

# CHALMERS



## Optimizing the steam reformers at AkzoNobel

*Master of Science Thesis within the  
Innovative and Sustainable Chemical Engineering Programme*

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Göteborg, Sweden, 2013



Master of Science thesis

# Optimizing the Steam reforms at AkzoNobel

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*ABSTRACT*

This thesis aims at optimizing the energy efficiency at two of AkzoNobel Pulp and Performance Chemicals' steam reformers. The steam reformers produce hydrogen and steam from a hydrocarbon feedstock. Since hydrogen, and not steam, is the primary product for AkzoNobel the optimized process must maintain the same level of hydrogen production but with less hydrocarbon feedstock consumption.

The thesis is divided into three sections; the first examines how the plants has been operated historically, the second reports the results of experiments performed at the plants to test possible strategies to improve energy efficiency and the third investigates the possibility to preheat the air to the burners with the flue gases.

The most important operating parameters in a steam reformer are the steam-to-carbon ratio and the temperature and pressure in the reformer. Therefore experiments have been performed with different temperature and steam-to-carbon ratio. It is possible to decrease the hydrocarbon feedstock consumption with up to 3% by changing the operating parameters and still maintain the same hydrogen production. However under these conditions the steam production decreases.

The air to the burners could be preheated with a heat exchanger with heat recovered from the flue gases. This could save 2 % of the hydrocarbon feedstock with a payback time of 1.3 years for the heat exchanger.

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## 1. INTRODUCTION

AkzoNobel Pulp and Performance Chemicals produces hydrogen as a feedstock for the production of hydrogen peroxide. The most economical way of producing hydrogen is by steam reforming (Rostrup-Nielsen, 2002). At three of AkzoNobel's plants the hydrogen is produced by steam reforming. This thesis will focus on optimizing two of the steam reformers, one in Bohus and one in Alby, both located in Sweden. The Bohus and Alby steam reformers have capacities of producing 6000 Nm<sup>3</sup> hydrogen/h and 3000 Nm<sup>3</sup> hydrogen/h respectively. The hydrocarbon feedstock is different for the plants; Bohus uses natural gas (NG) and Alby uses liquefied petroleum gas (LPG). The reformers also produce steam which is used for heating other processes at the site and for district heating. During most of the year all of the produced steam in Bohus is not utilized since heating demands are too low. Consequently, the Bohus reformer would ideally lower its steam production but keep the same level of hydrogen production with lower natural gas consumption.

The hydrocarbon feedstock cost for hydrogen production through steam reforming is normally about two thirds of the total production cost (Rostrup-Nielsen, 2002). With today's increasing energy prices it is therefore of importance to have a very efficient process and there are large economic incentives for optimization.

### 1.1 Aim

The aim of this study is to investigate the possibilities for AkzoNobel Pulp and Performance Chemicals of optimizing the two steam reformers in Alby and Bohus to decrease the feedstock consumptions and keep the same level of hydrogen production.

### 1.2 Structure of the thesis work

This report will focus on three different ways to optimize the steam reformers;

- 1) Differences between the steam reformers; Investigate how the plants have been operated historically and try to find the best operation settings. This part also includes comparing the two plants to find the most optimal operating conditions.
- 2) Experimental tests; Find the most important parameters of the plants and perform experiments in the plants by varying them.
- 3) Preheating of air to the burners; Investigate the possibility of preheating the air to the burners at the Bohus plant with the flue gases.

### 1.3 Delimitations

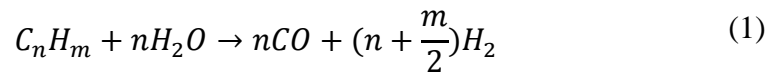
This report will focus mainly on the Bohus steam reformer since it is at the Bohus plant the study will be performed. The Alby steam reformer will also be considered but not to the same extent. The report will not focus on any other uses of excess steam, as for example electricity generation, since this already has been investigated by AkzoNobel Pulp and Performance Chemicals.

### 1.4 Short description of the reforming process

This section contains a short description of the reforming process (**Fel! Hittar inte referenskälla.**). The feedstock (NG in Bohus and LPG in Alby) is pretreated before entering the steam reformer which means that the LPG is evaporated and sulfur is removed from both the natural gas and the LPG. The feedstock is mixed with steam and

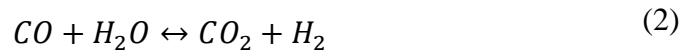


is fed to the reformer where it is heated in tubes and the following reaction mainly occurs:



The reaction is endothermic and therefore needs heat to be sustained. This is provided by a burner with NG (in Bohus) or LPG (in Alby) as fuel.

The heat from the reformer production stream and from the flue gases from the burners that leave the reformer are used to produce steam. The production stream is then fed to a high temperature shift converter (HTS) and carbon monoxide and steam is converted to hydrogen and carbon dioxide:



After the HTS the product stream is fed to a pressure swing absorption unit (PSA) where it is purified to 99.99% hydrogen.

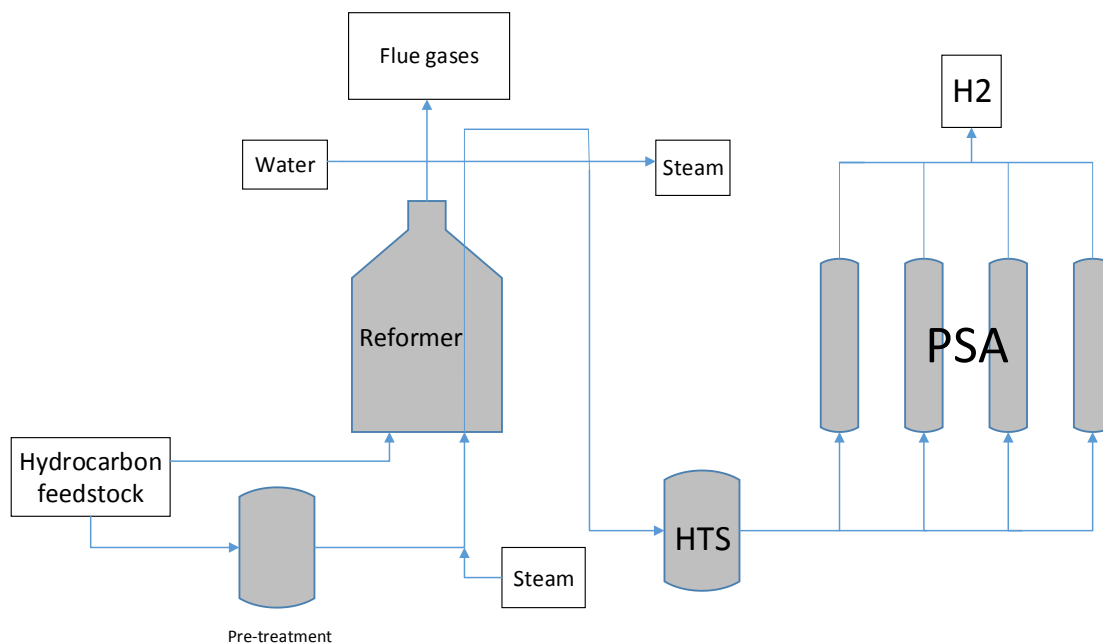


Figure 1: An overview of the steam reforming process at Alby and Bohus.

## 1.4 Background

AkzoNobel Pulp and Performance Chemicals (former Eka Chemicals) is a leading global force in pulp bleaching technologies, paper chemicals, colloidal silica and expandable microspheres. One of the products is hydrogen peroxide.

### 1.4.1 Hydrogen peroxide

The hydrogen produced in Bohus and Alby is used at the same site as a feedstock for hydrogen peroxide production. Hydrogen peroxide has strong oxidizing properties, low toxicity and is easy to handle and is therefore widely used as a bleaching chemical. In ambient conditions it spontaneously decomposes to water and oxygen and the growing environmental awareness the last decades have led to an increased use since other

bleaching agents tend to be more environmentally unfriendly. The most important application of hydrogen peroxide is for bleaching of chemical and mechanical pulp. It is also used for bleaching recycled paper, textile bleaching, as a raw material in the chemical industry, in the metal industry, for disinfection, laundry bleaching, hair bleaching and chemicals analysis (Eka).

AkzoNobel Pulp and Performance Chemicals manufactures hydrogen peroxide in five plants located in Sweden, Norway, the USA and Venezuela. There are two plants in Sweden, one in Alby and one in Bohus. The hydrogen peroxide is produced by oxidized hydrogen (Eka):



Hydrogen is produced in different ways in AkzoNobel's different plants. In the USA and Alby the hydrogen is a byproduct from other processes. In Alby this does not fully cover the need of hydrogen which is also produced from a steam reformer. The Bohus and Venezuela plants produce hydrogen only from steam reforming. In Norway the hydrogen is produced by water electrolysis.

#### 1.4.2 Important years for the steam reformers

To get a better overview of the steam reformers the most important changes are presented below:

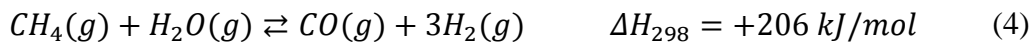
- 1990 The first Bohus steam reformer with LPG as feedstock was built in Bohus.
- 1997 The steam reformer in Bohus was replaced with a reformer with larger capacity.
- 1997 The Alby steam reformer was built.
- 2004 Bohus started to use natural gas as feedstock instead of LPG.
- 2005 A second reformer furnace was built in Bohus in order to double the production capacity.

## 2. THE STEAM REFORMING PROCESS

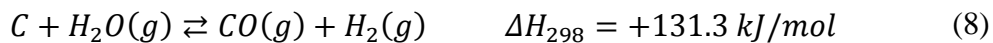
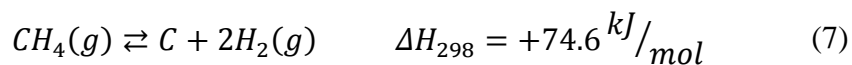
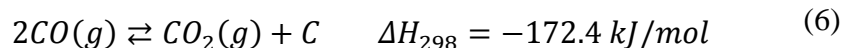
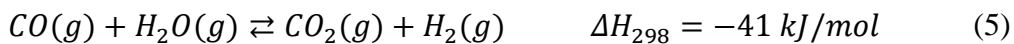
This section contains the theoretical information needed to understand the steam reforming process. It will explain the design of the reformer, the reactions, and the most common hazards for the equipment.

### 2.1 The reforming reactions

The basic reforming reaction for a hydrocarbon that occurs in the reformer tubes can be written as in equation 1. For natural gas methane reacts with steam in the presence of a supported nickel catalyst and by a reaction called steam methane reforming reaction (SMR) (Liu, Song, & Subramani, 2010) and is written below.



However, in reality the SMR is not just one reaction but involves contributions from several different catalytic reactions called the water-gas shift reaction (WGS), reverse water-gas shift reaction (RWGS), the Boudouard reaction and methane decomposition reaction which are presented below (Liu, Song, & Subramani, 2010).



The reforming reaction (4) normally reaches equilibrium over an active catalyst at high temperatures. Since the reaction is endothermic it is favored by high temperatures. The water shift reaction (5) is however exothermic and favored by lower temperatures. The reforming reaction is favored by low pressures because volume expansion occurs while the water shift reaction is independent of pressure (Liu J. A., 2006).

In general steam reforming of hydrocarbons is catalyzed by group VIII metals, with Nickel as the most cost effective catalyst. Steam reforming of methane is strongly endothermic and reversible. The equilibrium of reaction (4) depends on temperature, pressure and steam to carbon ratio. In order to have a high conversion of methane it is necessary to operate at high temperatures, low pressures and relatively high steam to carbon ratios (Joensen & Rostrup-Nielsen, March 2002). At too high temperatures however, (over 920 °C) the hydrocarbons may react in a parallel reaction by thermal cracking causing the formation of coke. The steam to carbon ratio is typically 3:1 in steam reformers (Liu J. A., 2006). To avoid carbon formation at the catalyst (coking), the steam-to-carbon ratio must be over 1:1 or greater (Cooper, 1998). The coking could deactivate the catalyst and it is therefore important to maintain a ratio that is sufficiently high. The relationship between conversion of methane, temperature, pressure and steam-to-carbon ratio is presented in Figure 2.

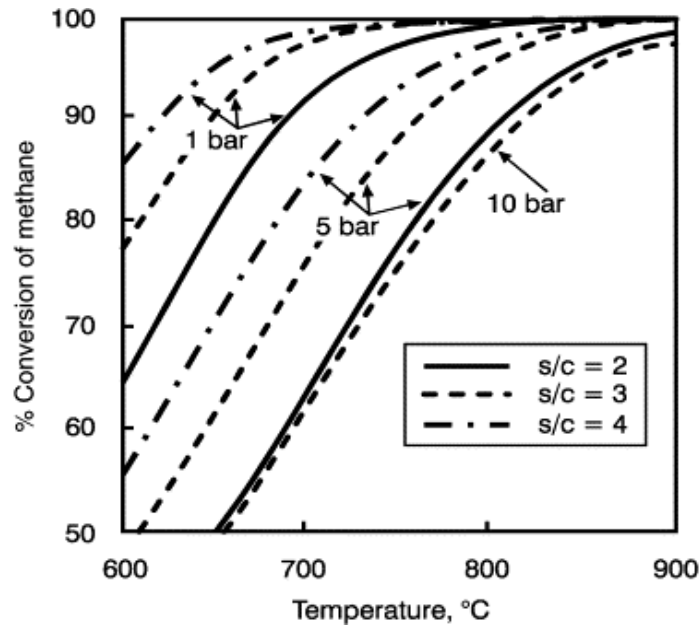


Figure 2: The equilibrium conversion of methane in steam reforming against temperature, pressure and steam-to-carbon (S/C) ratio

In tubular steam reformers, heat is supplied to the reaction by putting the tubes in a fired furnace. In a typical steam reformer only 50% of the supplied heat is transferred to the reforming process (Joensen & Rostrup-Nielsen, March 2002). The overall product gas from the reformer tubes is a mixture between hydrogen, carbon monoxide, carbon dioxide and unconverted methane and steam. The composition depends on the temperature of the reactor, the operating pressure, the composition of the feed gas and the proportion of steam fed to the reactor (Liu J. A., 2006). The amount of carbon monoxide from the reformer is quite high since equation 4 is favored by high temperatures. Due to this, a downstream process is necessary to reduce the carbon monoxide concentration in the product stream and increase the yield of hydrogen. In Bohus and Alby the process gas from the reformer tubes is fed to a high temperature shift converter to reduce the carbon monoxide concentration.

## 2.2 The design of the steam reformer plants at Bohus and Alby

The steam reformers at Alby and Bohus are built with the same design but with minor differences. The largest difference is that the feedstock to the Bohus reformer is natural gas and the feedstock to the Alby reformer is liquefied petroleum gas (LPG). The capacity of the Bohus reformer (6000 Nm<sup>3</sup>/h) is also twice as large as the Alby reformer (3000 Nm<sup>3</sup>/h). To manage this higher capacity the Bohus plant has two reformer furnaces instead of one. The following section contains a longer description of the components in the steam reformers. Figure 3 shows the Bohus reformer and Figure 4 shows the Alby reformers.

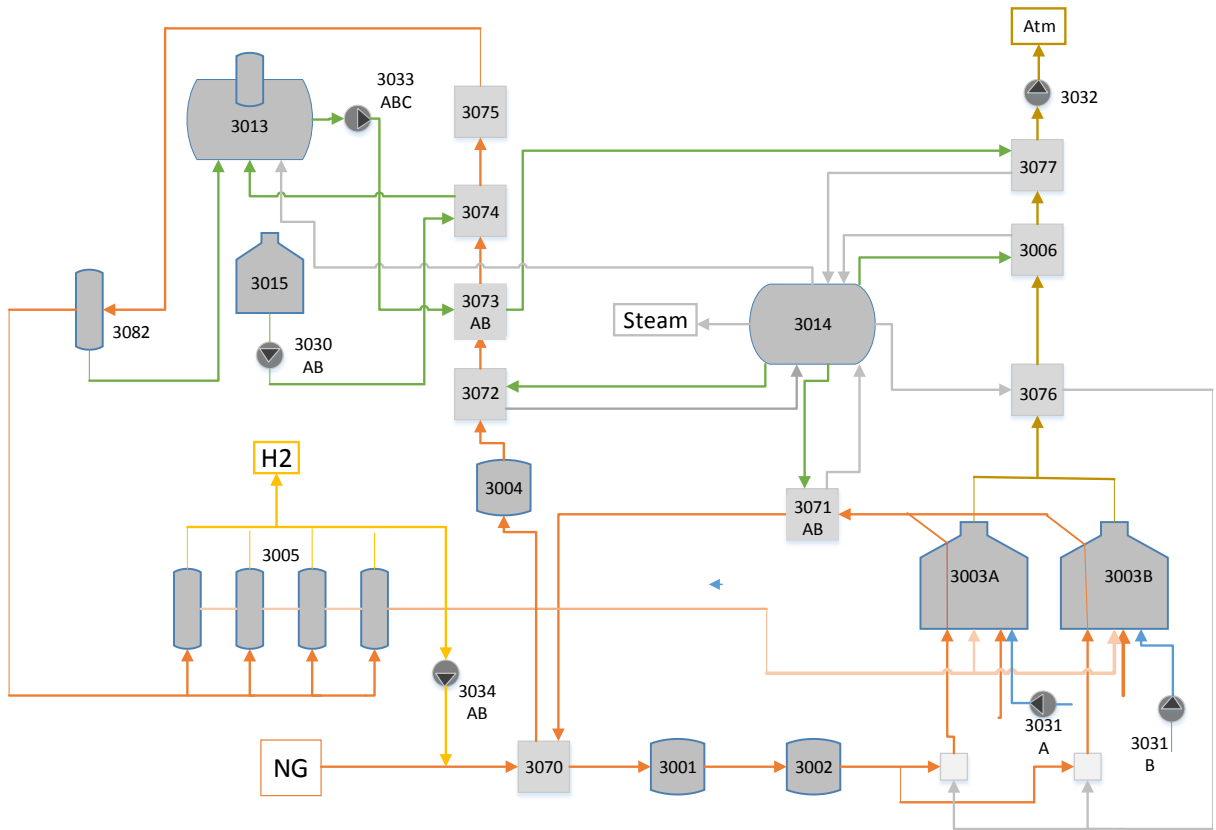


Figure 3: A detailed overview of the Bohus steam reformer.

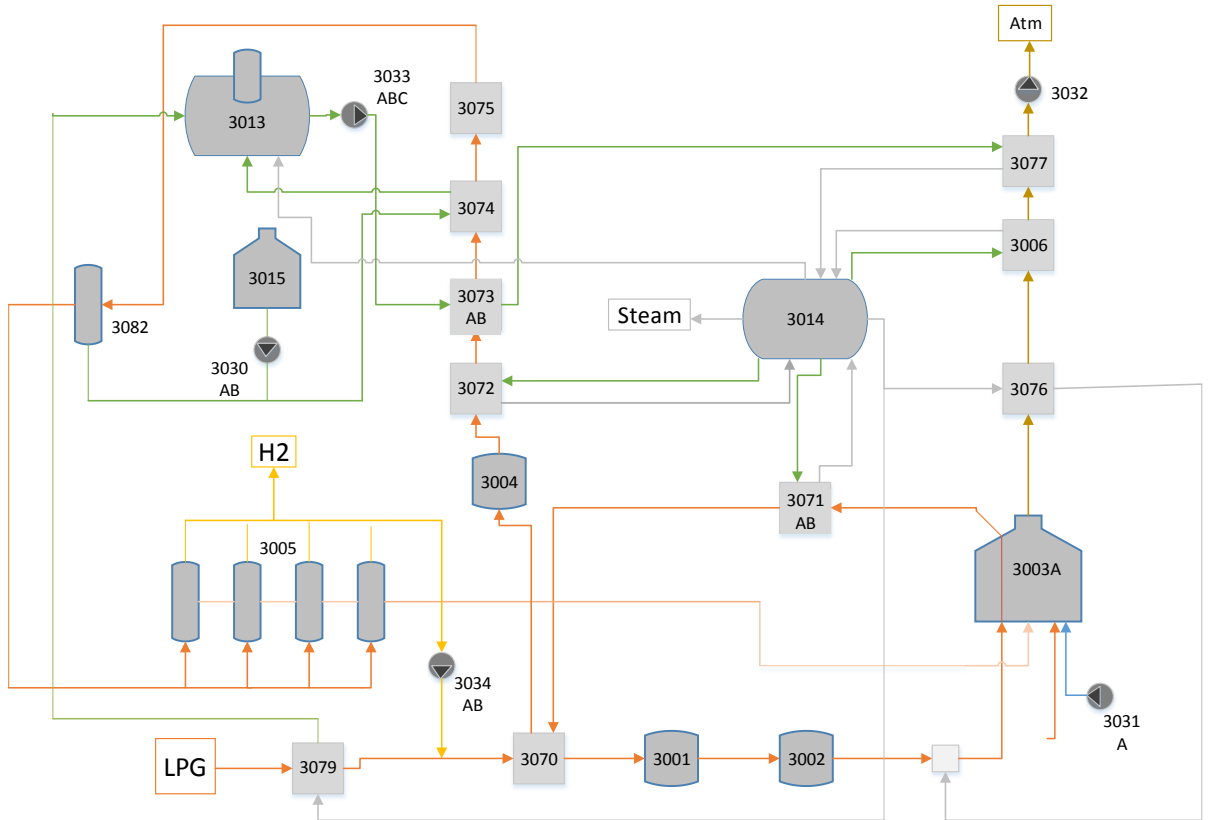


Figure 4: A detailed overview of the Alby steam reformer.

### **LPG Vaporizer (3079)**

The LPG is vaporized by using steam. Since the natural gas is already vaporized, this heat exchanger is only available at the Alby plant. In Alby most of the LPG is fed to the heat exchanger 3070 but some is fed to the burners as fuel.

### **Hydrogen recycle**

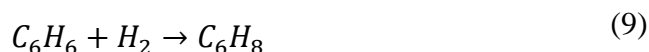
Pure hydrogen from the finished product is added to the LPG/NG stream to be used downstream in the process.

### **Feed gas heat exchanger (3070)**

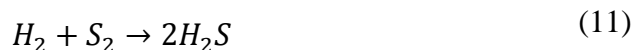
The natural gas /LPG to the reformer tubes are heated to approximately 400 °C with the product gas from the reformer tubes.

### **Co/Mo Unit (3001)**

The NG/LPG contains olefinic hydrocarbons which should be converted to a saturated hydrocarbon before entering the reformer tubes. The LPG/NG stream is fed to a vessel containing a cobalt-molybdate catalyst. In the presence of the catalyst the free hydrogen reacts with the olefinic hydrocarbons which are converted to a saturated hydrocarbon. Two examples:



The sulfur compounds in the natural gas and LPG, reacts in the presence of the Co/Mo-catalyst, with the free hydrogen to hydrogen sulfide. For example:



The reactions are all exothermic which results in increased temperature of the LPG/NG stream after the Co/Mo unit.

### **Zinc Oxide Desulfurizers (3002)**

After the Co/Mo unit the stream of LPG/NG is fed to a zinc oxide desulfurizer. The zinc oxide catalyst will absorb the hydrogen sulfide. The operating variables which affect the performance of the zinc oxide desulfurization catalyst are the flow rate of feed gas, type and total amount of sulfur in the feed gas, pressure and temperature (Hydro-Chem-Processing, 1991). The sulfur is removed since it is a severe poison for the reformer catalyst downstream in the process.

### **Mixture of steam and LPG/NG**

The LPG/NG is mixed with steam before it is fed to the reformer tubes. The ratio between the mixed steam and LPG/NG is called steam-to-carbon ratio.

### **The reformer (3003)**

The reformer is a vessel with tubes heated by burners. It is in these tubes the reforming reactions occur. The gases in the tubes are never mixed with the gases in the furnace from the burners. Therefore two streams are leaving the reformer, the production stream from the tubes and the flue gases from the burners.

The steam reforming reactions 4 occur in catalytic tubes heated by burners. The tubes are placed in a circle inside the reformer furnace. The tubes are fed with NG/LPG and overheated steam. The tubes can be seen in Figure 5. Reaction 4 almost goes to equilibrium and the process gas effluent will be a mixture of  $\text{CH}_4$ ,  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{H}_2$  and  $\text{H}_2\text{O}$ . The major variables in the operation of the reformer are as previously mentioned; the reformer outlet temperature, the reformer pressure and the steam-to-carbon ratio (Hydro-Chem-Processing, 1991).



**Figure 5: Picture taken inside the Bohus reformer furnace. The tubes are arranged in a circle inside the walls. The outlet for the flue gases is at the top of the reformer.**

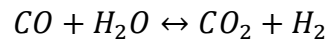
Since the steam reformer reaction 4 is endothermic the reaction needs heat to be sustained. The heat is provided by three burners in each reformer furnace. Most of the fuel requirement to the burners is supplied by the purge or vent gas from the PSA Hydrogen Purification unit. The rest of the fuel requirements are supplied from pure NG/LPG. Air is also fed to the burner to maintain the combustion. Besides maintaining the reformer reaction, the burners also heat the gases in the tubes and furnace. The burner should be operated to provide a long and slender flame and the flame should not impinge on the tubes. Ten percent excess air is normally required for satisfactory combustion of the fuel. If possible, however, it could be desirable to operate the furnace excess air percentage below those specified. (Hydro-Chem-Processing, 1991) It is in other words, desirable to operate the burner with as low air feed as possible since the air takes up heat (energy) which just produces more flue gases.

#### **Reformer effluent process boiler (3071)**

The process boiler utilizes the heat available in the effluent gases from the reformer tubes to increase steam production. The outlet temperature stream of the effluent gas can be controlled by this boiler.

### **3004 High temperature shift converter (HTS)**

In the high temperature shift converter most of the carbon monoxide in the effluent gas from the reformer is converted to carbon dioxide and water in the water gas shift reaction (WGS):



This reaction is facilitated by a chromium promoted iron oxide catalyst. The conversion is dependent on temperature, pressure, steam/carbon ration and flow rate. Temperature is an important parameter and can be used to optimize the performance of the high temperature shift converter. The higher the temperature, the faster the reaction rate, but the lower equilibrium CO content (Hydro-Chem-Processing, 1991). In order to achieve low CO without having significant excess steam it is desirable that the reaction is run at low temperatures. However, at low temperatures, reaction rates diminish and the process becomes kinetically controlled (Liu, Song, & Subramani, 2010). Hence, there is an optimal temperature for a given temperature activity. When the catalyst gets older this optimum temperature is often increased due to lower activity of the catalyst. The shift converter is designed to operate with an inlet temperature of 343 °C to 379 °C. The maximum allowable temperature is 426 °C on the outlet of the high shift temperature converter. Approximately 80% of the carbon monoxide is converted to carbon dioxide in the shift converter. The catalyst is sensitive to sulfur poisoning. (Hydro-Chem-Processing, 1991)

### **Process boiler exchanger (3072)**

The heat from the process gas from the HTS converter is used to produce steam in the process boiler exchanger.

### **Waste heat boiler feed water exchanger (3073)**

The heat from the process stream from the process boiler exchanger is used to preheat the water from the deaerator.

### **Deaerator feed water exchanger (3074)**

The heat from the process gas stream from the heat boiler feed water exchanger is used to heat the water to the deaerator.

### **Process gas cooler (3075)**

The process gas is further cooled so that the temperature is lowered and condensate dumped.

### **Condensate drums (3082)**

The condensate in the process stream is separated by the condensate drums and fed to the deaerator. The process stream is fed to the PSA unit.

### **Pressure swing absorption units (3005)**

The PSA system purifies the process stream from the high temperature shift converter to 99.99% pure hydrogen. The vent gas is fed to the burners in the reformer as fuel. From the purified hydrogen stream some hydrogen is taken and fed to the LPG/NG stream before the desulfurization unit.



**Steam pre-heat coil (3076)**

The heat in the reformer furnace stack gases is used to preheat the steam which should be mixed with the LPG/NG.

**Waste heat boiler (3006)**

The waste heat boiler recovers heat from the exhaust gases of combustion to produce steam.

**Boiler feed water economizer (3077)**

The economizer heats the feed water to the steam drum coming from the deaerator.

**Deaerator (3013)**

The deaerator removes carbon dioxide in the condensate water from the condensate drum.

**Steam drum (3014)**

A separate steam drum is used to provide adequate space for steam separation and aid natural circulation (Hydro-Chem-Processing, 1991).

**Water buffer tank (3015)**

The fresh water to the reformer is taken from the water buffer tank.

### 2.3 Four challenges for nickel steam-reforming catalysts

One of the largest producers of catalysts for steam reforming, Haldor Topsøe, claims that there are four challenges for nickel steam-reforming catalysts. They include activity, sulphur poisoning, carbon formation and sintering and the relationship between them are described in Figure 6 (Sehested, 2006).

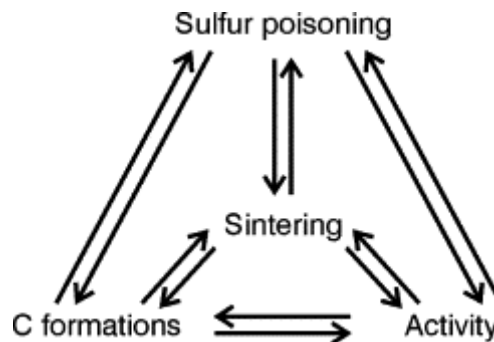
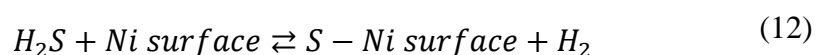


Figure 6: The relationship between carbon formation, activity, sintering and sulphur poisoning.

*Activity*-the catalyst must have sufficient activity to equilibrate the reaction mixture in the design catalyst volume. In a primary reformer the main reason for low activity is sulphur poisoning and sintering resulting in higher tube temperatures and even carbon formation.

*Sulphur poisoning*- Sulphur is a common and severe poison for nickel catalysts that blocks the active nickel sites. The sulphur-containing compounds in the feed react with hydrogen to hydrogen sulfide at reforming conditions. The sulphur atom in the hydrogen sulfide adsorbs strongly at the nickel active sites and blocks it as shown in equation 12.



*Carbon formation*-Carbon formation at the tubes can increase the pressure drop, crush the catalytic pellet, block the active nickel surface and decrease the heat transfer.

*Sintering*-Nickel particles in the catalyst may grow by fusion of smaller particles causing a reduction of the catalytic surface area.

## 2.4 Creep damage to the tubes

On account of the tough operating conditions in a steam reformer the tubes in the reformer furnace run close to their metallurgical limits and suffer so-called creep damage over time. Since local overheating occurs in the reformer, this damage does not occur with equal rate all over the tubes. The typical life time of reformer tubes is 100,000 hours (11.4 years if the reformer is operated constantly). Even under good conditions the tubes will undergo creep damage. There is however some things that can be avoided to prolong the life time of the tubes. Whenever reformer tubes are heated and cooled stresses are temporarily increased and this leads to an acceleration of creep damage. Therefore, every shut-down that can be avoided prolongs the lifetime of the tubes. Another way to prolong the tube lifetime is to control the catalyst charging in the tubes. The catalyst charging has a significant impact on the reformer's life time in two ways. Firstly, uneven catalyst loading of the tubes results in different pressure drops in different tubes and that, in turn, results in different gas compositions and a variation of wall temperature. The different wall temperatures of the tubes results in different life times. Secondly, packing within a tube must be uniform, otherwise there will be spots with no reaction, resulting in hot spots and decreased lifetime of the tubes. (Brightling, 2002)

## 2.5 The variation of natural gas

The raw material in the steam reformer at Bohus is natural gas. Natural gas is an odorless and colorless naturally occurring mixture of hydrocarbon and non-hydrocarbon gases found beneath the earth's surface, often together with petroleum or coal (Liu, Song, & Subramani, 2010). Natural gas consists mostly of methane but the composition of the gas can vary regionally. The natural gas is supplied to Bohus by a pipeline from Denmark (Swedegas, 2013). The composition of the natural gas is not constant and the following tables are monthly mean values for the natural gas used in Bohus provided by the supplier. It can be seen in these tables that both the energy content in the natural gas and the ratio between hydrogen and carbon can vary slightly. It is unknown how these variations affect the efficiency in the Bohus steam reformer.

**Table 1.** The composition of natural gas during 2012 in mol%.

	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	i-C <sub>4</sub> H <sub>10</sub>	n-C <sub>4</sub> H <sub>10</sub>	i-C <sub>5</sub> H <sub>12</sub>	n-C <sub>5</sub> H <sub>12</sub>	C <sub>6</sub> +	CO <sub>2</sub>	N <sub>2</sub>
<b>12-jan</b>	88,87	6,09	2,43	0,37	0,54	0,13	0,08	0,06	1,08	0,36
<b>12-feb</b>	88,94	6,07	2,47	0,38	0,55	0,13	0,09	0,06	1	0,32
<b>12-mar</b>	89,06	6,02	2,4	0,38	0,54	0,13	0,09	0,06	1	0,32
<b>12-apr</b>	88,57	6,24	2,57	0,38	0,56	0,13	0,09	0,06	1,1	0,32
<b>12-maj</b>	88,46	6,27	2,59	0,38	0,56	0,13	0,09	0,06	1,14	0,32
<b>12-jun</b>	88,25	6,36	2,65	0,39	0,57	0,12	0,08	0,06	1,18	0,32
<b>12-jul</b>	88,97	6,08	2,45	0,38	0,55	0,13	0,08	0,06	0,97	0,32
<b>12-aug</b>	89,27	6	2,34	0,37	0,52	0,13	0,08	0,05	0,92	0,31
<b>12-sep</b>	89,07	6,06	2,39	0,37	0,53	0,13	0,08	0,06	1	0,32
<b>12-okt</b>	88,86	6,14	2,48	0,38	0,55	0,13	0,08	0,05	1,02	0,31
<b>12-nov</b>	89,2	5,93	2,31	0,36	0,51	0,12	0,07	0,05	1	0,45
<b>12-dec</b>	89,25	5,91	2,19	0,33	0,47	0,11	0,07	0,05	1,1	0,53
<b>Mean value</b>	<b>88,9</b>	<b>6,1</b>	<b>2,44</b>	<b>0,37</b>	<b>0,54</b>	<b>0,13</b>	<b>0,08</b>	<b>0,06</b>	<b>1,04</b>	<b>0,35</b>

**Table 2** The heating value and density during 2012

	Higher heating value		Lower heating value		Density
	MJ/Nm <sup>3</sup>	kWh/Nm <sup>3</sup>	MJ/Nm <sup>3</sup>	kWh/Nm <sup>3</sup>	kg/Nm <sup>3</sup>
<b>12-jan</b>	43,72	12,15	39,55	10,99	0,83
<b>12-feb</b>	43,79	12,16	39,6	11	0,83
<b>12-mar</b>	43,74	12,15	39,56	10,99	0,83
<b>12-apr</b>	43,86	12,18	39,68	11,02	0,83
<b>11-may</b>	43,87	12,19	39,7	11,03	0,83
<b>12-jun</b>	43,94	12,21	39,75	11,04	0,83
<b>12-jul</b>	43,78	12,16	39,61	11	0,83
<b>12-aug</b>	43,66	12,13	39,5	10,97	0,82
<b>12-sep</b>	43,73	12,15	39,53	10,98	0,82
<b>12-okt</b>	43,8	12,17	39,61	11	0,83
<b>12-nov</b>	43,51	12,09	39,35	10,93	0,82
<b>12-dec</b>	43,29	12,02	39,14	10,87	0,82
<b>MV</b>	<b>43,72</b>	<b>12,17</b>	<b>39,55</b>	<b>11,01</b>	<b>0,83</b>

### 3 THE DIFFERENCES BETWEEN THE STEAM REFORMERS

The differences between the Bohus and Alby steam reformer were investigated. This was done by using and comparing data available at AkzoNobel from the plants.

#### 3.1 How to measure the consumption ratio

The consumption ratio between the consumed NG/LPG and the produced hydrogen is a measure of how efficiently the steam reformer operates. A lower consumption corresponds to higher efficiency. In the operating manuals the design ratios of steam reformers with natural gas and LPG can be found. The design consumption ratios have been compared with the actual consumption ratios of the reformers.

##### 3.1.1 Bohus

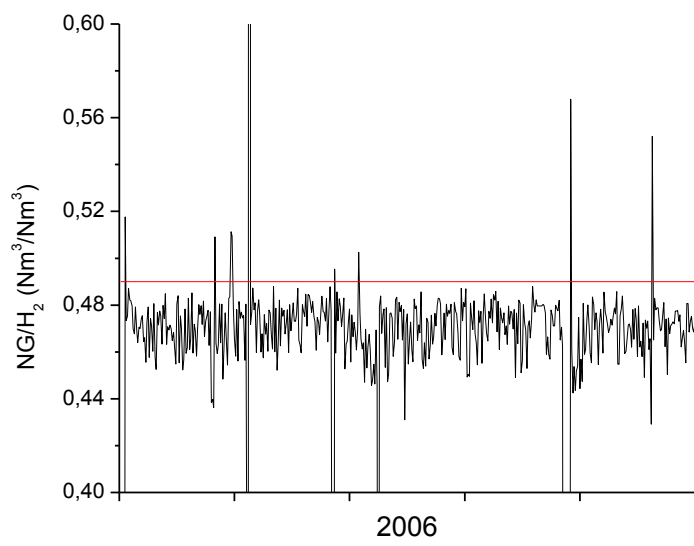
The consumption ratio of the Bohus steam reformer is calculated by dividing the natural gas consumption with the hydrogen production. The natural gas consumption is the natural gas to the tubes and the burners for both the A and B furnace. The produced hydrogen is the hydrogen leaving the reformer, the recycled hydrogen and the hydrogen to the PSA is not included here. This relationship is described in equation 13.

$$R_{NG/H_2}^{Bohus} = \frac{F_{NG,burner}^{Bohus,A} + F_{NG,burner}^{Bohus,B} + F_{NG,tubes}^{Bohus,A} + F_{NG,tubes}^{Bohus,B}}{F_{hydrogen\ prod}^{Bohus}} \quad (13)$$

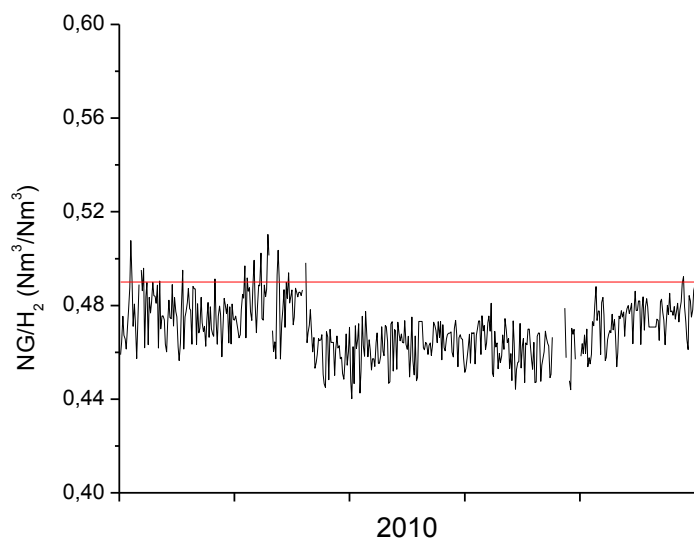
This can be compared with the design ratio given in the operating manual (Hydro-Chem, 1996) which is 0.49. The reformer also produces steam and the consumption ratio of the steam production can be measured as:

$$R_{NG/steam}^{Bohus} = \frac{F_{NG,burner}^{Bohus,A} + F_{NG,burner}^{Bohus,B} + F_{NG,tubes}^{Bohus,A} + F_{NG,tubes}^{Bohus,B}}{\dot{m}_{steam\ tot}^{Bohus}} \quad (14)$$

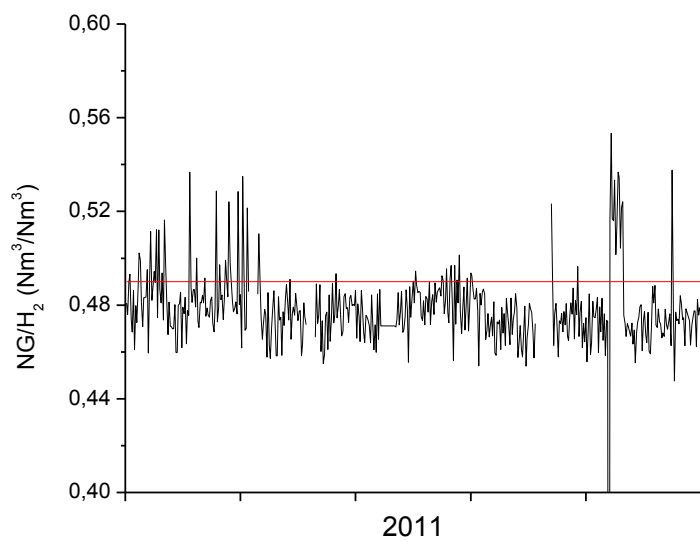
The steam is measured is the steam leaving the reformer to be used in other processes. The last three years (2010, 2011 and 2012) and 2006 are investigated and are shown in Figure 7Figure 10. 2006 is included since it is the first year with two furnaces and natural gas as feedstock. The consumption ratio from 1998 (Figure 11) is also included since the steam reformer was operated with liquefied petroleum gas during that time period and it is interesting to compare this with the consumption ratio in Alby.



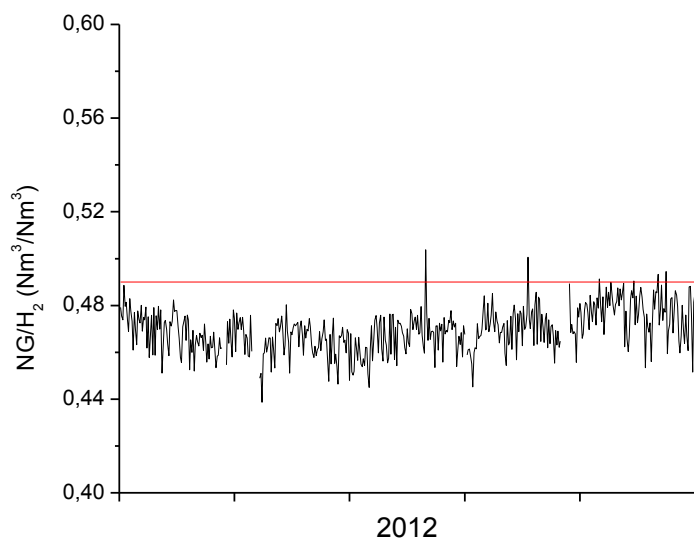
**Figure 7: The consumption ratio in Bohus 2006.**



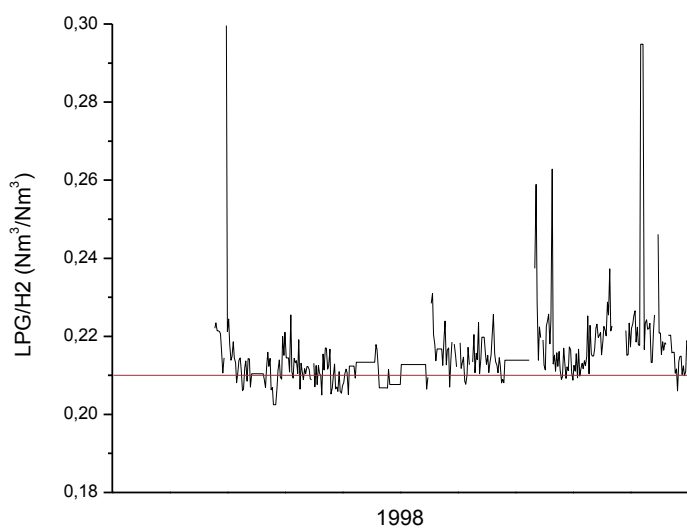
**Figure 8: The consumption ratio in Bohus 2010.**



**Figure 9: The consumption ratio in Bohus 2011.**



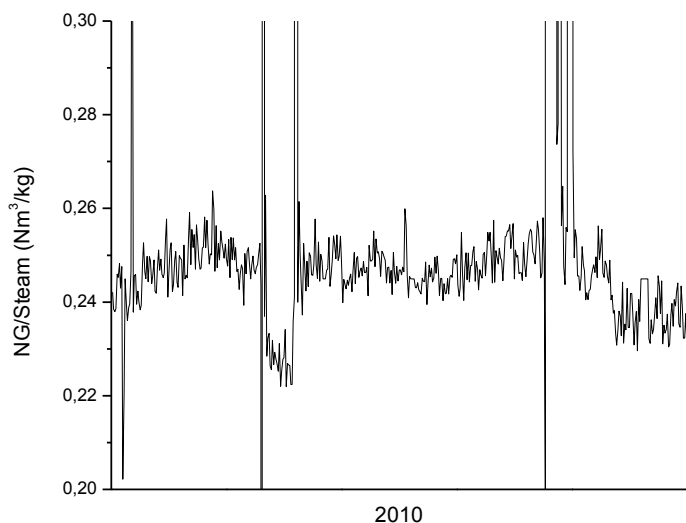
**Figure 10: The consumption ratio in Bohus 2012.**



**Figure 11: The consumption ratio in Bohus 1998.**

It can be seen in the figures that no significant change of the consumption ratio has occurred the last seven years. The consumption ratio is mostly lower than the design consumption ratio which indicates that the performance of the reformer is quite good. No connection can be seen between the consumption ratio and summer and winter, the performance of the reformer seems to be independent of the seasons.

The steam consumption ratio for 2010, 2011 and 2012 are shown below:



**Figure 12: The steam consumption ratio in Bohus 2010.**

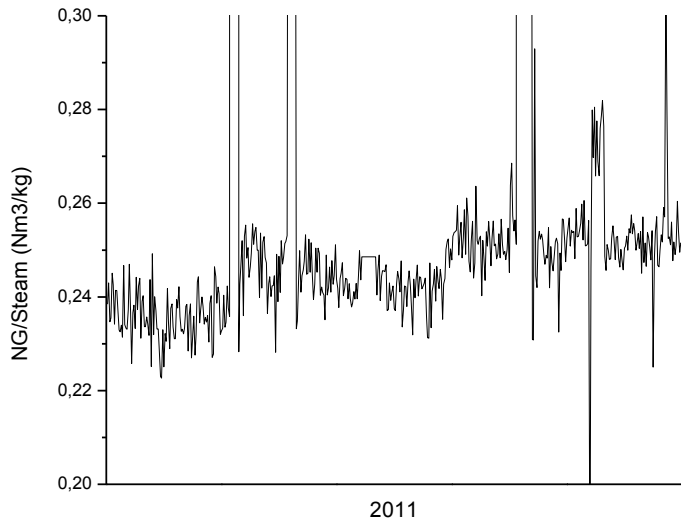


Figure 13: The steam consumption ratio in Bohus 2011.

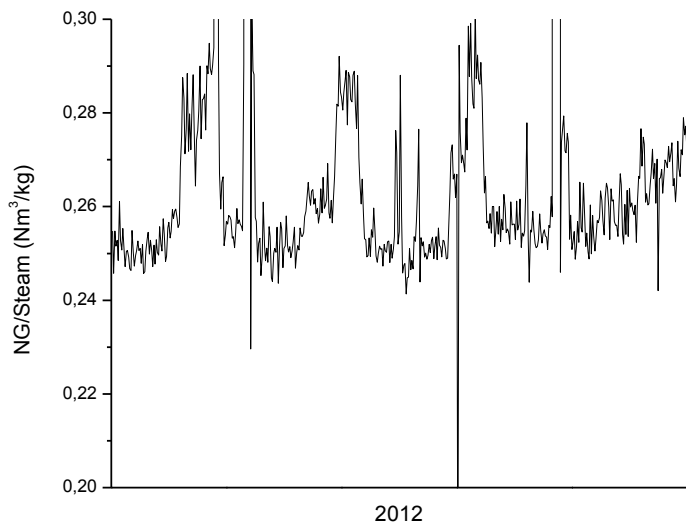


Figure 14: The steam consumption ratio in Bohus 2012.

In the graphs it can be seen that the steam consumption ratio varies substantially over time.

### 3.1.2 Alby

The consumption ratio of the Alby steam reformer is calculated by dividing the liquefied petroleum gas consumption with the hydrogen production:

$$R_{LPG/H_2}^{Alby} = \frac{F_{LPG,burner}^{Alby} + F_{LPG,tubes}^{Alby}}{F_{hydrogen\ prod}^{Alby}} \quad (15)$$



This can be compared with the value given in the design operating manual (Hydro-Chem, 1996) which is 0.21. The steam consumption ratio in Alby is calculated as:

$$R_{LPG/steam}^{Alby} = \frac{F_{LPG, burner}^{Alby} + F_{LPG, tubes}^{Alby}}{\dot{m}_{steam\ tot}^{Alby}} \quad (16)$$

The last three years (2010, 2011 and 2012) were investigated for both hydrogen and steam consumption ratio and the graphs are shown below:

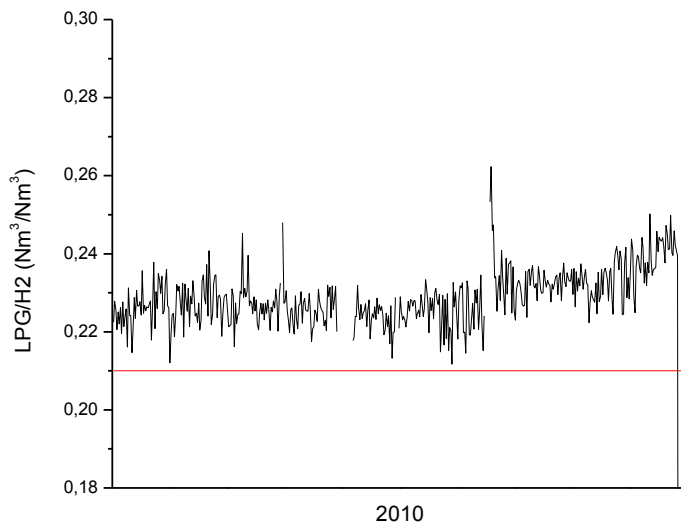


Figure 15: The consumption ratio in Alby 2010

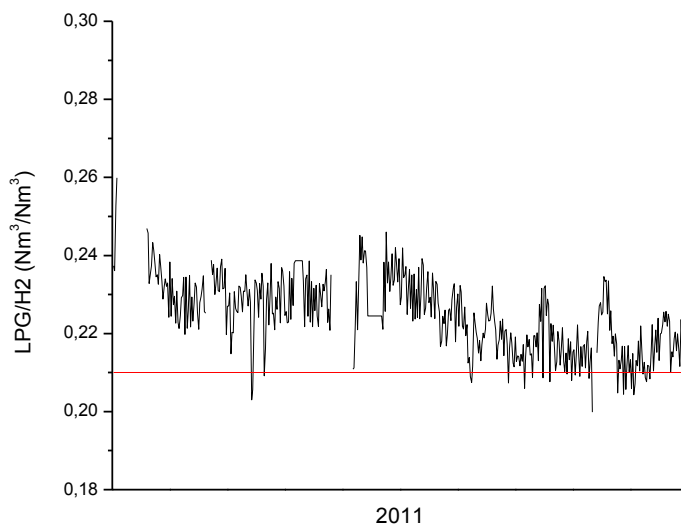
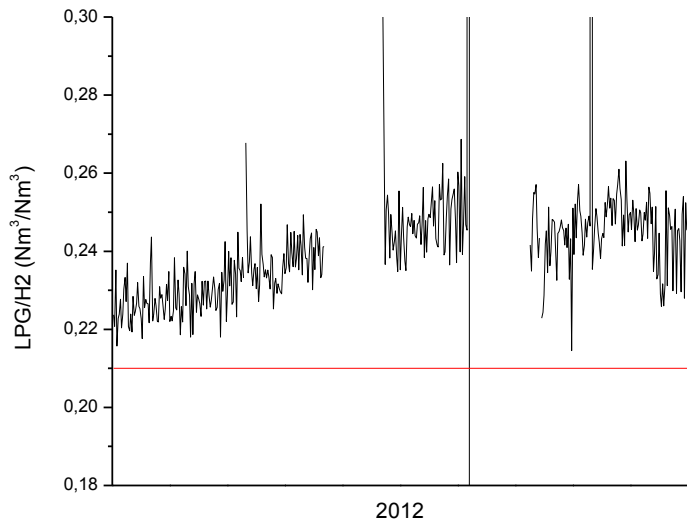
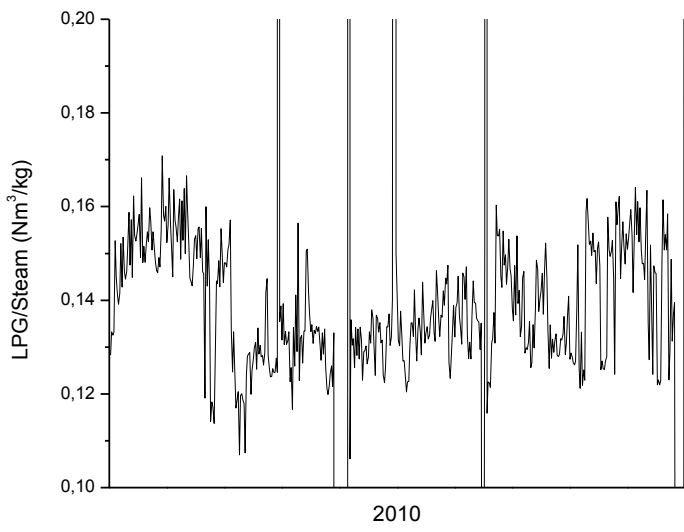


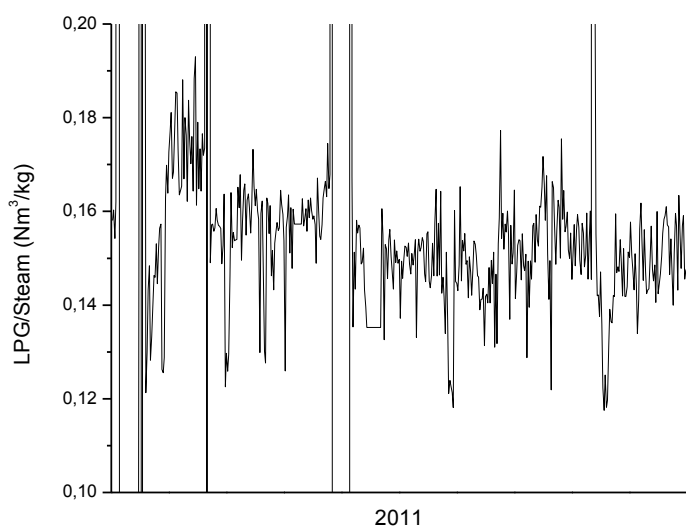
Figure 16: The consumption ratio in Alby 2011.



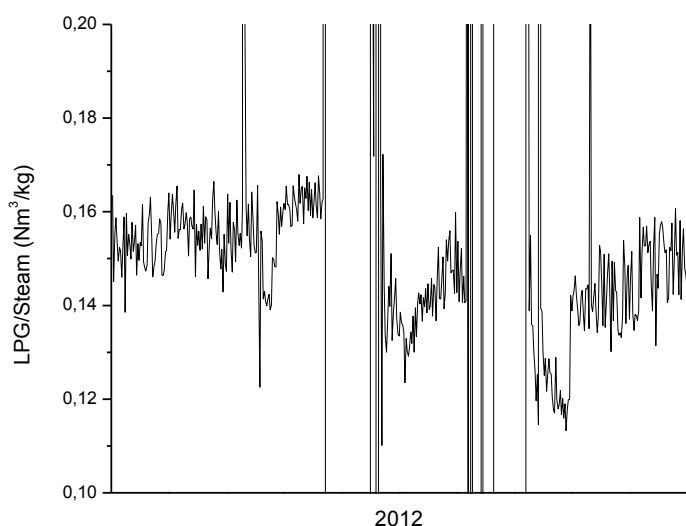
**Figure 17: The consumption ratio in Alby 2012.**



**Figure 18: The steam consumption ratio in Alby 2010.**



**Figure 19: The steam consumption ratio in Alby 2011.**



**Figure 20: The steam consumption ratio in Alby 2012.**

As in Bohus the consumption ratios for the Alby site varies significantly during different time periods. It can also be seen that the consumption ratio is higher than the design consumption ratio. It is also higher than the consumption ratio in Bohus 1998 (when Bohus used LPG as feedstock). Since the consumption ratio is higher than both the design ratio and the ratio in Bohus the performance of the Alby steam reformer has a potential to be better. As in Bohus no connection between the seasons of the year and the consumption ratio can be seen.

The following sections will examine different theories why the consumption ratio varies.

## 3.2 How the supplied energy is consumed

Since the reforming reaction 4 is endothermic heat must be supplied to the reformer furnaces by burners. The fuels for these burners are NG/LPG and also vent gas from the PSA hydrogen purification unit. The heat value of the NG and LPG is quite constant and known, but the heat value of the flue gases varies and the composition can only be estimated.

### 3.2.1 Bohus

To calculate how the energy is used in the steam reformers in Bohus the following assumptions are made:

- The natural gas has the same properties as methane.
- The only reaction occurring in the tubes at is  $CH_4 + H_2O \rightarrow CO + 3H_2$
- 100% conversion of natural gas in the reformer tubes.
- The vent gas from the PSA is assumed to consist of 50%  $H_2$  and 50%  $CO_2$  (Krans, 2011).

First, the total energy available is calculated. The energy available is the energy content in the fuel fed to the burners. The fuel consists of both natural gas and vent gas from the PSA-unit. In the control system the vent gas energy content is recalculated as the energy content of liquefied petroleum gas. This is done based on the ratio between NG and air fed to be burners,  $R_{air/fuel}^{Bohus}$ . The maximum energy to the furnaces can therefore be calculated as:

$$E_{max}^{Bohus} = \left( \frac{F_{air,burner}^{Bohus,A}}{R_{air/fuel}^{Bohus,A}} + \frac{F_{air,burner}^{Bohus,B}}{R_{air/fuel}^{Bohus,B}} \right) * \rho_{NG} * LHV_{NG} \quad (17)$$

Secondly, the energy demand for the endothermic reaction is estimated as:

$$E_{Reaction}^{Bohus} = \frac{F_{LPG,tubes}^{Bohus} * \Delta H_{SMR}^{Bohus}}{M_V} \quad (18)$$

Thirdly, some energy is used to heat the gases in the reformer. The gases in the reformer tubes, NG and steam, requires the energy for heating:

$$E_{NG,tubes}^{Bohus,A} = F_{NG,tubes}^{Bohus,A} * \rho_{NG} * Cp_{NG} * (T_{product\ gas}^{Bohus,A} - T_{NG,tubes}^{Bohus,A}) \quad (19)$$

$$E_{NG,tubes}^{Bohus,B} = F_{NG,tubes}^{Bohus,A} * \rho_{NG} * Cp_{NG} * (T_{product\ gas}^{Bohus,A} - T_{NG,tubes}^{Bohus,A}) \quad (20)$$

$$E_{steam}^{Bohus,A} = \dot{m}_{steam,tubes}^{Bohus,A} * Cp_{steam} * (T_{product\ gas}^{Bohus,A} - T_{steam,tubes}^{Bohus,A}) \quad (21)$$

$$E_{steam}^{Bohus,B} = \dot{m}_{steam,tubes}^{Bohus,B} * Cp_{steam} * (T_{product\ gas}^{Bohus,B} - T_{steam,tubes}^{Bohus,B}) \quad (22)$$

The gases in the furnace, NG, air and vent gas also require energy for heating:

$$E_{NG,burner}^{Bohus,A} = F_{NG,burner}^{Bohus,A} * \rho_{NG} * Cp_{NG} * (T_{flue\ gases}^{Bohus,A} - T_{NG,tubes}^{Bohus,A}) \quad (23)$$

$$E_{NG,burner}^{Bohus,B} = F_{NG,burner}^{Bohus,B} * \rho_{NG} * Cp_{NG} * (T_{flue\ gases}^{Bohus,B} - T_{NG,tubes}^{Bohus,B}) \quad (24)$$

$$E_{air}^{Bohus,A} = F_{air,burner}^{Bohus,A} * \rho_{air} * Cp_{air} * (T_{flue\ gases}^{Bohus,A} - T_{air,burner}^{Bohus,A}) \quad (25)$$

$$E_{air}^{Bohus,B} = F_{air,burner}^{Bohus,B} * \rho_{air} * Cp_{air} * (T_{flue\ gases}^{Bohus,B} - T_{air,burner}^{Bohus,B}) \quad (26)$$

$$E_{vent}^{Bohus,A} = F_{vent,A}^{Bohus} * (0.5 * \rho_{H2} * Cp_{H2} + 0.5 * \rho_{Co2} * Cp_{Co2}) * (T_{flue\ gases}^{Bohus,A} - T_{vent}^{Bohus}) \quad (27)$$

$$E_{vent}^{Bohus,B} = F_{vent,B}^{Bohus} * (0.5 * \rho_{H2} * Cp_{H2} + 0.5 * \rho_{Co2} * Cp_{Co2}) * (T_{flue\ gases}^{Bohus,A} - T_{vent}^{Bohus}) \quad (28)$$

The energy that is not used for sustaining the reaction is considered to be a loss. Losses could be due to incomplete combustion of the fuel or heat losses. The total loss is calculated in equation 29.

$$E_{loss} = E_{max}^{Bohus} - E_{reaction}^{Bohus} - E_{NG,tubes}^{Bohus,A} - E_{NG,tubes}^{Bohus,B} - E_{steam}^{Bohus,A} - E_{steam}^{Bohus,B} - E_{NG,burner}^{Bohus,A} - E_{NG,burner}^{Bohus,B} - E_{air}^{Bohus,A} - E_{air}^{Bohus,B} - E_{vent}^{Bohus} \quad (29)$$

Two examples of how the energy is distributed are shown below (Figure 21 and Figure 22). The first one is for maximum production and the second is for minimum production.

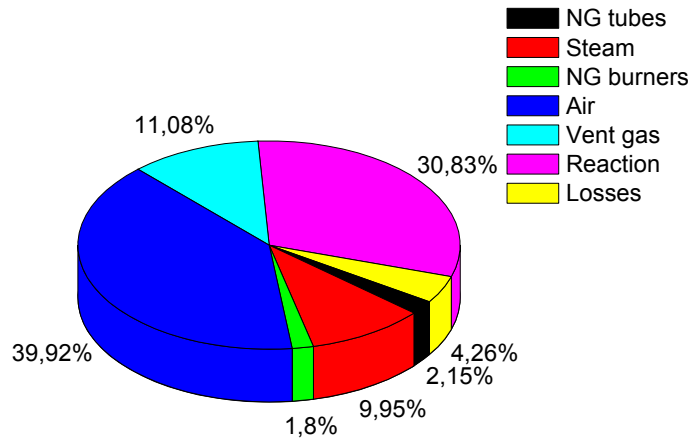


Figure 21: How the energy is utilized in the reformer in Bohus with maximum hydrogen production.

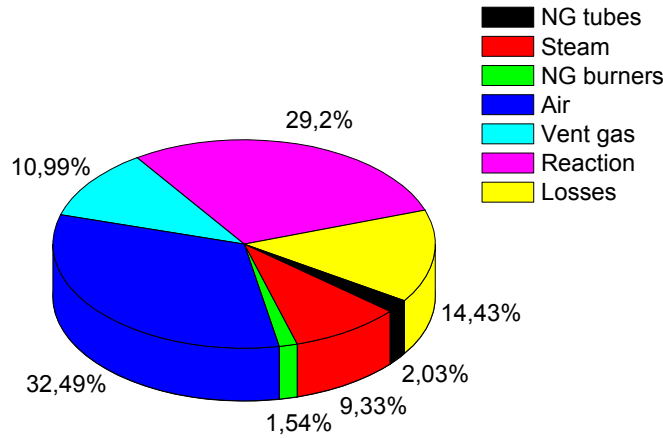


Figure 22: How the energy is utilized in the reformer in Bohus with minimum hydrogen production.

### 3.2.2 Alby

To calculate how the energy is used in the steam reformers in Alby the following assumptions are made:

- The LPG has the same properties as propane.
- The only reaction occurring in the tubes is  $C_3H_8 + 3H_2O \rightarrow 3CO + 7H_2$
- 100% conversion of the steam reforming reaction in the reformer tubes.
- The vent gas from the PSA is assumed to consist of 50%  $H_2$  and 50%  $CO_2$  (Krans, 2011).

The calculations are similar to those for Bohus. The maximum available energy is:

$$E_{max}^{Alby} = \frac{F_{air,burner}^{Alby}}{R_{air/fuel}^{Alby}} * \rho_{LPG} * LHV_{LPG} \quad (30)$$

Secondly, the energy demand for the endothermic reaction can be estimated as:

$$E_{Reaction}^{Alby} = \frac{F_{LPG,tubes}^{Alby} * \Delta H_{SMR}^{Alby}}{M_V} \quad (31)$$

Thirdly, some energy is used to heat the gases in the furnaces. The gases in the tubes, natural gas and steam, are heated as:

$$E_{LPG,tubes}^{Alby} = F_{LPG,tubes}^{Alby} * \rho_{LPG} * C_{pLPG} * (T_{product\ gas}^{Alby} - T_{LPG,tubes}^{Alby}) \quad (32)$$

$$E_{steam}^{Alby} = \dot{m}_{steam,tubes}^{Alby} * Cp_{steam} * (T_{product\ gas}^{Alby} - T_{steam,tubes}^{Alby}) \quad (33)$$

The gases in the furnace, liquefied petroleum gas, air and vent gas are heated as:

$$E_{LPG,burner}^{Alby} = F_{LPG,burner}^{Alby} * \rho_{LPG} * Cp_{LPG} * (T_{flue\ gases}^{Alby} - T_{LPG,tubes}^{Alby}) \quad (34)$$

$$E_{air}^{Alby} = F_{air,burner}^{Alby} * \rho_{air} * Cp_{air} * (T_{flue\ gases}^{Alby} - T_{air,burner}^{Alby}) \quad (35)$$

$$E_{vent}^{Alby} = F_{vent}^{Alby} * (0.5 * \rho_{H2} * Cp_{H2} + 0.5 * \rho_{Co2} * Cp_{Co2}) * (T_{flue\ gases}^{Alby} - T_{vent}^{Alby}) \quad (36)$$

The total loss in the Alby steam reformer is calculated as:

$$E_{loss}^{Alby} = E_{max}^{Alby} - E_{Reaction}^{Alby} - E_{LPG,tubes}^{Alby} - E_{steam}^{Alby} - E_{LPG,burner}^{Alby} - E_{air}^{Alby} - E_{vent}^{Alby} \quad (37)$$

Two examples of how the energy is distributed are shown below. The first one is for maximum production and the second is for minimum production.

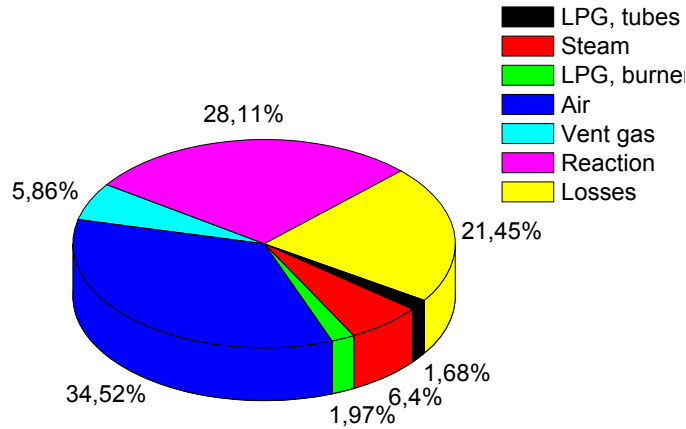
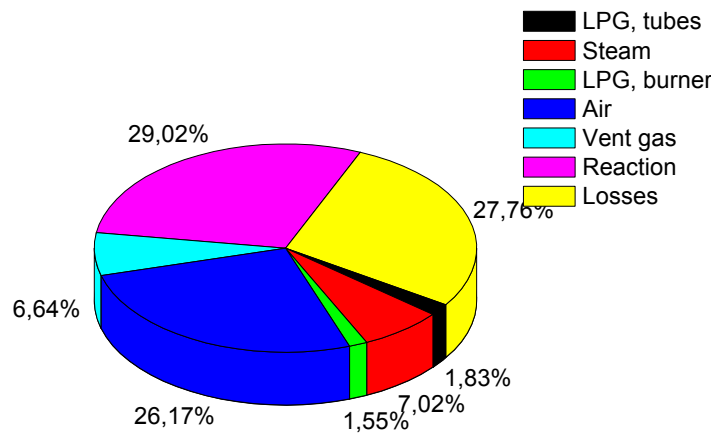


Figure 23: How the energy is utilized in the reformer in Alby with maximum hydrogen production.



**Figure 24: How the energy is utilized in the reformer in Alby with maximum hydrogen production.**

For both Alby and Bohus a considerable amount of energy (26-40%) is used to heat the air. The air is needed for the combustion in the burners. If this could be decreased fuel could be saved. One possibility is to preheat the air with the flue gases (see chapter 5). Another possibility is to decrease the air flow to the burners. The most economical air flow is investigated in section 3.5.

The possibilities of preheating the steam more is complicated since the steam already has an inlet temperature of 400-450 °C, so it would require more expensive materials for the piping. The plants are also built in a way which makes implementing a heat exchanger to the steam more complicated than to the air. The possibility of minimizing the steam flow is however examined in section 4.2 for Bohus and 4.3 for Alby.

The flows of NG/LPG to the tubes and burners are considered to be too small for any preheating to be economical.

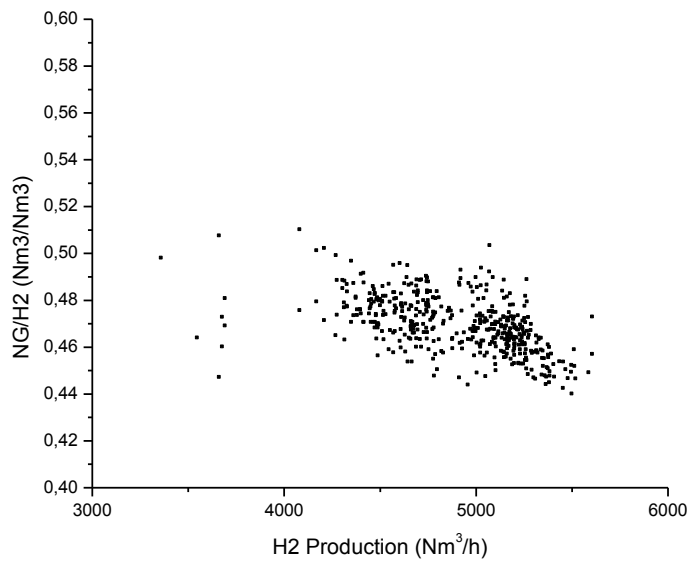
### 3.3 The relationship between consumption ratio and production level

Whether the efficiency of the steam reformers varies with the production level has been investigated. The consumption ratio of natural gas to hydrogen should not vary with different production levels according to the operating manual (Hydro-Chem-Processing, 1991). The steam production consumption ratio is also of interest since the steam is used in other processes.

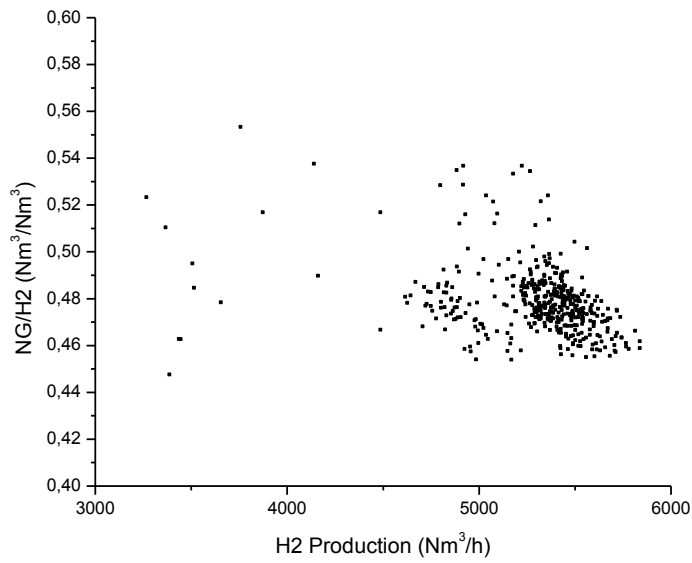
#### 3.3.1 Bohus

The production level the last three years (2010-2012) are plotted against the consumption ratio ( $R_{NG/H_2}^{Bohus}$ ) in Figure 25:

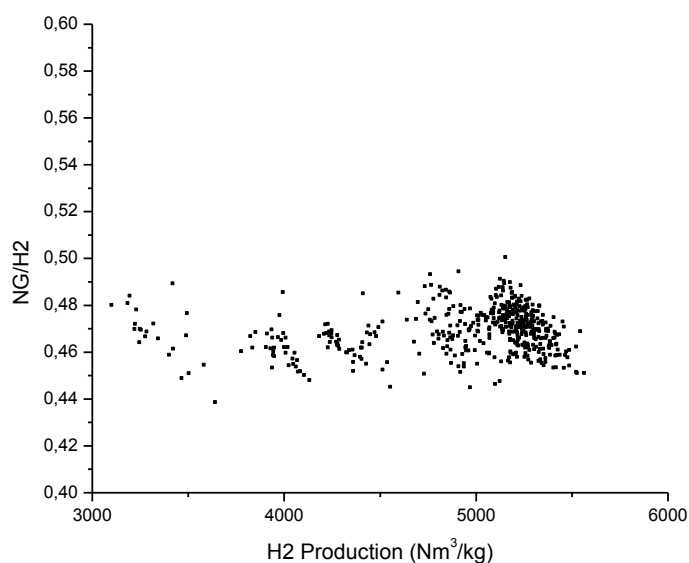




**Figure 25: The hydrogen production in Bohus 2010 plotted against the consumption ratio.**

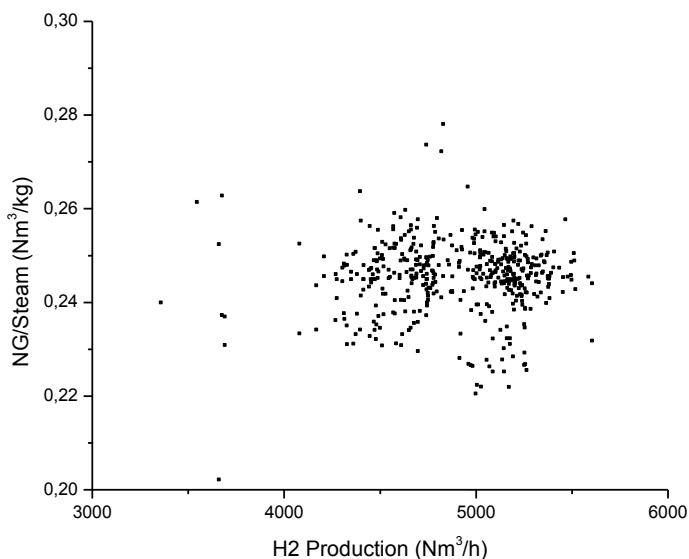


**Figure 26: The hydrogen production in Bohus 2011 plotted against the consumption ratio.**

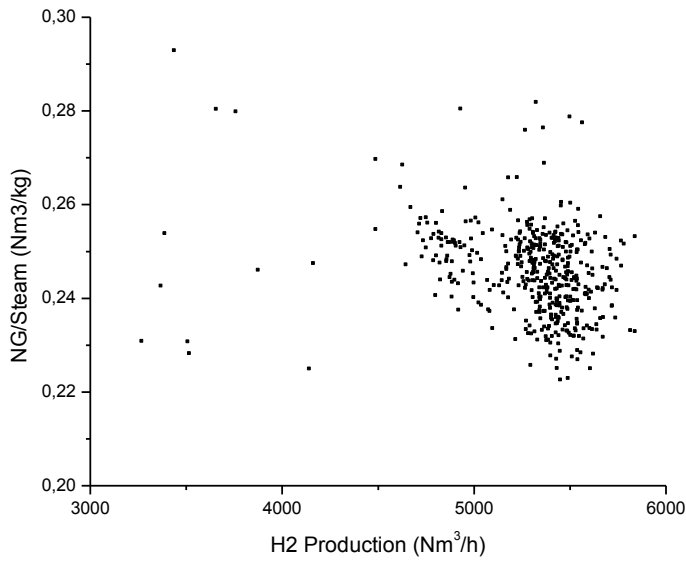


**Figure 27: The hydrogen production in Bohus 2012 plotted against the consumption ratio.**

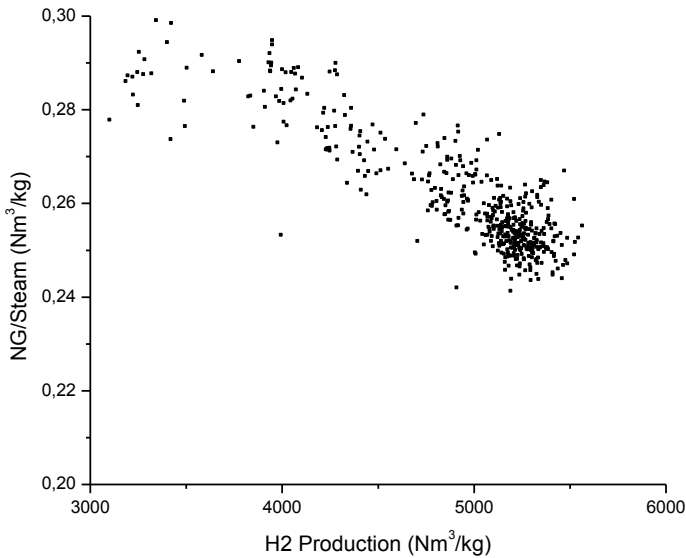
No trend can be seen that the production level has any impact on the consumption ratio which it should not according to the design. The same is done with the production level against the consumption ratio of consumed natural gas to produced steam ( $R_{NG/steam}^{Bohus}$ ) in Figure 28Figure 30: .



**Figure 28: The hydrogen production in Bohus 2010 plotted against the steam consumption ratio.**



**Figure 29: The hydrogen production in Bohus 2011 plotted against the steam consumption ratio.**

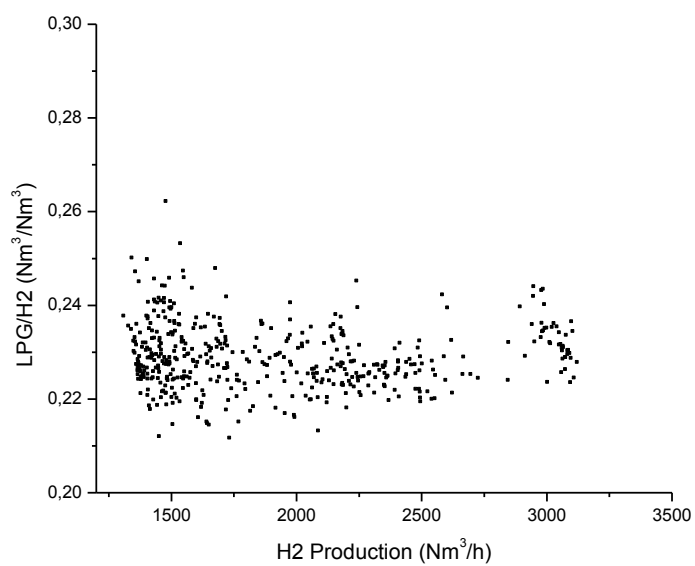


**Figure 30: The hydrogen production in Bohus 2012 plotted against the steam consumption ratio.**

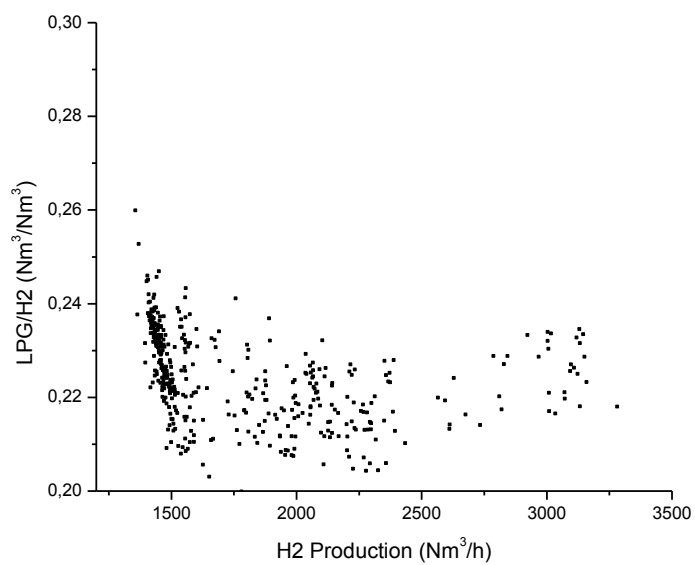
It can be seen in Figure 30 that the consumption ratio of natural gas to steam is much lower at higher production levels. In 2010 (Figure 28) and 2011 (Figure 29) this trend cannot be seen; this might depend on that that in 2010 and 2011 the hydrogen production was pretty constant.

### 3.3.2 Alby

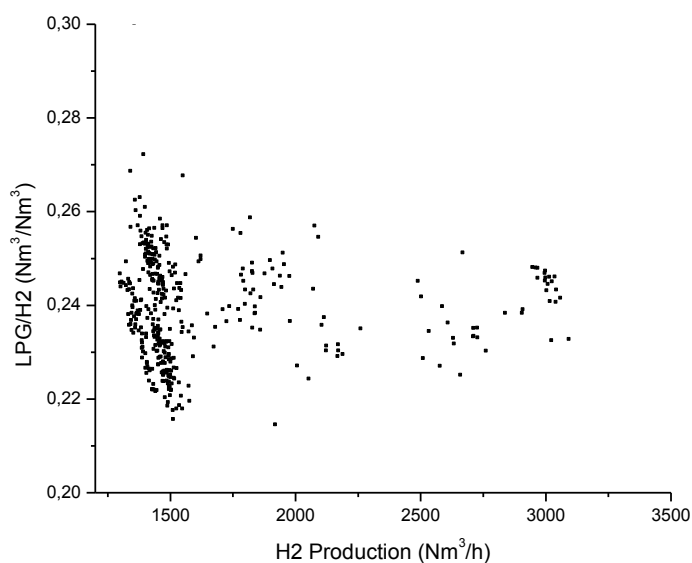
The same is done for the last three years in Alby. First the production level is plotted against the consumption ratio  $R_{LPG/H_2}^{Alby}$  in Figure 31Figure 33.



**Figure 31: The hydrogen production in Alby 2010 plotted against the consumption ratio.**

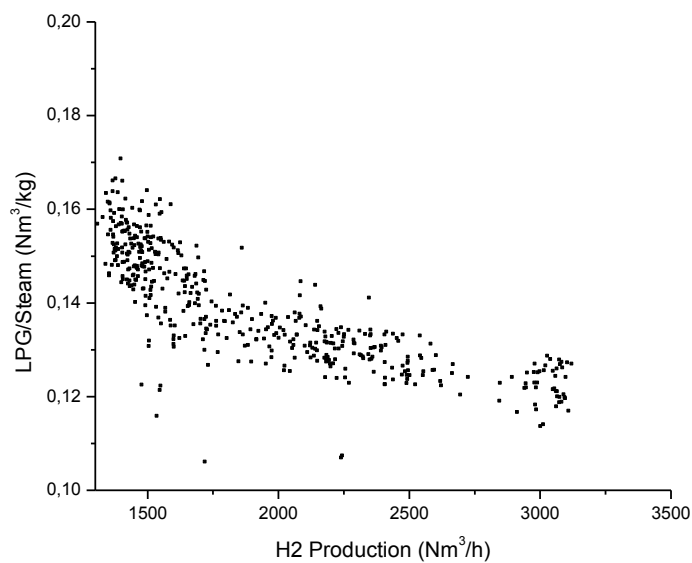


**Figure 32: The hydrogen production in Alby 2011 plotted against the consumption ratio.**

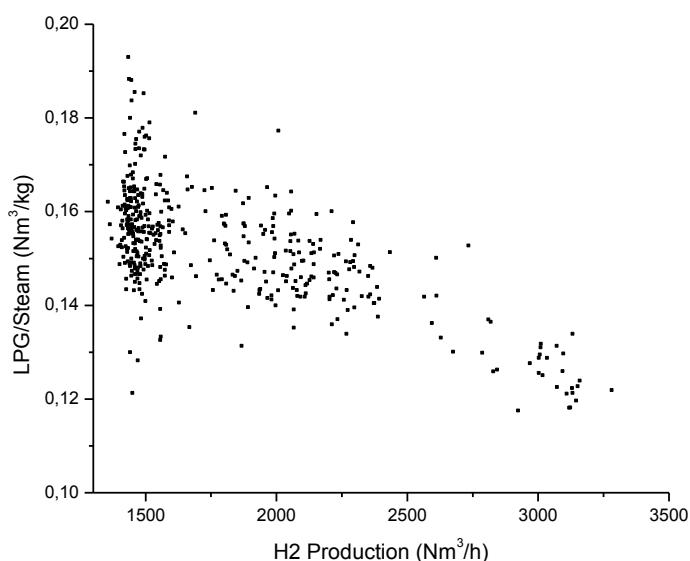


**Figure 33: The hydrogen production in Alby 2012 plotted against the consumption ratio.**

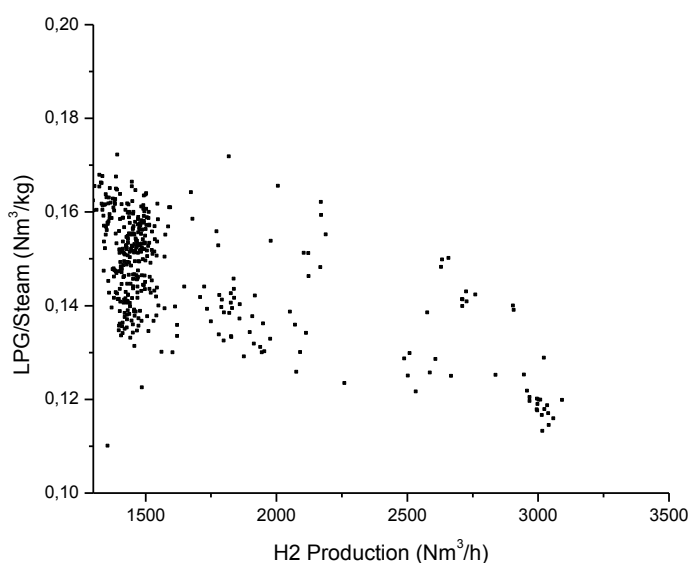
Neither in Alby can a connection between production level and consumption ratio be found. For the steam consumption ratio of liquefied petroleum gas the same trend can be seen as in Bohus with lower consumption ratio at higher production levels as can be seen in Figure 34Figure 36.



**Figure 34: The hydrogen production in Alby 2010 plotted against the steam consumption ratio.**



**Figure 35: The hydrogen production in Alby 2011 plotted against the steam consumption ratio.**



**Figure 36: The hydrogen production in Alby 2012 plotted against the steam consumption ratio.**

For the hydrogen production there is no connection between production level and consumption ratio. The differences in consumption ratio must involve other causes. However, the steam production is much more efficient at higher production levels.

### 3.4 The relationship between steam to carbon ratio and consumption ratio

One of the most important parameters in steam reformers is the steam to carbon ratio (Hydro-Chem-Processing, 1991) (Liu, Song, & Subramani, 2010) (Liu J. A., 2006). It is therefore of interest to examine if any connection between the efficiency and steam to carbon ratio can be found.

### 3.4.1 Bohus

In the Bohus steam reformer the steam to carbon ratio has been constant (3.5 kg steam /Nm<sup>3</sup> natural gas) since natural gas was introduced in 2004. Since the ratio has been this constant over the years it is hard to decide the ratio which is the most optimal.

### 3.4.2 Alby

In the Alby steam reformer the ratio varies much more and the steam-to-carbon ratio for last three years is plotted against the consumption ratio in Figures 37, 38 and 39 below.

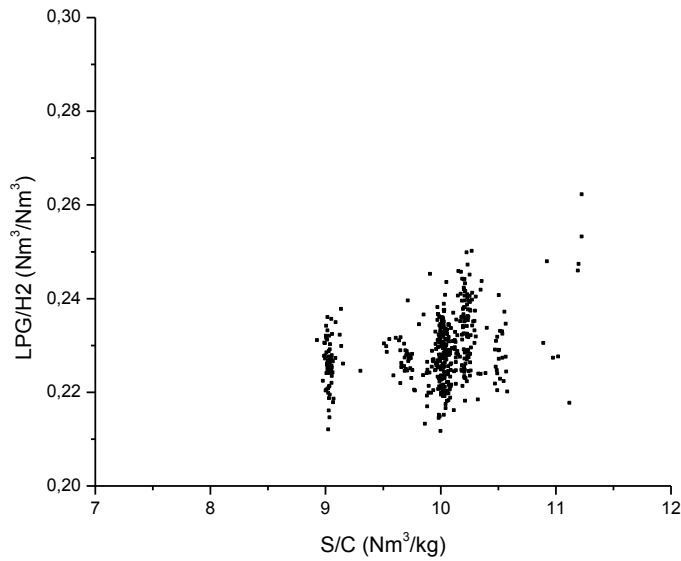


Figure 37: The steam-to-carbon ratio in Alby 2010 plotted against the consumption ratio.

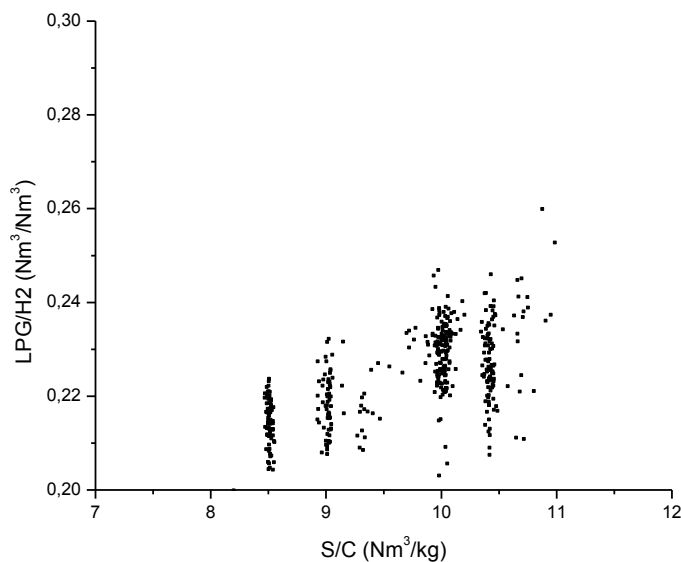
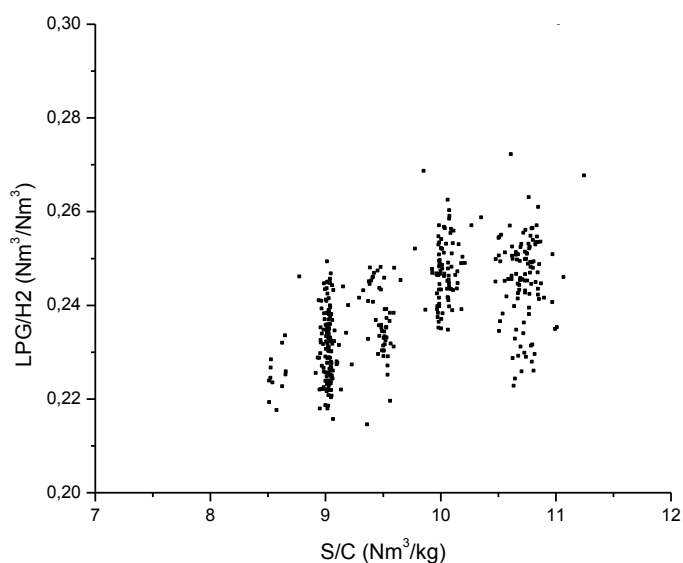


Figure 38: The steam-to-carbon ratio in Alby 2011 plotted against the consumption ratio.



**Figure 39: The steam-to-carbon ratio in Alby 2012 plotted against the consumption ratio.**

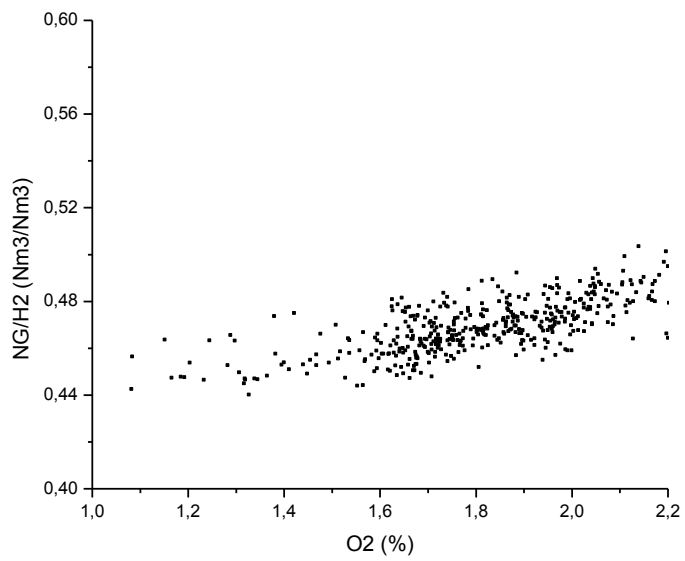
In the graphs a trend of lower consumption ratio can be seen with lower steam-to-carbon ratio for all three years. If the steam-to-carbon ratio is 9 kg/Nm<sup>3</sup> instead of 10.5 kg/Nm<sup>3</sup> the efficiency is increased with 2-6%. To confirm this hypothesized relationship, an experiment with lower steam-to-carbon ratio was performed in Alby, see section 4.3.

### 3.5 The relationship between air residual in flue gases and consumption ratio

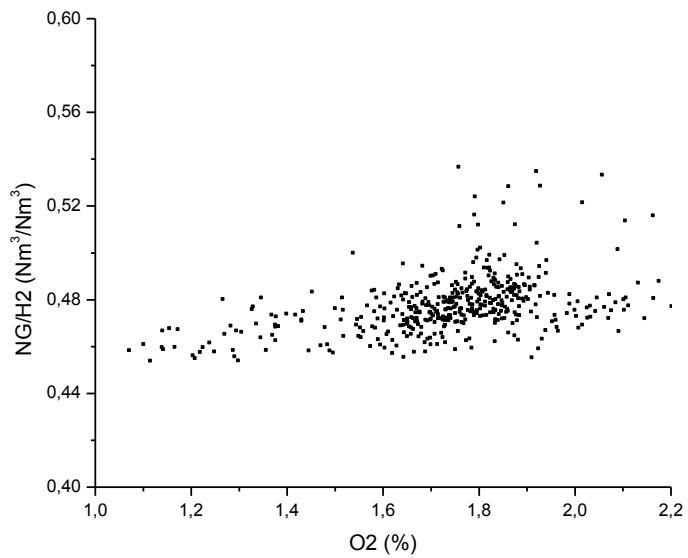
The flue gas from the burners in the reformer contains some residual oxygen. In theory the reformer should perform better if the oxygen concentration is lower. This is due to the fact that if there is a smaller air flow to the burners, less fuel is needed to heat the air.



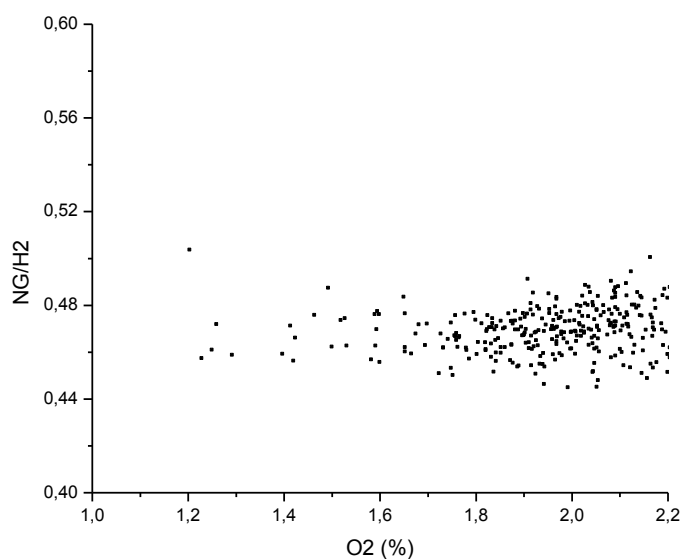
### 3.5.1 Bohus



**Figure 40: Oxygen percentage in flue gases 2010 in Bohus plotted against the consumption ratio.**



**Figure 41: Oxygen percentage in flue gases 2011 in Bohus plotted against the consumption ratio.**

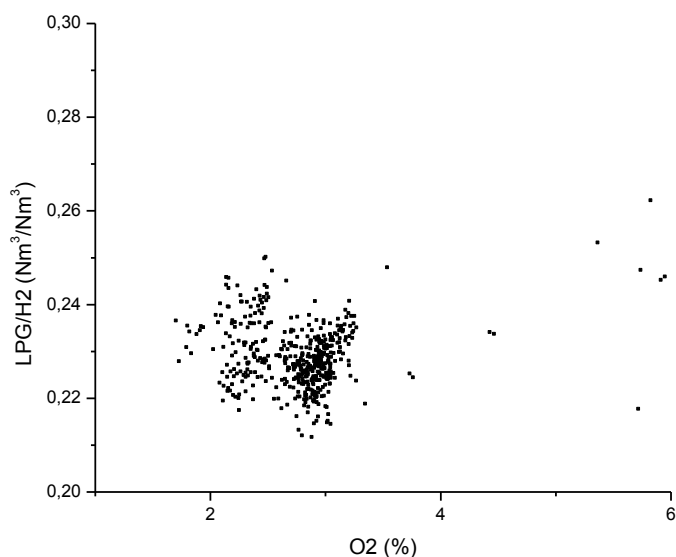


**Figure 42: Oxygen percentage in flue gases 2010 in Bohus plotted against the consumption ratio.**

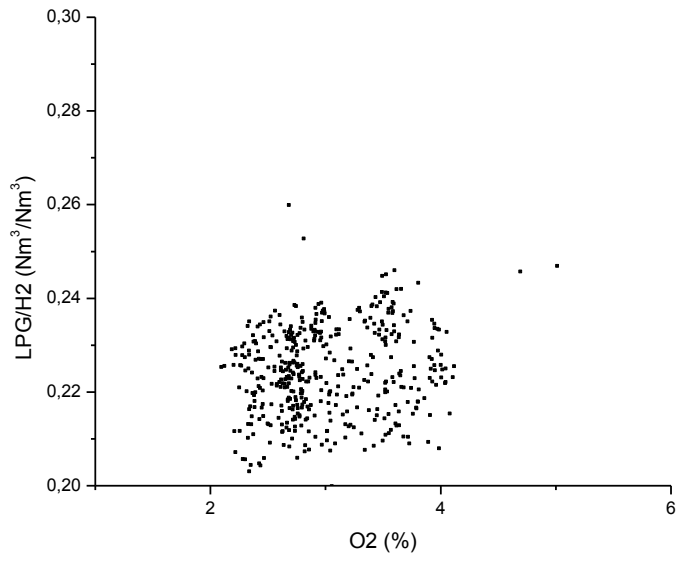
In Figure 40-Figure 42 a connection between low consumption ratio and low oxygen content can be observed. However, with the present control system the air is as low as possible in Bohus already. If the control system can be improved a considerable amount of fuel (natural gas) could be saved.

### 3.5.2 Alby

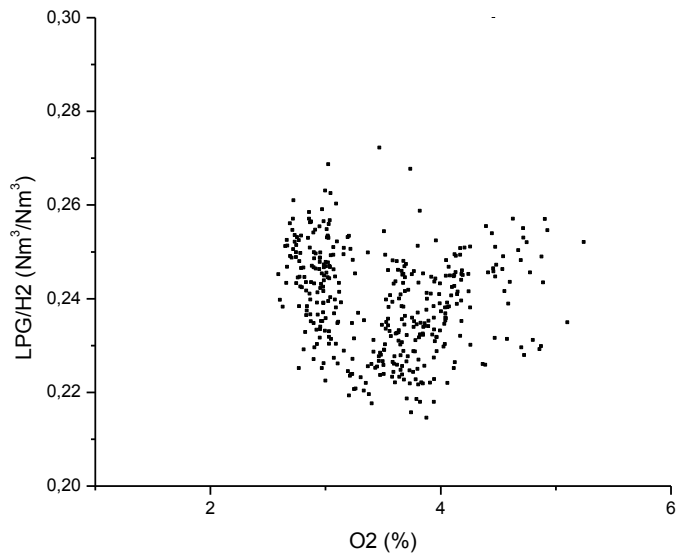
In Alby it is difficult to see a connection between the oxygen content in the flue gases and the consumption ratio. An experiment with lower oxygen is recommended but has not been performed in this thesis.



**Figure 43: Oxygen percentage in flue gases 2010 in Alby plotted against the consumption ratio.**



**Figure 44: Oxygen percentage in flue gases 2011 in Alby plotted against the consumption ratio.**



**Figure 45: Oxygen percentage in flue gases 2012 in Alby plotted against the consumption ratio.**

## 4 EXPERIMENTAL TESTS

This section contains the results and discussion of the experiments performed in the steam reformers at Bohus and Alby in the spring of 2013. The dates of the experiments are presented in Appendix I.

### 4.1 Furnace temperature in Bohus

The temperature is one of the most important parameters for the steam reforming reaction 4 (Liu, Song, & Subramani, 2010) (Hydro-Chem-Processing, 1991). The outlet stream from the reforming tubes has a temperature of 820°C. With a lower temperature the steam reforming reaction 4 will have a lower conversion of methane as explained in section 2.2. However with a lower temperature less fuel is needed to heat the tubes and therefore an optimal outlet temperature exists. An experiment done by Eka in 2006 indicated. The equilibrium conversion of methane in steam reforming against temperature, pressure and steam-to-carbon (S/C) ratio that 810°C gives a better consumption ratio between natural gas and hydrogen production than 820°C (Andersson & Thorén, 2006). This experiment lasted only for six hours and the results could be due to natural variations in the steam reformer. Therefore a new experiment with a temperature of 810°C was performed during a test period of one week.

#### 4.1.1 Predicted results

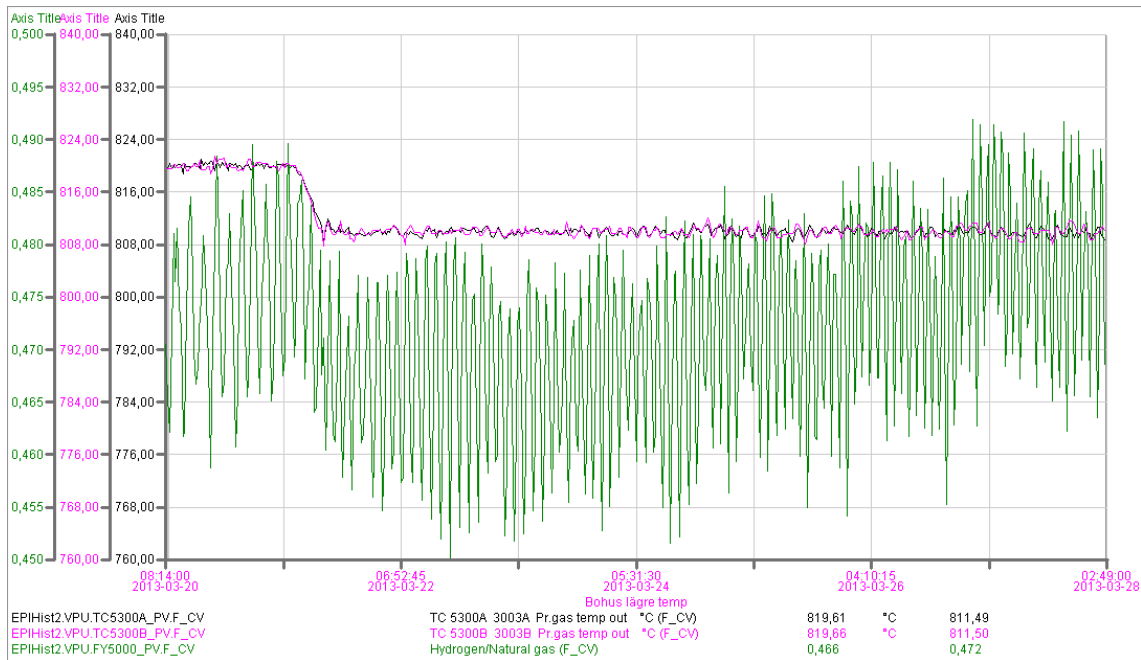
This is the predicted consequences of the experiment before it started:

1. Since the temperature is lowered, the conversion of natural gas should be decreased and more natural gas is needed to the tubes in order to have the same hydrogen production.
2. The vent gas after the PSA should contain more unconverted methane and will therefore be more energy rich. Because of this more energy-rich vent gas, less fuel in the form of natural gas is needed in the burners.
3. Since the temperature in the reformers is decreased, less fuel (natural gas) in the burners.
4. Since the outlet temperature of the product gas and flue gases is decreased, the steam production will also decrease.

If the experiment is successful the natural gas to the burners will decrease more than the required increase in natural gas to the tubes.

#### 4.1.2 Results

During the first days the results of the experiments went as hoped, the natural gas consumption to the burners decreased more than the natural gas consumption to the tubes increased. However after three days the consumption ratio increased again as can be seen in Figure 46.



**Figure 46:** The consumption ratio and the tubes outlet temperature during the experiment. It should be “Natural gas/Hydrogen” instead of “Hydrogen/Natural gas” for FY5000.

Due to this unknown increase of the consumption ratio the results are divided into three groups; before the experiment, after the experiment but before the increase of consumption ratio and after the increase of consumption ratio. The results are shown in table 3:

**Table 3.** The most important data before and during the experiment.

	19/3-21/3	21/3-23/3	26/3-28
R	0.476	0.468	0.477
H <sub>2</sub> production	4528 Nm <sup>3</sup> /h	4505 Nm <sup>3</sup> /h	4483 Nm <sup>3</sup> /h
NG to tubes A	760 Nm <sup>3</sup> /h	773 Nm <sup>3</sup> /h	783 Nm <sup>3</sup> /h
NG to tubes B	760 Nm <sup>3</sup> /h	773 Nm <sup>3</sup> /h	783 Nm <sup>3</sup> /h
NG to burner A	337 Nm <sup>3</sup> /h	302 Nm <sup>3</sup> /h	306 Nm <sup>3</sup> /h
NG to burner B	297 Nm <sup>3</sup> /h	260 Nm <sup>3</sup> /h	266 Nm <sup>3</sup> /h
Steam production	7.62 t/h	7.2 t/h	7.3 t/h
Tubes out temp A	820 °C	810 °C	810 °C
Tubes out temp B	820 °C	810 °C	810 °C

It can be seen in table 3 that the experiment went as predicted during the first three days. During these days the natural gas consumption decreased with 2.1 % with unchanged hydrogen production. However, after this the consumption ratio started to increase again. It is unknown why; it could be due to uncontrolled variations such as a temporary change of the heating value of the natural gas. The experiment should be performed again to see if the results are similar. It is important to investigate if the increased natural gas consumption after three days was a coincidence or a part of the experiment. The settings used in the experiment could potentially saving 2.1 % natural gas consumption without reducing the hydrogen production, but the steam production would decrease by 5.2 %. Before implementing this idea in the plant it should be considered if the savings in natural gas are worth the loss of steam.

## 4.2 Steam-to-carbon ratio in Bohus

Another important parameter in steam reforming is the steam to-carbon-ratio (section 2.2) to the tubes. In the Bohus steam reformer the ratio has always been 3.5 kg steam to 1 Nm<sup>3</sup> natural gas. Therefore it is of interest to test another ratio. A high steam-to-carbon ratio gives a high conversion of the steam reforming reaction (4). Excess steam is also needed to avoid carbon formation on the catalyst. However the heating of the steam requires extra fuel to the burners and therefore an optimal steam-to-carbon ratio exists in terms of energy consumption and stable operation of the catalyst.

### 4.2.1 Carbon formation

Although the stoichiometry for reaction 4 suggests that only 1 mol of H<sub>2</sub>O is required for 1 mol of CH<sub>4</sub>, the reaction in practice is being performed using high steam-carbon-ratio, typically in the range 2.5-3 mol/mol in order to reduce the risk of carbon deposition on the catalyst surface (Liu, Song, & Subramani, 2010). The steam to carbon ratio used in Bohus plant (3.5 kg/Nm<sup>3</sup> equivalent to 3.9 mol/mol) matches the recommended ratio from the manufacturer of the reformer, Hydro-Chem. However, this ratio is much higher than the recommended values found in most literature (around 3 mol/mol) and could probably be decreased without causing carbon formation on the catalyst. The contact person for the supplier of the catalyst, Johnson Matthey was therefore asked about the minimum steam-to-carbon ratio for the Bohus catalyst and he writes that the minimum steam-to-carbon ratio “will depend on feedstock, reformer outlet temperature, catalyst age etc. However, as a rule of thumb, for natural gas feeds, we would recommend a steam to carbon ratio of 2.8 mol/mol as a minimum. It is possible to run lower than this and there are plants that do this. However, there is a possibility to over-reduce the HTS catalyst if the steam to carbon ratio is reduced too far, as you will have too strong a reducing environment in the HTS. This will reduced the iron HTS catalyst to metallic iron and promote Fischer-Tropsch reactions, where higher hydrocarbons will be made over the catalyst bed.”

Based on this information it is considered safe to do an experiment with a steam to carbon ratio of 3.0 kg/Nm<sup>3</sup>.

### 4.2.2 Predicted results

This is the predicted consequences of the experiment before it started:

1. The conversion of natural gas in the reformer tubes as explained in section 2.1 will decrease due to less steam. To maintain the hydrogen production more natural gas to the tubes is needed.
2. The fuel (natural gas) to the burners will decrease due to less heating demand.
3. The temperature of the steam to the tubes will have a higher temperature due to a smaller flow of steam in the steam pre-heat coil (3076). It is important that the temperature is lower than 450 °C due to the properties of materials in the piping.
4. The condensate water flow from condensate drums (3082) will decrease due to less water in the system.
5. The steam production is believed to decrease due to lower flow of the production gas from the reformer tubes.

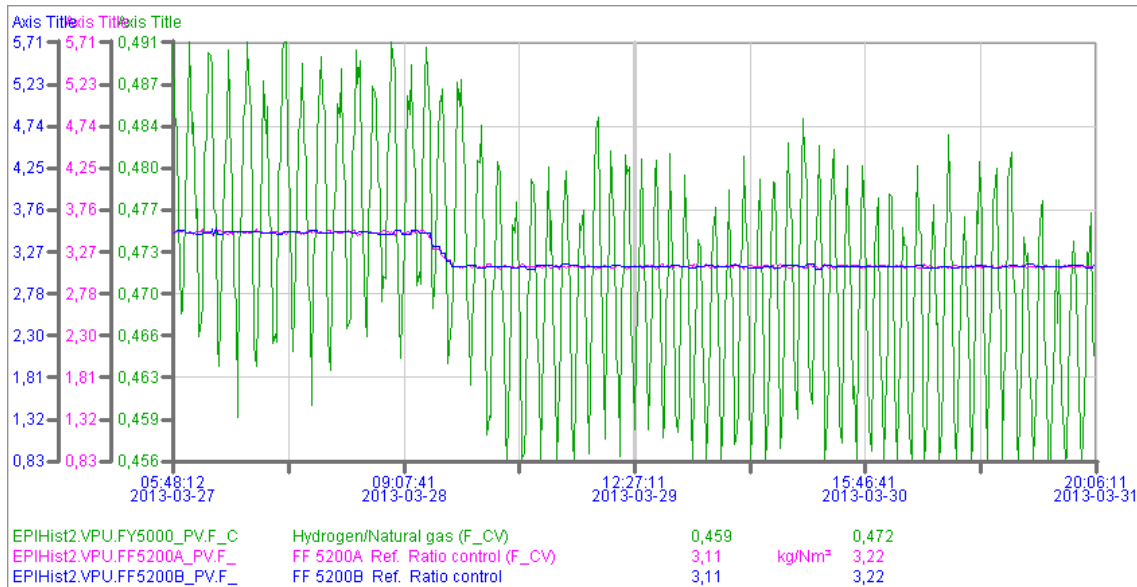
The experiment is successful if the decrease of natural gas to the burners is larger than the increase of natural gas to the tubes.

### 4.2.3 Results

The experiment with decreasing the steam-to-carbon ratio to 3.0 kg/ Nm<sup>3</sup> from 3.5 kg/ Nm<sup>3</sup> has been performed three times.

#### Experiment 1

The first experiment was performed just after the experiment with lower temperature. It was supposed to be one week but an unplanned shut-down of the reformer ended the experiment after just three days. Until then the results of the experiment were as predicted. In Figure 47 the consumption ratio before and during the experiment can be seen.



**Figure 47: The consumption ratio and the steam-to-carbon ratio during the first experiment. It should be “Natural gas/Hydrogen” instead of “Hydrogen/Natural gas” for FY5000.**

Since the experiment was performed just after the experiment with lower temperature the results have to be compared with conditions before any experiment. The results are presented in table 5.

**Table 5.** The most important data before and during the experiment.

	19/3-21/3	29/3-31/3
R	0.476	0.468
H <sub>2</sub> production	4528 Nm <sup>3</sup> /h	4459 Nm <sup>3</sup> /h
NG to tubes A	760 Nm <sup>3</sup> /h	774 Nm <sup>3</sup> /h
NG to tubes B	760 Nm <sup>3</sup> /h	773 Nm <sup>3</sup> /h
NG to burner A	337 Nm <sup>3</sup> /h	282 Nm <sup>3</sup> /h
NG to burner B	297 Nm <sup>3</sup> /h	258 Nm <sup>3</sup> /h
Steam production	7.62 t/h	7.44 t/h
S/C A	3.5 kg/ Nm <sup>3</sup>	3.1 kg/ Nm <sup>3</sup>
S/C B	3.5 kg/ Nm <sup>3</sup>	3.1 kg/ Nm <sup>3</sup>
Steam temp A	391 °C	402 °C
Steam temp B	391 °C	402 °C
Condensate water flow	3.00 Nm <sup>3</sup> /h	2.44 Nm <sup>3</sup> /h

The natural gas consumption is decreased with 1.7 % according to this experiment. The steam production is decreased with 0.8 %.

## Experiment 2

Due to the fact that experiment 1 was too short another experiment was performed. This experiment also started out with good results but after a few days something happened with the steam reformer which caused an increasing consumption ratio. This is believed to be unrelated to the experiment. This can be seen in Figure 48.

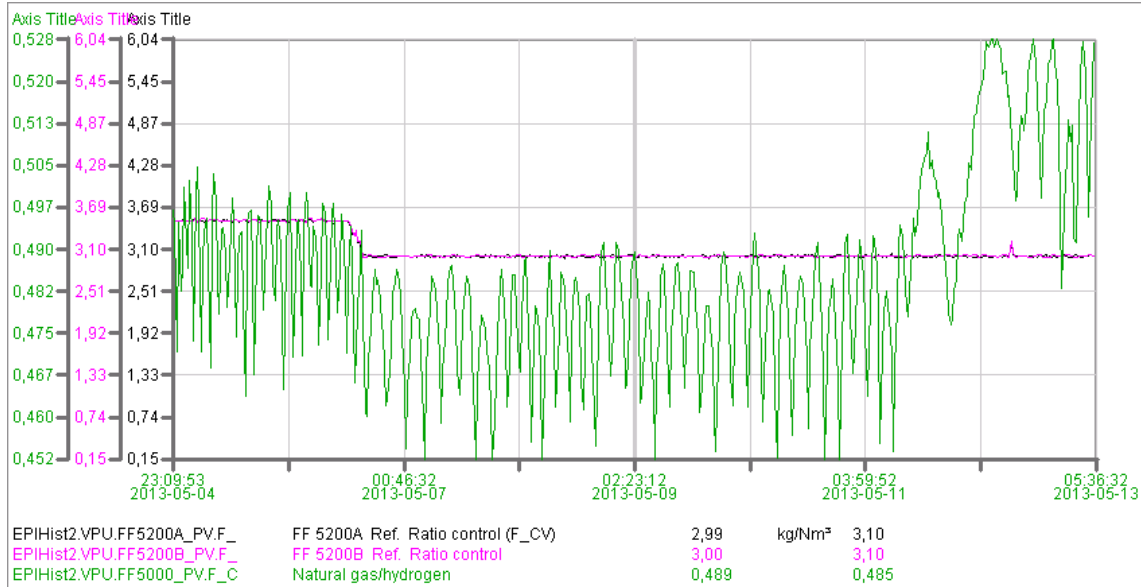


Figure 48: The consumption ratio and the steam-to-carbon ratio during the second experiment.

If the assumption is made that the increasing consumption of natural gas during the last days was due to something else (it became even worse when the experiment was finished) then the results are presented in table 6. If this assumption is not made, the results in Table 6 would be different.

Table 6. The most important data before and during the experiment.

	4/5-5/5	7/5-310/5
R	0.489	0.476
H <sub>2</sub> production	4979Nm <sup>3</sup> /h	4956 Nm <sup>3</sup> /h
NG to tubes A	874 Nm <sup>3</sup> /h	902 Nm <sup>3</sup> /h
NG to tubes B	874 Nm <sup>3</sup> /h	902 Nm <sup>3</sup> /h
NG to burner A	353 Nm <sup>3</sup> /h	291 Nm <sup>3</sup> /h
NG to burner B	333 Nm <sup>3</sup> /h	264 Nm <sup>3</sup> /h
Steam production	9.15 t/h	8.66 t/h
S/C A	3.5 kg/ Nm <sup>3</sup>	3.0 kg/ Nm <sup>3</sup>
S/C B	3.5 kg/ Nm <sup>3</sup>	3.0 kg/ Nm <sup>3</sup>
Steam temp A	387 °C	399 °C
Steam temp B	387 °C	399 °C

The natural gas consumption is decreased by 2.6 % with the same hydrogen production and the steam production is decreased by 2.4 %.

## Experiment 3

Since neither experiment 1 nor 2 went as predicted all days, a third experiment was performed. In this experiment all went well as can be seen in Figure 49 and table 7.



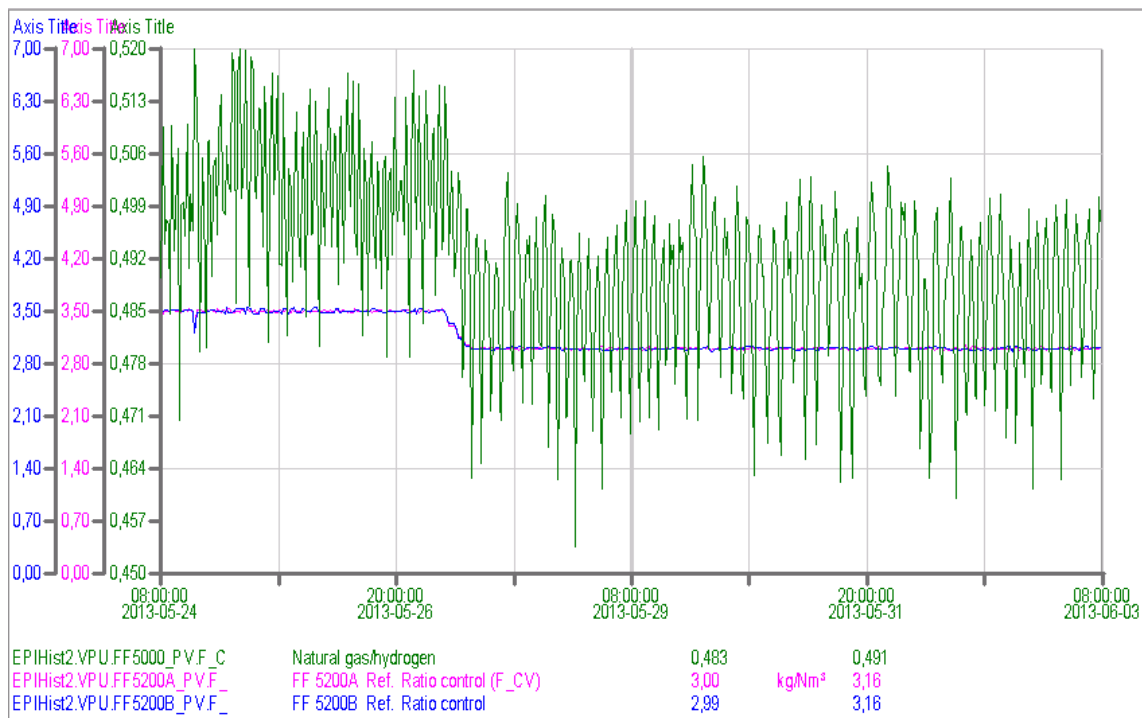


Figure 49: The consumption ratio and the steam-to-carbon ratio during the third experiment.

Table 7. The most important data before and during the experiment.

	24/5-26/5	28/5-3/6
R	0.502	0.487
H <sub>2</sub> production	5009 Nm <sup>3</sup> /h	5002 Nm <sup>3</sup> /h
NG to tubes A	902 Nm <sup>3</sup> /h	930 Nm <sup>3</sup> /h
NG to tubes B	902 Nm <sup>3</sup> /h	930 Nm <sup>3</sup> /h
NG to burner A	362 Nm <sup>3</sup> /h	295 Nm <sup>3</sup> /h
NG to burner B	346 Nm <sup>3</sup> /h	277 Nm <sup>3</sup> /h
Steam production	9.3 t/h	9.07 t/h
S/C A	3.5 kg/ Nm <sup>3</sup>	3.0 kg/ Nm <sup>3</sup>
S/C B	3.5 kg/ Nm <sup>3</sup>	3.0 kg/ Nm <sup>3</sup>
Steam temp A	388 °C	400 °C
Steam temp B	388 °C	399 °C

The results confirmed the findings in experiment 1 and 2. The natural gas consumption decreased with 3.0% and the steam production decreased with 2.5%. This indicated that a steam-to-carbon ratio of 3.0 is to be preferred and the steam reformer should be operated at this ratio in the future.

### 4.3 Steam to carbon ratio in Alby

Since Alby is using LPG instead of natural gas the results from Bohus cannot be directly implemented there. However, as in Bohus, an optimal steam-to-carbon ratio exists.

A steam-to-carbon ratio experiment has already been performed in 2008 by Alby, which indicated 10.5 kg/Nm<sup>3</sup> to be the optimal ratio. However, Figure 37, Figure 38 and Figure 39 indicates that the last three years a lower steam-to-carbon ratio is to be preferred.

### 4.3.1 Carbon formation

The operating manual recommends a steam-to-carbon ratio of 8.5 kg/Nm<sup>3</sup> and this has been tested before in both steam reformers in Alby and Bohus, so there is no risk of carbon formation on the catalyst due to lower ratio at this level.

### 4.3.2 Predicted results

The predicted results are the same as in section 4.2.2 except that the saved fuel is liquefied petroleum gas instead of natural gas.

### 4.3.3 Results

The temperature of the steam to the tubes increased from 439 °C to 448 °C when decreasing the steam-to-carbon ratio from 10.42 kg/Nm<sup>3</sup> to 9.9 kg/Nm<sup>3</sup>. Since the temperature should not exceed 450 °C the steam-to-carbon ratio could not be further decreased. The experiment lasted for a week and the results are presented in table 8.

**Table 8.** The most important data before and during the experiment.

	13/3-25/4	2/5-6/5
R	0.242	0.239
H <sub>2</sub> production	1430 Nm <sup>3</sup> /h	1418 Nm <sup>3</sup> /h
LPG to tubes	234 Nm <sup>3</sup> /h	234 Nm <sup>3</sup> /h
LPG to burner	113 Nm <sup>3</sup> /h	105 Nm <sup>3</sup> /h
Steam production	1431 kg/h	1417 kg/h
S/C	10.41 kg/ Nm <sup>3</sup>	9.9 kg/ Nm <sup>3</sup>
Steam temp	439 °C	448 °C
Condensate water flow	1.41 Nm <sup>3</sup> /h	1.27 Nm <sup>3</sup> /h

The liquefied petroleum gas consumption decreased by 1.2% with the same hydrogen production and the steam consumption decreased by 1.3 %. Since the steam-to-carbon ratio could not be decreased to less than 9.9 kg/Nm<sup>3</sup>, larger effect cannot be seen. It seems however that it is more efficient for the Alby steam reformer to operate at a lower steam-to-carbon ratio. It is important to consider if the saved LPG is enough to compensate for the lost steam.

## 5. PREHEATING OF THE AIR TO THE BURNERS

The air to the burners is taken from inside the steam reforming building. It has therefore the same temperature as the indoor temperature and has a small variation during the year, depending on the outside temperature. In Bohus the two furnaces have different air inlet temperature depending on the fact that A furnace has an air-intake higher from the ground and the air is therefore warmer. Inside the furnace the air is heated to around 1000 °C and as can be seen in Figure 21 and Figure 22 the heating of air accounts for a large part of the natural gas consumption. If the air was warmer when entering the burner it would need less energy for heating. The idea is that heat recovered from the flue gases could be used to preheat the air.

The savings in natural gas with a certain preheating temperature  $T_{spec}$ , can be calculated as:

$$\begin{aligned} \text{Energy saving} &= F_{NG,burner}^{Bohus,A} * \rho_{NG} * Cp_{NG} * (T_{spec} - T_{NG,tubes}^{Bohus,A}) \\ &+ F_{NG,burner}^{Bohus,B} * \rho_{NG} * Cp_{NG} * (T_{spec} - T_{NG,tubes}^{Bohus,B}) \end{aligned} \quad (38)$$

The flue gas leaving the steam reformer to the atmosphere has a temperature of 200 °C. This heat could be used in a heat exchanger to preheat the air to the burners. If a maximum temperature difference of 10 °C is chosen the preheating temperature can  $T_{spec}$  be calculated as:

$$\begin{aligned} F_{flue\ gases}^{Bohus} * \rho_{flue} * Cp_{flue} * (T_{flue\ out}^{Bohus} - (T_{spec} + 10)) \\ = F_{NG,burner}^{Bohus,A} * \rho_{NG} * Cp_{NG} * (T_{spec} - T_{NG,tubes}^{Bohus,A}) \\ + F_{NG,burner}^{Bohus,B} * \rho_{NG} * Cp_{NG} * (T_{spec} - T_{NG,tubes}^{Bohus,B}) \end{aligned} \quad (39)$$

Since the flow of the flue gases is not measured in the plant it has to be calculated. During the time the master thesis was written, an energy saving project was performed at AkzoNobel Pulp and Performance Chemicals. Both the flow and composition of the flue gases was calculated in this project. The results indicated that the heat exchanger could preheat the air to 127 °C, saving 4400 MWh or 155 000 euro each year.

A heat exchanger with these properties has an investment cost of around 200 000 euro with equipment, installation and engineering included. The design details regarding this heat exchanger are unfortunately confidential.

This gives a payback period of 1.3 years which could be small enough for AkzoNobel to do an investment. However, since it is not known in detail which equipment and piping are included in the investment cost (it is not for example certain that new fans are included in this cost) the payback period could increase.

## 6. CONCLUSIONS

The following conclusions were obtained in the thesis:

- It does not matter for the efficiency of the reformer whether it is summer time or winter time.
- The consumption ratio of natural gas to hydrogen is independent of the production level of hydrogen.
- The steam consumption ratio is lower at higher production levels of hydrogen.
- The steam-to-carbon ratio in Bohus should be decreased from 3.5 kg/Nm<sup>3</sup> to 3.0 kg/Nm<sup>3</sup> to improve the efficiency of the steam reformer. With this ratio it is probably no risk of carbon formation.
- The steam-to-carbon ratio in Alby should be decreased from 10.4 kg/Nm<sup>3</sup> to 9.9 kg/Nm<sup>3</sup> to improve efficiency of the steam reformer. With this new ratio it is no risk of carbon formation.
- A lower reformer temperature in Bohus has the possibility of making the reformer more efficient. The experiments to test this theory were however inconclusive and additional experiments are needed.
- The air to the burners could be preheated with heat recovered from flue gases with an estimated payback period of 1.3 years for required process revisions.

## *7. FUTURE WORK*

Since the master thesis is limited to a certain time period there was insufficient time to do as many experiments as wanted. Some suggestions on future experiments are listed below:

- Test other steam-to-carbon ratios in the reformers to find the optimal ratio.
- Test different pressures in the reformer tubes. A lower pressure could give a higher conversion of the reformer reaction in the tubes. The pressure could be varied by varying the pressure after the natural gas compressors. Beware however, that the PSA-unit might not be able to handle lower pressures.
- The experiment with lower temperature in the reformer furnace should be repeated since the result was so unexpected. A similar experiment could also be done in the Alby steam reformer.
- An experiment with higher temperatures in the furnace could be performed in both Alby and Bohus.
- An experiment with higher temperature before the HTS could be performed in Alby.
- If the composition of the product gas after the steam reformer and HTS could be investigated in both Alby and Bohus it would add much knowledge on how to optimize the reformers.

All experiments would ideally be performed with both high and low production rates.

## 8. REFERENCES

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## *APPENDIX I: THE DATES OF THE EXPERIMENTS*

<b>Experiment</b>	<b>Start date</b>	<b>Finish date</b>
Bohus: Temp from 820 °C to 810 °C	21 Mar 2013	28 Mar 2013
Bohus: S/C ratio from 3.5 kg/Nm <sup>3</sup> to 3.1 kg/Nm <sup>3</sup>	28 Mar 2013	31 Mar 2013
Bohus: S/C ratio from 3.5 kg/Nm <sup>3</sup> to 3.0 kg/Nm <sup>3</sup>	6 May 2013	13 May 2013
Bohus: S/C ratio from 3.5 kg/Nm <sup>3</sup> to 3.0 kg/Nm <sup>3</sup>	27 May 2013	3 Jun 2013
Alby: S/C ratio from 10.4 kg/Nm <sup>3</sup> to 9.9 kg/Nm <sup>3</sup>	2 May 2013	7 May 2013

## APPENDIX II: NOTATIONS

	<b>Liquefied petroleum gas</b>		
$\rho_{LPG}$	Density of LPG	1.99 kg/m <sup>3</sup>	(Mörstedt & Hellsten, 2005)
$M_{LPG}$	Molar mass of LPG	44.1 kg/kmol	(Mörstedt & Hellsten, 2005)
$Cp_{LPG}$	Specific heat of LPG	1.52 $\frac{kJ}{kg * K}$	(Mörstedt & Hellsten, 2005)
$LHV_{LPG}$	Lower heat value for LPG	12.8 kWh/kg	(Swedegas, 2013)
	<b>Natural gas</b>		
$LHV_{NG}$	Lower heat value for NG	11 kWh/kg	(Swedegas, 2013)
	<b>Water</b>		
$Cp_{water}$	Specific heat of water (liquid)	4.18 kJ/(kg * K)	(Mörstedt & Hellsten, 2005)
$Cp_{steam}$	Specific heat of steam	2.1 kJ/(kg * K)	(Mörstedt & Hellsten, 2005)
	<b>Air</b>		
$Cp_{air}$	Specific heat of air	1 kJ/(kg * K)	(Mörstedt & Hellsten, 2005)
$\rho_{air}$	Density of air	1.28 kg/m <sup>3</sup>	(Mörstedt & Hellsten, 2005)
	<b>Hydrogen</b>		
$Cp_{H2}$	Specific heat of hydrogen	0.09 kJ/(kg * K)	(Mörstedt & Hellsten, 2005)
$\rho_{H2}$	Density of hydrogen	14.2 kg/m <sup>3</sup>	(Mörstedt & Hellsten, 2005)
	<b>Carbon dioxide</b>		
$Cp_{CO2}$	Specific heat of carbon dioxide	1.95 kJ/(kg * K)	(Mörstedt & Hellsten, 2005)
$\rho_{CO2}$	Density of carbon dioxide	1.04 kg/m <sup>3</sup>	(Mörstedt & Hellsten, 2005)
	<b>Data for the SMR</b>		
$\Delta H_{SMR}^{Alby}$	Enthalpy of formation SMR for LPG at 825°C	537 kJ/mol	(Liu, Song, & Subramani, 2010)
$\Delta H_{SMR}^{Bohus}$	Enthalpy of formation SMR for LPG at 825°C	225 kJ/mol	(Liu, Song, & Subramani, 2010)
	<b>Others</b>		
$M_V$	Molar volume	0.0227 m <sup>3</sup> /mol	



### APPENDIX III: ALBY

Notation	Tag	Unit	Description	Min production 18/10-19/10 2012	Max production 10/10-12/10 2012
$F_{LPG,burner}^{Alby}$	FC5410A	$Nm^3/h$	Flow of LPG to burner	116	244
$T_{LPG,burner}^{Alby}$	TC5120	$^{\circ}C$	Temperature of LPG to burner	100	100
$F_{air,burner}^{Alby}$	FC5430A	$Nm^3/h$	Flow of air to burner	4317	9491
$T_{air,burner}^{Alby}$	Estimated	$^{\circ}C$	Temperature of air to burner	40	40
$F_{LPG,tubes}^{Alby}$	FC5100A	$Nm^3/h$	Flow of LPG to tubes	234	437
$T_{LPG,tubes}^{Alby}$	TI5102	$^{\circ}C$	Temperature of LPG to tubes	327	350
$\dot{m}_{steam,tubes}^{Alby}$	FC5200A	$kg/h$	Mass flow of steam to tubes	2484	4578
$T_{steam,tubes}^{Alby}$	TI5202A	$^{\circ}C$	Temperature of steam to tubes	436	404
$T_{product\ gas}^{Alby}$	TI5301A	$^{\circ}C$	Temperature of product gas from tubes	819	817
$T_{flue\ gases}^{Alby}$	TI45410A	$^{\circ}C$	Temperature of flue gases from furnace	951	1047
$R_{air/fuel}^{Alby}$	FF5430A	$Nm^3/Nm^3$	Ratio air/fuel to burner	20	23
$\dot{m}_{steam\ tot}^{Alby}$	FI5210	$kg/h$	Mass flow of total product steam	2374	5467
$F_{hydrogen\ prod}^{Alby}$	HC5000	$Nm^3/h$	Flow of product hydrogen	1436	3029
$F_{vent\ gas}^{Alby}$	FC5420A	$Nm^3/h$	Flow of vent gas to burners	1276	2202
$T_{vent\ gas}^{Alby}$	Estimated	$^{\circ}C$	Temperature of vent gas to burners	20	20

## APPENDIX IV: BOHUS

Notation	Tag	Unit	Description	Min production 18/8-20/8 2012	Max production 2/9-4/9 2012
$F_{NG,burner}^{Bohus,A}$	FC5410A	$Nm^3/h$	Flow of NG to burner A	212	362
$F_{NG,burner}^{Bohus,B}$	FC5410B	$Nm^3/h$	Flow of NG to burner B	217	335
$T_{NG,burner}^{Bohus}$	TI0113 TI0213 TI0313	$^{\circ}C$	Temperature of NG to burners	82	86
$F_{air,burner}^{Bohus,A}$	FC5430A	$Nm^3/h$	Flow of air to burner A	5167	9276
$F_{air,burner}^{Bohus,B}$	FC5430B	$Nm^3/h$	Flow of air to burner B	5284	8568
$T_{air,burner}^{Bohus,A}$	TI5433A	$^{\circ}C$	Temperature of air to burner A	48	48
$T_{air,burner}^{Bohus,B}$	TI5433B	$^{\circ}C$	Temperature of air to burner B	37	37
$F_{NG,tubes}^{Bohus,A}$	FC5100A	$Nm^3/h$	Flow of NG to tubes A	550	873
$F_{NG,tubes}^{Bohus,B}$	FC5100B	$Nm^3/h$	Flow of NG to tubes B	550	873
$T_{NG,tubes}^{Bohus}$	TI5102	$^{\circ}C$	Temperature of NG to tubes	372	371
$\dot{m}_{steam,burner}^{Bohus,A}$	FC5200A	$kg/h$	Flow of steam to tubes A	1926	3058
$\dot{m}_{steam,burner}^{Bohus,B}$	FC5200B	$kg/h$	Flow of steam to tubes B	1925	3059
$T_{steam,burner}^{Bohus,A}$	TI5202A	$^{\circ}C$	Temperature of steam to tubes A	400	393
$T_{steam,burner}^{Bohus,B}$	TI5202B	$^{\circ}C$	Temperature of steam to tubes B	401	395
$T_{product\ gas}^{Bohus,A}$	TC5300A	$^{\circ}C$	Temperature of product gas from tubes A	820	820
$T_{product\ gas}^{Bohus,B}$	TC5300B	$^{\circ}C$	Temperature of product gas from tubes B	820	820
$T_{flue\ gases}^{Bohus,A}$	TI45410A	$^{\circ}C$	Temperature of flue gases from furnace A	951	1024
$T_{flue\ gases}^{Bohus,B}$	TI45410B	$^{\circ}C$	Temperature of flue gases from furnace B	961	1038
$R_{air/fuel}^{Bohus,A}$	FF5430A	$Nm^3/Nm^3$	Ratio air/fuel to burner A	11	13
$R_{air/fuel}^{Bohus,B}$	FF5430B	$Nm^3/Nm^3$	Ratio air/fuel to burner B	11	12
$F_{hydrogen\ prod}^{Bohus}$	HC5000	$Nm^3/h$	Flow of product hydrogen	3246	5184
$F_{vent\ gas}^{Bohus}$	FC5420A	$Nm^3/h$	Flow of vent gas to A burners	1336	1874
$F_{vent\ gas}^{Bohus}$	FC5420B	$Nm^3/h$	Flow of vent gas to B burners	1336	1874
$T_{vent\ gas}^{Bohus}$	Estimated	$^{\circ}C$	Temperature of vent gas to burners	40	40