Hydrogen Pinch Analysis of Preemraff Göteborg and Preemraff Lysekil

A systematic analysis of hydrogen distribution systems

Master's Thesis within the Sustainable Energy Systems programme

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CHALMERS UNIVERSITY OF TECHNOLOGY
Göteborg, Sweden 2010

MASTER’S THESIS

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Cover:
Aerial photograph of Preemraff Lysekil with surroundings.

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ABSTRACT

Harder regulations regarding dearomatization and desulphurization of fuels in addition to increased yield of valuable products are making hydrogen scarce in the refinery process. Hydrogen demands not covered with gas from reforming of naphtha must be met by steam reforming. Hydrogen production from steam reforming is both costly and energy intensive, and refineries therefore aims at avoiding this.

In this thesis a relatively new tool, hydrogen pinch analysis, is used to review the hydrogen distribution system of two refineries: Preemraff Göteborg and Preemraff Lysekil. The reasons for the two refineries to participate in the project have been different, but the goal on both has been to identify shortcomings of the hydrogen distribution system. Preemraff Göteborg wants to be able to run their refinery at design capacity for all units, even after a revamp has been made in order to produce renewable based diesel. Preemraff Lysekil wants to cut down on their production of hydrogen from the steam reformer.

The analysis of the hydrogen distribution systems in Göteborg and Lysekil resulted in two respectively three suggestions for better hydrogen economy. This has mostly been achieved through redirection of off gases from the fuel gas net to an upgrading facility. The suggestions are all independent of each other, and have therefore been combined into a larger case covering all suggestions.

At Preemraff Göteborg, fresh hydrogen to the unit not working at maximum capacity was increased by 23 % with a payback time of 1.4 years. This could be achieved via one of the presented cases, which included purchase of a new compressor.

At Preemraff Lysekil, hydrogen production in the steam reformer could be lowered with 19 %, from approximately 70 100 Nm^3/h to 55 600 Nm^3/h. The suggestion achieving this also included a new compressor, since off gases with high purity but low pressure was found to be the most promising hydrogen source.

Key words: Hydrogen pinch analysis, hydrogen distribution system, refinery,

SAMMANFATTNING

Krav på lägre innehåll av aromater och svavel i bränslen samt ökat utbyte av värdefulla produkter har fått till följd att vätgas har blivit en bristvara i oljeraffinaderierna. Vätgasbehov som inte kan täckas av vätgasproduktion från nödvändig naftareformering måste täckas med hjälp av ångreformering. Vätgasproduktion från ångreformering är både dyrt och energiintensivt, varför det i största mån undviks av raffinaderierna.

I detta examensarbete används ett relativt nytt redskap, vätgaspinchanalys, för att utvärdera vätgassystemen på två raffinaderier: Preemraff Göteborg och Preemraff Lysekil. Skälen till att de två raffinaderierna har velat delta i studien har varit olika, men målet för båda har varit att identifiera brister i vätgassystemet. Preemraff Göteborg vill kunna utnyttja sin fulla kapacitet. Detta trots högre vätgasåtgång på en enhet beroende på en ombyggnation för att kunna producera förnyelsebart baserad diesel. Preemraff Lysekil vill minska vätgasproduktionen från sin ångreformator.

Analysen av vätgassystemen i Göteborg och Lysekil resulterade i två respektive tre förslag till förbättringar. Dessa har till största del resulterat i ett större användande av offgaser som tidigare gått till bränngasnätet. Dessa föreslås nu ledas tillbaka till reningsanläggningar, där de renas till mer användbara koncentrationer.

På Preemraff Göteborg kunde tillflödet av vätgas till den enhet som fått minska produktionstakten vid installationen av den ombyggda enheten ökas med 23 %, och investeringen betalar av sig på 1.4 år. Detta kunde åstadkommas i ett av de studerade fallen, som bland annat inkluderade köp av en ny kompressor.

På Preemraff Lysekil kunde produktionen av vätgas i ångreformern minskas med 19 %, från 70 100 Nm^3/h till 55 600 Nm^3/h. Även detta scenario inkluderade köp av en ny kompressor, eftersom off gaser med hög renhet men lågt tryck ansågs som den mest användbara källan till vätgas.

Nyckelord: Vätgaspinchanalys, vätgasystem, raffinaderi

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Preface

In this master's thesis, two hydrogen pinch analysis have been carried out at Preem Petroleum AB´s refineries in Göteborg and Lysekil. The study has been conducted in cooperation between the Department of Heat and Power Technology at Chalmers University of Technology, Sweden, and Preem Petroleum AB.

We would like to thank our examiner Thore Berntsson and our supervisor Daniella Johansson. We would also like to thank our supervisors at Preemraff Lysekil, Erika Wikström and Rebecka Fransson as well as our supervisor at Preemraff Göteborg, Henrik Rådberg. Our gratitude is also great for the whole staff at Preemraff who has helped us throughout this thesis.

Notations

C_e	Capital cost for equipment
C_p	Capital cost for pipes
CRYO	Cryogenic separator
d_i	Inner diameter of pipe
GHT	Hydro treating unit which will be able to refine tall oil
FG	Fuel gas system
IMO	International Maritime organization
L	Length
MK1	Swedish diesel standard and a denomination of an operation mode at Preemraff Göteborg
MK3	European diesel standard and a denomination of an operation mode at Preemraff Göteborg
PSA	Pressure swing absorption
TFOE	Tonne of fuel oil equivalent

1 Introduction

The refinery industry is facing great challenges within the coming years. Crude oils get heavier and sourer, i.e. higher sulphur content, at the same time as the demand is switched towards lighter and cleaner fuels i.e. diesel and aviation fuel (Fonseca et al, 2008). Diesel is nowadays more competitive than gasoline, at least in Europe. The gasoline is also restricted when it comes to benzene content. Furthermore, the refineries have begun to upgrade more residues from the production. All of these facts are pointing in the direction of more hydrogen usage in the refining process.

In the past, the shipping industry has been able to consume the sourest and heaviest fuel, but this has changed. Within the EU, regulations concerning sulphur concentrations in fuels have hardened in several steps since 1993 when the council directive 93/12/EEC was passed. Ships are forbidden to use oil with sulphur content above 0.1 mass% while in berth, while gasoline and diesel are allowed to have a sulphur content of 10 ppm (europa.eu). It is also decided by IMO that from 2020 (or 2025), it will be forbidden for ships globally to use fuels containing more than 0.5 % sulphur (www.naturskyddsforeningen.se). The refineries will thus have to produce less sulphur containing fuels even for shipping. The desulphurization of a fuel consumes large quantities of hydrogen.

Oil refineries over the world are struggling with their environmental profile. One path towards getting more environmentally friendly is to produce biomass based fuels. Preemraff Göteborg will produce diesel fuel from tall oil diesel. The refining process for this fuel demands a lot of hydrogen. When gasoline contains too much benzene, the same problem occurs. Hydrogen is the solution to many of the oil refineries´ problems. It is therefore essential for the refining companies to manage their hydrogen in an effective way.

There are also CO_2-emissions associated with hydrogen production, which with the current Emission Trading System demands permits for each ton of CO_2 that is emitted. This raises the cost for producing hydrogen.

Preemraff Göteborg has a capacity of refining 6 Mtonne crude oil each year, whereas Preemraff Lysekil can refine 11.4 Mtonne. Together they represent 80 % of the Swedish refining capacity. Both Preemraffs produce sulphur free gasoline and diesel and also fuel oil of environmental grade 1, with sulphur content of less than 10 ppm. The two refineries have rather similar structure, but one important difference is that Preemraff Lysekil has a vacuum unit that can increase the yield of valuable products from the crude oil (www.preem.se). The hydrogen production, translated into pure hydrogen, is for Göteborg 29 000 Nm^3/h and for Lysekil 128 000 Nm^3/h, whence 70100 comes from steam reforming.

Preem has taken an active role in decreasing its environmental impact, for example by supply some of the refineries excess heat to the district heating system. Preem also has an ongoing project for producing biodiesel from rapeseed, as well as a new project in Göteborg for making renewable diesel from tall oil. Renewable based diesel is more similar to regular diesel than the traditional biodiesel, e.g. RME. The renewable based diesel can completely replace regular fuel in an engine, which traditional biodiesel cannot.

1.1 Objective

The main objective of the thesis is to identify weaknesses in the hydrogen distribution system of Preemraff Lysekil and Göteborg and debottleneck these using a hydrogen pinch analysis. The system should make good use of off gases, while make up streams should be minimized. Hydrogen distribution will be evaluated with respect to both pressure differences and purities. The objective is also to suggest modifications to improve the existing distribution systems by rearranging or adding equipment. The additional costs will be reviewed including costs associated with fuel, electricity and CO_2 emissions. Furthermore, a sensitivity analysis will be carried out to investigate the influence of price fluctuations on the profitability of the retrofit. This will be carried out by studying different scenarios.

At Preemraff Lysekil, an investigation of the effects on hydrogen consumption when lowering the purity demands for certain units should be carried out.

Also, the methodology of hydrogen pinch analysis will be evaluated.

1.2 Problem analysis

A large part of the analysis was to collect data from the two refineries. In Göteborg, this was done continuously during a few weeks, and in Lysekil the gathering of data was performed during two stays in Lysekil. It was crucial to determine which streams were relevant, in order not to collect data that could be disregarded.

1.3 Limitations

Both Preemraff Göteborg and Preemraff Lysekil are currently doing modifications in their process. In Göteborg, a Green Hydrotreater (GHT) is to be installed, and in Lysekil a membrane unit is being exchanged. This may cause problems, since no data for real operation is available. At Preemraff Göteborg, design data of the GHT will be used when mapping the hydrogen system. This is because the new unit will have a fundamental impact on the process so it cannot be neglected.

At Preemraff Lysekil, however, the impact of the new membranes is rather small. It is also not decided how to use the new hydrogen made available. Therefore, data was used from the period chosen without taking the new membranes in consideration.

2 Theory

The hydrogen distribution systems of different refineries vary a lot. In this section the general structure and purpose of the hydrogen distribution system is described together with the theory about hydrogen pinch analysis.

2.1 Hydrogen distribution systems

Large quantities of hydrogen are used for different purposes at a refinery. There are three types of processes involved in the hydrogen distribution system; consuming processes, producing processes and purifying units (Hallale & Liu, 2001). The consumers often use hydrogen in order to increase the quality of the products e.g. by removing unwanted compounds or by converting certain groups of hydrocarbons into more desired groups. Common hydrogen consumers at a refinery are mild hydrocrackers, which is a process where heavy petroleum components are converted to lighter products, and hydrotreaters, where sulphur and nitrogen are removed from the products. Other hydrogen demands are associated with lubricant plants and isomerization processes.

In pinch analysis, a stream that takes hydrogen from the distribution system is called a ***sink***, whereas a stream that makes hydrogen available to the system is called a ***source*** (Alves & Towler, 2002). It is important to understand that the sink is defined as the stream entering the unit, i.e. after the mixing of recirculation stream and make up stream. Similar, the source is defined as the stream exiting the unit, i.e. before the stream is divided into recirculation and purge gas. Both the sink and the source are given as a flow rate at certain purity. A purifying unit will be both a sink and a source, and that also applies for many hydrogen consuming units, since hydrogen is present in the outlet gas (Hallale & Liu, 2001). Over the fence export of hydrogen is considered a sink, since it is specified to the customer regarding flow rate and purity.

Hydrogen is, in a refinery, commonly produced in two ways.

1. As a byproduct in catalytic reformers; where naphthenic hydrocarbons are converted to aromatics resulting in a lower hydrogen-carbon ratio.
2. As a main product in steam reformers; where hydrogen often is produced from natural gas together with steam according to:

$$CH_4 + H_2O \leftrightarrow 3H_2 + CO \qquad (1)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad (2)$$

The second reaction does not take place in the actual steam reformer, but in a shift reactor. The purpose of this reactor is to increase the conversion (Meyers, 2003).

If the onsite production is lower than the demand, import is necessary. To increase the concentration of hydrogen in the distribution system purifiers are used, such as pressure swing adsorption (PSA), cryogenic separation (CRYO) and membrane separation (Faraji et al, 2005). The production of hydrogen through steam reforming requires, besides steam and natural gas, heat since the net reaction is endothermic. This process as well as import of hydrogen is associated with a considerable cost for the refinery. Thus minimizing steam reforming and import of hydrogen is of great interest.

A typical hydrogen consuming unit is schematically shown in Figure 1. The reactor operates at a high partial pressure of hydrogen to ensure a sufficient reaction rate and to protect the catalyst from coking. This high concentration of hydrogen means that more is fed in to the reactor than what is actually used. The stream leaving the reactor therefore has a substantial fraction of hydrogen and is led to a separator where the product is separated from lighter gases. This gas stream is then often sent to an amine scrubber in order to remove hydrogen sulfide and ammonia. After the scrubber, a fraction of the gas is purged to prevent build-up of light hydrocarbons in the unit. The remaining stream with the excess hydrogen is mixed together with a make up stream with high hydrogen concentration. This mixture is then heated and led to the reactor (Alves & Towler, 2002). The green circle represents what is called a source, whereas the red circle represents a sink.

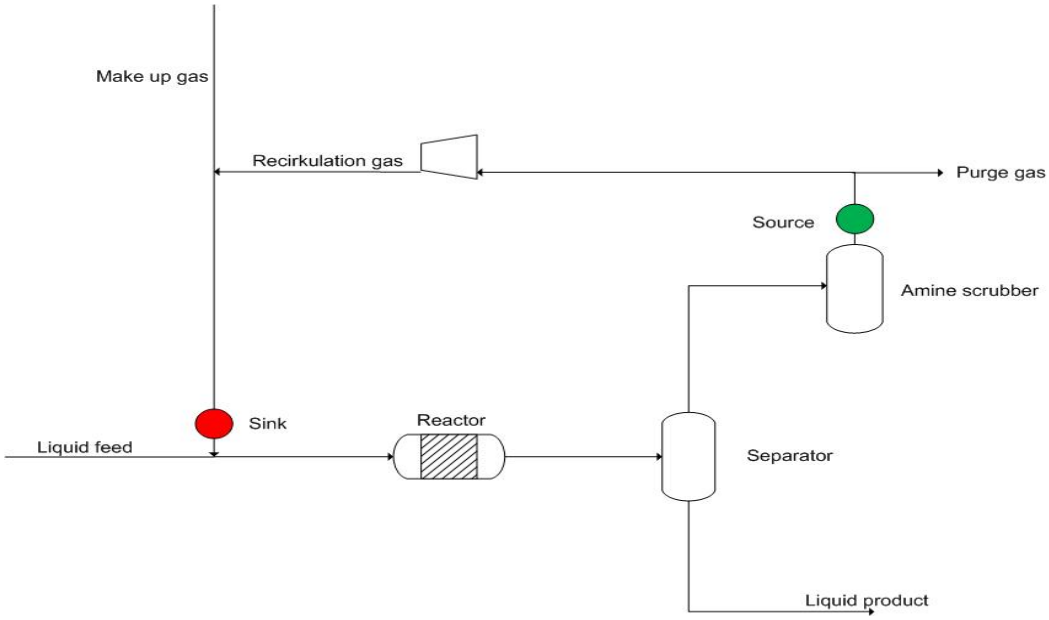

Figure 1: A typical hydrogen consuming unit. The green circle shows where the source is located and the red circle where there is a source.

2.2 Pinch analysis as a tool

The aim of a pinch analysis is to identify system surpluses and deficits of a certain utility, e.g. heat, water or hydrogen, at a given quality. This knowledge will then be used to obtain the theoretical minimum consumption of the utility, which then can be compared with the actual consumption. The difference constitutes a base for possible improvements. Since this thesis treats hydrogen usage, the quality will be purity.

The first step in performing a hydrogen pinch analysis is to put all sinks and sources into a purity profile (a diagram where flow rate is on the x-axis and purity on the y-axis)(Alves & Towler, 2002). This is done by starting with the sink of highest purity. This specific sink will constitute a horizontal line starting at x=0 with a certain length determined by the flow rate and with a distance from the x-axis determined by its purity. The next sink in the order of purity is then plotted in the diagram, also as a horizontal line, which will have a lower y-value since it has a lower purity. Once again the length will be determined by the flow rate of this sink, but it will now start at the same x-value as where the previous sink ended. The two plotted sinks are then connected by a vertical line. This is repeated until all sinks are presented in the diagram, which give a curve called the sink profile. The same procedure is carried out for the sources in the same diagram and the source profile is obtained. The result will look similar to Figure 2.

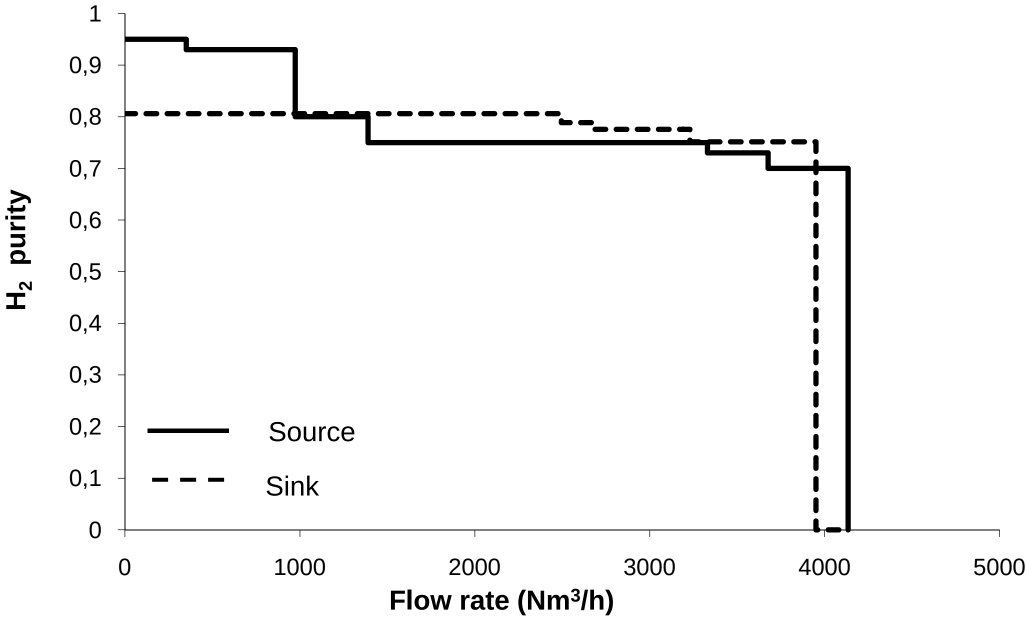

Figure 2: A purity profile showing all the sinks and sources of the hydrogen distribution system.

All sinks and sources used to create the purity profile shown in Figure 2 can are given in Table 1. In total 4 sinks and 7 sources constitute this fictive system.

Table 1: All sinks and sources of the fictive system that Figure 2 and Figure 3 represent.

Stream	Flow rate [Nm^3/h]	Purirty [%]
Sink 1	2495	80,6
Sink 2	180,2	78,9
Sink 3	554,4	77,6
Sink 4	720,7	75,1
Source 1	350	95
Source 2	623,8	93
Source 3	415,8	80
Source 4	1801,9	75
Source 5	138,6	75
Source 6	346,5	73
Source 7	457,4	70

The two curves in the purity profile diagram are discrete functions of the flow rate. These are now called y_{sink} (F) and y_{source} (F). A new function can be defined:

$$H(F) = \int_0^F (y_{source}(F) - y_{sink}(F))dF \qquad (3)$$

This is simply the net cumulative surplus of hydrogen in the hydrogen distribution system. In Figure 2 it can be seen that the source and sink profile create enclosed areas and it is clear that whenever the source profile is above the sink profile there will be a positive contribution to H(F) and vice versa.

To visualize the information given by H(F) in a good way a hydrogen surplus diagram is created. It can be done in two ways. Either the diagram is generated by plotting the highest of the purities y_{source} (F) and y_{sink} (F) against H(F) for every value of F as suggested by Alves & Towler (2002) or by plotting the lowest of the purities verses H(F) for every value of F. The latter way is used by Nelson and Liu (2008) who is the originator of the Excel macro mostly used in this project. The two different approaches give different shapes of the hydrogen surplus diagram. However, the essential information extracted from the two approaches is identical.

Figure 3 shows a hydrogen surplus diagram corresponding to the purity profile shown in Figure 2. Since it declares how much hydrogen excess there is on each purity level it is evident that as long as the curve does not reach the y-axis in the interval $(0, y_{sourceMAX})$, more hydrogen is provided to the system than what ideally is needed. By adjusting the flow rate of the variable sources, e.g. import or production by steam reforming, the shape of curve will change and the goal is to make the curve reach the y-axis without crossing it. The lower value of this segment that touches x=0 is the pinch purity and is of great interest.

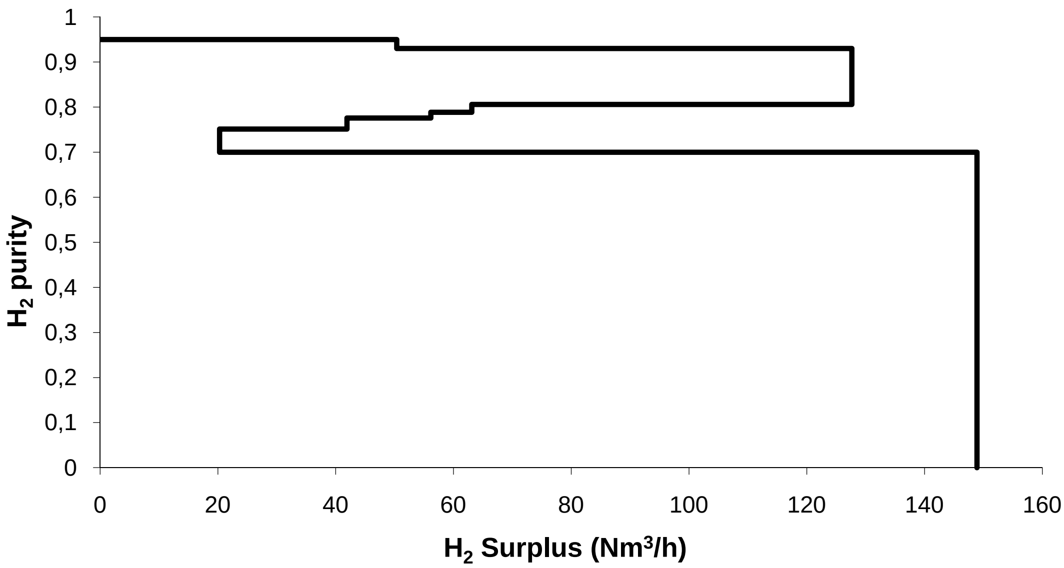

Figure 3: The figure shows the hydrogen surplus diagram corresponding to the purity profile in Figure 2. This shows whether there is an excess of hydrogen in the system.

Since no part of the hydrogen surplus diagram is touching the y-axis in Figure 3 (except for the starting point), the system is not pinched. This means that hydrogen at a high purity (95%) is wasted. If the source related to the production of high purity hydrogen is decreased in regard to flow rate, the surplus diagram will become pinched. This will result in a movement towards the y-axis for parts of the curve below production purity, which in this case is 95%. The pinched system is shown in Figure 4. The red circle shows where the pinch is located. The lowest y-value at the pinch is called the pinch purity.

The difference between the hydrogen production rate for the actual system and pinched system reveals the potential for hydrogen savings.

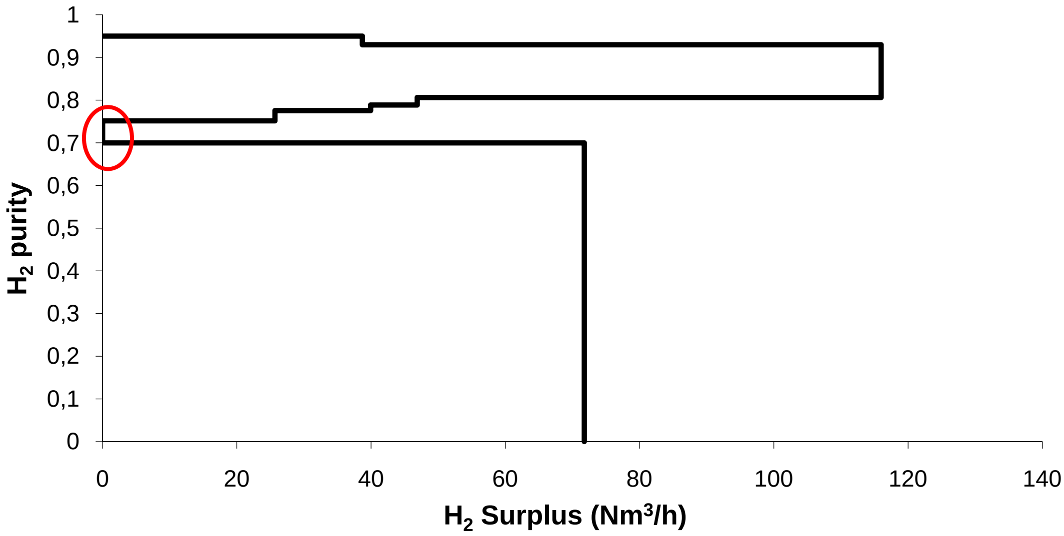

Figure 4: The hydrogen distribution system from Figure 2 and Figure 3. As can be seen, the cumulative flows in the system are smaller than in the unpinched system. The red circle marks the pinch of the system.

When the system is pinched it is possible to identify two subsystems; one region above and one below the pinch purity. In the upper subsystem the amount of available and demanded hydrogen is equal and is therefore said to be in balance. Below the pinch purity there is a surplus of hydrogen, except in the special case when the pinch purity is equal to zero.

With the knowledge from the hydrogen surplus diagram it is possible to point out the minimum usage and to identify theoretical shortcomings that explain why the present consumption is higher than the ideal. Notice that these shortcomings, called pinch violations, can be defended for economical or practical reasons. These could be expensive equipment purchases or long distances that make different sources hard to utilize. Actions that should be avoided if possible are (Hallale et al, 2006):

- flare hydrogen or use it as fuel if the concentration is higher than the pinch purity
- produce hydrogen at concentration lower than the pinch purity
- use streams with concentrations higher than the pinch purity to meet demands which requires a concentration lower than the pinch purity

A pinched system does not violate any of the three rules of thumb, meanwhile an unpinched system always violate at least one of them. By solving the pinch violation in a system the theoretical minimum consumptions can be achieved. This should be considered together with economical and practical aspects in order to create the most feasible hydrogen network.

3 Background

There are many different units involved with the hydrogen distributions system at Preemraff Göteborg and Preemraff Lysekil. Although the number of producers and purifiers is small, there is a large quantity of consumers. These and their main function are:

- ***DHT*** - Desulphurization unit, which receives the lighter components of the crude distillation unit.
- ***ICR*** - hydrogen cracker reactor, which desulphurize and cracks vacuum gas oil in order to produce more diesel.
- ***Isom*** - Isomerization unit which increase the octane number by converting straight chains of hydrocarbon to more branched compounds.
- ***MHC*** - Mild hydrocracker, which transform longer chains of hydrocarbons into shorter. It also removes sulphur from the products. At Preemraff Göteborg this unit will be converted to a green hydrotreater (GHT). It will then be able to operate as previous and also to accept a feed based on tall oil. In Lysekil this units is only used for desulphurization.
- ***NHTU*** - Naphta hydro treating unit, which receives the naphtha and desulphurize it before it is sent to gasoline mixture.
- ***Penex*** - is the name of the isomerization unit in Lysekil and is analogue with Isom unit in Göteborg.
- ***Synsat*** - Synergetic saturation unit, which desulphurize and decreases the amount of aromatic compounds in the diesel produced.
- ***T-2801*** - Column that cleans the entering hydrogen stream from hydrocarbons. Thus, the stream leaving T-2801 has a higher purity then the inlet.
- ***TGTU*** - tail gas treatment unit. The TGTU takes care of the last amount of sulphur that the desulphurizations units do not successfully remove.

Even though Preemraff Göteborg and Preemraff Lysekil have a lot in common, they still have different process and operation characteristics. Below follows a brief description of the two refineries.

3.1 Hydrogen distribution system, Preemraff Göteborg

For Preemraff Göteborg there is, as for many other refineries, a shortage of hydrogen. The amount of hydrogen available is the limiting factor when quantities of certain products are determined. Moreover, decisions on process modifications have been made in order to produce more fuels from renewable feedstock, which will make hydrogen sources of high purity even more desirable.

The requirements in regard to hydrogen vary a lot for different parts of the process. In total there are five relevant consumers connected to the hydrogen distribution. A principal sketch of the hydrogen system is shown in Figure 5. The amount of hydrogen produced at Preemraff Göteborg is 29 000 Nm^3/h.

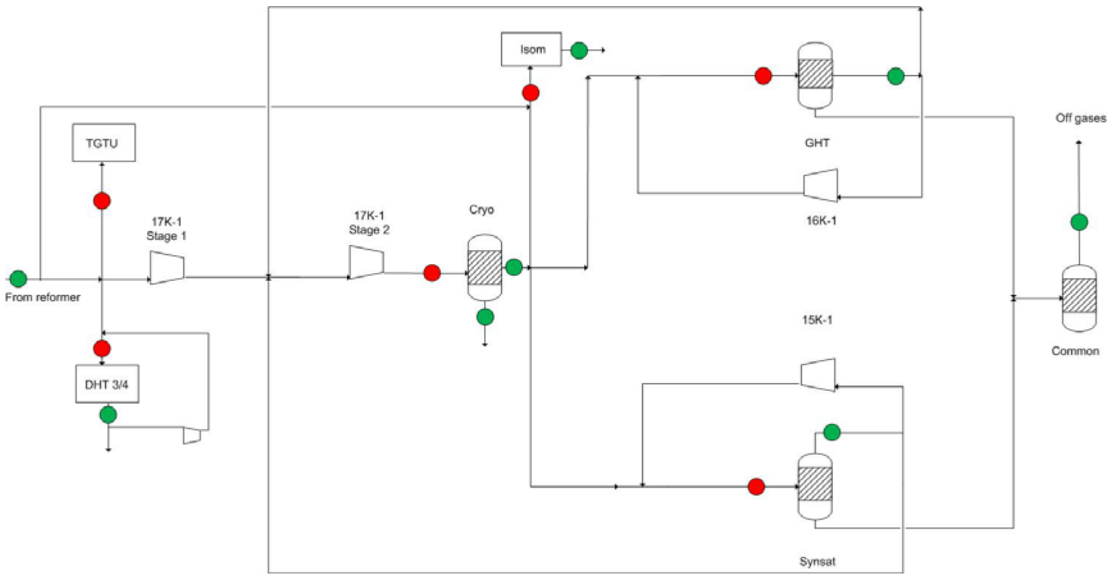

Figure 5: The hydrogen distribution system at Preemraff Göteborg. Red circles represent sinks and green circles represent sources.

There is no more hydrogen produced than what comes as a by-product in the catalytic reformer. It comes at a purity of around 83 %. However, to meet demands which require higher purities a cryogenic separator is used. This unit uses purge gases and hydrogen produced in the catalytic reformer to create two streams, one with high purity and one waste stream (sweet gas). The high purity stream has a concentration of about 95.5 vol% and is used as make up gas to the MHC and Synsat.

Since Preemraff Göteborg faces reconstructions in the near future, both present and future operation conditions were of interest. The refinery can be operated in different modes depending on which products the company prefer to produce. The most hydrogen consuming mode for the time being and for the future was investigated, since these are most critical. Before reconstructions the MK1 mode is the most hydrogen consuming. The hydrodearomatization process is then using large amounts of hydrogen (around 10000Nm^3/h) to reduce the presence of aromatics in the product. While the refinery works in this mode the Synsat receives the amount of hydrogen it needs from the cryogenic separator in order to work on full capacity. Meanwhile, the MHC obtains what is left of the highly purified hydrogen after a small part has been sent to the Isom.

The revamped MHC unit is called Green Hydrotreater, and it will be running after reconstruction. The unit will have a renewable and a standard mode for processing tall oil from the pulp and paper industry and HLGO (heavy light gas oil), respectively. When the GHT is in renewable mode, Synsat will operate in MK3 mode instead of MK1 mode and vice versa. Out of these two combinations the renewable/MK3 mode will be the most hydrogen demanding. Therefore, this scenario will be studied further.

The amount of hydrogen required for the two modes varies significantly. The production of renewable based diesel will consume more than double the amount of hydrogen compared to standard mode. This means that availability of hydrogen at a high purity will be even more critical in the future. To meet this new demand less hydrogen will be fed to the Synsat unit, which then produces diesel of European standard (MK3) instead of Swedish standard (MK1) which will be produced during standard mode. The GHT will run according to design and Synsat will be limited in operation because of hydrogen shortage. Thus, changes in the availability of usable hydrogen will affect Synsat operation alone.

3.2 Hydrogen distribution system, Preemraff Lysekil

At Preemraff Lysekil, conditions are more easily overviewed, but at the same time the system more complex. Here, it is not as interesting to look at different modes. This makes data gathering easier, since data can be collected during a long period.

Preemraff Lysekil has two producers of hydrogen; one catalytic reformer and one steam reformer that converts butane and naphtha to hydrogen and CO_2. Hydrogen production from steam reformer is expensive and not preferable. If hydrogen could be recovered, the steam reformer should work at a lower rate. Preemraff Lysekil is not in need of additional hydrogen, but rather to cut costs. Hydrogen produced in Lysekil amounts to 128 000 Nm^3/h, whence 70 100 comes from steam reforming.

There are also two upgrading facilities;

1. A ***membrane unit***, which delivers hydrogen at approximately 95% purity. The membranes are to be replaced during the spring of 2010 in order to be more effective and able to handle larger flows.
2. A ***PSA unit*** connected to the steam reformer. Currently, the PSA only treats gas from the steam reformer. Hydrogen that can be saved from the fuel gas network will be connected to the inlet of the PSA in order to decrease the hydrogen production from propane and naphtha. Out from the PSA unit, the hydrogen purity is 100 %.

One reason why it is convenient to put the recovered hydrogen to the PSA inlet is that many compressors at Preemraff Lysekil are working near maximum load.

The hydrogen system in Lysekil is viewed in Figure 6

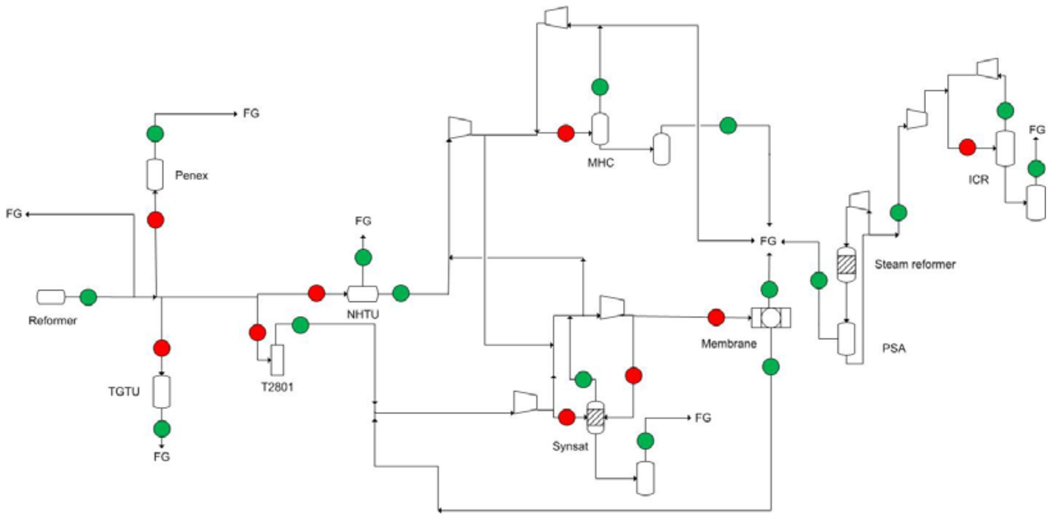

Figure 6: The hydrogen distribution system at Preemraff Lysekil. Red circles represent sinks and green circles represent sources.

3.3 Economy

All changes in the process proposed in this work will lead to new costs. There are different methods of estimating the cost when new equipment, as well as piping, must be purchased and installed. In the case of a new compressor, the capital cost is calculated via the formula

$$C_e = a + b \cdot S^n$$

and cost estimation parameters found in Sinnot & Towler(2009). In order to obtain correct costs, Chemical Engineering Index (CECPI) has been used. The cost is then transferred to today´s value with the expression

$$C_1 = C_0 \frac{Index\ 1}{Index\ 0}.$$

The cost for equipment alone is however not sufficient to describe the total cost for incorporating a unit in the process. An installation factor of 2.5, proposed by Hand (1958) was used to include costs for piping, labor etcetera (Sinnot & Towler, 2009). In order to calculate cost for single pipes, the formula

$$C_p = 880 d_i^{0.74} * L$$

was used, where L is the length in meter and d_i is the inner diameter of the pipe (Sinnot & Towler, 2009).

4 Methodology

The concept of hydrogen pinch analysis is new, and consequently not widely treated in literature. The concept was developed by Alves in 1999 (Hallale & liu, 2001). Therefore, the first step of this work was to gather a sufficient amount articles on the subject in order to obtain a comprehensive understanding of this type of analysis.

4.1 Hydrogen pinch analysis

The graphical results necessary to perform a general pinch analysis can be produced by several computer programs. However, the selection of corresponding programs for hydrogen pinch analysis is limited. Consequently, a Matlab-based program was created, which produces both a purity profile and a hydrogen surplus diagram from flows and purities given by the sinks and sources. The program code can be seen in Appendix . The program was used to control results which were obtained using a Microsoft Excel macro program by Nelson and Liu (2008). Figures used in this report however, were obtained via the Excel program.

Flow sheets of all process units were available and these describe the refinery on a detailed level. The relevant information concerning the hydrogen system was extracted and used in order to obtain a more simplified picture. This means that a unit, such as the Synsat, that holds several reactors was visualized with only one reactor since this is enough to describe the demands and accessibility of hydrogen associated with it. Furthermore, components that have no affect on hydrogen streams were neglected in these simplified pictures. This means that so called “once through units”, which do not have any recirculation of hydrogen, are represented as one component with a sink at the inlet and a source at the outlet.

4.1.1 Preemraff Göteborg

The major flows of hydrogen at Preem refinery in Göteborg are well documented. However, minor flows, particularly off gas streams are sometimes less surveyed. In order to perform a pinch analysis qualitatively all streams with a hydrogen content must be determined or estimated in regard to at least flow rate and purity.

After mapping the hydrogen network and identifying wanted measure points within the process, data was gathered using an AspenPlus excel add-in. Certain time intervals were found, when the refinery was operating under conditions which are interesting to study. This includes more than operation mode. There are variations in market prices and this will affect which products that are produced. Hence, there are many periods in the past that are not representative for a general case. It was desired that the reformer was running at maximum capacity and that the feed to the Isom unit was sufficiently high. Mean values of wanted data were then used to represent the actual conditions. Assumptions were made in discussion with process engineers regarding streams when data could not be found.

It was not very relevant to identify possible improvements on the present case since the reconstruction of the MHC will take place in the near future. Instead the identification was carried out for the future scenario when the renewable/MK3 mode will be critical. Calculations were performed on each improvement to estimate how much more hydrogen would be available and the corresponding increase in liquid feed to the Synsat unit.

4.1.2 Preemraff Lysekil

The hydrogen distribution system of Preemraff Lysekil is more complicated than the Göteborg system. It contains more connections and exchange of hydrogen between the different units. After mapping the system to obtain a clear picture, data was gathered in the same way as in Göteborg, using the same AspenPlus program. However, since the refinery does not switch between different operational modes, data could be gathered from a considerable longer time interval. The studied period of time was between 2009-01-01 and 2009-07-01 and the collected data was mean day averages. Also in this case, assumptions were made when some stream properties could not be measured.

The new membranes that was to be installed was treated as nonexistent. This was partly because no real data from the future case was available. Also, there were uncertainties where the extra hydrogen in the membrane inlet was to be taken from, and where increased flow of pure hydrogen was to be used.

When a complete simplified picture of the hydrogen distribution system was produced and all sinks and sources of hydrogen were determined the pinch analysis was carried out. This showed the efficiency of the hydrogen usage. Thereafter, four suggestions were made based on the information obtained from the analysis. Calculations were performed on each improvement to estimate how much the production of hydrogen could be reduced in the steam reformer.

One way to reduce the use of hydrogen is to lower the demanded purity at the inlet of units. This has been avoided earlier since it was desired to examine the potential hydrogen savings under normal operation conditions. However, it has been investigated for the MHC and the ICR units after discussion with process engineers. A reduction of the hydrogen concentration at the inlet by two percentages was studied with the ambition to discover possibilities for hydrogen savings. The amount of hydrogen entering should be the same and it was assumed that the consumption of hydrogen in the reactors were the same. Since a lower inlet concentration affects the outlet stream and therefore also the concentration of the recycling stream a correlation was needed. This was obtained by looking at the collected data. The inlet and outlet concentration of these units varies so it was possible to observe trends, which were used to establish the wanted correlation. This can be seen in Appendix E. It is important to add that this part of the study was carried out separately. A pinch analysis was performed with the new established demands in order to observe a new theoretical minimum consumption, but none of the suggestions made to improve the system includes the aspect of lower purity demands.

4.2 Economy

The investments proposed are evaluated in a payback period perspective. Interest rates are not taken into consideration, since the investments are in the order of magnitude that they should pay off in a short time perspective. In a short time span, the interest rates are not so important. The considered expenses were investments, changed costs for operation and emissions together. When new units were introduced to the hydrogen network these were simulated in Aspen HYSYS to estimate the size of the units.

4.2.1 Electricity

Due to larger and heavier flows, compressors can be forced to work harder. New units might also be installed. Compressors are units with high consumption of electricity. Thus, electricity consumption had to be taken into consideration. Electricity demands for the compressors were calculated via modeling in Aspen HYSYS. However, increased electricity use originating from pressure losses was not modeled.

4.2.2 Fuel cost

When hydrogen is made available for reuse in the process instead of being sent to the fuel gas network, this hydrogen must be replaced with another fuel in order to produce heat. At Preemraff Göteborg and Lysekil, the replacing fuel is natural gas and butane respectively. The amount of fuel needed is calculated through heating values of the streams being redirected from the flue gas net. Equations used are shown in Appendix B.

4.2.3 Emission cost

Since a company must buy permits in order to emit CO_2, the increased use of natural gas or butane will add a cost. The price used for carbon emissions is 15€/ton CO_2 (www.nordpool.com). Equations are accounted for in Appendix B.

4.3 Sensitivity Analysis Göteborg

To investigate the robustness of the results a sensitivity analysis was carried out. The chosen parameters for the analysis in Göteborg were:

- The marginal profit of products from Synsat operation. This parameter has large fluctuations and it is difficult to put a representative price on it. The marginal profit is supposed to be valid for the economic life time of the investment.
- The outlet concentration of hydrogen from Common off gases. The purity of the off gases leaving the Common unit is one of the more uncertain parameters of the calculations concerning the hydrogen network. The reason is that the purity of this stream only has been measured a few times during the last years and that it is assumed that the reconstruction of the MHC will not affect its composition.

4.4 Sensitivity analysis Lysekil

The suggestions made for Preemraff Lysekil had other uncertainties than Preemraff Göteborg. Therefore, the examined parameters were not the same. The parameters investigated at Preemraff Lysekil are:

- Price for butane. The price for butane is essential for both estimating the cost related to steam reformer operation and fuel gas substitution.
- Price for emitting CO_2. This is a cost that is likely to increase in the future. At Preemraff Lysekil, the savings of CO_2 emissions has a significant impact on the result.

5 Assumptions and approximations, Göteborg

Several assumptions and approximations have been carried out during this work. These are categorized into subgroups. Critical assumptions will be treated in the discussion.

5.1 Process equipment and process conditions

One of the most fundamental assumptions made in this work is that the mean values of data gathered from 2008-08-13 to 2008-08-14 and from 2009-01-12 to 2009-01-14 is representative for the MK1 and MK3 mode, respectively. This assumption concerns the operation of Synsat. Since the catalytic reformer, DHT and Isom units are independent of Synsat mode, their representative operational conditions have been assumed to be the same as during the selected time interval for MK1 mode regardless how the GHT and Synsat are operated. Furthermore, the cryogenic separator can deliver a hydrogen stream of varied purity due to several reasons. This purity was different for the two studied time periods (95,5mol% and 97,8mol% for the MK1 and MK3 case, respectively). However, the MK1 settings also determined the representative hydrogen concentration of cryogenic separator outlet, since it is closer to normal operation. The efficiency of this separation unit, defined as

$$\eta = \frac{F_{out}c_{out}}{F_{in}c_{in}}$$

was assumed to be 81%.

Since the MHC has not yet been reconstructed into a GHT unit, no data is available. Instead all flow properties of the streams within the future GHT unit originate from models created by Haldor Topsøe. Two models exist of this unit, describing the conditions in the start and end of a cycle. These differ due to catalyst deactivation etc. Mean values of necessary properties from these were used to perform calculations of the hydrogen distribution system after reconstruction.

The amount of hydrogen solved in the liquid petroleum product that leaves the Synsat unit is not measured and has instead been assumed to be 10% of the makeup flow of hydrogen entering this unit. The relation between the net added amounts of hydrogen (make up gas minus purge) and the liquid feed to Synsat is determined to be 50 Nm^3 H_2/m^3 liquid.

The TGTU requires a very small amount of hydrogen and therefore it has been neglected in order to simplify the system.

DHT3 and DHT4 are assumed to be identical. The concentrations of hydrogen in the recirculated streams are in general between 86-92%. Therefore, a value of 89% has been chosen.

It is assumed that all hydrogen goes over the top in low pressure separators. This means that no hydrogen is dissolved and lost in liquid going out from low pressure separators.

The hydrogen concentration of the Common off gas stream is not regularly measured. Lab samples indicate a purity of around 73%, which is used in this work. This assumption will be tested in the sensitivity analysis.

It is assumed that natural gas will replace shortages in the fuel gas network due to reuse off gases.

5.2 Economy

It has been assumed that the refinery only benefits a third of the year from the improvements suggested, since that is the assumed operational time for renewable/MK3 mode. Thus, any further use of these improvements during standard/MK1 is neglected.

When more hydrogen becomes available, which enable an increase of liquid feed to Synsat, the operating costs for this unit will rise. This will be included in the cost calculations.

When buying new equipment, e.g. a new compressor, the Hand factor for installing costs is assumed to cover the cost for piping.

5.3 Simulation in Aspen HYSYS

When simulating scenarios in Aspen HYSYS, a fluid package must be chosen. For all simulations in this work a Peng-Robinson-based fluid package was used.

All streams treated in the simulations have various compositions. These have been simplified by neglecting all components which occurs in concentrations lower than 2.5%.

To prevent an underestimate of electric costs, all isentropic efficiencies in compressors are set to 75% when modelled in Aspen HYSYS.

6 Results from hydrogen pinch analysis Göteborg

The pinch analysis results in, as mentioned in section 2.2, a purity profile and a hydrogen surplus diagram. These are different for the two modes, MK1 and renewable/MK3, and will be presented in separate sections below.

6.1 MK1 mode

The purity profile for MK1 mode is shown in Figure 7. It shows that there is a surplus of hydrogen at low purities in the system, since the “demand graph” end to the left of the “source graph”. The surplus may appear quite small, but is still significant.

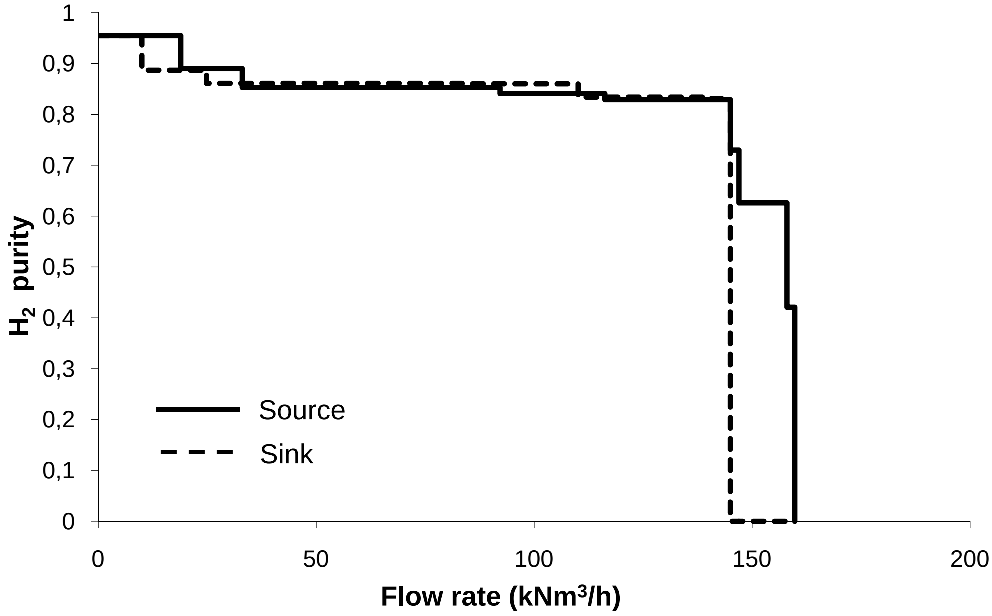

Figure 7: Purity profile for MK1 mode in Göteborg.

The hydrogen surplus diagram for MK1 mode is shown in Figure 8. As can be seen, the system is pinched, which means that no hydrogen with purity greater than the pinch purity is used to satisfy low purity demands or released to the fuel gas system. This is not surprising, considering the relatively simplicity of the system.

It is not possible to determine the exact pinch purity since there are several vertical segments in what appears to be one segment close to the y-axis. When closing up to this segment, it can be seen that it really consist of several sub-segments. The pinch purity is somewhere in the interval 0.73 - 0.834. This interval is highlighted with a circle in the diagram. However, the relevant information from this figure is that the system is optimal seen from a hydrogen pinch perspective.

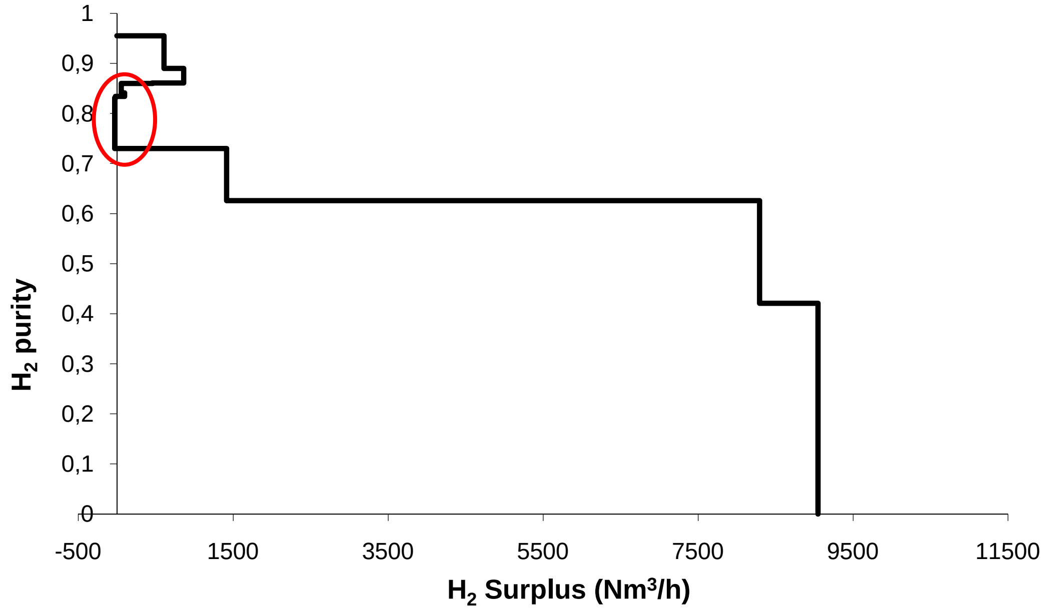

Figure 8: Hydrogen surplus diagram for MK1 mode, Göteborg. The red circle indicates the pinch.

6.2 Renewable/MK3 mode

A purity profile for renewable/MK3 mode is shown in Figure 9. As can be clearly seen, the cumulative flow rate is smaller in MK3 mode than in MK1 mode. This is mainly due to higher actual consumption in the units.

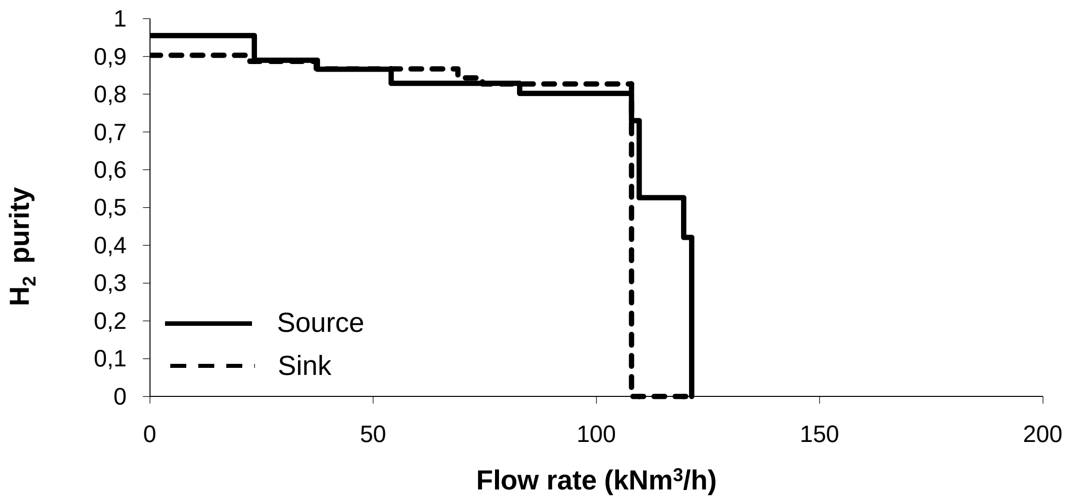

Figure 9: Purity profile for MK3 mode, Göteborg.

From the purity profile in Figure 9, the hydrogen surplus diagram for MK3 mode is constructed. This is shown in Figure 10. The system is pinched also in MK3 mode, and the pinch purity is 0.73. The pinch is circled in the figure.

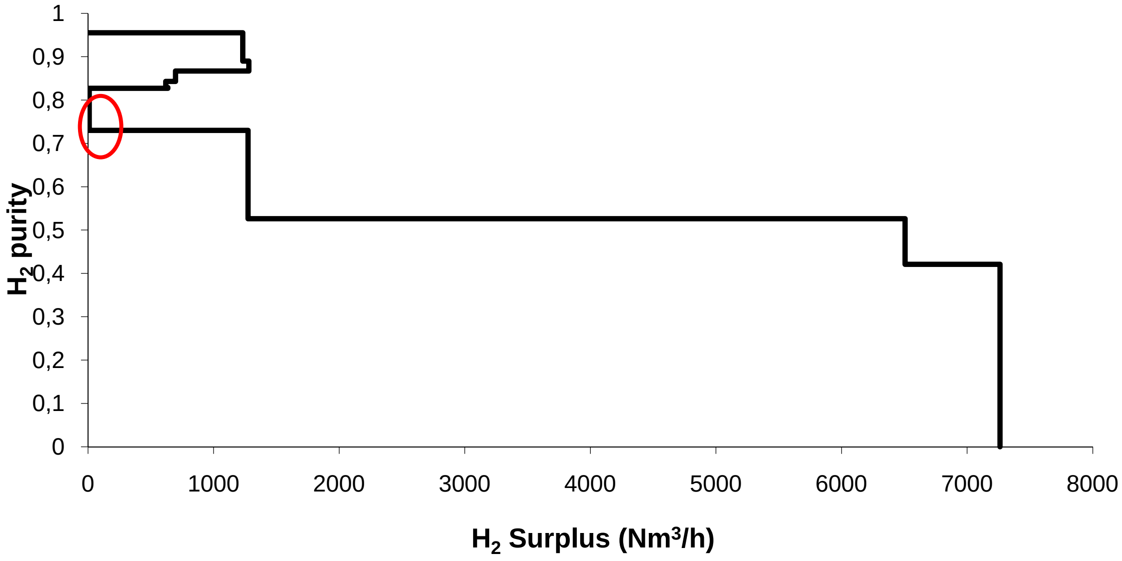

Figure 10: Hydrogen surplus diagram for MK3 mode. The red circle displays the pinch.

7 Options for hydrogen utilization, Göteborg

The hydrogen system at Preemraff Göteborg is pinched, but all the same there is an excess of hydrogen. A pinched system means that with determined sinks and sources it cannot be improved. However, by adjusting inlets to purifiers the system´s sinks change. When the sinks and sources change, the hydrogen surplus diagram also changes as a result of this. In this system, the amount of hydrogen that is located above the pinch purity can be increased, resulting in better hydrogen availability.

In order to utilize hydrogen that today is used as fuel gases, two different actions have been identified as interesting for further investigation. The two actions are independent of each other, and can therefore be combined into a third scenario. These cases are presented below. The DHT and TGTU units are disregarded in the process pictures, since they have little impact. It is important to notice that the pinch analysis itself did not provide any information about what can be modified in order to improve the system. The suggestions made are therefore not based on the result of the hydrogen pinch analysis.

7.1 Case 1: Reuse of off gas

Hydrogen is solved in the liquid products that are sent as feed to the diesel fractionators in the GHT and Synsat units. The lighter components including hydrogen are separated from this stream and continue to the Common unit. The hydrogen leaves this unit in form of off gases at a purity of 73%. These are at a low pressure (4.6 bar), and the feed to compressor 17K-1 is at 20 bar. In order to reuse this hydrogen, Preemraff Göteborg would therefore have to invest in a new compressor. This is, as previously stated, preferable to avoid but since the off gas stream is so large, it will still be worth considering. A flow chart of the modified process is shown in Figure 11.

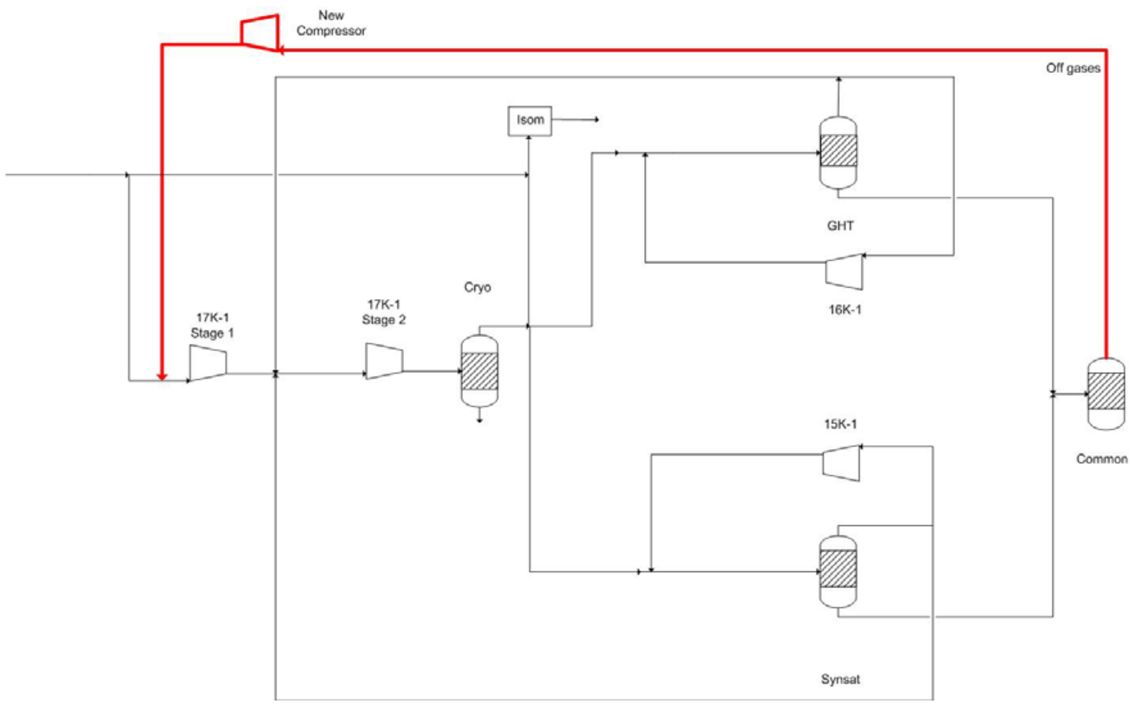

Figure 11: Flow chart of the process after adding a new compressor and redirecting the off gas flow back to 17K-1.

7.2 Case 2: Redirection of Synsat purge

The purge gas from the Synsat is currently being directed back to the cryogenic separator. However, this gas is above the pinch purity and could probably be used within the process without being upgraded. In the second scenario this gas is being redirected to be included in the treat gas to GHT, as illustrated in Figure 12. This will result in smaller amount of make up gas in order to reach up to the required purity of GHT treat gas, since the Synsat purge is more pure than the GHT outlet.

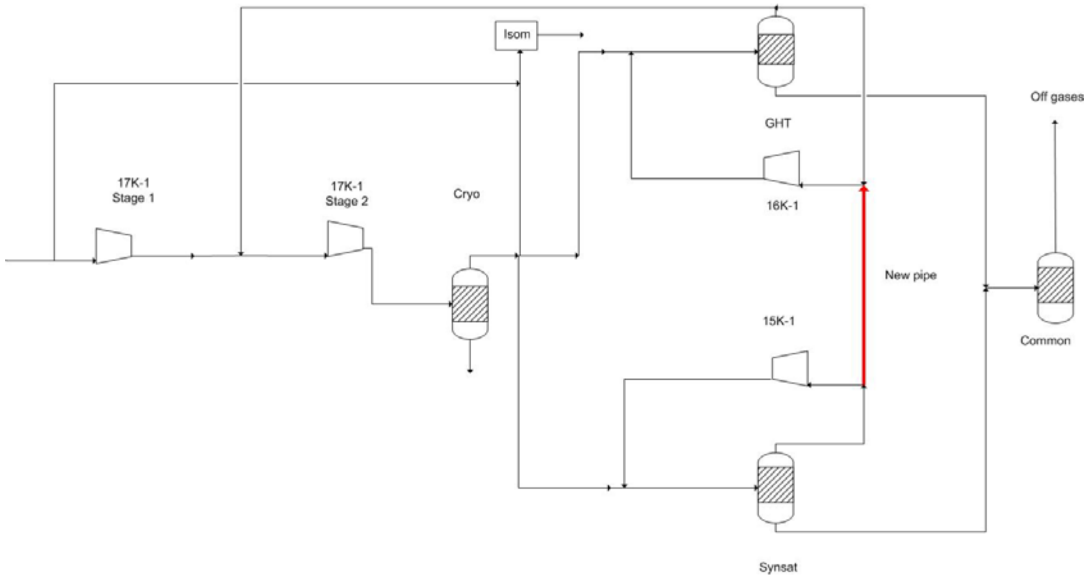

Figure 12 Flow chart of the process after redirecting Synsat purge to GHT inlet.

7.3 Case 3: A combination of off gas reuse and Synsat purge redirection

The two earlier suggestions do not involve the same streams, which makes it possible to suggest a combination of them. Hence, the hydrogen usage can be reduced by the advantages of both case 1 and 2 simultaneously. This can be seen in Figure 13.

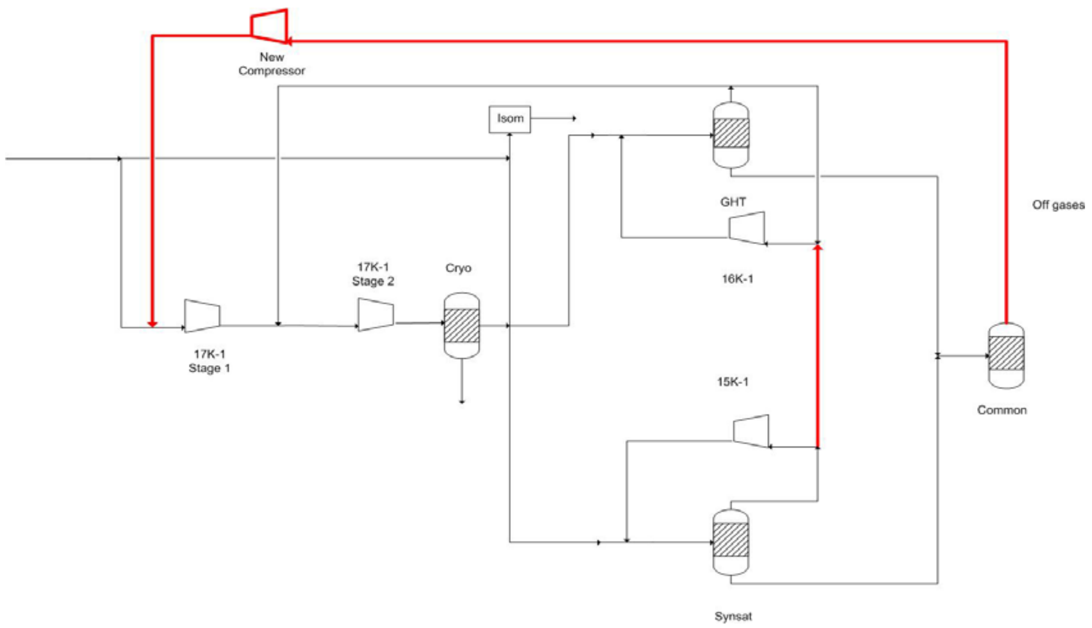

Figure 13: Flow chart of the process after carried out both earlier modifications.

8 Results from retrofit, Göteborg

The results are divided into effects on the process and economic results. A sensitivity analysis is also presented.

8.1 Process

All three suggestions increase the possibility to process more liquid feed in the Synsat unit, which can be seen in Table 2. Case 3 represents the largest difference in liquid feed to Synsat (23%) compared to the business as usual-scenario (BAU). Case 1 achieves an increase of 18%, whereas the second case has a more modest impact (4%).

Table 2: The difference in hydrogen usage for the three cases is shown together with the change in hydrogen and liquid feed

Case	BAU	1	2	3
H_2 to FG from Common and CRYO [Nm^3/h]	6 500	5 600	6 300	5 300
H_2 feed to Synsat [Nm^3/h]	9 300	11000	9 7000	11 500
Increased liquid feed to Synsat [m^3/d]	-	510	120	660

8.2 Economics

Since hydrogen is used in a more effective way, increased revenues from sales of diesel products are obtained. With a reasonable marginal profit of diesel product, the investments are evaluated. All costs related to the different modifications together with the payback periods are represented in Table 3. Case 3 is the most expensive option seen from an investment point of view, but it also generates the largest net revenue. The second case has the lowest investment cost and payback time. However, the annual net revenue is considerably lower for this alternative compared to the first and third.

Table 3: The costs and payback time associated with the three suggestions

Case	1	2	3
Capital cost [SEK]	15 570 000	78 000	15 730 000
Increased running costs [SEK/year]	512 000	300	532 000
Increased emission costs [SEK/year]	179 000	47 600	231 000
Increased fuel costs [SEK/year]	2 230 000	594 000	2 880 000
Increased revenues [SEK/year]	10 920 000	2 560 000	14 320 000
Net revenue [SEK/year]	8 000 000	1 920 000	10 670 000
Pay-back time [year]	**1,9**	**0,04**	**1,5**

8.3 Sensitivity analysis

In order to determine the robustness of the economic evaluation, a sensitivity analysis must be performed. In this analysis, two parameters are varied and the effects on the economic results are studied. As stated in section 4.3, the parameters chosen in this study are:

- Marginal net revenue from the sale of 1 m^3 diesel product.
- Hydrogen purity of common off gas

8.3.1 Marginal net profit of diesel products

Revenues are of course of great importance when making an economic decision. That, and the fact that the net marginal profit varies a lot from week to week in the oil business makes this a valid parameter to investigate in a sensitivity analysis. The net revenue is varied between 5-45 US$/$m^3$ diesel. The net income in relation to net revenue is shown in Figure 14.

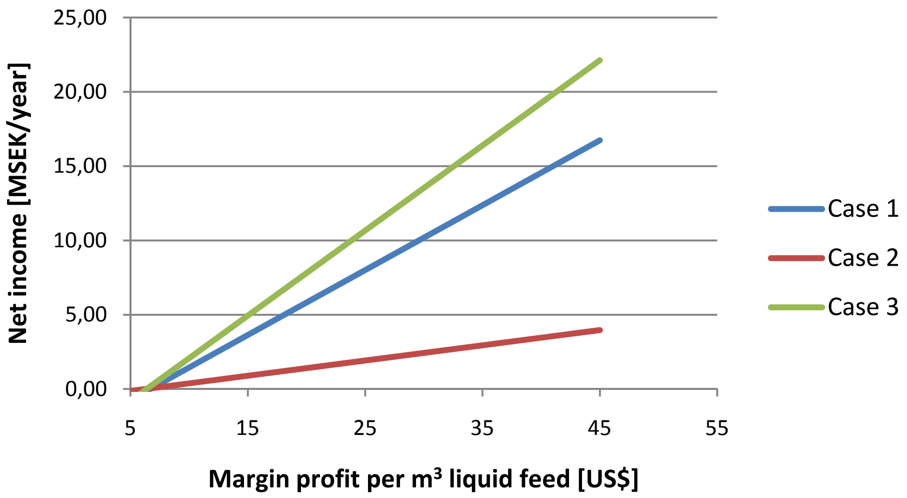

Figure 14: Net income in relation to marginal profit.

Note that the net income is below zero until the marginal profit reaches approximately 6-6.5 US$/$m^3$. This means that the investment will never pay off when the net revenue is below these numbers. In Figure 15, it is shown how the payback period correlates with net revenues. Here, the net revenue is varied between 10-45 US$/$m^3$ diesel.

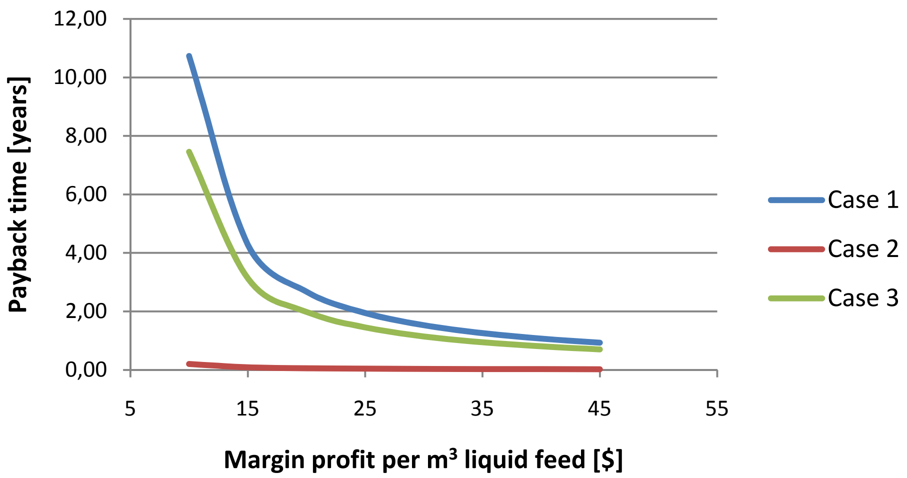

Figure 15: How payback time of the different cases depends on marginal profit.

As can be seen in Figure 15, the marginal profit must be approximately 20 US$ per m^3 diesel in order to achieve a payback period of less than 2 years. Case 2, however, is not so dependent on marginal profit since the investment cost is low.

8.3.2 Off gas purity

The composition of the off gases has an impact on both the compressor workload and the compressor size. Therefore, a re-modelling of the system is performed, changing the off gas purity between 69 and 77 %. As can be seen in Figure 16 though, the impact of off gas purity is not important. In case 2, the purity has no impact since the off gases are not recirkulated.

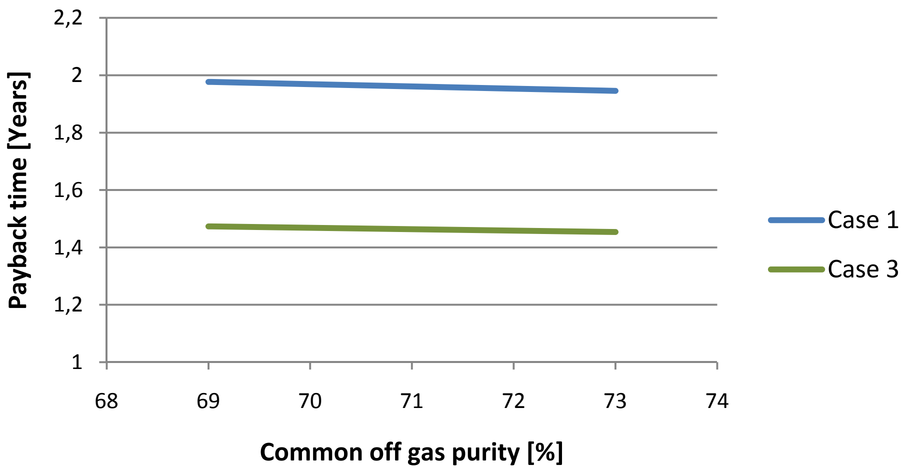

Figure 16: Payback time dependency of off gas purity.

The assumption of having 73% hydrogen purity in off gases is thus of little importance, since it has no greater impact on the results.

9 Discussion

Since the pinch concentration for MK3 is less than 82.9 %, it may seem strange that the reformer stream goes into the cryogenic separator. This is however essential. If a hydrogen pinch study would be performed before the separator was installed, there would be a shortage of hydrogen from the beginning, so the un-pinched “pinch purity” would certainly be higher than 82.9 %. After installing the separator and leading reformer gas into it though, it is not optimal to lead more gas over pinch purity into the separator.

Case 1 has the main advantage that the amount of hydrogen available for Synsat increases substantially. One other advantage is that the new GHT unit works under design specifications, i.e. with the hydrogen stream from CRYO and with the designed recirculation. However, there are also some drawbacks with this proposition. It has not been stated that the off gases from common contains only harmless substances. If the off gases contains some species harmful to the process, new cleaning devices must be installed, which would make the investment more expensive. Even now it is an expensive alternative, since a new compressor must be bought.

For ***case 2***, the major advantage is the low investment cost. This alternative cannot free as much hydrogen as the first case, but it has a short payback time. Also, it decreases the work load of 17K-1 and the cryogenic separator. The major disadvantage is that the outlet concentration of Synsat varies. The advantages are only valid when the Synsat purge is more pure than the GHT purge. The difference should most preferable be significant. Another disadvantage is that the GHT unit will be dependent on how Synsat is behaving. Large disturbances can therefore be transmitted in the process. It may be necessary to install more advanced forms of control systems if the inlet concentration to GHT is sensitive. This would increase the investment cost substantially. Since the conclusions from Figure 10 is that no pinch violations occur, it can be surprising that redirecting a stream can result in better hydrogen economy. However, when making the revamp the conditions for the system change. Since the more pure Synsat purge does not enter the cryogenic separator, the concentration at the inlet decreases. This causes a sink to become lower in purity demand.

Case 3 can combine the reuse of hydrogen with the lower load on compressor and cryogenic separator. This gives a situation with good availability of hydrogen, at the same time as the current equipment is not overloaded. The investment cost is marginally larger than in case 1, but the payback time is lower.

In case 2 and 3 it is suggested that the Synsat purge is led to the GHT recirculation compressor. This makes the total flow rate through the compressor to exceed 19 000 Nm^3/h by circa 5%, which is the maximum capacity. When estimating the increased electricity consumption, it has been assumed that this stream is compressed by one compressor which in is not possible in reality. There are however, two compressors available for recirculation and if both of them are used the entire stream can be compressed, but probably to a higher cost than what is estimated in the economic evaluation. It is worth to mention that the isentropic efficiency is assumed to be 75% for this compressor which is an underestimate and can therefore at least partly compensate for the inaccuracy. The two compressors occasionally work simultaneously also with current process conditions.

The sensitivity analysis shows that the purity of the off gases leaving the Common unit is not very important for the economical results. This is positive since this parameter was rather uncertain and gives the results increased credibility. It is also clear from the sensitivity analysis that the feasibility of the suggestions is highly dependent on the Synsat marginal profit. It is clear that none of the suggestions can be justified if this profit is low enough. However, with reasonable marginal profit all three alternatives are defendable.

It is assumed that no benefits can be drawn from the retrofit during standard/MK1 mode. In the second case this is probably true, since the difference in purity between Synsat and GHT purge is small during this mode. In case 1 and 3 however, this might not be accurate. If, in fact, the Common off gases could be utilized when producing MK1, the payback time for this option will decrease. The opposite is true if renewable/MK3 mode will be run less than a third of the year.

All assumptions will contribute with uncertainties in the results. Some are of course negligible, meanwhile others have considerable impact on the results. It is important to bear in mind that the work concerning Preemraff Göteborg is to a great extent based on data gathered during a few days. This means that several factors could have influenced the data in an undesired way. The studied time period consists of two discrete time intervals within a considerable time span. This means that the specification of the process may not be the same for the two intervals, e.g:

- the crude oil refined may have had different composition
- the markets demand for certain products are different and therefore the operation of the refinery units may have been prioritized differently
- the surrounding temperature was a lot higher during the studied MK1 period, since it occurred in the summer season and not during the winter, which was the case for renewable/MK3 mode

One drawback with the chosen time interval for renewable/MK3 is that the outlet concentration of the cryogenic separator was higher than normal (97.8 %). This means that the make up gas entering both the GHT and Synsat is higher than normal. The sink, which corresponds to the hydrogen inlet of these units, could therefore have been determined to be at a higher purity than what is actually needed for this mode.

10 Assumptions and approximations, Lysekil

Assumptions for Preemraff Lysekil will be stated for process and economy. All assumptions concerning HYSYS modelling are the same as for Preemraff Göteborg.

10.1 Process equipment and conditions

It is assumed that the data gathered is representative to describe the situation in Lysekil. This data was from between 2009-01-01 and 2009-07-01 and averages of all measured quantities were used to determine the streams in the hydrogen network. In most cases the data comes from surveying equipment that continuously performs measurements. However, concentrations of some streams are double-checked by taking lab samples. These are in general more correct and have been used when available.

The PSA unit is assumed to have an efficiency of 91% (defined in the same way as for the cryogenic separator in the Göteborg study). This is estimated through several measurements in the past. The measurements are accounted for in Appendix C.

The accuracy of the surveying equipment varies and it happened that mass balances did not add up due to error of measurements. This occurred at two places in the system:

- The measured volume from NHTU and Synsat, which are sent to the MHC make up compressor differed significantly from the measured volume leaving the very same compressor.
- The measured volume of the product stream from the membrane and the stream leaving T-2801, which constitute the make up gas to the Synsat did not correspond to the measured volume entering the Synsat make up compressor.

In these cases the error was distributed over the different streams, by adjusting the flows so that correct balances were obtained.

It was possible to see how much different valves had been open during the studied period of time. In order to get a picture of the relevant structure of the hydrogen distribution system some streams were neglected when valves controlling the flow were closed or barely open.

It is assumed that all hydrogen in the inlet of T-2801 is recovered when increasing the purity of the stream going to Synsat.

When densities has been needed and compositions was known, Aspen HYSYS has been use to estimate these densities.

It is assumed that when replacing hydrogen from the steam reformer, it is the butane feed that is decreasing. When it comes to replacing off gas in the fuel gas network it is assumed that the substitute is a mix with equal shares of propane and butane.

When the effect of reduced inlet purity to MHC and ICR was studied several assumptions were made. It was assumed that the same amount of liquid feed could be processed, which means that the consumption rates of hydrogen were unaffected. The outlet purities for the MHC and ICR were assumed to be 82.3 % and 86.6 %, respectively. These were estimated through looking at the behavior of the outlets stream when the inlet streams differed from the average values. In Appendix E it can be seen how the correlation between these streams was established.

10.2 Economy

It is assumed that average prices for 2009 are accurate regarding butane, naphtha and TFOE.

For the first suggestion, a new compressor is purchased. The Hand factor of 2.5 is assumed to cover the piping expences from the compressor to PSA inlet. However, the distance from the Synsat and ICR units to the PSA inlet is assumed to be too long to be included in a Hand factor. This is therefore calculated according to regular pipe cost. It is also assumed that the current piping cannot be reused. Hence, all pipes must be purchased.

11 Results from hydrogen pinch analysis Lysekil

The hydrogen distribution system in Lysekil was analyzed both in its current form, but also when a fictive change had been made to purity of the inlet to ICR and MHC.

11.1 Current distribution hydrogen network, Lysekil

The hydrogen distribution system in Lysekil is more complex, and therefore harder to utilize in an optimal way. A purity profile for the system is shown in Figure 17. The system shows prospects of improvement, since the difference between supply and demand are significant.

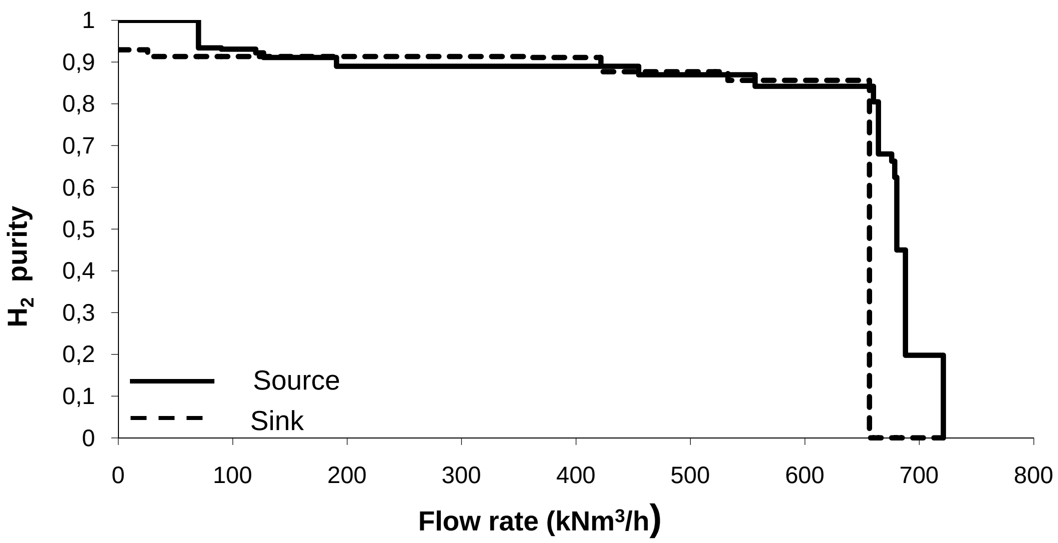

Figure 17: Purity profile for present hydrogen system in Lysekil.

As can be seen in Figure 18 the system is not pinched and is therefore not optimized today. This hydrogen surplus diagram indicates that there is a potential for hydrogen savings.

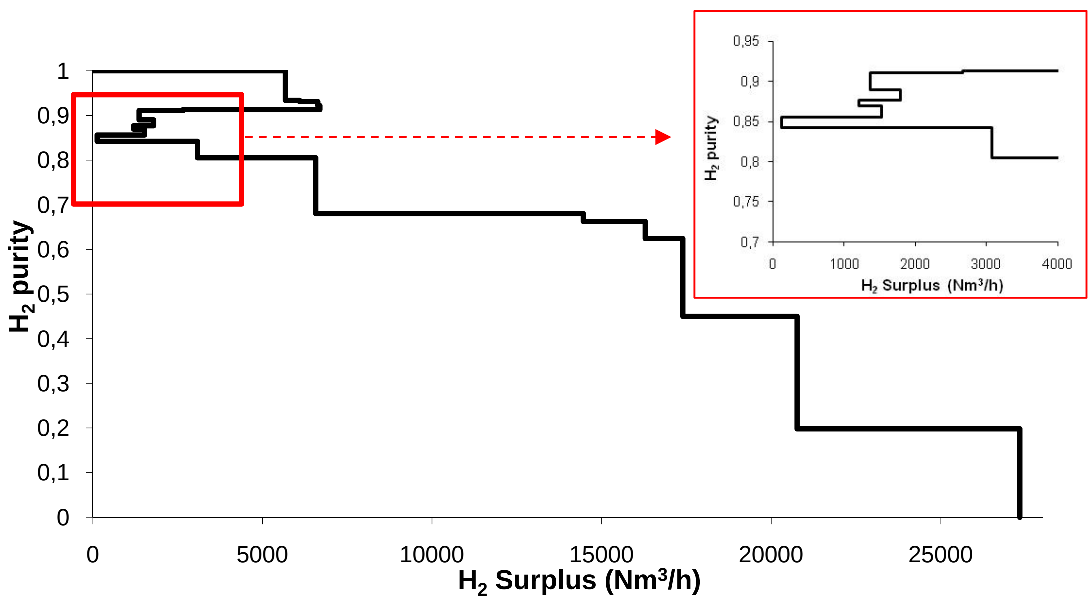

Figure 18: Hydrogen surplus diagram for present hydrogen system in Lysekil. A magnification of the area close to the y-axis is provided in the upper right corner.

Since the system is not pinched, it has to be determined what source should be lowered in order to optimize the system. In Lysekil, the desire is to lower the hydrogen production from steam reforming of butane. Before pinching, the steam reformer produces approximately 70 100 Nm^3/h. The resulting pinched system from pinch analysis is shown in Figure 19.

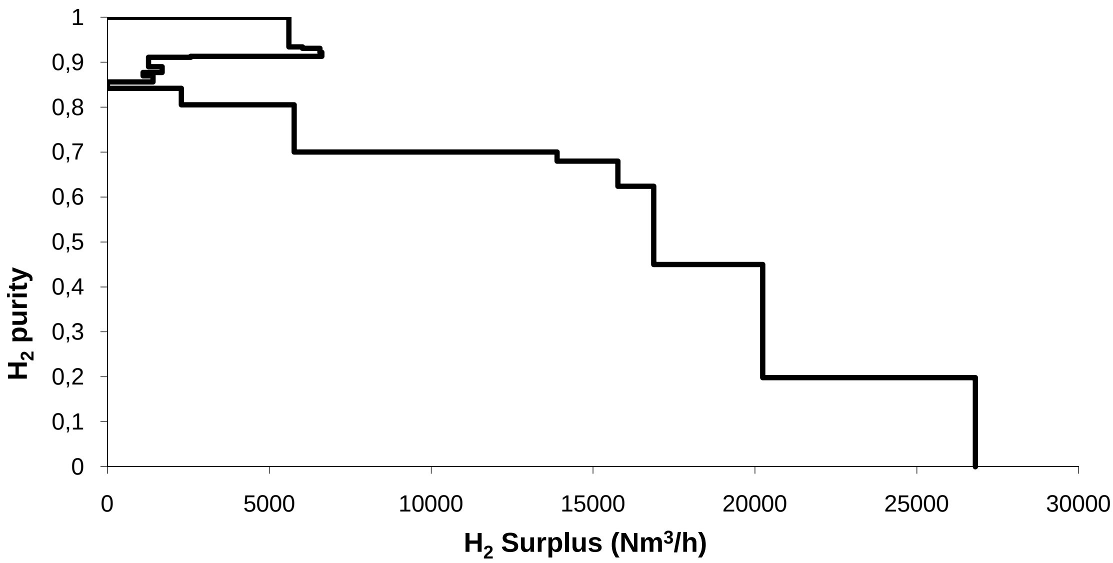

Figure 19: Hydrogen surplus diagram for pinched system in Lysekil.

The pinch purity could now be determined, and it is 84.2 %. After pinching the system, the required amount of hydrogen from the steam reformer is circa 69300 Nm^3/h. An obvious pinch violation is the bleed stream from reformer that transports hydrogen at a purity of 91.1 % directly to the fuel gas net. Thus, the system violates the first pinch rule mentioned in section 2.2.

11.2 Analysis of hydrogen network with low purity demands

The modified operation conditions for the ICR and MHC units affect the hydrogen distribution system. The examined inlet purities were 83.6% and 89.3% for the MHC and ICR, respectively. The outlet concentrations were determined to 82.3% and 86.6% (see Appendix D)

A hydrogen surplus diagram showing the new situation is shown in Figure 20. This is not a pinched system, which indicates that there is potential for hydrogen savings.

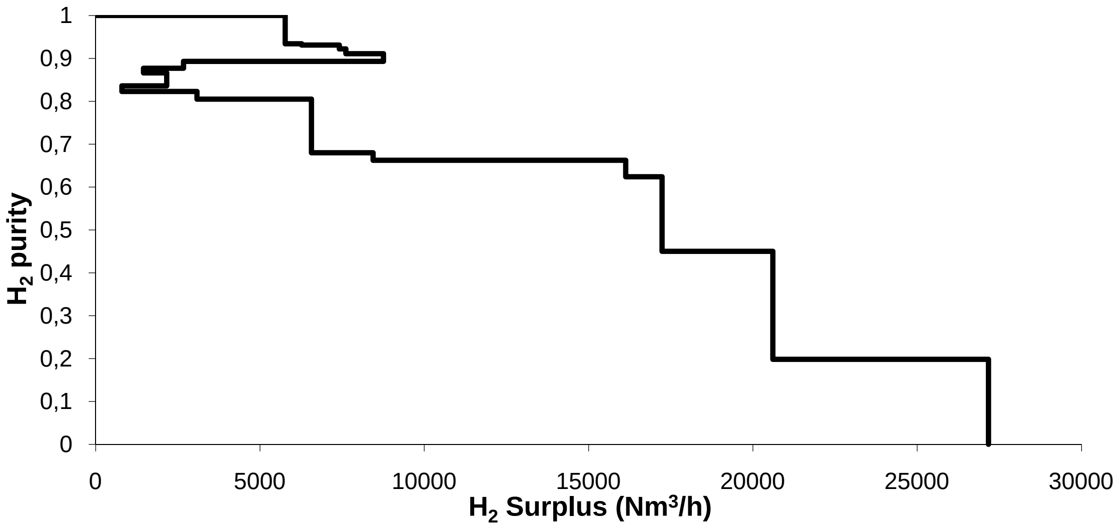

Figure 20: A hydrogen surplus diagram showing the surplus of hydrogen at the different purity level when the purity demand for ICR and MHC is lowered. All other flows and purities are held constant.

This modified system is pinched by reducing the amount of produced hydrogen at a purity of 100%. This can be seen in Figure 21. The pinch purity is then 80.5%, which is lower than before the changes. The only pinch violations possible to identify in this system is the hydrogen stream from the reformer to the fuel gas network. This scenario does not exist and it is therefore not possible to point out more pinch violations. However, if a purge gas from the MHC would be sent to the fuel gas network it would have been a pinch violation, since it has a purity of 82.3 %. When pinching this fictive system, the difference in hydrogen consumption is 4 400 Nm^3/h of pure hydrogen.

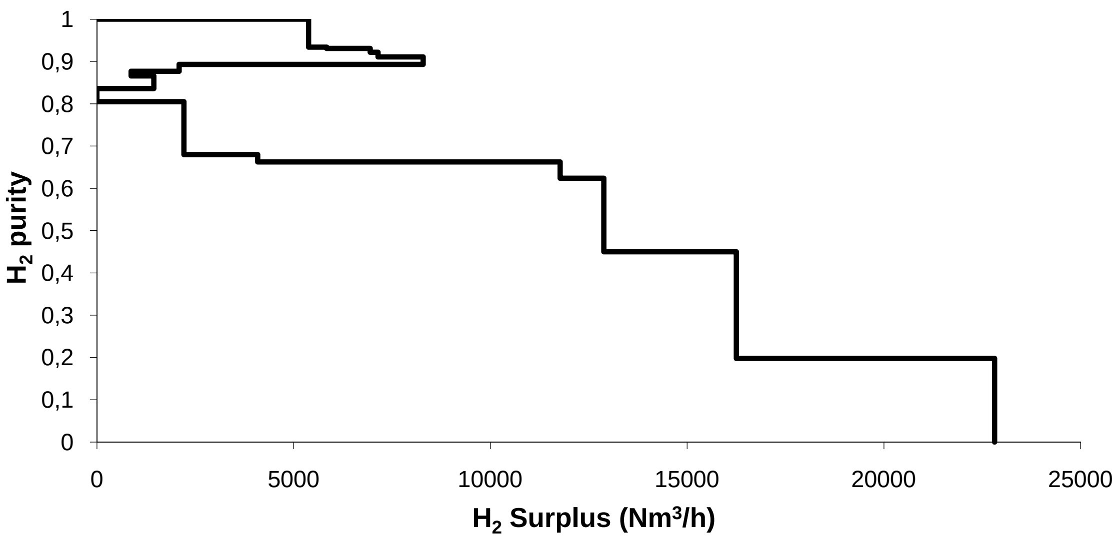

Figure 21: The pinched hydrogen surplus diagram of the hydrogen distribution system when the demands of the MHC and ICR are lowered by 2 percentages.

12 Options for hydrogen utilization, Lysekil

In Lysekil, three different options for increased usage of hydrogen were identified. All three actions are independent of each other, and a fourth scenario with all three actions simultaneously implemented will also be created. Unfortunately, the incorporation of the reformer bleed gas into the system is disregarded, due to very large fluctuations in flow. Therefore, no pinch violations can be resolved and the suggestions are not a result from the hydrogen pinch analysis. Similarly to the suggestions at Preemraff Göteborg, the suggestions aims more at recovering unused low purity hydrogen that today goes to the fuel gas network.

12.1 Case 1, reuse of off gases from Synsat and ICR

The low pressure separators off gases from Synsat and ICR have concentrations of 69.8 % and 66.3 % respectively. The difficulties with reusing these streams are that they are at a low pressure, around 3.7 bars. A compressor would have to be installed in order to utilize these streams. After compression they could be injected between the steam generator and PSA units. Between steam generator and PSA the gas already has a purity of around 70 %, which means that no large concentration change will occur in the inlet to the PSA unit. Too large concentration differences could otherwise cause the PSA to behave differently. A schematic of the process after modification is given in Figure 22.

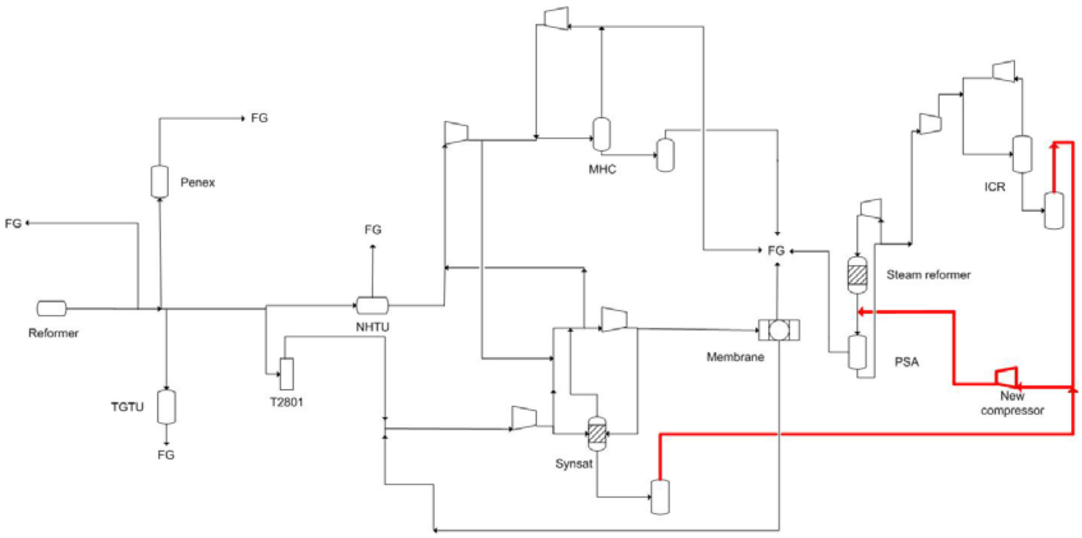

Figure 22: Process schematic after installing a new compressor.

12.2 Redirection of MHC purge

The purge gas from MHC contains 84.2 % hydrogen. Today, this stream is going directly to the fuel gas net. Since the gas is of high purity, it could be used in a better way. A new pipe could transfer gas to the pipe between steam reformer and PSA. The purge gas from MHC has high pressure, so a new compressor will not be necessary in this case. Here, the concentration of the purge gas is significantly higher than the PSA inlet, but the flow is relatively small so no larger impact of the inlet conditions are to expect. A schematic of the process after re-piping is given in Figure 23.

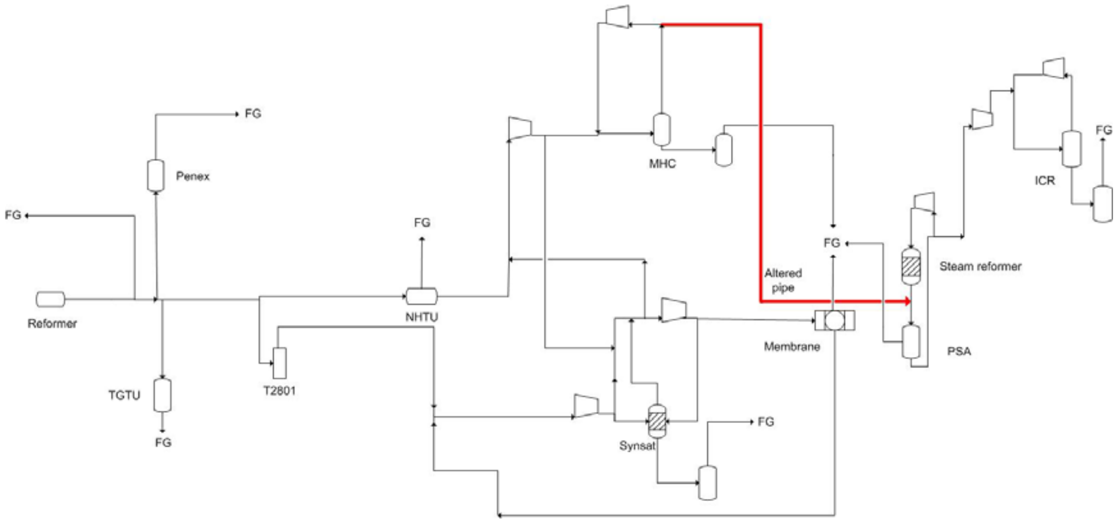

Figure 23: The hydrogen distribution system after redirecting MHC purge from fuel gas network to PSA.

12.3 Redirection of membrane retentate

Another stream that has a high purity but still goes to the fuel gas network is the rejected membrane stream. This gas currently has a purity of 80.5 % and a pressure level which makes it suitable for injection to PSA inlet. With the new membranes that are to be installed, the stream could become less pure but will still be suitable for reuse. Design data gives a purity of 66.5 % for the retentate. The distributions system after alteration is shown in Figure 24.

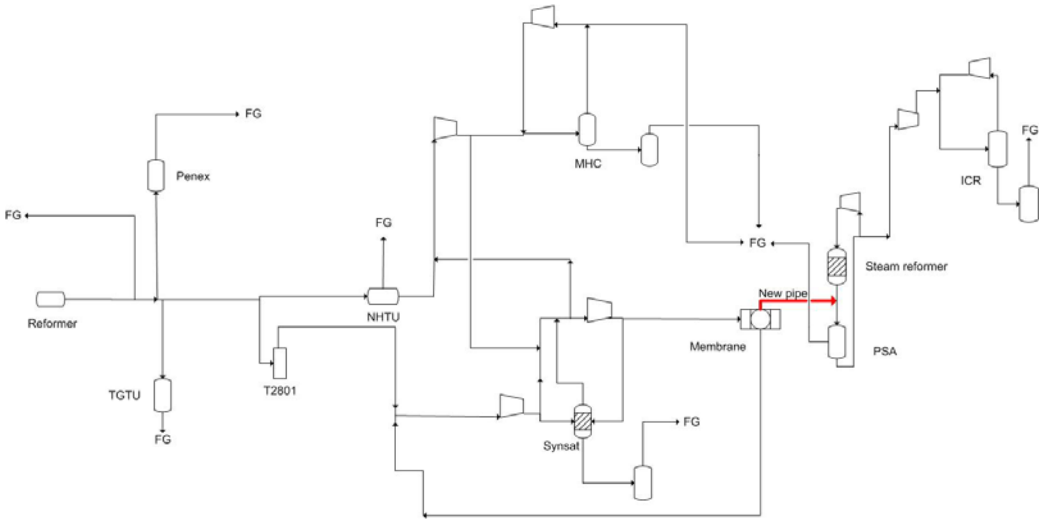

Figure 24: The hydrogen distribution system when redirecting membrane off gas to PSA inlet.

12.4 Combination of suggestions

As for Preemraff Göteborg, the different suggestions are all independent and can be combined. The production of hydrogen that can be avoided in the steam reformer then becomes substantial. In Figure 25, the hydrogen distribution system for Lysekil is shown, given that all three suggestions have been realized. Of course the actions can be realized by performing two of the actions, and not a third. In this thesis however, the option is to perform all three.

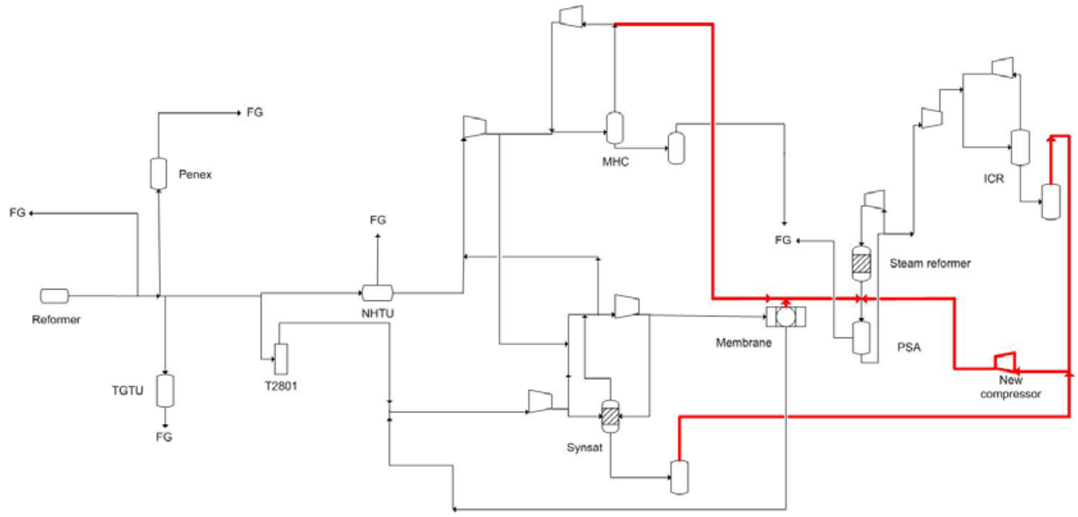

Figure 25: The hydrogen distribution system when performing a combination of all three suggestions for better hydrogen economy.

13 Results from retrofits, Lysekil

The results are divided into effects on the process and economic results. A sensitivity analysis is also presented.

13.1 Process

The process will not be altered to a great extent. Concentration in PSA inlet will be changed, and hydrogen that is led to PSA inlet will have to be replaced in the fuel gas network. In Table 4 the amounts of hydrogen being injected between the steam reformer and the PSA as well as PSA inlet concentrations are shown. The production of hydrogen in the steam reformer is also given. Different from Preemraff Göteborg, the improvements at Preemraff Lysekil does not aim at increasing the liquid feed to any unit, therefore all flows will still remain the same. The improvement is focused at minimizing hydrogen production by steam reforming.

Table 4: Amounts of hydrogen and PSA inlet concentrations given for the different scenarios.

Case	BAU	1	2	3	4
H_2 injected to PSA inlet [Nm3/h]	0	9 600	1 400	3 500	14 500
H_2 production in steam reformer [Nm3/h]	70 100	60 500	68 700	66 600	55 600
Concentration of H_2 in PSA inlet [mol%]	71.5	70.9	71.7	71.9	71.5

The production of hydrogen required in the steam reformer can be lowered from 70 100 to 55 600, which is a substantial fraction.

13.2 Economics

When hydrogen is reused in the system instead of going to the fuel gas network, the need for steam reforming of butane and naphtha will decline. This gives a decrease of cost. All costs related to the different modifications together with the payback periods are represented in Table 5. As for Preemraff Göteborg, the combined case is the one combining low payback time with large hydrogen savings. Case two and three only include pipes, and are therefore not so expensive. In the results, the fuel mix is assumed to be a 50/50 mix of propane and butane.

Table 5: The costs and payback period associated with the three suggestions.

Case	1	2	3	4
Capital cost [SEK]	36 030 000	97 000	240 000	36 370 000
Increased running costs [SEK/yr]	6 620 000	0	0	6 620 000
Increased emission costs [SEK/yr]	-1 570 000	-230 000	-570 000	-2 370 000
Increased fuel costs [SEK/yr]	88 320 000	13 120 000	32 040 000	133 480 000
Avoided costs [SEK/yr]	120 890 000	17 960 000	43 850 000	182 700 000
Net savings [SEK/yr]	27 510 000	5 070 000	12 380 000	44 960 000
Pay-back time [yr]	**1,3**	**0,02**	**0,02**	**0,8**

At Preemraff Lysekil, it would be first priority to replace lost fuel gases with propane, which is why a 50/50 mixture is used. However, if propane would not be available, pure butane could be used. Results for all the cases, but with butane as the only replacing fuel, are presented in Table 6.

Table 6: The costs and payback period associated with the three suggestions, if only butane is used as replacing fuel.

Case	1	2	3	4
Capital cost [SEK]	36 030 000	97 000	240 000	36 370 000
Increased running costs [SEK/yr]	6 620 000	0	0	6 620 000
Increased emission costs [SEK/yr]	-1 570 000	-230 000	-570 000	-2 370 000
Increased fuel costs [SEK/yr]	98 430 000	14 620 000	35 700 000	148 760 000
Avoided costs [SEK/yr]	120 890 000	17 960 000	43 850 000	182 700 000
Net savings [SEK/yr]	17 40 000	3 570 000	8 720 000	29 690 000
Pay-back time [yr]	**2,1**	**0,03**	**0,03**	**1,2**

13.3 Sensitivity analysis, Lysekil

Interesting parameters to look into when checking the viability of the economic results are the price for fuel and the price for emitting CO_2. The sensitivity analysis is carried out for the case with a 50/50 mixture of propane and butane as replacing fuel. The price of the two components is assumed to vary simultaneously.

13.3.1 Fuel price

The fuel price is an interesting parameter, since it fluctuates a lot during a year. In this thesis, an average price for 2009 has been used to estimate costs and revenues. The price for fuel is relevant since butane is the major cost in steam reforming, and the fuel used for supplementary firing when hydrogen is redirected away from the fuel gas net is large. Figure 26 shows how the payback time changes in correlation to the price for fuel.

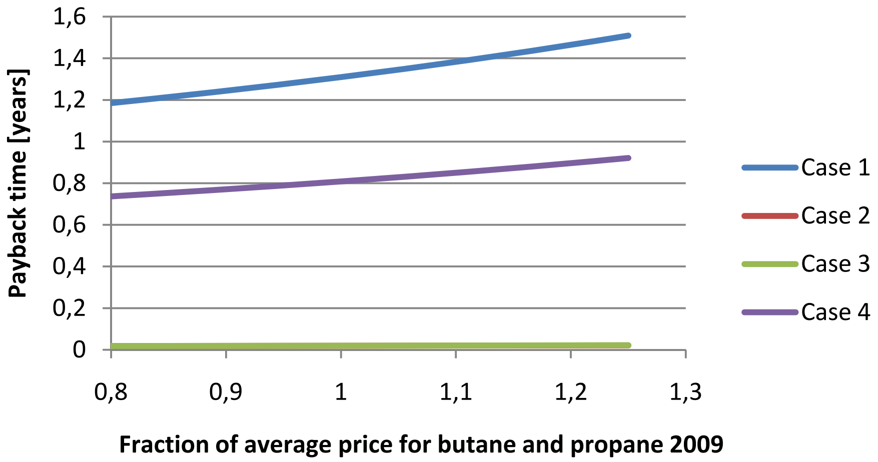

Figure 26: Payback time in respect to different butane and propane prices. The line representing case 2 is hidden under the line for case 3.

13.3.2 Cost for CO_2 emissions

Increased use of butane will result in larger emissions of CO_2. At the same time, less butane will be needed for steam reforming. All in all this leads to a reduction of CO_2 released to the atmosphere. The price per tonne emission is likely to increase in the future. It is therefore an interesting parameter to investigate. In Figure 27, the correlation between payback time and CO_2 price is shown.

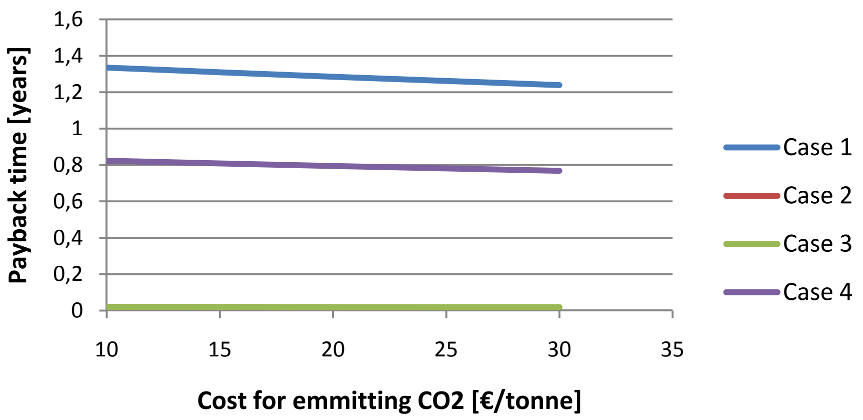

Figure 27: Payback time for the different cases versus the cost for emitting 1 tonne CO_2. The line representing case 2 is hidden under the line for case 3.

14 Discussion Lysekil

The scenarios at Preemraff Lysekil include both re-piping and more comprehensive measures like the purchase of a new compressor. The results cited are the results obtained when assuming a 50/50 mixture of propane and butane in the replacement fuel. It is beneficial for Preemraff Lysekil to increase the fraction of propane in this fuel, if possible.

Case 1 is expensive, since it includes the purchase of a new compressor. That said, it still has a payback time of 1.3 years, which could be considered reasonable. Large quantities of hydrogen could be utilized, instead of going to the fuel gas network.

Case 2 lets the purge gas from MHC go to PSA instead of going to the fuel gas network. This stream is at 64 bar, and in the inlet to the PSA unit is 27.5 bar. It could be seen as a waste to just throttle this stream. Instead, it could be interesting to inject the stream in the inlet of the membrane. The stream could then be upgraded in the membrane, and used in the process. The problem with this solution is that the production of hydrogen in the steam reformer is not lowered.

Case 3 uses the membrane off gases in the PSA unit. Here, the problem is that the membranes have been replaced with new ones. Therefore, no data (except design data for the new membranes) was available. The design data was also not consistent with current conditions. The feed into the membrane has a purity of 80 % according to design data. However, the stream currently has a purity of 87.7 %, and it will probably not decrease after change of membranes. It is thus difficult to forecast what purity will come out from the membrane, and how much hydrogen will be rejected, and thereby available for injection into the PSA.

Case 4 combines all three suggestions. The amount of hydrogen that does not have to be produced in steam reformer gets high, but also the investment cost. Since the investment costs for case 2 and 3 are small, the payback time for case 4 get shorter than for case 1.

The concentration of hydrogen in the PSA inlet for the different cases is shown in Table 4. As can be seen, all suggestions only results in minor changes in regard to hydrogen purity. This could be interpreted as if the PSA operation will not be affected. This is however not true. All streams proposed to go into the PSA unit contain a fraction of ethane, propane and butane. The effects these components would have on the PSA operation are not clear. A possible solution would be to change the number of beds used in the PSA from 10 to 12. This might however not overcome the problems with the adsorbents used. These are designed for a feed gas with a certain composition, and uncertainties exist regarding how they would respond to a change in this feed. There are also concerns about condensation of hydrocarbons heavier than methane. The concerns listed above are valid, but can be solved. Before realization of any changes, a thorough invesetigation of the PSA behavior needs to be performed. Such an investigation would of course cost money, and these are to be added to the capital cost.

The sensitivity analysis shows that if the price for butane and propane increase, the payback time is prolonged. However, while the prices for butane and propane change, the price per TFOE and naphtha stay the same. If the price for butane and propane would go up, it can be reasonable to assume that the other prices will follow. TFOE and naphtha are costs in the steam reformer, and could therefore attenuate the impact of the increased butane and propane prices. If that is not the case, the effect of increased prices does not make the payback time to exceed 1.5 years even with a 20 % increase.

The other parameter in the sensitivity analysis was the price for emitting 1 tonne of CO_2. Since the emissions are reduced when making the suggested retrofits, all suggestions get lower payback time when increasing the emission price. The impact is rather small though, when doubling the emission price the payback times only decreases about 5 %.

The composition of the fuel replacing hydrogen and steam reformer by-products has a major impact on the result. Since butane is considerable more expensive than propane, a large fraction of propane is desirable. In this work, both a 50/50 split and a pure butane stream have been investigated. Preemraff Lysekil should strive towards having a large fraction of propane in this fuel. Even if 100 % butane is used, the calculations show reasonable payback times. Preemraff Lysekil periodically has an excess of fuel gases. This means that all of the hydrogen that has been removed from the fuel gas net may not have to be replaced with another fuel. This has not been included into the report. When this is included, the payback time decreases.

A problem during the thesis was that the membrane separation unit was in the state of being changed. If proper process data had been available, it would have been interesting to model a pipeline with MHC purge going into the membrane, instead of to the PSA unit, which is discussed in this work. A fraction of the membrane outlet could then be used to replace PSA hydrogen in ICR make up gas.

When it comes to the investigation on how lower purity demands for the ICR and MHC units affects the hydrogen demand, the results look promising. 4 400 Nm^3/h of pure hydrogen has a great value since it would be very expensive to produce this amount in the steam reformer. It is important to have in mind that this is the difference between the present consumption and the theoretical minimum consumption. This saving could not be obtained without a reconstruction which is not treated in this thesis. Furthermore, several assumptions regarding this part of the work were needed. In order to obtain a more correct result a more rigorous study should be performed. Such a study should examine how the inlet and outlet stream of each unit would be affected by lowered inlet purity in a careful way. It should also make sure that the units can process the same amount of liquid feed. In this work it was assumed that lower inlet purity can be compensated by a higher flow rate as long as the total amount of hydrogen into the reactor is the same. This is most likely not true since that means that the mean residence time for the hydrogen in the reactor is lower. This part of the work shows tendencies which are interesting to bear in mind for future work. No conclusions can be drawn at this stage though.

15 Methodology discussion

It is relevant to question: To what extent did the hydrogen pinch analysis per se contribute to exposure of shortcomings in the hydrogen distribution systems? The answer would be that in the Göteborg case it was discovered that both the existing and reconstructed system are pinched. This means that the hydrogen network is designed in an optimal way, given the determined sinks and sources. In the Lysekil case one shortcoming was found, but it was discovered that it could not be addressed. These are indeed important conclusions. It means that the analysis itself did not give any indications of flaws. Still, two respectively three suggestions were made which increase the availability of hydrogen. This reveals a weakness of this analysis method; the pinch analysis cannot make a difference between solid demands/assets and variable ones. Example of a solid demand is for instance the required hydrogen stream entering a reactor. The concentration or the flow rate of hydrogen cannot change if the same product and quantity is to be produced, which is desired. Meanwhile, a variable demand corresponds to the stream entering a hydrogen separation unit, for example. It does not matter if the inlet and outlet of such a separator is changed as long as enough hydrogen is available to meet solid demands. Furthermore, if it is legitimate to assume a constant efficiency of the separation unit, the inlet stream can be adjusted without affecting the outlet stream which enables new possibilities for network design.

The method of hydrogen pinch analysis has another weakness. It only considers purity and flow rate of hydrogen. The graphical result from the analysis assumes that any stream of a higher purity can at least partly cover a demand of a lower purity. Hence, important factors e.g. impurities and pressure are excluded. If this method could be expanded to incorporate such important parameters, the pinch analysis would become a much more powerful tool.

The use of hydrogen pinch analysis increases with an increased complexity of a system. It can be difficult to identify shortcomings when the number of hydrogen stream is great without performing a hydrogen pinch analysis. The use of this method is also large when designing a plant from scratch in order to avoid inefficient solutions when it comes to hydrogen usage. In early stages of refinery planning the operation conditions for different units can be established with respect to a hydrogen pinch analysis so that the best overall system can be obtained.

It has been a general opinion when presenting the evaluation to engineers at Preemraff Göteborg and Preemraff Lysekil that capital costs for piping may be underestimated. The costs for compressors have been more reasonable, due to the use of Hand factors, but the piping costs do not include any form of engineering or installation costs.

16 Conclusions

Pinch violations do not exist at Preemraff Göteborg neither before nor after revamp of MHC. At Preemraff Lysekil one pinch violations was found, were hydrogen with a purity higher than the pinch purity were sent to the fuel gas network. This shortcoming however, was already known and is hard to eliminate in an economically defendable way.

It has been shown that even though a system is pinched there can still be possibilities for improvements regarding hydrogen usage by adjusting variable demands. A weakness with the hydrogen pinch analysis as a method is that it cannot treat variable demands and excesses.

Three suggestions are made for economical improvement at Preemraff Göteborg. These enable increased Synsat throughput and consequently larger revenue.

Four suggestions are made for economical improvement at Preemraff Lysekil. All suggestions leads to lower work load for the steam reformer, which reduces operation costs.

At both refineries large quantities of hydrogen can be retrieved from off gases in an economical way. In order to achieve substantial changes, compressors need to be implemented.

17 Further work

There is definitely a possibility to expand the work about efficient hydrogen usage. In the Göteborg study several assumptions where made since the reconstruction was not carried out completely. In the future data will be available, which describes the operating conditions in reality for both the renewable/MK3 and standard/MK1 mode. This would render the study less assumptions regarding the GHT. More correct properties of the Common off gases would also be available.

It could be interesting to see if any changes in the hydrogen distribution related to seasonal changes in the Göteborg case occurred. All gathered data concerning the MK1 are taken during summer time. To look for similar operational settings, which took place during other seasons, would reveal if the settings are dependent on season.

When it comes to the Lysekil study, future studies would preferably treat the new membranes which are supposed to replace old ones during 2010. With these new membranes more hydrogen will be available at higher purities and depending on how this surplus is decided to be used it might change the picture of the hydrogen distribution. This could be beneficial to analyze.

In Lysekil, it could also be interesting to investigate the effects of heavy hydrocarbons in the PSA unit. How would this affect the operation, and would there be increased costs? It could also be investigated whether it would be better to inject the streams before the steam reformer, so that the heavy hydrocarbons can react to form hydrogen and CO_2.

A more rigorous investigation of the effects of lowered purity demand to MHC and ICR would be interesting. If work would be concentrated on this, more complete balances and models over the revised hydrogen consumption could be obtained.

Moreover, it could possible to collect more advantages from the traditional energy pinch analysis in order to make the hydrogen pinch analysis more flexible. In hydrogen pinch analysis an upgrading unit (purifier) is not treated as a corresponding unit within energy pinch analysis (heat pump). In hydrogen pinch analysis the inlet and outlet of the upgrading unit is set to be a sink and a source, respectively (Alves & Towler, 2002). This makes the analysis less flexible compared to an energy pinch.

18 References

Alves, Joao J. and Towler Gavin P. 2002, “Analysis of Refinery Hydrogen Distribution Systems”, Industrial and Engineering Chemistry Research, vol. 41, no. 23 pp 5759-5769

Faraji, Sedigheh, Sotudeh-Gharabagh, Rahmat, Mostoufi, Navid, 2005, “Hydrogen Recovery from Refinery Off-gases”, Journal of Applied Sciences, vol. 5, iss. 3, pp 459.

Fonseca, André, Sá, Vítor, Bento, Hugo, Tavares, Manuel L.C., Pinto, Gilberto, Gomes, Luísa A.C.N 2008, “Hydrogen distribution network optimization: a refinery case study”, Journal of Cleaner Production, vol. 16, iss 16.

Hallale, N. and Liu, F. 2001, “Refinery hydrogen management for clean fuels production”,Advances in Environmental Research, vol.6 pp 81-98

Hallale, N., Moore, I. and Vauk D. 2006 Chapter26 “Hydrogen Under New Mangemant”, Practical Advances in Petroleum Processing, editor Hsu, C. S. and Robinson, P. R., Springer New York

Hellsten, Gunnar, 1992, ”Tabeller och Diagram”, Almqvist & Wiksell, Falköping.

Meyers, Robert A 2003, “Handbook of Petroleum Refining Processes”, 3rd edition, McGraw-Hill, New York

Nelson, April M. and Liu, Y. A. 2008, “Hydrogen-Pinch Analysis Made Easy”, Chemical Engineering, vol. 115, no. 6, pp 56-61

Sinnot, Ray and Towler, Gavin, 2009, “Chemical Engineering design”, 5th edition, Elsevier, Burlington

Lozowski, Dorothy, 2010, “Economic indicators”, Chemical Engineering, vol. 117, iss. 4, pp 79-80

Dagens Industri

http://www.di.se (2010-04-23)

European Union
http://europa.eu/legislation_summaries/internal_market/single_market_for_goods/motor_vehicles/interactions_industry_policies/l28077_en.htm (2010-01-21)

http://europa.eu/legislation_summaries/environment/air_pollution/l21050_en.htm

(2010-01-21)

Naturskyddsföreningen
http://www.naturskyddsforeningen.se/upload/Foreningsdokument/Remissvar/trafik/2009-09-11-yttrande-over-remiss-om-svavel-i-marint-bransle.pdf

Nordpool

http://www.nordpool.com/System/FinanceMarket/emissions/ (2010-04-26)

Preem Petroleum AB

http://www.preem.se (2010-03-04)

Swedish EPA

http://www.swedishepa.se/sv/Klimat-i-forandring/Minska-utslappen/Verktygslada-for-kommuner-och-foretag/Berakna-utslapp-av-vaxthusgaser/Emissionsfaktorer-koldioxid/ (2010-05-25)

Appendix A

Lower heating value for hydrogen	10.6 MJ/Nm^3
Lower heating value for natural gas	36.0 MJ/Nm^3
Lower heating value for methane	35.2 MJ/Nm^3
Lower heating value for ethane	63.3 MJ/Nm^3
Lower heating value for propane	92.1 MJ/Nm^3
Lower heating value for butane	121.6 MJ/Nm^3
Mass of CO_2 released when burning natural gas	56.8 g/MJ
Mass of CO_2 released when burning natural gas	65.1 g/MJ
Exchange rate US$	7.10 SEK/US$
Exchange rate €	9.73SEK/€
Price of emission rights	15 €/tonne CO_2
Energy content of 1 TFOE	40.2 GJ
Hand factor for compressor	2.5
Chemical engineering index of January 2007	532.9
Chemical engineering index of January 2010	509.7

Appendix B

In order to calculate increased revenues and costs for the different cases, the following equations have been used. List of all denotations are found at the bottom.

B.1 Göteborg

$$profit_{net} = profit_{inc} - c_{inc\ operation} - c_{inc\ emission} - c_{inc\ fuel}$$

$$payback\ period = \frac{c_{capital}}{profit_{net}}$$

$$profit_{inc} = \Delta\dot{V}_{liq\ Synsat} t_{op} profit_{margin\ Synsat} R_{US\$}$$

$$c_{inc\ operation} = \Delta P_{el} t_{op} c_{el}$$

Notice that there is an increased operational cost associated with the higher workload of the Synsat. However, this is accounted for when the increased profit is calculated.

$$c_{inc\ emission} = m_{carbon} c_{CER} R_{€} \dot{Q}_{shortage} t_{op} \frac{M_C}{M_{CO_2}}$$

where

$$\dot{Q}_{shortage} = \dot{Q}_{off\ gas\ BAU} + \dot{Q}_{sweet\ gas\ BAU} - (\dot{Q}_{off\ gas,case} + \dot{Q}_{sweet\ gas,case})$$

$$c_{inc\ fuel} = \frac{\dot{Q}_{shortage} \rho_{fuel} c_{fuel}}{H_{LHV\ NG}}$$

B.2 Lysekil

In order to calculate increased revenues and costs for the different cases at Preemraff Lysekil, the following equations have been used.

$$savings_{net} = c_{avoided} - c_{inc\ operation} - c_{inc\ emission} - c_{inc\ fuel}$$

$$payback\ time = \frac{c_{capital}}{profit_{net}}$$

$$c_{avoided} = \Delta\dot{V}_{feed\ sf} c_{butane} + c_{op,sf} \Delta\dot{V}_{H_2,sf}$$

$$c_{op,sf} = c_{cat} + c_{steam}$$

$$c_{inc\ operation} = \Delta P_{el} t_{op} c_{el}$$

$$c_{inc\ emission} = c_{CER} R_{€} t_{op} \left(m_{CO_2} (\dot{Q}_{shortage} - \Delta F_{fuel,sf} H_{LHV,fuel}) - \frac{F_{out,sf,new}}{F_{out,sf,old}} \frac{V_{CO_2,sf\ out}}{V_{sf\ out}} \right)$$

$$\dot{Q}_{shortage} = (F_{out,sf,new} - F_{out,sf,old}) H_{LHV,outlet}$$

$$c_{inc\ fuel} = \frac{\dot{Q}_{shortage} \rho_{fuel} c_{fuel}}{H_{LHV\ fuel}}$$

$c_{op,sf}$	operational cost for steam reformer
$c_{avoided}$	savings in steam reformer reducing the production of H_2
c_{butane}	cost for purchasing butane
$c_{capital}$	capital cost
c_{CER}	cost
c_{el}	price of electricity
$c_{inc\ emission}$	increased annual emission cost
$c_{inc\ fuel}$	increased annual fuel cost
$c_{inc\ operation}$	increased annual operational cost
c_{fuel}	Cost for purchasing fuel
$F_{out,sf,new}$	flow rate out from steam reformer after retrofit
$F_{out,sf,old}$	flow rate out from steam reformer before retrofit
$H_{LHV\ NG}$	Lower heating value for natural gas
M_C	molar mass of carbon
M_{CO_2}	molar mass of carbon dioxide
m_{carbon}	mass of carbon in fuel gas per energy content
$profit_{inc}$	increased annual profit
$profit_{margin\ Synsat}$	marginal profit for Synsat operation per volume of liquid feed
$profit_{net}$	net profit
$\dot{Q}_{off\ gas\ BAU}$	Heat content in off gases before reconstruction.
$\dot{Q}_{off\ gas\ case}$	Heat content in off gases in case.
$\dot{Q}_{sweet\ gas\ case}$	Heat content in Cryo sweet gas in case.
$\dot{Q}_{sweet\ gas\ BAU}$	Heat content in Cryo sweet gas before reconstruction.
$\dot{Q}_{shortage}$	heat loss in when streams are drawn from FG-system
$R_{\$}$	exchange rate from US$ to SEK
$R_{€}$	exchange rate from € to SEK
$savings_{net}$	total net savings per year with proposed retrofit
t_{op}	operation time
$V_{CO_2,sf\ out}$	volume flow rate of CO_2 out from steam reformer
$V_{sf\ out}$	volume flow rate out from steam reformer
$\Delta F_{fuel,sf}$	Change in fuel to steam reformer steam system
ΔP_{el}	change in power consumption
$\Delta\dot{V}_{liq\ Synsat}$	increased liquid feed to Synsat per time unit
ρ_{fuel}	Density for fuel

Appendix C

In order to estimate the efficiency of the PSA unit, measured recovery rates were used. The measure points are shown in Figure 28.

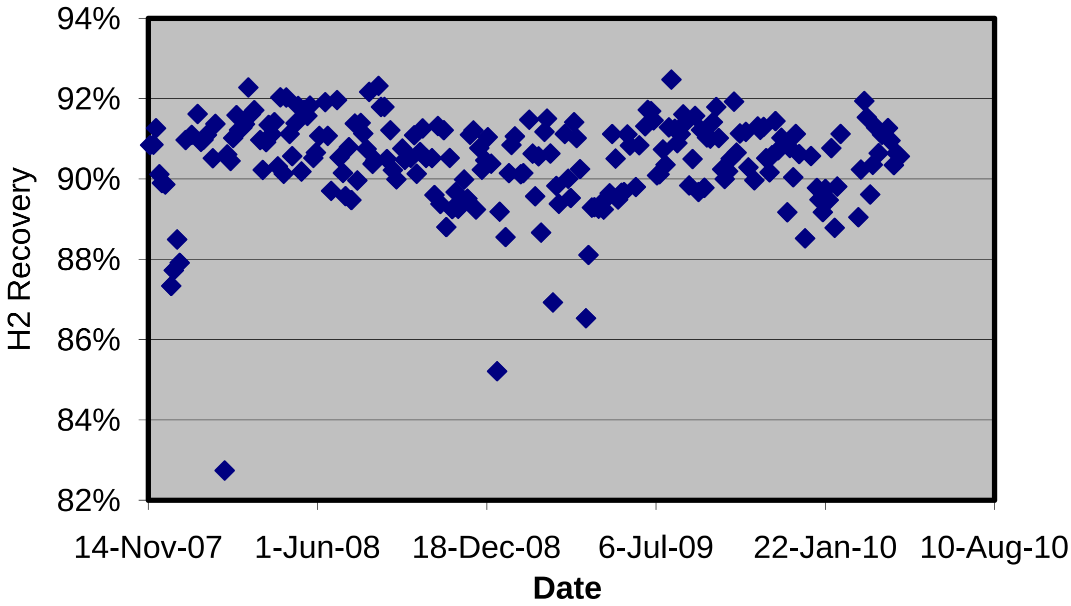

Figure 28: Measure points of PSA efficiency.

Appendix D

The outlet concentration from MHC and ICR depends on the inlet concentration. Below in Table 7 are data describing the situation for MHC. Corresponding data for ICR are located in Table 8. The concentration difference between inlet and outlet is plotted against inlet concentration in Figure 29 and Figure 30.

Table 7: Flow rate and purity is measured for the MHC make up gas and recirculation gas. From this inlet concentration is calculated and the difference between inlet and outlet purity.

Date	C_{MUG} [%]	C_{recirk} [%]	F_{MUG} [Nm^3/h]	F_{recirk} [Nm^3/h]	C_{inlet} [mol%]	ΔC(In-Out) [%]
09-01-14	93,23	85,46	19 801	108 027	86,6592	1,20
09-01-28	93,02	85,87	18 798	110 397	86,9138	1,04
09-02-25	93,95	82,11	21 993	102 117	84,2058	2,10
09-03-11	88,72	81,06	18 559	110 892	82,1593	1,10
09-03-25	92,31	86,61	20 956	101 735	87,5792	0,97
09-04-08	93,54	83,99	20 387	97 986	85,6347	1,64
09-04-22	91,79	84,93	19 170	100 437	86,0317	1,10
09-05-20	90,46	81,06	21 791	94 146	82,8283	1,77
09-06-17	92,31	86,61	20 365	107 353	87,5145	0,91
09-06-30	93,23	86,29	25 773	102 947	87,6807	1,34
Average	92,1	84,2	20 202	103 603	85,7	1,33

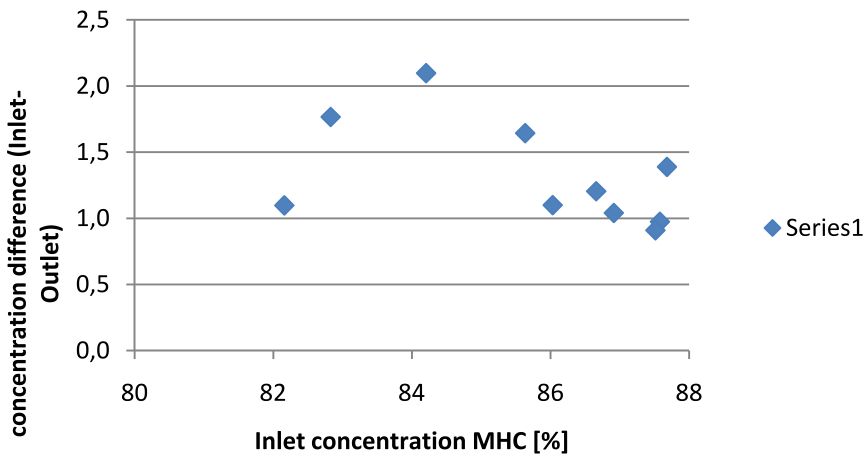

Figure 29: The concentration difference between inlet and outlet is plotted against inlet concentration for the MHC. No direct correlation can be observed from this and instead an average value was used to determine the outlet concentration when the inlet concentration was lowered.

Table 8: Flow rate and purity is measured for the ICR make up gas and recirculation gas. The inlet concentration is calculated as well as the difference between inlet and outlet purity.

Date	C_{MUG} [%]	C_{recirk} [%]	F_{MUG} [Nm^3/h]	F_{recirk} [Nm^3/h]	C_{inlet} [mol%]	ΔC(In-Out) [%]
09-01-13	100	89,7	70 664	257 999	91,91	2,21
09-01-20	100	90,8	68 462	273 399	92,64	1,84
09-01-26	100	90,3	71 307	250 557	92,45	2,15
09-02-03	100	89,3	76 378	271 245	91,65	2,35
09-02-10	100	89,4	78 087	271 915	91,76	2,36
09-02-24	100	87,6	72 182	275 205	90,18	2,58
09-03-03	100	90,3	67 732	264 395	92,28	1,98
09-03-10	100	89,7	69 717	264 737	91,85	2,15
09-03-17	100	87,8	68 268	267 403	90,28	2,48
09-03-24	100	89,1	69 206	266 418	91,35	2,25
09-03-31	100	89,7	70 366	256 032	91,92	2,22
09-04-07	100	89,7	72 271	257 720	91,96	2,26
09-04-14	100	89,2	70 174	254 263	91,54	2,34
09-04-21	100	86,1	66 057	292 021	88,66	2,56
09-04-29	100	88,4	73 085	283 350	90,78	2,38
09-05-05	100	86,2	70 453	292 558	88,88	2,68
09-05-12	100	88,9	65 630	258 380	91,15	2,25
09-05-26	100	89	70 202	270 166	91,27	2,27
09-06-02	100	89,9	69 883	250 083	92,11	2,21
09-06-09	100	88,8	69 307	259 867	91,16	2,36
09-06-16	100	85,9	72 341	250 240	89,06	3,16
09-06-23	100	88,9	72 760	252 506	91,38	2,48
09-06-30	100	91,8	54 134	250 179	93,26	1,46
Average	100	89,0	70 012	264 672	91,3	2,31

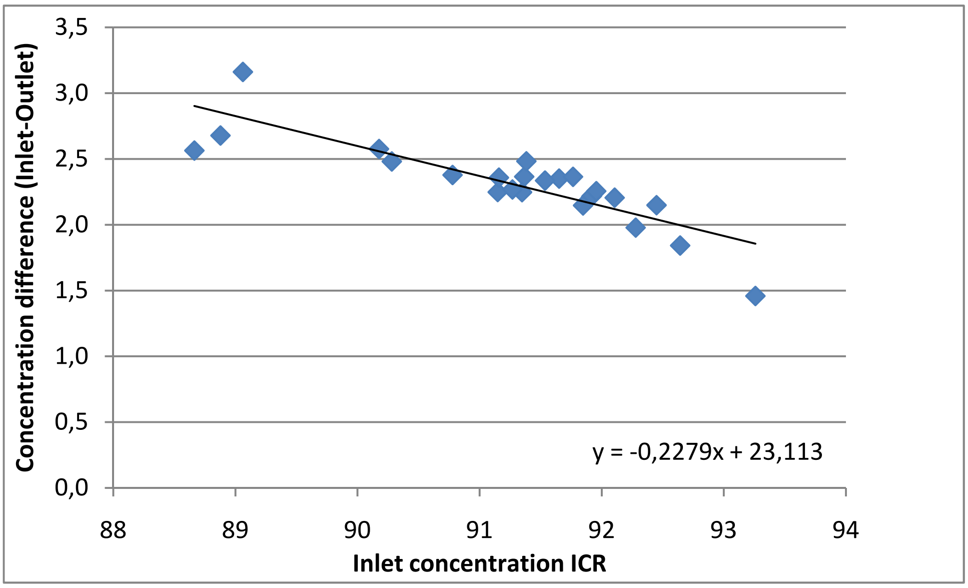

Figure 30: The concentration difference between inlet and outlet is plotted against inlet concentration for the ICR. The data shows a linear behavior and this correlation is used to estimate when the inlet concentration was lowered.

Appendix E

As mentioned in Assumptions and approximations, Lysekil there were two mass balances with large error according to collected data. The streams involved have been adjusted in order to achieve correct balances, which has been used when determining the hydrogen distribution system. In Table 9 and Table 10 the new flow rates can be seen. Following relations are used:

- Flow leaving MHC make up compressor = Flow leaving NHTU to MHC + Flow from Synsat to MHC
- Flow leaving Synsat make up compressor = Flow leaving membrane to Synsat + Flow leaving T-2801 to Synsat

Table 9: The measured and adjusted flows of the streams providing the MHC with hydrogen

	Flow leaving MHC MUG compressor	**Flow leaving NHTU to MHC**	**Flow from Synsat to MHC**	**Error**
Measured flows	24 977 Nm^3/h	21 074 Nm^3/h	6 874 Nm^3/h	2 971
Adjusted flows	25 909 Nm^3/h	20 000 Nm^3/h	5 909 Nm^3/h	0

Table 10: The measured and adjusted flows of the streams providing the Synsat with hydrogen

	Flow leaving Synsat MUG compressor	**Flow leaving membrane to Synsat**	**Flow leaving T-2801 to Synsat**	**Error**
Measured flows	36 936 Nm^3/h	8 000 Nm^3/h	31 430 Nm^3/h	2 494
Adjusted flows	36 936 Nm^3/h	6 892 Nm^3/h	30 044 Nm^3/h	0

Appendix F

The MatLab program constructed in order to make a hydrogen pinch analysis is shown below. This was used in combination with a Microsoft Excel macro.

```
%By Viktor Andersson och Albin Vadenbo
%Chalmers 2010-02-03
%Pinch
%Input:     Two matrixes, sinks and sources, with the dimensions m*2 and
%           n*2. The first column refers to flow rate, and the second to
%           purity.
%Output:    One purity profile, and two corresponding hydrogen surplus
%           diagrams. The first surplus diagram is according to Nelson and
%           Liu (2008), and the second according to Alves and Towler (2002)

function [F]=pinch_valid_edition(sinks,sources)

sort_sink_pures=sortrows(sinks,-2);
sort_source_pures=sortrows(sources,-2);


cum_flow_sinks(1)=sort_sink_pures(1,1);
%cum_flow_sinks [cumulative flow for sinks] is a vector where the cumulative flow
of sinks is shown
for n=2:1:length(sort_sink_pures)
   cum_flow_sinks(n)=sort_sink_pures(n,1)+cum_flow_sinks(n-1);
end

cum_sink_vector(1)=0;
%cum_sink_vector  is built up in order to create plots. If cum_flow_sinks=[ a b c]
then cum_sink_vector=[0 a a b b c c]
g=2;
for n=1:length(cum_flow_sinks)
   cum_sink_vector(g)=cum_flow_sinks(n);
   cum_sink_vector(g+1)=cum_flow_sinks(n);
   g=g+2;
end

g=1;
for m=1:length(sort_sink_pures)
   sink_purity_vector(g)=sort_sink_pures(m,2);
%sink_purity_vector a vector containing purities of the different streams. It is then
used in combination with cum_sink_vector in order to create a purity profile.
   sink_purity_vector(g+1)=sort_sink_pures(m,2);
   g=g+2;
end
sink_purity_vector(length(sink_purity_vector)+1)=0;
sort_source_pures(1,1)
cum_flow_sources(1)=sort_source_pures(1,1);
%cum_flow_sources is same as cum_flow_sink, bur for sources. The same procedure
will be done for sources as for sinks
```

```
for n=2:1:length(sort_source_pures)
   cum_flow_sources(n)=sort_source_pures(n,1)+cum_flow_sources(n-1);
end
cum_flow_source_vector(1)=0;
g=2;
for n=1:1:length(cum_flow_sources)
   cum_flow_source_vector(g)=cum_flow_sources(n);
   cum_flow_source_vector(g+1)=cum_flow_sources(n);
   g=g+2;
end

g=1;
for m=1:length(sort_source_pures)
   source_purity_vector(g)=sort_source_pures(m,2);
   source_purity_vector(g+1)=sort_source_pures(m,2);
   g=g+2;
end
source_purity_vector(length(source_purity_vector)+1)=0;


if
cum_flow_source_vector(length(cum_flow_source_vector))>cum_sink_vector(length
(cum_sink_vector))
%Does not really matter for the program, but makes the figure have suitable axis´s

A=cum_flow_source_vector(length(cum_flow_source_vector))+0.2*cum_flow_sourc
e_vector(length(cum_flow_source_vector));
else

A=cum_sink_vector(length(cum_sink_vector))+0.2*cum_sink_vector(length(cum_si
nk_vector));
end

figure(1)

plot(cum_sink_vector,sink_purity_vector,'m')
hold on
plot(cum_flow_source_vector,source_purity_vector,'g')
axis([0 A 0 1])
legend('Sinks','Sources')
xlabel('Flow rate')
ylabel('Purity')
title('Purity profile')

% Hydrogen surplus diagram should now be drawn. First with maximum purity
% on the y-axis, then with sink purity

cum_flow_tot(1)=0;
for i=2:length(cum_flow_sources)+1
   cum_flow_tot(i)=cum_flow_sources(i-1);
```

```
end
for i=1:length(cum_flow_sinks)
   cum_flow_tot(length(cum_flow_tot)+1)=cum_flow_sinks(i);
end
cum_flow_tot=sort(cum_flow_tot);

g=2;
for n=2:1:length(cum_flow_tot)
   cum_flow_tot_vector(g)=cum_flow_tot(n);
   cum_flow_tot_vector(g+1)=cum_flow_tot(n);
   g=g+2;
end


for i=1:2:length(cum_flow_tot_vector)
   j=ceil(i/2);
   interval(j,1)=cum_flow_tot_vector(i);
   if i<length(cum_flow_tot_vector)
      interval(j,2)=cum_flow_tot_vector(i+1);
   end
end


interval(length(interval),2)=interval(length(interval),1);
interval(:,3)=0;
cum_sinks=[cum_flow_sinks' sort_sink_pures(:,2)]
for i=length(cum_sinks):-1:1
   for j=1:length(interval)
      if cum_sinks(i,1)>=interval(j,2)
        interval(j,3)=cum_sinks(i,2);
      end
   end
end
interval(1,3)=cum_sinks(1,2);
interval(length(interval),3)=0;

interval(:,4)=0;
cum_sources=[cum_flow_sources' sort_source_pures(:,2)];
for i=length(cum_sources):-1:1
   for j=1:length(interval)
      if cum_sources(i,1)>=interval(j,2)
        interval(j,4)=cum_sources(i,2);
      end
   end
end
interval(1,4)=cum_sources(1,2);
interval(length(interval),4)=0;
```

```
for i=1:length(interval(:,1))
   if interval(i,3)<=interval(i,4)
      max_purity(i)=interval(i,4);
      min_purity(i)=interval(i,3);
   else
      max_purity(i)=interval(i,3);
      min_purity(i)=interval(i,4);
   end
end

interval(:,5)=min_purity;
interval(:,6)=max_purity;

area=0;
hyd_excess(1)=0;
hyd_excess_vector(1)=0;
for i=1:length(interval(:,1))-1
   sub_area=((interval(i,6)-interval(i,5))*(interval(i,2)-interval(i,1)));
   if interval(i,6)==interval(i,4)
      area=area+sub_area;
   else
      area=area-sub_area;
   end
   hyd_excess(i+1)=area;
   hyd_excess_vector(2*i)=hyd_excess(i+1);
   hyd_excess_vector(2*i+1)=hyd_excess(i+1);
   max_purity_vector(2*i-1)=interval(i,6);
   max_purity_vector(2*i)=interval(i,6);
   min_purity_vector(2*i-1)=interval(i,5);
   min_purity_vector(2*i)=interval(i,5);
end
max_purity_vector(2*length(interval(:,1))-1)=0;
min_purity_vector(2*length(interval(:,1))-1)=0;


figure(2)
plot(hyd_excess_vector,max_purity_vector)
hold on
title('Maximum purity used')
ylabel('purity')
xlabel('hydrogen flow rate')
axis([-50,25000 0,1])
figure(3)
plot(hyd_excess_vector,min_purity_vector,'k')
hold on
axis([-50,4600 0,1])
title('Minimum purity used')
ylabel('purity')
xlabel('hydrogen flow rate')
```