

**"The exergy efficiency of hydrogen-fired gas power plants"**

## Forord

Med denne oppgaven avslutter jeg mine studier ved Norges teknisk naturvitenskapelig universitet (NTNU) i Trondheim.

Opgaven er skrevet ved Institutt for Kjemi og Program for Industriell Økologi.

Det er mange som fortjener å blir nevnt når det gjelder hjelp til mitt arbeide. Først og fremst vil jeg takke stipendiat Anita Zvolinschi for alle hjelp og inspirasjon i forbindelse med oppgaven. Dette gjelder også min professor Signe Kjelstrup som på en svært entusiastisk måte har vært tilgjengelig med veiledning og kommentarer .

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Inger Austrem

## Abstract

The work includes an exergy analysis of the steam reforming process for conversion of natural gas to hydrogen rich gas for use in hydrogen-fired gas power plant. Based on the analysis two sustainability indicators were calculated, the exergetic efficiency and the renewability fraction. The same analysis has been performed for a system using auto thermal reformer (Zvolinschi, Kjelstrup, Bolland and van der Kooi 2002) instead of steam reformer, and the results were compared in order to find the better system of the two based on the indicators. The system using an auto thermal reformer had the best exergetic efficiency, and the renewability fraction was 0 for both systems. One should be aware of insecurities in the results, mainly related to assumptions and limitations with respect to the simulation process.

The two indicators were proposed by Zvolinschi et. al, as a contribution to the introduction of exergy analysis as a tool for industrial ecology. It was concluded that this will be a useful contribution, especially when using system boundaries that include the closure of material cycles. Then one can also calculate the third indicator proposed by Zvolinschi et al., namely the environmental efficiency.

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# 1 Introduction

“An exergy analysis, based on the first and second law of thermodynamics, shows the thermodynamic imperfection of a process, including all quality losses of materials and energy...”

*(Cornelissen, 1997)*

## 1.1 Motivation

The purpose of this thesis is to investigate exergy analysis as a tool in industrial ecology (IE), when discussing optimal process routes.

The use of Life cycle assessment (LCA) when analysing the performance of a process is an established tool in industrial ecology. Exergy analysis is also a much-used method (Cornelissen, 1997), but is not commonly used in IE. In an Exergetic life cycle analysis (ELCA) these two methods are combined. ELCA is a relatively new method and is not fully developed. Zvolinschi, Kjelstrup, Bolland and van der Kooi (2002) argue for the use of three different sustainability indicators, all based on exergy analysis. These indicators are the renewability fraction, the exergetic efficiency, and the environmental efficiency.

The renewability fraction and the exergetic efficiency will be calculated for the systems that will be looked at here in order to examine their applicability. Only a specific part of the life cycle will be looked at in the systems to be analysed, and the two indicators that will be calculated are therefore not based on an analysis of a closed cycle. The environmental efficiency deals with closing the cycle and will not be looked at here, since the material cycles in this work not will be closed.

To illustrate the applicability of exergy analysis, the process for reforming natural gas to hydrogen for use in hydrogen fired gas power plants is chosen as case study. An exergy balance had already been performed for such a system using an auto thermal reformer (Zvolinschi et al., 2002). It is interesting to look at alternatives for the reforming process to see if the performance of the system could be improved. Here the auto thermal reformer will be replaced with a steam reformer for the purpose of comparing the systems with respect to exergy losses and efficiency during the reforming process. Two parameters, the steam to carbon ratio and the reformer temperature, will be varied for the steam reformer alternative to see how this will affect the result. The system will however not be optimised.

Although the main subject is to discuss the application of exergy analysis and the sustainability indicators based on the analysis, an underlying goal is of course to get reliable values that can be used when choosing between the systems.

## 2 Exergy analysis

### 2.1 Industrial ecology

In 1987 the United Nations' World Commission on Environment and Development (WCED), also known as the Brundtland Commission released a report called *Our Common Future*. In this report they defined sustainable development as "development that meets the needs of the present without compromising the ability of future generations to meet their own needs." (WCED, 1987). After this report came out the concept of sustainable development has been a well-known and well-used term, although some have chosen to use alternative definitions of the concept.

Industrial ecology (IE) is an approach to sustainable manufacturing (Graedel & Allenby, 1995). Industrial ecology uses a long-term perspective and seeks holistic solutions. The solutions should not just include the manufacturing firms, but also human activities concerned with acts of production, including the energy and material transformations in household and consumption. Material resources, energy and capital are factors to be optimized. This optimization means reduction of resource-use and energy input, as well as pollution prevention. Connelly (1998) expresses it like this: "*IE reflects an ongoing shift from "end-of-pipe" pollution control methods towards more design-oriented, inter-industry strategies that emphasize re-use of industrial waste streams with the goal of developing "industrial ecosystems" that exhibit increasingly cyclical resource use patterns.*"

### 2.2 Exergetic life cycle analysis (ELCA)

Life-cycle assessment (LCA) is an established tool for industrial ecology. The essence of LCA is to locate and evaluate environmental burdens related to the whole life cycle of a product, a process or an activity, by identifying and quantifying material and energy use and environmental releases (Graedel & Allenby, 1995). LCA can be used to both look at one system to estimate potentials for improvement during the cycle, and also to compare two or more systems in respect of the environmental performance through the total life cycle of the systems.

In order to introduce exergy analysis into industrial ecology, an extension of the traditional LCA is proposed. Exergy analysis is not a new method, although Cornelissen (1997) on basis of a literature review concludes that use of the method is yet limited in process industry. In the same work he argues for how this extension can make LCA more powerful.

Energy balances are a common part of LCA, but an exergy balance can in many ways be more valuable. Cornelissen says: "*In an energy analysis, based on the first law of*



*thermodynamics, all forms of energy are considered to be equivalent. The loss of quality of energy is not taken into account. For example, the change of the quality of thermal energy as it is transferred from a higher to a lower temperature can not be demonstrated in an energy analysis. It shows the energy flow to be continuous. An exergy analysis, based on the first and second law of thermodynamics, shows the thermodynamic imperfection of a process, including all quality losses of materials and energy, including the one just described.”*

Also Connely (1998) emphasized in his thesis some advantages. He found the primary strengths to be:

- a) it is founded on first and second law principles and therefore allows variations and losses of energy quality to be considered,*
- b) since all physical resources have some level of exergy which may be defined relative to an environmental groundstate, a wide range of material and energy transformations may be included in analyses, and*
- c) thermodynamic representation of environmentally acceptable resource states may be used to optimise process design subject to specific environmental constraints.*

Cornelissen presented a method for performing ELCA. The framework is similar with the one for a traditional LCA, see for example Graedel and Allenby (1995).

This work concerns a cycle that is not closed. An exergy analysis will be performed for the system within its boundaries, and two sustainability indicators will be calculated based on this.

## 2.3 Exergy

The theory in this part is mainly taken from Kotas (1995).

The first law of thermodynamics states that when looking at the system and surroundings together, the total amount of energy will remain constant. The first law treats the different forms of energy as equivalent and does not distinguish the difference in quality between among other, mechanical and thermal energy.

From the second law of thermodynamics, we have that a process producing no other effect than the transfer of heat from a lower temperature body to a higher temperature body is impossible. In the same way, thermal energy cannot be fully converted to mechanical energy without losses. The losses in these processes are included in the second law of thermodynamics. This law can be expressed in terms of entropy. For an open system, the surroundings also has to be considered, giving the following entropy balance:

$$(\Delta S)_{\text{system}} + (\Delta S)_{\text{surroundings}} \geq 0 \quad (2.1)$$

Here  $(\Delta S)_{\text{system}}$  and  $(\Delta S)_{\text{surroundings}}$  are the change in entropy for system and surroundings respectively. If the process is reversible the sum of them will be zero. If the process is irreversible, the sum will be positive. All real processes are irreversible, and will thereby produce entropy.

Energy can be divided into two different forms of energy, ordered and disordered. Kotas says that disordered energy “characterised by entropy, is variable and depends both on the form of energy (chemical, thermal, etc.) and on the parameters of the energy carrier and of the environment.” While ordered energy “which are not characterised by entropy, have invariant quality and are fully convertible, through work interaction, to other forms of energy.”

Kotas refers to energy quality as “capacity to cause change”. Thermal energy is disordered energy and mechanical energy is ordered energy, and the same amount of these two energy forms is therefore able to cause different amounts of work. As a measure of the ability to do work, the concept of exergy is introduced. Exergy is defined as the maximal obtainable potential of work of a material or energy flow in relation to the environment.

Exergy analysis is a method that can determine how much potential work is lost during a process, and to identify where in the process the greatest losses are. The analysis can then be used as a starting point for process improvement.

When calculating the exergy content in a stream, effects caused by changes in kinetic, potential, nuclear and magnetic energy are commonly neglected. The two forms of exergy being important are physical and chemical exergy. Both forms will be discussed further below.

The total exergy associated with a stream is then given by:

$$\varepsilon = \varepsilon_{\text{ph}} + \varepsilon_{\text{ch}} \quad (2.2)$$

### 2.3.1 Physical exergy

Kotas (1995) defines physical exergy like this:

*Physical exergy is equal to the maximum amount of work obtainable when the stream of substance is brought from its initial state to the environmental state defined by  $P_0$  and  $T_0$ , by physical processes involving only thermal interaction with the environment.*

The physical exergy for a stream is given by the following expression:

$$\varepsilon_{\text{ph}} = h - h_0 - T_0 (s - s_0) \quad (2.3)$$

Here  $h$  and  $s$  are the enthalpy and entropy of the stream at the actual temperature  $T$  and pressure  $p$ , while  $h_0$  and  $s_0$  are the same properties at the environmental conditions  $T_0$  and  $p_0$ . Values for enthalpy and entropy can be found in thermodynamic tables.

### 2.3.2 Chemical exergy

In Kotas (1995), the following definition of chemical exergy is used:

*Chemical exergy is equal to the maximum amount of work obtainable when the substance under consideration is brought from the environmental state to the dead state by processes involving heat transfer and exchange of substances only with the environment.*

When calculating physical exergy, the final state of the stream is the environmental state, defined by  $P_0$  and  $T_0$ . For calculation of chemical exergy however, this will be the initial state in the reversible processes being used to establish a value for the chemical exergy of the stream. The final state will be what is called “dead state”, which means the substance is in thermal, mechanical and chemical equilibrium with the conceptual environment.

The chemical exergy for a substance is measured in relation to the chemical potential of a reference component. This reference component must be in equilibrium with the environment. As an example,  $N_2$  in the stream will have its reference component in atmospheric  $N_2$  in a state of environmental temperature and the partial pressure at which  $N_2$  exist in the atmosphere. If the system being analysed not is containing reference substances, the chemical exergy of the compound can be calculated from the standard exergy of reference species.

For a mixture of ideal gases the chemical exergy can be found using:

$$\varepsilon_{ch} = \sum(x_i \varepsilon_{0i}) + RT_0 \sum(x_i \ln x_i) \quad (2.4)$$

The chemical exergy is the sum of the exergy for the components of the mixture, in addition to the contribution gained when the pure components are being mixed into the stream.

The chemical exergy for component  $i$  is given by  $\varepsilon_{0i}$  and  $x_i$  represents the mole fraction of component  $i$  in the mixture.  $R$  is the gas constant and  $T_0$  is the temperature of the environment.

The last part of the equation is identical to the Gibbs energy of mixing:

$$\Delta G_{mix} = nRT \sum(x_i \ln x_i) \quad (2.5)$$

Where  $n$  gives the number of moles. The mixing of gases introduced into the same container is spontaneous and corresponds to a decrease in Gibbs energy.

## 2.4 Mass and energy balances

Mass and energy balances should be performed in consistency with the exergy balance. This can verify whether all the flows are included and balanced. All balances here are defined for a steady state process.

Mass balance for a unit or a control region can be written:

$$\Sigma m_{in} = \Sigma m_{out} \quad (2.6)$$

where  $m_{in}$  and  $m_{out}$  is mass flow entering and leaving the control region respectively.

The energy balance includes heat of reaction as well as work and heat. Heat entering ( $Q$ ) and work ( $\dot{W}$ ) leaving the system boundaries are defined as positive. The energy balance can then be written:

$$-\dot{W} + Q = \Sigma m_i (h_{out,i} - h_{in,i}) \quad (2.7)$$

Heat of reaction is the difference in enthalpy for the incoming and leaving stream ( $h_{out,i} - h_{in,i}$ ).

## 2.5 Exergy balance

The exergy balance can be written as:

$$\dot{E}_{in} + \dot{E}^Q = \dot{E}_{out} + \dot{I} + \dot{W} \quad (2.8)$$

The exergy associated with the mass streams are represented by  $\dot{E}_{in}$  and  $\dot{E}_{out}$ , for leaving and entering exergy respectively. This includes both chemical and physical exergy.

As in the energy balance,  $\dot{W}$  represents the work being exchanged between the system and the environment.

The irreversibility due to the process being real and not ideal is given by  $\dot{I}$ . From the second law of thermodynamics, it follows that  $\dot{I}$  has to be positive.

$\dot{E}^Q$  represents exergy connected to heat going in to or leaving the system/control region.

### 2.5.1 Efficiency defect

If the process contains more than one unit, it can be interesting to compare the irreversibility. One way to do this is to find the efficiency defect for each unit. The *efficiency defect* of the  $i$ -th unit (control region) is defined:

$$\delta_i = \dot{I}_i / \Sigma \Delta \dot{E}_{in} \quad (2.9)$$

Here the lost exergy, the irreversibility  $\dot{I}_i$ , for unit i is divided on the total exergy,  $\dot{E}_{in}$ , entering the system.

### 3 Indicators of sustainability

Zvolinschi et al. (2002) recommend the use of three indicators on basis of exergy analysis. The indicators are based on three restrictions required to assess long-term sustainability; “(1) the resource restriction caused by the scarcity and environmental impacts of resource consumption (the preferred resource is a renewable one); (2) the efficiency restriction caused by the second law of thermodynamics; and (3) the assimilation and degradation restrictions caused by the limited capacity of the ecological systems to offer natural material cycles that bring back all outputs flows of the technological system to the virgin state.” The three proposed indicators are the renewability fraction ( $\alpha$ ), the exergetic efficiency ( $\eta$ ), and the environmental efficiency ( $\xi$ ), based on restriction (1), (2) and (3) respectively.

The environmental efficiency includes the exergetic cost to close the material cycles for emissions and products at the end of their lifetime. Since the cycles are not closed in this work, only the renewability fraction ( $\alpha$ ) and the exergetic efficiency ( $\eta$ ) will be further discussed.

#### 3.1 Renewability fraction

The renewability fraction divides the input exergy, into renewable and non-renewable. Renewable resources include sun, water, CO<sub>2</sub>, while resources like minerals and fossil fuels are non-renewable. The condition of the resource is also of importance for how renewability is defined here. If energy or other resources (non-renewable) are required to bring the resources to desired conditions, it will not be seen as renewable.

The renewability fraction is defined:

$$\alpha = \frac{\sum E_{in}^{renewable}}{(\sum E_{in}^{renewable} + \sum E_{in}^{non-renewable})} \quad (3.1)$$

For a complete calculation, the exergy content of material and energy flows should be found throughout the productions process, the emission abatement process and the closing material cycle process. A complete analysis like this is not done in the work presented here. What is included will be discussed later.

## 3.2 Exergetic efficiency

Different definitions are being used for exergy efficiency. Cornelissen (1997) discusses three types, and they will shortly be presented here.

Common for the three types of efficiency is that they are valid for steady state processes, where the system boundaries are clearly defined and all irreversibilities associated with the process being considered are included.

### *a) Simple efficiency*

This form of efficiency is based on the exergy balance for incoming and outgoing flows;

$$\dot{E}_{in} = \dot{E}_{out} + \dot{I} \quad (3.2)$$

Where  $\dot{I}$  is the irreversibility, and all forms of exergy entering and leaving the control region are included in  $\dot{E}_{in}$  and  $\dot{E}_{out}$ . The efficiency is then given by the ratio of incoming and outgoing exergy:

$$\eta = \dot{E}_{out} / \dot{E}_{in} \quad (3.3)$$

### *b) Rational efficiency*

Rational efficiency is defined by Kotas (1995). This efficiency is given by the ratio of the desired exergy output to the exergy used:

$$\Psi = \dot{E}_{desired\ output} / \dot{E}_{used} \quad (3.4)$$

Desired exergy output is determined by examining the function of the system, but will also include exergy related to any useful by-product produced by the system.

### *c) Efficiency with transiting exergy*

Efficiency with transiting energy is seen as an improvement of the simple efficiency. Here untransformed components are subtracted from the incoming and the outgoing components. The efficiency will be defined by:

$$\eta_e = (\dot{E}_{out} - \dot{E}_{tr}) / (\dot{E}_{in} - \dot{E}_{tr}) \quad (3.5)$$

where  $\dot{E}_{tr}$  is the transiting energy. Sorin et. al. (1994) use this type of efficiency and says: "the transiting exergy can be considered as the part of the exergy which traverses a system without taking any part in the mechanical, thermal or chemical changes which take place in the system. To some extent, the transiting energy is analogous to an inert species traversing a chemical reactor without being involved in the chemical rearrangements taking place in the

reactor (for the analogy to be totally exact, the reactor should be isothermal and isobaric). The amount of transiting exergy does not affect the thermodynamic efficiency of the process and it should be subtracted from the incoming and outgoing exergy flows before the efficiency is computed.”

Zvolinschi et al. (2002) use in their report the following equation to calculate the exergetic efficiency:

$$\eta = E_{\text{out}}^{\text{useful}} / E_{\text{in}}^{\text{total}} \quad (3.6)$$

The useful exergy output includes both the exergy of the desired product as well as exergy of useful by-products. This is similar to the efficiency used by Kotas (1995), but with slightly different notation.

This type of efficiency will be used here.



## 4 Process description

### 4.1 Hydrogen-fired gas power plant

Norway is a country with large amounts of energy resources like natural gas, oil and hydropower. Traditionally the power production in Norway has almost entirely been based on hydropower.

During the last years, several gas-fired power plants have been planned around Norway. If conventional natural gas fired power plants are used, the total CO<sub>2</sub> emission for Norway will have a large increase. This will work against the Kyoto protocol where Norway among other countries has committed to lie within the individual quotas set for permission of total CO<sub>2</sub> emissions per country.

To be able to avoid the large emissions, different companies are working on the development of gas power plants with no or reduced amounts of CO<sub>2</sub> emissions. This can be realised through different solutions. One way is to take out CO<sub>2</sub> from the exhaust gas leaving the gas turbine. A problem with this method is that the exhaust gas is very diluted, making the separation of CO<sub>2</sub> both difficult and expensive. (Norsk Hydrogenforum, 2002)

A more efficient solution is to use a reformer to convert the natural gas before sending it to the gas turbine. The product gas from the reformer is as mixture of hydrogen and carbon oxides. This mixture is often referred to as synthesis gas (Hinderink, 1996). The CO<sub>2</sub> can then be captured before the turbine leaving a gas rich on hydrogen and with only minor amounts of carbon to be burned. The separated CO<sub>2</sub> can go to deposition or be utilized, for example to increase the extraction of oil (Norsk Hydrogenforum, 2002).

Synthesis gas can be produced for several purposes. Depending on factors like desired ratio between the gases and required capacity for the plant, different reforming solutions can be used. Other motives for choosing one reforming type over the other can be both economical as well as environmental.

In this work two solutions are being compared; the auto-thermal reformer and the steam reformer.

## 4.2 The systems

Zvolinschi et al. (2002) performed an exergy analysis for two gas power plants, both combined cycle. A conventional natural gas fired power plant was compared to a power plant using hydrogen as fuel. In the latter case an auto-thermal reformer was used to convert natural gas to hydrogen. The exergetic efficiency was found to be 44.9 % for the hydrogen fired gas power plant and 55.4 % for the natural gas fired power plant.

It is interesting to see if the efficiency of the hydrogen fired gas power plant can be improved. Here the auto-thermal reformer will be replaced with a steam reformer. An exergy analysis will then be performed for the new reforming system with the purpose of comparing the two systems. Both the exergetic efficiency and the renewability fraction will be calculated and compared. The reformer temperature and the steam to carbon ratio will be varied to see what effect this has on the results for the steam reformer.

The system using an auto-thermal reformer will not be analyzed again here. The results from the report of Zvolinschi et al. will be used instead.

A description of the two reforming systems is following. In this analysis, the main reformer makes the difference for the two systems. The other units are the same, although some conditions can be different. Figure 4.1 and 4.2 show the reforming process for the two each of the two systems.

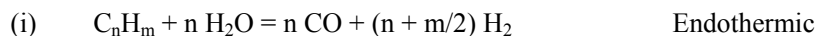
A discussion of the system boundaries will be presented later, and so will also the conditions. For simplicity the two systems using auto-thermal reformer and steam reformer will be named ATR and STR respectively.

## 4.3 The reforming process

Most of the reforming process is described as in Moulijn Moulijn, Makkee and van Diepen, (2001). Where other references are used, this is specified.

### 4.3.1 Pre-reformer

A pre-reformer is used when the fuel contains higher hydrocarbons. The pre-reformer is a catalytic fixed bed-reactor operating adiabatically installed upstream the steam reformer. Reaction (i) represents the reactions running in the pre-reformer.



The pre-reformer is equal for both reforming processes.

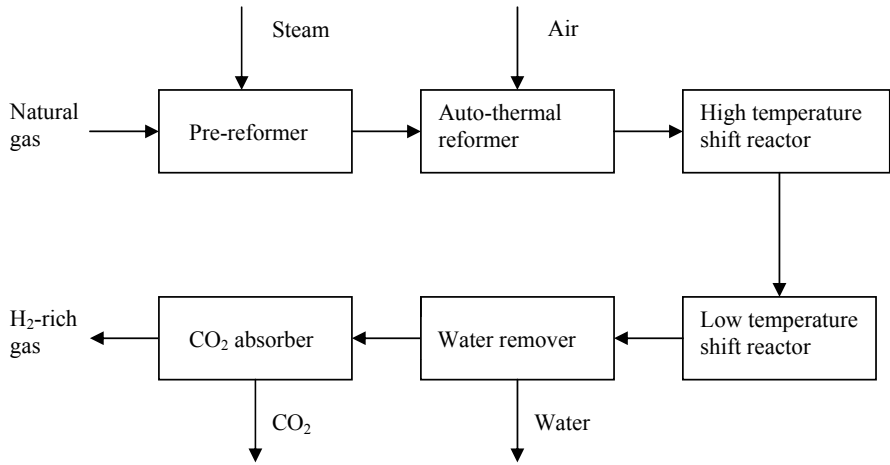


Figure 4.1: Reforming process for the ATR system

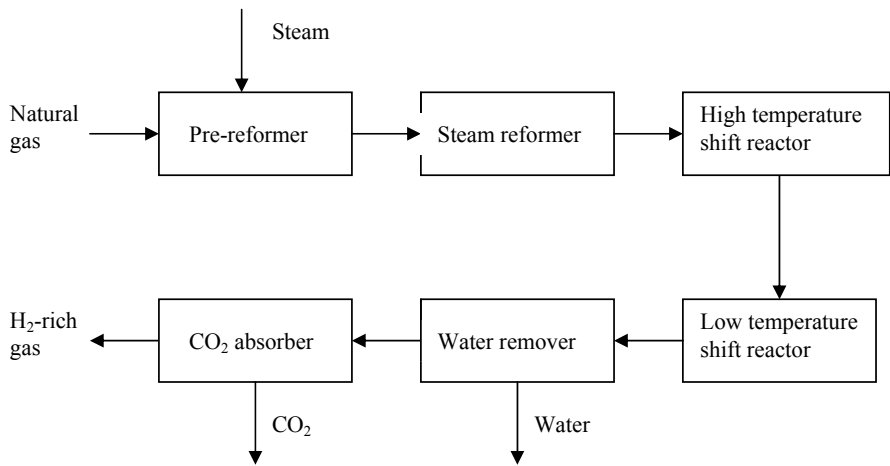


Figure 4.2: Reforming process for the STR system

### 4.3.2 Reformer

#### a) Auto-thermal reformer

The product stream from the pre-reformer is together with preheated air the feed streams in the ATR. Methane from the natural gas is converted in a partial oxidation reaction to hydrogen and CO (ii). A catalyst is present in the reformer.

The reaction and its corresponding Gibbs energy of reaction is given by:



Practically all of the available oxygen is consumed in this phase. The reaction is exothermic.

#### b) Steam reformer

In a steam reformer, methane and steam from the product stream of the pre-reformer are converted to synthesis gas in the presence of a catalyst. No additional steam or air is added.

The main reactions and corresponding Gibbs energy of reaction in a steam reforming process are:

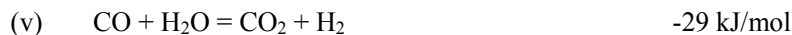


Methane and CO is converted to hydrogen and CO<sub>2</sub> as shown in reaction (iii) and (iv). Natural gas in the presence of air is burned in the reformer furnace to supply the heat needed to run the reactions.

### 4.3.3 Purification

The gas will in addition to hydrogen contain varying amounts of CO, CO<sub>2</sub>, H<sub>2</sub>O and CH<sub>4</sub> when it leaves the reformer unit. This mixture is also called synthesis gas.

In two shift reactors, high temperature and low temperature respectively; CO is converted to CO<sub>2</sub> in a water-gas reaction (v):



After the conversion reactors, the gases are being purified. Water will be removed in a physical separation, while CO<sub>2</sub> will be captured by means of chemical absorption using monoethanolamine at low temperature and high pressure.

Normally the natural gas has to be desulphurized before the reforming process, since sulphur

is a poison for metal catalysts. However, for the Norwegian natural gas the sulphur content is very low (IEA, 2000) and therefore this unit is not included in the analysis.

#### **4.3.4 Carbon formation**

One of the problems that can be experienced if the conditions not are right in the reformer is formation of carbon. If too much carbon is produced, the active sites of the catalyst can be deactivated by the coke deposition. In addition, the reformer tubes can be totally blocked when the carbon deposits grow that large, resulting in the development of what is called 'hot spots'. Choosing conditions that cause only limited carbon formation can prevent this.

#### **4.3.5 Catalysts**

Catalysts are required to run the reactions. This is important for the kinetics, but has no effect on the thermodynamic. The catalyst is not considered in the simulations and will not be discussed further in this work.

### **4.4 Power generation**

Although the intention with the systems is to produce power, the turbines that generate the power are outside the system boundaries. These units are still of interest since the total power gained from the system is required to find the exergetic efficiency.

In a combined cycle, power is produced both in a gas turbine and through a heat recovery steam generator (HRSG). A more detailed description of the power production processes can be found in Speich (2000).

## **5 Method**

### **5.1 The system**

The reforming process is already described, but the system boundaries are yet to be specified. They will be presented here together with a definition of the functional unit for the system.

#### **5.1.1 System boundaries**

The system boundaries for the STR system are shown in figure 5.1. The exergy analysis in this work is limited to the units within these boundaries.

The system starts with feed streams entering the reforming process or the combustion chamber. The steam reformer process was described in chapter 4. Conditions will be presented later.

In addition to the feed streams, power and duty are also added to the system. Steam used for heat exchangers is entering and leaving the system boundaries as well.

The units producing power are outside the boundaries. However they accomplish the function (as defined below) and the power production is included when calculating the exergetic efficiency. However, no exergy balance is performed for these units, in order to keep the focus on the reforming process.

Extraction of natural gas is not included in the boundaries and neither is treatment of exhaust gas and other unwanted by-products. This means that the system does not represent a closed cycle.

#### **5.1.2 Functional unit**

The system produces gas and steam for power production. Power production is defined as the function of the system, in order to decide how useful the exergy leaving the system is.

The functional unit was chosen to be 400 MW, which is the same used by Zvolinschi in the analysis of the ATR system. The proportions of the power generating units will then be the same for the two systems.

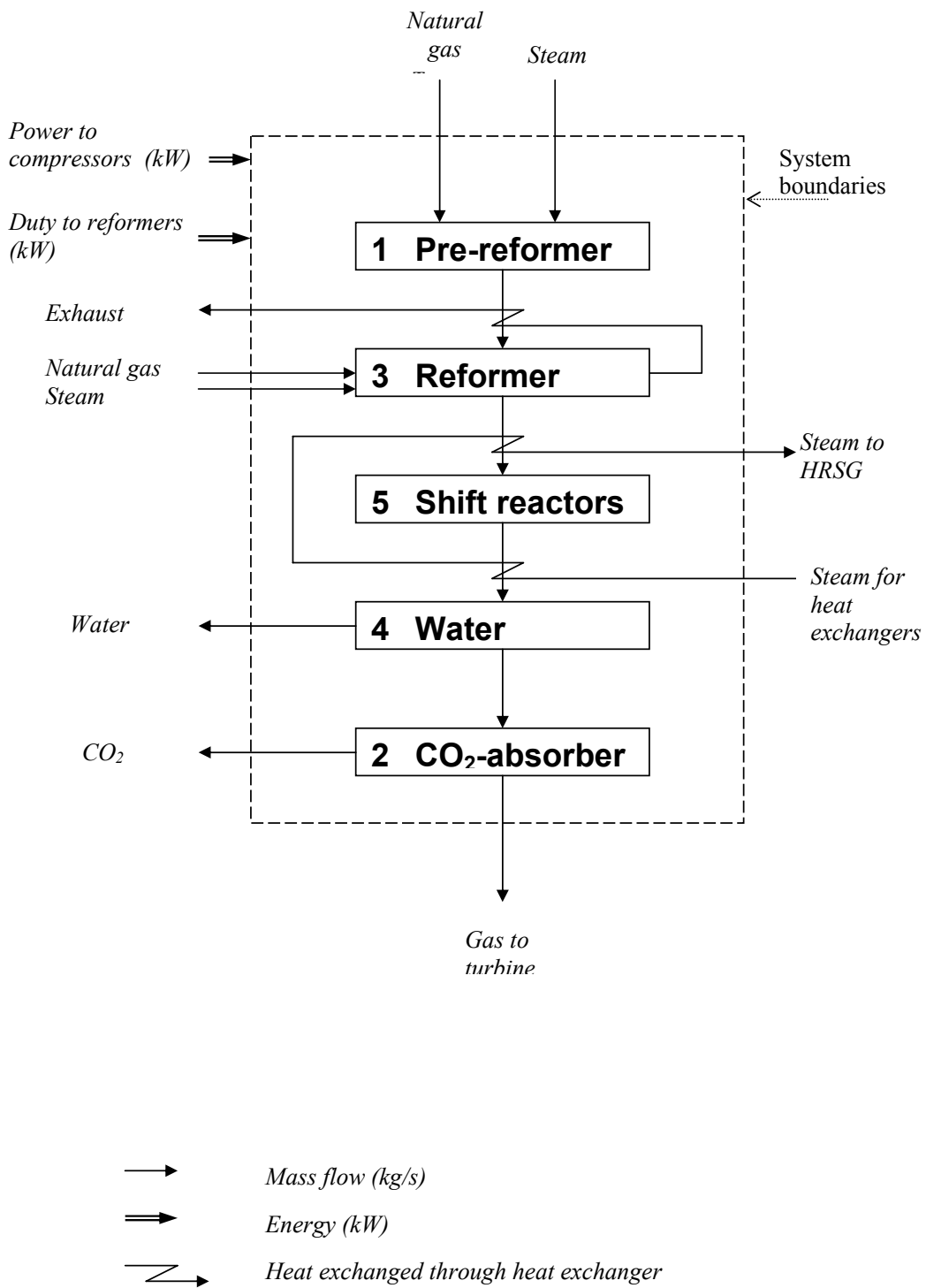


Figure 5.1: System boundaries for the STR system

## 5.2 Two variables - 7 Cases

It was decided to look at the effect of two variables, for the STR system. The temperature in the reformer and the steam to carbon ratio for the feed stream were chosen as variables, since it was assumed that these variables could affect the results.

Problems were experienced during the simulation for two of the cases. The error leading to these problems was not found and it was chosen to not look at these two alternatives further. The seven cases being left for analysis are presented in table 5.1.

Case	Steam/carbon (mol/mol)	Reformer temperature (°C)
1	3.5	815
2	3.5	850
3	3.5	900
4	3.0	815
6	3.0	900
8	2.5	850
9	2.5	900

**Table 5.1:** Overview of the two variables, in the 7 cases being analysed.

## 5.3 Simulation with PRO/II

The simulation tool PRO/II was used to simulate the reforming process and to provide flow sheet calculations. Before the simulations in PRO/II could be carried out, conditions for the units and the streams included in the reforming process had to be given. Flow sheet calculations could be provided when all required data was set.

Tables in Appendix 2 give data related to each stream in the flow sheet (see Appendix 1) for each of the seven cases being analysed.

### 5.3.1 Operating conditions

Some operating conditions will be presented here. In Appendix 5 more conditions for the STR system are given.

#### *Conditions of the environment*

For the simulation process and calculations it is assumed that the conditions of the environment is 15° C and 1.013 bar. It is not considered whether more extreme conditions can have an impact of relevance on the results.



## Feed streams

### a) Composition

Natural gas and steam are the only feed streams for the reforming process in the STR system. In addition, air is required for the combustion process; while natural gas is being burned to give heat for the reforming process.

In the ATR system, natural gas is mixed with steam before the pre-reformer and then air is mixed in, in the main reformer.

The composition of the feed streams on mole fraction are given in table 5.2.

Component	Natural gas	Steam	Air
O <sub>2</sub>			0.2085
N <sub>2</sub>	0.004		0.7702
CO <sub>2</sub>	0.018		0.0030
H <sub>2</sub> O		1	0.0101
Methane	0.839		
Ethane	0.092		
Propane	0.033		
Butane	0.014		
Ar			0.0082

**Table 5.2:** Composition of feed streams on mole fraction

The composition of the natural gas is based on a pipeline quality gas from the southern part of the Norwegian offshore reserves (IEA, 2000).

**Merknad:** Taken from "Leading options for the capture of CO<sub>2</sub> emissions at power stations"

### b) Conditions

The conditions of the feed streams entering the STR system were the same as for streams entering the ATR system. Pressure and temperature for the incoming streams are given in table 5.3.

Stream	Temperature (°C)	Pressure (bar)
Air	15	1.01
Natural gas	25	14.00
Steam	470	23.10

**Table 5.3:** Conditions for feed streams

In the STR system, the natural gas going to the reforming process was compressed to a pressure of 30 bar and a temperature of 5°C before being mixed with steam. The air was compressed to 14 bar and 360°C before entering the combustor.

### 5.3.2 Modelling the units in PRO/II

Adjustments with respect to the actual units, had to be done when modelling some of the units in the simulation program. Some of these adjustments have an influence on the calculations and they will therefore be commented here.

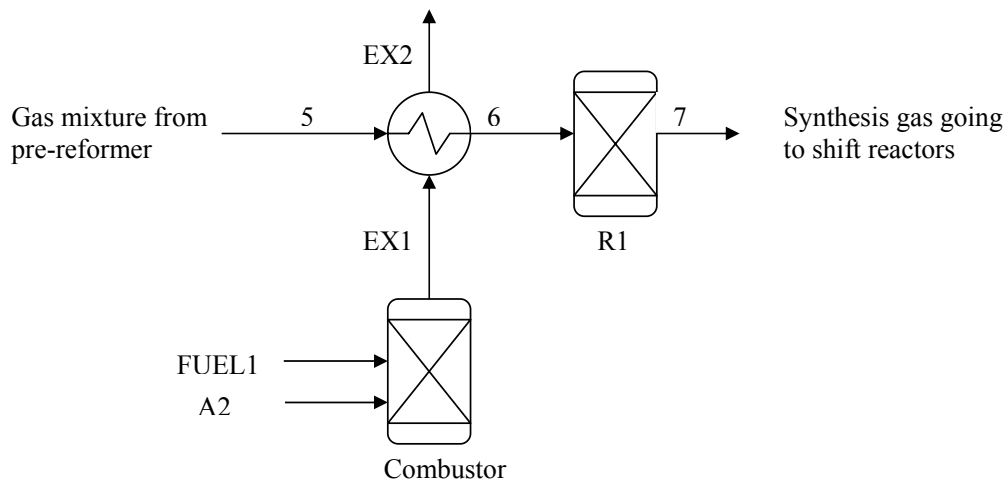
#### *Reactors*

PRO/II allows the user to choose between different reactors with individual specifications. In this simulation Gibbs reactor was used to model all reactor units. The Gibbs Reactor simulates a chemical reactor by solving the heat and material balances based on minimizing the free energy of the components in the reaction.

The reactors can be either adiabatic or isothermal. Adiabatic reactors were used for both the pre-reformer and the shift-reactors (HTS and LTS). A description of the steam reformer model will be given below.

#### *Modelling the steam reformer*

PRO/II do not contain a single unit that could model the steam reformer satisfyingly. Instead different units were arranged so that they together could represent a steam reformer. Figure 5.2 shows what units the model was compounded of. Names on streams and units are identical to what is used in the simulation in PRO/II (see flow sheet in Appendix 1).



**Figur 5.1:** Model of the steam reformer arrangement used in simulation in PRO/II

Fuel (natural gas) was burned in the combustor unit in order to supply the reforming reaction with required heat. The heat was transferred from the exhaust gas to the reaction mixture by a heat exchanger upstream the reformer. The gas mixture was heated up to the reforming temperature. In order to keep this temperature through the reforming process an isothermal reformer was used. This means however that additional heat was required. If an adiabatic reactor was used instead, the temperature would decrease through the reactor. In order to have the desired outlet temperature, the gas mixture would need to be heated up to a very high temperature before going in to the reformer unit. As discussed earlier, carbon formation is a problem at to high temperatures and this was therefore not seen as an alternative.

For the calculations all units “included” in the steam reformer model was treated as one unit. The modifications in the model, with respect to a real reactor will in all probability impact the results.

#### *Stream calculators*

In the simulations in PRO/II a stream calculator was used to model both the water removal unit and the unit that absorbs CO<sub>2</sub>. The stream calculator allows you to split the input stream into two streams with different composition. This was wanted for both these units, in order to take out water and CO<sub>2</sub>.

##### *a) CO<sub>2</sub> absorption*

90% of the CO<sub>2</sub> is taken out in this unit. PRO/II calculated the duty required for this, but it is assumed that extra duty needs to be added in the absorbing process. Corti and Lombardi (2002) describe the process, saying that 3.4 MJ is required per kilo CO<sub>2</sub> removed. This value is much higher than the value calculated by PRO/II. It is assumed 3.4 MJ/ kg CO<sub>2</sub> can be used here even though the conditions are somewhat different from the conditions in Corti and Lombardis work.

The purpose with the energy balance is to make sure all streams and energy transfers included in the simulation by PRO/II are included and balanced. The extra duty will therefore not be included in the energy balance. However it will be included in the exergy balance. A conversion factor of 0.3 will be used, since the exergy content in a heat stream is lower than the energy content.

##### *b) Water removal*

A stream calculator was also used to model the water removal unit. The energy required for this unit is calculated from PRO/II, and it is assumed that no additional heat or work had to be added.

#### *Heat exchangers*

The heat exchangers transfer heat between two streams. The heat transfer is balanced by having one stream being heated and one cooled. The streams do not come into direct contact with each other, but are separated by the tube wall.

The heat exchangers in this work are all counter current. Desired outlet temperature is set for one of the streams, and the outlet temperature related to the other stream will then be calculated.

In the simulated process one of the heat exchangers (E7) was not balanced with two streams. PRO/II calculated the duty required in order to balance the energy balance for this unit.

## 5.4 GT PRO

GT PRO was used to calculate total amount of power that could be generated from the systems output streams. Feed streams to the power-producing units included both the gas mixture from the reforming process and steam used in heat exchangers. The conditions and composition of the streams had to be given, together with some ambient conditions, before the power production could be calculated.

### *Gas turbine*

The product gas from the reforming process has a concentration of more than 90 % hydrogen when it is fed to the gas turbine. For a conventional turbine the gas would need to be diluted with an inert gas.

It is assumed that the gas mixture can be used like this, either now or in the future. GT PRO calculates how much power can be generated from the streams entering the power plant based on thermodynamic computations. If an inert gas needs to be added, there is reason to believe that additional exergy would be required in order to supply the inert gas at desired conditions. The effect this would have on the exergy efficiency depend on the choice of inert gas and on at what conditions.

## 5.5 Calculations

### 5.5.1 Exergy

Calculations of physical and chemical exergy were done separately.

#### *a) Physical exergy*

The values needed to calculate physical exergy was provided from PRO/II. In PRO/II they define the availability function:

$$B = H - TS \quad (5.1)$$

Where:

B = availability

H = enthalpy

T = temperature

S = entropy

PRO/II provides different availability functions. Physical exergy as defined in equation (2.3) can be found by using two of these availability functions, namely B(EXS) and B(EVS). B(EXS) is the availability function at existing state while B(EVS) is at environmental state. From equation (2.3) we have the definition of physical exergy:

$$\varepsilon_{ph} = h - h_0 - T_0 (s - s_0) \quad (2.3)$$

If using the two availability functions, physical exergy can be written as:

$$\varepsilon_{ph} = B(EXS) - B(EVS) \quad (5.2)$$

The environmental temperature  $T_0$  in equation (2.3) is the same as T used in equation (5.1). For B(EXS), H and S in equation (5.1) is the same as h and s in equation (2.3), while for B(EVS), H and S are equal to  $h_0$  and  $s_0$ .

#### *b) Chemical exergy*

The chemical exergy was calculated from equation (2.4).

The environmental temperature,  $T_0$ , was chosen to be 15° C. A table showing the values used for the chemical exergy of each component is given in Appendix 6. All values are taken from Kotas (1995).

### *c) Exergy balance*

Exergy balances are performed according to equation (?). Exergy in and out of each unit include the physical and chemical exergy. Work supplied to the compressors are found by calculations done by PRO/II .

Duty is required for the steam reformer and the CO<sub>2</sub> absorber unit.

The exergy content of the duty to the reformer is not specified. Duty required to the steam reformer is included in the exergy balance without using any conversion factor. This represents an inaccuracy in the calculations since the duty is heat that should come from combustion of natural gas. To be correct the exergy value should be equal to the exergy that would enter with natural gas required to contribute with the additional duty.

The exergy coming with required duty to the CO<sub>2</sub> absorber is calculated as described in chapter 5.3.2.

## **5.5.2 Energy and mass-balance calculations**

The mass and energy balances are defined in equation (2.6) and (2.7). All required values for these balances were provided by PRO/II.

Duty required to the steam reformer is calculated by PRO/II and is included in the energy balance.

For the CO<sub>2</sub> absorber the additional duty is not included in the energy balance since this value is not taken from the simulation in PRO/II.

## **5.5.3 Sustainability indicators**

The sustainability indicators were calculated according to equation (3.1) and (3.6).

### *a) Renewability fraction*

Air is the only renewable resource entering the system boundaries when the process is running at steady state. All other resources where considered as non-renewable.

### *b) Exergetic efficiency*

The exergy input includes all exergy input to the system boundaries. This includes both exergy in connection to the mass stream and exergy with supplied power and duty.

Useful exergy output is found by calculating how much power can be generated from the output of the system. Power required for the compressors in the system is deducted.

## 6 Results

### 6.1 Steam reformer

Here the results from the simulation and calculations for the seven cases for the STR system will be presented.

#### 6.1.1 Results from simulation in PRO/II

The results from simulations of the STR system in PRO/II are presented in tables in Appendix 2. These tables include the composition on mole fraction, together with stream properties and conditions for each stream included in the STR system. The flow-sheet showing the process simulated in PRO/II is given in Appendix 1

More detailed results used for the mass, energy and exergy balances are presented later.

It is important to notice that not all of the presented results are related to a total power production of 400 MW. It will be specified when the values are scaled to match a power production of 400 MW.

#### 6.1.2 Power production

For the simulations in PRO/II the proportions of the mass flows were chosen arbitrarily. GT PRO calculated the power production based on these numbers. Some results are scaled to match a power production of 400 MW.

The total power production before scaling and the scaling factor for each case are given in table 6.1.

Case	Power produced (MW)	Scaling factor
1	432	0.93
2	436	0.92
3	447	0.90
4	512	0.78
6	514	0.78
8	588	0.68
9	607	0.66

**Table 6.1:** Power production and scaling factor

The scaling factor was used to find how much natural gas was required to produce 400 MW for each case. The total feed of natural gas is given for each case in table 6.2. This includes both natural gas going to the reforming process, and natural gas going to the combustion chamber. As commented earlier, extra duty need to be supplied, in order to keep the temperature as high as required in the steam reformer. Even though this duty should come from natural gas, this is not compensated for in the value for total feed of natural gas. In table 6.2 the value for duty required is also given, the value is scaled to match a power production of 400 MW.

Case	Total feed NG (kg/s)	Duty for steam reformer (MW)
1	14.8	112
2	14.7	123
3	14.3	130
4	14.6	106
6	14.6	131
8	15.2	118
9	14.7	130

**Table 6.2:** Total feed stream of natural gas and duty for steam reformer required - for 400 MW

From table 6.2 it can be seen that case 3 requires the lowest amount of natural gas in order to produce 400 MW, while case 4 requires the least amount of extra duty in the steam reformer.

### 6.1.3 Mass- and energy balances

Results from these balances for each of the STR cases, are given in Appendix 4. The error in percentage for the mass- and energy balances is also included in the tables.

Total mass flow rate in and out of the different units are calculated by PRO/II. The energy balance is also based on the calculation in PRO.

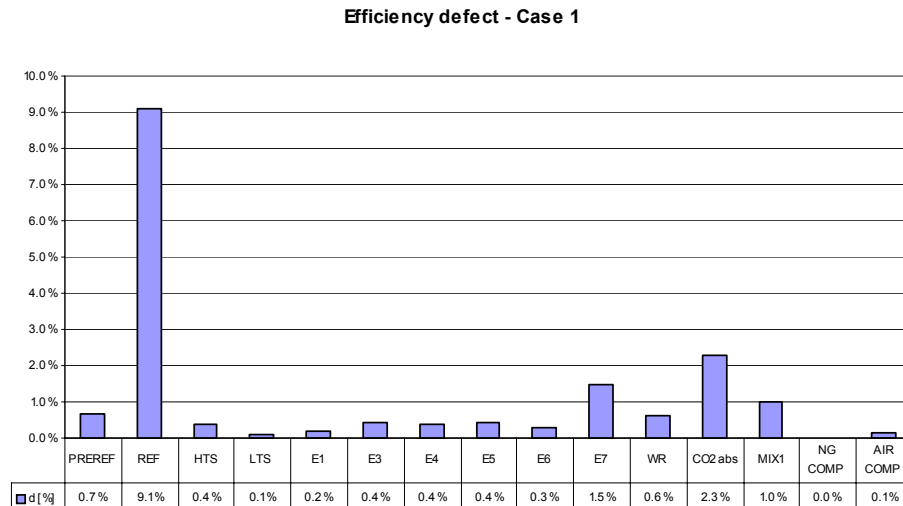
The mass balances show that all mass streams are well balanced through the whole process for all seven cases

The energy is not balanced for all units. All reactor units have some energy losses. The losses are mainly heat going to the environment.



### 6.1.4 Exergy balance

The results from the exergy balances are given in tables in Appendix 4 together with the mass- and energy balances. The efficiency defect for each unit is presented both in the tables (Appendix 4), and in diagrams (Appendix 7). A diagram showing the proportions of the efficiency defect for each unit in case1 is shown in figure 6.1



**Figure 6.1:** The efficiency defect for units in the STR system – Case 1

From the figure it can be seen that the greatest exergy loss is from the steam reforming process. The distribution is similar for the other cases. Between 9.0 % and 10.4 % of the total incoming exergy is lost from the steam reformer. This is not an unexpected result due to the irreversibility in the combustor.

### 6.1.5 Sustainability indicators

#### a) Renewability fraction

The renewability fraction is defined in equation (3.1). For the STR system air was the only renewable resource, however the exergy of air at environmental conditions is 0. This means the renewability fraction is 0 for all 7 cases, with system boundaries as given in figure 5.1.

#### b) Exergetic efficiency

The results of exergy efficiency for the seven cases of the STR system are given in table 6.3. Exergy input includes total exergy for all input streams, in addition to the duty required for the reformer and the CO<sub>2</sub> absorber unit. Power used for compressors is deducted from the power output and is therefore not included in the exergy input.

Case	Exergetic efficiency ( $\eta$ )
1	41,6 %
2	41,4 %
3	41,9 %
4	43,1 %
6	41,9 %
8	41,6 %
9	42,2 %

**Table 6.3:** Exergetic efficiency for STR cases

The differences in exergy efficiency for the seven cases are relatively small ranging from 41.4 % to 43.1 %. Case 4 has the highest efficiency of the seven cases. For this case the reformer temperature was 815 °C and the steam to carbon ratio was 3.0.

## 6.2 SR vs. ATR

Results from the analysis of the ATR system are taken from Zvolinschi et al. (2002). The renewability fraction and exergetic efficiency for ATR are given in table 6.4.

As for the STR system, the results for the ATR system are valid when the cycle is not closed with respect to material resources.

Case	Renewability fraction ( $\alpha$ )	Exergetic efficiency ( $\eta$ )
ATR	0.05 %	44.9 %

**Table 6.4:** Renewability fraction and exergetic efficiency for the ATR system

It is important to be aware that in the calculation of the renewability fraction for the ATR system, the power plant was included. The renewable resource is seawater used in the cooling tower at the power plant.

If looking at the ATR system with the same system boundaries as the STR system, the renewability fraction would also be 0, since the same type of resources are entering the two reforming systems. In the same way would the renewability fraction be greater than 0 also for the STR system if the power plant was included in the system boundaries. The plant is assumed to be the same as the one for the ATR system, requiring the same amount of cooling water per power production.

## 7 Discussion

### 7.1 STR system

#### *Renewability fraction*

The renewability fraction is 0 for all cases and will therefore not indicate anything about which is the better case. Air is a renewable resource but since it enters at environmental conditions it has 0 exergy. It is important to notice that air is still a resource that is required in the system for the combustion process, but does not contribute with any exergy.

#### *Exergetic efficiency*

The difference in the exergetic efficiency is only about 1.7 % between worst and best case. The insecurities in the results related to assumptions and simplification in the simulation process makes the difference almost insignificant.

#### *The effect of the variables*

Even if the results were more reliable would it be hard to draw any conclusions with respect to the effect of the variables since only seven cases are analysed. There is no clear pattern when comparing increasing temperature for the three different steam to carbon ratios. For the steam to carbon ratio compared at three different temperatures, lower ratio seems to correspond with higher efficiency. If this pattern is valid, it is reason to believe that the conditions that would define “lost” case 7 (Steam/carbon= 2.5. reformer temperature is 815 °C) would give the best results. A new analysis where the two “lost” cases are included is recommended in order to verify this.

A sensitivity analysis to illustrate effects of using inaccurate data would be helpful when deciding how reliable the results are.

#### *Exergy balance*

The exergy balances for the units within the system boundaries show that the greatest exergy loss is related to the steam reformer unit. Many of the insecurity factors are related to the steam reformer model in the simulations. It is still reason to believe that this unit has the greatest loss but the value for the exergy loss can be somewhat different. It is hard to indicate how great the insecurity in the results is.

The effect it would have on the results if an inert gas would have to be added to the gas mixture upstream the gas turbine would be similar for all results and would not cause that one case would be more or less favoured than the others. In the same way would the extra exergy required to treat the exhaust gas lead to similar decrease in the exergetic efficiency for all cases.

### *Conditions*

The analysis is not based on numbers from a specific plant. The conditions both in the environment and for the feed streams can change from plant to plant and one need to be aware of the local variations before using the results. It is recommended to go through all conditions and assumptions.

It was not expected in this analysis to reach optimal conditions. By extending the analysis to include more variables one can come closer to find an optimisation.

## 7.2 Steam reformer vs. Auto thermal reformer

### *Renewability fraction*

The choice of system boundaries affects the renewability fraction. The renewable resource used in the ATR system is related to the cooling water used in the power plant. This would be similar for the STR system if the boundaries were extended to include the power-producing units. In the same way would the renewability fraction for the ATR system be 0 if only the reforming process were looked at.

For both choices of system boundaries the renewability fraction is very small.

### *Exergetic efficiency*

For all cases of the STR system, is the exergy efficiency lower than it is for the ATR system. Even though the results are very insecure is it reason to believe that they give an indication of what system is the better with respect to exergetic efficiency.

### *Exhaust gas*

The exhaust gas from the combustion process is leaving the system without being treated in any way. This exhaust gas contains among others CO<sub>2</sub> that has a negative effect on the environment. One of the purposes with converting the natural gas to a hydrogen rich gas before entering the gas turbine is to be able to collect the CO<sub>2</sub> and thereby reduce the total CO<sub>2</sub> emissions to the environment. If treatment of the exhaust gas were to be included, the required exergy input would increase, leading to lower exergetic efficiency. The ATR system has no similar emissions meaning that this would favour the ATR system even more with respect to exergetic efficiency.

### *The best system*

Based on the results presented and the discussion given, the ATR system seems to be better than the STR system with respect to exergetic efficiency. For the renewability fraction the two systems seems to be similar. However, the insecurities are significant and the results will be seen as an indication rather than a conclusion.

### 7.3 Experiences from using the method

#### *Insecurities in the results*

A simulation will always include simplifications and assumptions that make an impact on the results. For the STR system the effect of two variables was looked at, but no sensitivity analysis was performed in order to get an indication of the inaccuracy in the data. The limitations and weaknesses related to the use of the tool and indicators are associated to the simulation process and collection of data. The accuracy in the result will never be better than the accuracy in the input data used. It is therefore necessary to be aware of all simplifications and assumptions made when one decides how to use the result.

Even if the results are somewhat insecure, it can in most cases probably give an indication of which system is better. Based on this, the method can be useful in a decision-making process, but one should not rely blindly on the results only.

#### *The renewability fraction*

In this work the results are not saying much about which case is the better one based on the renewability fraction since it was 0 for all cases. For other processes however the renewability fraction would still have potential to be an interesting indicator. When looking at systems using renewable resources that contribute with exergy this indicator will be much more useful. It is important to emphasize that the renewability fraction does not say anything about the relation between renewable and non-renewable resources based on mass flow. The renewability fraction will only say something about the fraction of exergy being renewable, and nothing about the size of the mass streams of renewable resources compared to mass streams of non-renewable resources. In this work, the renewable resource air did not contribute with exergy, but it was still a resource that was required.

#### *The exergetic efficiency*

The exergetic efficiency was useful in this analysis. The insecurities make it hard to draw conclusions, but the result can be used as an indication. The results should however not be used alone, but together with other decision tools that consider other factors of the systems.

#### *Impacts on the environment*

A reforming process like the one being discussed here will impact the environment in ways where the effect not will be included in the two indicators calculated. A more comprehensive analysis with respect to the environmental performance can lead to other conclusions of what system is the better one. If using the ELCA tool that was described in chapter 2, a better picture of the environmental performance would be given. When choosing to look at the system with closed material cycles, also the third indicator proposed by Zvolinschi et al. (2002) can be calculated in addition to traditional parameters from the LCA. Other indicators can probably also be used. The method ELCA is still new with a potential to develop.

## 7.4 The results in the perspective of industrial ecology

In order to obtain sustainable development, the use of renewable resources should be preferred over non-renewable. As can be seen from the discussion of the renewability fraction, most resources entering the reforming process - and all resources containing exergy - are non-renewable resources. However the results are similar for the two systems being compared, making no conclusion which is the better based on this.

The exergy efficiency is indicating that the ATR system will be the better one, but both systems could probably be improved from an environmental view. Based on an attempt to reach sustainable development, alternatives using renewable resources should be used rather than the one being discussed in this work. Systems based on the use of natural gas, can obviously not be made strictly sustainable, but they can be improved. An optimisation should be searched for with respect to the running conditions and other reforming processes could also be considered in order to optimise the exergetic efficiency, as well as the renewability fraction. The exergy analysis will be a useful tool in such an optimisation process.

Another important area for improvements is related to closing the material cycle. The third sustainability indicator proposed by Zvolinschi et al. (2002) could then also be considered. This indicator, the environmental efficiency parameter, includes the exergy inputs necessary to close the material cycles for emissions and products at the end of their lifetime as well as the exergy inputs for the production and the abatement process. This would give an important contribution to the discussion of the best reforming system with respect to environmental performance. From an industrial ecology view this is maybe the most interesting indicator and it is recommended to extend the analysis to include the closure of all cycles, in order to find this third indicator.

## 8 Concluding remarks

The ATR system seems to be the best alternative based on the analysis performed. The results are somewhat insecure and one should be aware of all assumptions and simplifications made when using the results. It is recommended to extend the system boundaries in order to get a better estimation with respect to environmental performance. This should include closing the material cycles as well as searching for optimized conditions for the system.

The method used in the work, seem functional also within the perspective of industrial ecology. However the two indicators calculated here should not be used alone but in addition to other parameters, as the ones used in a traditional LCA, when making decision based on environmental performance. The environmental efficiency indicator, proposed by Zvolinschi et al. (2002) should also be used.

How useful the results are depend a great deal on the simplifications and assumptions made through the simulation process. This should all be included in an overall evaluation based on the analysis.

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## List of symbols

$\partial_i$	=	efficiency defect for component i
$\varepsilon$	=	exergy
$\varepsilon_{ch}$	=	chemical exergy
$\varepsilon_{ph}$	=	physical exergy
$\varepsilon_{0i}$	=	chemical exergy for component i
$\varepsilon$	=	chemical exergy for component i
$\eta$	=	exergy efficiency
$\eta_e$	=	efficiency with transiting exergy
$\Psi$	=	rational efficiency
$h_0$	=	enthalpy at environmental conditions
$h$	=	enthalpy at actual conditions
$n$	=	moles
$m$	=	mass flow
$s_0$	=	entropy at environmental conditions
$s$	=	entropy at actual conditions
$x_i$	=	mole fraction of component i
$B$	=	availability
$\dot{E}^q$	=	exergy connected to heat going into or leaving the system
$\dot{E}_{in}$	=	exergy going into the system
$\dot{E}_{out}$	=	exergy leaving the system
$H$	=	enthalpy
$\dot{I}$	=	Irreversibility
$\dot{I}_i$	=	irreversibility for component i
$Q$	=	heat
$R$	=	gas constant
$S$	=	entropy
$T$	=	actual temperature
$T_0$	=	environmental temperature
$\dot{W}$	=	work
$B(EXS)$	=	availability function at existing state
$B(EVS)$	=	availability function at environmental state
$(\Delta S)_{surroundings}$	=	change in entropy for surroundings
$(\Delta S)_{system}$	=	change in entropy for system