CO₂ Mitigation in Advanced Power Cycles

- Chemical Looping Combustion and Steam-Based Gasification

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Abstract

This thesis encompasses CO₂ mitigation using three different processes: i) natural gas-fired combined cycle with chemical looping combustion (CLC), ii) tri-generation of electrical power, hydrogen and district heating with extended CLC, iii) steam-based gasification of biomass integrated in an advanced power cycle.

In CLC, a solid oxygen carrier circulates between two fluidised-bed reactors and transports oxygen from the combustion air to the fuel; thus, the fuel is not mixed with air and an inherent CO₂ separation occurs. In this thesis, CLC has been studied as an alternative process for CO₂ capture in a natural gas-fired combined cycle (NGCC). The potential efficiency of such a process using a turbine inlet temperature of 1200 °C and a pressure ratio of 13 is between 52 and 53 % when including the penalty for CO₂ compression to 110 bar. It is shown that this efficiency cannot be further improved by including an additional CO₂ turbine. Two conceivable reactor designs for CLC in an NGCC are presented. Top-firing has been studied as an option to overcome a temperature limitation in the CLC reactor system. The degree of CO₂ capture is shown versus the temperature in the CLC reactor and its combustion efficiency. CLC has the potential to reach both a higher efficiency and a higher degree of CO₂ capture than conventional post combustion CO₂ capture technique. However, further research is needed to solve technical problems as, for example, temperature limitations in the reactor to reach this potential.

Extended CLC (exCLC) is introduced, in which hydrogen is not only produced but also inherently purified. The potential efficiency of a novel tri-generation process for hydrogen, electricity and district heating using exCLC for CO₂ capture is investigated. The results show that a thermal efficiency of about 54% might be achieved.

A novel power process named evaporative biomass air turbine (EvGT-BAT) for biomass feedstock is presented. This process contains a steam-based gasification of biomass, which is integrated in an externally fired gas turbine cycle with top-firing. In the EvGT-BAT process, the steam-based gasification is conducted in an entrained-flow tubular reactor that is installed in the SFC as a heat exchanger. The EvGT-BAT process has the potential to generate electrical power from biomass with an efficiency of 41%.
Keywords: chemical looping combustion, CO₂ capture, hydrogen production, tri-generation, co-generation, natural gas, biomass fuel, steam-based gasification, combined cycle, externally-fired gas turbine, evaporative gas turbine, steam injected gas turbine, advanced power generation
List of Appended Papers


II. Wolf, J., Anheden, M. and Yan, J., _Comparison of Nickel Oxide and Iron Oxide as Oxygen Carrier in Chemical Looping Combustion for CO₂ Capture_, accepted by Fuel.


My contribution to the attended papers

Papers I, II, III, IV to V are my own work

Paper VI is based on a master's thesis, whose simulation part I supervised. Additionally, I wrote the paper.
# Table of Contents

Abstract iii  
List of Appended Papers v  
Table of Contents vii  

1 INTRODUCTION..................................................................................................................1  
1.1 Thesis outline ..............................................................................................................2  
1.2 Objective of this thesis ...............................................................................................3  

2 BACKGROUND.................................................................................................................5  
2.1 CO₂ mitigation ............................................................................................................5  
2.1.1 Three natural gas-fired power plant concepts with CO₂ capture .........................6  
2.2 Chemical Looping Combustion ................................................................................8  
2.2.1 Technical background ............................................................................................8  
2.2.2 Research activities in chemical looping combustion ............................................9  
2.2.3 Previous work on potential oxygen carriers .........................................................11  
2.2.4 Previous work on reactor design ..........................................................................14  
2.3 Steam-based gasification of biomass ........................................................................15  
2.3.1 Externally fired gas turbines with topping combustion .......................................15  
2.3.2 The evaporative gas turbine cycles (EvGT) ..........................................................16  
2.3.3 Previous work .......................................................................................................17  
2.3.4 Technical background of steam based gasification of biomass .........................19  

3 GENERAL METHOD .....................................................................................................23  
3.1 General method of studying chemical looping combustion .....................................23  
3.2 General method of studying the EvGT-BAT process ...............................................24  

4 CO₂-FREE POWER GENERATION USING CHEMICAL LOOPING COMBUSTION.................................................................................................................25  
4.1 The studied systems ..................................................................................................25  
4.1.1 Description of the reference NGCC .................................................................26  
4.1.2 Description of studied systems (CC-CLC) .........................................................27  
4.1.3 Assumptions for the performance studies of the system ....................................29  
4.2 Comparison of a standard NGCC to an NGCC using CLC for CO₂ capture ............30  
4.2.1 Results of the system simulation ....................................................................30  
4.2.2 Discussion ............................................................................................................30
4.3 Performance study of a CC-CLC process including a CO₂ expander .......... 32
   4.3.1 Description of the system with CO₂ expander .......................................................... 32
   4.3.2 Results ................................................................................................................... 33
   4.3.3 Discussion ............................................................................................................. 34

4.4 Comparison of nickel oxides and iron oxides as oxygen carrier .......... 36
   4.4.1 Method .................................................................................................................. 36
   4.4.2 Description of the studied cases ............................................................................ 38
   4.4.3 Results of the CLC Parameter Mapping ............................................................... 39
   4.4.4 The impact of pressure drop and fan power .......................................................... 41
   4.4.5 Results of the system analysis ............................................................................... 43
   4.4.6 Discussion ............................................................................................................. 43

4.5 Impact of the degree of conversion in the fuel reactor on the thermal efficiency of the system ................................................................. 45
   4.5.1 Description of studied cases.................................................................................. 45
   4.5.2 Separation of methane and CO₂ by a "simple" condensation in Case II ............ 46
   4.5.3 Results .................................................................................................................. 48
   4.5.4 Discussion ............................................................................................................. 49

4.6 Top-firing to overcome temperature limitation in the air reactor .......... 50
   4.6.1 Definition of the avoided CO₂............................................................................... 50
   4.6.2 Results .................................................................................................................. 51
   4.6.3 Discussion ............................................................................................................. 52

4.7 Conceivable reactor design ........................................................................ 53
   4.7.1 The boundary for the flow of oxygen carrier – the MTPFR ................................. 54
   4.7.2 Assumption for calculating the hydrodynamic behaviour of the IPFBR .............. 55
   4.7.3 IPFBR_A: A riser and a stationary fluidised bed ................................................. 56
   4.7.4 IPFBR_B: Two circulating fluidised bed reactors ................................................ 56
   4.7.5 Discussion ............................................................................................................. 58

5 CO₂-FREE COGENERATION OF POWER AND HYDROGEN WITH CHEMICAL LOOPING COMBUSTION ....................................................59

5.1 The principle of hydrogen production with chemical looping combustion ... 60
   5.1.1 Hydrogen production with chemical looping combustion .................................... 60
   5.1.2 Separation of hydrogen and carbon dioxide in the exCLC ..................................... 61

5.2 Consideration of a conceivable reactor layout ........................................ 63

5.3 Nickel as potential oxygen carrier in exCLC ............................................. 64

5.4 The system of an extended CLC in a steam-injected gas turbine cycle (exCLC-STIG) ................................................................................................................. 65
   5.4.1 Description of the system ..................................................................................... 65
   5.4.2 Assumptions .......................................................................................................... 67

5.5 Methods ............................................................................................................. 68
   5.5.1 Process analysis method ...................................................................................... 68
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.6</td>
<td>Results of the thermo-chemical analysis</td>
<td>71</td>
</tr>
<tr>
<td>5.6.1</td>
<td>Thermo-chemical analysis of the gas composition in the reactors</td>
<td>71</td>
</tr>
<tr>
<td>5.6.2</td>
<td>Requirements for the regeneration of the carbon carrier</td>
<td>72</td>
</tr>
<tr>
<td>5.7</td>
<td>Results and discussion of the parametric study of the exCLC-STIG process</td>
<td>74</td>
</tr>
<tr>
<td>5.7.1</td>
<td>Impact of the steam to carbon carrier ratio during calcination</td>
<td>74</td>
</tr>
<tr>
<td>5.7.2</td>
<td>Impact of the amount of solids circulating between the air reactor and the calcination reactor</td>
<td>76</td>
</tr>
<tr>
<td>5.7.3</td>
<td>Impact of the temperature in the air reactor</td>
<td>76</td>
</tr>
<tr>
<td>5.7.4</td>
<td>Effect of the temperature of the topping combustor</td>
<td>77</td>
</tr>
<tr>
<td>5.7.5</td>
<td>Effect of introducing steam to the fuel reactor</td>
<td>78</td>
</tr>
<tr>
<td>5.7.6</td>
<td>Impact of the oxygen carrier’s reactivity on cycle performance</td>
<td>78</td>
</tr>
<tr>
<td>5.8</td>
<td>Optimisation of the system</td>
<td>79</td>
</tr>
<tr>
<td>6</td>
<td>INTEGRATION OF A STEAM-BASED GASIFICATION IN AN EVAPORATIVE GAS TURBINE CYCLE (EVGT-BAT)</td>
<td>81</td>
</tr>
<tr>
<td>6.1</td>
<td>Description of the EvGT-BAT process</td>
<td>81</td>
</tr>
<tr>
<td>6.2</td>
<td>Method and assumption</td>
<td>83</td>
</tr>
<tr>
<td>6.2.1</td>
<td>Simulation of the steam-based gasification of biomass</td>
<td>83</td>
</tr>
<tr>
<td>6.3</td>
<td>Results and discussion of the performance analysis</td>
<td>86</td>
</tr>
<tr>
<td>6.4</td>
<td>Advantages with EvGT-BAT compared to IGCC</td>
<td>88</td>
</tr>
<tr>
<td>7</td>
<td>CONCLUDING REMARKS</td>
<td>91</td>
</tr>
<tr>
<td>7.1</td>
<td>Chemical looping combustion</td>
<td>91</td>
</tr>
<tr>
<td>7.2</td>
<td>Steam-based gasification in EvGT-BAT</td>
<td>94</td>
</tr>
<tr>
<td>8</td>
<td>RECOMMENDATIONS FOR FURTHER RESEARCH</td>
<td>95</td>
</tr>
<tr>
<td>8.1</td>
<td>Chemical looping combustion</td>
<td>95</td>
</tr>
<tr>
<td>8.2</td>
<td>Steam based gasification in EvGT-BAT</td>
<td>97</td>
</tr>
<tr>
<td>9</td>
<td>ACKNOWLEDGEMENT</td>
<td>99</td>
</tr>
<tr>
<td>10</td>
<td>REFERENCES</td>
<td>101</td>
</tr>
<tr>
<td>11</td>
<td>NOMENCLATURE</td>
<td>109</td>
</tr>
<tr>
<td>11.1</td>
<td>Greek letters</td>
<td>110</td>
</tr>
<tr>
<td>11.2</td>
<td>Indices</td>
<td>110</td>
</tr>
</tbody>
</table>
### 12 APPENDIX

12.1 The freeboard-entrainment model ..................................................... 113

12.2 Two modes of operation in the IPFBR.................................................. 114

12.2.1 First mode of operation in IPFBR_A: Controlling the residence time in the air reactor .................................................................................................................. 116

12.2.2 Second mode of operation in IPFBR_A: Controlling the flow rate between the fuel and the air reactor ................................................................. 116

12.3 Terminal velocity.................................................................................... 118

12.3.1 The model from Basu et al. (1991) ................................................... 119

12.3.2 The model found in Kunii and Levenspiel (1991) ............................. 119

12.3.3 The model found in Bolland (2001) ................................................... 120

12.4 Calculation of the pressure loss in the IPFBR........................................ 120

12.4.1 Pressure drop in the fluidised bed ................................................... 121

12.4.2 Pressure drop in a cyclone.............................................................. 122

12.4.3 Power requirement for the booster fan ........................................... 124

12.5 Height of the fluidised bed in the fuel reactor ....................................... 124

12.6 Calculation of the pressure shell............................................................ 125

12.6.1 The cylinder .................................................................................... 125

12.6.2 The ellipsoidal head ........................................................................ 126

12.7 Results of dimensioning of the IPFBR .................................................. 126

12.7.1 The dimensions of the CLC reactor ................................................ 127

12.7.2 The pressure shell ........................................................................... 131

12.7.3 Amount of required material ......................................................... 131
Europe's park of power plants is growing old at the same time as the demand on electrical power increases. For the next 20 years, it is predicted that power plants with a total capacity of 200 GW will be installed in the EU-15 countries (Epple et al., 2004). Due to the lack of competitive alternatives and due to the beginning nuclear power phase-out in some European countries, it can be expected that most of these plants will be fuelled by fossil fuels. These new plants will probably be built under more strict environmental constraints including not only the local emissions such as particulates, SOx and NOx, but also their contribution to global CO\textsubscript{2} emissions. There is a growing interest in reducing global CO\textsubscript{2} emissions since CO\textsubscript{2} is the most important anthropogenic greenhouse gas. According to the Kyoto protocol from 1997, the countries in the European Union (EU 15) have to reduce their emission of CO\textsubscript{2} and five other greenhouse gases by at least 8% by 2008 to 2012 compared to levels in 1990 (UNFCCC, 2004). Because electric power plants using fossil fuels produce more than one third of the global carbon emissions and because a limited number of centralized and large emitters are easier to control than millions of vehicle emitters or small boilers, the power production sector is likely to become a prime target for CO\textsubscript{2} emission control and mitigation (IPCC, 2001b).

Approaches to mitigating CO\textsubscript{2} from power generation include the improvement of the plants' efficiencies, increased use of renewable energy sources, and the capture and sequestration of CO\textsubscript{2} emissions from energy systems. In addition, switching to low-carbon fuels such as natural gas is considered as a further option for CO\textsubscript{2} mitigation (IPCC, 2001b). A switch from coal to natural gas allows the use of combined cycle technology with high efficiency and low capital cost. However, natural gas is a fossil fuel and an important source of CO\textsubscript{2} emissions. Today, natural gas stands for 22% of the world energy mix (McKee, 2002). With this background power plants using natural gas as fuel are an interesting field for new advanced technology for low or zero CO\textsubscript{2} emissions.
1.1 Thesis outline

This thesis includes the combination of three approaches for CO₂ mitigation. These approaches are capture and sequestration of CO₂ emissions from a natural gas-fired power generation process, the use of biomass and the improvement of the plants’ efficiency. Two power generation processes with almost zero CO₂ emissions and high efficiencies are presented. The first process, which makes up the main part of this thesis, integrates a novel technique for CO₂ capture in a natural gas-fired power plant. This technique is known as Chemical Looping Combustion (CLC) and has the potential to separate CO₂ from a power generation process with only small penalties in efficiency. The second process contains a steam-based gasification process of biomass to substitute coal and natural gas in an advanced power generation process. Biomass is a renewable energy resource and does not contribute to CO₂ emissions as long as the reforestation exceeds the consumption. Therefore, using biomass in place of fossil fuels for power generation reduces CO₂ emissions.

In Chapter 2 the technical backgrounds of these processes are described along with more detailed information about the Kyoto protocol and the previous work on CLC. Chapter 3 gives an introduction to the methods of approach for the studies of CLC and the novel power process integrated with steam-based gasification of biomass.

Chapter 4 contains the results of five studies with CLC integrated in a natural gas-fired combined cycle (NGCC) and the resulting dimensions of two conceivable reactor layouts. Chapter 4 is based on the work published in Papers I and II and an MS thesis project under supervision of the author (Hicking, 2002).

In Chapter 5, an extended CLC (exCLC) process for producing and purifying hydrogen is presented. The potential efficiency of a novel tri-generation process for hydrogen, electricity and district heating using exCLC for CO₂ capture is investigated. In Chapter 5, the work published in Papers III and IV is summarised.

In Chapter 6, a power process named evaporative biomass air turbine (EvGT-BAT¹) is presented. This process includes steam-based gasification of biomass, which is integrated in an externally fired evaporative gas turbine cycle with top-firing. The potential efficiency of this process is studied by varying, for example, the moisture content of biomass. The work presented in Chapter 6 refers to Papers V and VI.

¹ EvGT stands for evaporative gas turbine and BAT stands for Biomass Air Turbine
Chapter 7 contains the conclusions of this work and in Chapter 8 the author gives recommendations for continued research in the field of CLC and EvGT-BAT. All used abbreviations and chemical compounds are listed in Chapter 11.

In the Appendix (Chapter 12), a hydrodynamic model for a CLC reactor is described and initial estimations for the dimensions of two conceivable layouts for a CLC reactor are presented.

1.2 Objective of this thesis

This thesis has two major topics: CLC and biomass gasification for advanced power cycles.

The aim of this thesis is to evaluate the performance of CLC compared to existing techniques for CO$_2$ capture in a natural gas-fired power plant under consideration of technical limitations in temperature and mass flowrates in the CLC reactor. A further objective is to find additional applications for CLC as, for example, cogeneration of hydrogen and electricity together with CO$_2$ capture.

Steam-based gasification of biomass has been studied as an alternative fuel to natural gas in a new power generation process that uses the advantages of existing concepts and minimises their technical problems such as temperature limitation, the large size of gasifiers and the low efficiency of power plants using biomass feedstock. The aim of this work is to evaluate the impact of the process parameters of the gasification on the overall electrical efficiency.
2 Background

2.1 CO₂ mitigation

Since the late 18th century to the present, the atmospheric concentration of CO₂ has increased from 280 ppm to 367 ppm, which is an increase by 31%. During the same time period the global average temperature has increased by 0.6 °C (IPCC, 2001a). Although, there is no evidence that the increasing concentration of CO₂ is the reason for the global warming, many scientists agree that a connection between these two phenomena is possible. For this reason, in December 1997, the so called Kyoto protocol was adopted at the third session of the Conference of Parties (COP3) to the United Nations. The protocol contains legally binding emissions targets for 36 industrialised countries. These counties are to reduce their collective emissions of six key greenhouse gases (CO₂, CH₄, N₂O, HFCs, PFC, and SF₆) by at least 5% by 2008 to 2012 compared to levels 1990. According to the agreement, the European Union (EU 15) has to reduce their emission of the six greenhouse gases by at least 8% in the same time frame (UNFCCC, 2004). This first five-year period is only the first step.

Especially since the commitment to the Kyoto protocol in 1997, numerous studies have been conducted on CO₂ capture in natural gas-fired power generation systems. It has been shown that removing CO₂ from flue gases is expensive and consumes a significant amount energy. For instance, previous investigations have indicated that the electrical efficiency of a natural gas-fired combined cycle (NGCC) will be decreased by about eight to ten percentage points when using available concepts for CO₂ capture (Audus, 2000; Herzog et al., 1997; Göttlicher and Pruschek, 1997; Bolland, 2003).
2.1.1 Three natural gas-fired power plant concepts with CO₂ capture

*Figure 2-1* shows three frequently discussed concepts for CO₂ capture, in which the CO₂ is separated after (a), during (b) or before (c) the combustion process (*Bolland, 2003*):

(a) Technologies for separation of CO₂ from flue gases after combustion include the use of chemical absorption and adsorption. The exhaust gas from the gas turbine flows into a CO₂ capture plant consisting of exhaust gas preparation (cooling and a booster fan to overcome the exhaust gas pressure drop in the CO₂ capture plant), absorption, stripping of CO₂ from the absorbent and CO₂ compression. Low-pressure steam extracted from the steam turbine in the CC is used to cover the heat demand in the stripping process.

(b) Separation during combustion is based on a combined cycle with a near stoichiometric combustion using pure oxygen from an air separation unit (ASU) to oxidise the natural gas in an atmosphere of re-circulated flue gases. CO₂ and steam are produced in the combustion and the working medium in the gas turbine is mainly CO₂. The CO₂ can be purified by simply condensing the water (*Göttlicher, 1997; Bolland, 2003*). Flue gas re-circulation can also be applied with air instead of oxygen. In this case, an ASU is not necessary but instead a chemical absorption unit is used. The exhaust gas contains a higher partial pressure of CO₂ than in a standard combined cycle which eases the absorption (*Audus, 2000*).

(c) Separation before combustion includes steam reforming, partial oxidation or auto-thermal reforming plus a CO/H₂ shift reactor and a high pressure CO₂ capture unit to produce a hydrogen rich (H++) fuel gas. When using auto-thermal reforming (*Figure 2-1*) compressed air and steam are extracted from the combined

![Figure 2-1. Three natural-gas fired power plant concepts with CO₂ capture (Bolland, 2002)](image)
cycle and used for the reforming. Some high pressure steam is transferred back into the combined cycle (Bolland, 2001, 2003).

All these technologies reduce the thermal efficiency of the power generation process by about 10 percentage points. More detailed data about the penalty in efficiency for CO₂ capture in an NGCC based on state-of-the-art technologies is summarised in Table 1-1. The table shows the efficiency of a reference system without CO₂ capture and the efficiencies when the above described concepts for CO₂ capture are used.

**Table 1-1. Thermal efficiencies of a NGCC with CO₂ capture after (A) and before (C) combustion and with re-circulated flue gas (B).**

<table>
<thead>
<tr>
<th>Technology</th>
<th>η&lt;sub&gt;th&lt;/sub&gt; [%]</th>
<th>ref. sys. [%]</th>
<th>η&lt;sub&gt;th&lt;/sub&gt; [%]</th>
<th>ref. sys. [%]</th>
<th>η&lt;sub&gt;th&lt;/sub&gt; [%]</th>
<th>ref. sys. [%]</th>
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<tr>
<td>A</td>
<td>50</td>
<td>57.5</td>
<td>47</td>
<td>56</td>
<td>49.6</td>
<td>58</td>
</tr>
<tr>
<td>B</td>
<td>48&lt;sup&gt;a)&lt;/sup&gt;</td>
<td></td>
<td>48&lt;sup&gt;b)&lt;/sup&gt;</td>
<td>56</td>
<td>47.2&lt;sup&gt;d)&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>42&lt;sup&gt;g)&lt;/sup&gt;</td>
<td></td>
<td>48&lt;sup&gt;f)&lt;/sup&gt;</td>
<td></td>
<td>45.3&lt;sup&gt;e)&lt;/sup&gt;</td>
<td></td>
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</table>

1) CO₂ leaves the process at atmospheric pressure  
2) CO₂ leaves the process at 110 bar  
3) CO₂ leaves the process at 100 bar and 90 % of CO₂ is captured  
4) Combustion with O₂ by using ASU  
5) Combustion with air, no ASU  
6) Steam reforming and absorption with MDEA  
7) Partial oxidation with O₂ by using ASU and a physio-chemical solvent for CO₂ capture  
8) Air-blown autothermal reforming (ATR)
2.2 Chemical Looping Combustion

2.2.1 Technical background

Chemical looping combustion (CLC) is a new concept for CO$_2$ capture. The separation of CO$_2$ from the combustion product gases occurs like in concept (b) during the combustion process, but in CLC no ASU is necessary. Direct contact of fuel and combustion air is avoided; thus, the CO$_2$ is inherently separated from nitrogen which normally makes up the main fraction of the exhaust. In CLC a solid oxygen carrier performs the task of carrying the oxygen from the air to the fuel gas. Figure 2-2 illustrates the principle of a CLC process. The oxygen carrier is a metal oxide that is reduced in a fuel reactor (also called reduction reactor) at the same time as the fuel is oxidised (Reaction Eq. 2-1). The oxygen carrier is then transported into an air reactor (also called oxidation reactor) where it is re-oxidised by air (Reaction Eq. 2-2). After passing through a cyclone to separate the solid oxygen carrier from the hot gases (N$_2$ and O$_2$), the oxygen carrier is recycled back into the fuel reactor. The gaseous reaction products from the fuel reactor consist of carbon dioxide and water.

\[ C_x H_y + \Phi \cdot \left( \frac{2a + b}{2} \right) \cdot Me_{x_1}O_{y_1} \rightarrow aCO_2 + \left( \frac{b}{2} \right)H_2O + \Omega \cdot \left( \frac{2a + b}{2} \right) \cdot Me_{x_2}O_{y_2} \quad (2-1) \]

\[ \Omega \cdot \left( \frac{2a + b}{2} \right) \cdot Me_{x_2}O_{y_2} + \left( \frac{a + b}{4} \right) \rightarrow \Phi \cdot \left( \frac{2a + b}{2} \right) \cdot Me_{x_1}O_{y_1} \quad (2-2) \]

The coefficients $\Phi$ and $\Omega$ in Eqs. 2-1 and 2-2 can be calculated from the compositions of the oxides (Eqs. 2-3 and 2-4).

\[ \Phi = \frac{x_2}{y_1 \cdot x_2 - y_2 \cdot x_1} \quad (2-3) \]

\[ \Omega = \frac{x_1}{y_1 \cdot x_2 - y_2 \cdot x_1} \quad (2-4) \]
Nitrogen is inert in the Reaction Eq. (2-2). Therefore, the gas phase leaving the air reactor consists of nitrogen and excess oxygen, depending on the reaction conditions. In this way, CO$_2$ is obtained in a stream separate from nitrogen. In order to obtain pure CO$_2$, the gas mixture from the fuel reactor is cooled and the remaining water is condensed. In addition to its inherent CO$_2$ separation, a further advantage of CLC is that no significant formation of nitrogen oxides takes place during combustion (Ishida and Jin, 1996).

### 2.2.2 Research activities in chemical looping combustion

The principles of CLC were first introduced in 1983 by Richter and Knoche (1983) and later, this novel combustion process was given the name Chemical Looping Combustion (Ishida et al., 1987). The main object of introducing CLC at that time was to increase the energy conversion efficiency in thermal power processes by decreasing the entropy production in the combustion. However, it has been shown that an advantage in the overall thermal efficiency of processes with CLC can only be achieved if the separation of CO$_2$ from the exhaust gases is included in the calculation (Grönkvist, 1995; Anheden, 2000; Paper II).

Since 1983, several studies have been performed on process integration, selection and preparation of oxygen carriers, and reactor design. The Laboratory of Resource Utilization at the Tokyo Institute of Technology in Japan has conducted both
systems analysis (Ishida et al., 1987, 1997; Ishida and Jin, 1994a; Jin and Ishida, 1997) and experimental studies on oxygen carriers (Ishida and Jin, 1994b; Ishida et al., 1996; 1998, 1999, 2002). Some experimental studies on CLC have also been performed at the National Institute for Resources and Environment (NIRE), Japan, (Hatanaka et al., 1997).

At the Royal Institute of Technology in Stockholm, Sweden, the first studies on CLC were started in 1995. These studies focused on performance analysis of combined power cycles with CLC using ABB’s gas turbines GT24/26 with a maximum pressure of 30 bar, a TIT of 1235 °C, and a reheat at 15 bar (Anheden et al., 1995). In a later study, coal gasification was included in a combined cycle with a simpler gas turbine that operates at 17 bar and a TIT of 1280 °C (Anheden and Svedberg, 1996). A comprehensive exergy analysis was conducted of these two systems (Anheden and Svedberg, 1997).

In the late nineties an increasing number of new groups started research on CLC as a novel method for CO₂ capture. A research team at Chalmers University of Technology in Gothenburg, Sweden, focuses on a suitable reactor design for CLC and performs experimental work on oxygen carriers (Mattisson and Lyngfelt, 1998, 2001; Mattisson et al., 2001; Lyngfelt et al., 2001, 2004; Johansson, 2002; Johansson et al., 2002, 2004; Cho et al. 2002, 2004). Another group worked at TDA Research, Inc. in Colorado, USA. Their project was supported by the US Department of Energy (DOE) and their proposed system is called “Sorbent Energy Transfer Systems” (SETS), which is based on a principle similar to CLC (Copeland et al., 2000, 2002). Further research on particle preparation of oxygen carriers and process design is being conducted at the Norwegian University of Science and Technology in Trondheim, Norway (Brandvoll and Bolland, 2002; Brandvoll et al., 2004; Naqvi et al., 2004). Further activities, especially in particle design and reactor design, have been reported from the Instituto de Carboquímica (CSIC) in Zaragoza, Spain (Adánes et al., 2003, 2004) and from Italy (Villa et al., 2003). In Korea at the Institute of Research, NiO with betonite and hexaaluminate as support material has been investigated (Ryu et al., 2002). At the Vienna University of Technology in Austria practical experiments on fluidisation in a CLC reactor model have been conducted (Kronberger et al., 2004a, 2004b, 2004c).

Recently, research has been started on CLC for hydrogen production. A process study on an NGCC with CLC for CO₂ capture and hydrogen production has been conducted by Hicking (2002) at the Royal Institute of Technology in Stockholm, Sweden. At Chalmers University of Technology in Gothenburg, Sweden, Mattisson et al. (2004) has shown experimentally that hydrogen can be produced in the fuel reactor of a CLC system. An advanced gasification-combustion (AGC) process
with integrated CO₂ capture was presented by GE Energy and Environmental Research Corporation (Rizeq, 2001). In this process an oxygen and a carbon carrier circulate between a gasification reactor, a CO₂-release reactor and an oxygen-transfer reactor. The process resembles CLC and produces pure hydrogen and CO₂ ready for sequestration.

2.2.3 Previous work on potential oxygen carriers

In chemical looping combustion, special particles must be manufactured that can meet the challenging conditions in CLC. Some of these demands are:

- A high operating temperature
- A high gas velocity in the air reactor causing mechanical stress
- Alternately a reducing and an oxidising atmosphere
- High reactivity
- High transport capacity for oxygen

Many potential oxygen carriers have been proposed, including combinations of copper, manganese, iron, and nickel as the active agent and aluminium oxide, titanium dioxide, zirconium dioxide and silicon dioxide as the inert material (Ishida and Jin, 1994b; Ishida et al., 1996, 1999, 2002; Mattisson et al., 2001a, 2001b; Lyngfelt et al., 2001, 2002, 2004; Cho et al., 2002, 2004; Copeland et al., 2000, 2002; Brandvoll and Bolland, 2002, Brandvoll et al., 2004; Ryu et al., 2002; Adánes et al., 2004; Villa et al., 2003). In this thesis, three oxygen carriers, that belong among the most promising alternatives, are further studied:

1. Pure Fe₂O₃,
2. Fe₂O₃ stabilised with Al₂O₃ with a composition of 60 wt% Fe₂O₃ and 40 wt% Al₂O₃, and
3. A nickel-based oxygen carrier that consists of 50 wt% active NiO and 50 wt% inert NiAl₂O₄.

TDA Research, Inc, tested pure Fe₂O₃ as oxygen carrier at 720°C to 800°C and found excellent chemical stability and no loss of activity with cycling (Copeland et al., 2002). However, at 900°C the same particles began to agglomerate. Though the agglomeration rate was slow, the authors concluded that the agglomeration would continue and make the particles unusable. Experiments have been conducted with iron-based oxygen carriers, which were stabilized with Al₂O₃, and no agglomeration or breakage was found at 950°C (Cho et al., 2002). An oxygen carrier composed of 60 wt% NiO and 40 wt% NiAl₂O₄ has been studied and no agglomeration at 1200 °C was reported (Ishida et al., 2002). Moreover, the first kinetic data for the
reaction of nickel oxide with hydrogen have recently be published (Brandvoll and Bolland, 2004).

### 2.2.3.1 Nickel oxide

Nickel belongs to group VIII of the transition metals. The melting point of pure nickel is 1453 °C. The most common nickel oxide is nickel monoxide. Its melting point is at 1990 °C. Higher nickel oxides such as Ni₂O₃ and NiO₂ are formed only through oxidation of nickel(II)hydroxide. NiO₂ can be formed by using a strong oxidation agent such as an aqueous peroxodisulfate solution to oxidise nickel(II)hydroxide (Falbe and Regitz, 1995). In CLC, apparently, the conditions for forming higher nickel oxides do not occur, i.e., only NiO has to be considered. This means that, if nickel is used as oxygen carrier, Reaction Eq. 2-1 becomes Reaction Eq. 2-5. In the air reactor nickel is re-oxidised according to Reaction Eq. (2-6).

\[
\text{Fuel reactor} \\
\text{CH}_4 + 4\text{NiO} \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + 4\text{Ni} \quad \text{(endothermic)} \\
\text{Air reactor} \\
4\text{Ni} + 2\text{O}_2 \rightarrow 4\text{NiO} \quad \text{(exothermic)}
\]

Nickel oxide in combination with aluminium(III)oxide (Al₂O₃) was found to be very interesting as oxygen carrier in CLC. The reason is the formation of water-free nickel aluminates when calcining particles of these materials. The water-free nickel aluminates are also named nickel-aluminium spinel (NiO*Al₂O₃-spinel). The spinel seems to make the particles very heat resistant and therefore suitable for CLC. For example, Ishida et al. (2002) tested particles of nickel oxide stabilised with NiAl₂O₄ (NiO*Al₂O₃-spinel) for CLC. The authors concluded that their particles had good circulation properties, high mechanical strength, high reactivity and, therefore, they are highly applicable in CLC. Cho et al. (2004) also come to the conclusion that nickel oxide is the most promising oxygen carrier for CLC.

However, nickel and nickel oxide have a major disadvantage. Nickel and many of its chemical components, including nickel oxide, are referred to be carcinogen and for many compounds containing nickel it was found that they have the potential to generate allergies and mutations (Falbe and Regitz, 1995).
2.2.3.2 Iron oxide

Iron, just as nickel, belongs to group VIII of the transition metals. The melting point of pure iron is 1535 °C. Iron forms the oxides wustite (FeO), hematite (Fe₂O₃), and magnetite (Fe₃O₄). The formation of one or the other iron oxide is dependent on the amount of oxide in relation to the amount of methane in the fuel reactor. The Reaction Eqs. 2-7 to 2-16 demonstrate the high number of possible reactions in the fuel reactor and Figure 2-3 shows the actual reaction products as a function of the ratio of hematite to methane if chemical equilibrium is assumed.

\[
\begin{align*}
\text{CH}_4 + \text{Fe}_2\text{O}_3 & \leftrightarrow 2 \text{ Fe} + 0.15 \text{ CO}_2 + 0.85 \text{ CO} + 0.5 \text{ H}_2\text{O} + 1.5 \text{ H}_2 \\
\text{CH}_4 + \text{Fe}_2\text{O}_3 & \leftrightarrow \text{Fe} + \text{FeO} + 0.15 \text{ CO}_2 + 0.85 \text{ CO} + 0.5 \text{ H}_2\text{O} + 1.5 \text{ H}_2 \\
\text{CH}_4 + 2 \text{Fe}_2\text{O}_3 & \leftrightarrow 4 \text{FeO} + 0.5 \text{ CO}_2 + 0.5 \text{ CO} + 0.5 \text{ H}_2\text{O} + \text{H}_2 \\
\text{CH}_4 + 3 \text{Fe}_2\text{O}_3 & \leftrightarrow 6 \text{FeO} + 0.5 \text{ CO}_2 + 0.5 \text{ CO} + 1.5 \text{ H}_2\text{O} + 0.5 \text{ H}_2 \\
\text{CH}_4 + 3 \text{Fe}_2\text{O}_3 & \leftrightarrow 2 \text{Fe}_3\text{O}_4 + \text{CO} + 2 \text{H}_2 \\
\text{CH}_4 + 3 \text{Fe}_2\text{O}_3 & \leftrightarrow \text{Fe}_3\text{O}_4 + 3 \text{FeO} + \text{CO} + 2 \text{H}_2 \\
\text{CH}_4 + 4 \text{Fe}_2\text{O}_3 & \leftrightarrow \text{Fe}_3\text{O}_4 + 5 \text{FeO} + \text{CO}_2 + \text{H}_2\text{O} + \text{H}_2 \\
\text{CH}_4 + 4 \text{Fe}_2\text{O}_3 & \leftrightarrow 8 \text{FeO} + \text{CO}_2 + 2 \text{H}_2\text{O} \\
\text{CH}_4 + 5 \text{Fe}_2\text{O}_3 & \leftrightarrow \text{Fe}_3\text{O}_4 + 7 \text{FeO} + \text{CO}_2 + 2 \text{H}_2\text{O} \\
\text{CH}_4 + 12\text{Fe}_2\text{O}_3 & \rightarrow 8\text{Fe}_3\text{O}_4 + \text{CO}_2 + 2\text{H}_2\text{O}
\end{align*}
\]

Figure 2-3 shows that at a low concentration of hematite in the fuel reactor even pure iron will occur. In this case a high concentration of carbon monoxide and hydrogen can be expected while only a small amount of CO₂ will be produced. This means that, in order to achieve a high fuel conversion in the fuel reactor, it is
necessary to increase the amount of hematite. From Figure 2-3a, one can realise, that at an input of 5 mole hematite into the reactor and one mole methane, there will still be some carbon monoxide and hydrogen left after the reaction. A complete conversion of methane to CO$_2$ and water will be achieved if 12 mole hematite reacts with one mole methane (Figure 2-3b). For this reason Reaction Eq. 2-16 will dominate if enough hematite is in the fuel reactor. The re-oxidation of the formed magnetite occurs according to Reaction eq. 2-17.

\[
8\text{Fe}_3\text{O}_4 + 2\text{O}_2 \rightarrow 12\text{Fe}_2\text{O}_3
\]  

(2-17)

In CLC, apparently all oxides will appear at the same time on each particle of oxygen carrier. The reason is that the surface of the particles is more exposed to the reducing gas phase in the fuel reactor than the inner porous body of the particle. This may lead to a significant amount of wustite in the fuel reactor. However, due to considerable changes in the structure of the particle, when magnetite and hematite are reduced to wustite, the formation of wustite in the inner structure of the particle is not desirable. In order to simplify the calculations only the presence of magnetite has been considered in this thesis.

2.2.4 Previous work on reactor design

A suitable reactor system for CLC in an NGCC has to meet the following requirements:

- Enable sufficient particle transport between the fuel reactor and the air reactor to guarantee an efficient fuel conversion
- Prevent gas exchange between the two reactors
- Provide a sufficient reaction time for the reactions
- Reach a sufficiently high temperature to meet the turbine inlet temperature of a modern gas turbine
- Withstand the required pressure of a turbine combustor

The last named requirement assumes that the CLC reactor is pressurised. Initial research on reactor design, however, has been focused on an atmospheric reactor concept. A dual fluidised-bed reactor consisting of a riser and a stationary fluidised bed of the bubble bed type has been suggested. In this design scheme, the riser is the air reactor and the combustion air transports the particles into a cyclone that separates them from the hot oxygen-lean air. From the cyclone the particles flow via a particle pot seal into the fuel reactor. The particle pot seal prevents gas leakage.
from the fuel reactor into the cyclone. From the fuel reactor, which is designed as a bubble bed reactor, the particles flow via a second particle pot seal back into the air reactor. An initial feasibility study of this concept was presented by Lyngfelt et al. (2001). First experiments with a cold model were conducted by Johanson et al. (2002, 2004). Andanz et al. (2003) have presented a kinetic model to optimise the dimensions of the fuel reactor. In 2003, experimental work with a prototype of such a CLC reactor with a thermal capacity of 10 kWth started at Chalmers University of Technology in Gothenburg, Sweden (Lyngfelt et al., 2004).

2.3 Steam-based gasification of biomass

This section provides the reader a background to the studied EvGT-BAT system. This novel process is an integration of externally fired gas turbines (EFGT) with top-firing, evaporative gas turbines (EvGT) and steam-based gasification of biomass (SBGoB). In this section, the relevant technologies for the present work are explained (Sections 2.3.1 and 2.3.2) and previous work on the new process is presented (Section 2.3.3). Section 2.3.4 gives the technical background of the steam-based gasification.

2.3.1 Externally fired gas turbines with topping combustion

A proposed technique for using solid fuels such as coal and biomass in power generation is the concept of externally fired gas turbines (EFGT). The basic idea in EFGT is the application of a high-temperature heat exchanger (HTHx), that indirectly heats the working medium of a gas turbine up to the required turbine inlet temperature (TIT\(^1\)). In this way, the working medium, which is humid air in this study, is heated without mixing with the combustion products, which usually contain traces of the alkali metals sodium and potassium and particles damaging to the gas turbine blades. In EFGT, no combustion products enter the turbine and, therefore, it is possible to use a wide variety of solid fuels such as waste, all types of coal, and biomass without jeopardising the gas turbine. A disadvantage, today, is the temperature limitation of the HTHx. It is a challenge to develop a heat exchanger that withstands the temperature and pressure necessary to meet the requirements of modern gas turbines, which use a TIT of above 1200°C. The maximum temperature of the HTHx, today, may be 900 to 1000 °C (Anheden and Abroth, 1997). Additionally, the melting point of the ash particles may also lead to a

\(^1\) TIT in this work is defined as the temperature of the hot gas when it leaves the combustion and before cooling air is mixed to it.
limitation of temperature in the combustion. Previous work on research and development of EFGT has been reviewed by Yan (1998b).

In the present process, top-firing is used to increase the temperature of the working medium to the desired TIT and, thereby, improve the performance of the process. If top-firing is used, the pressurised air may be heated to the highest possible temperature in the HTHx before entering the topping combustor. In this additional furnace, the air temperature is further increased by combusting a fuel gas. The fuel gas for the topping combustion could be natural gas as in the previous work (Section 2.3.3) or cleaned product gas from a gasification as in the studied EvGT-BAT process (Chapter 6). The exhaust gas from the gas turbine may be used as combustion air in the furnace as suggested in Paper V or it can be used in a heat recovery (HR) to supply heat for humidifying the combustion air as proposed in the EvGT-BAT process.

2.3.2 The evaporative gas turbine cycles (EvGT)

EvGT cycles belong to a group of humidified gas turbine (HGT) cycles that have been studied as an alternative to the combined cycle (CC) and diesel motors for power generation (Ågren, 2000; Bartlett and Westermark, 2003; Dalili, 2003; Jonsson and Yan, 2004). This group consists of gas turbine cycles that utilise cycle heat sources to evaporate water, which in turn augments the expander flowrate. Water can be evaporated in a steam generator as in steam injected gas turbine (STIG) technology, a humidification tower as in the EvGT-BAT cycle, or through water injection into the warm working fluid. The important aspect of HGT cycles is that the turbine flow increase occurs without increasing the compressor flow. The additional work from the larger turbine expander can be utilised in the generator, raising the specific power output and the electrical efficiency of the cycle (Bartlett, 2002).

In EvGT cycles the water vapour is produced directly in the working fluid, which is realised in a humidification tower. The humidification tower is a refinement of a water injection, in which the temperature of the injected water is rapidly raised above its boiling point when mixing with the warm working fluid. In the humidification tower the evaporation of water occurs below its boiling point. The principle is the same as when drying clothes on a clothesline, i.e., despite the air temperature being below the boiling point of water at atmospheric pressure (100°C) water still evaporates into the air (Bartlett, 2002). The physical explanation of this evaporation is that the partial pressure of water at the water-air interface exceeds the partial pressure of water in the air, which causes a mass transport of water molecules driven by diffusion from the water-air interface into the gaseous
phase. Assuming the air-water mixture is an ideal gas, this mass transport continues until the air is saturated, i.e., the partial pressure of water at the interface and in the air are the same. At this state the two-phase system is in phase equilibrium. In order to allow the water and air to come closer to equilibrium, in the humidification tower, water flows in a counter-current direction to the compressed air as a thin film on a packing surface. The flowrate of water decreases on its way through the humidification tower while the flowrate of the water-air mixture increases. Because only a part of the water stream that is flowing down the tower is evaporated, the remaining chilled\(^2\) water at the bottom can be used as an internal heat sink in the cycle. The result of this process is an increased water flowrate, which can be used to recover more heat from the flue gas than is the case with steam or water injection. Hence a humidification tower is a very useful unit to recover larger quantities of low temperature heat, after either a recuperator or a heat recovery steam generator (HRSG). From a comprehensive literature review presented in Jonsson and Yan (2004), the authors concluded that for gasified coal or biomass, the evaporative cycles have a potentially higher efficiency than combined cycles. Moreover, especially in case of smaller power output they also have the potential for lower investment costs and cost of electricity than combined cycles.

2.3.3 Previous work

The studied EvGT-BAT system is a further development of a hybrid process using biomass in a solid fuel combustion (SFC) and natural gas for top-firing. This process has been studied earlier by Yan et al, (1995). The original system (Figure 2-4) contains a gas turbine (T), an intercooler (IC), an aftercooler (AC), a recuperator (RC), a humidification tower (HT), two air preheaters (PH), two economizers (ECO), a solid fuel combustion (SFC), a humid air heater (HAHx), and a high temperature heat exchanger (HTHx). The SFC, fuelled with biomass, provides the main part of the thermal energy for producing electricity. The high-temperature heat exchanger (HTHx) heats the air to about 900 °C. Before entering the turbine, the air temperature is further increased by mixing with the flue gas from the topping combustion to the required turbine inlet temperature of 1100 °C. After being expanded from 12 bar to atmospheric pressure, the exhaust gas is cooled in recuperator, a preheater, and an economizer before it leaves the process at a temperature of about 100 °C. The flue gas from the SFC is cooled in the HTHx, HAH, a preheater for the combustion air and an economizer and leaves the process

\(^2\)The principle for the cooling effect is the same as in an atmospheric cooling tower, in which a water stream is cooled by evaporating a part of it. The cooling effect comes from the heat of evaporation that is consumed during the evaporation.
as well as about 100 °C. The energy for the humidification comes from four sources; these are the intercooler, the aftercooler, and the two economizers.

The original system has been studied and optimised earlier by Yan et al. (1995). Natural gas was used for top-firing and biomass with a heating value of 8.25 MJ/kg at a moisture content of 50 wt% was fed into the SFC. The optimum thermal efficiency of this process was 45%. Initial studies on the integration of a steam-based gasification were conducted in an MS thesis under the co-supervision of the author (Barone, 2000).

![Fig. 2-4. Flowsheet of the reference process using natural gas for top-firing](image)

C = compressor, T = turbine expander, G = generator, IC = intercooler, AC = aftercooler, HT = humidification tower, RC = recuperator, PH = preheater, ECO = economizer, HAHx = humid air heat exchanger, HTHx = high temperature heat exchanger, SFC = solid fuel combustion
2.3.4 Technical background of steam based gasification of biomass

In the EvGT-BAT system, the natural gas is replaced by fuel gas produced from biomass in a steam-based gasification process. This section gives the technical background for this process.

During the twentieth century, a wide variety of gasifiers was investigated (Beenackers, 1994; Brightstar Synfuels Co, 1999; Ising et al., 1998; Kaltschmitt et al., 1998; Yan, 1998b). The main difference between these techniques is the method of heat transfer, heating rate, temperature, pressure and the way of transporting the feedstock the reactor. The mechanism of gasification, however, always follows the same pattern (Figure 2-5). First, the material is preheated and dried. Then the temperature is raised to about 250°C to 700°C where devolatilisation of the volatile matter takes place. This process step is called pyrolysis. In the next step, a great variety of substances consisting of both solid and gaseous components exist. The temperature here is between 700 °C (CFB Gasifier of Lurgi, Frankfurt) and 1400 °C (Carbo V process of UET, Freiberg) and the gaseous components are reacting with the pyrolysis char and with each other (Kaltschmitt, 1998). This step is mainly controlled by char conversion and is called gasification\(^3\). In order to gain a product gas with a higher heating value, steam may be added to the process initialising steam reforming. During this reforming process, more hydrogen and

---

\(^3\) Commonly, the term gasification is used for the whole conversion of a solid matter into a gas.
carbon dioxide are formed. All these steps, preheating, pyrolysis, gasification and steam reforming require energy, which can be supplied in several ways.

The most conventional way of generating the required thermal energy for the gasification is through partial oxidation within the gasification reactor. However, in this direct heating method the product gas is contaminated with flue gas from the incomplete combustion. The stack gas decreases the heating value and, moreover, if air is used as gasifying medium, nitrogen will further dilute the product gas and form nitrogen oxides in the top-firing. These drawbacks can be avoided by indirect methods such as external heating.

The main feature of externally heated gasification is the separation of gas production and heat generation. Similar to externally fired gas turbines, many types of fuel, both solid and gaseous, may be used for heat generation. However, also similar to externally fired gas turbines, a heat exchange system is required limiting the operating temperature of the gasifier. The highest possible temperature is about 850 °C maybe 900 °C. Primary investigations with coal have shown that this

![Diagram of steam-based gasification process](image)

**Figure 2-6. Principle scheme of the steam-based gasification process conducted in an entrained-flow tubular reactor housed in the furnace**
temperature is too low for an efficient conversion. This may be a reason why externally heated gasifiers have not been studied more intensively. Biomass on the other hand can attain very high gasification efficiencies with operation temperatures lower than those required for coal (Consonni and Larson, 1996; Várhegyi et al., 1997; Klass, 1998). A survey of introduced types of gasifier are given by Yan, 1998a; Consonni and Larson, 1996; Klass, 1998.

In the presented EvGT-BAT cycle an externally heated entrained-flow tubular reactor is installed in the SFC. The principle of this gasifier is shown in Figure 2-6. The idea is to propel biomass very rapidly through a tube, which is heated by the SFC. The medium that carries the biomass is recycled product gas, which contains up to 50% steam. Because the tube is installed in the combustion chamber of the SFC, the fuel for heating the gasification is also biomass. Installing the gasification reactor within the SFC reduces the numbers of units for the EvGT-BAT cycle. An advantage of this technique is that moisture from the raw material can be used for the reforming process. Therefore, drying the biomass is not necessary in order to produce a medium-energy fuel gas. Brightstar Synfuels Co. (BSC) has been developing an entrained flow tubular gasifier, which is able to use moist biomass with a water content of up to 60% (Brightstar Synfuels Co, 1999). The advantages of entrained flow tubular reactors for biomass gasification are summarised by Bohn and Benham (1984):

- Very rapid heating rates, of the order of $10^4$ °C/s, thereby minimising char and tar production
- Product gases are not contaminated by products of combustion or nitrogen
- Syngas with a higher heating value up to about 17 MJ/Nm$^3$
- Maximum quantities of hydrogen, carbon monoxide and the unsaturated hydrocarbon species
- Wide variety of heating methods including combustion of solid feedstock, process offgas, natural gas, fuel oil or use of solar energy
- Continuous mode
- High throughput capability
- Compact design

Bohn and Benham (1984) and Brightstar Synfuels Co (1999) discovered that the composition of the product gas is relatively insensitive to the used biomass type. Due to the very high heating rate in the reactor, this process is also called flash pyrolysis. More details about this flash pyrolysis can be found in Paper V.
3 General method

This chapter introduces the general methods that were used to investigate CLC and the EvGT-BAT process. Parameter definitions and specific methods for the individual studies are explained in the chapters where they are applied.

3.1 General method of studying chemical looping combustion

For the studies with CLC the method of approach was to find first a promising power process with CLC for CO₂ capture, if natural gas is used as fuel. In the process the pressure and temperature demands for the CLC reactor were determined in order to reach a sufficiently high thermal efficiency. The mass flowrates of the oxygen carrier, combustion air and natural gas were calculated by a mass and energy balance of the CLC reactor. For this step, including the process simulations and the calculations of the chemical equilibrium of the CLC reactions, the simulation software Aspen Plus® was used.

The second step was to find a suitable reactor design and to define the demands for the particles of oxygen carrier in order to realise the CLC process in a conceivable reactor design. A hydrodynamic analysis of the reactor was conducted to find the required dimensions of the air reactor, the fuel reactor, and the cyclone system. A theoretically possible maximum flowrate of oxygen carrier from the air reactor into the fuel reactor (MTPFR) was defined as the border of feasibility for the CLC reactor. The calculations for the hydrodynamic analysis were implemented in MS Excel®.

The third step was to look at potential oxygen carriers that meet the requirements determined in step one and two. For this task, a new method was developed, in
which the key parameters of CLC are plotted in a diagram called CLC parameter mapping (CLC-PM). The CLC-PM can be seen as an interface between the oxygen carriers’ properties, the requirements of the CLC reactor, and the input data of the system study. The CLC-PM is explained in Section 4.6.1.

### 3.2 General method of studying the EvGT-BAT process

For the studies of the EvGT-BAT process, the method of approach was, first, to gain knowledge of the requirements of the steam-based gasification, if it is conducted in an entrained tubular flow reactor. It was necessary to collect information about the composition of the produced fuel gas at different conditions during the gasification such as heating rate, final temperature, and moisture content. For this step, data from the literature and calculations of equilibria were used (Paper V).

The second step was to implement the steam-based gasification process in Aspen Plus®. An existing model of the same process, but with natural gas for top-firing, was used. For the EvGT-BAT process the stream of natural gas was replaced by the gasifier. The original process was used as a reference process and is described in Section 2.3.3.

In a third step the gasifier was integrated in the process as well as possible in order to reduce the penalty in efficiency caused by the gasification process. The process was simulated with different moisture contents of the biomass used in the gasifier. More details about the integration of the gasifier can be found in Section 6.1.
4 CO₂-free power generation using chemical looping combustion

In this chapter the studied NGCC cycles with CLC for CO₂ capture are described and the results of the conducted studies are presented. In Section 4.1, the studied system and a reference system are described. The results of five system studies with CLC for CO₂ capture in an NGCC are presented in Sections 4.2 to 4.6. Section 4.7 contains the presentation of two conceivable reactor designs and Section 12.7 presents the results of a hydrodynamic analysis of the conceivable reactor designs and the resulting dimensions of a CLC reactor with a thermal capacity of 800 MWₜₐₜ. This study is also published in Papers III and IV.

4.1 The studied systems

In this work, the assumed fuel is natural gas (methane). The fuel input has been set to 16 kg/s (1 kmol CH₄/s) which corresponds to 802 MWₜₐₜ (LHV). A future power generation process using CLC for CO₂ capture will compete with the most efficient technology using gaseous fuels. Today, natural gas-fired combined cycles (NGCC) achieve the highest electrical efficiencies to 60% (Jeffs, 1998). Assuming a penalty in efficiency by 8 to 10 percentage points for CO₂ capture and compression if MEA absorption or an air separation unit is used, these processes will reach an efficiency of about 50% or even higher. In order to find a power process with CLC, that in the future can compete with commercially available techniques, the potential efficiency of a NGCC integrated with CLC has been studied.

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¹ In order to facilitate the calculations, methane has been used throughout this thesis instead of natural gas.
4.1.1 Description of the reference NGCC

The reference system contains only commercially available components and is therefore called the conventional combined cycle (CCC) and is shown in Figure 4-1. The compressor ratio is 13 and the turbine inlet temperature (TTT) of the gas turbine is 1200°C. For turbine cooling, 11% of the compressor air bypasses the combustion chamber. After the combustion gas is expanded in the gas turbine, it enters a tri-pressure reheat steam cycle that contains three boilers (A3, A6, and A9), which operate at 110 bar, 20 bar and 1.7 bar (Figure 4-1). The superheaters A1 and A2 heat the steam to 450°C before the high-pressure turbine (hp turbine) and 470°C before the intermediate-pressure turbine (ip turbine). The heat exchangers A4, A8, and A10 are economizers and pre-heat the water close to the boiling point. The stack gas leaves the process at 74°C and is a mixture of N₂, H₂O, O₂ and CO₂.

This power cycle was chosen as a the reference system, because a TIT of 1200 °C may be the minimum requirement for a modern gas turbine used in a combined cycle and the maximum reachable temperature of the air reactor in CLC. This power cycle is especially suitable for studying the necessary changes in order to integrate CLC into the process, because the TIT and the pressure in the

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Figure 4-1. Flowsheet of the reference system, here denoted conventional combined cycle (CCC)

---

2 TTT in this work is defined as the temperature of the hot gas when it leaves the combustion and before cooling air is mixed to it.
Combustion chamber are the same as in the studied NGCC with CLC. Comparing the new power cycle with CLC with this reference system will show the impact of applying CLC on the efficiency.

4.1.2 Description of studied systems (CC-CLC)

The studied power process is a natural gas-fired combined cycle, which is based on the reference process (CCC), with CLC for CO₂ capture (CC-CLC). In the CC-CLC system the combustor of the gas turbine is replaced by the CLC (Figure 4-2). Due to the principle of the CLC, the main difference between the two processes is that two streams of combustion products enter the bottoming steam cycle. The first one comes from the gas turbine and consists of nitrogen and some excess air. The second one is much smaller and comes directly from the fuel reactor. It contains only steam and CO₂. The temperature of this stream is much higher than the temperature of the gas from the gas turbine outlet. The CO₂/H₂O stream is, therefore, used to increase the steam temperature before the high-pressure and the intermediate-pressure steam turbines (superheaters B1 and B2 in Figure 4-2). In this way, higher inlet temperatures for the high-pressure and the intermediate-pressure steam turbines are reached in the CC-CLC than in the CCC. Another feature of the

**Figure 4-2. Flowsheet of the studied combined cycle with CLC for CO₂ capture (CC-CLC)**

A1, A3, A6 = superheater; A2, A5, A9 = evaporator; A4, A7, A8, A10 = preheater
B1, B2 = superheater; B3 economizer; B4 = supplemental evaporator; B5 = preheater
P = pump; C = condenser; G = generator
CC-CLC is that the dew point of the compressed CO\textsubscript{2}/H\textsubscript{2}O stream is above the boiling point of the water in the evaporator of the low-pressure steam turbine (evaporator B4 in Figure 4-2). Hence a part of the heat of evaporation of the steam generated in the fuel reactor can be recovered in the steam cycle, which increases the efficiency of the whole process. The CC-CLC includes a CO\textsubscript{2} compressor, which compresses the separated CO\textsubscript{2} to 110 bar. More information can be found in Section 4.2.1.

\begin{table}[h]
\centering
\caption{Assumptions for the cycle calculations}
\begin{tabular}{|l|c|c|}
\hline
\textbf{Fuel input (1 kmolCH\textsubscript{4}/s = 16 kg/s) [MW]} & CCC & CC-CLC \\
\hline
\textbf{Efficiencies} & & \\
Isentropic efficiency of the gas turbine [%] & 90 & 90 \\
Isentropic efficiency of the compressor [%] & 85 & 85 \\
Isentropic efficiency of the steam turbine [%] & 91 & 91 \\
Isentropic efficiency of the pumps [%] & 65 & 65 \\
Isentropic efficiency of the booster fan [%] & 88 & 88 \\
Mechanical efficiency of the gas turbine [%] & 99 & 99 \\
Mechanical efficiency of the compressor [%] & 100 & 100 \\
Mechanical efficiency of the steam turbine [%] & 98 & 98 \\
Mechanical efficiency of the booster fan [%] & 100 & 100 \\
Mechanical efficiency of the pumps [%] & 100 & 100 \\
Efficiency of the generator [%] & 100 & 100 \\
\hline
\textbf{Gas turbine compressor} & & \\
Pressure ratio [-] & 13 & 13 \\
Inlet temperature [°C] & 15 & 15 \\
Intet air pressure [bar] & 1 & 1 \\
\hline
\textbf{Gas turbine expander} & & \\
TIT [°C] & 1200 & 1200 \\
Partial flow of compressor air used for cooling [%] & 11 & 11 \\
\hline
\textbf{hp steam turbine} & & \\
Inlet temperature [°C] & 450 & 570 \\
Pressure change [bar] & 110/20 & 150/20 \\
\hline
\textbf{ip steam turbine} & & \\
Inlet temperature [°C] & 470 & 570 \\
Pressure change [bar] & 20/1.7 & 20/1.7 \\
\hline
\textbf{lp steam turbine} & & \\
Inlet temperature [°C] & 180 & 190 \\
Pressure change [bar] & 1.7/0.06 & 1.7/0.06 \\
\hline
\textbf{Heat exchanger – minimum temperature difference} & & \\
gas – gas heat exchanger [°C] & 30 & 30 \\
gas – water heat exchanger [°C] & 10 & 10 \\
water – water heat exchanger [°C] & 10 & 10 \\
\hline
\end{tabular}
\end{table}
4.1.3 Assumptions for the performance studies of the system

The CCC and the CC-CLC systems were simulated with Aspen Plus® using the same assumptions for the gas turbine and the heat exchangers’ pinch points. The heat losses in heat exchangers, steam generators or the CLC reactor are not included. The pressure drops in the heat exchangers and pipes are neglected. The pressure drop over the CLC reactor, however, is considered in Section 4.4. Detailed information about the assumptions for the system analysis can be found in Table 4-1.
4.2 Comparison of a standard NGCC to an NGCC using CLC for CO₂ capture

In this study, the potential efficiency of a CC-CLC is compared to the CCC using MEA absorption for CO₂ capture (CCC-MEA). The MEA absorption was not simulated in this thesis, but a penalty in electrical efficiency of 8 to 10 percentage points for the absorption process was assumed referring to the literature (Audus, 2000; Herzog et al., 1997; Göttlicher, 1997; Bolland, 2002). As can be seen in Section 4.1.3, all pressure losses and heat losses in pipes, heat exchangers and combustion are neglected in both processes. This study was published in Paper I. A further comparison of these to processes by using an exergy analysis can be found in Paper II.

4.2.1 Results of the system simulation

The resulting temperature profile of the optimised steam cycles for the reference system is shown in Figure 4-3. The x-axis gives the amount of exchanged heat and the y-axis shows the temperature at which the heat exchange occurs. Figure 4-3a shows the results of the reference system. Figure 4-3b shows the optimised steam cycles of CC-CLC.

The thermal efficiency of the reference system was about 55% (LHV) without considering CO₂ capture. According to Göttlicher (1997) and Audus (2000), the CO₂ separation reduces this efficiency by about eight percentage points and the compression of CO₂ up to 110 bar by about two percentage points. Thus, the CCC-MEA process will achieve a maximum thermal efficiency of 45%. The maximum thermal efficiency for the CC-CLC process is between 52 and 53%.

4.2.2 Discussion

The comparison between the CC-CLC and the reference system with state-of-the-art technology for CO₂ capture (CCC-MEA) showed that the CC-CLC process has the potential to achieve five percentage points greater efficiency if both processes operate at a TIT of 1200°C. While an available CO₂ capture technology reduces the efficiency of an NGCC by about eight percentage points plus two percentage
points for CO₂ compression, CLC only causes two to three percentage points penalty in efficiency.

This study also shows that the CC-CLC system is only more efficient than a CCC if CO₂ capture is included. The efficiency of the CC-CLC system was 2 to 3 percentage points lower than the efficiency of the CCC cycle without CO₂ capture. In Paper II an exergy analysis is presented that confirms this conclusion.

*Figure 4-3. Heat exchanger profile. Q is the exchanged heat based on 1 kmol CH₄/s and Ax/Bx refers to Figures 4-1 and 4-2.*
4.3 Performance study of a CC-CLC process including a CO₂ expander

Previous researchers suggested a CO₂ expander to produce extra power from the CO₂/H₂O stream (Ishida et al., 1987; Anheden et al., 1995; Brandvoll et al., 2002; Naqvi, 2004). However, in these previous studies, the conclusions were based on process simulations, in which no CO₂ compression was considered. In this study the CC-CLC process has been extended with a CO₂ expander, in order to investigate whether a CO₂ expander will improve the overall efficiency if CO₂ compression is included. The bottoming steam cycle has been re-designed. The new configuration of the CC-CLC is called CC-CLC-CO2ex. The same assumptions are used as for the CC-CLC system in Section 4.2. A more detailed study concerning the integration of a CO₂ expander in an NGCC with CLC can be found in Paper I.

4.3.1 Description of the system with CO₂ expander

The flowsheet of the CC-CLC-CO2ex is shown in Figure 4-4. The application of the CO₂ expander has two major effects on the design of the bottoming steam cycle. One change is that the temperature of the CO₂/H₂O stream is reduced by about 400°C after the CO₂ expander. Due to the lower temperature of this stream when entering the steam cycle, lower steam data will be reached in the superheaters. Therefore, the inlet pressure of the high-pressure steam turbine is reduced from 150 bar to 120 bar and the inlet temperatures for the three turbine steps are reduced from 570 to 483 °C (hp turbine), from 570 to 503 °C (ip turbine) and from 190 to 175 °C (lp turbine), respectively. Another consequence of introducing the CO₂ expander is that the CO₂/H₂O mixture has atmospheric pressure when passing through the steam cycle. The dew point of this mixture is below 100°C; thus, the integration of a condenser and an evaporator, as in the CC-CLC process, is impossible according to the two-phase behaviour of the CO₂/H₂O mixture at atmospheric pressure.
4.3.2 Results

The main result of this study is that the efficiency of the CC-CLC-CO2ex configuration also reached a value between 52 and 53%. Figure 4-5 shows the heat exchanger profile of the CC-CLC-CO2ex. It can be seen that the outlet temperature of the CO₂ expander is about 200°C higher than that of the gas turbine. This is due to the lower isentropic coefficient of the CO₂/H₂O stream (1.24) compared to the one of nitrogen (1.38). The smaller isentropic coefficient results in a smaller temperature drop when expanding both streams by the same pressure ratio.

From a comparison of Figures 4-5 and 4-3b, one can see that in spite of the complexity of the bottoming steam cycle of the process CC-CLC-CO2ex, the amount of recovered heat is about 100 MW larger in the CC-CLC configuration.
4.3.3 Discussion

Although CC-CLC-CO2ex contains a CO₂ expander, the efficiency is similar to that for CC-CLC. This may be due to the following two reasons. The first is that the CO₂ must be compressed to 110 bar in the studied systems. The calculations showed that the required compression work for compressing the CO₂ stream from 1 bar to 110 bar reduces the efficiency by about two percentage points in the process CC-CLC-CO2ex. In the CC-CLC process, after condensing the water from the CO₂/H₂O-mixture, the stream of pure CO₂ still has a pressure of 13 bar. Thus, the CO₂ stream has to be compressed from 13 bar to 110 bar instead of from 1 bar to 110 bar. Since the critical pressure of CO₂ is at 73.9 bar (Perry, 1997), the major compression work is already performed for the compression from 1 to 13 bar. In this way, power is saved for compressing the CO₂ in the CC-CLC. Compressing the CO₂ diminishes the efficiency by only 0.8 percentage points in the CC-CLC.

The second reason is that the dew point at 13 bar of a CO₂/H₂O-mixture is at 171°C which is above the boiling point of the water for the second reheat stream (1.7 bar, boiling temperature 115 °C). The high temperature of the dew point makes it possible to use a part of the latent heat from the pressurised steam in the CO₂/H₂O mixture to evaporate water for the second reheat. At 1 bar the dew point of the CO₂/H₂O mixture is at 88 °C and thereby below the boiling point of the water for the second reheat (1.7 bar). For this reason, the latent heat in the CO₂/H₂O stream of process CC-CLC-CO2ex cannot be recovered for power production which leads to losses in the thermal efficiency compared the CC-CLC.

![Heat exchanger profile of the CC-CLC-CO2ex. Q is the exchanged heat based on 1 kmolCH₄/s and Ax/Bx refers to Figure 4-4.](image-url)
The result from this study indicates that the investment in a CO₂ expander in the CC-CLC with a TIT of 1200 °C and a compressor ratio of 13 cannot be recommended, because the extra power gained by the CO₂-expander will be lost again due to a less efficient bottoming steam cycle and the extra power required for the CO₂ compression. Moreover, the CO₂ expander that operates at such high temperature has to be cooled by, e.g., steam which would reduce the efficiency further.
4.4 Comparison of nickel oxides and iron oxides as oxygen carrier

Previous studies showed that both iron and nickel-based particles are promising oxygen carriers. The advantage of nickel-based oxygen carriers is that they apparently withstand a higher operating temperature and that they are more efficient in transporting oxygen. The disadvantages of nickel are its high price and that it can be hazardous to personnel (Section 2.2.3). Therefore, it is relevant to study iron as an alternative oxygen carrier. Advantages with iron are the environmental compatibility of its oxides magnetite (Fe₃O₄), hematite (Fe₂O₃), and wustite (FeO) and the lower price of hematite than of nickel oxide (NiO).

This study is to investigate whether iron-based oxygen carriers are a possible alternative to nickel-based oxygen carriers and what technical requirements have to be fulfilled so that CLC can be used efficiently in an NGCC. The technical constraints of different oxygen carriers from the viewpoint of the system’s performance and the feasibility of the reactor have been considered, including the reaction kinetics, required mass flowrates and agglomeration of the particles resulting in temperature limitations.

As previously stated (Section 3.1), CLC parameter mapping (CLC-PM) has been developed, in which the key parameters of CLC are plotted in a diagram. The CLC-PM can be seen as an interface between the oxygen carriers’ properties, the requirements of the CLC reactor, and the input data for a system study. This new method is described in Section 4.4.1. In Section 4.4.2, the studied cases are introduced and in Sections 4.4.3 to 4.4.5 the results of the parameter mapping and a system analysis are presented and discussed. This study was published in Paper II.

4.4.1 Method

The CLC-PM is based on a mass and energy balance over the CLC reactor and summarises the key parameters in a comprehensive diagram. Figure 4-6 shows the principles of the CLC-PM. The diagram includes the mass flowrate of solids entering the air reactor (x-axis) and the mass flowrate of combustion air (y-axis). The lines in the diagram are isotherms of the air reactor (negative slope) and the fuel reactor (positive slope). The vertical dashed lines give the conversion degree
CO₂-free power generation using chemical looping combustion

(x) of metal oxide in the fuel reactor. By knowing two independent parameters, for example, the conversion degree and the temperature in the air reactor, the remaining parameters can be read from the diagram (Point A in Figure 4-6).

The conversion degree of the oxygen carrier (X) is defined as the ratio of the number of moles of the oxygen carrier that are reduced in the fuel reactor to the number of moles of the oxidised form that enter the reduction reactor. If the conversion of one mole methane to one CO₂ and two mole H₂O is assumed, the conversion of the nickel and iron-based oxygen carriers is described by Eqs. 4-1 and 4-2, respectively (referring to Reaction Eqs. 2-5 and 2-16).

\[
x_{\text{Nickel}} = \frac{n_{\text{NiO(input)}} - n_{\text{NiO(output)}}}{n_{\text{NiO(input)}}} = \frac{n_{\text{NiO(reduced)}}}{n_{\text{NiO(input)}}} = \frac{4 \cdot n_{\text{CH}_4}}{n_{\text{NiO(input)}}}
\]

\[
x_{\text{Iron}} = \frac{n_{\text{Fe}_2\text{O}_3(input)} - n_{\text{Fe}_2\text{O}_3(output)}}{n_{\text{Fe}_2\text{O}_3(input)}} = \frac{n_{\text{Fe}_2\text{O}_3(reduced)}}{n_{\text{Fe}_2\text{O}_3(input)}} = \frac{12 \cdot n_{\text{CH}_4}}{n_{\text{Fe}_2\text{O}_3(input)}}
\]

In addition to the conversion degree, another property of the oxygen carrier is the mass flowrate of oxygen carrier (oxidised form) that is necessary to transport the oxygen. This mass ratio between oxygen and oxygen carrier, we define as the mass

\[3\text{ In the case of nickel, this assumption is not entirely correct, because about 1% of the methane is converted to hydrogen and carbon monoxide.}\]
per transported oxygen value (MOV). For example: the reaction of pure hematite to magnetite follows Eq. (4-3)

\[3\text{Fe}_2\text{O}_3 \leftrightarrow 2\text{Fe}_2\text{O}_4 + \frac{1}{2}\text{O}_2. \quad (4-3)\]

The MOV for pure hematite to magnetite is therefore \(3 \times 159.7 / 16 = 29.9\) kg hematite/kg oxygen. If the hematite is stabilised with \(\text{Al}_2\text{O}_3\) in a mixture of 60 wt\% \(\text{Fe}_2\text{O}_3\) and 40 wt\% \(\text{Al}_2\text{O}_3\), the MOV\(_{\text{Fe}_2\text{O}_3,\text{Al}_2\text{O}_3}\) increases to 49.9 kg/kg. The MOV for the nickel-based particle can be calculated in the same way and results in MOV\(_{\text{NiO},\text{NiAl}_2\text{O}_4}\) = 9.3 kg/kg, if the mixture consists of 50 wt\% NiO.

An important information for the evaluation of oxygen-carrier material is the maximum mass flowrate of oxygen carrier, that can be circulated in the CLC reactor. In this thesis the maximum theoretically possible flowrate of oxygen carrier from the air reactor into the fuel reactor (MTPFR) is introduced. This flowrate is specific for each reactor design and is explained later in Section 4.7.1. In this section an MTPFR, based on the conceivable reactor designs described later in Section 4.7, is included.

### 4.4.2 Description of the studied cases

Seven cases are considered for the simulations of the CC-CLC system (Table 4-2). Four parameters have been varied: the three oxygen carriers, two different turbine inlet temperatures, two different pressure levels in the CLC, and three different conversion degrees of the oxygen carriers. The flowrate of fuel gas (methane) is 1 kmol/s which corresponds to a thermal capacity of the CLC of about 802 MW (LHV). The temperature in the air reactor was set to 1200°C and the pressure ratio in the gas turbine was 13 in the cases with \(\text{Fe}_2\text{O}_3\) stabilised with 40 wt\% \(\text{Al}_2\text{O}_3\) (cases C and D) and in the cases with NiO stabilised with 50 wt\% NiAl\(_2\text{O}_4\) (cases E to G). Two cases with a TIT of 1000°C and a pressure ratio of 9 have been studied.

Two more cases (\(C_A'\) and \(C_B'\), derived from case C) are analysed, in which the residence time of the oxygen carrier in the air reactor is varied. These two cases are further described in Appendix 12.2. They are interesting for the system study because the increased residence time results in an increased pressure drop in the CLC reactor.
Table 4-2. Studied cases with combination of oxygen carriers, turbine inlet temperature, pressure of CLC reactors, and conversion degree of active metal oxide in the fuel reactor

<table>
<thead>
<tr>
<th>Case</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen carrier</td>
<td>Fe₂O₃</td>
<td>Fe₂O₃</td>
<td>Fe₂O₃/Al₂O₃</td>
<td>Fe₂O₃/Al₂O₃</td>
<td>NiO/NiAl₂O₄</td>
<td>NiO/NiAl₂O₄</td>
<td>NiO/NiAl₂O₄</td>
</tr>
<tr>
<td>TIT [°C]</td>
<td>1000</td>
<td>1000</td>
<td>1200</td>
<td>1200</td>
<td>1200</td>
<td>1200</td>
<td>1200</td>
</tr>
<tr>
<td>P_CLC [bar]</td>
<td>9</td>
<td>9</td>
<td>13</td>
<td>13</td>
<td>13</td>
<td>13</td>
<td>13</td>
</tr>
<tr>
<td>X [%]</td>
<td>70</td>
<td>20</td>
<td>70</td>
<td>20</td>
<td>70</td>
<td>40</td>
<td>20</td>
</tr>
</tbody>
</table>

P_CLC = Pressure in CLC reactors
X = Conversion of active metal oxide in the fuel reactor; the inert material is not considered

4.4.3 Results of the CLC Parameter Mapping

Figure 4-7 shows the CLC-PMs for

a) Pure Fe₂O₃ for 9 bar,

b) Fe₂O₃ with 40 wt% Al₂O₃ as inert material for 13 bar, and

c) NiO with 50 wt% NiAl₂O₄ as inert material for 13 bar.

In all cases, the natural gas (methane) is preheated to 180 °C and the combustion air has a temperature depending on the gas turbine pressure ratio. For example, the combustion air has a temperature of 306 °C at 9 bar or 372 °C at 13 bar before it enters the air reactor.

Figure 4-7a) shows the CLC-PM for pure Fe₂O₃. The points A and B mark the system’s positions in the chart for cases A and B. In case A, for example, the required mass flowrate of the solids is 2670 kg/s, the mass flowrate of the combustion air is 970 kg/s, and the temperature in the fuel reactor is 913 °C. From the chart can be seen that the mass flowrate of the circulating solids has to increase by more than three times if the conversion degree decreases from 0.7 to 0.2. At the same time, more heat will be transferred from the air reactor to the fuel reactor; thus, the temperature in the fuel reactor increases from about 910°C in case A to 975 °C in case B. The mass flowrate of combustion air, which also cools the reactor, will slightly decrease from about 970 to 960 kg/kmol CH₄, because the mass flowrate of oxygen carrier, which has to be heated in the air reactor, is greater.
Figure 4-7. **a)** CLC-PM for Fe₂O₃ at 9 bar; **b)** CLC-PM for Fe₂O₃/Al₂O₃ at 13 bar; the particles contain 40 wt% Al₂O₃; **c)** CLC-PM for NiO/NiAl₂O₄ at 13 bar, the particle contains 50 wt% NiAl₂O₄.
Figure 4-7b) shows the CLC-PM for Fe$_2$O$_3$ with 40 wt% Al$_2$O$_3$. Due to the presence of inert aluminium oxide, the required mass flowrate of circulating solids is much larger in cases C and D than that in the respective cases A and B. In case D, about 16 t/s oxygen carrier would have to be circulated in an 800 MW$_{th}$ reactor. At this high circulation rate, the temperature in the air and fuel reactors will almost be equal.

Figure 4-7c) shows the CLC-PM for NiO with 50 wt% NiAl$_2$O$_4$. The mass flowrate of solids is much smaller than in the cases with iron-based oxygen carriers. A comparison of cases D and G shows that the mass flowrate of solids is 80% less when the nickel-based particle is used instead of the iron/aluminium-based particle.

Figure 4-7b shows the impact of the MTPFR on the feasibility of CLC in the IPFBR. An operating line divides the chart into two regions. On the left hand side of the operating line (case C), the required flow of oxygen carrier is less than the MTPFR and on the right hand side (case D) the required mass flow is not possible in the suggested reactor. The same can be concluded for case B in Figure 4-7a. Cases B and D are, therefore, not included in the performance analysis. The result indicates that when using the suggested reactor, a conversion degree of about 60% is necessary for the Fe$_2$O$_3$/Al$_2$O$_3$ particles in order to realise CLC with a TIT of 1200 °C. Generally, this result suggests that an oxygen carrier with a MOV of about 50 kg/kg should react fast enough for a conversion of 60% to be achieved in the available reaction time. Figure 4-7c shows the impact of the oxygen carriers’ MOV on the reactor design. If NiO is used as the oxygen carrier, the required mass flow is much less compared to the Fe$_2$O$_3$/Al$_2$O$_3$ case, because of the lower MOV of NiO. Even at a conversion degree of less than 20%, the MTPFR will not be reached. This shows that NiO is a suitable oxygen carrier even if the oxidation would be slower than in case of an iron-based oxygen carrier.

When using the first mode of operation, case C turns into case C’ (Figure 4-7b). In case C’ the reactor works at the operating point and, therefore, its flow of oxygen carrier is always the MTPFR. This means for case C’ that more particles circulate in the reactor than necessary or that conversion degree of about 58% of the oxygen carrier is required in order to reach 1200 °C in the air reactor.

4.4.4 The impact of pressure drop and fan power

The efficiency losses due to the pressure drop over the CLC reactor are different for different oxygen carriers because the circulating flowrate of the solid particles depends on the MOV and the conversion degree of the oxygen carrier. The
The pressure drop over the air reactor plus cyclones was calculated by using the dimensions that are presented later in Section 12.7. Table 4-3 shows the pressure drops over the air reactor plus four pairs of cyclones and the fuel reactor, the resulting fan power, and the total required fan power for the 800 MWth CLC reactor.

The pressure drop over the air reactor plus cyclones is largest in cases C_B’ (0.5 bar), because of the great amount of bed material. In cases A, B, E, F, and G, the pressure loss is only half of that in case C_B’. The pressure drop over the fuel reactor is higher, because the 60 s residence time of the oxygen carrier in the fuel reactor leads to a much greater amount of bed material in this reactor than in the air reactor. However, the volume flowrate of the gases through the air reactor is almost forty times the one through the fuel reactor. Due to this large difference in the volume flowrate, the required fan power is much less for the fuel reactor than for the air reactor. The total required fan power is greatest in case C_B’ with about 11 MW. Case A requires more fan power than the cases C, E, F, and G. This is due to the lower pressure in the CLC which leads to a larger volume flowrate and consequently to a greater volumetric work for compression.

<table>
<thead>
<tr>
<th>Case</th>
<th>A</th>
<th>C</th>
<th>C_A'</th>
<th>C_B'</th>
<th>E</th>
<th>F</th>
<th>G</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔP air reactor plus cyclones [bar]</td>
<td>0.47</td>
<td>0.24</td>
<td>0.37</td>
<td>0.49</td>
<td>0.24</td>
<td>0.24</td>
<td>0.24</td>
</tr>
<tr>
<td>ΔP fuel reactor [bar]</td>
<td>0.26</td>
<td>0.62</td>
<td>0.80</td>
<td>0.80</td>
<td>0.11</td>
<td>0.20</td>
<td>0.41</td>
</tr>
<tr>
<td>Fan power air reactor [MW]</td>
<td>9.4</td>
<td>3.0</td>
<td>4.5</td>
<td>6.0</td>
<td>3.1</td>
<td>3.1</td>
<td>3.0</td>
</tr>
<tr>
<td>Fan power fuel reactor [MW]</td>
<td>0.1</td>
<td>0.2</td>
<td>0.3</td>
<td>0.3</td>
<td>&lt;0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Total fan power [MW]</td>
<td>9.5</td>
<td>3.2</td>
<td>4.8</td>
<td>6.3</td>
<td>3.2</td>
<td>3.1</td>
<td>3.1</td>
</tr>
<tr>
<td>Mean residence time in air reactor [s]</td>
<td>4.8</td>
<td>4.8</td>
<td>8.1</td>
<td>11.4</td>
<td>4.8</td>
<td>4.8</td>
<td>4.8</td>
</tr>
<tr>
<td>Diameter of the air reactor [m]</td>
<td>7.1</td>
<td>5.7</td>
<td>5.7</td>
<td>5.7</td>
<td>5.8</td>
<td>5.7</td>
<td>5.7</td>
</tr>
<tr>
<td>Total bed mass in the air reactor [t]</td>
<td>13</td>
<td>22</td>
<td>47</td>
<td>66</td>
<td>4</td>
<td>7</td>
<td>14</td>
</tr>
<tr>
<td>Total bed mass in the fuel reactor [t]</td>
<td>160</td>
<td>270</td>
<td>345</td>
<td>345</td>
<td>48</td>
<td>86</td>
<td>176</td>
</tr>
<tr>
<td>Flowrate of oxygen carrier [t/s]</td>
<td>2.7</td>
<td>4.5</td>
<td>5.8</td>
<td>5.8</td>
<td>0.8</td>
<td>1.4</td>
<td>2.9</td>
</tr>
</tbody>
</table>
4.4.5 Results of the system analysis

The turbine inlet temperature (TIT) has the most important impact on the efficiency of the combined cycle (Table 4-4). The efficiency decreases by about 4 percentage points when the TIT is reduced 200 °C, i.e., from 1200 °C to 1000 °C (Case A). This shows the disadvantage of systems with pure Fe₂O₃ as oxygen carrier because the maximum operation temperature for pure Fe₂O₃ is limited to 1000°C (Section 2.2.3).

When comparing the oxygen carriers NiO and Fe₂O₃ stabilised with Al₂O₃, no significant difference in efficiency could be found, though the pressure drop over the CLC reactor differs significantly. Systems C, E and F all have efficiencies of about 52 to 53%. The penalty in efficiency for the power consumption of the booster is relatively small (max: case Cₐ with 0.8 percentage points; min: cases C, E-G with 0.4 percentage points, Table 4-4). This shows that the loss due to the pressure drop in the CLC reactor, caused by a larger MOV or a longer residence time of an oxygen carrier, is less important than the TIT.

Other parameters linked to the oxygen carrier, which may have an impact on the process’ efficiencies, include the temperature in the fuel reactor and the combustion air flowrate (CLC PM in Figure 4-7). However, the system analysis has shown that these variations have no significant impact on the overall electrical efficiency of the studied CC-CLC system.

<table>
<thead>
<tr>
<th>Case</th>
<th>A</th>
<th>C</th>
<th>Cₐ</th>
<th>Cₐ</th>
<th>E</th>
<th>F</th>
<th>G</th>
</tr>
</thead>
<tbody>
<tr>
<td>η₁ [1]</td>
<td>49.2</td>
<td>52.5</td>
<td>52.5</td>
<td>52.5</td>
<td>53.0</td>
<td>52.8</td>
<td>52.1</td>
</tr>
<tr>
<td>η₂ [2]</td>
<td>48.6</td>
<td>52.1</td>
<td>51.9</td>
<td>51.7</td>
<td>52.6</td>
<td>52.4</td>
<td>51.7</td>
</tr>
</tbody>
</table>

1) The electrical efficiency without the power consumption of the booster fan
2) The electrical efficiency including the power consumption of the booster fan

4.4.6 Discussion

The question was raised, whether it is possible to use an iron-based oxygen carrier instead of a nickel-based one in an efficient NGCC using CLC for CO₂ capture and what are the requirements on that oxygen carrier. The following answers are found:

- If the conversion degree of hematite stabilised with 40 wt% aluminium oxide is over 60 %, and the operating temperature is not limited to below the
desired TIT (e.g., 1200 °C), this oxygen carrier might be an alternative to nickel oxide.

- Pure hematite is, due to its temperature limitation, apparently no option as oxygen carrier if CLC is used in an NGCC. If the temperature in the air reactor is limited to 1000 °C, the electrical efficiency would be between 48 % and 49 %. This is about the same efficiency as for an NGCC with a post-combustion CO₂ absorption process. In this case there would be no incentive for the power industry to adopt CLC.

An important aspect concerning the MOV of an oxygen carrier may be an unwanted gas transport between the air and the fuel reactor. Due to the porosity of the oxygen carrier, gas will be enclosed in the particles when they circulate between the two reactors. If the particles, for example, flow from the air reactor into the fuel reactor nitrogen will travel with them and be released in the fuel reactor. The same mechanism will lead to a transport of CO₂ into the air reactor and thereby reduce the degree of CO₂ capture. Assuming that 5 t of oxygen carrier circulate per second in the CLC reactor this gas exchange might be significant, especially if the reactor is pressurised as necessary for the use in an NGCC. The unwanted gas exchange in CLC may be an advantage for nickel-based oxygen carriers, because they result in a smaller flowrate of particles.
4.5 Impact of the degree of conversion in the fuel reactor on the thermal efficiency of the system

An NGCC with CLC for CO₂ capture has the potential to reach a thermal efficiency of 52 to 53 %, if a temperature of 1200 °C can be reached in the air reactor and if the combustion efficiency in the fuel reactor reaches 100 %. A combustion efficiency of 100% means that all methane is converted to CO₂ and steam. However, if the fuel reactor contains a fluidised bed, some methane may stay unconverted. Bubbles of methane are formed, which move through the bed material faster than all the methane can react. This may occur because of slow convection and diffusion processes within the bubbles. The combustion efficiency depends among other variables on the amount of bed material and the gas velocity in the reactor. Assuming a thermal efficiency of 53%, each percentage point loss in combustion efficiency reduces the overall efficiency by 0.53 percentage points. Moreover, in the studied systems, the compression of CO₂ to 110 bar is included, which means that all unconverted methane will also be compressed and thereby consume some compressor work. In this section the impact of the combustion efficiency on the overall efficiency is presented and a simple separation step is studied as a potential solution to this problem. Initial work for this study was done in an MS thesis under supervision of the author (Hicking, 2002).

4.5.1 Description of studied cases

In order to investigate the importance of the combustion efficiency, three cases were studied. In all cases the steam of the CO₂/H₂O stream is completely condensed while the gas mixture is compressed and cooled. The unconverted methane does not condense and remains in the gaseous phase. In Case I, the methane was compressed to 110 bar along with the CO₂. The methane leaves the process unused. In Case II, it was assumed that a part of the unconverted methane is separated by a one-step condenser after the gas mixtures was compressed to 71 bar, which is close to the critical point of CO₂ (73.9 bar, Perry et al., 1997). This one-step condensation is further explained in Section 4.5.2. In Case II, no additional energy was necessary for separating the unconverted methane from the CO₂. The separated methane is recycled into the fuel reactor. Case III is a hypothetical case. Complete recycling of the unconverted methane back into the fuel reactor, after
compression to 110 bar, is assumed while the energy for the required separation of methane from the outgoing CO₂ stream is not included. This case shows the efficiency losses caused by the additional compressor work for the unconverted methane and is defined as a reference case for comparison with Cases I and II.

4.5.2 Separation of methane and CO₂ by a "simple" condensation in Case II

The potential efficiency of a condenser is connected to the two-phase behaviour of the mixture under the prevailing pressure. Figure 4-8 shows the two-phase behaviour of a methane-CO₂ mixture at 71.2 bar. The upper line of the two-phase region is the dew-point curve (green curve in Figure 4-8) and the lower line is the boiling-point curve (blue curve Figure 4-8). When reducing the total pressure, the two-phase region will move towards lower temperatures such that cooling of the condenser below 15°C will be necessary. Since one of the features in Case II was to avoid the use of external cooling sources or extra power for the separation process, 71.2 bar was chosen for the condensation. A further increase of the total pressure will lead to an increase in power consumption and, moreover, above a partial pressure of 73.9 bar CO₂ is supercritical and no separation would be possible.

From Figure 4-8 can be seen that a complete separation in one step is impossible, assuming a gas mixture of 15% methane and 85% CO₂ at a total pressure of 71.2

![Figure 4-8. Two-phase behaviour of methane and CO₂ at 71.2 bar based on the Peng-Robinson equation of state (Aspen Plus®)](image)
bar is cooled from 30 °C to 15 °C (Points A and B in Figure 4-8). At phase equilibrium the liquid phase will have a methane concentration of 9 % (Point B') and the gas phase will contain 17 % methane (Point B''). The fraction $G$ of the original amount of gas ($F$) that will stay in the gas phase can be calculated by Eq. 4-4. The fraction $L$ that will condense can be calculated by Eq. 4-5,

$$G = \frac{|B'B|}{|B'B''|} \cdot F \quad [\text{mol}]$$  \hspace{1cm} (4-4)$$

$$L = \frac{|BB''|}{|B'B''|} \cdot F \quad [\text{mol}]$$  \hspace{1cm} (4-5)$$

where $F$ has the unit mole and $|B'B|$, $|B'B''|$ and $|BB''|$ are the distances from the respective points to each other in Figure 4-8. According to Eq. 4-6 and Figure 4-8, when condensing the gas mixture at 15°C, the ratio of the recycled amount of methane ($n_{\text{CH}_4, \text{recycle}}$) to the amount of unconverted methane ($n_{\text{CH}_4, \text{unconv}}$) is about 78 % (Eq. 4-6). This means that about 78% of the unconverted methane could be recycled by a one-step condenser at 15°C.

$$\frac{n_{\text{CH}_4, \text{recycle}, 15^\circ\text{C}}}{n_{\text{CH}_4, \text{unconv}}} = G \cdot f(B'') = \frac{2}{3} \cdot 0.175 \cdot \frac{F}{0.15} = \frac{0.117}{0.15} = 0.78$$  \hspace{1cm} (4-6)$$

However, the recycle stream will contain 83 % CO$_2$ (point B'' in Figure 4-8), which will lead to a significant increase of the gas volume in the fuel reactor. Moreover, this large recycle stream ($G = 67 \%$) has to be preheated in order to maintain the temperature in the fuel reactor. Preheating consumes energy which will reduce the overall efficiency. An alternative is to reduce the temperature in the condenser to 10°C (Point C in Figure 4-8). In this way, 76 % of the recycle stream would be CO$_2$ (point C'' in Figure 4-8) and only 25% of the original stream would be recycled. However, only 40% of the unconverted methane can be recovered (Eq. 4-5).

$$\frac{n_{\text{CH}_4, \text{recycle}, 10^\circ\text{C}}}{n_{\text{CH}_4, \text{unconv}}} = \frac{G \cdot f(C'')}{0.15} = \frac{1}{4} \cdot 0.24 \cdot \frac{F}{0.15} = \frac{0.06}{0.15} = 0.4$$  \hspace{1cm} (4-7)$$
This example shows that finding the right temperature for the condenser is an optimisation problem. In Case II, the simulation software Aspen Plus® has been used to perform this optimisation.

From Figure 4-8 it can also be concluded that the higher the fraction of methane is, the lower is the necessary temperature of the condenser. If, for example, the methane fraction is 47% (Point D in Figure 4-8), the condenser must be cooled below -10°C to condense any CO₂. If no external cooling is accessible, the cooling could be generated by flash-expanding the gas mixture from a higher pressure. However this method requires even more compressor work.

4.5.3 Results

Figure 4-9 shows the efficiencies of the CC-CLC process for the studied cases in a range from 70 to 100 % of methane conversion in the fuel reactor. From the curve of Case I can be read that a loss in combustion efficiency of 5 percentage points will lead to a decrease in overall efficiency to beneath 50 %. The curve of Case II shows the potential improvement of the system by applying one step condensation. If 95 to 100% of the methane is converted in the fuel reactor, the application of a condenser provides only a slight improvement, which comes from the low efficiency of this "simple" separation step at low methane concentrations. At higher methane concentrations in the exhaust of the fuel reactor, the efficiency of the separation increases and the efficiency can be improved half way to the curve of
the hypothetic Case III. However, it is not possible to increase the efficiency over 50%. In Case III, a no-power-consuming separation is assumed. Only the power loss for compressing the unconverted methane is considered. This case shows that the additional power consumption for the unconverted methane has a relatively small impact. The major loss comes from the fuel loss.

4.5.4 Discussion

This study demonstrates the importance of high combustion efficiency in CLC. The combustion efficiency should be close to 100%, since it is not possible to recover the unconverted methane sufficiently by a one-step condensation. If combustion efficiency cannot be achieved it may be necessary to use a more complex separation such as a separation column. However, a costly and energy consuming separation unit would question the concept of CLC, because the special feature of CLC is just that no post-combustion separation unit is required.
4.6 Top-firing to overcome temperature limitation in the air reactor

From previous discussion, it can be concluded that the TIT is a very important parameter in order to achieve a competitive efficiency for the CC-CLC process. However, it is uncertain if the particles of oxygen carrier or the reactor can withstand the sufficiently high temperature of about 1200°C. In this case, additional natural gas can be used for top-firing to increase the TIT, which offers an option to achieve a high electrical efficiency even if the temperature in the air reactor is limited. However, this will increase the CO₂ emissions, because the carbon contained in the additional natural gas will be emitted as CO₂. The quantity of CO₂ emitted depends on the temperature in the air reactor. This section presents a study concerning the impact of the temperature of the air reactor on the avoided amount of CO₂ if the air temperature is increased to 1200 °C by using top-firing with additional natural gas. The results are compared to the same NGCC with monoethanolamine (MEA) absorption for CO₂ capture (CCC-MEA). A part of the study is published in Paper II.

4.6.1 Definition of the avoided CO₂

The avoided CO₂ per kilowatt hour (z) in either CC-CLC or CC-MEA was calculated using Eq. 4-8 and Eq. 4-9, respective,

\[
Z_{\text{CLC}} = \left( \frac{m_{\text{CO}_2}}{W_{\text{net}}} \right)_{55.2, \text{CCC}} - \left( \frac{m_{\text{CO}_2}}{W_{\text{net}}} \right)_{\eta, \text{CC-CLC}} \quad [\text{kg/kWh}] \quad (4-8)
\]

\[
Z_{\text{MEA}} = \left( \frac{m_{\text{CO}_2}}{W_{\text{net}}} \right)_{55.2, \text{CCC}} - \left( \frac{m_{\text{CO}_2}}{W_{\text{net}}} \right)_{\eta, \text{CCC-MEA}} \quad [\text{kg/kWh}] \quad (4-9)
\]

where \( m_{\text{CO}_2} \) is the emitted CO₂ and \( W_{\text{net}} \) is the generated power. The first term in Eqs. 4-8 and 4-9 is the emitted CO₂ from the reference system with an electrical efficiency of 55.2% (CCC, Section 4.2.1). The second term in Eqs. 4-8 and 4-9 is the emitted CO₂ from the CC-CLC system and the CCC-MEA system, receptively, at
the calculated efficiencies ($\eta$). For the CCC-MEA system two cases are considered: a) CO$_2$ absorption of 95% with an efficiency penalty of eight to ten percentage points, and b) 80% of the CO$_2$ is captured with an efficiency loss of eight to ten percentage points.

4.6.2 Results

*Figure 4-9* shows the avoided CO$_2$ emissions and the electrical efficiency of the CC-CLC system at a temperature range in the air reactor from 800 to 1200°C and a methane conversion in the fuel reactor from 75 to 100%. The TIT was raised to 1200°C in all cases by using top-firing with additional methane. The impact of the degree of methane conversion on the system's efficiency is presented in *Section 4.5*. For this study, the results of Case II, where a one-step condenser was applied to recover a part of the unconverted methane, are used to calculate the penalty in efficiency. By including the methane conversion in *Figure 4-9*, the CC-CLC's efficiency covers a range of 45 to 52.5% and the avoided CO$_2$ varies from 0.145 to 0.35 kg CO$_2$/kWh. The CCC-MEA system can be found in this diagram in an area defined by the points 1 and 2 for Case a) and the points 2 and 4 for Case b), respectively. Assuming a trade-off between a high degree of CO$_2$ capture and a good electrical efficiency for the CCC-MEA system the points 2 and 3 may be irrelevant.

*Figure 4-9. Comparison of the amount of avoided CO$_2$ - emission of the CC-CLC system with top-firing to the CCC-MEA system*
Comparing the CC-CLC with the CCC-MEA system, Figure 4-9 shows that CLC has the potential to avoid more CO$_2$ emissions than a MEA absorption, if the oxidation temperature can be as high as the required TIT. Assuming the temperature in the oxidation reactor is limited to 1100 °C the CCC-MEA system would avoid an equal or even higher amount of CO$_2$ if an efficiency loss of about 10 percentage points is accepted. However, in this case the CC-CLC system with top-firing will still have an efficiency of five to seven percentage points higher than the CCC-MEA system, if 100% methane conversion can be realised. By including the "simple" condenser to recover unconverted methane, the CC-CLC system has the potential to reach a higher efficiency than the CCC-MEA system down to a methane conversion of about 80%.

CLC has also the potential to reach both a higher efficiency and to avoid more CO$_2$ emissions than today's most advanced combined cycles with an electrical efficiency of 60% combined with a MEA absorption causing about 10 percentage points in efficiency, in order to absorb 95% of the produced CO$_2$ (future CC-MEA in Figure 4-9). However, in order to compete with these advanced processes, a complete methane conversion and an oxidation temperature close to the TIT are necessary.

4.6.3 Discussion

From this study it can be concluded that, compared to today's conventional technology for CO$_2$ capture, CLC will provide a higher efficiency even if top-firing with methane is used to overcome a temperature limitation in the air reactor. However, in order to compete in the future with other CO$_2$ capture processes such as MEA absorption integrated in future combined cycles, CLC should reach at least 1200 °C in the air reactor.

This study also shows that CLC has the potential to reach an high efficiency of 53% while almost 100% of the produced CO$_2$ is captured. This potential, however, can only be used if both the reactor and the particles can withstand at least 13 bar and 1200 °C. Additionally, the combustion efficiency must be close to 100%.
4.7 Conceivable reactor design

The conclusions of the previous sections have shown that the CLC reactor is a key component in the CLC concept. This reactor consisting of a fuel reactor and an air reactor is different from conventional equipment in power plants. Previous research on the CLC reactor has been focused on atmospheric dual fluidised-bed reactors (Section 2.2.4). However, for the application of CLC in the systems

![Diagram of the studied CLC reactor, version IPFBR_A1](image)

*Figure 4-10. Layout of the studied CLC reactor, version IPFBR_A1*
presented in this thesis a pressurised reactor system is required. This section presents two conceivable design alternatives of the CLC reactor. The design alternatives are denoted IPFBR_A and IPFBR_B. IPFBR stands for interconnected pressurised fluidised bed reactor (Figure 4-10). Both design alternatives have in common that they are installed in a pressure shell similar to those in pressurised fluidised bed combustion (PFBC) technology. After the air reactor, the oxygen carrier particles are separated from the hot gases by a cyclone system as in PFBC technology. The mathematical models for both IPFBR designs are similar and limitations of the flow of oxygen carrier can be calculated using the same equations. This boundary of the flow of oxygen carrier is called the maximum theoretically possible flowrate of oxygen carrier from the air reactor into the fuel reactor (MTPFR) and is discussed in the next section. In Sections 4.7.3 and 4.7.4 the alternative designs are described. A hydrodynamic model of the IPFBR is presented in Appendix 12.2 to 12.4. The dimensions and the required amount of the essential materials for the two reactor alternatives are shown in Appendix 12.7.

4.7.1 The boundary for the flow of oxygen carrier – the MTPFR

This section explains why the maximum theoretically possible flowrate of oxygen carrier from the air reactor into the fuel reactor (MTPFR) is introduced and why it is important to study this boundary of feasibility.

In the IPFBR, the amount of material which can be transported from the air reactor into the cyclone is limited by the maximum transport capacity of the air flow. At a constant gas velocity and an increasing amount of particles entering the riser, the first very dilute gas-solid mixture will reach a state, in which the gas stream is saturated with particles. Here the MTPFR is reached. If the particle input increases further, the gas stream is not able to entrain all particles and the riser will fill with particles. The MTPFR is strongly connected to the mass flowrate of the combustion air. A higher mass flowrate of combustion air results in a larger diameter of the reactor or in a higher gas velocity which would increase the MTPFR. The mass flowrate of air can be increased by reducing the temperature in the air reactor while keeping the fuel flowrate into the fuel reactor constant. Since the released heat in the reactor remains the same, more air is needed to cool the reactor and the MTPFR increases. In this way, an operating point for the suggested reactor can be determined. This operating point marks a theoretical limitation for the flow of oxygen carrier in the IPFBR and is important in finding the requirements for the oxygen carrier. However, a suitable model is missing for calculating the MTPFR in the studied air reactor, because of its high gas velocity.
(u₀ = 6 to 10 m/s) and the large diameter (Dₐ = 5 to 6 m). In order to obtain a preliminary estimation, a freeboard entrainment model for fast fluidisation has been extrapolated. The model was described by Kunii and Levenspiel (1991) and is derived from experimental results obtained in vessels with a diameter of less than 0.5 m. More details about the model can be found in Appendix 12.1. Since there will be a significant difference in fluidisation behaviour in large (D = 5 to 6 m) and small (D = 0.5 m) vessels, the calculations in this study can only give an indication of the MTPFR.

The MTPFR is calculated as a function of the superficial gas velocity (u₀), the terminal velocity (uₜ) of the particles and their density (ρₛ) (Eq. 4-10):

\[
\text{MTPFR} = A_a \cdot G_{sc} = A_a \cdot \rho_s \cdot \varepsilon_{sc} \cdot (u_0 - u_t)
\]  

(4-10)

εₛₑ is the solid fraction at the exit of the reactor and Aᵦ is its cross-sectional area. The particle diameter (dₚ) is also important for the MTPFR, because the terminal velocity (uₜ) is a function of the diameter (dₚ). By decreasing dₚ the MTPFR can be increased. The calculation of the terminal velocity (uₜ) is based on a force balance (Kunii and Levenspiel, 1991; Appendix 12.3).

**Table 4-5. Assumptions for the hydrodynamic calculations**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle diameter</td>
<td>125 µm</td>
</tr>
<tr>
<td>Particle density</td>
<td>2400 kg/m³</td>
</tr>
<tr>
<td>Gas composition in the fuel reactor</td>
<td>CH₄/H₂O/CO₂ = 0.1/0.6/0.3¹)</td>
</tr>
<tr>
<td>Isentropic coefficient (n = f(T))</td>
<td>From Aspen Plus</td>
</tr>
<tr>
<td>Air reactor</td>
<td>1.4</td>
</tr>
<tr>
<td>Fuel reactor (methane)</td>
<td>1.237</td>
</tr>
<tr>
<td>cp(T)</td>
<td>from Aspen Plus</td>
</tr>
<tr>
<td>Air reactor</td>
<td>1 kJ/(kg,K)</td>
</tr>
<tr>
<td>Fuel reactor (methane)</td>
<td>2.74 kJ/(kg,K)</td>
</tr>
</tbody>
</table>

¹) mole fraction

4.7.2 Assumption for calculating the hydrodynamic behaviour of the IPFBR

Table 4-5 gives more assumptions for the hydrodynamic calculations. The particle diameter (dₚ), the particle density (ρₛ), and the residence time (τ) are based on literature (Copeland et al., 2002; Cho et al., 2002; Lyngfelt, 2001; Johansson, 2002; Ishida 2002). The gas composition, CH₄/H₂O/CO₂ = 0.1/0.6/0.3, is assumed to be the
average composition in the fuel reactor. However, there is still great uncertainty about these parameters because no experience in a full scale CLC reactor are available. Therefore, the values in Table 4-5 should be considered as an example for the initial calculations in this thesis.

### 4.7.3 IPFBR_A: A riser and a stationary fluidised bed

The design of the IPFBR_A is a further development of the layout presented in Lyngfelt et al., 2001 (Section 2.2.4) The fuel reactor is of the bubble bed type and the air reactor is essentially a pneumatic transport reactor (Figure 4-10). Using design A of the IPFBR, two cases with a difference in the cyclone system and two modes of operation are investigated. In the first mode, it is possible to control the mass flowrate of solids from the fuel reactor into the air reactor and in the second mode, this flowrate is determined by the gas flowrate of combustion air into the air reactor. A detailed discussion about the two modes of operation can be found in Appendix 12.2.

### 4.7.4 IPFBR_B: Two circulating fluidised bed reactors

The second design is a further development of the IPFBR_A based on the experiences gained from studying the cyclone system. In contrast to PFBC systems, in CLC the bed material consists of especially prepared particles with a well-defined diameter, for example, 125 µm (Table 4-2). According to the VDI-Wärmeatlas (2002), the cyclones (with dimensions presented in Appendix 12.7) will separate all particles with a diameter larger than 55 µm to 100 %. In the ideal case, which means very strong particles, no breakage, and no abrasion, there are no particles, which are smaller in diameter than 125 µm. Theoretically, the cyclones in CLC will separate all particles. However, no particle will be so strong that it never breaks. This means that after a period of operation the diameter of the particles will be reduced and smaller particles will exist in the CLC reactor. The particle-size distribution will approach a profile that is promoted by the cyclone system and the particle discharge from the fuel reactor. If the IPFBR_A is used for CLC, the particle discharge from the fuel reactor will dominate, because the design velocity of the gas in the fuel reactor is close to the terminal velocity of the particles with a diameter of 125 µm. Particle fragments with a diameter smaller than 115 µm will be carried out of the reactor.
Figure 4-11. IPFBR (B) for a CLC reactor system of about 800 MW
The risk of particle discharge from the fuel reactor can be reduced by increasing the diameter of the reactor or by installing a second system of cyclones for the fuel reactor. The second option may be the better one, because the fuel reactor can have a smaller diameter and the particle discharge becomes independent of the flowrate of methane, which may be an advantage if the methane flowrate varies in, for example, off-design operation.

Figure 4-11 shows the layout of the IPFBR_B. The air reactor on the left hand side and the fuel reactor on the right hand side are shadowed in yellow. The top-view picture shows the arrangement of the cyclones better. For the air reactor, four cyclones in parallel are assumed and for the fuel reactor, three primary cyclones and one secondary cyclone are suggested for the initial calculations in this thesis. In this arrangement the smallest particles will be collected in the downcomer of the secondary cyclone. Optionally, this particle fraction can be removed from the system in order to protect the gas turbine for particle fragments. More data about the dimensions of the reactor can be found in Appendix 12.7.

4.7.5 Discussion

The suggested IPFBR is a promising reactor design for CLC because it uses to some extent available technology similar to that of PFBC. Major differences to PFBC are:

- No heat exchanger pipes have to be installed in the reactors. This facilitates the construction of the fluidised beds.
- The maximum temperature in the cyclones should be at least 1200 °C. This increases the demands on the material.
- The arrangement of the reactors within the pressure shell is more complicated.

The IPFBR_B is an interesting design for a CLC reactor. It is less sensible to varying fuel gas flowrates than the IPFBR_A. Due to the compact construction, significant material savings for the pressure shell are possible (detailed results about the required amount of essential materials for the IPFBR version A and B, respectively, can be found in Appendix 12.7.)
Chapter 4 has shown that a combined cycle will have a higher efficiency with CLC than conventional techniques for CO₂ capture, if the temperature in the air reactor can be raised to 1200 °C or higher. Furthermore, top-firing with additional natural gas may improve the efficiency of CLC systems with lower temperature in the air reactor but will increase the CO₂ emissions. Another option is to use hydrogen for top-firing. In this way, the temperature of the combustion air can be raised to the required TIT while the degree of CO₂ capture stays close to 100 %. A major disadvantage is the high price for hydrogen. A third option is to produce the hydrogen in the process itself, purify it and use it either for top-firing to increase the efficiency of the process or trade it as a valuable by-product. In this chapter, a process is presented that tri-generates hydrogen, electrical power and district heating. The special feature with this new process is that the hydrogen is produced and purified in an extended CLC (exCLC) process. The objective of this study is to find a new interesting application for CLC by reducing the demands on the material in the air reactor while keeping the thermal efficiency high. It has been investigated whether a thermal efficiency of over 50 % can be achieved with a temperature in the air reactor not exceeding 1000 °C by far. The suggested process is denoted extended CLC in steam-injected gas turbine (exCLC-STIG) cycle.
5.1 The principle of hydrogen production with chemical looping combustion

This section presents the development from the classic CLC (Chapter 4), to an extended CLC (exCLC). In exCLC hydrogen is produced and inherently separated from CO₂. Section 5.1.1 describes the mechanism that makes hydrogen production possible in CLC and Section 5.1.2 shows the concept of separating the hydrogen from CO₂.

5.1.1 Hydrogen production with chemical looping combustion

Hydrogen production can be realised in the fuel reactor of the classic CLC by reducing the amount of oxygen carrier so that the oxygen present is not sufficient for a complete oxidation of the fuel. Partial oxidation (Reaction Eqs. 5-1 – 5-3) and steam reforming (Reaction Eq. 5-4) then take place at the same time. The amount of active oxygen carrier controls the yield of produced hydrogen and carbon monoxide (Reaction Eqs. 5-5 and 5-6).

\[
\begin{align*}
\text{CH}_4 + 2 \text{NiO} & \rightarrow 2 \text{Ni} + \text{CO}_2 + 2 \text{H}_2 \quad \text{(5-1)} \\
\text{CH}_4 + 2 \text{NiO} & \rightarrow 2 \text{Ni} + \text{CO} + \text{H}_2\text{O} + \text{H}_2 \quad \text{(5-2)} \\
\text{CH}_4 + 2 \text{NiO} & \rightarrow 2 \text{Ni} + \text{C} + 2 \text{H}_2\text{O} \quad \text{(5-3)} \\
\text{CH}_4 + \text{H}_2\text{O} & \rightarrow \text{CO} + 3 \text{H}_2 \quad \text{(5-4)} \\
\text{NiO} + \text{H}_2 & \rightarrow \text{Ni} + \text{H}_2\text{O} \quad \text{(5-5)} \\
\text{NiO} + \text{CO} & \rightarrow \text{CO}_2 \quad \text{(5-6)} \\
\text{CO} + \text{H}_2\text{O} & \leftrightarrow \text{CO}_2 + \text{H}_2 \quad \text{(5-7)} \\
\text{C} + \text{H}_2\text{O} & \leftrightarrow \text{CO} + \text{H}_2 \quad \text{(5-8)}
\end{align*}
\]

The homogeneous and the heterogeneous water-gas shift reaction (Reaction Eqs. 5-7 and 5-8) control the composition of the gaseous phase and are heavily dependent on the reaction temperature. If there is too little steam or oxygen available in the fuel reactor, the decomposition of methane will cause deposits of carbon on the particles of the carrier material (Reaction Eqs. 5-3 and 5-8). The composition of the thermo-chemical equilibrium in the fuel reactor for various temperatures is shown in Section 5.6.1.
5.1.2 Separation of hydrogen and carbon dioxide in the exCLC

So far, the gaseous products of the fuel reactor are CO$_2$, hydrogen, and steam. In order to separate the hydrogen from the CO$_2$ a carbon carrier (calcium oxide in this study) is used that circulates along with the oxygen carrier between the reactors. Due to the presence of calcium oxide in the fuel reactor, the CO$_2$ will react to calcium carbonate (CaCO$_3$) according to Reaction Eq. 5-9.

\[
\text{CaO} + \text{CO}_2 \leftrightarrow \text{CaCO}_3 \quad (5-9)
\]

In this way, CO$_2$ is removed from the gaseous phase where only hydrogen and steam remain. In order to regenerate the carbon carrier, a third reactor (the calcination reactor) is added. Figure 5-1 illustrates the principles of the exCLC. In order to operate the fuel reactor at an appropriate temperature, the very hot particles that return from their regeneration have to be cooled. This is necessary for the formation of calcium carbonate. In Figure 5-1 a configuration is proposed, in which steam is used to cool the particles before they enter the fuel reactor. To regenerate the carbon carrier, the particles flow into a calcination reactor where calcium carbonate decomposes into calcium oxide and CO$_2$ (calcination reactor in Figure 5-1). In this reactor, the temperature must be above the decomposition
temperature of calcium carbonate, i.e., the equilibrium of Reaction 5-9 must be on the left hand side. However, this desorption reaction is endothermic; thus, additional heat is needed. For the heat supply, a partial flow of the hot particle steam leaving the third reactor (the air reactor), in which the oxygen carrier is regenerated, can be used. However, depending on the temperature in the air reactor, the achievable temperature with this measure will be too low for calcination (CO₂-desorption). Therefore, a second measure is used, additionally. The hot steam, that cools the fuel reactor, is introduced into the calcination reactor in order to reduce the partial pressure of CO₂ in the calcination. The only gaseous products of the calcination reactor are CO₂ and steam. The oxygen carrier is inert in the calcination reactor and has to be regenerated in the air reactor (also called oxidation reactor), where the reduced nickel oxide re-oxidises according to Reaction Eq. 2-6.
5.2 Consideration of a conceivable reactor layout

As in classical CLC it will be a challenge to build a reactor for the exCLC because of the high flowrates of solids. Figure 5-2 shows a conceivable reactor layout where the whole reactor system is built within a pressure shell as in PFBC and as suggested for the classic CLC (Section 4.7). From the air reactor (a transport reactor), the particles are transported into a system of cyclones where the gaseous products are separated from the particles and flow towards the gas turbine. The particle flow is divided into two, of which one partial flow enters the calcination and the other the solid-gas heat exchanger (HX). The HX may be a bubble bed reactor where pressurised steam fluidises the particles and then flows into the calcination. The cooled particles flow from the HX into the fuel reactor, that also contains a bubble bed. After the fuel reactor, the particles enter the calcination.
before they return into the air reactor. In the calcination, the fluidising medium is the steam from the HX and the desorbed CO$_2$. Compared to the IPFBR presented in Section 4.7 the suggested reactor for exCLC has more complicated layout. On the other hand, due to the concept of exCLC-STIG the temperature in the air reactor can be much lower as discussed later in Sections 5.7 and 5.8.

5.3 Nickel as potential oxygen carrier in exCLC

Nickel is a promising oxygen carrier for the exCLC with hydrogen production. This is due to its good properties for CLC (Sections 2.2.3 and 4.4) and nickel has been recognized as the most suitable catalyst when steam reforming hydrocarbons (Twigg, 1989). Recent experiments on nickel-based particles for hydrogen production in CLC have confirmed its promising properties for this type of processes (Mattisson et al., 2004). However, nickel catalysts are sensible to sulphur and it is necessary to install a fuel gas cleaning before the reformer (Twigg, 1989).

Calcium carbonate is commonly used in power industry for removing sulphur dioxide from the exhaust gases from coal combustion. However, in that process, the carbonate is not recycled. If it is used in an exCLC, the carbon carrier must be regenerated. Previous experiments showed that it is difficult to regenerate calcium carbonate (Abanades, 2002). Only after a few cycles the material had lost much of its activity. It seems to be necessary to develop special particles as in classical CLC.
5.4 The system of an extended CLC in a steam-injected gas turbine cycle (exCLC-STIG)

In this section, a STIG (Steam Injected Gas Turbine) cycle is integrated with exCLC which has the potential to cogenerate the three products of heat, hydrogen and power by using a simple cycle configuration.

5.4.1 Description of the system

Figure 5-3 shows the flowchart of the exCLC-STIG process. In the process the compressed air flows from the compressor into the air reactor along with steam,
oxygen carrier and carbon carrier particles. After the air reactor, the hot gas consisting of nitrogen and a little excess oxygen is separated and enters a the top-firing, in which, a partial flow of the hydrogen/steam mixture that comes from the fuel reactor is used to increase the temperature of the combustion gas stream up to the desired TIT before it enters the gas turbine. The turbine exhaust and the remaining hydrogen/steam are used for steam generation and district heating (heat exchangers A1 to A4 and B1 plus B2 in Figure 5-3).

The mixture of steam and CO₂ leaving from the exCLC is mainly used to generate the steam that is needed to operate the calcination with low CO₂ partial pressure. In order to generate enough steam, it is necessary to compress the stream between evaporators C4 and C5 from 10 bar to 20 bar. In this way, the dew point increases so that most of the steam can be condensed in the evaporator C5; thus, the heat of vaporization can be used to generate more steam. When all the steam has been removed from the CO₂ after heat exchanger C6, the CO₂ is compressed to 110 bar for final storage.

<table>
<thead>
<tr>
<th>Table 5-1. Assumption for the process study of the exCLC-STIG</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Efficiencies</strong></td>
</tr>
<tr>
<td>Isentropic efficiency of the gas turbine</td>
</tr>
<tr>
<td>Isentropic efficiency of the compressor</td>
</tr>
<tr>
<td>Isentropic efficiency of the booster fans</td>
</tr>
<tr>
<td>Isentropic efficiency of the pumps</td>
</tr>
<tr>
<td>Mechanical efficiency of the gas turbine</td>
</tr>
<tr>
<td>Mechanical efficiency of the compressor</td>
</tr>
<tr>
<td>Mechanical efficiency of the booster fans</td>
</tr>
<tr>
<td>Mechanical efficiency of the pumps</td>
</tr>
<tr>
<td>Efficiency of the generator</td>
</tr>
<tr>
<td><strong>Heat exchanger – min. temp. difference</strong></td>
</tr>
<tr>
<td>Gas – gas heat exchanger</td>
</tr>
<tr>
<td>Gas – water heat exchanger</td>
</tr>
<tr>
<td>Water – water heat exchanger</td>
</tr>
<tr>
<td><strong>Cooling of gas turbine</strong></td>
</tr>
<tr>
<td>Percentage of compressor air</td>
</tr>
<tr>
<td><strong>District heating</strong></td>
</tr>
<tr>
<td>Temperature of incoming water</td>
</tr>
<tr>
<td>Temperature of heated water</td>
</tr>
<tr>
<td><strong>Lower heating value (LHV)</strong></td>
</tr>
<tr>
<td>Methane</td>
</tr>
<tr>
<td>Hydrogen</td>
</tr>
</tbody>
</table>
5.4.2 Assumptions

The assumptions are summarized in Table 5-1. It should be mentioned, a smaller temperature difference in the heat exchangers may be feasible, which would lead to a higher efficiency of the system. In particular, the efficiency for district heating could be increased.
5.5 Methods

Two aspects of the exCLC-STIG have been analyses. The first was a thermo-chemical analysis of the fuel reactor and the calcination reactor and the second was a parameter study of the whole process. The results of the thermo-chemical analysis improve the understanding of the reactions occurring in the fuel reactor and the calcination. The results from the thermo-chemical analysis are presented in Section 5.6. A parameter study reveals the required conditions in the reactors. The definitions of the studied parameters are given in Section 5.5.1 and the results are presented and discussed in Section 5.7.

5.5.1 Process analysis method

Five independent process parameters were identified for the analysis of the exCLC-STIG, \( f \), \( T_{AR} \), \( T_{TC} \), \( R_{SM} \) and \( z \).

Parameter \( f \) determines the mass flowrate of particles that circulate between the air and the calcination reactor in order to heat the calcination process. Here, \( f \) is the ratio of the particle stream that comes from the air reactor (\( m_{AR, out} \)) to the part flow that enters the fuel reactor (\( m_{FR, in} \)).

\[
f = \frac{m_{AR, out}}{m_{FR, in}} \quad (5-10)
\]

\[
m_{CR, in} = m_{AR, out} - m_{FR, in} \quad (5-11)
\]

\[
m_{CR, in} = (f - 1) \cdot m_{FR, in} \quad (5-12)
\]

From Eqs. 5-11 and 5-12 it can be seen the larger \( f \) is, the larger is the flowrate of solids into the calcination reactor (\( m_{CR, in} \)).

\( T_{AR} \) is the temperature in the air reactor,

\( T_{TC} \) is the temperature in the topping combustion,

\( R_{SM} \) is the ratio of the mass flowrate of steam to fuel (methane) entering the fuel reactor and
z is the mass fraction of inactive material in the oxygen carrier particle.

The system’s efficiencies are defined as the thermal efficiency, Eq. 5-13, the hydrogen efficiency, Eq. 5-14, the efficiency of electrical power, Eq. 5-15, the degree of CO₂ capture Eq. 5-16, and the efficiency of district heating Eq. 5-17.

\[
\eta_{th} = \frac{\dot{n}_{H2, out} \cdot LHV_{H2} + P}{\dot{n}_{CH4} \cdot LHV_{CH4}} \tag{5-13}
\]

\[
\eta_{H2} = \frac{\dot{n}_{H2, out} \cdot LHV_{H2}}{\dot{n}_{CH4} \cdot LHV_{CH4}} \tag{5-14}
\]

\[
\eta_P = \frac{P}{\dot{n}_{CH4} \cdot LHV_{CH4}} \tag{5-15}
\]

\[
D_{CO2} = \frac{\dot{m}_{CO2, captured}}{\dot{m}_{CO2, produced}} \tag{5-16}
\]

\[
\eta_{DH} = \frac{Q_{DH}}{\dot{n}_{CH4} \cdot LHV_{CH4}} \tag{5-17}
\]

A model of the whole system was implemented in the simulation software Aspen Plus® and five series of simulations were conducted, in which the five parameters were varied starting from a base case. In order to study the impact on the system of each parameter, only one parameter was changed during a series and the others kept as in the base case (if possible). The settings for the base case were \( f = 8 \), \( T_{AR} = 1000 \, ^\circ C \), \( T_{TC} = 1150 \, ^\circ C \), \( R_{SM} = 0.6 \), \( z = 0.4 \). This base case was chosen because it could be used over a wide range in most of the series. However, it should be pointed out that in some cases it was necessary to change two parameters in order to obtain the required \( T_{AR} \).

Another important parameter is the ratio of the mass flowrate of steam to the mass flowrate of calcium carbonate into the calcination reactor (\( R_{SCa} \)). \( R_{SCa} \) controls the partial pressure of CO₂ in the calcinator. In contrast to the above defined parameters, \( R_{SCa} \) is not independent. On the contrary, \( T_{AR} \), \( R_{SM} \), and \( z \) influence the amount of steam passing the gas-solid heat exchanger (HX in Figure 5-3 and thereby they change \( R_{SCa} \). This means that some of the effects of the independent parameters on the system's performance, and here especially the CO₂ capture, are caused by changing \( R_{SCa} \). Therefore, for a better understanding of the system, a series was simulated, in which only \( R_{SCa} \) was varied while the other five parameters were kept as in the base case. In this simulation series, steam was added into the
calcination reactor via heat exchanger C1 in Figure 5-2. In all other series, this stream was set to zero.

A further assumption was that all calcium oxide reacts to calcium carbonate in the fuel reactor. In practice, a fraction of the particles will be inactive, as is the case with the oxygen carrier.
5.6 Results of the thermo-chemical analysis

This section contains the results of a thermo-chemical study of the fuel reactor (Section 5.6.1) and the calcination reactor (Section 5.6.2).

5.6.1 Thermo-chemical analysis of the gas composition in the reactors

The amount of metal oxide controls which reactions in the fuel reactor are dominant. More oxygen carrier means that more oxygen is in the reactor and consequently a fraction of the hydrogen will react to water (Reaction Eq. 5-5). Less oxygen carrier, therefore, increases the hydrogen production. However, less oxygen in the reactor leads to a reduced conversion of methane which must be avoided in order to achieve a high efficiency of the combustion. In this study, it was found that a ratio of three mol active nickel oxide to one mol methane gives a good conversion of methane and a good hydrogen production.

Figure 5-4a shows the thermo-chemical equilibrium of the fuel reactor versus the temperature of reaction at 10 bar for hydrogen production in the classic CLC. From the diagram, it can be read that the concentration of hydrogen is highest at a temperature of about 750 °C. At increasing temperatures, the yield of hydrogen decreases while the concentration of carbon monoxide increases. The concentration of carbon dioxide follows the concentration of hydrogen. Since the desired products are carbon dioxide and hydrogen, a lower temperature is favourable. However, even when assuming thermo-chemical equilibrium, some methane will be left unconverted at 750 °C.

By introducing calcium oxide in the fuel reactor, the gas composition at the equilibrium can be shifted. Figure 5-4b shows that in the temperature range of 600 °C to 700 °C the gaseous phase consists of almost 50 % hydrogen while the rest is steam. All carbon is bonded as carbonate and removed from the gas phase. At a temperature above 700 °C calcination will start and CO₂ will be released. Due to Reaction 5-7, carbon monoxide will also be formed. This result shows that an inherent separation of hydrogen and carbon dioxide is theoretically possible, if the required conditions in the reactors can be reached and the extended CLC can be heat balanced.
5.6.2 Requirements for the regeneration of the carbon carrier

In the calcination reactor, a complete regeneration of the carbon carrier is desired. If some calcium carbonate enters the air reactor it will release its CO$_2$ during the very exothermic oxidation of the nickel. In this case, all CO$_2$ released in the air reactor will leave the process through the stack along with nitrogen and the excess oxygen. This means that an incomplete calcination will decreases the efficiency of
CO₂ capture. One way to achieve a complete regeneration (if this is possible) is to increase the temperature in the calcination (T_{CR}) and the other is to reduce the partial pressure of CO₂ (P_{CO₂,CR}). The temperature in the calcination can be raised by increasing the stream of solids from the air reactor into the calcination and/or by increasing the temperature in the air reactor. P_{CO₂,CR} can be reduced by introducing steam in the calcination along with the calcium carbonate.

*Figure 5-5* shows the degree of regeneration F versus the ratio of the molar flow rate of steam into the calcination to the molar flow rate of calcium carbonate (R_{SCa}) at various calcination temperatures (T_{CR}). F is the molar fraction of regenerated carbon carrier. This means that at F equal to one all calcium carbonate has reacted to calcium oxide and all CO₂ has been captured. If F is below one, for example, 0.8 as in point A in *Figure 5-4*, some calcium carbonate will enter the air reactor and the maximum degree of CO₂ capture can only reach 80%. Point B in *Figure 5-5* shows that at a temperature of 947 °C a steam to calcium carbonate ratio of R_{SCa} equal to four will be sufficient to achieve a complete regeneration. For a temperature of 905 °C a ratio of about 7.5 would be necessary (Point C in *Figure 5-5*).

*Figure 5-6* shows the saturation pressure of CO₂ over calcium carbonate versus T_{CR}. This is the partial pressure that exists in the gaseous phase over solid calcium carbonate, if equilibrium is assumed. Under these conditions the gaseous phase is saturated with CO₂. This means that at a higher partial pressure, the calcium carbonate is stable and regeneration is impossible. By inserting points A and B from *Figure 5-5* into *Figure 5-6*, one can see that the partial pressure of CO₂ at 950 °C must be less than two bar. This means that, at a total pressure of 10 bar, it is necessary to introduce at least 4 mole steam to release one mole CO₂ from the calcium carbonate (therefore R_{SCa} = 4 at point B in *Figure 4*). When the total pressure increases, the required amount of steam increases as well and, thereby, the reactor size and the heat demand for steam generation. In this study we found that a total pressure of 10 bar is the limit of feasibility in order to maintain a temperature of about 1050 °C as the maximum allowed temperature in the exCLC.

![Figure 5-6. Saturation curve of the partial pressure of CO₂ over calcium carbonate versus temperature](image_url)
5.7 Results and discussion of the parametric study of the exCLC-STIG process

The results from the parametric study are summarised in Sections 5.7.1 and 5.7.2 and Figure 5-7. All absolute figures in this chapter refer to an 800 MWth exCLC, i.e., one kilomole methane per second is used as feedstock. In Figure 5-7, the simulations where a second parameter was changed are marked with a yellow background. Section 5.8 contains an optimisation of the system for the production of hydrogen and electrical power.

5.7.1 Impact of the steam to carbon carrier ratio during calcination

Figure 5-7a shows the impact of the amount of steam that is injected into the calcination reactor in order to maintain a low CO₂ partial pressure during calcination. The diagram shows the power, the hydrogen, the district heating and the thermal efficiencies versus R_{SCa}. The y-axis on the right is the degree of capturing CO₂ in the process. The fraction of captured CO₂ increases when increasing R_{SCa}, although the temperature in the calcinator decreases from 938 °C (when R_{SCa}=0.6) down to 922 °C (R_{SCa}=1.5). This is because the steam that comes from heat exchanger C1 enters the calcinator at 700 °C which cools the reactor. Figure 5-7a shows that the diluting effect of increasing R_{SCa} has a stronger impact on the degree of CO₂ capture than its cooling effect.

When increasing R_{SCa}, the thermal efficiency decreases slightly, with an increase in η_{H₂} offsetting a decrease in η_{P}. This occurs because the more steam that enters the calcination reactor, the more steam passes the vapour compression, which consumes some of the generated electrical power. This means the degree of CO₂ capture increases at the cost of power efficiency. The increase of the hydrogen efficiency occurs because less hydrogen is consumed in the topping combustion. The reason for this is a lower temperature of the oxygen and carbon carrier after calcination when R_{SCa} is high. The lower temperature of the solid stream after calcination leads to a reduced combustion-air flow into the air reactor, because less air is required to cool the exothermic oxidation of the oxygen carrier. Therefore, less gas, which has to be heated by top-firing, will enter the topping combustion;
thus, less hydrogen is needed in the topping combustion. The hydrogen that is saved increases the hydrogen efficiency slightly.

In the process, the waste heat in the hydrogen stream and the turbine exhaust are used for generating district heating. The efficiency of district heating in this case is about 18 % and it is fairly constant over the studied range of $\text{R}_{\text{SCa}}$. 

Figure 5-7. Results of the parameter study. The first y-axis shows the thermal efficiency ($\eta_{\text{th}}$), the power efficiency ($\eta_{\text{P}}$), the hydrogen efficiency ($\eta_{\text{H2}}$), and the efficiency of district heating ($\eta_{\text{DH}}$). The y-axis on the right shows the degree of CO$_2$ capture ($D_{\text{CO2}}$).
It can be concluded that increasing $R_{SCa}$ is a very efficient way to improve the degree of CO$_2$ capture and it favours hydrogen production. However, if a high power efficiency is desired, $R_{SCa}$ should be kept as small as possible.

5.7.2 Impact of the amount of solids circulating between the air reactor and the calcination reactor

In Figure 5-7b, $f$ is the independent variable which controls the flowrate of inert solids into the calcination reactor. The studied efficiencies are only a little affected by increasing the rate of particle circulation between the air and the calcination reactors, except that the efficiency of district heating increases by 10 percentage points and that the degree of CO$_2$ capture increases from 60% to 96% over the studied range. The reason for this is the rising temperature in the calcination ($T_{CR}$) which increases from 924 °C to 955 °C when $f$ increases from 7 to 16. However, the disadvantage of increasing the efficiency of CO$_2$ capture by increasing the circulation rate is the increasing size of the air and calcination reactors. For an 800 MW$_{th}$ exCLC, the mass flowrate of the carrier materials into the calcination reactor will increase from 2300 kg/s to 5800 kg/s over the studied range of $f$. Depending on the reactor construction, the feasible circulation rate will be limited. Moreover, more particles are necessary for operating the cycle, which will increase the costs. However, $f$ is an effective parameter for controlling the temperature in the calcination reactor without affecting $R_{SCa}$.

5.7.3 Impact of the temperature in the air reactor

Figure 5-7c shows the impact of raising the temperature in the air reactor. The thermal efficiency is almost constant at 52% over a temperature range of 1000 to 1080 °C. However, the degree of CO$_2$ capture increases from 55% at 1000 °C to 96% at 1080 °C. The strong impact of $T_{AR}$ on the degree of CO$_2$ capture comes from the induced increase of both $R_{SCa}$ and $T_{CR}$, which is favourable for the regeneration of the carbon carrier. The diagram indicates that 96% of CO$_2$ capture is the maximum that can be achieved. The final 4% of CO$_2$ cannot be captured because the temperature in the fuel reactor (732 °C) is too high to allow all CO$_2$ to be absorbed by the carbon carrier (Figure 5-4b in Section 5.6.1). This means the produced hydrogen contains some CO$_2$, of which a part escapes from the process via the topping combustion.

Figure 5-7c shows another feature of the system. It is possible to optimise the process for hydrogen production or for power production. A lower temperature in
the air reactor favours the power efficiency, because the gas flow through the cyclone and therewith through the turbine expander is larger. In this way, however, more hydrogen is consumed in the topping combustor, which decreases the hydrogen efficiency. If the temperature in the air reactor is higher, less hydrogen is required for top-firing and therefore more hydrogen can be saved in the process.

The figure also shows an increased production of district heating when the temperature in the air reactor is raised to 1040 °C. This occurs as the oxygen factor in the air reactor is reduced because less heat has to be removed from the air reactor. The decreasing oxygen factor in the air reactor, however, is also a limiting parameter for the amount of steam that can be injected into this reactor. If the oxygen factor were to fall below one, not all nickel will be re-oxidized leading to less oxygen transport, and the thermal capacity of the exCLC will be reduced. In order to extend the feasible temperature range, the steam injection into the air reactor can be decreased while more steam is injected into the fuel reactor. Therefore, the flowrate of steam into the fuel reactor was set to 30 kg/s in this simulation series instead of 10 kg/s, as in the base case. If $T_{AR}$ increases above 1040 °C, $\eta_{DH}$ decreases, because of an increased demand for steam in the gas-solid heat exchanger (HX in Figure 5-3). This means more heat is consumed in the economizer (A3 in Figure 3-3) which leaves less heat for district heating.

It can be concluded that increasing $T_{AR}$ is an efficient way of improving CO₂ capture while retaining a high thermal efficiency. However, if electrical power is the desired product, then $T_{AR}$ should be chosen as low as possible. Moreover, the material of the cyclones should be considered as the limiting factor for the temperature.

### 5.7.4 Effect of the temperature of the topping combustor

The temperature of the topping combustion is an effective parameter to shift the degree of efficiency between hydrogen and power production. Figure 5-7d shows that, starting from the base case, the hydrogen efficiency increases from about 25% to 40% when no top-firing is used. The hydrogen efficiency increases even more than the power efficiency decreases; thus, the combined hydrogen and power efficiency ($\eta_{th}$) increases from 52% to 54% when no top-firing is used. However, without top-firing the power efficiency will only be about 18%. 


5.7.5 Effect of introducing steam to the fuel reactor

Injecting steam into the fuel reactor seems to have no positive effect on the cycle’s efficiencies (Figure 5-7e). Moreover, the degree of CO₂ capture decreases from 70 % if no steam is added into the fuel reactor (R_SM = 0) to 40 %, when R_SM is equal to three. The decrease of CO₂ capture is caused by a reduction of R_SCa. Due to the increased steam flow into the fuel reactor, less steam is required to cool the solids entering the fuel reactor. This reduces the R_SCa value in the calcination reactor, thus, the partial pressure of CO₂ in the calcination increases which leads to an incomplete regeneration of the carbon carrier.

Despite the negative effects of increasing R_SM on the efficiencies, it might be necessary to introduce some steam into the fuel reactor in order to avoid the formation of carbon on the particles. The conditions in the fuel reactor will be similar to those in steam reforming where an R_SM of at least 1.7 is recommended (Twigg, 1989). This would lead to a CO₂ capture of only 55 % which is not sufficient. Some of the other parameters have to be changed, for example, the temperature in the air reactor. From Figure 5-7c, in which R_SM was equal to 1.9, it can be seen that a temperature in the air reactor of 1060 °C would be sufficient to achieve the maximum possible CO₂ capture at a thermal efficiency of 52 %.

5.7.6 Impact of the oxygen carrier’s reactivity on cycle performance

If the particle reactivity decreases, the circulation rate of solids through the fuel reactor and the calcination reactor will increase. This has a positive impact on CO₂ capture and heat production (Figure 5-7f). Since more steam is required in the HX to maintain 732 °C in the fuel reactor, more steam enters the calcination reactor and R_SCa increases. A second reason is that T_CR increases because of the increased flowrate of solids from the air reactor. The increase of η_DH can be explained by reduction of the oxygen factor. Less air is required in the air reactor because of the larger amount of solids that has to be heated by the oxidation reaction. For z equal to 0.6 and 0.7, the oxygen factor will fall below one if the steam fraction in the air reactor is not decreased by increasing the steam flowrate into the fuel reactor. If z is larger than 0.7, more parameter have to be changed in order to achieve 1000 °C in the air reactor, for example, reducing f. Nevertheless, this indicates that the inactive fraction of the oxygen carrier should be far below 0.7.
5.8 Optimisation of the system

The results from Sections 5.7.1 to 5.7.6 can be used to optimise the tri-generation process for either power generation or hydrogen production. Table 5-2 shows the results of an optimisation of the power and the hydrogen efficiencies. The table shows the settings of the input parameters and the results of the efficiencies.

<table>
<thead>
<tr>
<th>Optimised Efficiency</th>
<th>Input Parameter</th>
<th>Results of efficiencies [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>f</td>
<td>T_{AR}</td>
</tr>
<tr>
<td>\eta_P</td>
<td>12</td>
<td>1000</td>
</tr>
<tr>
<td>\eta_{H2}</td>
<td>10</td>
<td>1040</td>
</tr>
<tr>
<td>\eta_P^{1)}</td>
<td>10</td>
<td>1000</td>
</tr>
</tbody>
</table>

1) The fraction of active oxygen carrier is increased so that less hydrogen is produced in the fuel reactor.

2) The supply temperature for district heating is reduced from 80°C to 70°C.

\(\eta_P\) has been optimised by increasing \(f\) to 12 and \(z\) to 0.5; \(T_{AR}\) and \(T_{TC}\) are kept constant from the base case. \(R_{SM}\) was set to 1.9 in order to avoid carbon deposits on the particles in the fuel reactor. The results show that a power efficiency of 24\% can be achieved while the hydrogen efficiency is 23\% and the degree of CO\(_2\) capture is 95\%. A further increase of the power efficiency could be possible by increasing the amount of active oxygen carrier in the fuel reactor (case \(\eta_P^{1)}\) in Table 5-2). However, even less hydrogen would be produced and the thermal efficiency \(\eta_{th}\) would fall below 40\%.

When optimising the process for hydrogen production, a high thermal efficiency of about 54\% may be achieved. The hydrogen efficiency will be 40\% while the power efficiency decreases to 14\%. If hydrogen is the desired product, the topping combustion can be removed. In order to keep the degree of CO\(_2\) capture above 95\%, it is necessary to increase \(T_{AR}\) to 1040 \(^\circ\)C. These settings are also an optimisation for the thermal efficiency, given that a high degree of CO\(_2\) capture is required and \(T_{AR}\) should be as low as possible in order to facilitate the reactor design.
From Table 5-2 one can read that the total efficiency of the system ($\eta_{th} + \eta_{DH}$) is about 75 %, if the supply-temperature for the district-heating net is set to 80 °C. The total efficiency can be improved by lowering the output temperature for the district heating from 80 °C to 70 °C, for example. Figure 5-8 shows the temperature profile of the heat recovery with heat exchangers A4 and B2 for district heating. One can see that the output temperature of the exhaust gas after A4 is high above 80 °C, which would be enough to produce more district heating. The dew-point of the exhaust gas, however, is too low to produce this district heating at a supply temperature of 80 °C. Further calculations showed that at a supply temperature of 70 °C a total efficiency of over 90 % is possible (case $\eta_P^{1}$) in Table 5-2.)
This chapter contains the study of the EvGT-BAT (evaporative biomass air turbine) process with a steam-based gasification of biomass. The process is described in Section 6.1 and the model of the gasifier implemented in Aspen Plus® is explained in Section 6.2. Section 6.3 presents the results of a performance analysis and in Section 6.4 some advantages with EvGT-BAT compared to available integrated gasification combined (IGCC) cycles. This chapter is based on studies published in Papers V and VI.

6.1 Description of the EvGT-BAT process

Figure 6-1 shows the steam-based gasification integrated in a previous studied process introduced in Section 2.3.3. A screw feeder transports the biomass feedstock into a carrier gas injector. The carrier gas is a high temperature product gas, which is accelerated and slightly pressurised by a compressor (not illustrated in Figure 6-1). The carrier gas conveys the biomass very rapidly through an entrained flow tubular reactor. The mixture of product gas and biomass that enters the gasifier is heated up to about 800°C in less than 1 sec. Under these conditions flash pyrolysis occurs. After the pyrolysis, the gaseous products are separated from the pyrolysis char by a cyclone and the char is transported into the SFC. The stream of gaseous products is divided into a recycle stream, which flows back into the carrier gas injector, and the product gas stream. The produced fuel gas stream is cooled down to about 40°C and then compressed before it can be fed into the topping combustor. The fuel gas leaves the gasifier at about 800°C, is cooled down to 40°C and then compressed to
12 bar. After compression, the fuel gas of 12 bar and about 130 °C is used for firing. Heat from the fuel gas cooler is recovered for preheating the fuel gas stream after the compression and preheating the combustion air for the HITAF.

![Flowsheet of the EvGT-BAT cycle](image)

C = compressor, T = turbine expander, G = generator, IC = intercooler, AC = aftercooler, HT = humidification tower, RC = recuperator, PH = preheater, ECO = economizer, HAHx = humid air heat exchanger, HTHx = high temperature heat exchanger, SFC = solid fuel combustion, SBG = steam-based gasification, SGC = synfuel cooler, GC = gas cleaning/cooling/water knock out, M = motor, SGC = Syngas compressor

*Fig. 6-1. Flowsheet of the EvGT-BAT cycle*
6.2 Method and assumption

6.2.1 Simulation of the steam-based gasification of biomass

*Figure 6-2* shows how the steam-based gasification process is simulated in Aspen Plus®. The biomass is heated to 400 °C (heater B1 in *Figure 6-2*) by using heat from the SFC (heater S1 in *Figure 6-2*). The conversion of biomass to fuel gas is simulated by a so called "yield reactor". In this unit the gas composition and the fraction of char is inserted manually considering the mole balance of the substances carbon, oxygen and hydrogen. The resulting fuel gas composition after a water knock out, is shown in *Table 6-2*. The gas composition is adjusted to the results published in *Paper V*. After the yield reactor the pyrolysis char is separated from the fuel gas into a char stream and a fuel gas stream. Both streams are heated to 800 °C, which is the final temperature in the gasifier (heater B2 and B3). The moisture content of the biomass in the gasifier is simulated by mixing steam to the fuel gas (Mixer). The required heat for the steam generation is taken from the SFC.

*Figure 6-2. Scheme of the Aspen Plus® model of the gasifier*
(heaters M1 and S2). The devolatilisation energy is considered as heat loss in heater S2.

The devolatilisation energy for the pyrolysis process is calculated by an energy balance over the pyrolysis (Table 6-1). The LHV for the moist biomass is calculated using Eq. 6-1, where LHV* is the LHV of dry biomass in MJ/kg, $\gamma_w$ is the water fraction by weight and $\gamma_A$ is the ash fraction by weight. The value for LHV* in this work refers to forest wood and is 16.66 MJ/kg. The ash fraction is set to 0.005 (Beahr, 1989).

$$\text{LHV}_{(25^\circ\text{C})} = \text{LHV}^* \left( 1 - \gamma_w - \gamma_A \right)$$  \hspace{1cm} 6-1

The LHV of the produced fuel gas and the char are calculated with Aspen Plus®. In the model, the pyrolysis char consists only of carbon with an LHV of 32.8 MJ/kg. Assuming a char fraction of 9.6 wt% the required devolatilisation energy is 2 MJ/kg biomass. Further Input data for the performance analysis is summarized in Table 6-2.

<table>
<thead>
<tr>
<th></th>
<th>LHV [MJ/kg]</th>
<th>[wt%]</th>
<th>[MJ/kg Biomass]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biomass (50 water)</td>
<td>8.25</td>
<td></td>
<td>8.25</td>
</tr>
<tr>
<td>Fuel gas(^1)</td>
<td>-7.85</td>
<td>90.4</td>
<td>-7.10</td>
</tr>
<tr>
<td>Char(^2)</td>
<td>-32.8</td>
<td>9.6</td>
<td>-3.15</td>
</tr>
<tr>
<td>Devolatilisation energy</td>
<td></td>
<td></td>
<td>-2.00</td>
</tr>
</tbody>
</table>

1) wet gas composition [wt%]: CO = 28; H = 1; CO\(_2\) = 7; CH\(_4\) = 5; C\(_2\)H\(_4\) = 3; H\(_2\)O = 55; N\(_2\) = 1
2) 100% carbon
Table 6-2. Assumption for the performance analysis

<table>
<thead>
<tr>
<th>Inputs for Gas turbine</th>
<th>Economizers</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Compressor</strong></td>
<td></td>
</tr>
<tr>
<td>Cold side pressure loss [%]</td>
<td>2</td>
</tr>
<tr>
<td>Inlet pressure loss [%]</td>
<td>0.01</td>
</tr>
<tr>
<td>Pressure ratio [13.6]</td>
<td>13.6</td>
</tr>
<tr>
<td>Isentropic efficiency [-]</td>
<td>0.88</td>
</tr>
<tr>
<td><strong>Topping combustor</strong></td>
<td></td>
</tr>
<tr>
<td>Min. stack temperature</td>
<td>100</td>
</tr>
<tr>
<td>Pressure loss [%]</td>
<td>3</td>
</tr>
<tr>
<td>Outlet temperature [°C]</td>
<td>1100</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Inputs for the biomass combustion system</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Turbine</strong></td>
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<tr>
<td>Isentropic efficiency [-]</td>
</tr>
<tr>
<td>Pressure loss [%]</td>
</tr>
<tr>
<td>Mechanical efficiency [%]</td>
</tr>
<tr>
<td><strong>Intercooler</strong></td>
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<tr>
<td>Cold side pressure loss [%]</td>
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<tr>
<td>Hot side pressure loss [%]</td>
</tr>
<tr>
<td><strong>Gasifier</strong></td>
</tr>
<tr>
<td>Minimum temp. difference [°C]</td>
</tr>
<tr>
<td><strong>High temp. heat exchanger</strong></td>
</tr>
<tr>
<td>Max outlet humid air temperature [°C]</td>
</tr>
<tr>
<td>Cold side pressure loss [%]</td>
</tr>
<tr>
<td><strong>Recuperator</strong></td>
</tr>
<tr>
<td>Cold side pressure loss [%]</td>
</tr>
<tr>
<td>Hot side pressure loss [%]</td>
</tr>
<tr>
<td>Minimum temp. difference [°C]</td>
</tr>
<tr>
<td><strong>Biomass composition</strong></td>
</tr>
<tr>
<td>CO</td>
</tr>
<tr>
<td>O</td>
</tr>
<tr>
<td>H</td>
</tr>
<tr>
<td><strong>Humidification tower</strong></td>
</tr>
<tr>
<td>Pressure loss [%]</td>
</tr>
<tr>
<td>Min. temp. difference of outlet water to wet-bulb point [°C]</td>
</tr>
<tr>
<td>Outlet air state</td>
</tr>
<tr>
<td><strong>Dry fuel gas composition</strong></td>
</tr>
<tr>
<td>CO</td>
</tr>
<tr>
<td>H2</td>
</tr>
<tr>
<td><strong>Combustion air preheater</strong></td>
</tr>
<tr>
<td>Cold side pressure loss [%]</td>
</tr>
<tr>
<td>Hot side pressure loss [%]</td>
</tr>
<tr>
<td><strong>Char composition</strong></td>
</tr>
<tr>
<td>Min. temp. difference [°C]</td>
</tr>
</tbody>
</table>

<table>
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<tr>
<th>Inputs for the HR</th>
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</thead>
<tbody>
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<td><strong>Aftercooler</strong></td>
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<tr>
<td>Cold side pressure loss [%]</td>
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<tr>
<td>Hot side pressure loss [%]</td>
</tr>
<tr>
<td>Minimum temp. difference [°C]</td>
</tr>
<tr>
<td><strong>Biomass composition</strong></td>
</tr>
<tr>
<td>CO</td>
</tr>
<tr>
<td>H2</td>
</tr>
<tr>
<td>CO2</td>
</tr>
<tr>
<td>CH4</td>
</tr>
<tr>
<td>C2H4</td>
</tr>
<tr>
<td>H2O</td>
</tr>
<tr>
<td><strong>Combustion air preheater</strong></td>
</tr>
<tr>
<td>Cold side pressure loss [%]</td>
</tr>
<tr>
<td>Hot side pressure loss [%]</td>
</tr>
<tr>
<td><strong>Char composition</strong></td>
</tr>
<tr>
<td>Carbon fraction [wt%]</td>
</tr>
<tr>
<td>Inlet air temperature [°C]</td>
</tr>
<tr>
<td>Relative humidity [%]</td>
</tr>
<tr>
<td>Pressure [bar]</td>
</tr>
</tbody>
</table>
6.3 Results and discussion of the performance analysis

A process study including the effects of moisture content and temperature of the HTHx on the electrical efficiency and the mass flow rates into the gasifier and the SFC has been conducted. Figure 6-3 shows the electrical efficiency of the EvGT-BAT process at various temperature of the HTHx and at different water-to-air ratios. The moisture content of the biomass used in the gasification is 20 wt% (Figure 6-3a) and 50 wt% (Figure 6-3b). The moisture content of the biomass burned in the SFC is in all cases 50 wt%. A comparison of Figure 6-3a and b reveals the effect of the biomass' moisture content on the electrical efficiency. The efficiency of the process is between 38.5 % and 41 % if biomass with 20 wt% moisture content is used. The efficiency is about 2.5 percentage points lower if biomass with 50 wt% moisture is used as in the SFC. The reason is that more biomass is required in the SFC to evaporate the water in the biomass passing through the gasifier. The generated steam is then condensed before the gas cleaning and its latent heat is lost. The system could be improved by using a part of the heat to increase the water-to-air ratio as shown in Paper VI. A significant increase in electrical efficiency can be achieved by using dry biomass also for the SFC as shown in Paper VI. Alternatively, the waste heat could be used for district heating.

![Figure 6-3. The electrical efficiency of the EvGT-BAT process versus the HTHx temperature and the water-to-air ratio. The moisture content of the biomass used in the gasifier was 20 wt% in a) and 50 wt% in b).](image-url)
From Figure 6-3 can also be seen that the effect of the HTHx temperature on the electrical efficiency changes if drier biomass is used. In Figure 6-3a, the efficiency increases if the HTHx temperature decreases by a constant water-to-air ratio and, in Figure 6-3b, the efficiency decreases if the HTHx temperature decreases. The water-to-air ratio is varied to optimise the heat recovery; thus, the exhaust streams from the SFC and the one from the gas turbine have a temperature close to 100 °C. Figure 6-3a shows an optimum water-to-air ratio of 0.23 if the HTHx temperature is 900 °C, of 0.21 if the HTHx temperature is between 800 °C and 900 °C and of 0.20 if the HTHx temperature is between 700 °C and 800 °C. The figure indicates that studying more water-to-air ratios would show that also for the dry biomass a higher HTHx temperature is recommended. This result shows that the temperature in the HTHx should be as high as possible especially if dry biomass is not available. The reason is that in the EvGT-BAT, the gasifier is installed within the SFC and if the HTHx temperature is low, more fuel gas is needed for top firing to heat the humidified air up to 1100 °C. If more fuel gas is needed, more biomass has to be gasified and consequently more biomass is consumed in the SFC. If the biomass for the gasifier has a high moisture content, more water has to be evaporated which leads to a further increased heat loss in the gas cleaning unit. Additionally, the biomass used in the SFC contains 50 wt% water which must be evaporated in the SFC and all its heat of evaporation is lost because the exhaust gas from the SFC leaves the process at 100 °C, which is above the dew point.

Figure 6-4 shows the specific power output of the EvGT-BAT process versus the HTHx temperature. From a comparison of Figures 6-4a and b one can see that a

![Figure 6-4](image-url)

*Figure 6-4. The specific power output of the EvGT-BAT process and the mass flowrates of biomass versus the HTHx temperature. The moisture content of the biomass used in the gasifier was 20 wt% in a) and 50 wt% in b)*
higher moisture content results in a larger specific power output. The higher the water-to-air ratio, the larger the specific power output. The curves of the biomass flowrates confirm that a higher moisture content results in an increased demand on biomass input for both the gasifier and the SFC which also means that more heat is available in the heat recovery.

*Figure 6-4a and b* also shows that the ratio of flowrates into the gasifier and the SFC can be changed by increasing the HTHx temperature from 700 °C to 900 °C. At a HTHx temperature of 900 °C, the biomass flowrate into the SFC is more than twice that in the gasifier. At lower temperature, more biomass is needed in the gasifier than in the air SFC. However, it will become increasingly complicated to design the SFC, if the size of the gasifier increases while the feedstock into the SFC decreases. This discussion indicates that it is not possible to decrease the HTHx by much. Furthermore, the investment cost for the gasifier, the fuel gas compressor, the fuel gas cooler and the cleaning unit will also rise if the fuel gas demand and consequently the dimensions of the gasifier increase.

### 6.4 Advantages with EvGT-BAT compared to IGCC

The EvGT-BAT cycle is an approach to use commercially available equipment as much as possible and new technologies only if necessary. For example, combustion occurs in a conventional atmospheric furnace. By using top-firing to increase the turbine inlet temperature, the temperature of the high-temperature heat exchanger (HTHx) can be selected in a reasonable temperature range based on the development of the material and manufacturing technique. Moreover, due to the application of the EvGT concept, no expensive bottoming steam cycle is required.

The gasification of biomass to produce the additional fuel for the topping combustion is a simple pyrolysis process, which does not require a high conversion rate from biomass to gaseous fuel because the unconverted char can be further used in the SFC. Additionally, In comparison to IGCC, the EvGT-BAT system requires a smaller flowrate of fuel gas to heat the compressed air to the turbine inlet temperature. This has two reasons:

- In the EvGT-BAT process less heat is needed in the topping combustion than in the turbine combustor in IGCC, because the combustion air that enters the topping combustor has a much higher temperature after the HTHx than the compressed air in IGCC has when it enters the turbine combustor.
The heating value of the fuel gas produced in the steam-based gasification process is about 16 MJ/Nm³ if a water knock out unit is used (Paper V). In standard IGCC, if the fuel gas is produced by partial oxidation its LHV is only 5-6 MJ/Nm³.

The high investment cost for gasification in IGCC is one of the obstacles for adopting this technology in commercial applications. The concept of EvGT-BAT will reduce the size of the gasifier. Figure 6-5 shows an initial comparison of the flowrate of fuel gas that is needed in the topping combustor in EvGT-BAT to the flowrate of fuel gas that is needed in the turbine combustor in an integrated gasification combined cycle (IGCC) using an air-blow gasifier. The columns in Figure 6-5 are based on the flowrates shown in Figure 6-4a for the EvGT-BAT system. For IGCC it has been assumed that the total flow of biomass is converted into a fuel gas with an LHV of 5 MJ/Nm³. It can be seen that in EvGT-BAT the required flowrate of fuel gas can be reduced by the factor 11, if an HTHx temperature of 900 °C is possible. If the HTHx temperature is only 700 °C the required fuel gas flowrate in EvGT-BAT will still be 6.5 times smaller than in IGCC.

Figure 6-5. Comparison of the fuel gas volume flow into the combustor in EvGT-BAT at different HTHx temperature and in IGCC using an air-blown gasifier
7 Concluding remarks

7.1 Chemical looping combustion

The studies with chemical looping combustion (CLC) have addressed the question of whether CLC can be a competitive alternative for CO₂ capture in natural gas-fired power plants. This question has been investigated on three levels: the process, the reactor and the oxygen carrier. Additionally, the possibility of hydrogen production and purification with an extended CLC has been studied:

**The process**

- A new natural gas-fired power cycle with CO₂ capture should have a thermal efficiency over 50% (based on the lower heating value) while the degree of CO₂ capture should be at least 90% in order to compete with existing technology.

- Capturing CO₂ from a combined cycle using a turbine inlet temperature of 1200 °C, a pressure ratio of 13 bar and a tri-pressure reheat bottoming steam cycle is a promising application for CLC. Potentially this process achieves an electrical efficiency of 52% to 53% while almost 100% of the produced CO₂ is captured and compressed to 110 bar.

- Expanding the CO₂/H₂O stream coming from the fuel reactor with an additional CO₂ expander is not recommended, because the gained power will be needed for compressing the CO₂ for final storage.
Regarding the competitiveness of CLC, top-firing with additional natural gas is only a short-term solution to overcome temperature limitations in CLC, because future combined cycles with post-combustion CO₂ capture (e.g., chemical absorption with monoethanolamine) will probably also reach an efficiency above 50%, while providing a similar degree of CO₂ capture as CLC with top-firing.

The CLC reactor

- In order to use the high potential of the combined cycle with CLC, the reactor must withstand a temperature of 1200 °C, a pressure of 13 bar and achieve a fuel conversion of almost 100%. Additionally, the reactor must realise the circulation of large mass flowrates of particles and the separation of them from the gas flow in order to protect the gas turbine. Moreover, gas leakage between the fuel and air reactor must be avoided to realise a complete CO₂ capture.

- An atmospheric dual fluidised-bed reactor system suggested in previous studies has been further developed for using CLC in a combined cycle. This reactor system is installed in a pressure shell and comprises a riser (air reactor), a cyclone system and a stationary fluidised bed (fuel reactor). An important parameter for the CLC reactor is the maximum possible flow of oxygen carrier. A maximum theoretical possible flowrate from the air reactor into the fuel reactor of 5 to 6 t/s has been calculated for such a reactor with a thermal capacity of 800 MW. The diameter of the pressure shell is about 20 meters and the height of it may be between 25 and 30 metres.

- A disadvantage with this layout is a large diameter of the fuel reactor. The large diameter is necessary to keep the gas velocity low enough to prevent the particles from being transported out of the reactor. Therefore, a second interesting reactor layout has been studied including two cyclone systems, one for the air reactor and a smaller one for the fuel reactor. This concept enables a more compact construction of the CLC reactor resulting in significant material savings for the pressure shell. The diameter of the pressure shell can be reduced to 16 to 17 metres for CLC reactor of 800 MW.

- The concept of two interconnected pressurised fluidised bed reactors may be a possible design to realise CLC. However, current PFBC technology, which
is similar to the technology required for an IPFBR, operates under 1000°C. The implications of increasing the temperature have to be investigated.

The oxygen carrier

- In order to use the potential of the combined cycle with CLC, the oxygen carrier particles must withstand a temperature of 1200 °C while they are exposed to great mechanical stress in the CLC reactor. The particle velocity may be above 15 m/s at the inlet of the cyclone system. Additionally, the reactivity must be sufficient and the capacity for transporting oxygen must not be too low, because of the limitation of the flow of oxygen carrier in the CLC reactor.

- A new diagram for mapping the CLC reactor parameters (CLC-PM) has been developed. The CLC-PM diagram can be seen as an interface between the process, the reactor and the particles of oxygen carrier. It seems to be a good tool to identify the requirements for the particles that are necessary to realise CLC in the CLC reactor and the chosen process. The impact of the oxygen carrier’s properties on the system’s efficiency and the reactor design can be quickly identified.

- Iron-based oxygen carriers were investigated as a possible alternative to nickel-based oxygen carriers. The conclusion is that, if the conversion degree of hematite stabilised with 40 wt% aluminium oxide is over 60%, and the operating temperature is not limited to under the desired TIT (e.g., 1200°C), this oxygen carrier might be an alternative to nickel oxide, which apparently is a suitable material for CLC. Since pure hematite cannot operate in temperatures above 900 °C, it is probably no option as oxygen carrier if CLC is used in a combined cycle.

Hydrogen production and purification in exCLC:

- Co-generation of electrical power and hydrogen is a promising new application for CLC, even if the temperature in the air reactor cannot be raised over 1050 °C. The produced hydrogen can be traded as a valuable by-product or can be used in the process itself for top-firing.
• A novel process is developed, in which hydrogen is not only produced but also purified. The process applies steam injection instead of a bottoming steam cycle. The core process of this concept is an extended CLC comprising three reactors, an air reactor, a fuel reactor and a calcinator. Additionally to the oxygen carrier, a carbon carrier circulates between the tree reactors. The process tri-generates electrical power, hydrogen and district heating with a thermal efficiency of over 50 % and an degree of CO₂ separation of 95 %.

• Experiments are required to confirm the results of this study and to find suitable compositions of oxygen and carbon carrier particles. It may be necessary to develop special particles for both oxygen carrier and carbon carrier for application in the exCLC.

7.2 Steam-based gasification in EvGT-BAT

A new power process for biomass feedstock has been suggested. The process is denoted as EvGT-BAT and integrates three technologies, steam-based gasification of biomass (SBGoB), externally-fired gas turbine (EFGT) cycles and evaporative gas turbines (EvGT) cycles. A special feature of the presented EvGT-BAT process is that the steam-based gasification is conducted in an entrained-flow tubular reactor that is installed in a solid fuel combustion chamber as a heat exchanger.

The process converts solid fuel such as biomass into electrical power with a thermal efficiency of almost 41 % if half of the biomass has a moisture content of 20% and the other half has a moisture content of 50 %.

A comparison between the required fuel gas generation for IGCC and the presented EvGT-BAT system shows that the EvGT-BAT system has a great potential to reduce the size of the gasification unit.

A key component in this concept is a high temperature heat exchanger, in which humid combustion air is heated before it is used for top-firing. For this unit it can be concluded that the temperature should be as high as possible in order to reach a high electrical efficiency if all biomass has a moisture content of 50 wt%. However, if the biomass used in the gasifier has a moisture content of 20 wt% almost the same efficiency can be reached whether the HTHx temperature is 900 °C or 650 °C.
8 Recommendations for further research

8.1 Chemical looping combustion

Recommendation for continued process studies

It is necessary to estimate the investment cost and the variable costs for a power plant with CLC. Therefore, a process should be studied that applies a commercial gas turbine. For the process, this means that steam has to be injected into the air reactor in order to provide the same ratio of gas flowrates through the gas turbine's compressor and expander as the gas turbine is designed for. This is necessary, because in CLC no combustion gases pass through the turbine expander. On the contrary, the flowrate through the expander is reduced because a partial flow of oxygen is removed from the combustion air and transported into the fuel reactor by the oxygen carrier. Today's gas turbines are not designed for these conditions and initial studies on the required process changes indicated that the electrical efficiency will decrease somewhat if these changes are applied to a natural gas-fired combined cycle with CLC for CO₂ capture.

Off-design is a very important mode of operation. Therefore, the behaviour for a power plant using CLC should be investigated when the mode of operation is shifted from the design point into off-design. Especially interesting will be the fuel reactor, if designed as stationary fluidised bed, because in part-load operation the fuel gas flowrate into the fuel reactor will be reduced which leads to a reduced superficial gas velocity and this may have a strong impact on the fluidisation. A question will be how much fuel cut is allowed before the stationary fluidised bed stops operating properly.
To model the dynamic behaviour of a CLC reactor is an interesting subject for continued research. Since natural gas-fired power plants are often used for peak-load supply, it would be desirable that NGCC plants with CLC provide this possibility. Therefore, it is important to study start-up procedures and other types of mode switching by including the dynamic of a CLC reactor.

Due to the porosity of the oxygen carrier, gas will be enclosed in the particles when they circulate between the two reactors. This will lead to a leakage of CO$_2$ into the air reactor when the oxygen carrier circulates from the fuel reactor back into the air reactor. In the same way, nitrogen will leak into the fuel reactor. The impact of this unwanted gas transport on the degree of CO$_2$ capture should be investigated.

**Recommendation for further research on the CLC reactor**

This thesis showed the importance of the temperature in the air reactor for CLC to be competitive on the power market, regarding efficiency and degree of CO$_2$ capture. It is important to find the maximum possible temperature in a real CLC reactor, because this is important for the choice of a process.

**Recommendation for further research on oxygen carrier**

Nickel oxide has been found to be the most promising material for CLC. However, it is an expensive material and can be hazardous to personnel. In this thesis, a new tool (CLC-PM) has been developed that facilitates the evaluation of whether a new oxygen carrier particle is suitable for CLC or not. New oxygen carrier particles should be evaluated by considering the process requirements.

**Further applications for CLC**

Since it has been shown that CLC provides the possibility of hydrogen production, numerous conceivable process alternatives are interesting to study including, for example, combined cycles and supercritical steam cycles. A problem is the separation of hydrogen and CO$_2$ in most process alternatives. This problem is known from hydrogen production using steam reforming processes. However, in hydrogen production with CLC the partial pressure of CO$_2$ is higher, which may open new ways for the separation.
In this thesis a novel tri-generation process for hydrogen, power and heat generation has been developed. The power generation part of the process is based on a steam-injected gas turbine cycle which leads to a relatively low electrical efficiency compared to a combined cycle or an evaporative gas turbine (EvGT) cycle. Therefore, process studies with other power cycles integrated with extended CLC will be interesting.

A breakthrough for CLC might be the possibility to use CLC for CO₂ capture from coal-fired power plants. For this application a gasification process using as gasifying agent a re-cycled partial flow of the CO₂/H₂O stream from the fuel reactor would be an interesting option. In order to reach a complete coal conversion, additional oxygen can be added into the gasifier. The oxygen can be produced in an air separation unit as discussed in the oxy-fuel concept for coal-fired power plants. An investigation of this process idea may show that less oxygen is needed in the process with CLC and gasification than in an oxy-fuel process, which could lead to a higher efficiency.

**8.2 Steam based gasification in EvGT-BAT**

Further studies should focus on a detailed investigation of the entrained-flow tubular reactor installed in the SFC. The required surface for the heat exchange from the furnace into the gasifier has to be determined. This is essential for the EvGT-BAT concept, because the electrical efficiency of the EvGT-BAT process will decease if the conversion from biomass to fuel gas decreases. This holds although the char can be used in the SFC.
First, my heartfelt thanks go out to Anna, my wonderful wife, for helping me through this last period filled with deadlines, writing and moving. Thank you for being by my side!

To Professor Jinyue Yan, my supervisor, who gave me the chance to work on such an interesting project and guided me through these years. Thank you for many encouraging discussions and those many late hours you spent on reading my papers.

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And last but never least, I would like to thank my family for all the support I have received and for providing the stimulating environment in which I grew up.
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## 11 Nomenclature

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<tr>
<th>Symbol</th>
<th>Definition</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>area</td>
<td>$\text{m}^2$</td>
</tr>
<tr>
<td>$C_D$</td>
<td>drag coefficient</td>
<td>[-]</td>
</tr>
<tr>
<td>$c_p$</td>
<td>heat capacity</td>
<td>$\text{kJ/kg,K}$</td>
</tr>
<tr>
<td>$D$</td>
<td>diameter of the shell</td>
<td>$\text{mm}$</td>
</tr>
<tr>
<td>$d_p$</td>
<td>particle diameter</td>
<td>$\text{mm}$</td>
</tr>
<tr>
<td>$g$</td>
<td>gravitation constant</td>
<td>$\text{m/s}^2$</td>
</tr>
<tr>
<td>$H_{Bf}$</td>
<td>height of the fluidised bed in the fuel reactor</td>
<td>$\text{m}$</td>
</tr>
<tr>
<td>$H_d$</td>
<td>height of the dense region</td>
<td>$\text{m}$</td>
</tr>
<tr>
<td>$H_F$</td>
<td>height of the freeboard</td>
<td>$\text{m}$</td>
</tr>
<tr>
<td>$H_f$</td>
<td>height of the fuel reactor</td>
<td>$\text{m}$</td>
</tr>
<tr>
<td>$h_i$</td>
<td>specific enthalpy</td>
<td>$\text{kJ/kg}$</td>
</tr>
<tr>
<td>$M$</td>
<td>mass of fluidised bed material</td>
<td>$\text{kg}$</td>
</tr>
<tr>
<td>$m$</td>
<td>mass flowrate</td>
<td>$\text{kg/s}$</td>
</tr>
<tr>
<td>$n$</td>
<td>isentropic coefficient</td>
<td>[-]</td>
</tr>
<tr>
<td>$P$</td>
<td>pressure</td>
<td>$\text{bar}$</td>
</tr>
<tr>
<td>$P_T$</td>
<td>pressure [bar] = Reynolds number for particles at $u_T$</td>
<td>[-]</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature</td>
<td>$\text{°C}$</td>
</tr>
<tr>
<td>$u_0$</td>
<td>superficial gas velocity</td>
<td>$\text{m/s}$</td>
</tr>
<tr>
<td>$u_T$</td>
<td>terminal velocity</td>
<td>$\text{m/s}$</td>
</tr>
<tr>
<td>$\dot{W}_f$</td>
<td>fan power</td>
<td>$\text{MW}$</td>
</tr>
<tr>
<td>$z$</td>
<td>variable of height</td>
<td>$\text{m}$</td>
</tr>
<tr>
<td>$z$</td>
<td>strength factor</td>
<td>(Eq. 12-28 + 12-29)</td>
</tr>
</tbody>
</table>
11.1 Greek letters

\[\varepsilon\] = voidage \(= \frac{V_g - V_s}{V_g}\) [-]
\[\varepsilon_s\] = solid fraction \(= 1 - \varepsilon\) [-]
\[\bar{\varepsilon}_s\] = mean solid fraction [-]
\[\varepsilon_{sd}\] = solid fraction in the dense region [-]
\[\varepsilon_{sp}\] = solid fraction at saturated pneumatic conditions [-]
\[\eta_{fan}\] = isentropic efficiency of the fan [-]
\[\mu\] = dynamic viscosity \([N.s/m^2]\)
\[\rho_g\] = gas density \([kg/m^3]\)
\[\rho_f\] = fluid density \([kg/m^3]\)
\[\rho_s\] = particle density \([kg/m^3]\)
\[\tau\] = residence time/ reaction time \([s]\)

11.2 Indices

\[a\] = air reactor
\[B\] = fluidised bed
\[C\] = cyclone
\[d\] = dense region
\[D\] = distributor
\[F\] = freeboard
\[f\] = fuel reactor
\[g\] = gas
\[s\] = solid

11.3 Abbreviations

CC = combined cycle
CLC = chemical-looping combustion
CLC-PM = CLC parameter mapping
EFGT = externally fired gas turbine
EvGT = evaporative gas turbine
EvGT-BAT = evaporative biomass air turbine
11.4 Chemicals Compounds

\[
\begin{align*}
\text{Al}_2\text{O}_3 & = \text{aluminium(III)oxide} \\
\text{C} & = \text{carbon} \\
\text{C}_2\text{H}_2 & = \text{acetylene} \\
\text{C}_2\text{H}_4 & = \text{ethylene} \\
\text{C}_2\text{H}_6 & = \text{ethane} \\
\text{C}_3\text{H}_6 & = \text{propylene} \\
\text{CH}_4 & = \text{methane} \\
\text{CO} & = \text{carbon monoxide} \\
\text{CO}_2 & = \text{carbon dioxide} \\
\text{Fe} & = \text{iron} \\
\text{Fe}_2\text{O}_3 & = \text{iron(III)oxide (hematite)} \\
\text{Fe}_3\text{O}_4 & = \text{magnetite} \\
\text{FeO} & = \text{iron(II)oxide (wustite)} \\
\text{H}_2 & = \text{hydrogen} \\
\text{H}_2\text{O} & = \text{water} \\
\text{HFC} & = \text{hydroflorocarbons (hydrogenated fluorocarbons)} \\
\text{N}_2 & = \text{nitrogen} \\
\text{N}_2\text{O} & = \text{nitrous oxide} \\
\text{Ni} & = \text{nickel} \\
\text{NiAl}_2\text{O}_4 & = \text{nickelaluminat} \\
\text{NiO} & = \text{nickel oxide} \\
\text{NiO}\text{*Al}_2\text{O}_3\text{-spinel} & = \text{nickel-aluminium spinel} \\
\text{O}_2 & = \text{oxygen} \\
\text{PFCs} & = \text{perfluorocarbon} \\
\text{SF}_6 & = \text{sulphur hexafluoride}
\end{align*}
\]
SOx  = sulphur oxides
NOx  = nitrogen oxides
In this thesis, a reactor type called an interconnected pressurised fluidised bed reactor (IPFBR) is investigated for realising CLC in a power generation process. The layout of the reactor is described in Section 4.7. In Appendix 12.1 to 12.4 a mathematical model for calculating the hydrodynamic features of the IPFBR is presented.

12.1 The freeboard-entrainment model

In order to calculate the amount of bed material in the air reactor, a freeboard entrainment model for fast fluidisation has been extrapolated. The model was described by Kunii and Levenspiel (1991) and is derived from experimental results from vessels with a diameter of less than 0.5 m. According to this model, a fluidised bed may be divided into four fluidisation regions:

- At the bottom is a relatively short entry zone. Because the contribution of this zone to the total mass of solids in the reactor is of minor importance, the entry zone has been neglected in the following calculations.

- Following the entry zone, there is a portion of the vessel of almost constant solid fraction. These lower portions may be called the dense region (Figure 12-1). The solid fraction $\varepsilon_{sd}$ in this region was calculated by Eq. 12-1, which is a regression equation over experimental data (Kunii and Levenspiel, 1991) using superficial gas velocities from 2 to 6 m/s. (Note: This equation gives too low values for a superficial gas velocity less than 2 m/s).
The section of the vessel between the surface of the dense phase and the exit of the reactor is called the freeboard, and its height is called the freeboard height ($H_f$).

- Above the dense region is an upper entrained region where the solid fraction decreases progressively to about $\varepsilon_{sd} = 0.01 - 0.02$. When increasing the freeboard height, eventually, a solid fraction of 0.01 is reached. This may be called the transport disengaging height (TDH in Figure 12-1). When the freeboard height exceeds the TDH, the entrainment rate does not change significantly.

- At the TDH, the fast fluidised bed may turn into a saturated pneumatic transport with a particle fraction of $\varepsilon_{sd} = 0.01$.

If the freeboard is higher than the TDH, the maximum flowrate of solids between the air reactor and the fuel reactor is limited by the saturated pneumatic transport flow.

### 12.2 Two modes of operation in the IPFBR

In Section 4.7, the IPFBR is presented and in Section 4.4.2 two modes of operation are introduced. These two operating modes mark two extreme cases. If the second mode (Section 12.2.2) is used, the flow of oxygen carrier can be controlled (for example, case C in Figure 12-1 and Figure 4-7b) and with the first mode (Section 12.2.1), the residence time of the oxygen carrier in the air reactor can be controlled (cases C, C_A, and C_b'). The transition from mode one to mode two is illustrated by the points C and C' in Figure 12-1. In case C, a homogeneous pneumatic transport flow exists in the air reactor and in case C' the mass flowrate of solids has increased so much that the pneumatic transport flow is saturated and the formation of a bottom bed begins. The figure shows the regions of different fraction of solids, $\varepsilon_s$, in the air reactor for cases C', C_A', C_b', and C. Z is the height of the reactor. The solid fraction $\varepsilon_{sp} = 0.01$ is the fraction of solids existing in a saturated pneumatic transport flow. It can be seen that in case C, the solid fraction is less than 0.01. In the other three cases, the solid fraction at the bottom of the reactor is much larger than in a saturated pneumatic transport flow. This region is called the dense region.
This means that in cases C', C_A', and C_B' the total bed mass is much greater than in case C. According to Eq. 12-2, the residence time increases when increasing the bed mass and keeping the flow of oxygen carrier constant.

\[
\tau = \frac{M}{\dot{m}} \tag{12-2}
\]

In case C_B', the residence time is about 11 seconds which is more than twice that in case C. The second mode of operation is advantageous if the oxidation reactions is slower and therefore more residence time is required.

Figure 12-1. Distribution of solid fraction \(\varepsilon_s\) in the air reactor at different amounts of total bed material in the air reactor. Curves B and C are calculated for cases C_A' and C_B' with a bed mass of 47 t and 66 t in the air reactor, respectively. The particles’ properties are according to Table 4-5.
12.2.1 First mode of operation in IPFBR_A: Controlling the residence time in the air reactor

If the first mode of operation is applied in the IPFBR_A, the reactor works at the operating point (Section 4.7.1). This means the combustion air flowrate controls the flow of oxygen carrier, which is equal to the MTPFR. The total height of the fluidised bed in the fuel reactor maybe determined by a ring of overflow holes in the reactor wall. If the amount of bed material in the bubble bed (fuel reactor) increases, the excess material flows through the overflow hole back into the air reactor. The reactor can be seen as a pot with boiling water. If one tries to fill more water into the pot than fits, the water will pour over the lip out of the pot. This means, if the gas velocity is constant in the air reactor, the amount of total bed material in this reactor can be controlled by the total amount of bed material in the whole reactor system. All excess carrier material will accumulate in the air reactor, because for each kilogram oxygen carrier being transported into the fuel reactor, one kilogram will flow back into the air reactor through the ring of overflow holes. In this way, theoretically, the reaction time in the air reactor can be controlled. An advantage is that in this design the residence time can be adjusted to the requirement of the oxygen carrier. Disadvantages are the large amount of particles that circulate in the IPFBR and the large amount of particles needed in the whole reactor. More about the reactor dimensions can be found in Section 12.7.

12.2.2 Second mode of operation in IPFBR_A: Controlling the flow rate between the fuel and the air reactor

In the second mode of operation, the mass flowrate of oxygen carrier from the fuel reactor into the air reactor can be controlled. This may be realised by a control device between the fuel and the air reactor, for example, a valve with a determined diameter such that only a particles at a given flowrate can flow through it. The principle would be the same as in an hourglass. Alternatively, a particle pot-seal, in which the particles are fluidised with steam, can be installed between the fuel and the air reactor. In this way the particle flow can be controlled by the steam flowrate. More steam would lead to an increased flowrate through the pot-seal, while a reduced steam flowrate would decrease the particle flow into the air reactor. The main feature with this mode of operation is that the flowrate of particles from the fuel reactor into the air reactor is below the MTPFR and because the gas velocity in the air reactor is far above the necessary velocity for pneumatic transport, all

---

1 Here, it is assumed that the particles are not stuck in the cyclone system or a particle pot-seal.
particles entering the air reactor are almost immediately transported into the cyclone system. There would be no dense region in the air reactor. An advantage is that the amount of fluidised particles is minimal and therefore the pressure loss is less than in the first mode of operation. Moreover, the mass flowrate of particles is independent from the air flowrate in the air reactor which eases the control of the reactor. A disadvantage is a relatively short residence time of the particles in the air reactor. The residence time depends on the height of the reactor and the particle diameter in the first place. Results concerning the dimensions of the reactor can be found in Section 12.7.
12.3 Terminal velocity

The terminal velocity exists when the velocity drag force equals the gravitational force. At this state, each particle is individually supported and they no longer rest upon one another (Eq. 12-3).

\[
\begin{align*}
  u_T &= \left[ \frac{4 \cdot g \cdot d_p}{3 \cdot C_D} \left( \frac{\rho_s}{\rho_g} - 1 \right) \right]^{1/2} \\
  (12-3)
\end{align*}
\]

The drag coefficient, \(C_D\), is a function of the Reynolds number for particles at terminal velocity (\(Re_T\)).

\[
Re_T = \frac{u_T \cdot d_p \cdot \rho_g}{\mu}
\]

(12-4)

The dynamic viscosity (\(\mu \text{ [N}s\text{/m}^2\)) is a function of temperature. A regression equation over data derived from Aspen Plus® gives Eq. (12-5).

\[
\mu = 5.55556 \cdot 10^{-15} \cdot T^3 - 2.04475 \cdot 10^{-11} \cdot T^2 + 4.79114 \cdot 10^{-8} \cdot T + 1.57354 \cdot 10^{-5}
\]

(12-5)

This equation is only valid in a temperature range from \(T = 700^\circ\text{C}\) to \(1250^\circ\text{C}\). The density of the gas (\(\rho_g\)) is calculated by using the ideal-gas law (Eq. 12-6),

\[
\rho_g = \frac{P \cdot M_{\text{air}}}{R \cdot (T + 273.15)} \text{ [kg/m}^3\text{]} \]

(12-6)

where

\(P\) = pressure [Pa],
\(M_{\text{air}}\) = molar mass of air = 28.8 g/mol,
\(R\) = universal gas constant = 8.3142 J/(mol*K),
\(T\) = temperature [°C]
Three models for calculating the drag coefficient have been compared. The first model from Basu et al. (1991) is described in Appendix 12.3.1. This model gives lower values for the drag coefficient if the particle diameter \( d_p \) is below 300 \( \mu m \) than the other two. Appendix 12.2.2 presents the second model, which is taken from Kunii and Levenspiel (1991). The third model can be found in Bolland (2001) and is shown in Appendix 12.3.3

### 12.3.1 The model from Basu et al. (1991)

The drag coefficient, \( C_D \), is calculated as a function of the Reynolds number for particles at terminal velocity (\( Re_T \)).

\[
C_D = \frac{a_1}{Re_T^b} \quad \text{(12-7)}
\]

\[
Re_T = \frac{u_T \cdot d_p \cdot \rho_s}{\mu} \quad \text{(12-8)}
\]

The constants \( a_1 \) and \( b \) were approximated according to Howard (1989) (Table 12-1).

<table>
<thead>
<tr>
<th>Range of ( Re_p )</th>
<th>Region</th>
<th>( a_1 )</th>
<th>( b )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 &lt; ( Re_p &lt; 0.4 )</td>
<td>Stoke’s law</td>
<td>24</td>
<td>1</td>
</tr>
<tr>
<td>0.4 &lt; ( Re_p &lt; 500 )</td>
<td>Intermediate law</td>
<td>10</td>
<td>0.5</td>
</tr>
<tr>
<td>( 500 &lt; Re_p )</td>
<td>Newton’s law</td>
<td>0.43</td>
<td>0</td>
</tr>
</tbody>
</table>

### 12.3.2 The model found in Kunii and Levenspiel (1991)

\[
C_D = \frac{24}{Re_T} \left[ 1 + \left( 8.1716 \cdot e^{-4.0655 \cdot \Phi_s} \right) \cdot Re_T^{0.0964+0.5565 \cdot \Phi_s} \right] + \frac{73.69 \cdot \left( e^{-5.0748 \cdot \Phi_s} \right) \cdot Re_T^{5.378 \cdot e^{6.2122 \cdot \Phi_s}}}{Re_T + 5.378 \cdot e^{6.2122 \cdot \Phi_s}} \quad \text{(12-9)}
\]

where \( \Phi_s \) is the sphericity, defined as follows:

\[
\Phi_s = \left( \frac{S_{\text{sphere}}}{S_{\text{particle}}} \right)_{\text{same volume}} \quad \text{(12-10)}
\]
A round sand particle has got a sphericity of 0.86, for example (Kunii and Levenspiel, 1991). When the sphericity is set to one Eq. 12-10 can be reduced to:

\[ C_D = \frac{24}{Re_T} + 3.3643 \cdot Re_T^{-0.3471} + \frac{0.4607 \cdot Re_T}{Re_T + 2682.5} \]  

\[ (12-11) \]

### 12.3.3 The model found in Bolland (2001)

The model found by Bolland gives similar results for \( C_D \) as the previous one. The calculated values are, however, a little lower than those calculated with Kunii and Levenspiel's model, if the particle diameter is between 125 and 300 µm.

\[ C_D = \frac{24}{Re_T} + \frac{4}{\sqrt{Re_T}} + 0.4 \quad \text{for } Re < 10^5 \]  

\[ (12-12) \]

### 12.4 Calculation of the pressure loss in the IPFBR

Compared to a commercial gas turbine combustor the IPFBR will cause a higher pressure drop when integrated in a power generation process such as, for example, a natural gas-fired combined cycle. The pressure loss mainly comes from the force necessary to fluidise the large amount of particles in the two reactors, the pressure drop in the cyclone, and the pressure drop for the gas distribution at the fuel gas and combustion air inlet.

The pressure drops of the fuel reactor and air reactor are calculated using Eqs. 12-12 and 12-13:

\[ \Delta P_f = \Delta P_{b,f} + \Delta P_{d,f} \]  

\[ (12-12) \]

\[ \Delta P_a = \Delta P_{b,a} + \Delta P_{d,a} + \Delta P_c \]  

\[ (12-13) \]

where \( \Delta P_B \) is the pressure drop in the fluidised bed and \( \Delta P_D \) the pressure drop caused by the gas distribution. \( \Delta P_C \) is the pressure drop over the cyclone. The pressure drop across the gas distributors is calculated from Eq. 12-14.
\[ \Delta P_B = 0.4 \cdot \Delta P_{B_0} \quad (12-14) \]

12.4.1 Pressure drop in the fluidised bed

The pressure drop over the fluidised bed \( \Delta P_B \) is calculated using \textit{Eq. 12-15}, which is derived from the hydrodynamics described by \textit{Carberry and Varma (1986)} and \textit{Kunii and Levenspiel (1991)}.

\[ \Delta P_B = 1.2 \cdot \frac{M \cdot g}{A} \quad (12-15) \]

According to \textit{Eq. 12-15}, the pressure drop is the total fluidised mass \( (M) \) per area \( (A) \) of the reactor multiplied by the gravitation constant. Because of the large diameter of the reactors, the pressure loss caused by friction against the wall is neglected.

The fluidised mass in the fuel reactor \( M_f \) is calculated as the product of the flow of oxygen carrier \( (\dot{m}_s) \) and the residence time \( (\tau_f) \) of the particles in the fuel reactor \textit{(Eq. 12-16)}.

\[ M_f = \dot{m}_s \cdot \tau_f \quad (12-16) \]

The fluidised mass in the air reactor \( M_a \) is calculated using \textit{Eq. 12-17},

\[ M_a = \left( H_d \cdot \varepsilon_{sd} + H_f \cdot \varepsilon_{sf} \right) \cdot A_a \cdot \rho_s \quad (12-17) \]

where \( H_d \) is the height of the dense region, \( \varepsilon_{sd} \) its solid fraction and \( H_f \) is the height of the freeboard. \( \varepsilon_{sf} \) is the mean value of the solid fraction over the freeboard \textit{(Eqs. 12-18 to 12-20)}.
\[ \bar{\varepsilon}_{sf} = \frac{1}{H_f} \int_0^{H_f} \varepsilon_{sf} \cdot dz = \varepsilon_{sp} + \frac{\varepsilon_{sd} - \varepsilon_{sp}}{a \cdot H_f} \left(1 - e^{-a \cdot H_f}\right) \]  

(12-18)

\[ \frac{\varepsilon_{sf} - \varepsilon_{sp}}{\varepsilon_{sd} - \varepsilon_{sp}} = e^{-a \cdot z_f} \]  

(12-19)

\[ a \cdot u_0 = \text{constant (for constant } d_p) \]  

(12-20)

The coefficient \( a \) in \( \text{Eq. 9-19} \) is estimated from \( \text{Eq. 9-20} \). The constant is estimated to five based on experimental results presented by Kunii and Levenspiel (1991). However, the constant should be determined experimentally for the particles of oxygen carrier and the relatively large diameter of the air reactor for a fast fluidisation.

12.4.2 Pressure drop in a cyclone

According to Sinnott et al. (1996), Stairmand developed two standard designs for gas-solid cyclones: a high efficiency cyclone and a high throughput design. The high throughput design, Figure 12-2, is suitable for high gas rates as occurring in the IPFBR. The pressure drop in the cyclone will be due to the entry and exit losses,
and friction kinetic energy losses in the cyclone. The empirical equation given by Stairman was used to estimate the pressure drop ($\Delta P_c$):

$$\Delta P_c = \frac{\rho_r}{203} \left[ u_1^2 \left( 1 + 2\phi \left( \frac{r_t}{r_e} - 1 \right) \right) + 2u_2^2 \right]$$

(12-21)

Here the inlet duct velocity is $u_1$ and the exit duct velocity is $u_2$; $r_t$ is the radius of the circle to which the center line of the inlet is tangential and $r_e$ is the radius of the exit pipe. The factor $\phi$ can be taken from Figure 9-3, where the parameter $\Psi$ is proportional the ratio of $\Lambda_s$, which is the surface area of the cyclone exposed to the

---

*Fig. 12-3. Cyclone pressure drop factor (Sinnott et al., 1996)*
spinning fluid, and \( A_1 \), which is the area of the inlet duct:

\[
\psi = f_c \frac{A}{A_1}
\]  
(12-22)

The friction factor \( f_c \) is 0.005 for gases. For design purpose \( A_s \) can be taken as equal to the surface area of a cylinder with the same diameter as the cyclone and length equal to the total height of the cylinder (barrel plus cone).

### 12.4.3 Power requirement for the booster fan

The gas turbine compressor or an additional booster fan has to overcome the pressure loss in the fluidised beds. This booster power \( W_f \) was calculated by the flow equation for a reversible adiabatic process and the isentropic efficiency of the fan (Eq. 12-23).

\[
W_f = \frac{m}{\eta_{fan}} (h_2 - h_1) = \frac{m}{\eta_{fan}} \cdot c_p \cdot (T_2 - T_1)
\]  
(12-23)

By assuming a perfect gas, \( T_2 \) is calculated for the reversible adiabatic process where \( n \) is equal to the isentropic coefficient (Eq. 12-24).

\[
T_2 = T_1 \left( \frac{P_1}{P_1 + \Delta P} \right)^{\frac{1-n}{n}}
\]  
(12-24)

For the power loss in the air reactor, \( T_1 \) is the temperature of the air after compression. For the fuel reactor \( T_1 \) was 180°C, because the natural gas was preheated to 180°C. The heat capacity \( (c_p) \) was assumed to be constant.

### 12.5 Height of the fluidised bed in the fuel reactor

The height of the fluidised bed in the fuel reactor was calculated using Eq. 12-25.

\[
H_{fr} \cdot (1 - \varepsilon_f) = \frac{M}{A_f \cdot \rho_s}
\]  
(12-25)

The overall voidage \( \varepsilon_f \) of the bubble bed (fuel reactor) is calculated by Eqs. 12-26 and 12-27. Eq. 12-27 is a regression equation over data published in Carberry and Varma (1987) and is only valid for Reynolds numbers from 200 to 1000.
\[ \frac{u_0}{u_r} = \varepsilon_r^m \]  

\[ m = -0.2632 \cdot \ln(R_r) + 4.152 \]  

12.6 Calculation of the pressure shell

The dimensions of the pressure shell can be calculated according to the Swedish standards for pressure vessels (Tryckkärlskommissionen, 1987a). In order to simplify the calculation no holes and welding seams are considered.

12.6.1 The cylinder

The minimum thickness of the wall ($S_{\text{min}}$) for the cylinder was calculated with Eq. 12-28.

\[ S_{\text{min}} = \frac{D \cdot P}{20 \cdot \sigma_{\text{des}} \cdot Z} \]  

$D$ is the inner diameter of the shell and $P$ is the design pressure (overpressure). The security factor was taken as $S_f = 1.5$. $Z$ is a strength factor, which depends on holes and welding seams in the shell. Here, the impact of holes and welding seams is neglected and the strength factor is set to one.

$\sigma_{\text{des}}$ is the design stress for the steel and can be found, for example, in the Swedish standards for pressure vessels (Tryckkärlskommissionen, 1987b). These calculations are only valid for $S_{\text{min}}/D \leq 0.05$. 

125
12.6.2 The ellipsoidal head

The minimum wall thickness of the head can be calculated according to Eq. 12-29.

\[
S_{\text{min}} = \frac{D_y \cdot P \cdot y}{20 \cdot \sigma_{\text{des}} \cdot z}
\]  

(12-29)

Here $D_y$ is the outer diameter of the ellipsoidal head and $y$ is a form factor, depending on the shape of the head. If the form for the head is determined by Eqs. 12-30 to 12-32, the form factor is $y = 1.3$.

\[
h = \text{height of the ellipsoidal head} = 0.25 \cdot D_y \quad [\text{mm}] \quad (12-30)
\]

\[
R = \text{crown radius} = 0.8 \cdot D_y \quad [\text{mm}] \quad (12-31)
\]

\[
r = \text{knuckle radius} = 0.154 \cdot D_y \quad [\text{mm}] \quad (12-32)
\]

For the ellipsoidal head, the security factor is $S_f = 1.1$

12.7 Results of dimensioning of the IPFBR

In this section an initial estimation of the dimensions of a CLC reactor in a combined cycle is presented. The results of the hydrodynamic study of the IPFBR versions A and B and the two already introduced modes of operation are summarised. Additionally, the impact of the number of cyclones on the total height of the reactor and the required amount of steel has been studied. Two cases have been calculated, in Case 1 four pairs of cyclones are used and in Case 2 eight cyclones are used in parallel.
12.7.1 The dimensions of the CLC reactor

Essential design parameters are the height and the diameter of the pressure shell. Therefore, it is necessary to determine first the height of the air reactor and the fuel reactor and the diameter, respectively.

The height of the air reactor is mainly determined by the size of the cyclones, the fuel reactor, and a particle pot-seal between the cyclones and the fuel reactor. The height of the cyclones depends on the volume flow of gas flowing through it (VDI-Wärmeatlas, 2002; Sinnott et al., 1996). If the gas stream is divided into smaller streams and more cyclones are used parallel, the height of each cyclone can be reduced. Table 12-2 lists the assumptions for the required input data for the reactor model in order to calculate the hydrodynamic behaviour and the dimensions of the IPFBR. This data set is an example which refers to Case C which was investigated in Section 4.4.

<table>
<thead>
<tr>
<th>Table 12-2 Input data for calculating the dimensions of the IPFBR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp. oxidation (TIT) (turbine Inlet)</td>
</tr>
<tr>
<td>Temp. reduction (fuel reactor)</td>
</tr>
<tr>
<td>Particles flow (oxidation outlet)</td>
</tr>
<tr>
<td>Airflow into air reactor</td>
</tr>
<tr>
<td>Methane flow into fuel reactor (800 MW\text{n})</td>
</tr>
<tr>
<td>Residence time of fuel reactor</td>
</tr>
</tbody>
</table>

Table 12-2 shows the results from the hydrodynamic analysis of the IPFBR\_A when operating in the first and the second modes. IPFBR\_A1 stands for the design with four pairs of cyclones (Figure 4-10) and IPFBR\_A2 for the one with 8 cyclones in parallel. The figures in the grey shadowed boxes are not equal for the two cases.

From Table 12-3 can be seen that the total height of the air reactor can be reduced by four metres, if eight cyclones are used parallel instead of four pair of cyclones. When increasing the number of cyclones the gas flowrate through each cyclone is reduced and, therefore, the cyclone can be scaled down in its dimensions.

After all, the pressure drop in each cyclone does not change significantly. The difference in pressure drop from 66 to 32 mbar comes from the fact that in the IPFBR\_A1 two cyclones are coupled in series and therefore the pressure drop is twice the one in the IPFBR\_A2.
Table 12-3. Results of the reactor design for the IPFBR (A) for 800 MWth

<table>
<thead>
<tr>
<th></th>
<th>IPFBR (A)</th>
<th>IPFBR A1</th>
<th>IPFBR A2</th>
</tr>
</thead>
<tbody>
<tr>
<td>uT in air reactor1)</td>
<td>[m/s]</td>
<td>0.28</td>
<td>0.28</td>
</tr>
<tr>
<td>uT in fuel reactor</td>
<td>[m/s]</td>
<td>0.29</td>
<td>0.29</td>
</tr>
<tr>
<td>u0 of gas inlet in air reactor2)</td>
<td>[m/s]</td>
<td>10</td>
<td>6</td>
</tr>
<tr>
<td>u0 of gas inlet in fuel reactor</td>
<td>[m/s]</td>
<td>0.07</td>
<td>0.07</td>
</tr>
<tr>
<td>Total height of the fuel reactor</td>
<td>[m]</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Height of the downcomer and particle seal</td>
<td>[m]</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Height of the bubble bed</td>
<td>[m]</td>
<td>2.8</td>
<td>2.8</td>
</tr>
<tr>
<td>Total height of the air reactor</td>
<td>[m]</td>
<td>25</td>
<td>21</td>
</tr>
<tr>
<td>Height of the cyclone system</td>
<td>[m]</td>
<td>15.5</td>
<td>11.1</td>
</tr>
<tr>
<td>Diameter of the cyclones</td>
<td>[m]</td>
<td>3.3</td>
<td>2.3</td>
</tr>
<tr>
<td>Inlet gas velocity of the cyclones</td>
<td>[m/s]</td>
<td>22</td>
<td>21</td>
</tr>
<tr>
<td>ΔP in the cyclone system</td>
<td>[mbar]</td>
<td>66</td>
<td>32</td>
</tr>
<tr>
<td>Diameter of the air reactor</td>
<td>[m]</td>
<td>5.7</td>
<td>7.3</td>
</tr>
<tr>
<td>Diameter of the fuel reactor</td>
<td>[m]</td>
<td>13</td>
<td>13</td>
</tr>
<tr>
<td>ΔP fuel reactor3)</td>
<td>[mbar]</td>
<td>320</td>
<td>320</td>
</tr>
<tr>
<td>Mean residence time in fuel reactor</td>
<td>[s]</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>Total bed mass in the fuel reactor</td>
<td>[t]</td>
<td>270</td>
<td>270</td>
</tr>
<tr>
<td>Maximum flow of oxygen carrier (MTFFR)</td>
<td>[t/s]</td>
<td>5.9</td>
<td>5.8</td>
</tr>
</tbody>
</table>

**First mode of operation4)**
| ΔP air reactor3) | [mbar] | 151 | 145 |
| Mean residence time in air reactor | [s] | 4.7 | 6.4 |
| Total bed mass in the air reactor | [t] | 28 | 37 |
| Flow of oxygen carrier | [t/s] | 5.9 | 5.8 |

**Second mode of operation5)**
| ΔP air reactor3) | [mbar] | 54 | 46 |
| Mean residence time in air reactor | [s] | 2.6 | 3.7 |
| Total bed mass in the air reactor | [t] | 12 | 17 |
| Flow of oxygen carrier | [t/s] | 4.5 | 4.5 |

1) uT = Terminal velocity
2) u0 = Superficial gas velocity [m/s]
3) Pressure loss of gas distribution and fluidisation
4) Mode of operation 1 represents Case C in Section 4.6 and Figure 9-1
5) Mode of operation 2 represents Case C' in Section 4.6 and Figure 9-1
6) Four pairs of cyclones
7) Eight cyclones in parallel

The increase of the air reactor's diameter from 5.7 to 7.3 m in design A2 can be explained by the much higher superficial gas velocity (u0) in design A1. If the gas velocity is 10 m/s instead of 6 m/s, the air reactor can be more compact and the MTFFR increases from 5800 kg/s to 5900 kg. The disadvantage is the reduced
residence time from 6.4 s to 4.7 s in the first operating mode and from 3.7 s to 2.6 s in the second operating mode. Moreover, 10 m/s is rather unconventionally high for circulating fluidised bed reactors and questionable in CLC, because of the great mechanical stress on the particles of the oxygen carrier.

When comparing the first and the second modes of operation, one can see the great difference in total mass of bed material in the air reactor. More than the double amount of particles is fluidised in the air reactor if the mode of operation is changed from the second one to the first one. This figure will be even more impressive if a nickel-based oxygen carrier is used. If, for example, the stream data of Case F from the CLC-PM (Section 4.4.3) is used, the amount of bed material in the second mode will be only 3.7 ton instead of 28 ton. For this reason, the second mode of operation provides advantages concerning the pressure drop and the required amount of particles. The residence time, however is shorter in the second mode that in the first one and this might be a very important disadvantage, if the kinetics of the oxidation reaction is too slow.

Table 12-4 shows the dimensions for an 800 MW\textsubscript{th} version of the IPFBR\textsubscript{B}. The assumptions for the hydrodynamic calculations are the same as for the IPFBR\textsubscript{A} (Table 12-3). This design example of the IPFBR\textsubscript{B} includes four parallel cyclones for the air reactor and it operates in the second mode of operation, i.e., the flowrate of oxygen carrier into the air reactor is controlled. It is also possible to operate the IPFBR\textsubscript{B} in the first mode and to extend it to eight cyclones. Here, however, the simplest layout is studied.

The most interesting result from a comparison of designs A and B is the diameter of the fuel reactor. In the IPFBR\textsubscript{B}, the discharge of particles from the fuel reactor is a minor problem, such that the superficial gas velocity in the fuel reactor can be increased enabling the diameter to be reduced. In this way the CLC reactor can be more compactly constructed. A disadvantage is the higher pressure loss in the fuel reactor caused by the higher fluidised bed.
### Table 12-4. Technical data of the IPFBR (B) with two cyclone systems

<table>
<thead>
<tr>
<th>Unit</th>
<th>IPFBR_B</th>
</tr>
</thead>
<tbody>
<tr>
<td>$u_T$ in air reactor $^1$</td>
<td>0.28</td>
</tr>
<tr>
<td>$u_T$ in fuel reactor</td>
<td>0.29</td>
</tr>
<tr>
<td>$u_0$ of gas inlet in air reactor $^2$</td>
<td>6</td>
</tr>
<tr>
<td>$u_0$ of gas inlet in fuel reactor</td>
<td>0.18</td>
</tr>
<tr>
<td>Total height of the fuel reactor</td>
<td>5</td>
</tr>
<tr>
<td>Height of the dense region in the fuel reactor</td>
<td>4</td>
</tr>
<tr>
<td>Total height of the air reactor</td>
<td>25</td>
</tr>
<tr>
<td>$\Delta P$ air reactor $^3$</td>
<td>55</td>
</tr>
<tr>
<td>$\Delta P$ fuel reactor $^3$</td>
<td>633</td>
</tr>
<tr>
<td>Mean residence time in air reactor</td>
<td>4.4</td>
</tr>
<tr>
<td>Mean residence time in fuel reactor</td>
<td>60</td>
</tr>
<tr>
<td>Diameter of the air reactor</td>
<td>7.3</td>
</tr>
<tr>
<td>Diameter of the fuel reactor</td>
<td>8</td>
</tr>
<tr>
<td>Total bed mass in the air reactor</td>
<td>19.7</td>
</tr>
<tr>
<td>Total bed mass in the fuel reactor</td>
<td>270</td>
</tr>
<tr>
<td>Flow of oxygen carrier</td>
<td>4.5</td>
</tr>
<tr>
<td>Maximum flow of oxygen carrier (MTFFR)</td>
<td>5.8</td>
</tr>
</tbody>
</table>

#### Four cyclones for the air reactor

<table>
<thead>
<tr>
<th>Unit</th>
<th>IPFBR_B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter of the cyclone ($D_c$)</td>
<td>3.2</td>
</tr>
<tr>
<td>Inlet duct velocity of the cyclone</td>
<td>22</td>
</tr>
<tr>
<td>Total height of the cyclone</td>
<td>15.5</td>
</tr>
<tr>
<td>$\Delta P$ cyclone</td>
<td>23</td>
</tr>
<tr>
<td>Height of the downcomer and particle seal</td>
<td>2</td>
</tr>
</tbody>
</table>

#### Three primary cyclones for the fuel reactor

<table>
<thead>
<tr>
<th>Unit</th>
<th>IPFBR_B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter of the cyclone ($D_c$)</td>
<td>1.3</td>
</tr>
<tr>
<td>Inlet duct velocity of the cyclone</td>
<td>20</td>
</tr>
<tr>
<td>Total height of the cyclone</td>
<td>9.5</td>
</tr>
<tr>
<td>$\Delta P$ cyclone</td>
<td>8</td>
</tr>
</tbody>
</table>

#### Secondary cyclone for the fuel reactor

<table>
<thead>
<tr>
<th>Unit</th>
<th>IPFBR_B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter of the cyclone ($D_c$)</td>
<td>2.2</td>
</tr>
<tr>
<td>Inlet duct velocity of the cyclone</td>
<td>21</td>
</tr>
<tr>
<td>Total height of the cyclone</td>
<td>9</td>
</tr>
<tr>
<td>$\Delta P$ cyclone</td>
<td>43</td>
</tr>
</tbody>
</table>

---

1) $u_T$ = Terminal velocity  
2) $u_0$ = Superficial gas velocity [m/s]  
3) Pressure loss of gas distribution and fluidisation
12.7.2 The pressure shell

The wall thickness of the pressure shell is calculated according to the Swedish norm for pressure vessels (Appendix 12.6). For the pressure shell, it is assumed that the inner side of the shell is covered with a refractory insulation, which protects the steel from the heat. For the calculations of the wall thickness a steel temperature of max. 20°C is assumed. An even better insulation is desirable in order to avoid heat losses through the pressure shell. The used steel is of the type SS-steal 13 31 (Swedish steel standard). Table 12-5 shows the approximate size of the pressure shell and the thickness of the wall, which is necessary to withstand the pressure.

<table>
<thead>
<tr>
<th>Units</th>
<th>IPFBR A1</th>
<th>IPFBR A2</th>
<th>IPFBR B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inner diameter of the shell</td>
<td>[m]</td>
<td>20</td>
<td>21.5</td>
</tr>
<tr>
<td>Total height of the shell</td>
<td>[m]</td>
<td>31</td>
<td>26.5</td>
</tr>
<tr>
<td>Wall thickness</td>
<td>[mm]</td>
<td>83</td>
<td>90</td>
</tr>
</tbody>
</table>

The inner diameter of the pressure shell is determined by the diameters of the air and the fuel reactor. The IPFBR of type B has a four metres smaller diameter due to its more compact construction. The smaller diameter leads to less mechanical stress in the pressure shell which reduces the required wall thickness (Appendix 12.6).

12.7.3 Amount of required material

The most interesting result from this initial estimation calculation of the required amount of material is that the IPFBR_B design requires a smaller pressure shell compared to the IPFBR_A design. This leads to significant material savings of the steel and the refractory insulation for the pressure shell. Table 4-10 shows that 57 m³ less steel is required for IPFBR_B than for IPFBR_A1. Moreover, this savings can be reached although the IPFBR_B was designed for a superficial gas velocity of 6 m/s while the IPFBR_A1 uses 10 m/s in this study, which allows a smaller diameter of the air reactor (Table 4-7, Section 12.7.1). If comparing the IPFBR_B with design IPFBR_A2 (both designs use superficial gas velocities of 6 m/s in the air reactor) the material savings for design IPFBR_B are 62 m³ although the IPFBR_A1 includes eight parallel cyclones instead of four, respectively. Section 12.7.2 showed that using four smaller cyclones instead for four
larger ones reduces the height of the pressure shell. For the insulation of the inner side of the pressure shell material savings of 300 m$^2$ to 400 m$^2$ is possible.

The fact that the superficial gas velocity in the air reactor of the IPFBR$_B$ is 6 m/s and that only four parallel cyclones are used results in a larger material demand of the air reactor. The IPFBR$_B$ needs more material for the air reactor than the both versions of IPFBR$_A$. The reason that more material is needed for the fuel reactor, although the diameter is much smaller, is the tapered head (Figure 4.11) of the reactor. If such a head would be used in the IPFBR$_A$ as well, for example, to reduce the particle discharge, the required amount of material would be much larger than in the IPFBR$_B$.

The steel for the cyclone has to withstand very high temperature, thus, it might be necessary to build the cyclones in refractory bricks or ceramic. Since there is no pressure difference between the inside and the outside, the material only has to withstand high temperatures. Another option might be to cover the inside of the cyclones with a refractory lining. From Table 12-6 can be seen that material savings are also possible for the material of the cyclone system. These figures for the cyclone system, however, are somewhat misleading, because in IPFBR$_B$ only four cyclones are considered for the air reactor compared to eight in IPFBR$_A$. In fact, for the cyclones, more material would be is required in IPFBR$_B$ because of the cyclone system for the fuel reactor. However, these cyclones are smaller and because the temperature is lower in the fuel reactor, the demands on the material are smaller.

<table>
<thead>
<tr>
<th>Table 12-6. Amount of material needed for the CLC reactor</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Unit</strong></td>
</tr>
<tr>
<td>Steel for pressure shell, SS-steel 13 31</td>
</tr>
<tr>
<td>Steel for cyclones including ducting</td>
</tr>
<tr>
<td>Refractory insulation material for the inside of the shell to keep an outer temp of &lt; 15°C of the shell</td>
</tr>
<tr>
<td>Refractory brick for the air reactor</td>
</tr>
<tr>
<td>Refractory brick for the fuel reactor</td>
</tr>
<tr>
<td>Gas distributor fuel reactor</td>
</tr>
<tr>
<td>Gas distributor air reactor</td>
</tr>
<tr>
<td>Total mass of oxygen carrier</td>
</tr>
</tbody>
</table>

1) First mode of operation
2) Second mode of operation