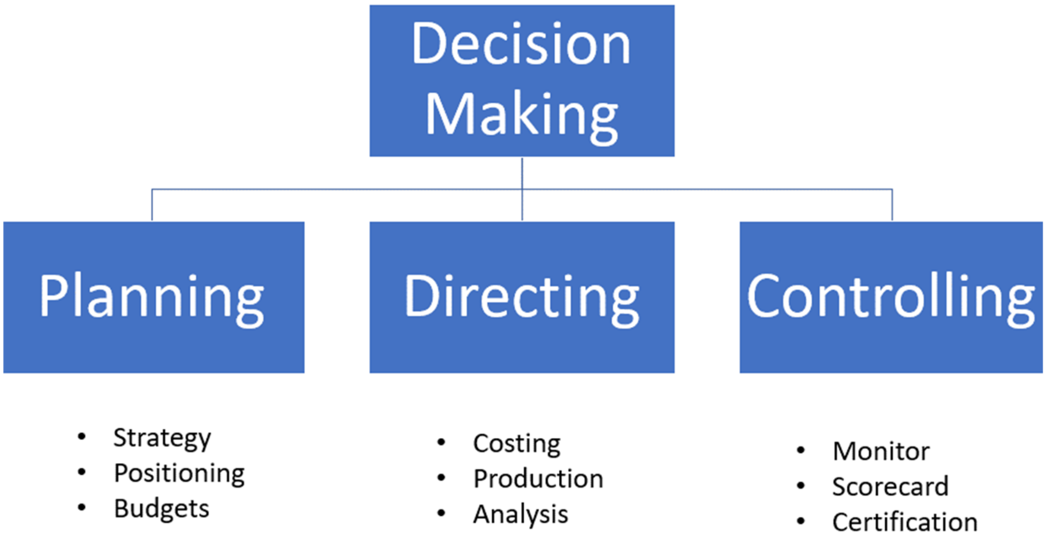

Figure 42: Decision Making Tree for Business Value Creation[89]

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[86] Walther, L. M.; Skousen, C.J. (2009): p. 98

[87] Walther, L. M.; Skousen, C.J. (2009): p. 100

[88] Topic, M. personal communication, 08.01.2020

[89] Walther, L. M.; Skousen, C.J. (2009): p. 11

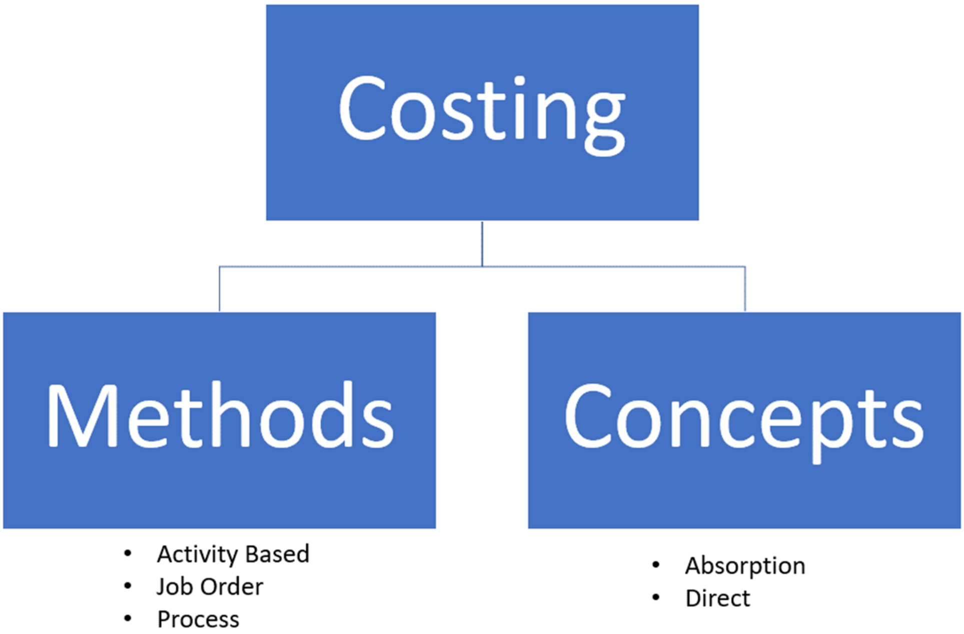

Figure 43: Cost Accounting Tree[90]

Process Costing is a costing method that pools together the aggregate cost of producing a homogenous item. The output of this process is then measured in aggregate quantities, where the "Process Cost" is defined as:[91]

$$Cost\ per\ unit = \frac{Cost\ of\ inputs}{Expected\ Output\ in\ Units} \tag{29}$$

Equation 30: Definition Process Unit Cost

The method is used to average the total cost of the process during production and takes into account all costs incurred during the process cycle, which mainly are:

- Labor cost (Operating Labor, Supervision, Quality Control and Maintenance)
- Material cost (Raw Material, Catalysts and Solvents)
- Overhead cost
- Utility cost (Electricity, Fuel, Steam, Water)

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[90] Walther, L. M.; Skousen, C.J. (2009): p. 17

[91] Association of Chartered Certified Accountants (ACCA): "Process Costing" Technical Paper; https://www.accaglobal.com/content/dam/acca/global/pdf/sa_june11_process2.pdf; Accessed 21.1.2019

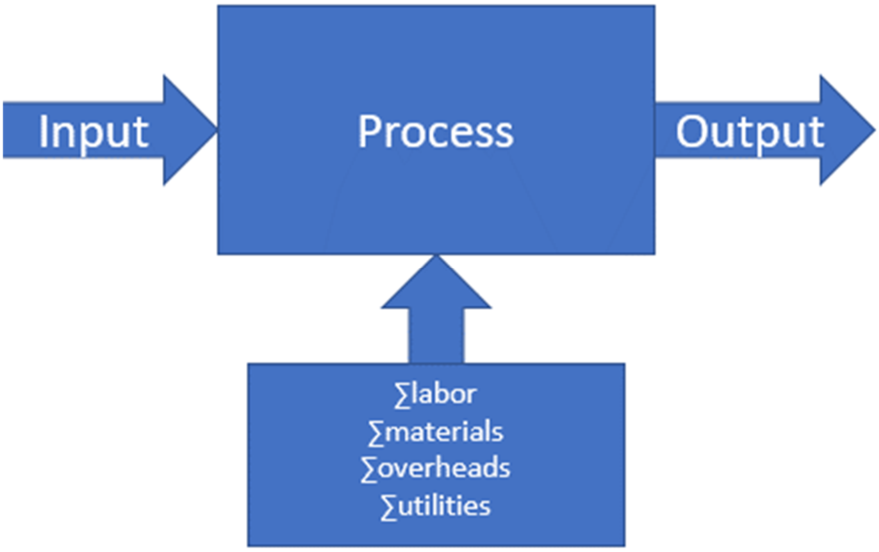

Figure 44: Process Cost flow chart[92]

7.3.2 Assumptions

In Figure 44 the concept of Process Costing is shown. With the application of this concept, he summation of all costs generated by the process are attached to the process itself, where they are incurred. **Error! Reference source not found.** shows the process system boundary used for this study during cost estimation. That means, that all the calculations start with using the already available sour gas input (H_2S) stream, finish with the output of hydrogen (H_2) and sulfur (S) streams, and consequently do not account for treating the recycled gases.

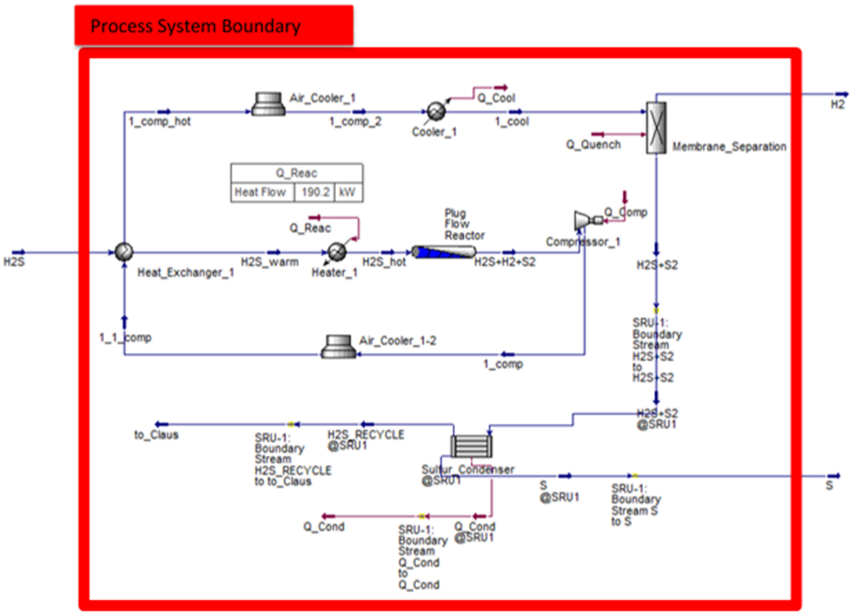

Figure 45: Process System Boundary for Cost Estimation

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[92] Source: Kaplan Financial Knowledge Bank; https://kfknowledgebank.kaplan.co.uk/management-accounting/costing/process-costing; Accessed 21.1.2019

Furthermore, as an additional assumption for cost estimation, it is assumed that the plant is already bought and fully depreciated, as a full economic analysis with capital estimation for such an experimental process would expand the scope of this work too much. [93] In the following section, all assumptions for all cost drivers utilized in this study will be analyzed and explained. Keeping the levels of accuracy of cost analyses depicted in Figure 46 in mind, this study should not be used as an accurate representation situation but rather as a rough estimation. With the amount of uncertainties and assumptions that are presented in this thesis, this analysis is done with best practices in mind, while relying on assumptions based on literature and former research on top of the simulation-related uncertainties. This is why a ± 30 – 40% accuracy can be expected.

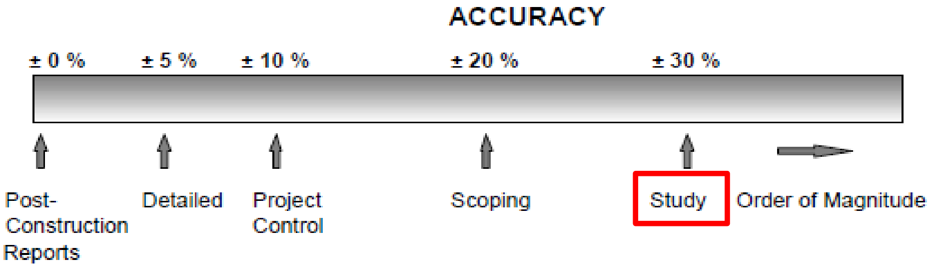

Figure 46: Levels of Accuracy for Cost Analyses[94]

7.3.2.1 Material Cost

The only raw material used for this process is sour gas, mainly containing H_2S, which usually acts not as a resource, but rather a byproduct of petroleum processing and production as already discussed in section 7.2.4 during market research summary. As this is a pollutant, neutralization inquires cost and, depending on business cases, it can be procured from external sources by either credit or cost. Depending on the business case, the credit for H_2S procurement was assumed at 25 [$/ton] for a best-case scenario, which was based on the cost of treating gas containing 19% of H_2S with conventional technologies. [95] For the other scenarios, it was assumed that the sour gas was produced on site without additional feedstock cost. As this process is non-catalytic, no catalysts or solvents were used.

$$Raw\ Material\ Cost = Amount\ x\ Cost \tag{31}$$

Equation 32: Raw Material Cost Estimation[96]

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[93] Siegmeth, F. personal communication, 08.01.2020

[94] Source: Sorrels, J. L.; Walton, T. G. (2017): p. 7

[95] Lockhart, T.; Crescenzi, F. (2007): p. 245

[96] Silla, H. (2003): p. 47

7.3.2.2 Utility Cost

As the thermal decomposition of sour gas is a highly endothermic process, as discussed in the beginning of this study, a large amount of electrical energy is needed. In the best-case scenario, this energy could be provided by on-site supplied gas generation, which could be fueled by self-supplied natural gas, which does not inquire cost, but rather opportunity cost by not selling this gas. As CIS states (Commonwealth of independent states) should be the operational focus of this study, this gas price was estimated as the weighted average annual price for industrial consumers in Russia (2018) as 4316.4 [Rub/1000m^3], which translates to 69.83 [\$/1000m^3].[97] As total power requirements do not exceed 700[kW], two 350[kW] gas generators, running on full load should suffice for this operation. The total gas fuel consumption was estimated at 127.4[m^3/h] for full load. [98] In a worst-case scenario, the full power consumption is supplied by grid electricity, at a price of 0.052[\$/kWh] for the industrial sector in Kazakhstan. [99] Water requirements for cooling were not included in this estimate.

$$Utility\ Cost = Power\ Consumed\ x\ Cost \tag{33}$$

Equation 34: Utility Cost Estimation [100]

7.3.2.3 Labor Cost

Cost of labor is difficult to estimate.[101]Labor is a function of the numbers of operators per shift required for the process and the hourly rates. The number of operators depends on the size of the facility and the hourly rates depend on the geographic location of the plant. Furthermore, the level of automation, number of production steps and the level of productivity needs to be accounted for. [100]For labor cost, an average hourly rate of 4.79[€/h] was used in order to simulate a plant location in Russia/CIS, which equates to 5.32[\$/h] (21.1.2020).[102] Usually, especially in the chemical industry, the overall labor cost percentage of total product cost is low (11% in EU including overhead and maintenance).[103]

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[97] Gazprom (2018): p. 123

[98] Generatorsource.com: Approximate Natural Gas Consumption Chart; https://www.generatorsource.com/Natural_Gas_Fuel_Consumption.aspx; Accessed 21.1.2020

[99] Energypedia : Kazakhstan Energy Situation; https://energypedia.info/wiki/Kazakhstan_Energy_Situation; Accessed 21.1.2020

[100] Silla, H. (2003): p. 47

[101] Smith, R. (2005): p. 28

[102] Boulamanti, A.; Moya, J. A. (2017): p.1208

[103] JRC Science for Policy Report, European Commission (2016): p.21

7.3.2.4 Operating Labor

Operating Labor Cost is estimated by multiplying the operating-labor man-hours [h/kg] and multiplying by the cost per hour [$/h] as stated in Equation 36 below. The overall assumption includes a 24-hour production cycle, 365 days of the year and as it is assumed that this process is part of a plant-complex with high automation level, one main operator plus supervision and quality control plus maintenance personnel is calculated into the cost estimation.

$$Operating\ Labor\ Cost = L\ x\ Cost \tag{35}$$

Equation 36: Operating Labor cost estimation[101]

Where:

- L = operating-labor man hours [h/kg]
- Cost = hourly rates [$/h]

7.3.2.5 Operating Supervision

Every Operator needs to be assigned a supervising manager, which needs to be accounted for in cost estimation and were estimated at 0.20 x Operating Labor Cost. [101]

7.3.2.6 Quality Control and Maintenance

For Quality Control purposes and Maintenance during the entire production process, a quality control cost needs to be added. This cost was estimated at 0.20 x Operating Labor Cost. [101]

7.3.2.7 Plant Overhead Cost

Fringe benefits and overhead cost where estimated at 0.22 x (Labor Cost + Supervision) and 0.5 x (Labor Cost + Supervision) respectively.[101]

7.3.2.8 General Costs

For Marketing and Administration, 0.045 x Production cost and 0.135 x Production cost respectively were accounted for.[101]Additionally, 0.0575 x Production Cost as Research and Development Cost were added.

7.3.3 Total Production Cost

The total production cost was calculated as the sum of all items from section 7.3.2.1 to 7.3.2.8 and is shown in Table 9.

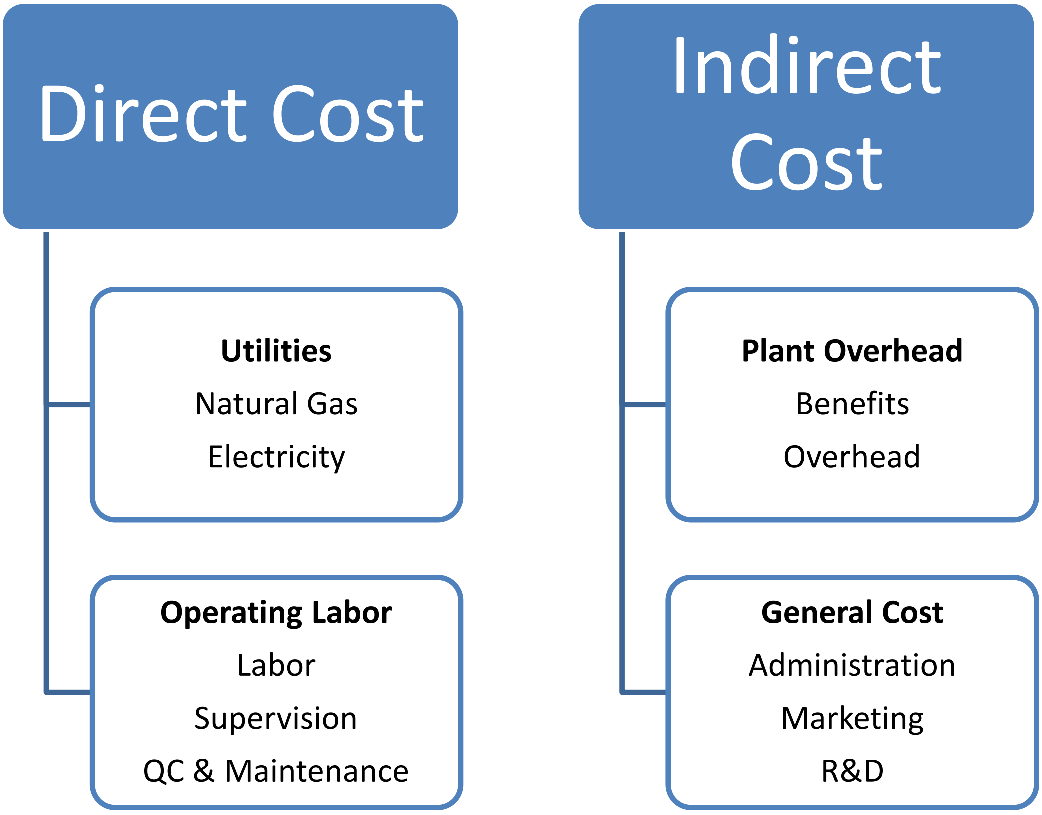

Figure 47: Cost Structure for Production Cost Estimation

Direct Cost	**Type**	**Calculation**
Raw Materials	H_2S	Amount x Cost
Utilities	Natural Gas	Power Consumed x Cost
	Electricity	Power Consumed x Cost
Operating Labor	Labor	L x Cost
	Supervision	0.20 x Labor Cost
	QC and Maintenance	0.20 x Labor Cost
Indirect Cost		
Plant Overhead	Benefits	0.22 x (Labor Cost + Supervision Cost)
	Overhead	0.50 x (Labor Cost + Supervision Cost)
General Costs		
Administration		0.045 x Production Cost
Marketing		0.135 x Production Cost
R&D		0.0575 x Production Cost
Production Cost		Σ of Above Items

Table 9: Calculation Procedure for Total Production Cost (Cf. Winter (1969), Humphreys (1970))

7.3.4 Business Scenarios for Cost Estimation

Three business case scenarios were established to include a wide range of possibilities into the cost calculation procedure. The business scenarios for cost calculation are:

1. Best Case Scenario:
    a. Natural gas on-site used for utility (power generation)
    b. Full credit for H_2S procurement granted (assumed equal storage cost from desulphurization, as discussed in chapter 7.3.2.1)
2. Medium Case Scenario:
    a. Natural gas procured for utility (power generation)
    b. “Free” H_2S from former process
3. Worst Case Scenario:
    a. Grid electricity used for utility (power generation)
    b. H_2S procured at a price (assumed equal storage cost from desulphurization, as discussed in chapter 7.3.2.1)

7.4 Cost Estimation Results and Business Scenarios

Scenario 1 (Best case)	
Direct Cost	*Cost* [$/tH2]
Raw Materials	-$8 387.05
Utilities	$4 299.28
Operating Labor	$2 570.966
	$514.193
	$514.193
Indirect Cost	
Plant Overhead	$678.735
	$1 542.579
General Costs	
Administration	$455.40
Marketing	$1 366.19
R&D	$581.90
Production Cost	$4 136.39

Table 10: Best Case Scenario for Cost Estimation

Scenario 3 (Medium case)	
Direct Cost	*Cost* [$/tH2]
Raw Materials	$0.00
Utilities	$10 010.93
Operating Labor	$2 570.966
	$514.193
	$514.193
Indirect Cost	
Plant Overhead	$678.735
	$1 542.579
General Costs	
Administration	$712.42
Marketing	$2 137.27
R&D	$910.32
Production Cost	$19 591.61

Table 11: Medium Case Scenario for Cost Estimation

Scenario 3 (Worst case)	
Direct Cost	*Cost* [$/tH2]
Raw Materials	$8 387.05
Utilities	$16 407.29
Operating Labor	$2 570.966
	$514.193
	$514.193
Indirect Cost	
Plant Overhead	$678.735
	$1 542.579
General Costs	
Administration	$1 377.68
Marketing	$4 133.03
R&D	$1 760.36
Production Cost	$37 886.07

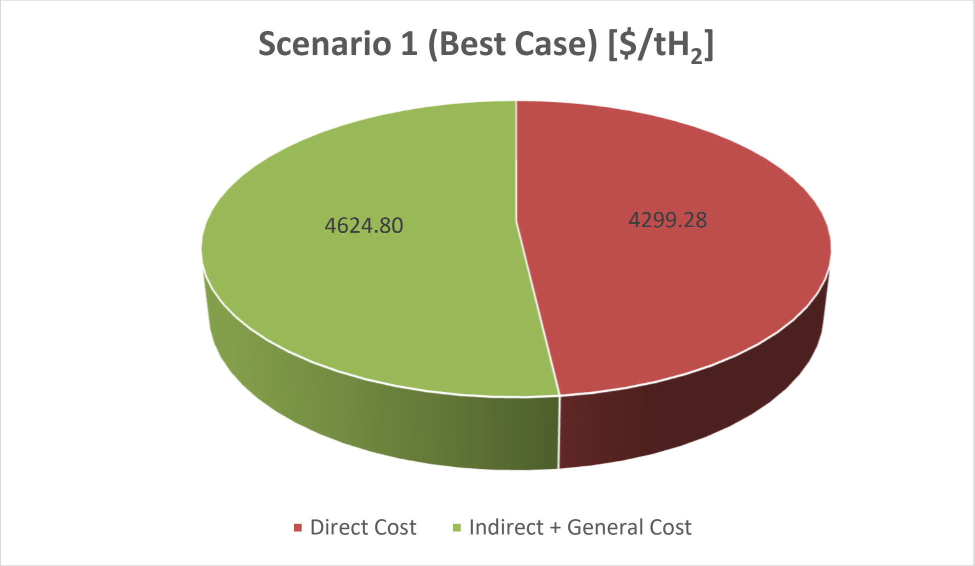

Figure 48: Direct vs Indirect + General Cost Scenario 1

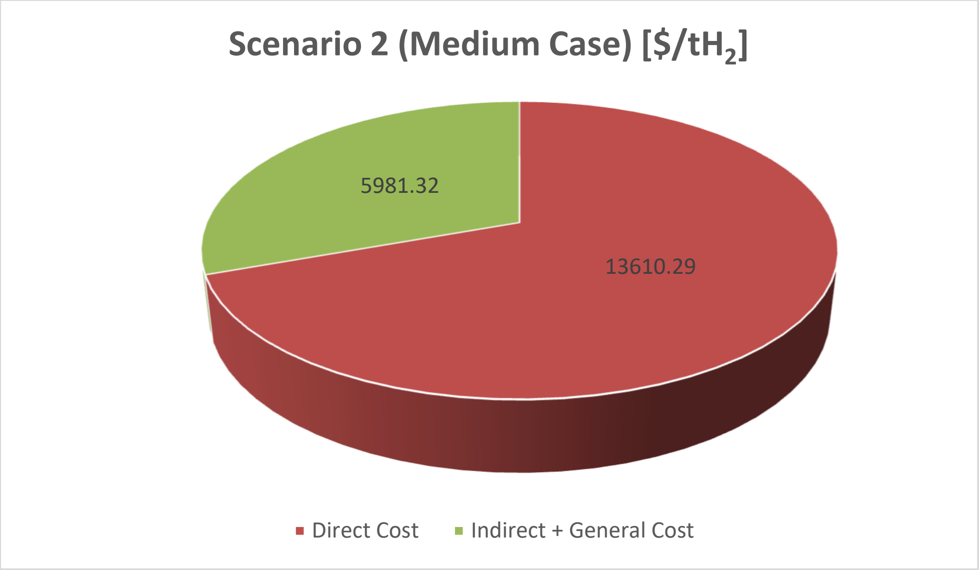

Figure 49: Direct vs Indirect + General Cost Scenario 2

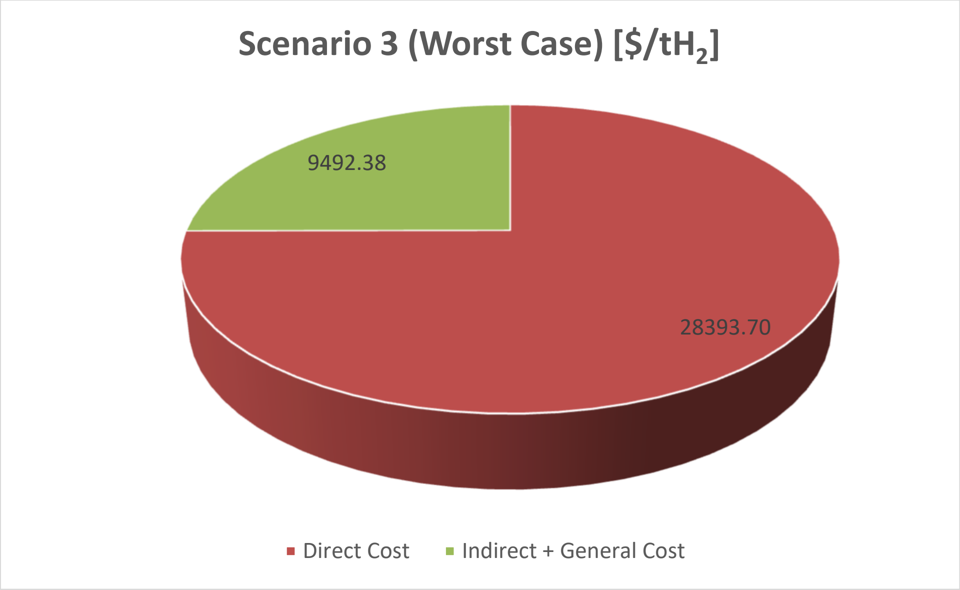

Figure 50: Direct vs Indirect + General Cost Scenario 3

As seen in Figure 48 to Figure 50, most costs are accrued as direct costs. Because of the credit for sour gas in scenario 1, direct material costs are held low. In scenarios 2 and 3 because of increasing utility costs and material costs, direct costs account for 50-75% of production costs, which is in-line with reports of the European Commission for the chemical industry.[104]

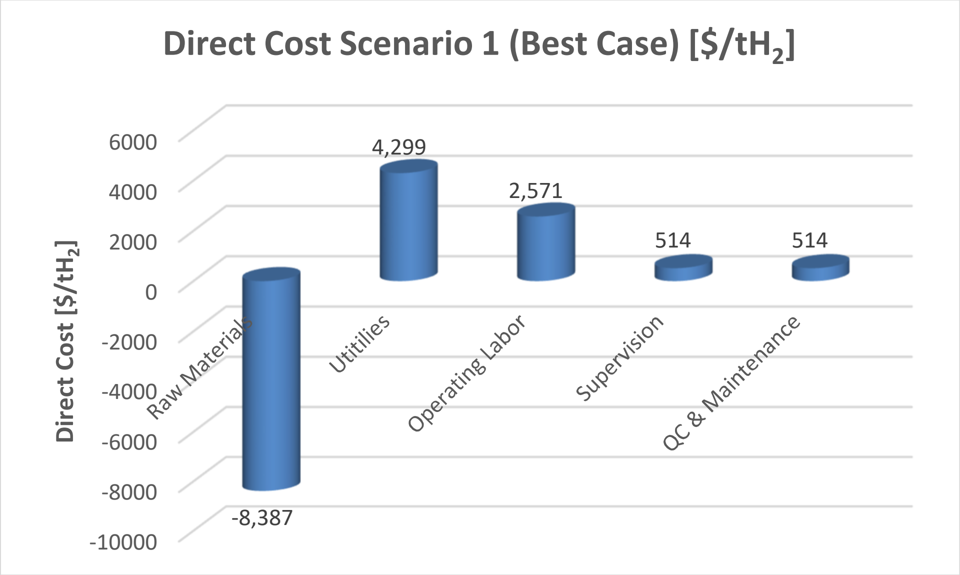

Figure 51: Direct Cost Composition Scenario 1

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[104] JRC Science for Policy Report, European Commission (2016): p.21

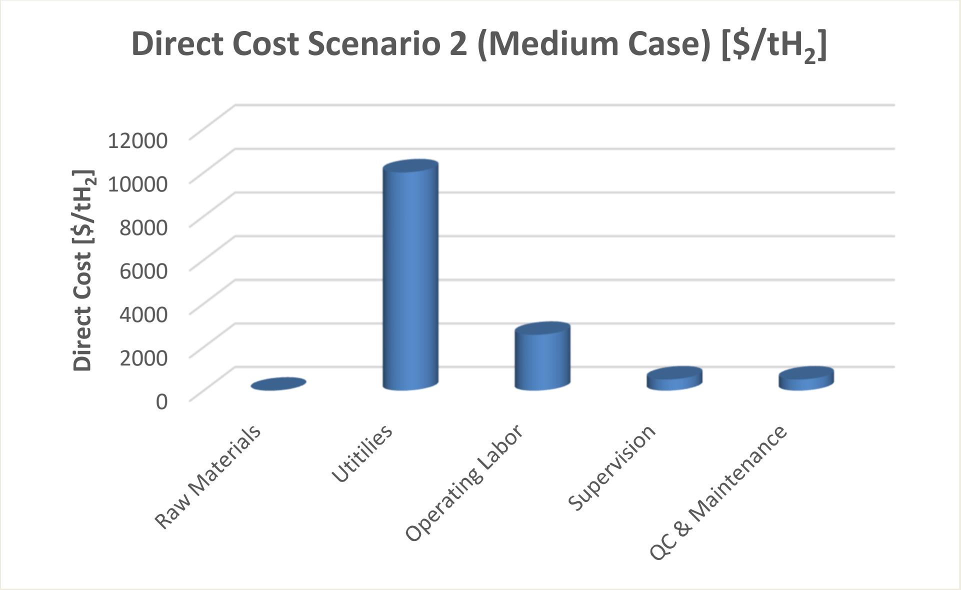

Figure 52: Direct Cost Composition Scenario 2

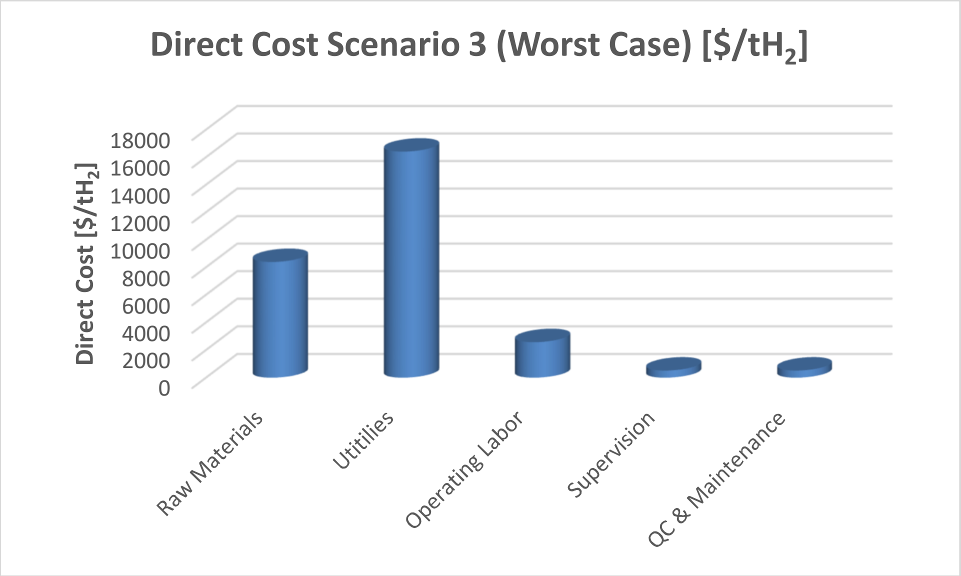

Figure 53: Direct Cost Composition Scenario 3

From Figure 51 to Figure 53 it can be seen that, because of the highly endothermic nature of the thermal dissociation reaction, most costs come from utilities and energy costs, especially in scenario 1 and 2, where material costs are seen as credit or zero respectively.

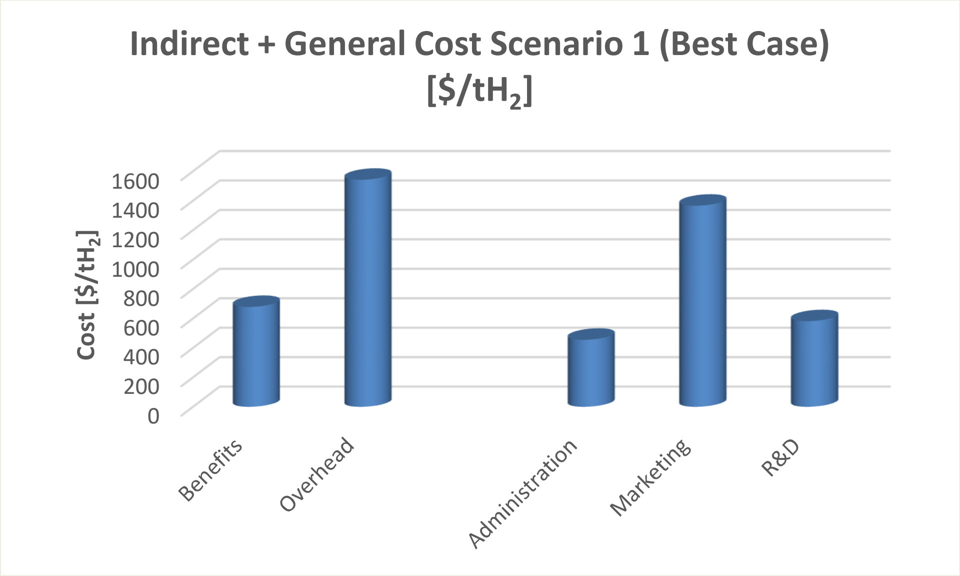

Figure 54: Indirect + General Cost Composition Scenario 1

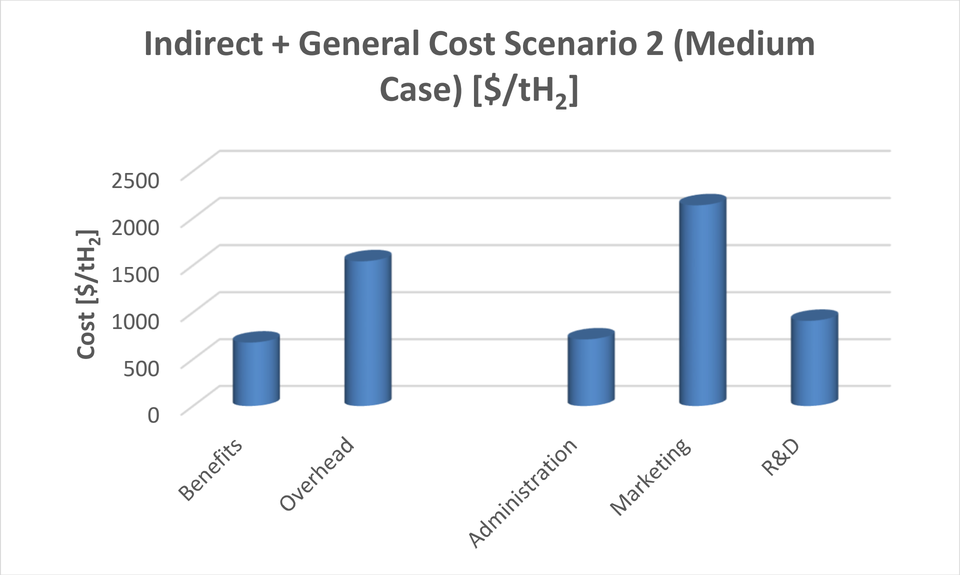

Figure 55: Indirect + General Cost Composition Scenario 2

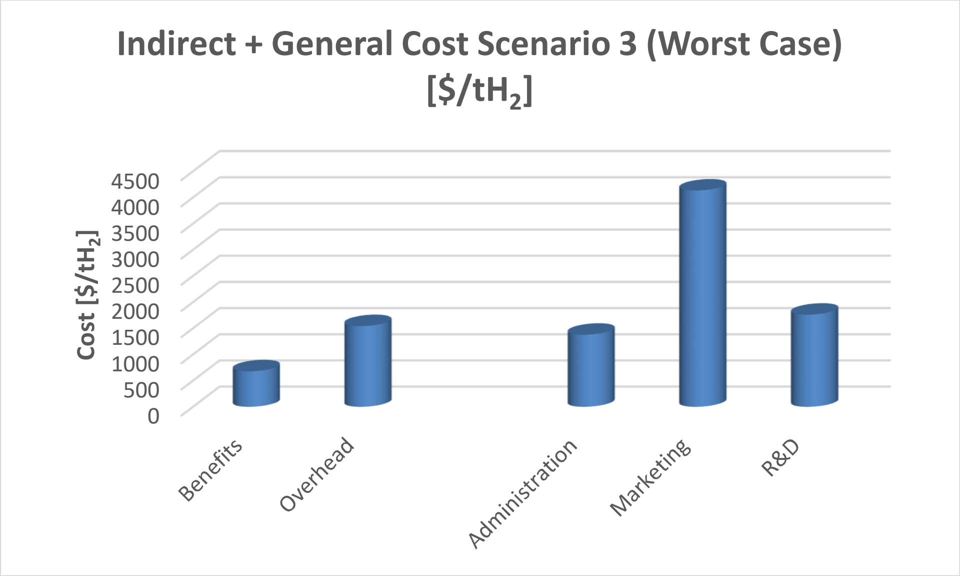

Figure 56: Indirect + General Cost Composition Scenario 3

As seen in Figure 54 to Figure 56, most indirect and general cost is due to marketing expenses, with Administration, Research & Development and general plant overhead on par.

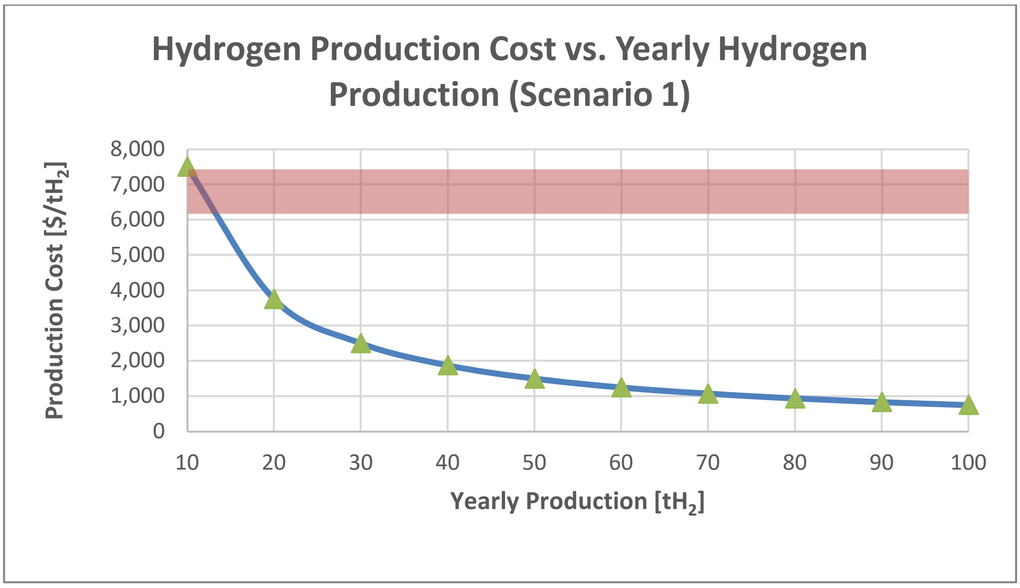

Figure 57: Hydrogen Production Cost vs. Yearly Hydrogen Production (Scenario 1)

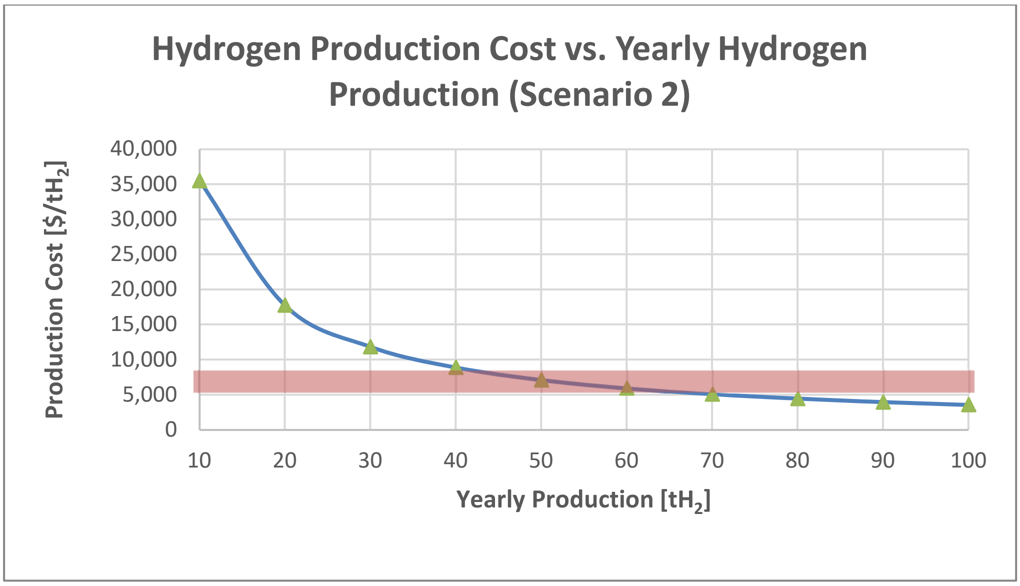

Figure 58: Hydrogen Production Cost vs. Yearly Hydrogen Production (Scenario 2)

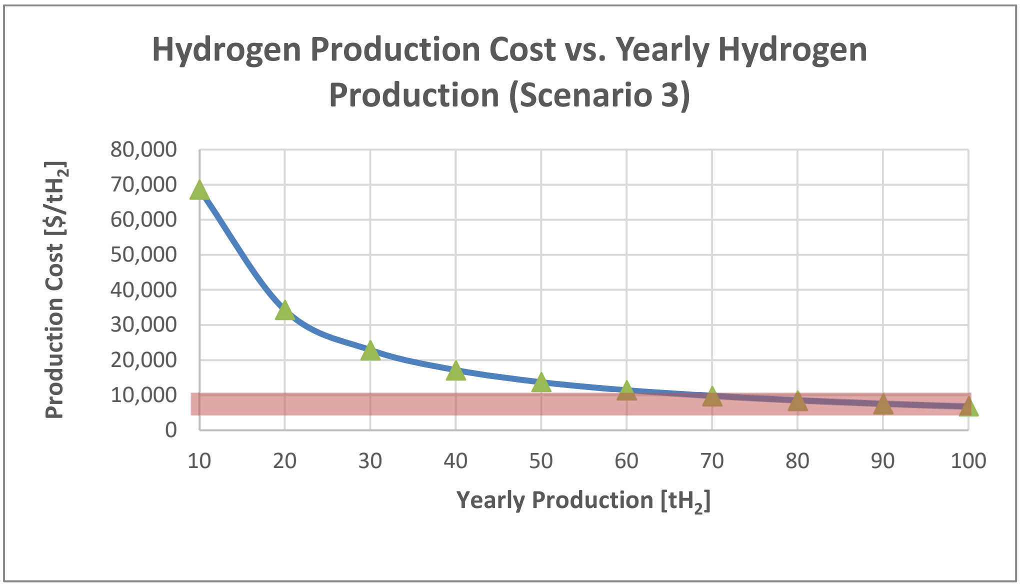

Figure 59: Hydrogen Production Cost vs. Yearly Hydrogen Production (Scenario 3)

Figure 57 to Figure 59 show the production cost for 1 ton of gaseous hydrogen vs yearly production. It can be seen that prices drop rapidly from a cumulative production of 10-20 tons per year and smooth out afterward. The red area is indicating expected sales prices. (No storage and transport cost)

7.5 Revenue Estimation and Scenarios

In this chapter, the assumptions for revenue estimation are given and revenue is calculated.

7.5.1 Hydrogen Price

Hydrogen is expected to be sold as gaseous hydrogen (BHY) with an approximate dispensed price of 6.4 [$/kg] to 7.3 [$/kg]. [105,106] Depending on scenario, pipeline or tube-trailer truck transport cost is subtracted from gross revenue sales at a rate of 199.8 [$/t$H_2$] and 610.5 [$/tH_2] respectively. (Per 100km)[107]

Transport Type	**Cost [$/t$H_2$]**
Tanker [LH]	777
Pipeline [GH]	999
Trailer Truck [GH]	3053

Table 12: Estimated Hydrogen Transport Cost

7.5.2 Sulfur Price

Depending on scenario, sulfur is expected to be sold in molten state at a price of 130 – 150 [$/t] CFR (cost and freight). [108] As discussed in chapter 7.2.2 during market research, this price is expected to drop because of the aforementioned situation. Sulfur storage cost was estimated at 8 [$/t].[96]

7.5.3 Business Scenarios for Revenue Estimation

Three business scenarios for revenue estimation were constructed to incorporate many uncertain factors in order to achieve a realistic view on the situation. The scenarios for revenue estimation are:

1. Best Case Scenario:
    a. Best price Scenario for Hydrogen Sales
    b. No transport cost, directly into pipeline (CFR)
    c. Molten Sulfur sold immediately, no transport cost, no storage cost

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[105] Bonner, B. (2013): “Current Hydrogen Cost”, U.S. Dpt. Of Energy, p. 9

[106] Verheul, B. (2019): “Overview of hydrogen and fuel cell developments in China”, Holland Innovation Network, p. 50

[107] Energy Technology System Analysis Programme (2014): “Hydrogen Production & Distribution “, p.1

[108] Argus Sulphur (2018): Executive Summary, Issue 18-39, p. 2

2. Medium Case Scenario:
    a. Average price for Hydrogen Sales
    b. Transport via pipeline (500km)
    c. Sulfur sold at average price + storage cost included
3. Worst Case Scenario:
    a. Bad Hydrogen Price, cost for storage and transport via trailer tube-truck
    b. Sulfur is not sold and deposited (storage cost included)

7.5.4 Sales Revenue Estimation Results

Scenario 1(Best case)	
Revenues	Revenue [$/tH2]
Hydrogen Sales	7300.00
Transport Cost	0.00
Sulfur Sales	2384.24
Storage Cost	0.00
Total	9684.24

Table 13: Best Case Scenario for Revenue Estimation

Scenario 2(Medium case)	
Revenues	Revenue [$/tH2]
Hydrogen Sales	7000.00
Transport Cost	999.00
Sulfur Sales	2066.34
Storage Cost	127.16
Total	7940.18

Table 14: Medium Case Scenario for Revenue Estimation

Scenario 3(Worst case)	
Revenues	Revenue [$/tH2]
Hydrogen Sales	6400.00
Transport Cost	3053.00
Sulfur Sales	0.00
Storage Cost	127.16
Total	3219.84

Table 15: Worst Case Scenario for Revenue Estimation

As seen in Table 13 to 15, expected sales revenues range from 9684[$/tH2] to 3220[$/tH2]. In Figure 60, a graphic representation of the composition of revenue for the best case (scenario 1) is shown.

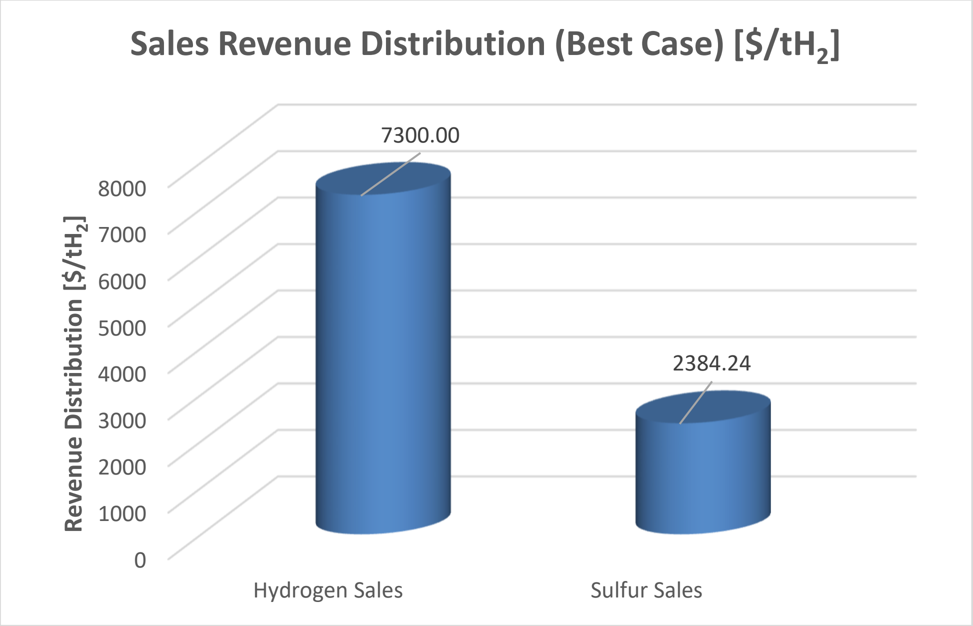

Figure 60: Sales Revenue Distribution (Scenario 1)

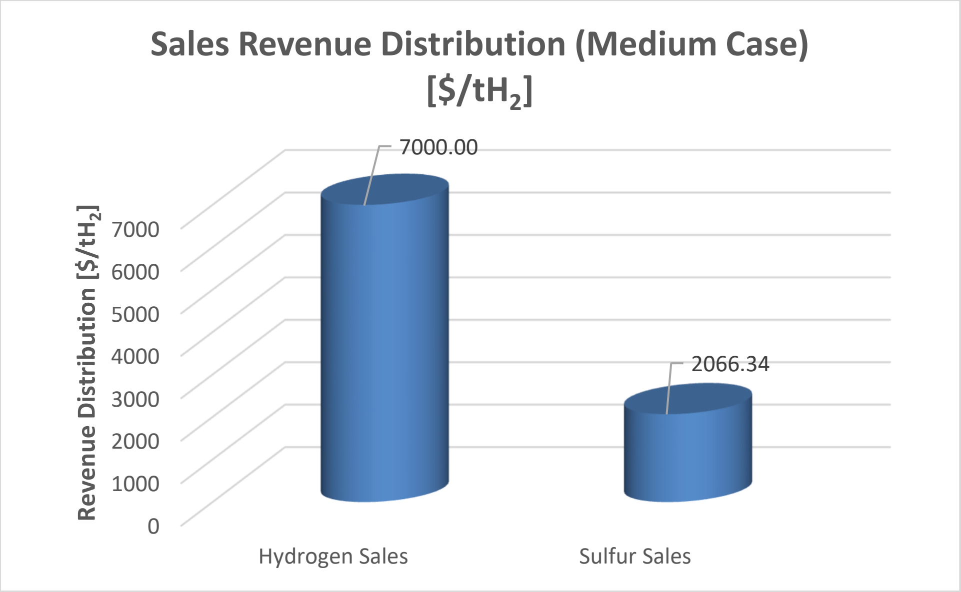

Figure 61: Sales Revenue Distribution (Scenario 2)

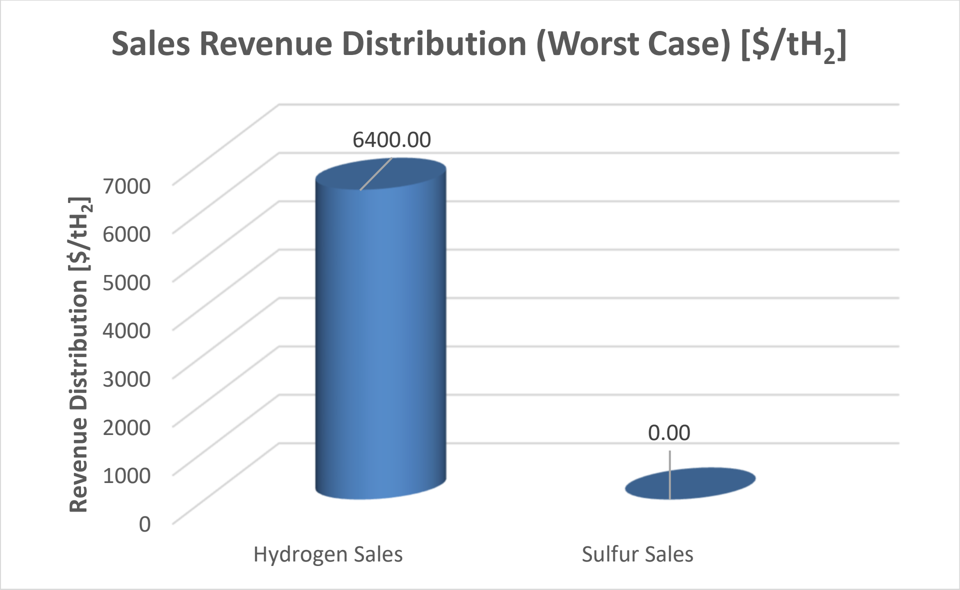

Figure 62: Sales Revenue Distribution (Scenario 3)

As seen in Figure 60 to Figure 62, Sales revenue distribution is always in favor of hydrogen and in scenario 3, the expected generated revenue from sulfur sales is zero.

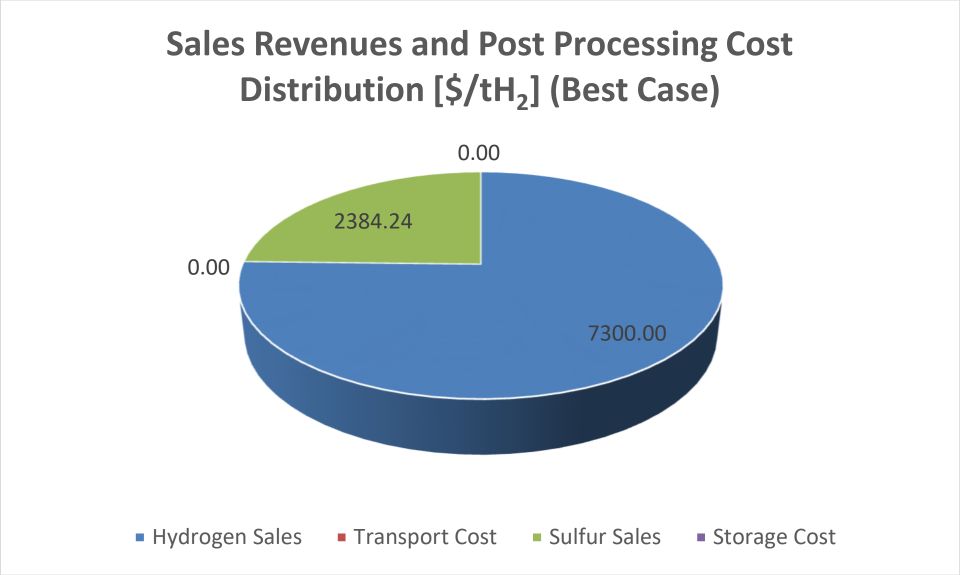

Figure 63: Sales Revenues and Post Processing Cost Distribution [$/tH2] (Best Case)

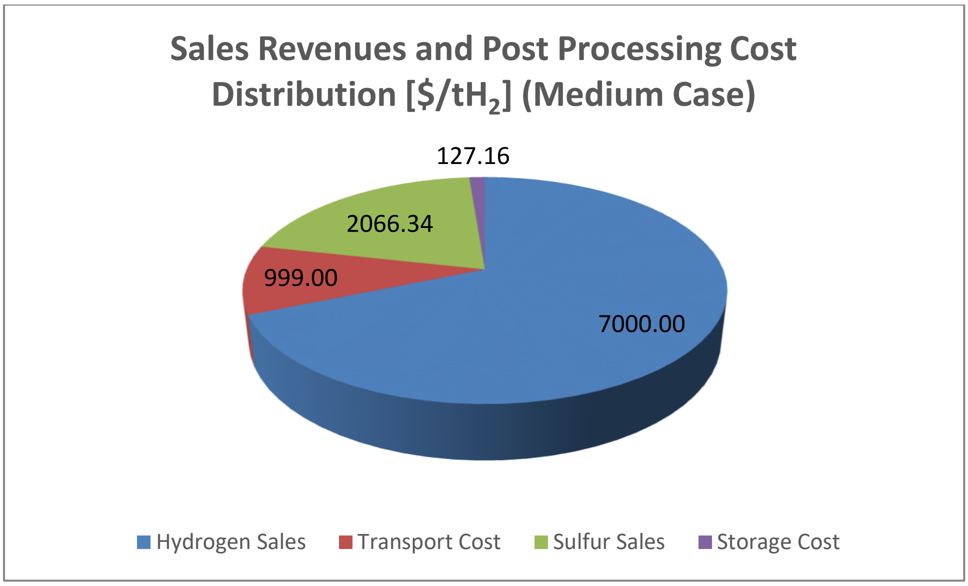

Figure 64: Sales Revenues and Post Processing Cost Distribution [$/tH2] (Medium Case)

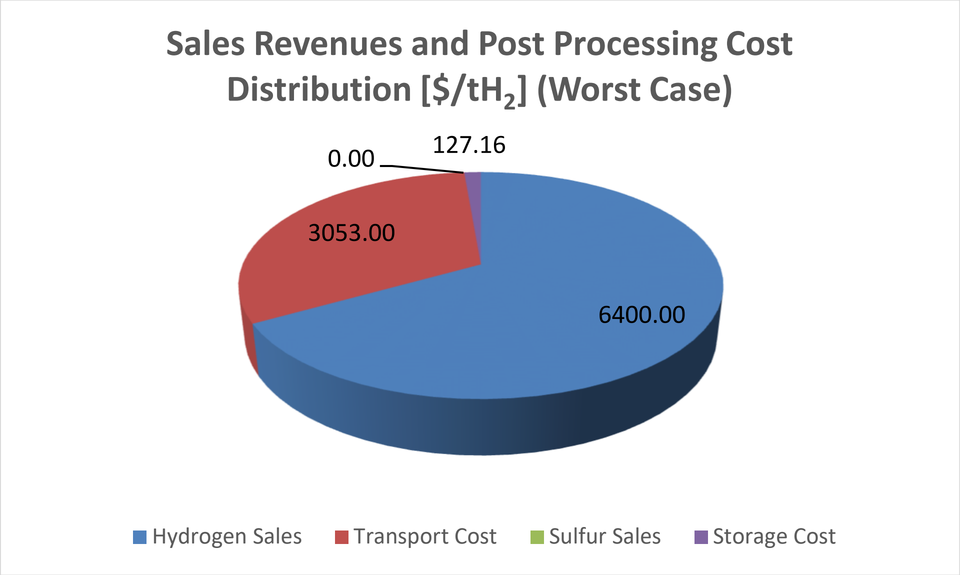

Figure 65: Sales Revenues and Post Processing Cost Distribution [$/tH2] (Worst Case)

Figure 63 to Figure 65 indicate gross sales revenues vs storage and transport costs in each scenario. It can be seen that most post-processing expenses in scenario 3 come from trailer-truck transport. Storage costs for sulfur due to hydrogen production are seemingly negligible.

7.6 Economic Results Discussion

To evaluate the economic potential of an investment, economic criteria are needed. Sales revenue must pay for fixed costs that are independent of the rate of production and variable costs, which in fact depend on the rate of production. Usually, taxes are deducted afterwards to calculate a net profit.[109] In this work, taxes have not been included in final calculations because of the scope of this study and furthermore, the plethora of different fiscal systems worldwide.

As simple economic criteria, the Economic Potential (EP) and Total Annual Cost (TAC) is used:[110]

$$EP = value\ of\ products - fixed\ costs - variable\ costs - taxes \qquad (37)$$

Equation 38: Economic Potential Definition

and

$$TAC = fixed\ costs + variable\ costs + taxes \qquad (39)$$

Equation 40: Total Annual Cost Definition

For this, all production cost business scenario (1-3) and all sales revenue scenarios (1-3) will be combined to calculate an EP value for profitability estimation.

Economic Potential Matrix [$/tH2]			
	Sales Scenario		
Cost Scenario	1	2	3
1	5548	3804	-917
2	-9907	-11651	-16372
3	-28202	-29946	-34666

Table 16: Economic Potential Matrix for all Business Cases Combinations (negative EP in red)

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[109] Smith, R. (2005): p. 29

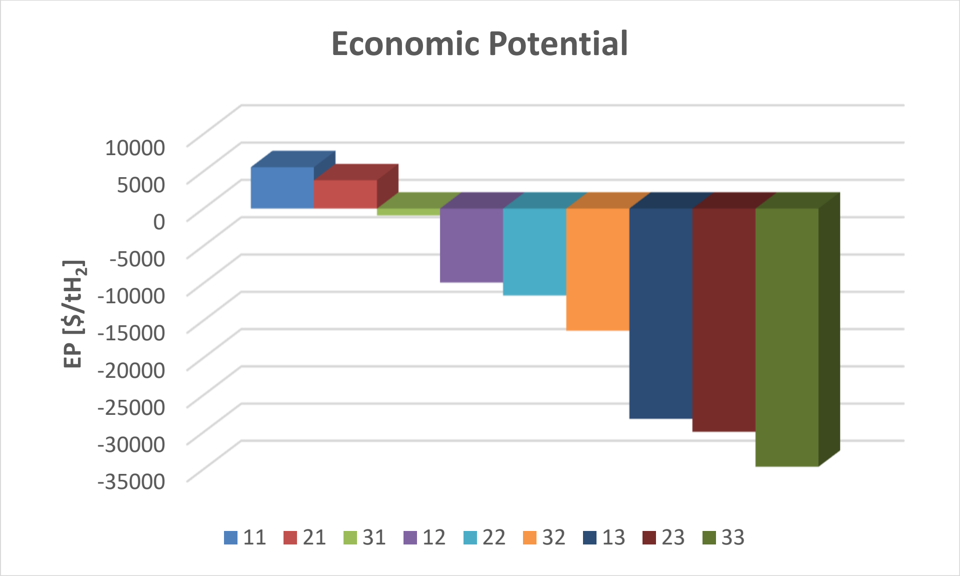

Figure 66: Economic Potential (Legend signifies sales- and cost-scenario index combination; i=Sales Scenario, j=Cost Scenario)

As seen from Figure 66, the Economic potential is only positive when specifically combining two cases, the best case of the sales scenario (1) and the best cost scenario(1) and the medium sales scenario(2) with the best cost scenario(1).

That means, only if (1)

a. Natural Gas on-site used for utility (power generation)
b. Full credit for H_2S procurement granted (assumed equal storage cost from desulfurization, as discussed in chapter 7.3.2.1)

and either (1):

a. Best price Scenario for Hydrogen Sales (7.3 $ /kg)
b. No transport cost, directly into pipeline (CFR)
c. Molten Sulfur sold immediately, no transport cost, no storage cost (150$/t)

or (2):

a. Average price for Hydrogen Sales (7$/kg)
b. Transport via pipeline (500km)
c. Sulfur sold at average price + storage cost included (130$/t)

Keeping these specific cases in mind, this work did not include a tax calculation, which would diminish positive EP’s even further.

Looking at the cost of hydrogen production, Figure 67 shows the comparison of hydrogen production for thermal decomposition to two other commercial methods. It can be seen that after 100 [tH_2/year] the same production costs per ton of hydrogen could be achieved with steam methane reforming methods.

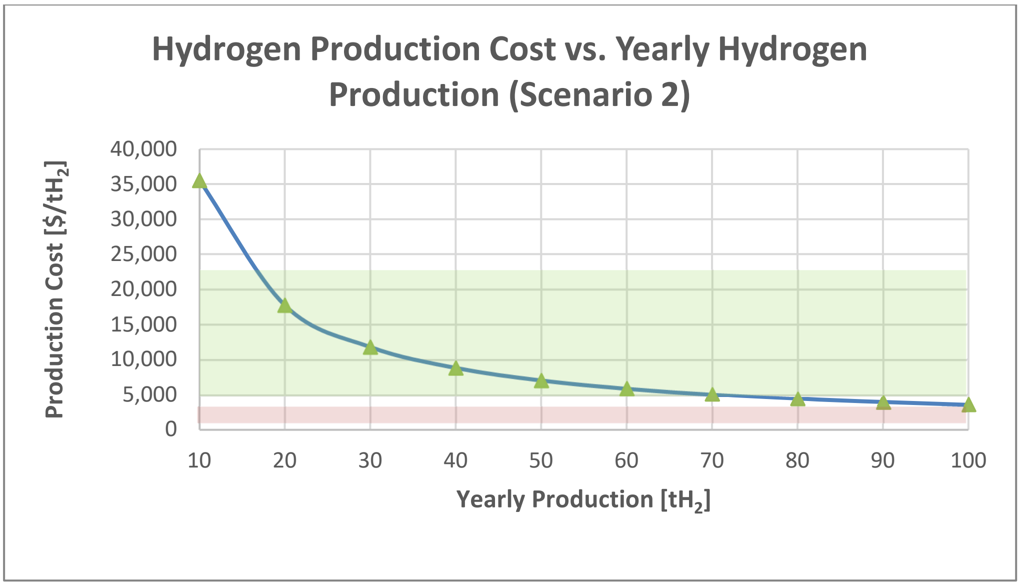

Figure 67: Hydrogen Production Cost comparison vs. commercial methods (green= electrolysis, red= SMR)[111]

Unfortunately, analyzing the economic potential and cost for utility during the process itself and high transport cost, this process at the moment seems to be still too expensive overall to be seen as a sound financial investment, which is in-line with previous research. Efficiencies during the chemical process itself need to be increased, as losses are decreased.

The bottom line is: Production costs are still, in most of the cases, too high to recommend this method of producing hydrogen to the economically sound investor.

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[111] Kayfeci, M.; Kecebas, A.; Bayat, M. (2019): p. 83

8 Risk Analysis

Talking about hydrogen and hydrogen-related compounds, it is mandatory to look at the risk and hazard-related considerations of this potentially harmful substance to human life and the environment. Properly evaluating risk is not only relevant from an economic standpoint, but more-so from a Health, Safety & Environmental (HSE) perspective. In the first section, a summary of all HSE-related considerations to hydrogen handling and storage are given, following a risk identification and analysis in compliance with the ISO 31000 Risk Management Standard with further recommendations afterwards.

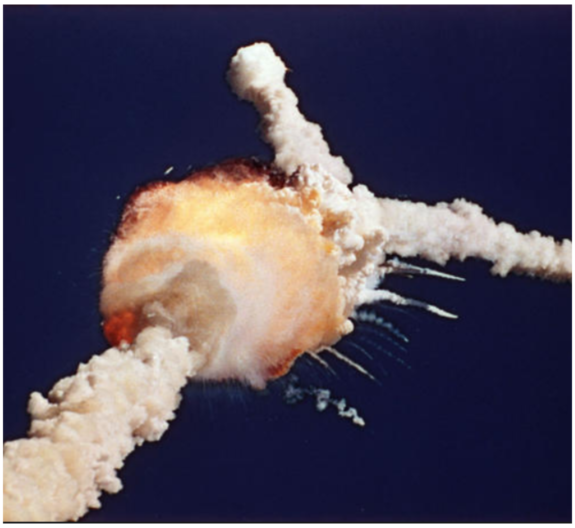

Figure 68: Challenger Accident 1986[112]

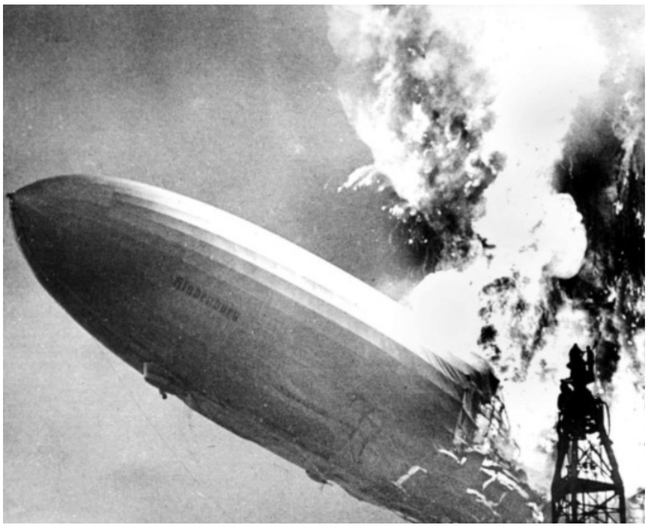

Figure 69: Hindenburg Accident 1937[113]

8.1 Properties and Characteristics of Hydrogen:

According to the Safety Data Sheet provided by Air Liquide[114], hydrogen is classified as a colourless, odourless gas at ambient conditions (20°C/101.3 kPa) with no adequate odour threshold to warn of overexposure and a wide range of flammability (4-77 vol% in air with a minimum ignition temperature of hydrogen-air mixtures of 500°C). The boiling point is defined at -263°C, with a very close melting point and critical temperature of -259°C and -240°C respectively. The p-T diagram of hydrogen can be seen in Figure 70.

---

[112] Source: CBS News (2016): https://www.cbsnews.com/news/january-28th-1986-space-shuttle-challenger-disaster-plays-out-on-live-tv/; Accessed 24.1.2020

[113] Source: Der Tagesspiegel (2017): https://www.tagesspiegel.de/gesellschaft/panorama/hindenburg-katastrophe-das-ende-der-luftschifffahrt/19762944.html; Accessed 24.1.2019

[114] Air Liquide (2016): Safety Data Sheet; p. 1 ff.

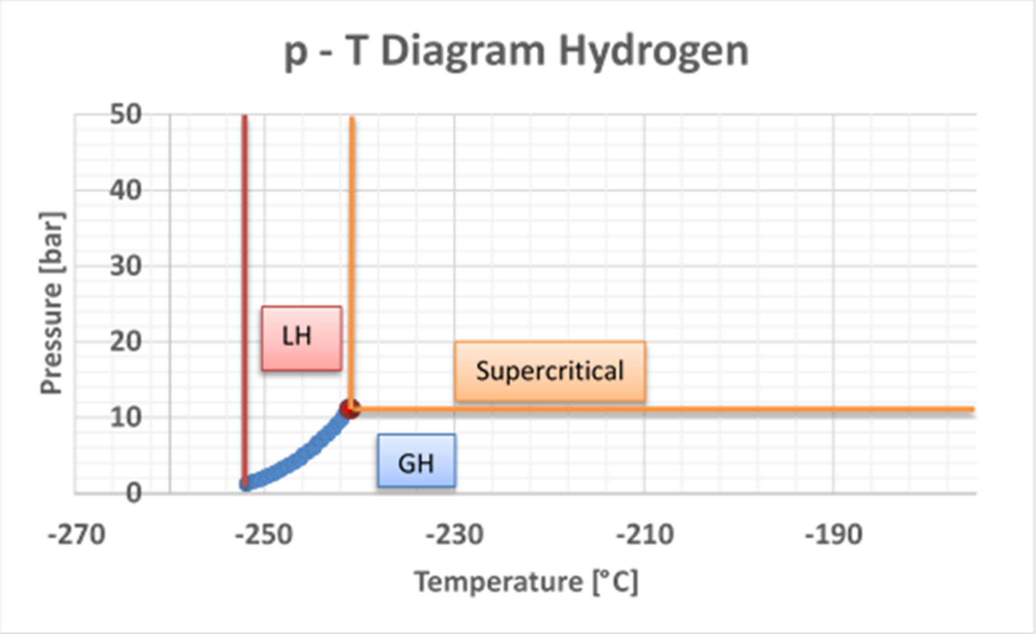

Figure 70: p-T Diagram Hydrogen[115]

8.2 Hydrogen and Hydrogen Compounds related HSE considerations

8.2.1 Fire and explosion hazards of Hydrogen

Hydrogen has some significantly different properties from more common used gases, which need to be fully considered to achieve safety compliance according to newest standards. Hydrogen may be stored in a number of ways:[116]

- Compressed Gas (GHY): Pressure of 200+ bar, temperature range between -40°C and 175°C
- Liquid (LHY): Below -250°C
- Complex hydrides (i.e. sodium aluminium hydrides): Flammable solids, creates corrosive solutions in reactions with water

8.2.2 Pressure Hazard of Hydrogen

Hydrogen has a significant expansion ratio in its conversion from a liquid to a gaseous state. Therefore, overpressure is a hazard to be considered and is comprised of: [117]

- Excessive deformation and subsequent release of hydrogen

---

[115] Source: Self (2019); constructed via Antoine Eq. with values from nist.gov chemistry webbook, SRD 69

[116] Health and Safety Laboratory UK (2009): p. 5

[117] NASA (2003): Guide for Hydrogen Hazards Analysis on Components and Systems; p. 2

- Rupture of pressure vessels with subsequent release of hydrogen, simultaneously acting as a potential ignition source and producing shrapnel

8.2.3 Hydrogen-Related injuries of Hydrogen

Potential injuries related to the hazards stated above are:[118]

- Asphyxiation because of displacement of oxygen in a breathable atmosphere
- Blast overpressure resulting from an expansion of compressed gas or detonation
- Burn can result from contact with hydrogen fire or thermal radiation
- Fragments/shrapnel related injuries or damages
- Frostbite/Freezing/Cryogenic burn due to contact with a cold fluid or surface
- Hypothermia because of lowering of body-temperature in a cold environment

Therefore, most systems with hydrogen-related functions functionally isolate personnel from direct exposure via protective equipment and/or insulation barriers.[119]

8.3 Hydrogen related environmental damage mechanisms

The most important environmental degradation effects due to hydrogen via pipelines are attributed to:[120]

1. Hydrogen Gas Embrittlement (HGE): Internal Corrosion at ambient temperature
2. Stress Corrosive Cracking (SSC): External Corrosion in underground environments

These two effects may cause catastrophic failures if not handled correctly by minimizing local stress levels and careful material selection for hydrogen-related applications.

Depending on the exact application for the material, following significant metallurgical considerations need to be addressed:[121]

1. Use of alloys with homogenous fine-grained microstructure
2. Avoidance of excessive hard/high strength alloys
3. Use of steels with enhanced cleanliness to non-metallic inclusions to reduce toughness
4. Components free from significant defects

Overall, API 5L (X52 or lower, PSL 2) pipe grade carbon steel is recommended.[121]

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[118] NASA (2003): Guide for Hydrogen Hazards Analysis on Components and Systems; p. 2

[119] NASA (2003): Guide for Hydrogen Hazards Analysis on Components and Systems; p. 3

[120] Health and Safety Laboratory UK (2009): p. 6

[121] Health and Safety Laboratory UK (2009): p. 7 ff.

8.4 Risk Management

For this risk analysis, the framework of the Industrial Risk Management Standard ISO 31000 was used to establish conclusions regarding hydrogen-related risks for future operations and where efforts of companies need to be made in order to minimize hazards in the field of hydrogen-production and handling.

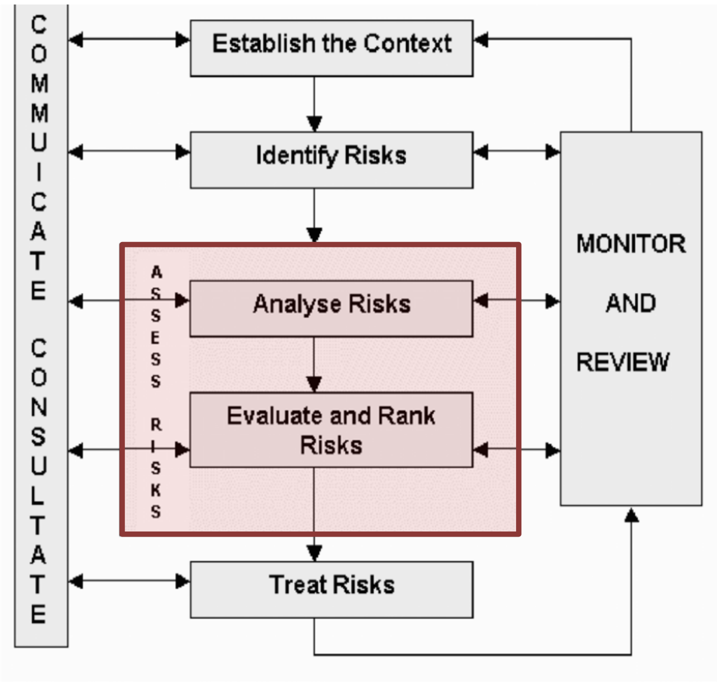

Figure 71: ISO 31000 Risk Management framework[122]

This work will focus on Identification of Risks and Risk Assessment (Analyse and Evaluate/Rank risks qualitatively).

8.4.1 Data Collection and Analysis

This Risk Assessment is based on the data collected from the H2LL (Hydrogen Lessons Learned) database, where hydrogen-related incidents are recorded by a variety of global sources, including industrial, government and academic facilities. This database is supported by the U.S. Dpt. Of Energy and is intended to be used as a knowledge base to ensuing lessons learned from those events.[123] Those events are then compared to NASA established data and analyses.

8.4.2 Risk Identification

Risk Identification was already conducted during section 8.2.

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[122] Cf. ISO 31000:2009

[123] U.S. Dpt. Of Energy (2020): H2LL database; https://h2tools.org/lessons

8.4.3 Analyse Risks and Evaluate and Rank Risks

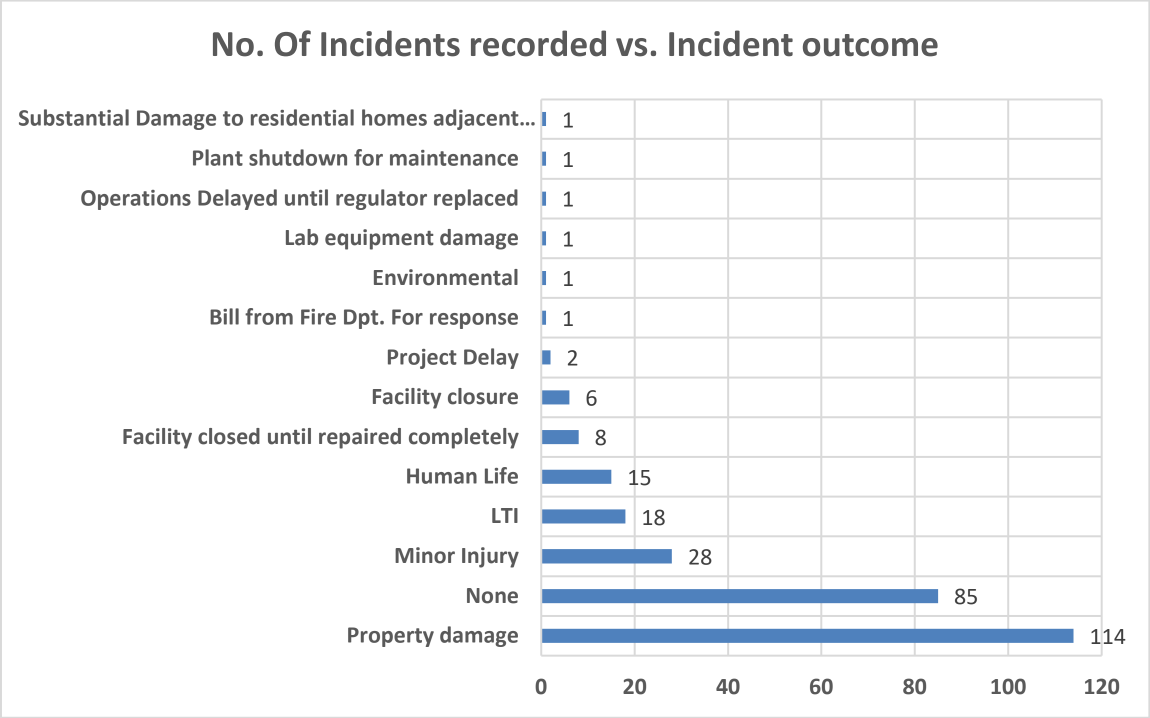

Figure 72: No. of hydrogen-related incidents vs. outcome

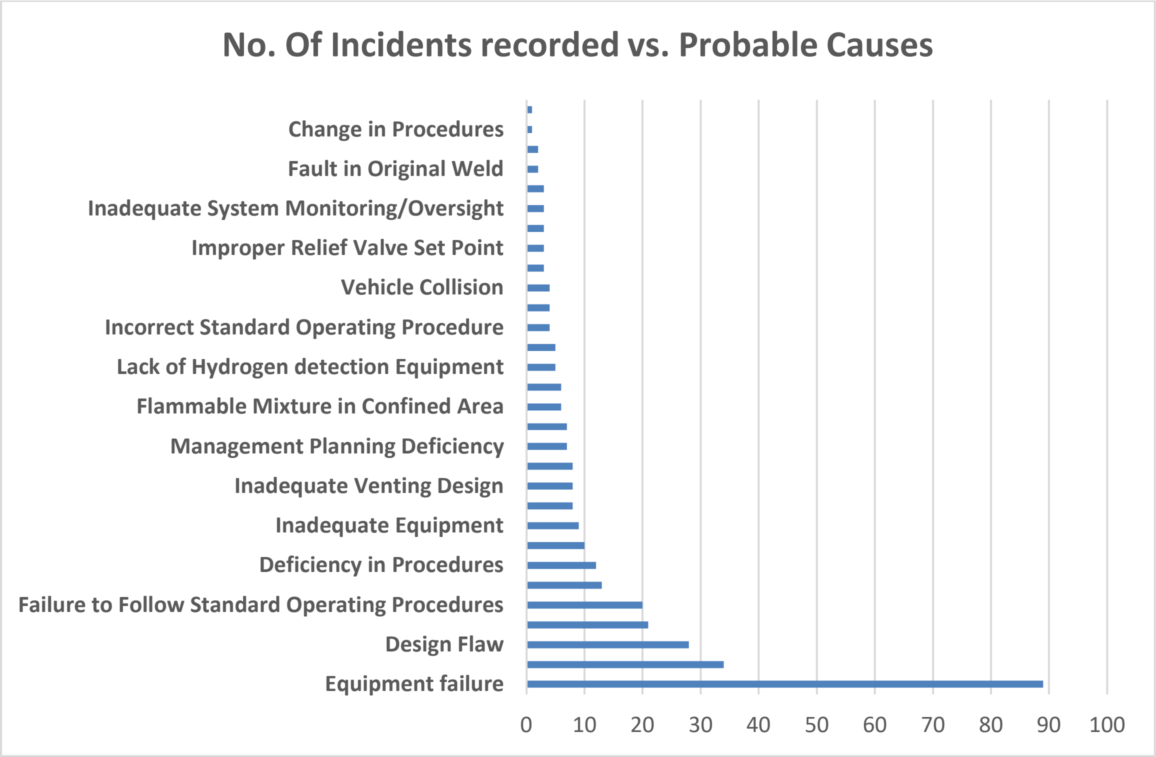

Figure 73: No. of hydrogen-related incidents recorded vs. Probable Causes

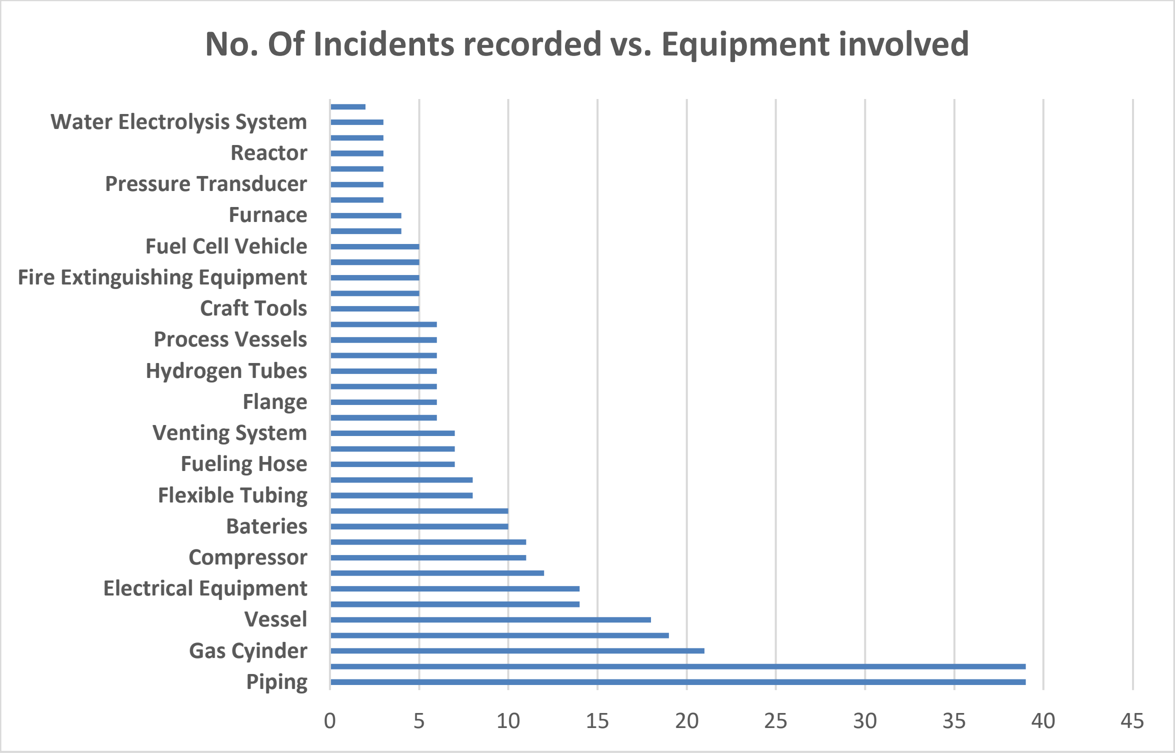

Figure 74: No. of hydrogen-related incidents recorded vs. Equipment involved

From Figure 72 to Figure 74 it can be identified, that most hydrogen-related incidents are attributed to the overall causes of (in descending order):

1. Equipment failure
2. Design Flaws
3. Failure to comply with Operating Procedure (human error) and
4. Deficiencies in Operating Procedures itself

Furthermore, the most critical parts of equipment-related failures seem to be (in descending order):

1. Piping
2. Gas cylinders
3. Vessel

These findings with already established data from one of the most experienced institutions related hydrogen-usage (NASA). NASA released a technical review of “hydrogen accidents and incidents in NASA operations” in 1996.

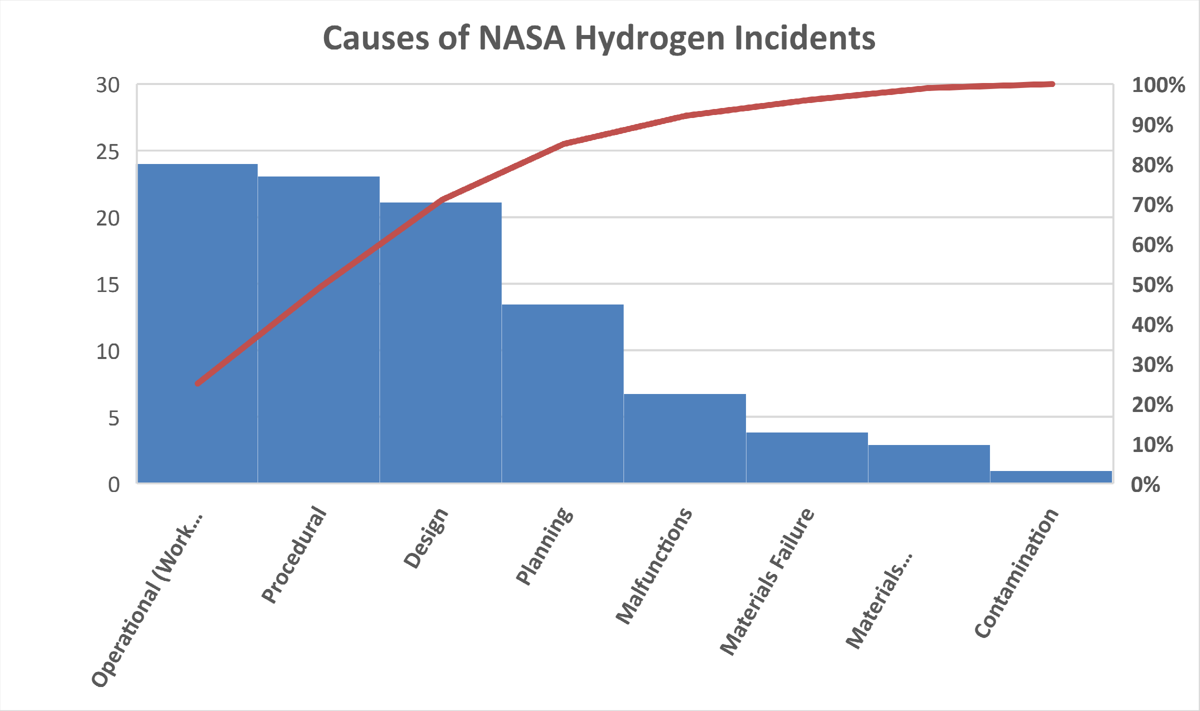

Figure 75: Causes of NASA Hydrogen Incidents (96)[124]

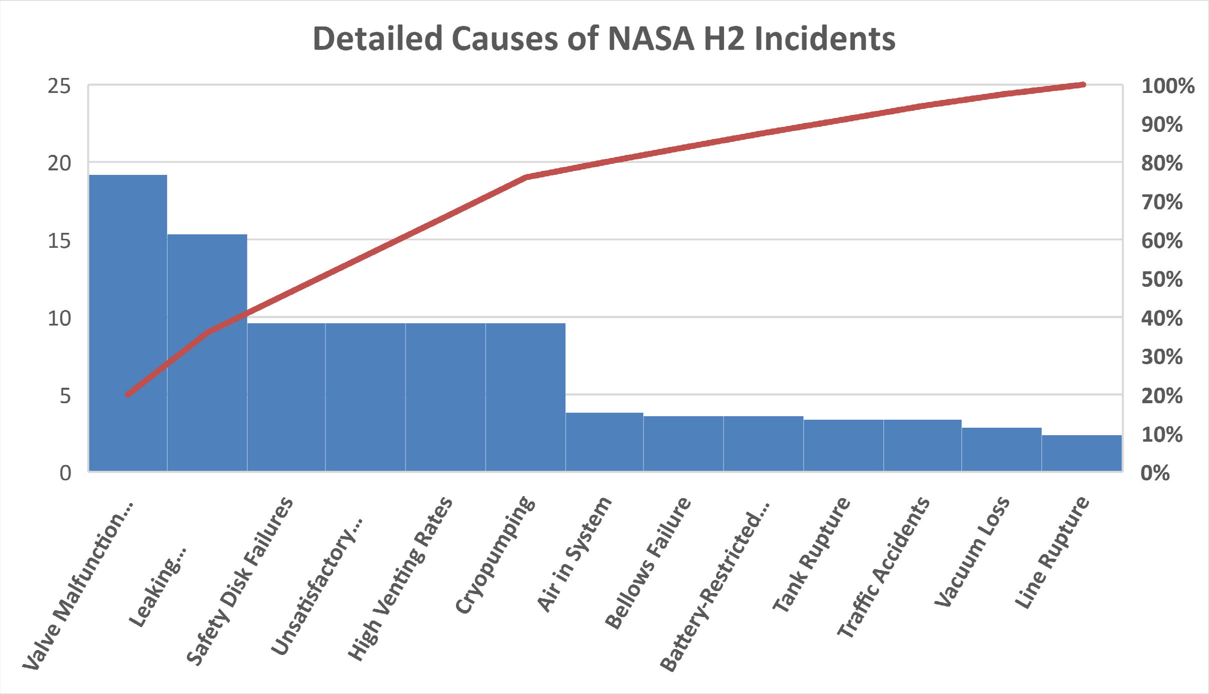

Figure 76: Detailed Causes of NASA Hydrogen Incidents (96)

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[124] NASA(1996): NASA TM -X71565

Comparing the overall causes of hydrogen incidents from NASA seen in Figure 75 and the findings from the H2LL database in Figure 73, it can be identified that both statistics coincide in ways that indicate a similar ranking of the top causes relating hydrogen-related mishaps:

1. Operational Problems (human error)
2. Procedural Deficiencies
3. Design Flaws

8.4.4 Risk Treatment

Looking at the results, the most common causes overall seem to be:

- Operational mistakes due to lack of training
- Procedures not according to safety standards
- Design failure

In order to avoid incidents in the future, considerations and recommendations to gain value from lessons learned are:

1. Design equipment and systems fit for purpose regarding hydrogen related standards
2. Specialized training for personnel in handling hydrogen-related substances
3. Technical and Operational Procedures updated according to latest standards (i.e. OSHA Standard 1910.103)[125]

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[125] Occupational Safety and Health Administration: OSHA Standard 1910.103) https://www.osha.gov/laws-regs/regulations/standardnumber/1910/1910.103

9 Conclusions and Recommendations

This technical and economic evaluation of hydrogen production from sour gas has shown that it is technically possible to produce a substantial amount of hydrogen gas from off-gases during the petroleum production process. Nevertheless, the economic analysis has shown that the economic potential from a direct thermal decomposition reaction of hydrogen sulphide to elemental sulfur and hydrogen is not economically viable with current estimated market-prices compared to modern steam reforming methods, even with its sustainability-focus in mind. The main culprit are high energy requirements during production and further processing of the hydrogen itself. Furthermore, risk analysis has estimated that most mishaps during hydrogen production and handling come from equipment failure, design flaws and flaws in operational procedures due to mishandled planning and not sufficient training of personnel regarding hydrogen safety.

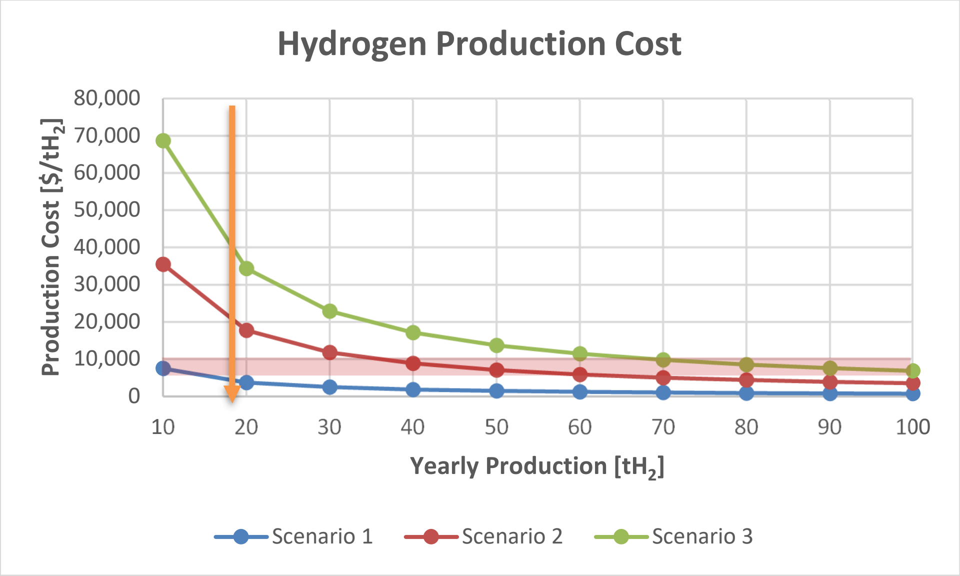

Figure 77: Hydrogen Production Cost Summary (Red bar = estimated sales price, orange arrow = production at current efficiencies)

Looking at the favourable market outlook for hydrogen one could recommend a shift of research focus on other methods of potential hydrogen-producing methods, including hydrogen sulphide methane reforming, which was not possible to analyse during this study due to technical limitations. Also, a recommendation would be a bottom-up approach in reactor design by exploring catalytic reactions and a focus on increasing efficiencies on a process-technological level.

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Abbreviations

B	Billion
BHY	Gaseous Hydrogen
CO2	Carbon Dioxide
CFR	Cost and Freight
EF	Economic Feasibility
GH	Gaseous Hydrogen
H_2S	Hydrogen Sulfide
LH	Liquid Hydrogen
Mcm	1000 m^3
MM	Million
PFD	Process Flow Diagram
Rub	Rouble
SAC	Superadiabatic Decomposition
scf	Standard cubic feet
TC	Technical Challenge

Appendices

Appendix A

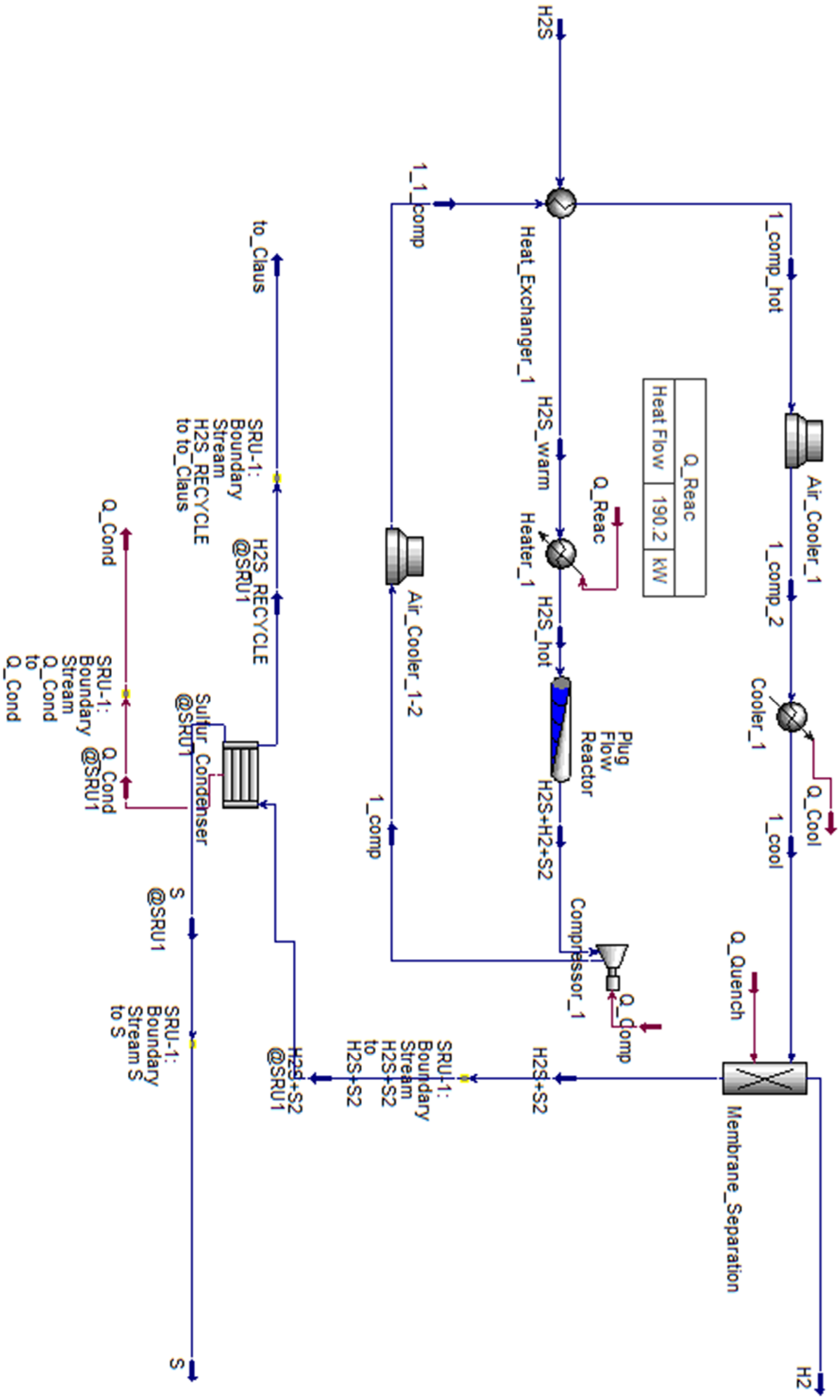

Figure 78: Optimized PFD Direct Thermal Decomposition

Years	Hydrogen Production [tons/day]	Hydrogen Production [tons]	Hydrogen Production cum. [tons]
0.25	0.0463	4.227536404	4.227536404
0.5	0.0463	4.227536404	12.68260921
0.75	0.0463	4.227536404	25.36521842
1	0.0463	4.227536404	42.27536404
1.25	0.0520	4.748413004	63.93392266
1.5	0.0511	4.662412336	73.344748
1.75	0.0511	4.662412336	82.66957267
2	0.0500	4.557979471	119.8644385
2.25	0.0500	4.557979471	128.9803974
2.5	0.0500	4.557979471	174.5601921
2.75	0.0546	4.978507188	225.118494
3	0.0544	4.962550558	235.0595518
3.25	0.0574	5.241681541	245.2637839
3.5	0.0593	5.409500678	255.9149661
3.75	0.0580	5.291845586	266.6163124
4	0.0559	5.105190573	277.0133485
4.25	0.0491	4.482757516	286.6012966
4.5	0.0491	4.482757516	295.5668116
4.75	0.0526	4.803391854	381.0598388
5	0.0541	4.940487054	390.8037177
5.25	0.0534	4.868315997	400.6125207
5.5	0.0496	4.530404786	410.0112415
5.75	0.0499	4.551119053	419.0927654

6	0.0499	4.551119053	428.1950035
6.25	0.0523	4.771765304	542.193626
6.5	0.0516	4.710673667	551.676065
6.75	0.0525	4.792620304	561.179359
7	0.0528	4.820992865	570.7929721
7.25	0.0520	4.741371633	580.3553366
7.5	0.0505	4.609860925	589.7065692
7.75	0.0491	4.480914441	598.7973446
8	0.0501	4.569188725	607.8474477
8.25	0.0476	4.347045745	616.7636822
8.5	0.0478	4.36544673	625.4761747
8.75	0.0478	4.36544673	634.2070681
9	0.0451	4.115560675	791.1132644
9.25	0.0453	4.131762536	799.3605876
9.5	0.0466	4.249021722	807.7413718
9.75	0.0459	4.188582845	816.1789764
10	0.0447	4.077646946	824.4452062
10.25	0.0453	4.129536987	832.6523901
10.5	0.0440	4.013297775	840.7952249
10.75	0.0436	3.977200482	848.7857231
11	0.0457	4.169430207	856.9323538
11.25	0.0449	4.098947637	865.2007317
11.5	0.0458	4.178359677	873.478039
11.75	0.0463	4.227437148	881.8838358

Table 17: Dynamic Hydrogen Production Data HYSYS Output

Years	Sulfur Production [tons/day]	Sulfur Production [tons]	Sulfur Production cum. [tons]
0.25	0.7363	67.18423365	67.18423365
0.5	0.7363	67.18423365	134.3684673
0.75	0.7363	67.18423365	201.5527009
1	0.7363	67.18423365	268.7369346
1.25	0.7363	67.18423365	335.9211682
1.5	0.8272	75.48614124	411.4073095
1.75	0.8123	74.11861453	485.525924
2	0.8123	74.11861453	559.6445385
2.25	0.7940	72.45498091	632.0995194
2.5	0.7940	72.45498091	704.5545004
2.75	0.7940	72.45498091	777.0094813
3	0.8673	79.13809239	856.1475737
3.25	0.8645	78.88470362	935.0322773
3.5	0.9132	83.32610334	1018.358381
3.75	0.9424	85.99511166	1104.353492
4	0.9219	84.12240035	1188.475893
4.25	0.8894	81.15804426	1269.633937
4.5	0.7809	71.25723318	1340.89117
4.75	0.7809	71.25723318	1412.148403
5	0.8367	76.35243111	1488.500834
5.25	0.8607	78.53466614	1567.035501
5.5	0.8481	77.38967857	1644.425179
5.75	0.7893	72.02548269	1716.450662

6	0.7929	72.35209886	1788.802761
6.25	0.7929	72.35209886	1861.154859
6.5	0.8312	75.85106596	1937.005925
6.75	0.8206	74.87604062	2011.881966
7	0.8348	76.17696358	2088.05893
7.25	0.8397	76.6263051	2164.685235
7.5	0.8259	75.36362349	2240.048858
7.75	0.8030	73.27204414	2313.320902
8	0.7805	71.21850819	2384.539411
8.25	0.7958	72.62058968	2457.16
8.5	0.7571	69.08436465	2526.244365
8.75	0.7604	69.38503312	2595.629398
9	0.7604	69.38503312	2665.014431
9.25	0.7168	65.40894011	2730.423371
9.5	0.7196	65.66454661	2796.087918
9.75	0.7401	67.53186718	2863.619785
10	0.7295	66.56900667	2930.188792
10.25	0.7102	64.80967142	2994.998463
10.5	0.7193	65.63346332	3060.631926
10.75	0.6990	63.78389229	3124.415819
11	0.6927	63.20956326	3187.625382
11.25	0.7262	66.26841261	3253.893795
11.5	0.7140	65.14862778	3319.042422
11.75	0.7278	66.40900646	3385.451429

Table 18: Dynamic Sulfur Production Data HYSYS Output

Years	**Reactor Power [kW]**	**Compressor Power [kW]**
0.25	190.2269966	216.8511
0.5	190.2269966	216.8511
0.75	190.2269966	216.8511
1	190.2269966	216.8511
1.25	186.149394	212.9657593
1.5	183.1672784	209.4072335
1.75	183.1672784	209.4072335
2	182.8523956	208.9054931
2.25	182.8523956	208.9054931
2.5	182.8523956	208.9054931
2.75	200.6747307	229.9744394
3	199.7755198	228.8883269
3.25	206.4385936	236.788148
3.5	211.6683017	242.9987505
3.75	209.4656424	240.3452922
4	199.5754737	228.7110889
4.25	182.025302	207.7964694
4.5	182.025302	207.7964694
4.75	196.2139645	224.5255076
5	198.3692926	227.0837145
5.25	193.2907252	221.1255912
5.5	173.291803	197.6374885
5.75	176.5387222	201.3894327

6	176.5387222	201.3894327
6.25	193.5696892	221.134148
6.5	195.53287	223.315484
6.75	200.4900233	229.2287175
7	203.3828257	232.6676822
7.25	197.0202612	225.2422001
7.5	193.0606441	220.5383556
7.75	192.3347433	219.4891101
8	197.1979846	225.0185466
8.25	194.4599669	221.7252968
8.5	185.5718625	211.5520298
8.75	185.5718625	211.5520298
9	180.3848389	205.2418179
9.25	183.2323572	208.6472643
9.5	183.7997248	209.4561954
9.75	183.9403262	209.537203
10	174.9182654	198.9628883
10.25	178.1218106	202.7236718
10.5	175.7102587	199.8472721
10.75	174.9538317	198.901197
11	178.7983793	203.491681
11.25	175.372845	199.4600064
11.5	180.6914112	205.6771119
11.75	190.2271187	216.8498113

Table 19: Dynamic Power Requirements Data HYSYS Output (Reactor, Compressor)

Years	**Cooler Power [kW]**	**Sulfur Condenser Power [kW]**	**Quenching and Separation Power [kW]**
0.25	27.06798452	16.7836562	204.6702633
0.5	27.06798452	16.7836562	204.6702633
0.75	27.06798452	16.7836562	204.6702633
1	27.06798452	16.7836562	204.6702633
1.25	26.50711882	18.85208526	202.2347963
1.5	26.08340269	18.51061886	198.9428555
1.75	26.08340269	18.51061886	198.9428555
2	26.03558692	18.09598376	198.2925289
2.25	26.03558692	18.09598376	198.2925289
2.5	26.03558692	18.09598376	198.2925289
2.75	28.56518346	19.76547131	217.6300062
3	28.43791198	19.70211793	216.6733032
3.25	29.38829112	20.81040344	224.2830074
3.5	30.13220705	21.47670033	230.0971479
3.75	29.81724126	21.00953898	227.4979382
4	28.41500744	20.26854734	216.9137959
4.25	25.9167608	17.79729803	197.2123781
4.5	25.9167608	17.79729803	197.2123781
4.75	27.93036344	19.0702349	212.5651614
5	28.23954788	19.61454309	215.1731634
5.25	27.5203474	19.32805171	209.8096108
5.5	24.68640401	17.98663805	188.5244938
5.75	25.1454659	18.06881978	191.8744827

6	25.1454659	18.06881978	191.8744827
6.25	27.55779385	18.94465578	209.7757159
6.5	27.83307855	18.70207453	211.5593928
6.75	28.53506312	19.02737726	216.8338553
7	28.94405237	19.13998375	219.8495812
7.25	28.04306464	18.82394046	213.1705562
7.5	27.4797246	18.3017978	208.7476416
7.75	27.37365432	17.78977063	207.6064404
8	28.06419423	18.14020815	212.7837855
8.25	27.67023071	17.25813946	209.3130664
8.5	26.41506735	17.33139139	200.404587
8.75	26.41506735	17.33139139	200.404587
9	25.6751543	16.33920969	194.3596698
9.25	26.07724248	16.40348568	197.3000524
9.5	26.16075016	16.8691062	198.2484115
9.75	26.17889861	16.62910293	198.1936597
10	24.90151212	16.18876678	188.7296511
10.25	25.35552102	16.39475388	192.1323134
10.5	25.01119976	15.93322046	189.3253225
10.75	24.90348419	15.7898957	188.446492
11	25.45262007	16.55315562	192.9424303
11.25	24.96668453	16.27334281	189.2550294
11.5	25.72029481	16.58857609	194.8791478
11.75	27.06800143	16.78326216	204.6700714

Table 20: Dynamic Power Requirements Data HYSYS Output (Cooler, Condenser, Sep.)

Appendix B

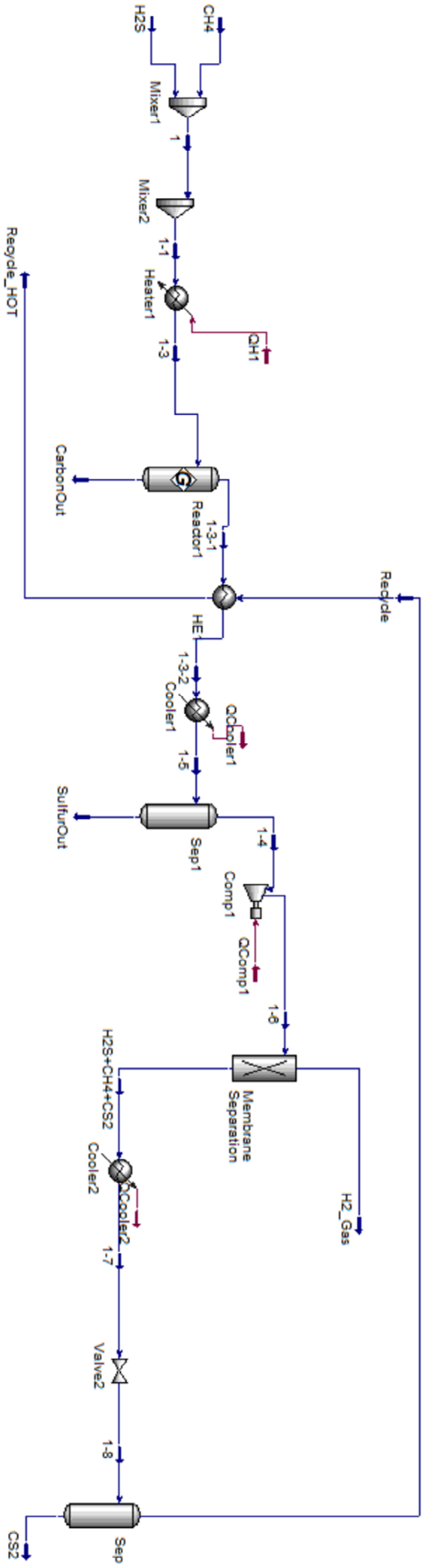

Figure 79: Preliminary PFD H_2SMR

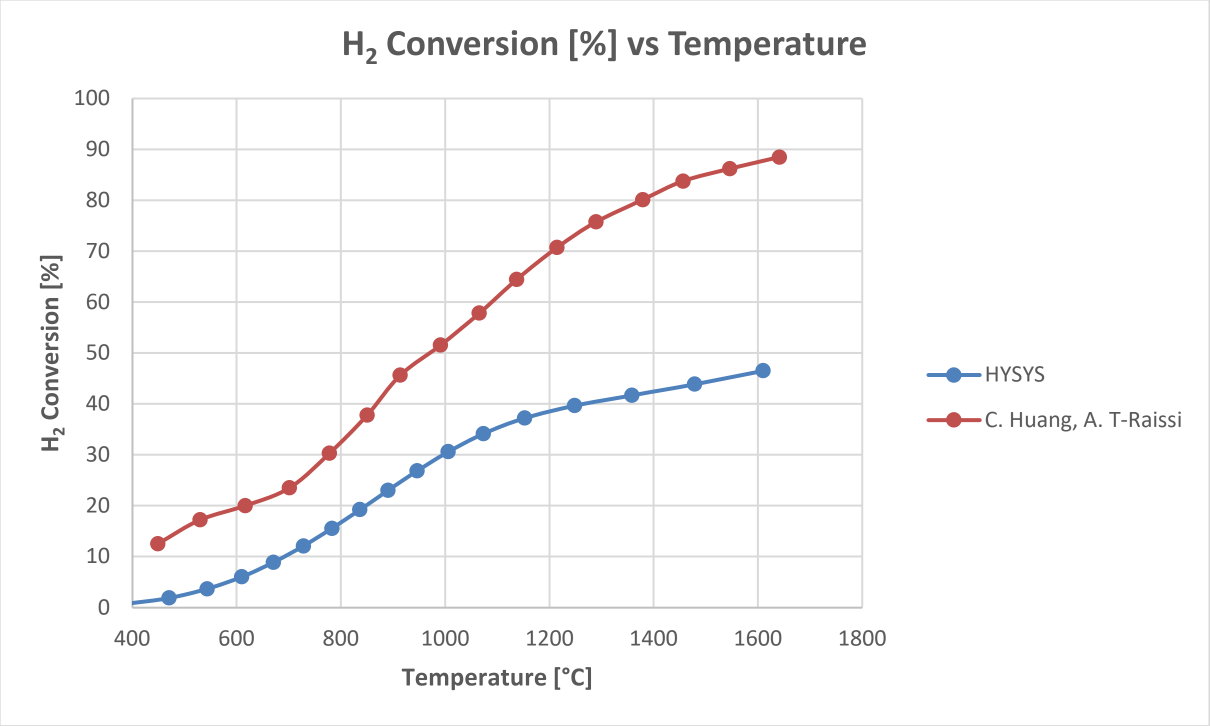

Figure 80: Verification Results H_2SMR; H_2 Conversion [%] vs Temperature

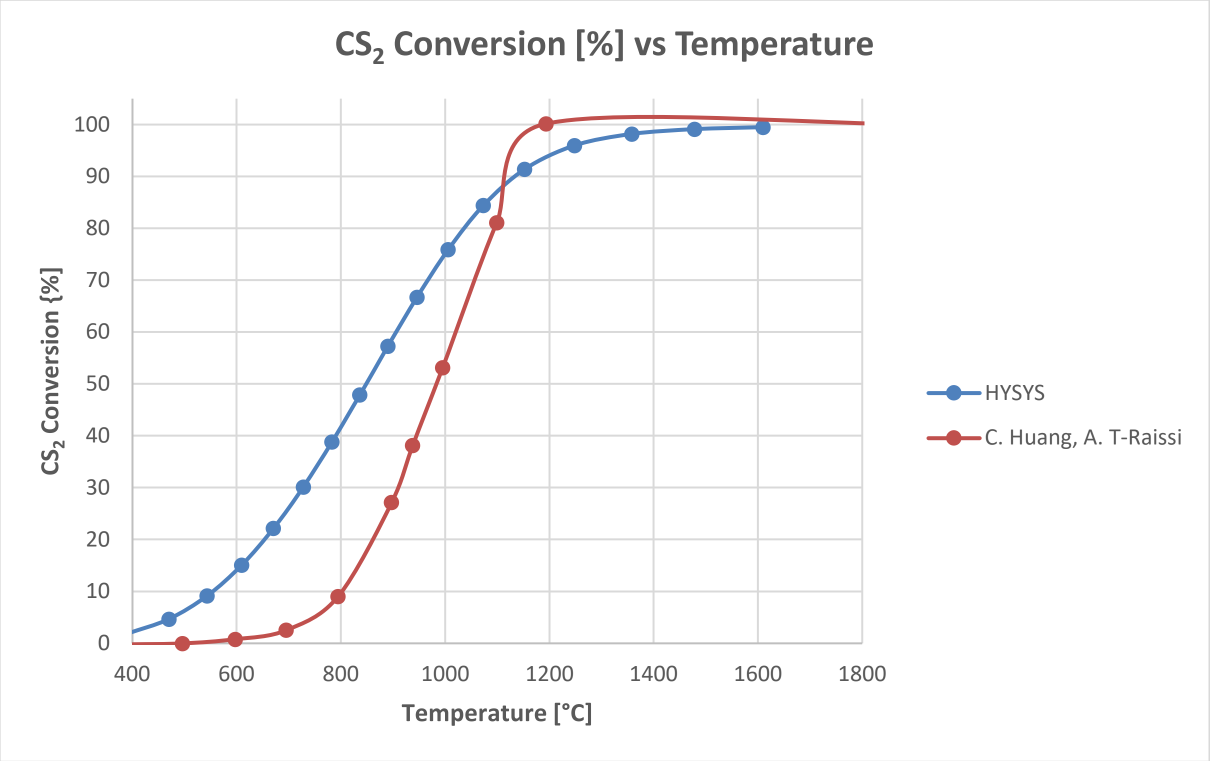

Figure 81: Verification Results H_2SMR; CS_2 Conversion [%] vs Temperature

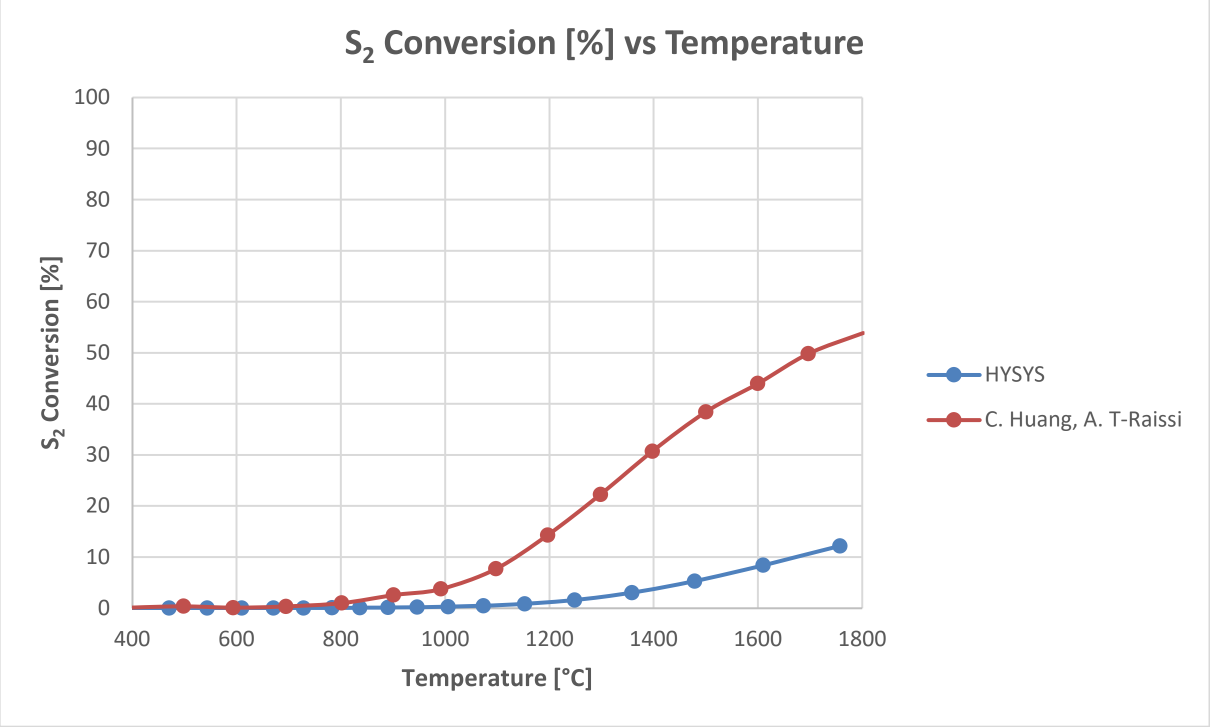

Figure 82: Verification Results H_2SMR; S_2 Conversion [%] vs Temperature