

LAPPEENRANTA UNIVERSITY OF TECHNOLOGY
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OPTIMIZATION OF HYDROGEN PLANT EFFICIENCY

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ABSTRACT

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Optimization of hydrogen plant efficiency

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The purpose of this master's thesis was to study ways to increase the operating cost-efficiency of the hydrogen production process by optimizing the process parameters while, at the same time, maintaining plant reliability and safety. The literature part reviewed other hydrogen production and purification processes as well as raw material alternatives for hydrogen production.

The experimental part of the master's thesis was conducted at Solvay Chemicals Finland Oy's hydrogen plant in spring 2012. It was performed by changing the process parameters, first, one by one, aiming for a more efficient process with clean product gas and lower natural gas consumption. The values of the process parameters were tested based on the information from the literature, process simulation and experiences of previous similar processes. The studied parameters were reformer outlet temperature, shift converter inlet temperature and steam/carbon ratio. The results show that the optimal process conditions are a lower steam/carbon ratio and reformer outlet temperature than the current values of 3.0 and 798 °C. An increase/decrease in the shift conversion inlet temperature does not affect natural gas consumption, but it has an effect on minimizing the process steam overload.

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Työssä tutkittiin tapoja parantaa vetylaitoksen käyttökustannustehokkuutta optimoimalla prosessiparametreja taloudellisempaan ja tehokkaampaan suuntaan. Työssä vertailtiin myös muita vedynvalmistus- ja puhdistusprosesseja ja raaka-aineita, joilla maakaasun höyryreformointiprosessi voitaisiin mahdollisesti korvata.

Diplomityön soveltava osa toteutettiin Solvay Chemicals Finland Oy:n vetyperoksiditehtaan vetylaitoksella keväällä 2012. Toteutus tapahtui parametrien manuaalisesti yksittäisinä muutoksina. Tavoitteena oli parantaa reformointiprosessin hyötysuhteita. Muutokset pohjautuivat kirjallisuuden tietoihin, prosessin simulointiin ja samankaltaisten laitoksien kokemuksiin. Testattavat parametrit prosessissa olivat reformerin ulostulolämpötila, veden siirtoreaktion sisääntulolämpötila ja esilämmitetyn raaka-ainevirtaan lisätyn höyryn määrän suhde raaka-ainevirran hiileen. Tuloksien perusteella optimaalisin suuntaus prosessiparametreille on laskea höyry/hiilisuhdetta ja reformerin ulostulolämpötilaa niiden alkuperäisistä arvoista 3.0 ja 798 °C. Veden siirtoreaktion lämpötilan muutoksilla ei havaittu olevan vaikutusta maakaasun kulutukseen, mutta sen nostaminen vähentää höyryn ylijäämää prosessissa.

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TABLE OF CONTENTS

1	INTRODUCTION	1
	LITERATURE PART	2
2	PROPERTIES OF HYDROGEN	2
3	POTENTIAL RAW MATERIALS	4
3.1	Hydrocarbons	4
3.1.1	Natural gas	4
3.1.2	Naphtha.....	5
3.1.3	Liquefied petroleum gas	6
3.1.4	Fuel oils	7
3.2	Other raw materials	8
3.2.1	Coal.....	8
3.2.2	Biomass	9
3.3	Comparison of alternative raw materials	10
4	HYDROGEN PRODUCTION BY STEAM REFORMING	13
4.1	Steam reforming process.....	13
4.1.1	Feed purification	14
4.1.2	Steam reforming	15
4.1.3	Shift conversion	15
4.1.4	Product purification	16
4.1.5	Process utilities	19
4.1.6	Heat recovery.....	20
4.2	Reformer structure	22
4.3	Reformer types	22
4.4	Reforming options	24
4.5	Steam reforming catalyst design	25
4.6	Operating conditions at a steam reforming plant	26
4.7	Economic aspects	27
4.8	Safety aspects	28
4.8.1	Safety of the hydrogen plant.....	28
4.8.2	Reformer bottlenecks and failure mechanisms.....	29
5	OTHER MANUFACTURING TECHNOLOGIES	31
5.1	Electrolysis.....	31
5.2	Partial oxidation	33
5.3	Auto-thermal reforming	34
5.4	Coal/biomass gasification	35
5.5	Biomass pyrolysis	36
5.6	Thermo-catalytic cracking of methane and ammonia.....	39
5.7	Comparison of the technology alternatives.....	40
6	OTHER HYDROGEN PURIFICATION PROCESSES.....	42
6.1	Partial condensation process	42
6.2	Solid polymer electrolyte cell.....	43
6.3	Palladium membrane diffusion	44

EXPERIMENTAL PART	46
7 SOLVAY CHEMICALS FINLAND OY.....	46
8 SIMULATION OF A HYDROGEN PRODUCTION PROCESS PLANT ..	49
8.1 Simulation of the process.....	49
8.2 Simulation results.....	51
8.3 Parameter selection based on simulation	52
8.4 Evaluation of the importance of the parameters	54
9 FIELD EXPERIMENTS AT SOLVAY CHEMICALS FINLAND OY	56
9.1 Execution of the test runs.....	56
9.2 Results.....	57
9.3 Result analysis	62
10 CONCLUSIONS	67
REFERENCES	69

APPENDIXES

APPENDIX I	Aspen simulation
APPENDIX II	Results from the field experiments
APPENDIX III	Results from the test run

1 INTRODUCTION

Solvay Chemicals Finland Oy produces hydrogen in a process plant in Kouvola. Hydrogen is not a natural resource on earth. This means that it has to be produced from other resources, like natural gas. Hydrogen is used as a raw material in the hydrogen peroxide production process. The hydrogen process also produces so-called process steam as a side product. This process steam is mainly used for the process itself but also for other purposes.

The aim of this master's thesis was to increase the operating cost-efficiency of the current process by optimizing process parameters in a more economical direction. In order to find the best solutions for the process, different raw materials and process technology alternatives for natural gas steam reforming were studied and compared with the steam reforming process.

The application part of the master's thesis consists of the Aspen simulation of the process, which is used as a base for the test run plans. Test runs were performed by changing three of the most important parameters: the steam/carbon ratio, the reformer outlet temperature and the shift conversion inlet temperature, in order to increase the efficiencies of the process. The final test runs were performed to confirm the results and conclusions of the first test runs and to finalize the values to which the parameters were changed for the regular process run.

LITERATURE PART

2 PROPERTIES OF HYDROGEN

Hydrogen, H, is the simplest and lightest of the known elements. It exists in nature in the molecular form H₂. This form makes its total molecular weight 2.016 g/mol. The melting point of hydrogen is -259 °C and the boiling point is -252.7 °C. At a temperature of 20 °C and pressure of 101.325 kPa, hydrogen is in a gaseous state. Hydrogen is a light gas, having a density of 0.08988 kg/m³ and a specific gravity of 0.06998 (when air is equal to 1). It rises and dissipates quickly. It has a high capacity of absorption and its solubility is relatively high in water, and high in alcohols and ethers. Hydrogen is odourless, non-irritating, non-poisonous, tasteless and colourless, but it is very reactive and flammable. It has a flammability range of 4-74 % of hydrogen in air by volume. The auto-ignition temperature of hydrogen varies from 500 °C to 571 °C. The minimum ignition energy for hydrogen, depending on the hydrogen concentration in hydrogen-air mixtures, is 0.017 mJ. Due to the properties of hydrogen gas, it is essential that hydrogen detectors are installed at the plant to notify leaks and improve safety [1].

Hydrogen has high calorimetric values, as the higher heat value is 141.86 kJ/g and the lower heat value (effective) is 119.93 kJ/g. However, hydrogen has a low molecular weight, which means that the advantage of high heat values is reduced by its need for volume. In order to take advantage of the heat values, hydrogen gas has to be stored at high pressure [1].

Hydrogen forms compounds with all the other known elements except the noble gases. Hydrogen can form chemical compounds with metals, covalent bonds with non-metals and halogens, and numerous compounds with carbon. This is based on the electronegativity (2.2) of hydrogen and the unique 1s¹ electron configuration of its atoms. In order to separate hydrogen from these compounds, they have to be processed to release the hydrogen that is present, for example, when converting hydrogen from fossil fuels. The structure of a hydrogen atom is presented in Figure 1.

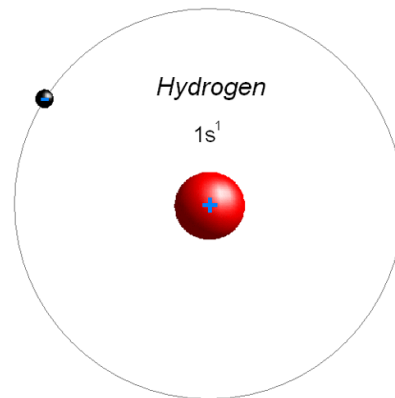


Figure 1. Structure of a hydrogen atom [2]

Hydrogen is an energy carrier rather than an energy source. It can store and give out energy in a usable form, but it must be produced from compounds that contain it. Hydrogen has high energy content per weight, at three times that of petrol. These properties are mainly used to maintain the energy levels of the next steps in industrial processes. This makes hydrogen an efficient raw material to use. In industry, hydrogen is mostly consumed in ammonia production, oil refining, methanol synthesis, space exploration and other processes like hydrogen peroxide production. Other hydrogen consumers are refineries, which require hydrogen for, for example, hydrocracking, dearomatization and desulphurization processes.

3 POTENTIAL RAW MATERIALS

Natural gas is one of the most used raw materials in hydrogen production. However, it is not the only alternative available. In order to find a more efficient raw material for natural gas-based steam, reforming of the other potential raw materials has to be considered. There is also a need for new solutions to replace fossil fuels, as the reservoirs of fossil fuels are continuing to decrease and their prices increase.

3.1 Hydrocarbons

Hydrocarbons are the main constituents of petroleum and generally account for up to 97 % of the total mass of the fuel. The rest of the mass is mainly organic compounds of sulphur, nitrogen and oxygen. Fuel may also include water, salts and various metal-containing constituents. Steam reforming from hydrocarbons is the most common hydrogen production method. It has many advantages, such as less severe operating conditions, in terms of design temperature and metal dusting, than other technologies used. The most common hydrocarbons for steam reforming are natural gas, naphtha, liquefied petroleum gas and fuel oils.

3.1.1 Natural gas

Natural gas is a hydrocarbon-based gas that can be converted into carbon dioxide and hydrogen at high temperature and in gaseous phases by steam reforming. With this method, additional H₂ and CO₂ can be produced in the later stages of the process using CO. The composition of natural gas varies greatly depending on the mining location. The general composition ranges of natural gas estimated from all of the world's reservoirs are presented in Table I.

Table I. General composition of natural gas [3]

Constituents	Chemical Structure	Amount present, (%)
Methane	CH ₄	70-90
Ethane	C ₂ H ₆	0-20
Propane	C ₃ H ₈	0-20
Butane	C ₄ H ₁₀	0-10
Pentane and higher hydrocarbons	C ₅ H ₁₂	0-10
Carbon dioxide	CO ₂	0-8
Oxygen	O ₂	0-0.2
Nitrogen	N ₂	0-5
Hydrogen sulphide, carbonyl sulphide	H ₂ S, COS	0-5
Rare gases, argon, helium, neon, xenon	A, He, Ne, Xe	Trace

According to the Finnish Gas Association [4], the natural gas used in Finland consists of a very low amount of sulphur compounds, so the corrosion risk to the process equipment caused by sulphur oxides or sulphuric acid formed during burning is also low. As no other impurities are involved in natural gas feed, desulphurization can be used as the only feed purification method. The methane content of the natural gas can even be as high as 98 % in natural gases imported from Russia. Natural gas is a cost-effective feed for hydrogen production due to its high methane content and higher purity compared with other raw materials. Due to the high methane content, the yield of hydrogen produced from natural gas is very high. Natural gas also only produces low amounts of environmentally harmful products when burned, and the process emissions are low.

3.1.2 Naphtha

Naphtha is a colourless or reddish-brown mobile liquid with an aromatic odour. It is an inflammable, heavy cut fraction from the distillation of petroleum that boils below 150 °C and includes mostly C₆–C₉ hydrocarbons. It is also one of the most used raw materials in steam reforming besides natural gas. The general composition of naphtha is shown in Table II.

Table II. General composition of naphtha [5]

Constituents	Chemical Structure	Amount present (w-%)
N-hexane	C_6H_{14}	25-35
Xylene	C_8H_{10} , $C_6H_4(CH_3)_2$ or $C_6H_4C_2H_6$	25-35
Toluene	C_7H_8 or $C_6H_5CH_3$	15-25
Cyclohexane	C_6H_{12}	15-20
Pentane	C_5H_{12}	15-20
Heptane	C_7H_{16}	12.5-15
Ethylbenzene	$C_6H_5CH_2CH_3$	5-7
Benzene	C_6H_6	3-5
1,2,4-Trimethylbenzene	C_9H_{12}	2-3
Sulphur	S	0-1.5

As shown in Table II, naphtha is a mixture of alkanes, cycloalkanes and aromatic hydrocarbons, but it also contains sulphur. The composition is dependent on the origin of the naphtha: if it is obtained directly from crude oil distillation and the type of crude oil used. When compared with natural gas, reactions of naphtha are more complex, mainly because the components of naphtha are more complicated and have complex structures. Due to these chemical structures, there is a higher risk of non-desirable reactions in the reactor. An example of this kind of reaction is coke formation in the reformer. This has a negative effect on the catalyst's activity and reduces its lifetime.

When comparing naphtha and natural gas plants, the reformer designs used are identical. A fundamental difference between the natural gas process and the naphtha process is the catalyst. If the natural gas is replaced by, for example, naphtha, a pre-reformer, naphtha drain system and liquid feed section are needed. From a safety point of view, naphtha also creates a fire risk at the plant. This is also the case if naphtha is used as back-up raw material and natural gas remains the main feed.

3.1.3 Liquefied petroleum gas

Liquefied petroleum gas (LPG) is an odourless, colourless, non-corrosive and non-toxic mixture of hydrocarbon gases, mainly propane $CH_3CH_2CH_3$, butane $CH_3CH_2CH_2CH_3$ and isobutane $CH_3CH(CH_3)CH_3$, which exist in a gaseous state under atmospheric ambient conditions. Like all hydrocarbon-based fuels, LPG is a flammable gas and is similar to natural gas. It is stored and transported in

pressurized tanks in which it is partly in its liquid form. LPG differs from natural gas by its higher levels of heavier hydrocarbons. As natural gas consists mostly of methane, LPG consists mostly of propane. It is also more expensive than natural gas because of its partly liquid form and content of heavier hydrocarbons. The general composition of liquefied petroleum gas is shown in Table III.

Table III. General composition of liquefied petroleum gas [6]

Constituents	Chemical Structure	Amount present (w-%)
Propane	$\text{CH}_3\text{CH}_2\text{CH}_3$,	60-90
Butane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$	10-30
Isobutane	$\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_3$	1-5
Propene, Propylene	C_3H_6	1-5

The advantages of liquefied petroleum gas are its high energy content, high burning temperature and ability to burn purely without formation of smoke and coke. Liquefied petroleum gas is also easily transported in liquid form. The main disadvantage is the composition of LPG, which may include low amounts of sulphur and chlorides, which act as catalyst poisons. Their amounts vary greatly. These impurities require a special kind of purification before LPG can be used as a raw material in steam reforming. LPG also consists of heavier hydrocarbons than natural gas, so a pre-reformer is necessary. Due to the heavier hydrocarbons, the yield of hydrogen is lower than the yields from natural gas.

3.1.4 Fuel oils

Fuel oils are liquid products from various refinery streams, usually from residues. The composition of the oil is complex and varies with the source of the crude oil. Fuel oils can be divided into light fuel oil (LFO), Medium Fuel Oil (MFO) and Heavy Fuel Oil (HFO) based on their distillate form to fit small to large industrial heating and combustion processes. LFO is a low viscosity fuel oil for industrial applications. It is blended with a good quality fuel oil and formulated for use in small-scale industrial heating processes in which fuel oil is required. Ease of use is an important factor. MFO is a mixture of distillate and heavier fuel oils. It is a standard fuel blended for use in industry boilers and a possible fuel alternative for power plants and other industrial operations. HFO is a higher density fuel oil product that is specifically designed for large-scale industrial plants to generate

more heat and energy. The main difference between the fuel oils is their viscosities. These are shown in Table IV.

Table IV. Viscosities and specific energy densities of the fuel oils [7]

Fuel oil type	Viscosity at 100 °C, 10^{-5} m ² /s	Specific energy density, MJ/kg
Light	0.82	42.5
Medium	0.82-2.00	41.3
Heavy	2.001-4.00	42.7

Like the fuels introduced in earlier chapters, fuel oils are hydrocarbon based and contain cracked components in which polycyclic aromatic compounds are present. They also contain sulphur, oxygen and nitrogen compounds as well as organo-metallic compounds. Normally, the sulphur content of fuel oils is below 1 %. They can therefore be considered pure enough for catalyzed hydrogen production. However, gasification equipment, a pre-reformer, oil drain system and liquid feed section would be needed in order to use fuel oils as raw material in a steam methane reforming plant.

3.2 Other raw materials

Other alternatives containing carbon and hydrogen that can be used as raw material in hydrogen production are coal and biomass.

3.2.1 Coal

One potential raw material for hydrogen production is coal. It is a combustible black or brownish-black organic rock formed from highly compressed residues of plants, thus consisting mainly of carbon, silicates, metals and some sulphur. The general composition of coal is shown in Table V.

Table V. General composition of bituminous coal [8]

Constituent	Chemical Structure	Approximate amount present (w-%)
Carbon	C	75-90
Hydrogen	H	4.5-5.5
Sulphur	S	1-2
Oxygen	O	5-20
Ash		2-10
Moisture (Water)	H ₂ O	1-10

Coal appears in different forms depending on its formation temperature and pressure, and other environmental conditions. In hydrogen production, coal is gasified and used in similar ways to natural gas in steam reforming. The disadvantage of coal-based hydrogen production is coal's impurities like ash. Coal requires purification after gasification, which affects the economics of the process. Coal gas has to be cooled and filtered after gasification in order to purify it. A drain system for the gasification wastes would also be needed. Another disadvantage of the use of coal is its continuously decreasing reservoirs. However, the coal reservoirs will last longer than the oil reservoirs and they could be a temporary solution to replace the oil-based raw materials.

3.2.2 Biomass

Future scenarios show continuously decreasing world reservoirs of fossil fuels. This means that possibilities other than fossil fuels have to be considered as alternative raw materials.

One of the most promising is biomass, which is an organic material originating from plants or animals. The main components of biomass are cellulose, hemicelluloses, lignin, lipids, proteins, simple-structured sugars, starches, water, hydrocarbons, ash-forming constituents and extractable compounds. Biogas produced from biomass has the potential to reduce greenhouse gas emissions when used as an energy source.

The energy from the sun is stored in plants via photosynthesis in the form of chemical energy and released when burned. This energy can also be converted into other energy forms by a conversion process such as anaerobic digestion, gasification or biorefinery-type fermentation. Energy from biomaterials is most

commonly produced from wood, but also from food crops, grasses, forestry and agricultural by-products, manure and other organic municipal solid wastes. Normally, biomass is gasified into a biogas form in decomposition conditions with controlled amounts of oxygen. The application with most potential for biomass gasification is pyrolysis, i.e. gasification performed in oxygen-free conditions. The typical composition of gasified biomass is shown in Table VI.

Table VI. General composition of gasified biomass according to Speight [3]

Constituent	Chemical Structure	Amount present (%)
Methane	CH ₄	55-65
Carbon dioxide	CO ₂	35-45
Hydrogen sulphide	H ₂ S	0-1
Nitrogen	N ₂	0-3
Hydrogen	H ₂	0-1
Oxygen	O ₂	0-2
Ammonia	NH ₃	0-1

The advantages of using biomass as a hydrogen production raw material are its abundance and cheap price. The disadvantages for efficient hydrogen production are its low methane and high carbon dioxide contents. The low hydrogen content of the raw material also makes efficient hydrogen production from biomass difficult and energy consuming. Impurities in biomass vary depending on the origin of the biomass. Like coal, biomass has to be gasified and then cooled and filtered in order to be suitable for steam reforming. Biomass also needs to be pre-treated before it is suitable for efficient gasification. A drain system for the gasification waste is also needed. The technology is still either at its the development stage or only used in small plants.

3.3 Comparison of alternative raw materials

The raw materials presented in Sections 3.1-3.2 differ from each other in their properties, energy values and prices. A comparison of the economic and energy values of different raw materials is shown in Table VII. The values and prices are based on information gained from the Sustainable Energy Authority of Ireland (SEAI) [9] and Finland's Ministry of Employment and Economy [10], published in 2011.

Table VII. Alternative raw materials and their energy and economic values [9, 10, 11]

Raw material	Specific energy density, MJ/kg	Hydrogen to carbon ratio	Energy per unit, kWh/kg (solid), kWh/L (liquids), kWh/m ³ (gases)	Average price, (2011), cent/kWh	Average Price, (2010)
Natural gas	47-52	4	10	2.49-4.22	0.249-0.422 €/m ³
Naphtha	45-48	1.5-2.5	11	8.48	0.895 €/L
LPG	47	2.5-2.7	13	7.09	0.732-0.803 €/L
LFO	43	1.6-2.1	11	7.26	0.814 €/L
MFO	41	1.6-2.1	11	6.87	0.778 €/L
HFO	43	1.6-2.1	11	6.64	0.760 €/L
Biomass	15-20	0.7-2	5	3.95-5.54	0.19-0.27 €/kg
Coal	23-24	<1	8	0.71	0.055 €/kg

When new raw materials for hydrogen production are considered, the aspects of impurities, reliability of supply, stability of composition and current plant design have to be taken into account. Changing to a completely new raw material requires changes in equipment, process conditions and/or catalyst. This leads to additional investment costs as well as operational risks due to the presence of impurities and variable operating conditions. The most commonly used new equipment installed to switch to a different kind of feedstock is pre-reformer or other gasifying equipment. The form of the raw material also affects the choice of equipment. If the equipment used is designed for gaseous raw materials, the use of liquid feed requires new liquid feed systems and drain systems.

The two most important aspects in the selection of raw materials are the yield of hydrogen and the cost-efficiency of the raw material. The optimal raw material would be one that is cheap enough and can be used efficiently in hydrogen production. This also means that the technology used for production and the possible need for feed purification would have to be taken into account.

Coal has the highest sulphur content of all the raw materials. Its ash content is also high, which makes it expensive to use, as purification is needed. Other raw materials have lower sulphur contents, which allow simpler and cheaper purifications techniques to be applied. The hydrogen yield from the processing of

coal is also significantly lower than from the processing of other raw materials, and coal also has the second lowest specific energy content of all the alternatives.

Biomass also has low specific energy and hydrocarbon contents. The yield of produced hydrogen is therefore low. Even with low prices, coal and biomass efficiency in hydrogen production are not sufficient to make the process profitable. However, a breakthrough in biomass technology is likely in the near future, as it has already been widely studied by, for example, the Technical Research Centre of Finland (VTT) in co-operation with industrial companies [12]. Over the next ten years, biomass will most probably become a raw material with great potential, after the development of the technology and the possible rise in the prices of the other raw materials.

The other alternative raw materials for hydrogen production, natural gas, naphtha, liquefied petroleum gas and fuel oils, have the same specific contents of hydrocarbons and low contents of sulphur compounds. The differences are mostly in the price and phase of the fuels. Only natural gas and partly liquefied petroleum gas are in their gaseous form. The fuel oils and naphtha are in their liquid forms. These raw materials need to be gasified and, thus, new equipment has to be installed. This increases the investment costs for the company. There is also a difference between the gas and liquid states of raw materials and their maximum CO₂ yields. The maximum CO₂ yield is generally lower for the gaseous fuels. The water yield is lower for the flue gases produced from the liquid fuels. This increases the heat transfer properties of the flue gases.

The equipment available at the plant affects the choice of raw material with most potential. If the gaseous fuel is changed into a liquid or solid fuel, investment in extra equipment for gasification and new arrangements for raw material transportation to the process plant will be needed.

If the price of the original raw material rises or its availability decreases considerably, a replacement for natural gas will be needed. The first choice would be the heavier hydrocarbons containing raw materials; the most likely is heavy

fuel oil. This means investments, however, like gasification equipment, a liquid drain and pump system and most probably a pre-reformer.

4 HYDROGEN PRODUCTION BY STEAM REFORMING

Steam-methane reforming is a catalytic process that involves a reaction between light hydrocarbons and steam. It is one of the best known and most used hydrogen production processes in the industry. In the reforming process, hydrocarbons react with steam at high temperatures and moderate pressures in catalyst-filled tubes, generating a mixture of hydrogen, carbon monoxide and carbon dioxide, so-called synthesis gas. The steam reforming process consists of several process steps that are greatly affected by the operating conditions.

4.1 Steam reforming process

Steam reforming of hydrocarbons is a metal-catalyzed reaction in which the hydrocarbons dissociate on the metal surface. Different hydrocarbons can be used as raw materials, but the basic structures of the different steam reforming plants are generally the same, with minor equipment differences. The structure of a general hydrogen process plant using fossil fuels is presented in Figure 2.

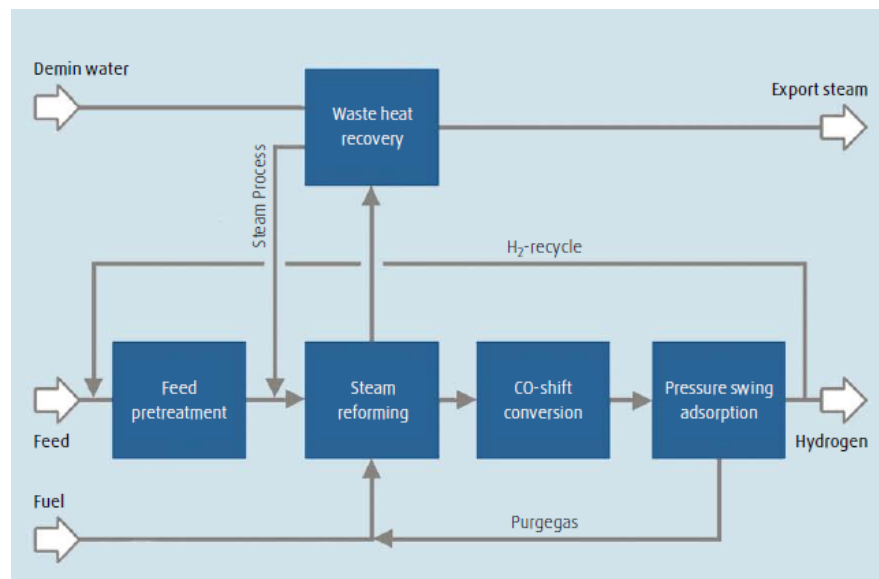


Figure 2. General structure of a hydrocarbon steam reforming plant [13]

The hydrogen process can be divided into four (4) main blocks: hydrocarbon feed with feed purification, reforming, shift conversion and product purification. The fifth block of the process is waste heat recovery, which will be studied further in Section 6.2.

4.1.1 Feed purification

The first unit process in the hydrogen plant is feed purification. The process pre-steps for the hydrocarbon feed purification are normally compression of the feed, mixing feed with recycled hydrogen and heating of the feed stream. These pre-steps are followed by feed purification. In the feed purification, the hydrocarbon feed is purified and mixed with steam before the reforming process. Purification is needed because the feed may contain catalyst poisons like sulphur- and chlorine-containing compounds or olefins. In this purification process, various different catalysts can be used. The catalysts used vary by manufacturer, but most of them are metal-based oxides, for example, CoMo/Al₂O₃ and ZnO.

The most important factors affecting feed purification are the catalyst bed lifetime, the flow rate of the feed and the impurity concentration in the feed. The catalyst bed life affects how long the same bed can be used before the efficiency decreases and the catalyst bed has to be changed. The flow rate affects the pressure directed at the bed and with that its lifetime. The impurity concentration has an important role in feed purification because the impurities act as catalyst poisons in the process. The composition of the impurities also affects the choice of purification method. For example, chloride removal is performed by scrubbing the chloride compounds to an amount below 5 ppm with alkaline-treated Al₂O₃. Chloride compounds are known for corroding heat exchangers and poisoning downstream catalysts. This is most likely to occur in the low temperature copper shift catalysts in the later part of the process plant

Sulphur removal is performed by converting sulphur compounds into H₂S using the hydrosulphurization process method. In the hydrosulphurization method, the compounds are scrubbed by a reaction with an adsorbent such as ZnO according to equation 1.



The sulphur amount is reduced to a level of less than 0.01 ppm of the combined HDS/ZnO scrubbing process.

4.1.2 Steam reforming

After the purification processes, the feed is reformed in the reforming process. In practice, the production part of the process is divided into two sections. The first part is a section at high temperature and pressure, typically 800-1000 °C and 30-40 bar, in which the reforming occurs and shift reactions start. The reforming process is a highly endothermic catalytic process and is shown in reaction 2.



The reaction of natural gas with steam to form CO and H₂ requires a large amount of heat. In current commercial practice, this heat is added using fired furnaces containing tubular reactors filled with a catalyst. The most typically used reforming catalysts are Ni/MgO, Ni/CaAl₂O₄ and Ni/ α -Al₂O₃.

4.1.3 Shift conversion

The synthesis gas that comes from the steam reforming is cooled before entering the shift conversion, which acts as a second part of the production part of the process. In shift conversion, carbon monoxide reacts with process steam to form carbon dioxide and hydrogen. This reaction begins already in the reformer and the cooling after the reformer, but the shift reaction mainly takes place inside the shift converter. The shift conversion takes place at a lower temperature than the reforming in order to maximize the CO conversion and decrease the CO concentrations of the process as much as possible. This conversion is independent of pressure. The shift conversion is more favourable at lower temperatures, high steam quality and higher H₂O:CH₄ ratios than in steam reforming. The H₂:CH₄

ratio is greatly dependent on the operating temperatures. The process gas therefore has to be cooled after reforming. The exothermic shift reaction is shown in reaction 3.



Shift conversion can occur at different shift temperatures. Based on the temperature, the shift conversion can be named low temperature shift converter (LT shift), medium temperature shift converter (MT shift) and high temperature shift converter (HT shift). The temperature ranges of all the shift converters are introduced in Table VIII. One of these shift converters, or combinations of two, can be used. The most typical shift converter catalysts used for shift converters are based on CuO and Cu/Fe-oxide/Cr-oxide.

Table VIII. Temperature ranges of all shift converters according to The Linde Group [13]

Shift converter type	Temperature range
Low temperature shift converter	180-250
Medium temperature shift converter	220-270
High temperature shift converter	300-450

The hydrogen-rich exit stream from the shift converter is cooled and then flashed in order to remove the excess steam as condensate. Finally, the hydrogen produced from the exit steam is purified. Nowadays, the purification is performed with pressure swing adsorption. In traditional product purification, the HT shift converter is used first and then the LT shift converter. In more modern plants, the HT shift is combined with pressure swing adsorption.

4.1.4 Product purification

Pressure swing adsorption (PSA) is a unit process designed for the recovery of pure hydrogen from different hydrogen-rich streams, such as synthesis gases from a steam reforming process or gasification. In the PSA purification process, the impurities in the gas are adsorbed into the fixed adsorbent bed at high pressure.

Subsequently, the impurities of the gas are desorbed at comparatively low pressure into an off-gas stream.

PSA capacities range from a few hundred Nm³/h to large-scale plants with a capacity of more than 400,000 Nm³/h. The hydrogen product meets every purity requirement up to 99.9999 mol-% at the highest recovery rates. Numerous hydrogen-rich feedstocks can be treated by this process. The purity requirements and feed gas composition can be managed by adjustments in the PSA cycle and the type of adsorbents. The number of PSA beds needed depends on the amount of the gas flow and the required purity of the product gas. The typical number of PSA beds in industrial use varies between 4 and 12. A PSA structure with 6 beds is shown in Figure 3.

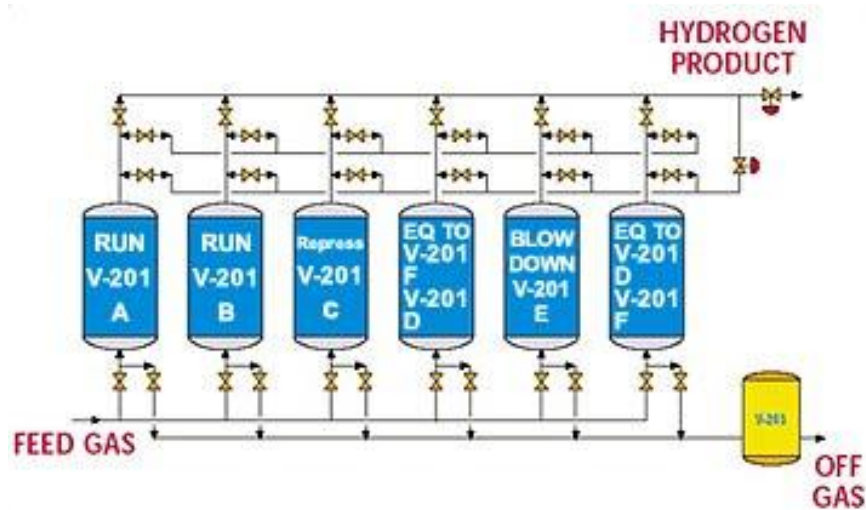


Figure 3. Six- bed PSA purification System [14]

For applications that demand higher hydrogen recoveries, additional adsorbers can easily be added. Multiple beds are used effectively to reduce the size of vessels and the quantity of adsorbent. Although the process is a batch operation, continuous product and off-gas flows can be achieved by employing multiple adsorbers that operate in a stepwise manner. The PSA process cycle has five basic steps. These are shown in Figure 4.

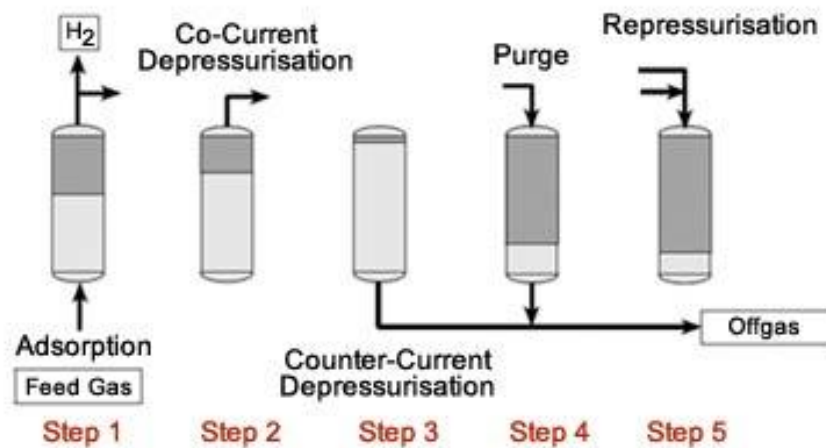


Figure 4. PSA process cycle with five basic steps [14]

The steps are

- I. Adsorption Process
- II. Co-Current Depressurization Process
- III. Counter-Current Depressurization Process
- IV. Purge Process
- V. Counter-Current Repressurization Process

In the adsorption process (I), the gas to be purified flows into a vessel containing a PSA bed under high pressure. The purified air passes through this on-line PSA bed and the impurities remain trapped on the internal surfaces of the adsorbent due their larger molecular size. This leaves the product gas in the void spaces on the vessel where it is then withdrawn from the top of the vessel by pressure on the co-current depressurization process (II). When product gas is withdrawn, the pressure is decreased (III) and the product gas remaining in the void spaces is removed. The adsorbed impurities are released into the gas phase and directed in the purge process (IV) to the low-pressured purge gas stream. This also regenerates the adsorbent bed. The vessel is then purged with a small amount of purified product gas to complete the regeneration of the bed. The vessel is then repressurized (V) with a mixture of production gas from the depressurization step, feed gas and high purity product gas

Product purification aims to produce hydrogen of the required purity at the required recovery and produce a stable flow of PSA purge gas. A small portion of the produced pure H₂ is recycled back to the feed in order to keep the catalyst in the active state in the early part of the reformer tubes.

4.1.5 Process utilities

In addition to raw material, some utilities are needed in production and in maintaining the process conditions. The utilities needed are demineralized water (DMW), steam generated from the DMW and combustion air. The flow sheet of the process with these utilities is shown in Figure 5.

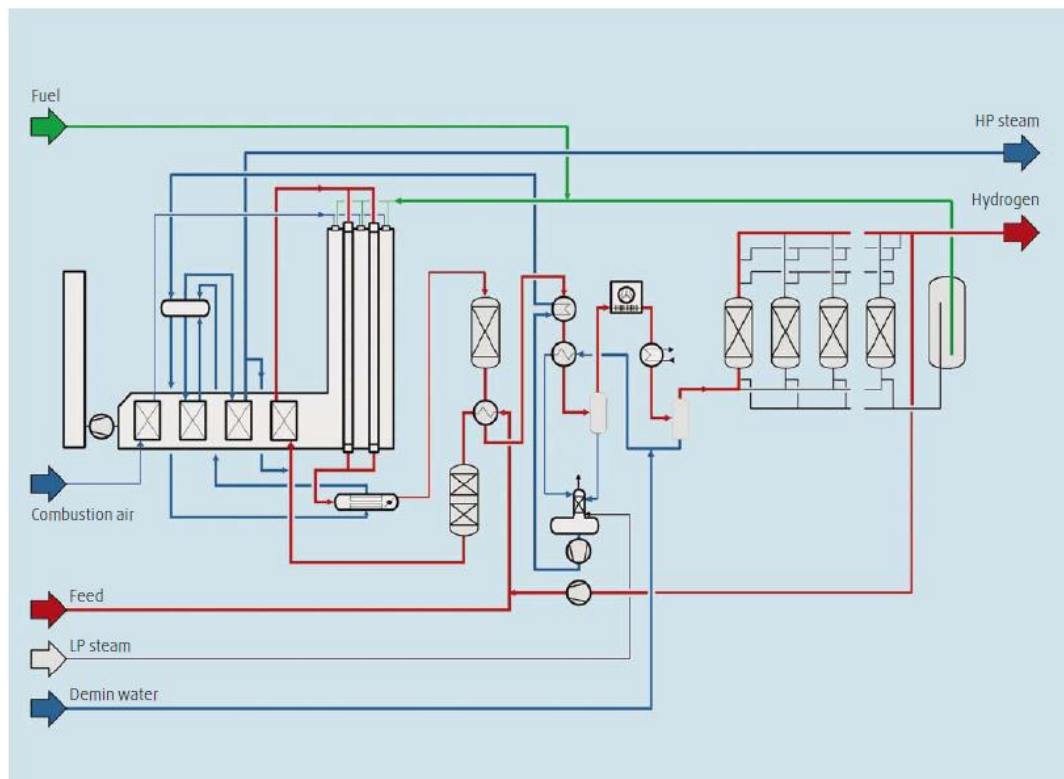


Figure 5. Flow sheet of the steam reforming hydrogen plant showing the main utilities used in the process plant [13]

Demineralized water is used to produce steam for the steam reformer and other purposes. It can also be used for the cooling of the process gas after shift conversion and in some cases to control the temperature of the process gas after reforming. The product steam that is generated is an essential part of the process as it is the main side product.

Combustion air is used to enhance the burning of the fuel and purge gas in the reformer furnaces. Purge and flue gas can also be considered utilities if they are used in the process. Purge gas is a separated part of the process gas in PSA in which hydrogen is purified. It can be fed to the reformer furnaces as a fuel and thus decrease the need for other fuels for the burning.

4.1.6 Heat recovery

Heat recovery from the process unit operations is an important way to decrease operational utility costs by using the heat processed from one unit process to heat the other unit process. The energy costs can be calculated for the process by calculating the hot utility requirement of the process prior to the heat recovery and calculating the energy gained from the heat recovery waste stream.

The energy conversion efficiency can be calculated by equation 4

$$\text{energy conversion efficiency} = \frac{\text{hydrogen out (higher heating value (HHV))}}{\text{energy input}} \quad (4)$$

The energy conversion efficiency for large-scale steam methane reformers is typically 75-80 %, but even 85 % efficiencies may be achieved with good waste heat recovery and use, which decrease the energy input. The reformer feed gas is heated with hot flue gas from furnaces. This heat is also used to generate steam in the boiler by heating the water. After using the heat from the flue gas it flows via the flue gas fan into the atmosphere.

The process also produces steam as a side product. Steam is used in the reforming and shift conversion reactions as process steam. If the amount of steam produced is high enough, the rest of the steam produced is used for other heating purposes in the factory area. Figure 6 shows a block diagram of the hydrogen process in which the steam system is connected to the process.

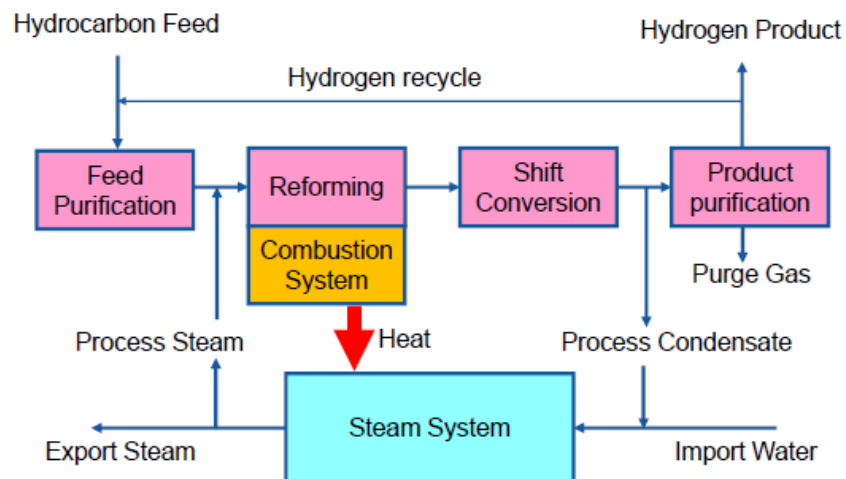


Figure 6. Block diagram of a hydrogen process with a steam system [15]

For the unit process of the plant that consumes most heat, the steam reformer, the required heat must be produced by external firing as the heat balance for the main reactions is endothermic. This is performed by burning the purge gas from the PSA and natural gas with combustion air in the reformer furnaces. The heating value of the purge gas affects the need for natural gas used as a fuel. The higher the heating value of purge gas, the less natural gas is needed.

When burning natural gas as a fuel, 1 m³ of methane produces 10.6 m³ of flue gas including 2 m³ of steam. This flue gas consists mainly of steam, nitrogen and carbon dioxide. It may also contain oxygen if the air constant is higher than 1.0. This constant affects the amount of combustion air needed in the furnaces. By increasing the air constant, nitrogen and oxygen yields in the flue gases increase, and carbon monoxide and the steam yields decrease.

4.2 Reformer structure

In the reformer, the natural gas is mostly converted into synthesis gas. This reaction is called a reforming reaction. Reforming is normally followed by a water-shift conversion reaction that begins already in the reformer. The general structure of the steam reformer is presented in Figure 7.

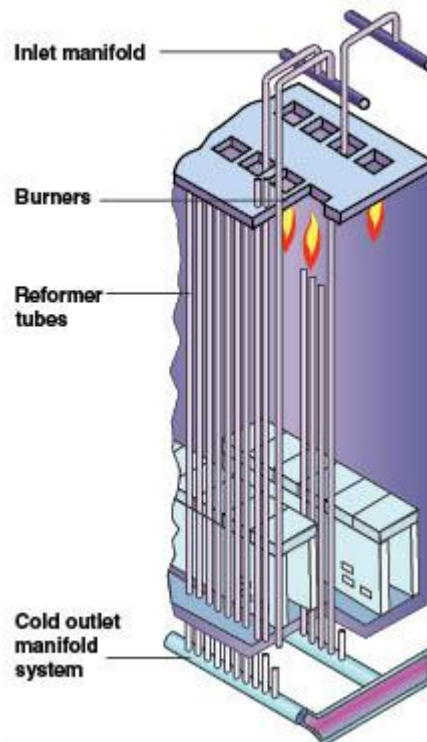


Figure 7. General reformer structure [16]

In the steam reforming process, the pre-purified and pre-heated hydrocarbon feed is mixed with superheated process steam in accordance with the steam/carbon ratio necessary for the reforming process. The gas mixture is then heated and distributed in the catalyst-filled reformer tubes. While flowing through the tubes, which are heated from the outside, the hydrocarbon/steam mixture reacts according to equation 2, which was introduced earlier in Section 4.1.2.

4.3 Reformer types

Different types of reformers are used for steam reforming. The difference is in the position of the burners on the reformer. The selection of the reformer type differs from the reformer wall temperatures and heat flux profiles and thus from the need for capacity for the plant. The three most used reformer types in hydrogen

production are top-fired, side-fired and bottom-fired reformers, as presented in Figure 8.

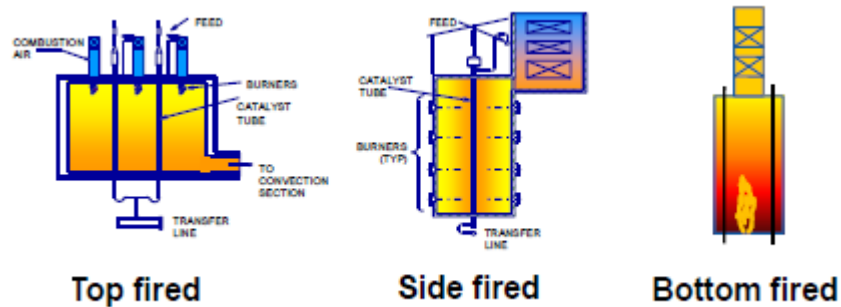


Figure 8. Reformer types [17]

The top-fired reformer is the most common reformer type in the industry. In this reformer type, the reformer heater is usually a rectangular box. The tubes are vertical and the inlet and outlet pigtailed are used to connect the inlet header and the outlet transfer line. All the burners are on top of the reformer. With this reformer type, a large range of capacities can be achieved. The top-fired steam reformer must be operated even more carefully than the other types of reformers as the tube wall temperature and heat flux show a peak in the upper part of the reformer.

The side-fired reformer has the most effective design and is also the most flexible reformer, both in design and operation. It has the highest total heat flux possible combined with the lowest heat flux where the tube skin temperature is at its highest. In a side-fired reformer it is possible to combine a low steam-to-carbon ratio with a high outlet temperature. The most critical operation parameter for this reformer type is the maximum temperature difference over the tube wall, not the maximum heat flux as in other reformer types.

The bottom-fired reformer type is mainly used for small reformers, which are mainly operated from grade. In this reformer type, the tubes are fired from one side only. The bottom-fired reformer has a low process temperature and high flue gas temperature in the lower parts of the reformer, which makes the peak/average flux 1.8. For the top- and side-fired reformers, the peak/average flux is 1.2. In the

bottom-fired reformer, natural draft application is allowed. The bottom-fired reformers achieve a stable heat flux profile along the tube length, which causes high tube skin temperatures at the reactor outlet.

4.4 Reforming options

Reforming can be done as direct reforming, with the use of a pre-reformer or using heat exchange reforming. Pre-reforming allows operation at a low steam to carbon ratio. This reduces the overall energy consumption. The pre-reformer is also used if the raw material stream consists of heavier hydrocarbons. The pre-reformer also increases the lifetime of the reformer tube catalyst and the shift catalysts, as the sulphur present in the hydrocarbon feed and process steam is absorbed by the pre-reforming catalyst. The aim of the pre-reformer is to produce methane-rich products suitable for further downstream reforming. This is done by reforming the hydrocarbon feed with steam over a high Ni catalyst. It will shift the potential for carbon formation away from the steam reformer or even eliminate the carbon deposition on the reformer. Successful pre-reforming requires a good catalyst, and careful start-up, operation and monitoring. An example of the hydrogen process reforming with a pre-reformer is shown in Figure 8.

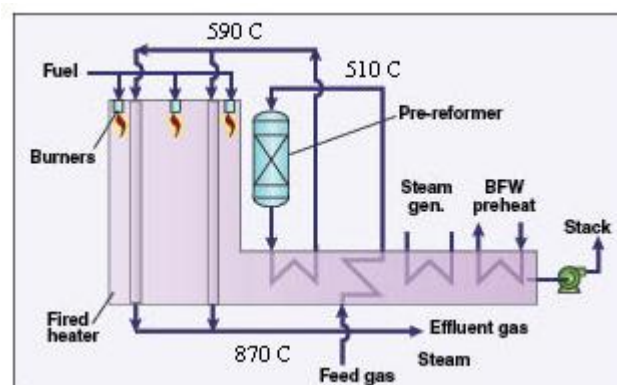


Figure 9. Reforming process with a pre-reformer [15]

The advantages of a pre-reformer are the fuel savings over the standalone primary reformer, reduced capital cost of the reformer, higher primary reformer preheat temperatures, increased feedstock flexibility, lower involuntary steam production and overall steam/carbon ratios, and the provided protection for the main reformer. The use of a pre-reformer offers an opportunity to use different raw material feeds.

Installing a pre-reformer in the plant means that a larger pre-treatment section is needed as the product stream going to the shift conversion increases. This also increases the amount of catalysts needed in the process. Replacing the reformer tubes with better, upgraded metallurgy and thinner walls also allows more throughput and a higher heat flux in the reformer. Even though it is expensive, the pre-reformer increases the capacity of the reformer and the safety of the plant.

The heat exchange reforming has a gas-heated reformer in which the hot reformer effluent at high pressure is used as a heating medium. This high pressure enables a more effective convective heat transfer compared with the convection reforming concept. The novel reactor design in the heat exchange reformer uses a bayonet type or two-bed system with a catalyst on the inside and outside of the tubes, allowing optimal use of the heat transfer areas.

4.5 Steam reforming catalyst design

Steam reforming catalysts comprise active metal or metals, dispersed substrate strong enough for high pressures and temperatures, and promoters to fine tune activity and selectivity. The catalyst design also has some key features like activity on the used metal's surface area, stability and good pressure drop performance. The shape and size of the catalyst are also important to the activity of the catalysts.

Even if the catalyst is suitable for the process, it can be damaged and deactivated.

Damage and deactivation can happen in three different ways:

- physical processes
- poisons
- carbon deposition

Physical processes are catalyst loading, steam condensation and thermal cycling. The most typical physical process is incorrect catalyst loading. Catalysts must be loaded uniformly in specially designed parts of the reactor. Non-uniform loading causes problems of stability and efficiency of the catalyst. Poisons that deactivate

the catalysts are chlorides, heavy metals and sulphur that enter the process in the used feedstock. Carbon deposition occurs if natural gas feeds lead to carbon at high temperature by cracking. Possible carbon removal from the catalyst can be performed by steaming or steam/air decoking depending on the weight of the deposits. Treatment may not fully restore the performance of the catalyst but should enable sufficient activity to be recovered for a continuing satisfactory operation.

Nickel has been used in catalysts because it is an active metal with good activity. It decomposes tar and ammonia simultaneously but it deactivates easily with coke and sulphur compounds. It also requires temperatures above 900 °C. ZrO₂ could also be used as a catalyst in reforming as it tolerates catalyst poisons and can be used at lower operating temperatures than nickel catalysts (~700 °C). However, it is still at the development stage. Other possible active precious metals that could be used in reforming are ruthenium-, rhodium- and palladium-based catalysts. However, they are very expensive and their long-term stability has not been studied much.

4.6 Operating conditions at a steam reforming plant

Operating conditions are strongly affected by the operation of the plant. The plant is controlled by the temperature, pressure, and quantity and quality parameters. A change in these operating conditions affects the production conversions and safety of the process. In the steam reforming plant, these operating parameters are the steam/carbon ratio, steam reformer and shift converter temperatures.

According to Beurden [18] and Armstrong [16], a higher yield of the product hydrogen is achieved by increasing the temperature of the reformer and decreasing the pressure. Reforming is favoured by high temperature and low pressure due to its endothermic character. As reforming is accompanied by volume expansion, it is also favoured by low pressure. In contrast, the exothermic shift reaction is favoured by low temperature, while it is unaffected by changes in pressure. Increasing the amount of steam will enhance the CH₄ conversion but requires additional energy to produce the steam. In practice, steam/carbon ratios

of about 3 are applied. This value for the steam/carbon ratio will also suppress coke formation during the reaction.

Hydrogen production, even with suitable equipment, is a compromise within the operating conditions. Changing one parameter will have a positive and negative effect on the process, making a change of only one parameter and only one eligible result impossible to achieve. Table IX introduces some of the main hydrogen yield driver parameters.

Table IX. Hydrogen yield drivers according to Armstrong (2011) [16]

How to Reduce...	...feed	...fuel
Reforming	High temperature Low pressure High steam/carbon ratio	Low temperature High pressure Low steam/carbon ratio
Shift conversion	High steam/carbon ratio Low temperature	Low steam/carbon ratio High temperature
Product purification	High pressure Low CO content	Low pressure High CO content

At lower temperatures in reforming and shift conversion, operational costs caused by heating are reduced. Lowering operating temperatures in the reformer reduces fuel consumption but in turn decreases the hydrogen yield. Lowering the shift conversion temperature in turn increases the hydrogen yield.

4.7 Economic aspects

Economic aspects are a relevant part of hydrogen production. There are multiple variables affecting the profitability of the process. An already efficient process plant can be optimized to become even more efficient with better heat recovery, thus making relevant savings on the operational costs.

The overall production cost can be estimated over the life of the hydrogen plant using the different cost parameters of constructing, operating and maintaining the hydrogen plant. This reflects a complete picture of the hydrogen plant economics. The efficiency of hydrogen production is the most important parameter when minimizing the production cost. The use of the correct type of catalysts also

ensures proper efficiency for the process reactions. Using the catalysts in the proper conditions will maximize their lifetime and efficiency.

According to Boyce et al. [19], the reforming section makes up about 60-80 % of the total cost of the plant. The main operating cost comes from the utilities. The overall operating cost changes significantly if the raw material price varies. It is the biggest part of the utility costs. Other main parameters affecting the utility costs is the fixed rate of the raw material and the amount of furnace fuel required to fire the reformer. Other utilities than these, even if combined, make up less than 10 % of the utility costs. The other economic parameters include capital costs, start-up costs, catalyst replacement costs, tube replacement costs and maintenance costs.

4.8 Safety aspects

4.8.1 Safety of the hydrogen plant

Safety of the process is an essential part of the production. The most severe hazards in the hydrogen plant are material over-stressing, fire and explosion. Over-stressing is caused by incorrect operation in the plant, or inadequate maintenance or repair work. Incorrect operation means exposing process equipment to conditions for which it is not designed, such as pressure, temperature, corrosion, erosion, mechanical forces, vibrations, alternating stress or thermal expansion.

In order to maintain the safety of the plant, hydrogen's flammable properties have to be taken into account. Hydrogen burns above 2000 °C with colourless flames that are extremely dangerous and difficult to detect in time. Hydrogen also has a rather low auto-ignition temperature of 500-571 °C. The risk of hydrogen auto-igniting is considerable. Simultaneous monitoring of UV and IR radiation at two wavelengths could be used to detect the fire.

In an enclosed area, small leaks of hydrogen pose a danger of exposure to hydrogen, fire and even explosion since hydrogen diffuses quickly to fill the volume. According to Press et al. [20], exposure to hydrogen can cause oxygen

deficiency in the human body, the effects of which may include rapid breathing, diminished mental alertness, impaired muscular co-ordination, faulty judgment, depression of all sensations, emotional instability and fatigue.

The safety of the raw material also has to be taken into account. Natural gas does not have a characteristic smell, so leakages cannot be detected from smell without adding sulphur-containing compounds. Sulphur cannot be used because it acts as a catalyst poison. Natural gas is also lighter than air. Natural gas fuel may cause a risk of water formation in reforming furnaces. Burning hydrocarbon-based fuel can form water if the equipment materials or catalysts are not suitable. The formation of water causes risks of weathering and freeze-up of the furnaces. Incomplete burning of natural gas caused by temperature and pressure changes may cause the formation of toxic carbon monoxide. This can be avoided by ensuring that sufficient combustion air is fed to the furnace and that the flue gases are successfully removed from the furnaces by a closed system, vent system or a combination thereof.

The equipment safety determines the maximum and minimum values for process parameters. These are taken into account in the equipment design parameters. These alarm values should be avoided in order to ensure plant safety and minimize the risks caused by process condition changes. Possible risks caused by the use of incorrect process conditions are process shut-down, low quality of product, equipment breakage and even an explosion in the plant.

4.8.2 Reformer bottlenecks and failure mechanisms

The steam reformer is the most important and expensive part of the hydrogen plant. Its tubes have a certain lifetime and the replacement is expensive. The right timing of the tube change and correct operation are therefore essential.

The main bottlenecks with reformers are usually the reformer tubes, radiant box, convection section, fuel cell (FC) fans and burners. The most common steam reformer tube failure mechanisms are normal 'end-of-life' failures and accelerated normal 'end-of-life' by overheating and thermal cycling. One of the most

dominant damage mechanisms in reformer tubes is creep damage. Creep damage is a slow, sustained increase in the diameter of the tube caused by stress at elevated temperatures.

Less common steam reformer tube failure mechanisms are unidense loading, burner firing, thermal shock, stress corrosion cracking, dissimilar weld cracking and the tube support system. Consequences of these kinds of failure mechanisms include flames from the furnace burners accidentally impinging directly on the outside surface of one or two tubes, the activity of the catalyst in the odd tube becoming impaired by carbon formation, reducing the reaction rate and creep damage on the reformer tubes.

In order to replace the tubes in time, reformer tubes have to be inspected regularly. For this kind of inspection, two kinds of testing methods are used: non-destructive testing (NDT) and destructive testing. In non-destructive testing, reformer tubes are tested without removing the tubes from the process by visual examination, radiography or tube outer diameter measurement. The most used non-destructive testing methods are the detailed mapping and the Laser optical tube inspection system (LOTIS). In destructive testing methods, in which the tubes are removed from the process, the testing is mainly based on metallurgical examination. Monitoring and testing of the reformer tubes is necessary in order to maximize the tube lifetime and maintain the safety of the reformer. The tube life can also be maximized by temperature control by maintaining the temperature as low as possible. Using improved metallurgy at the investment stage of the plant also maximizes the tube lifetime.

5 OTHER MANUFACTURING TECHNOLOGIES

Besides steam reforming, multiple other technologies are used for hydrogen production. These methods differ from steam reforming in their structure and principle, raw materials or efficiencies. Chemical processes, in which hydrogen is produced by a chemical reaction or reactions, are called synthesis processes.

Hydrogen can be produced from water via electrolysis. Another method is to produce hydrogen from a gas mixture of hydrocarbons, as in partial oxidation and auto-thermal reforming. Hydrogen can also be produced from solid and liquid materials as in coal/biomass gasification and biomass pyrolysis. The combination of gas and liquid hydrogen production technology is called thermo-catalytic cracking of methane and ammonia.

5.1 Electrolysis

Electrolysis of water is a process in which water is transformed into its elemental parts with an electric current. It is the simplest and cleanest way to produce hydrogen. Due to the need for water, electrolysis processes are often located near large areas of water. There are large-scale electrolysis processes located in, for example, Brazil, Egypt, Canada and Norway. In 2006, 4 % of the world's hydrogen used in industry was produced from electrolysis of water. The basic principle of electrolysis is presented in Figure 10.

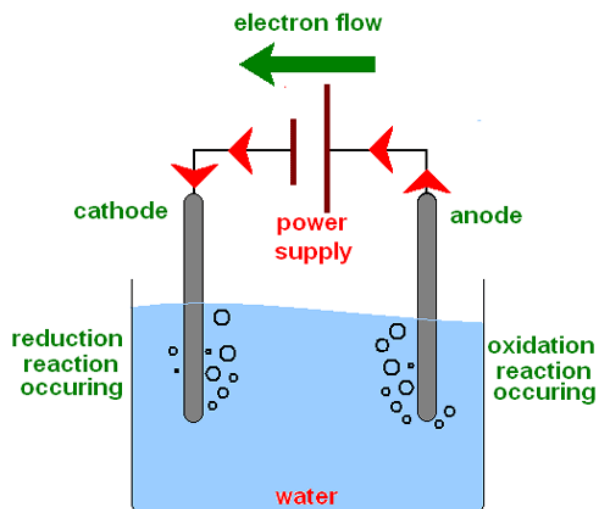
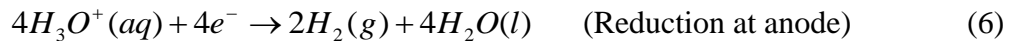
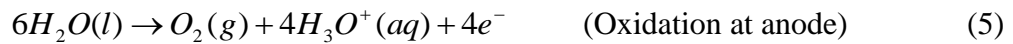


Figure 10. Basic principle of electrolysis [22]

The process of electrolysis breaks water into its constituent elements of hydrogen and oxygen by charging water with an electrical current. It takes about 142 MJ to produce 1 kg of hydrogen. In electrolysis from water, hydrogen ions capture electrons from the cathode and water molecules lose electrons to the anode according to reactions 5 and 6. The overall process reaction is introduced in reaction 7.



In the production of hydrogen gas through electrolysis of water, a dedicated electrolyser is needed. The electrolyser is chosen depending on the electrolyte used in electrolysis cells. The two most common types of electrolysers are a potassium hydroxide electrolyte and a solid polymer membrane electrolyte. Hydrogen can also be produced via electrolysis as a side product when electrolyzing HCl in order to produce Cl-based products.

Electrolysis is very expensive in terms of the amounts of electricity used and hydrogen gas produced from water. The electricity needed for electrolysis can cost more than 80 % of the price of the hydrogen produced. However, if a cheap option for the source of the electricity is available, the process will be profitable. One option is to produce electricity via water power.

5.2 Partial oxidation

In partial oxidation, hydrogen is produced by converting raw material with an oxidant like air, pure oxygen and/or steam. Applicable raw materials for a partial oxidation process are natural gas, LPG, naphtha, residual oil, asphalt, petrol coke and coal. The reaction is exothermic and, hence, no indirect heat exchanger or catalysts are required. However, the hydrogen yield per mole of methane feed and the system efficiency can be significantly enhanced with catalysts. Partial oxidation is introduced in equation 8.



The process is carried out by injecting preheated hydrocarbon and steam through a specially designed burner into a closed combustion vessel. Partial oxidation occurs at 1290-1400 °C. In practice, the reaction needs less than a stoichiometric amount of oxygen to complete the combustion reaction. The structure of a partial oxidation process is presented in Figure 10.

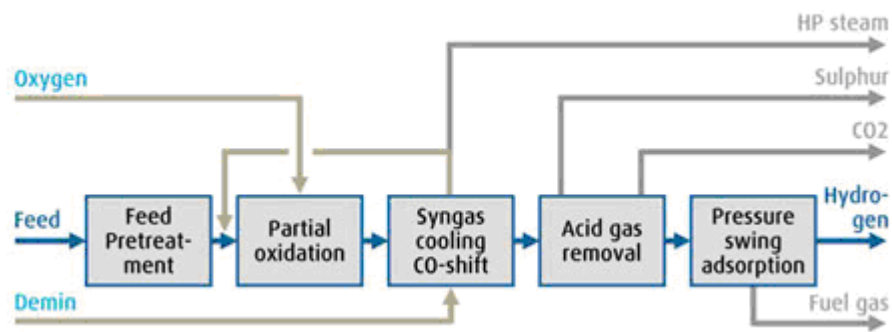


Figure 11. Structure of the partial oxidation process [14]

The principal advantage of the partial oxidation process over steam reforming is that any hydrocarbon feed can be used by changing certain parameters. No desulphurization is required prior to the partial oxidation step. The principal disadvantage is that a supply of 95 % pure oxygen has to be provided to the process. This increases the investment and operating costs of the process plant.

The efficiency of the partial oxidation unit is relatively low (70-80 %) compared with steam reforming. Partial oxidation systems are typically less energy efficient

because of the higher temperatures involved. Lower energy efficiency is mainly caused by a less efficient heat recovery process. In a steam methane reforming plant, heat can be recovered from the flue gas to generate steam for the reaction, and PSA purge gas can be used as a reformer burner fuel to provide heat for the endothermic steam reforming reaction. In an exothermic partial oxidation reactor, the energy in the PSA purge gas cannot be recovered as fully as in steam reforming. The process is profitable if 95 % pure oxygen can be purchased at a reasonable price and the heat recovery does not need to be as efficient as in steam reforming.

5.3 Auto-thermal reforming

Auto-thermal reforming, sometimes called tandem reforming, is a combination of steam reforming and partial oxidation for the generation of synthesis gas. Unlike the steam methane reformer, the auto-thermal reformer requires no external heat source and no indirect heat exchangers. This makes auto-thermal reformers simpler and more compact than steam reformers, and it is likely that auto-thermal reformers will have a lower capital cost. The structure of the auto-thermal reforming process is shown in Figure 12.

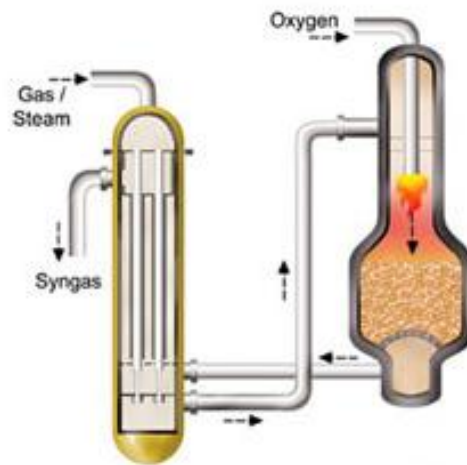
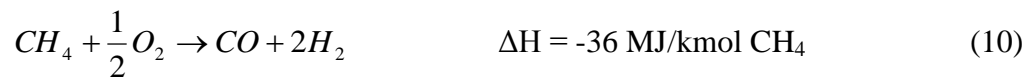


Figure 12. Structure of the auto-thermal reforming process [23]

In auto-thermal reforming, a hydrocarbon feed reacts with both steam and air to produce a hydrogen-rich gas. The steam reforming and partial oxidation reactions take place simultaneously. The synthesis gas from the process heats the tube reactors.

The reaction equations for the autothermal reforming are introduced as equations 9 and 10.



In an auto-thermal reformer, all the heat generated by the partial oxidation reaction is used in full to drive the steam reforming reaction. Thus, auto-thermal reformers typically offer higher system efficiency than partial oxidation systems from which excess heat is not easily recovered. As with a steam reformer or partial oxidation system, water gas shift reactors and a hydrogen purification stage are needed. The process is normally used for the production of hydrogen from heavier hydrocarbons if steam reforming cannot be used.

5.4 Coal/biomass gasification

Gasification is a conversion of carbon-containing materials into carbon monoxide and hydrogen at high temperatures with a controlled amount of oxygen. Coal is converted into synthesis gas, which is a mixture of CO and H₂O, or liquefied and used as a substitute for petroleum. The coal gasification temperature is 1100-1300 °C after which the hydrogen gas is separated from the hydrogen monoxide. The reaction equation for the coal conversion into hydrogen is introduced as equation 11.



The highest yield in the primary gasification step is achieved with pulverized coal gasified with oxygen at high temperatures. In coal gasification, sulphur capture is needed to purify the product gas from sulphur compounds. In order to purify the gas from the char and ash particles, gas has to be cooled and then filtered to remove the particles. As many different purification techniques are needed, coal gasification for hydrogen production is expensive. Even if the highest yield of hydrogen is achieved, gasification is approximately twice as expensive as natural gas-based hydrogen production

Gasification is also used for hydrogen production from biomass. Ohkubo et al. [23] studied the use of biogas as a raw material for hydrogen plants in 2010. In this study, the biogas was generated from high-water-content biomass using methane fermentation technology consisting of acid and gas fermentation processes. These reactions are shown below in 12 and 13.



After purification, the methane from the process can be used to produce hydrogen by steam reforming. Compared with coal, biomass is easier to gasify because it is more reactive with higher ignition stability. This also makes it easier to thermochemically process higher value fuels such as methanol and hydrogen. Biomass gasification gas has impurities, however, like tars and nitrogen compounds, which is the greatest disadvantage of using biogas. Biomass has to be pretreated before it can be used in a gasification process to have it as dry pulver or an oil-like liquid. The biomass gasification process is profitable if biomass can be purchased cheaply and is already in usable form, such as from paper and pulp industry waste, and is easily transported. This requires a cheap option for a purification method, however, and the impurities in the biomass used should remain the same.

5.5 Biomass pyrolysis

Pyrolysis is the heating of biomass at a temperature of 380-630 °C at 0.1-0.5 MPa. The products from pyrolysis are liquid pyrolysis oils, solid charcoal and gaseous compounds. Pyrolysis is performed in zero-oxygen conditions. Pyrolysis can be further classified into slow pyrolysis and fast pyrolysis. As the product is mainly charcoal, slow pyrolysis is normally not considered for hydrogen production. Fast pyrolysis is a high temperature process in which the biomass feedstock is heated rapidly in the absence of oxygen to form vapour and subsequently condensed into a dark brown mobile bio-liquid.

The products of fast pyrolysis can be found in all gas, liquid and solid phases:

- I. Gaseous products include H₂, CH₄, CO, CO₂ and other gases depending on the organic nature of the biomass for pyrolysis.
- II. Liquid products include tar and oils that remain in liquid form at room temperature, like acetone, acetic acid, etc.
- III. Solid products are mainly composed of char and almost pure carbon plus other inert materials

The basic structure of the pyrolysis process is presented in Figure 13.

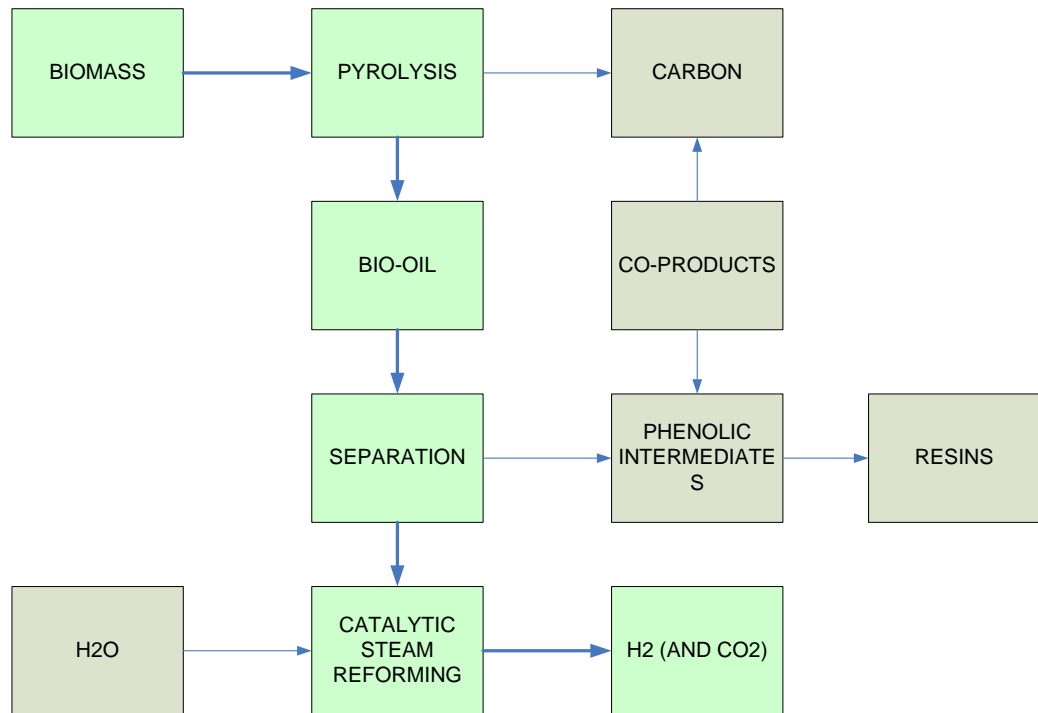
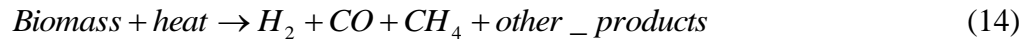


Figure 13. Block diagram of biomass pyrolysis [25]

In the biomass pyrolysis process, biomass and flue gas are fed to the pyrolysis reactor. The products from the pyrolysis are 30 % bio-oil, 30 % H₂O, 5 % pyrolysis gas and 35 % pyrolysis char, which is removed from the process from the bottom of the reactor. Product bio-oil is fed to the separation where the phenolic intermediates are separated from the bio-oil. After separation, the remaining bio-oil is fed to the catalytic steam reforming with water. Products of the reforming are 7 % H₂, 60 % CO₂, 11 % CO and 2 % CH₄. The results are based on the studies by Evans et al. [25] in 2003.

Although most pyrolysis processes are designed for biofuel production, hydrogen can be produced directly through fast or flash pyrolysis if a high temperature and sufficient volatile phase residence time are allowed, as in equation 14:



Methane and other hydrocarbon vapours produced can be steam reformed to produce more hydrogen as shown in equation 15:



In order to increase the hydrogen production, a water-gas shift reaction can be applied as shown in equation 16:



The temperature, heating rate, residence time and type of catalyst used are important pyrolysis process control parameters. In favour of gaseous products, especially in hydrogen production, a high temperature, high heating rate and long volatile phase residence time are required. As pyrolysis is an application of biomass gasification, it has the same disadvantages, like impurities (tars and nitrogen compounds) that remain in the pyrolysis and the need for pre-treatment. As for biomass gasification, if biomass can be purchased cheaply and in a suitable form and be transported easily then even with a lower efficiency process, it could be made profitable. However, pyrolysis is mostly still in its development stage and a profitable and efficient process is not yet on the market.

5.6 Thermo-catalytic cracking of methane and ammonia

Hydrogen can also be produced by thermo-catalytic cracking of methane consisting of hydrocarbons. In this approach, methane is broken down into carbon and hydrogen in the presence of a catalyst at a high temperature of 850-1200 °C, according to reaction 17.



This reaction is endothermic, requiring an energy input of about 10 % of the natural gas feedstock. Thermo-catalytic cracking technology is still far from a commercial application for hydrogen production. The primary issues are low efficiency of conversion and carbon fouling of the catalyst. Frequent regeneration of the catalyst is required to remove accumulated carbon, but relatively low capital costs are achieved because of the system's simplicity.

Ammonia cracking is a process of dissociation of gaseous anhydrous ammonia into a mixture of hydrogen and nitrogen according to reaction 18.



This endothermic process is performed at an increased temperature within the range 850-950°C in the presence of a nickel catalyst. Ammonia cracking takes place in indirectly heated catalyst-filled tubes. The dissociation rate depends on the temperature, pressure and catalyst type. Ammonia is widely distributed to consumers today. Ammonia is also cheap and relatively easy to transport and store compared with hydrogen. This makes it a potential candidate for use as a hydrogen carrier for fuel cell applications.

The main impurities are traces of unreacted ammonia and nitrogen oxides. The concentration of unreacted ammonia must be reduced to the ppm level for use in polymer electrolyte membrane (PEM) fuel cells, although alkaline fuel cells are not as sensitive to this. A potential advantage of ammonia cracking for hydrogen generation in a fuel cell system is simplicity. Unlike a steam reformer system,

water is not required as a co-feed with the fuel, and no water gas shift reactors are needed. When an ammonia cracker is closely coupled to a fuel cell no final hydrogen purification stage is needed. As nitrogen is inert in the fuel cell, it is simply passed through as a diluent.

For pure hydrogen production based on ammonia cracking, however, a costly separation of H₂ and N₂ would be required, for example, by using a PSA unit or a hydrogen-selective membrane. The process is used when methane or ammonia is easily and cheaply available.

5.7 Comparison of the technology alternatives

The comparison of different technology alternatives for hydrogen production concentrates on the efficiency of the processes. Investment and operational costs also have to be considered. The raw material selection and alternatives are important, especially for the operational cost. The need for a catalyst and special equipment also affects the potential of the process alternative. In Table X, an approximation of the operational costs of the technologies compared with steam reforming technology and process efficiencies is introduced. The efficiency of the process illustrates the hydrogen yields that can be achieved by the current technology. The information is based on studies by T-Raissi et al. [26] and information from the Florida Solar Energy Center (FSEC) [27].

Table X. Comparison of synthesis technology alternatives [26, 27]

Technology	Raw materials	Efficiency, %	Operational costs relative number to SMR calculated by <u>other technology steam reforming</u>
Steam reforming	Natural gas, naphtha, methanol	95-99	1
Electrolysis	Water	75-80	3-10
Coal gasification	Coal	35-45	1.4-2.6
Biomass gasification	Biomass	45-50	2.0-2.6
Partial oxidation	Heavier hydrocarbons than naphtha	70-80	1.8
Auto-thermal reforming	Natural gas, methane	90	>1.8
Pyrolysis	Biomass	<95	0.9
Thermal cracking	Methane (Natural gas)	low	Not known
Ammonia cracking	Ammonia	<85	Not known

The steam reformer has the best efficiency of all the alternatives, with pyrolysis and ammonia cracking the second and third best options. From an efficiency point of view, auto-thermal reforming and electrolysis of water can also be considered for hydrogen production. The main disadvantage of auto-thermal reforming is the difficulty of scaling up if there is existing production equipment. Changing to auto-thermal reforming would require much more equipment for the plant area. Electrolysis does not have the potential to be economically efficient for hydrogen production due to its high electricity costs. All the other alternative synthesis processes studied have significantly lower efficiencies. The efficiency of coal gasification is clearly the lowest of all the studied processes. Comparing the efficiency and the operational costs of the technology alternatives, the best combination is steam reforming and pyrolysis. Pyrolysis efficiency is only theoretical for now, however, and in order to achieve suitable efficiencies the technology needs more development.

6 OTHER HYDROGEN PURIFICATION PROCESSES

Pressure swing adsorption is the most common hydrogen purification method used in industrial hydrogen production via steam methane reforming. There are other alternative methods for hydrogen purification depending on the hydrogen production method used. Besides pressure swing adsorption, the most used hydrogen purification methods are partial condensation, solid polymer electrolyte cell and palladium membrane diffusion.

A proper purification method is needed in all hydrogen production processes in order to reduce the CO and CO₂ contents, which decrease the heating value of the hydrogen. High contents of CO and CO₂ also mean lower purity of hydrogen, which lessens the hydrogen properties in further uses.

6.1 Partial condensation process

A partial condensation process is used to recover pure carbon monoxide from synthesis gas if hydrogen is produced by a partial oxidation or catalytic reforming process. In the partial condensation process the synthesis gas fed to the process has to be absolutely free of water and other components that could freeze at low operating temperatures. To prevent the risk of freezing, the process gas is initially dried in a molecular sieve adsorber station.

Synthesis gas from partial oxidation is normally supplied with high pressure, and a high CO and low CH₄ content to the partial condensation process. Alternatively, syntheses gases from catalytic reforming processes are supplied with lower pressure, lower CO and elevated CH₄ content. If catalytic reforming is used as a production method, a methane wash is needed before the reforming.

Partial condensation processes exist in several alternative configurations, depending on the required product purity, recovery rate and presence of other impurities like N₂ and Ar in the feed. One of the simplest flow sheet of a condensation process is presented in Figure 14.

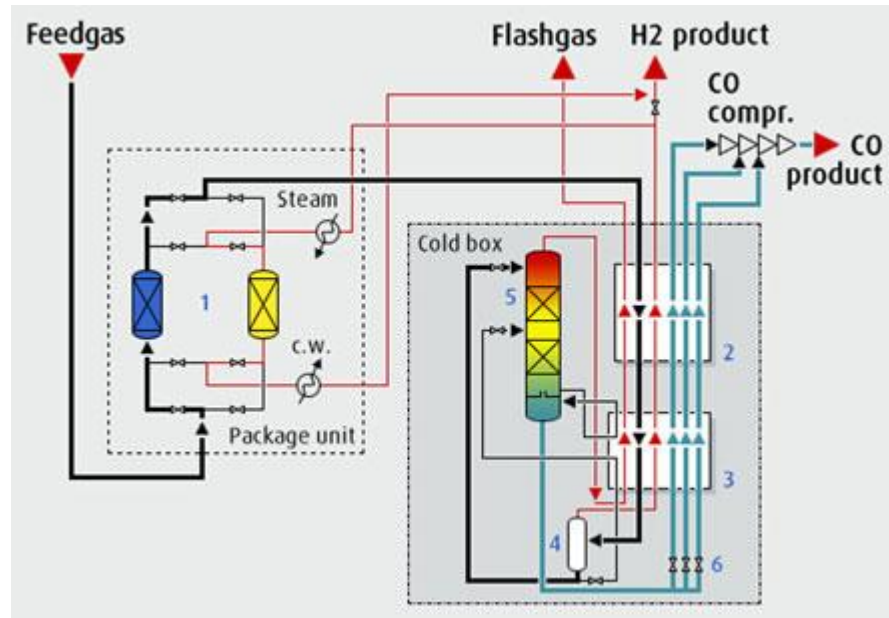


Figure 14. Flow sheet of a partial condensation process [14]

A partial condensation process includes an adsorber station, a coldbox containing the plate heat exchangers for the pre-cooling of the feed gas against product streams, the hydrogen separator and stripping column. A dry piston or integrally geared centrifugal compressor is usually used as a carbon monoxide compressor.

6.2 Solid polymer electrolyte cell

A solid polymer electrolyte cell is used in the purification of hydrogen produced by thermo-chemical cycles. In this method, an electrolytic passage of hydrogen ions crosses a solid polymer electrolyte membrane. The hydrogen output purity is 99.8 % and the hydrogen output recovery 95 %. Sulphur-containing compounds contaminate the electro-catalysts, which has to be taken into account when choosing a raw material for hydrogen production. The feed can also be purified before the production process.

Polymer electrolyte membrane (PEM) fuel cells, also called proton exchange membrane fuel cells, deliver high-power density and offer the advantages of low weight and volume compared with other fuel cells. PEM fuel cells use a solid polymer as an electrolyte and porous carbon as electrodes that contain a noble metal catalyst. They need only hydrogen, oxygen from the air and water to operate. They are typically fuelled with pure hydrogen supplied from storage tanks or on-

board reformers. The structure and principle of a polymer electrolyte cell is presented in Figure 15.

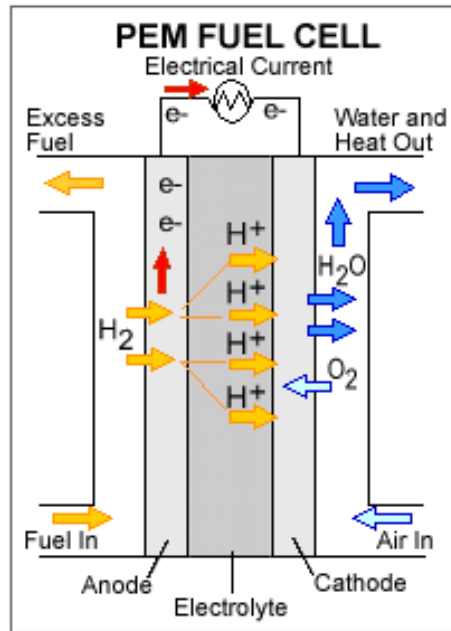


Figure 15. Principle of polymer electrolyte cell [28]

Polymer electrolyte membrane fuel cells operate at relatively low temperatures, around 80 °C. Low temperature operation allows them to be started quickly because of the short warm-up time and results in less wear on the system components, resulting in better durability. However, a noble metal catalyst, typically platinum, is required to separate the hydrogen's electrons and protons. This increases the costs of the system. The platinum catalyst is also extremely sensitive to CO poisoning, making it necessary to employ an additional reactor to reduce CO in the fuel gas if the hydrogen is derived from an alcohol or hydrocarbon fuel. This also adds to the costs of the process. This technology is still mainly in the development stage.

6.3 Palladium membrane diffusion

Palladium membrane diffusion is a hydrogen purification method in which hydrogen purifiers operate via pressure-driven diffusion across palladium membranes. The method is based on palladium diffusion properties as hydrogen is an element that can diffuse through palladium. Palladium membrane diffusion can

achieve a purity of 99.9999 % and hydrogen recovery of up to 99 %. This method is normally used in small to medium size process plants. The principle of palladium membrane diffusion is shown in Figure 16.

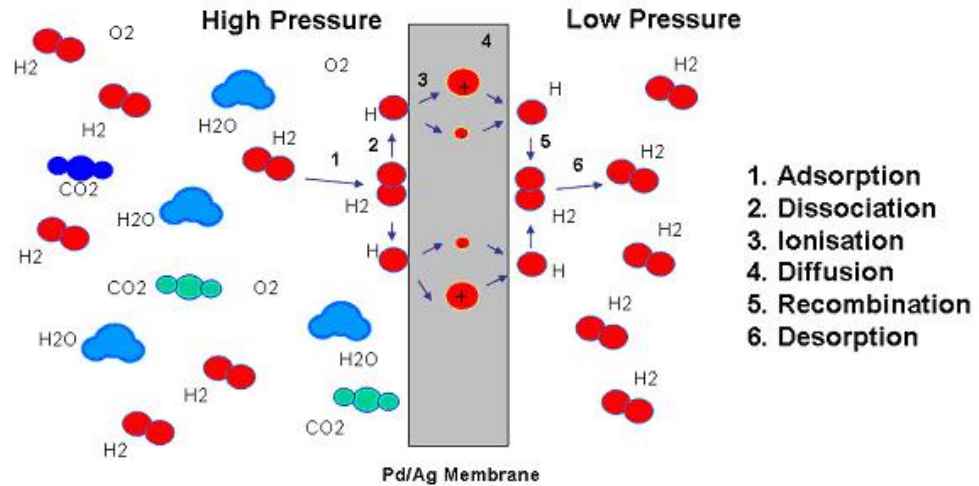


Figure 16. Principle of membrane diffusion [29]

Only hydrogen can diffuse through the palladium. The palladium membrane is typically a metallic tube comprising a palladium and silver alloy material possessing the unique property of allowing only monatomic hydrogen to pass through its crystal lattice when it is heated above nominally 300 °C. When the hydrogen gas molecule comes into contact with the palladium membrane surface, it dissociates into monatomic hydrogen and passes through the membrane. On the other surface of the palladium membrane, the monatomic hydrogen is recombined into molecular hydrogen – the ultrapure hydrogen used in the semiconductor process.

Palladium purifiers provide <1 ppb purity with any inlet gas quality. The impurities removed include O₂, H₂O, CO, CO₂, N₂ and all hydrocarbons including methane. The maximum operating pressure is 17 bar at a temperature of 300-400 °C. The normal life expectancy of a palladium membrane purifier is five years, and no routine maintenance is required. In this method, the sulphur-containing compounds and unsaturated hydrocarbon decrease the permeability of the membrane.

EXPERIMENTAL PART

The experimental part consists of an introduction to the hydrogen plant at Solvay Chemicals Finland Oy, a process simulation based on the hydrogen plant and an introduction to the prevailing operating conditions and results of the field experiments. After the analysis of the results of the field experiments and the interpretation of these results, suggestions for further development of the process and final conclusions are given.

7 SOLVAY CHEMICALS FINLAND OY

Solvay Chemicals Finland Oy produces hydrogen as a raw material for its hydrogen peroxide process. For hydrogen production, Solvay Chemicals Finland Oy uses a continuous steam reforming process with a feedstock of natural gas. The plant is designed for a maximum production of 7700 Nm³/h of hydrogen with a possible decrease of 35 %. The plant can also produce 10 t/h of low pressure steam as a by-product of the process. This is partly used for the hydrogen production process as a process steam and partly for other purposes. Purge gas separated from the product flow is used as a reformer fuel with the second natural gas flow.

The process reactors are two bottom-fired reformers and a high temperature shift converter. The application of only one shift converter instead of two is relevant because PSA technology is used in product purification. The application of PSA technology has many advantages, such as a significant reduction in the amount of equipment and the extreme purity (>99.99 %) of produced hydrogen. A flow sheet of the production process is shown in Figure 17.

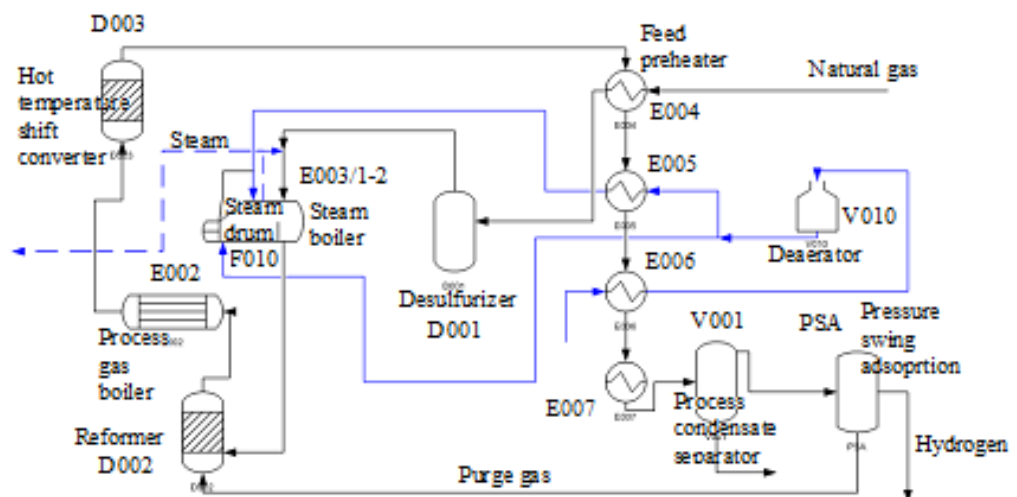


Figure 17. A flow sheet of the hydrogen production process at Solvay Chemicals Finland Oy

Natural gas is used as the feed and fuel in the process. There is no alternative back-up raw material for the feed to change into. Natural gas is purchased from Gasum and fed to the process from the natural gas pipe at a temperature of 10 °C and a pressure of 23 bar. The production process begins by preheating the natural gas and possible recycled hydrogen with a converted gas in feed pre-heater E004. Preheating is then followed by hydro-desulphurization in desulphurizer reactor D001 in order to remove the sulphur compounds from the feed stream. After hydro-desulphurization, the feed is mixed with process steam, then superheated to 540 °C and fed to the catalyst-filled reformer, D002, tubes for the reforming. The reforming reaction occurs at a temperature of 800 °C and pressure of 15.5 bar. After reforming, the process gas is cooled with cooling water in heat exchanger E002 to 330 °C and fed into high temperature shift converter D003 for the water shift conversion. After the shift conversion process, the gas is cooled to 35 °C by four heat-exchangers: E004, E005, E006 and E007. After cooling, the process gas flows to the process condensate separator V001 and to the PSA, from which the purified hydrogen flows forward as a product stream. Part of the pure H₂ product can be recycled back to the feedstock. The rest of the process gas is separated from the hydrogen stream as a purge stream. Purge gas from the hydrogen purification in PSA is used as a fraction of the feed fuel. This purge gas, natural gas and air are used as a fuel in the reformer furnaces to heat the reformer. The

rest of the fuel is released from the furnaces as a flue gas. This flue gas is then used in steam generation and then released to the atmosphere.

Other main utilities used in the hydrogen plant are demineralized water (DMW) for steam production and air for the reforming reaction. DMW is first heated by heat exchanger E006 with a hot process gas. After this, the heated DMW flows to boiler V010; it is then divided into two fractions. The first fraction flows to heat exchanger E004 for preheating and the second fraction flows via heat exchanger E005 to E003-3. Before entering heat exchanger E003-3, the preheated steam from E014 is mixed with the second stream. In E003, the DMW is converted to 210 °C steam. A fraction of the steam is mixed with the natural gas stream coming from the hydro-desulphurization, and the other fraction is used for other heating purposes like heating the air for the reforming furnaces.

Different catalysts are used in the reactions in the hydrogen production process. The choice of catalyst depends on the operating conditions and plant manufacturer. Different kinds of catalysts can be used in similar kinds of reactors because of the different operating conditions. Catalysts used in the Solvay Chemicals Finland Oy hydrogen plant are shown in Table XI.

Table XI. Catalysts used at Solvay Chemicals Finland Oy until 2011

Service	Position	Catalyst type (Linde)	Catalyst name	Volume [m ³]	Bulk density [kg/m ³]	Expected lifetime [a]
De-sulphurization Reactor	D001	Süd-Chemie G1	Copper and Molybdenum-promoted Zinc Oxide	1.34	1.15	3
Reformer Tubes	D002 -1/2	Süd-Chemie C14	Nickel on Alumina	0.2	1.14	4
		G90LDP	Nickel catalyst on a calcium aluminate support	5.0	0.8	4
HT shift Reactor	D003	Süd-Chemie G3C	Iron-based catalyst with chromium and copper promoter	4.8	1.1	4

As seen from Table XI, the expected lifetime of the catalysts varies from three to four years, at which point catalysts have to be changed according to the suppliers' recommendation. This expected lifetime is approximated for a 100 % production rate, which is not the case at Solvay Chemicals Finland Oy. Normally, the production rate is about 60-70 %, which increases the expected lifetime of the catalysts. The catalyst lifetime is also affected by possible problems in the process, which include the number of shutdowns and start-ups needed at the plant. Catalysts from Solvay Chemicals Finland Oy have been used since 2005 and their replacement will become necessary in the next few years.

8 SIMULATION OF A HYDROGEN PRODUCTION PROCESS PLANT

8.1 Simulation of the process

Aspen Plus simulation software is used to model a hydrogen production process plant at Solvay Chemicals Finland Oy. The simulation is based on the presently used equipment and set-up parameters. After simulating the present process set-up, the changes in the operating conditions of the hydrogen plant are tested to find their effect on the process efficiency.

The process is simulated by the Aspen Plus User Interface program. To simplify the simulation of the process mixers, the splitters and heat exchangers are modified differently from the existing flow sheet. The reformer is shown as two separate reactors having two different reactions because the water shift reaction begins straight after the reforming and continues in the high temperature shift converter. The purge and flue gas heat flows are not simulated, but their effect on the process is taken into account in the natural gas consumption and optimization calculations. Solvay Chemicals Finland Oy's hydrogen production plant flow sheet used in the simulation is shown in Figure 18.

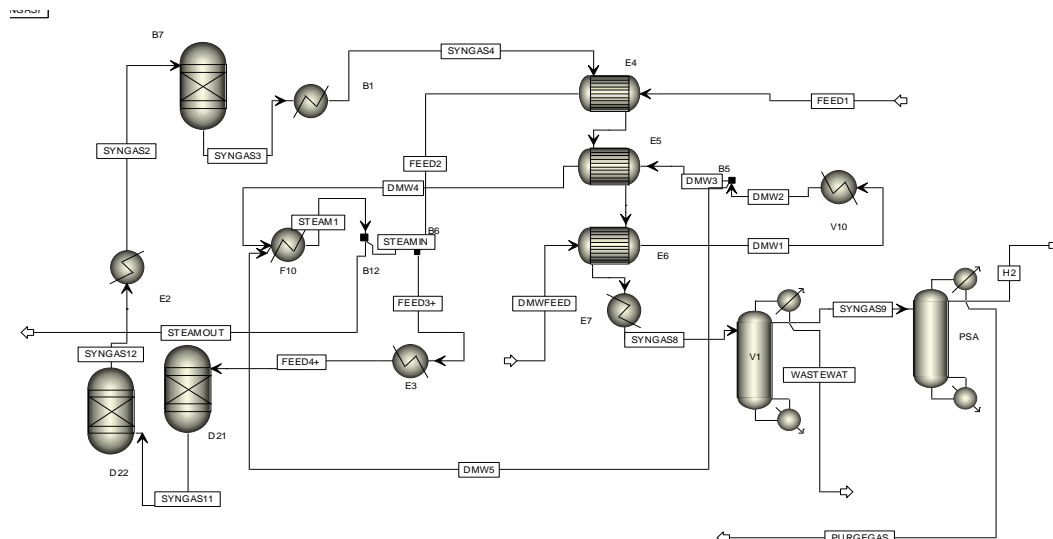


Figure 18. Flow sheet of the hydrogen production plant by the Aspen Plus User Interface

The composition of the natural gas was calculated based on the analysis results provided by the gas supplier Gasum Oy. The average values from January to November 2011 were taken into account. In order to reach 100 mol-% for the simulation, the average values were rounded. The average composition of the natural gas used in the simulation is shown in Table XII.

Table XII. Average composition of the natural gas stream

Composition	Average composition values
Methane	97.84±0.1
Ethane	0.9±0.01
Propane	0.3±0.02
Butane	0.1±0.01
Pentane	0.01±0.01
Hexane	0±0.00
Nitrogen	0.8±0.02
CO ₂	0.05±0.05
O ₂	0±0.000

The simulation is performed using process data gathered on 18.3.2008 and 17.10.2008. During the periods, the production capacity was 67-68 % from the maximum 7700 Nm³/h (5160 Nm³/h). Data for the natural gas and process gas compositions were gathered from the recorded laboratory analyses. The reaction yields and conversions were used as the main simulation parameters. The temperature and pressure parameters were taken from the data gathered in October

2011. The process gas compositions used in the simulation are shown in Table XIII and the temperature and pressure parameters in Table XIV.

Table XIII. Composition of the process gas used at the plant with 67 % of the maximum production capacity

	Process gas composition after reforming %	Process gas composition before PSA, %
H ₂	73.36	75.92
N ₂	0.45	0.20
CO	12.16	2.75
CH ₄	4.86	4.36
CO ₂	9.18	16.77
total	100	100

Table XIV. Temperature and pressure parameters used in the simulation of the plant with 67 % of the maximum capacity

Equipment position	Equipment name	Temperature, °C	Pressure, bar
E004	Feed preheater	390	21.9
D001	Desulphurizer	380	16.5
E003/1-2	Steam boiler	540	16.5
F010	Steam drum	210	21.0
D002	Reformer	890	15.5
E002	Process gas boiler	335	15.5
D003	Hot temperature shift converter	330	15.5
V001	Process condensate separator	35	15.0
PSA	Pressure swing adsorption	20	15.0
V010	Deaerator	107	21.0

8.2 Simulation results

The results of the simulation are shown in Appendix I in Table I. The results show that under the simulation conditions of 1540 kg/h of natural gas, it is possible to produce 606 kg/h of hydrogen as well as 7500 kg/h of steam. In an ideal process, more natural gas, process steam and carbon monoxide are converted into valuable products. The real process is not as efficient as the ideal process, but the effect of the parameter changes can be seen from the simulation results. The results also show that the process produces a large amount of steam (1972 kg/h) that can be used for other purposes. This is shown as the stream WASTEWAT from daerator V010.

8.3 Parameter selection based on simulation

Process optimization is continued on a plant scale by choosing the most important process parameters to optimize. The parameters are chosen according to the results of the simulation of the process the already known theory of the hydrogen plant parameters and discussions with the operating staff and management of Solvay Chemicals Finland Oy. The parameters that can be considered for use in the optimization and plant experiments are

- Temperature of the feed pre-heater E004
- Steam/carbon ratio before reformer D002
- Reformer inlet temperature from pre-heaters E003-1 and E003-2
- Reforming temperature in D002
- Shift conversion temperature in D003
- PSA operating factor
- Oxygen residue in the purge gas going to the reformer furnaces

The feed preheater heats the natural gas feed to 390 °C before hydro-desulphurization. The feed is heated in the heat exchanger with the cooling process gas coming from the shift conversion. The temperature parameter of the pre-heater is dependent on the temperature of the process gas and hence it cannot be used for optimization as an independent parameter, only as a shift-conversion-dependent parameter.

The steam/carbon ratio controls the amount of steam mixed with natural gas before the reformer. The existing value of the steam/carbon ratio is 3.0, which means that the amount of steam is three times the amount of natural gas. All the steam will not react in the reactions. This is also shown in the simulation. Decreasing the steam/carbon ratio reduces the amount of steam and water that need to be separated from the process stream in the V001. However, too low a steam/carbon ratio leads to the formation of coal in the reformer. Hence, the value of the steam/carbon ratio needs to be kept near 3.0 to suppress coke formation during the reaction.

The reformer inlet temperature is controlled by process gas pre-heaters E003-1 and E003-2. With regard to the steam/carbon ratio, a controlled amount of steam is mixed with the natural gas feed and preheated before entering the reformer at a temperature of 540 °C. The reforming temperature is kept constant at a value of 796 °C. By reducing this temperature, less energy and heat are needed in the reforming. This in turn increases the amount of natural gas used as a fuel and decreases the conversion of the methane and the yield of hydrogen. The decrease in the conversion is based on endothermic reaction 2 of the reforming, as studied in Section 4.1.2. Under the lower temperature, the reaction equilibrium shifts to the side of the raw materials.

For the shift conversion temperature there is a theory that the catalyst in the shift converter has a temperature memory, as stated by Hinton [30]. According to the theory, the catalyst becomes used to its operational temperature and will not work properly at lower temperatures. The outlet temperature of the shift conversion affects the preheating of the feed as the feed pre-heater is also used to cool the process gas. The temperature after the cooling in pre-heater E004 affects the temperature of demineralized water in heat exchangers E005 and E006.

The operating factor in the PSA affects the composition of the purge gas going to the reforming furnaces and thus the heating value of the purge gas. A lower heating value for the purge gas means that more natural gas has to be used as a fuel to reach the process temperature in the reformer and, vice versa, a higher heating value will decrease the amount of natural gas feed needed.

The oxygen residue is the amount of combustion air oxygen left unburned. Its amount in the flue gas depends on the amount of combustion air in the reformer furnaces. Sufficient combustion air prevents incomplete burning of the purge gas and natural gas fuel in the furnaces.

8.4 Evaluation of the importance of the parameters

The process parameters have various effects on the hydrogen production process. The effect can be small or significant depending on the size of the change in the value of a parameter. Based on the literature reviewed in Chapter 4 and the experiences of the process plant, the effects of the process parameters can be predicted. The process parameters and their predicted effect on the natural gas consumption and the hydrogen and steam production are shown in Table XV.

Table XV. Process parameters in hydrogen production and their predicted effect on natural gas consumption, hydrogen production and/or steam production

Process parameter	Effect of the change on natural gas consumption, hydrogen production and/or steam production	Importance of the parameter (5=most important, 1=least important)
Pre-heat temperature	No significant effect on natural gas consumption or hydrogen/steam production	2
Steam/carbon ratio	Increases the reaction conversions in the reformer and in the shift converter and increases the consumption of process steam when the S/C is increased	5
Reformer inlet temperature	Higher temperature in inlet means less heating in the reforming furnaces is needed, saving fuel	3
Reforming temperature	Lower reacting temperature decreases fuel consumption	4
Shift conversion temperature	Higher temperature increases the yield of hydrogen produced enabling lower temperatures in reformer and decreasing fuel consumption	4
PSA operating factor	Effects on purity of the product and the heating value of purge gas and thus the amount of fuel needed	2
Oxygen residue from reforming	Effects on the purity of the burning in reformer furnaces, the more complete the burning, the more heat energy is produced and the less carbon monoxide is generated, decreasing the consumption of fuel	1

The three parameters with the biggest effects on the process are the reforming temperature, shift conversion temperature and steam/carbon ratio. These parameters are chosen for the experimental study of the plant experiments at the

Solvay Chemicals Finland Oy process plant. The ranges of the values of the tested process parameters are shown in Table XVI.

Table XVI. Values of the process parameters chosen for the optimization of hydrogen production

Parameter	Plant's current operating value	Range of the change	Size of the change	Unit
Outlet temperature of the reformer	798	788-798	5	°C
Temperature of the shift reactor	330	325-345	10	°C
S/C ratio	3	2.8-3.2	0.1	-

In optimum process conditions, a certain hydrogen production capacity can be reached with the lowest possible amount of natural gas feed. Besides the amount of natural gas feed, the purity of the product and the amount of steam generated are important process parameters and have to be taken into account. In order to find the optimum process conditions, the balance between the natural gas feed, product purity and amount of steam generated is tested.

The field experiments were performed at the Solvay Chemicals Finland Oy hydrogen plant in Voikkaa in spring 2012. The tests were performed by changing one process parameter at a time. The parameters were changed manually with a distributed control system (DCS) by the process operator.

Every test is performed by changing only one parameter and keeping the other parameters unchanged. During the test run, the hydrogen production rate is kept as constant as possible. The parameter is changed at 9:00 o'clock in the morning and the process conditions are kept constant for 24 hours. The gas samples are taken to specially designed steel cylinders from the gas lines after the reformer and before the PSA. Compositions of the process gas after the reformer and before the PSA are analysed in the laboratory after each test period. A gas analysis is performed with gas chromatograph Agilent 6890N. First, the device is calibrated with two calibration samples. If the calibration results match, the test samples can be analysed. Every sample is analysed twice and the results are compared. If the

results do not match, the analysis is repeated. The results are recorded and any differences from the normal results are reported to the operating staff. The purity of the product has to be kept at a sufficiently high level because a decrease in the gas purity will affect further processes in the plant and the lifetime of the catalyst. The specification for the purity of the product hydrogen in the process industry according to *Linde AG* [13] is

- H_2 content ≥ 99.9 vol-%
- N_2 ~500 vppm
- $\text{O}_2 < 1$ vppm
- $\text{CO} < 1$ vppm
- $\text{CH}_4 < 10$ vppm
- $\text{CO}_2 < 1$ vppm
- $\text{H}_2\text{O} < 10$ vppm
- $\text{H}_2\text{S} < 0.02$ vppm
- pressure of 16 bar and temperature of 40 °C

9 FIELD EXPERIMENTS AT SOLVAY CHEMICALS FINLAND OY

9.1 Execution of the test runs

Field experiments were performed at the Solvay Chemicals Finland Oy hydrogen plant in Voikkaa on 31.1.-10.2.2012. In every test, one parameter was changed at a time and kept unchanged for 24 hours. These parameters were reformer outlet temperature, shift conversion temperature and steam/carbon ratio. The first reformer outlet temperature was decreased from 798 °C to 793 °C and to 788 °C. The reformer outlet temperature was then returned back to its initial value of 798 °C. Then the shift conversion temperature was decreased, first to 325 °C and then increased to 345 °C and then returned to its initial value of 335 °C. In the third test, the steam/carbon ratio was decreased from 3.0, first to 2.9 and then to 2.8. After that, the steam/carbon ratio was returned to 3.0 and then increased, first to 3.1 and then to 3.2. The initial conditions in the hydrogen plant and the gas

analysis results for the initial conditions are shown in Appendix II in Tables I and II. The test conditions are shown in Appendix II in Table III.

9.2 Results

The results of the field experiments were all calculated to match the production rate of 70 % in order to have comparable information from all the field experiments. After this, average values for natural gas consumption, hydrogen production and process steam consumption were calculated and rounded to the nearest integer value. These average values for natural gas consumption, hydrogen production and steam production with different process parameter values are shown in Table XVII. The effects of the process parameters on natural gas consumption, hydrogen production, process steam consumption and steam generation are shown in Figures 20, 22 and 24. The natural gas consumption, divided into natural gas used as fuel and as feed, is shown in Appendix III in Tables I, II and III and Figures 1, 3 and 5. The natural gas consumption is divided into feed and fuel in order to have information on how much natural gas is used in the process reactions.

The relationship between the natural gas consumed and the hydrogen produced is calculated from the test results in order to measure the efficiency determinants for different test runs. Efficiency determinants are used to illustrate the economic efficiency of the process. They describe how efficiently natural gas is used in hydrogen production and steam generation. The smaller the efficiency determinant, the better the operating point of the process. The efficiency determinants are calculated by equations 19 and 20 and shown in Figures 20, 22 and 24

$$\eta_1 = \frac{m(CH_4 \text{ consumed})}{m(H_2 \text{ produced})} \quad (19)$$

$$\eta_2 = \frac{m(CH_4 \text{ consumed}) - m(CH_4 \text{ used for steam production})}{m(H_2 \text{ produced})} \quad (20)$$

Efficiency determinant 1 shows the ratio of total natural gas consumption to hydrogen production. It shows that the smaller efficiency determinant 1, the less natural gas is consumed in the process to produce a certain amount of hydrogen. Efficiency determinant 2 shows the ratio of natural gas consumption as a feed to hydrogen production. It shows that the smaller efficiency determinant 2, the less natural gas is consumed in hydrogen production reactions as a feed to produce a certain amount of hydrogen.

Due to the purity requirements of the produced hydrogen, the purity has to be monitored and kept at sufficient levels. The purity of the hydrogen produced in each test run is shown in Figures 21, 23 and 25.

Table XVII. Process parameters, natural gas and process steam consumption and amounts of produced hydrogen and steam in the test runs

Process parameter	Process parameter value	Natural gas consumption, kg/h	Process steam consumption, kg/h	Hydrogen production, kg/h	Steam generation, kg/h
Reformer outlet temperature, °C	788	1872	4633	5356	5583
	793	1907	4616	5412	6053
	798	1943	4600	5476	6482
Shift conversion temperature, °C	325	1949	4608	5470	6615
	335	1943	4600	5476	6482
	345	1933	4383	5417	6468
Steam/carbon Ratio, -	2.8	1891	4316	5370	6322
	2.9	1900	4442	5395	6245
	3.0	1943	4600	5476	6482
	3.1	1964	4727	5528	6605
	3.2	1992	4698	5588	6703

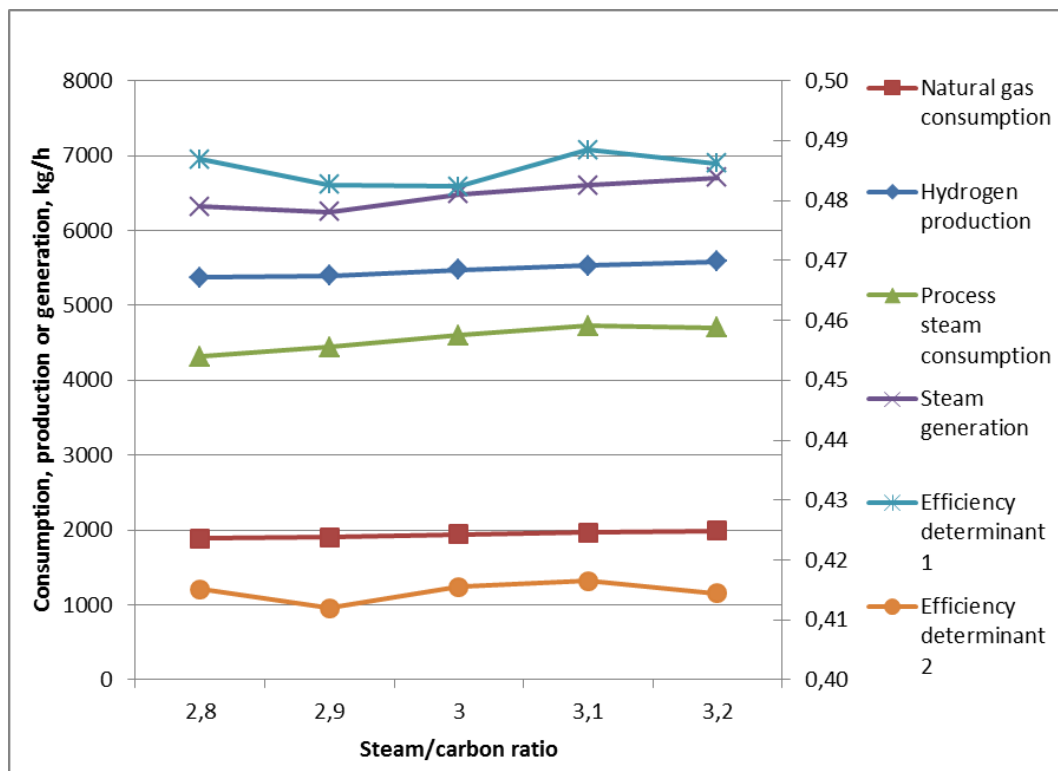


Figure 20. Natural gas consumption, hydrogen production, steam generated, process steam consumed and efficiency determinants for different steam/carbon ratios

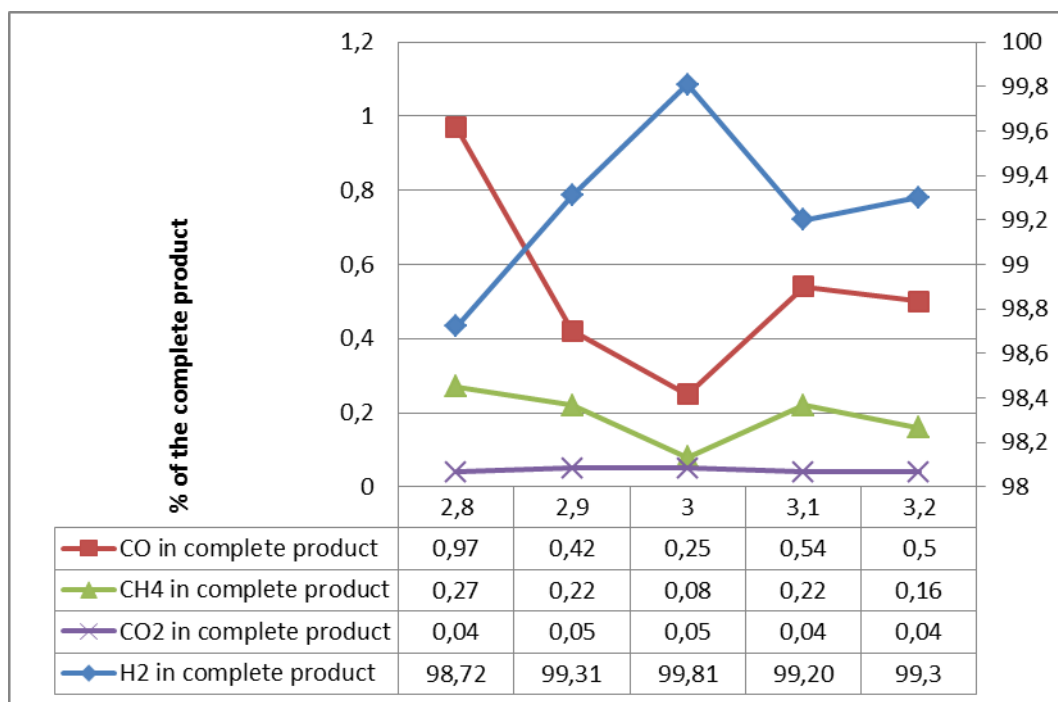


Figure 21. Effect of the steam/carbon ratio on the H₂ yield and main product impurities

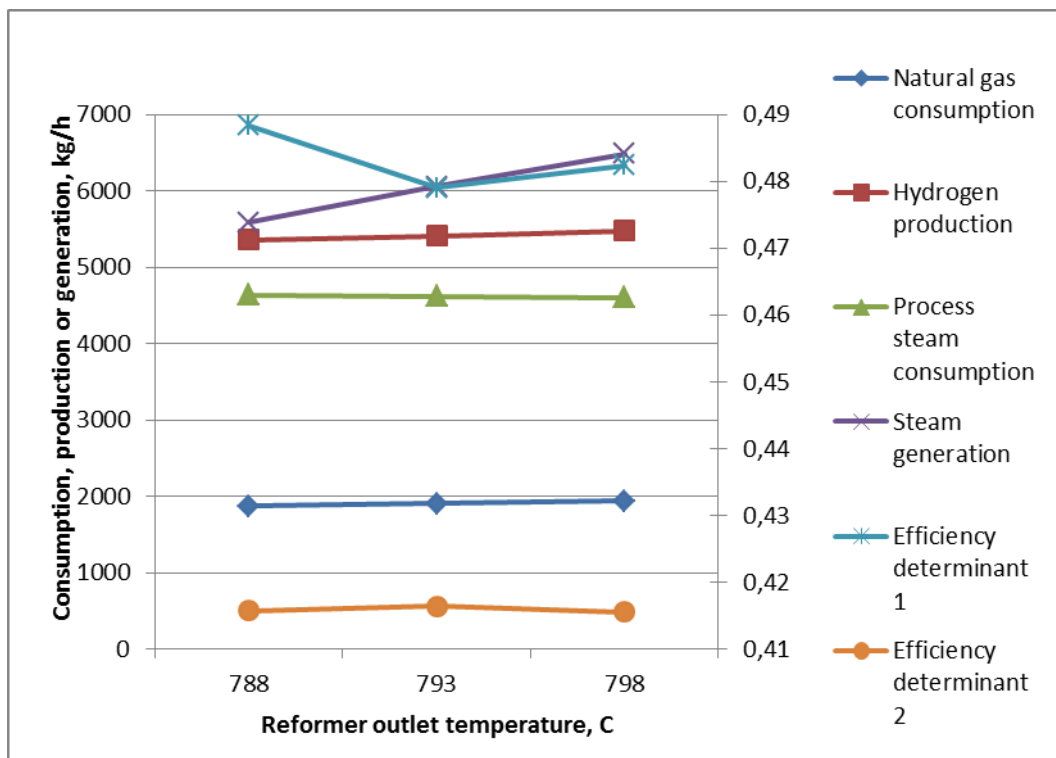


Figure 22. Natural gas consumption, hydrogen production, steam generated, process steam consumed and efficiency determinants for different reformer outlet temperatures

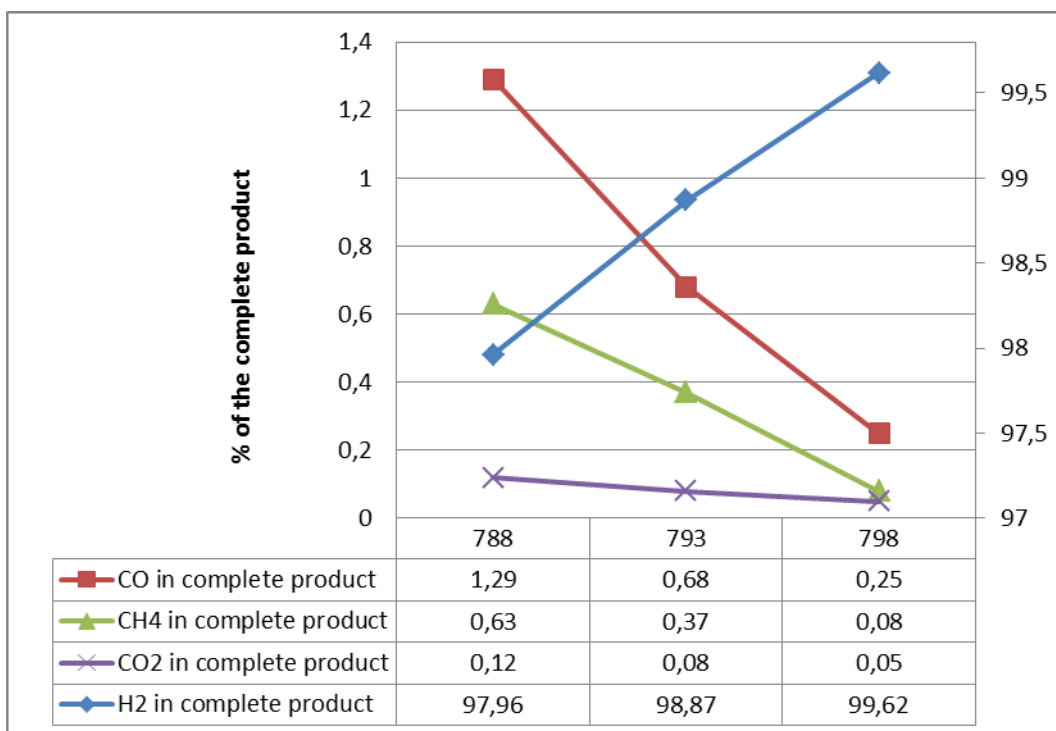


Figure 23. Effect of the reformer outlet temperature on the H₂ yield and the main product impurities

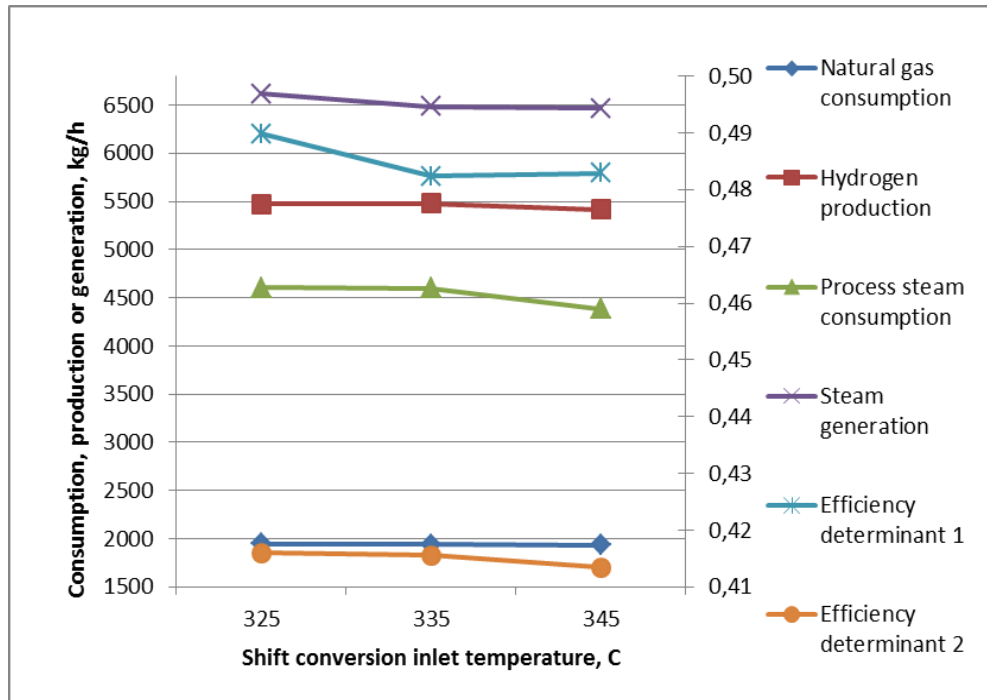


Figure 24. Natural gas consumption, hydrogen production, steam generated and process steam consumed for different shift conversion temperatures

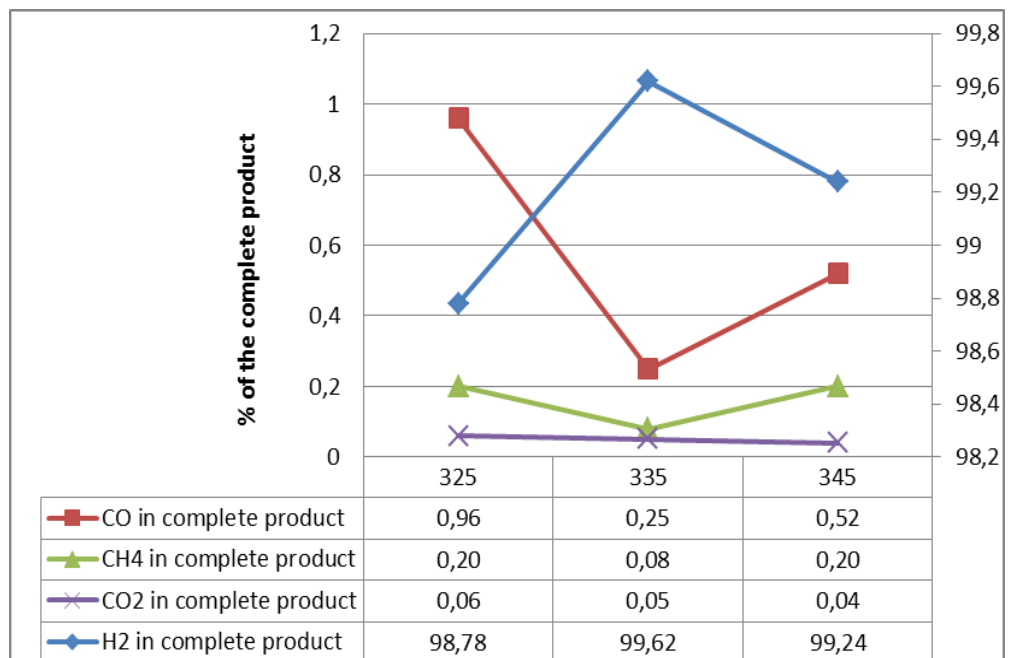


Figure 25. Effect of the shift conversion inlet temperature on the H₂ yield and the main product impurities

9.3 Result analysis

The most important process variables to be studied in different operating conditions were natural gas consumption, process steam consumption, amount of steam generated, amount of hydrogen produced and purity of the hydrogen. The effects of the operating conditions on these parameters are shown in Figures 20, 22 and 24

As shown in Figure 20, the natural gas consumption increases with the steam/carbon ratio. The steam/carbon ratio seems to have the greatest impact of all the process parameters. This can be seen from the test results:

Decreasing the steam/carbon ratio from 3.0 to 2.9 and 2.8:

- Decreases the process steam consumption as can be seen from Figure 20
 - Decreases the overload of steam as can be seen from Appendix III, Figure 2
- Decreases the CH₄ conversion as can be seen from Figure 21
- Decreases the total natural gas consumption
 - The amount of natural gas used as feed decreases when the steam/carbon ratio is decreased from 3.0 to 2.9 and increases slightly when it is further decreased to 2.8 as can be seen from Appendix III, Figure 1.
 - The amount of natural gas used as fuel decreases as can be seen from Appendix III, Figure 1.

Decreases the amount of hydrogen produced rate as can be seen from Figure 20

- Decreases the purity of the product as can be seen from Figure 21
- Decreases the efficiency determinants at 2.9
 - With a steam/carbon ratio of 2.9, efficiency determinant 2 has the lowest value of all the results as can be seen from Figure 20. This means that with this steam/carbon ratio, the natural gas is consumed most efficiently to produce hydrogen.

Increasing the steam/carbon ratio from 3.0 to 3.1 and 3.2:

- Decreases the CH₄ conversion as can be seen from Figure 21
- Increases the overload of steam with a steam/carbon ratio of 3.1 as can be seen from Appendix III, Figure 2
- Keeps the overload constant with a steam/carbon ratio of 3.2 compared with the initial value of 3.0 as can be seen from Appendix III, Figure 2
- Increases efficiency determinants 1 and 2 slightly at steam/carbon ratios of 3.1 and 3.2 as can be seen from Figure 21

As can be seen from Figure 22, natural gas consumption is dependent on the reformer outlet temperature. This also matches the earlier findings shown in Section 8.3. A decrease in the temperature from 798 °C to 788 °C reduces the total natural gas consumption. The reason is the endothermic nature of the reforming reactions and the fact that at higher temperatures more feed is burned in order to achieve a higher temperature.

Based on the field experiments, the decrease in the reformer outlet temperature

- Decreases the total natural gas consumption
 - Increases the amount of natural gas used as feed as can be seen from Appendix III, Figure 3
 - Decreases the amount of natural gas used as fuel as can be seen from Appendix III, Figure 3
- Decreases the amount of hydrogen produced as can be seen from Figure 22
- Increases process steam consumption
 - Increases the overload of process steam as can be seen from Appendix III, Figure 4
- Decreases CH₄ conversion as can be seen from Figure 23
- Decreases product purities as can be seen from Figure 23
- At a reformer outlet temperature of 793 °C, the efficient determinant 1 has the lowest of all the results
- Keeps the efficiency determinant 2 almost constant as can be seen from Figure 22

The shift conversion inlet temperature was the third tested parameter. As shown in Table XVII, the natural gas consumption decreases when the shift conversion inlet temperature increases. The other effects when the shift conversion inlet temperature is decreased from 335 C to 325 are

- Increases the total natural gas consumption
 - Increases the natural gas used as a feed and a fuel as can be seen from Appendix III, Figure 5
- Keeps the process steam consumption almost constant as can be seen from Figure 24
 - Increases the process steam overload as can be seen from Appendix III, Figure 6
- Decreases CH₄ conversion as can be seen from Figure 25
- Decreases product purity below 335 °C as can be seen from Figure 25
- Increases efficiency determinant 1 as can be seen from Figure 24
- Keeps efficiency determinant 2 almost constant as can be seen from Figure 24

Increasing the shift conversion inlet temperature from 335 C to 345 C

- Decreases the total natural gas consumption as can be seen from Table XVII
 - Decreases the amounts of natural gas used as feed and as fuel as can be seen from Appendix III, Figure 5
- Decreases the hydrogen production as can be seen from Figure 24
- Decreases the process steam consumption as can be seen from Figure 24
 - Decreases the process steam overload as can be seen from Appendix III, Figure 6
- Decreases the CH₄ conversion as can be seen from Figure 25
- Decreases the product purity as can be seen from Figure 25
- Increases efficiency determinant 1
- Decreases efficiency determinant 2

The results show that all the process parameters studied have an effect on natural gas consumption, hydrogen production, process steam consumption, total steam generation and product purity. The results also show that steam/carbon ratios higher than 3.0 should only be considered if the target is to increase the capacity of hydrogen production despite the other effects on product purity. The optimal operating point is found by decreasing the steam/carbon ratio from 3.0 to 2.9, but below the value of 2.9 the purity of the produced hydrogen begins to decrease. Efficiency determinant 2 reaches its lowest value of 0.412 at a steam/carbon ratio of 2.9. This means that efficiency determinant 1 remains almost constant compared with the initial conditions. This means that the value of 2.9 for the steam/carbon ratio is the optimal operating point for the process.

The results also show that a decrease in the reformer inlet temperature reduces the natural gas needed for reforming furnaces. However, it decreases the amount of hydrogen produced in the process. The amount of process steam needed is lowest at a temperature of 793 °C. This decreases the consumption of natural gas used as fuel and the consumption of the process steam while keeping the purity of the product at a sufficient level. The total amount of steam generated also decreases at lower temperatures. Efficiency determinant 1 has its optimal value of 0.4790 at a reformer temperature of 793 °C. Efficiency determinant 2 remains almost constant compared with the initial conditions.

The results show that an increase in the shift conversion temperature decreases the natural gas and process steam consumption while the purity of the product remains at a sufficient level. Efficiency determinants 1 and 2 also reach their optimal values when the shift conversion temperature is increased. However, the overload of the process steam is small at a temperature of 345 °C. At this temperature, the theoretical and real amounts of steam used are about the same, which means that the overload of the process steam is 0 kg/h. This does not meet the demands of the error margin required by the amount of steam in order to maintain the safety and activity of the process. The shift in conversion temperature can therefore be increased from 335 °C but kept under 345 °C. The shift conversion temperature should be studied further with different steam/carbon

ratios and reformer inlet temperatures in order to find the optimal temperature inside the range 335-345 °C.

9.4 Further development of the process

Based on the literature study and the field experiment results, it can be seen that the process type and the raw material selected, i.e. the natural gas-based steam reforming process for hydrogen production, is the optimal one for Solvay Chemicals Finland Oy. Changing the process type or raw material would lead to investment costs for new equipment. This would not decrease the operational costs of the plant sufficiently within an appropriate time frame because of the high price of the equipment.

Based on the test results, the next stage in hydrogen plant optimization is to adjust the chosen process parameters closer to the optimal values and to study their effect on the process in the long run. Due to the need for a pure product and long lifetime of the equipment, regular monitoring is required, especially of the product quality, metallurgical state of the reformer tubes and process conditions in the reformer. Based on the test run results, the most optimal process parameters are

- steam/carbon ratio 2.9
- $T_{\text{Reformer outlet}} 793 \text{ °C}$
- $335 \text{ °C} < T_{\text{shift conversion inlet}} < 345 \text{ °C}$

It is recommended that final test runs are performed in the future in order to test the effect of a decrease in the steam/carbon ratio and reformer outlet temperature and an increase in the shift conversion inlet temperature. The tests should be performed by first decreasing the reformer temperature and steam/carbon ratio and then increasing the shift conversion temperature in addition to the former changes.

10 CONCLUSIONS

Hydrogen is an efficient raw material for hydrogen peroxide production and many other industries. It can be produced from natural gas via the steam reforming process. During this process, low pressure steam is also generated. It is partly used in the process itself; the excess can be used for other heating purposes. In the literature part of this thesis, different raw materials and production technologies for hydrogen production were studied as well as different product gas purification methods. The production technologies were compared with natural gas-based steam reforming, and purification methods were linked to the technologies introduced.

When comparing different raw materials for hydrogen production by steam reforming at Solvay Chemicals Finland Oy, natural gas seemed to be the most efficient one. It has the greatest hydrogen production efficiency compared with other raw materials available. The need for extra equipment if the other raw materials are used also helps to keep natural gas the optimal raw material. If other raw material is used, the extra equipment needed increases the investment cost. However, if the raw material is changed because of low availability or high price of the material, it should be changed to heavy fuel oil because of its better availability in the future. Biomass gasification applications should also be seen as a potential alternative if the technology development continues. The next ten years are critical to this development; after this, biomass gasification may be considered a potential alternative for steam reforming of natural gas or heavy fuel oil.

In the experimental part of this thesis, the hydrogen plant at Solvay Chemicals Finland Oy was introduced. The current process conditions and equipment were presented and this information was used to simulate the plant. Simulation was used to approximate the effect of different process parameters on natural gas consumption, hydrogen production, process steam consumption and hydrogen product purity. The process parameters that were found to have the highest effects on process variables were the steam/carbon ratio, reformer outlet temperature and shift conversion inlet temperature. These parameters were further studied in the field experiments. The efficiency determinants η_1 and η_2 were calculated from the

values of these variables in order to find the optimal operating point of the process. At this point, hydrogen production from natural gas has the lowest efficiency determinant value, which means that a certain amount of hydrogen is produced from as small amount of methane as possible.

The results of the field experiments also show that the steam/carbon ratio can be decreased from the current value of 3.0 to a value of 2.9. Generally, the steam/carbon ratio was the most effective parameter in hydrogen production. Steam generation was affected most by the steam/carbon ratio and reformer outlet temperature, and process steam consumption by the steam/carbon ratio and shift conversion temperature.

The results also show that the reformer outlet temperature could be decreased to 793 °C. At this temperature the efficiency of the hydrogen production has the best value η_1 at this temperature, which means that the more optimal operating point of the process could be reached at lower temperatures than the current 798 °C. However, the reformer outlet temperature should not be decreased below 793 °C, in order to keep the hydrogen product purity at a sufficient level. Natural gas consumption was also the most dependent on it. This is based on the lower consumption of natural gas as a fuel in reformer furnaces.

From the results, it can also be seen that in order to improve the efficiency of the process, the shift conversion temperature should also be increased. The shift conversion temperature should be between 335 °C and 345 °C. To specify the optimal temperature, more studies on the steam/carbon ratio of 2.9 and reformer outlet temperature of 793°C are needed.

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