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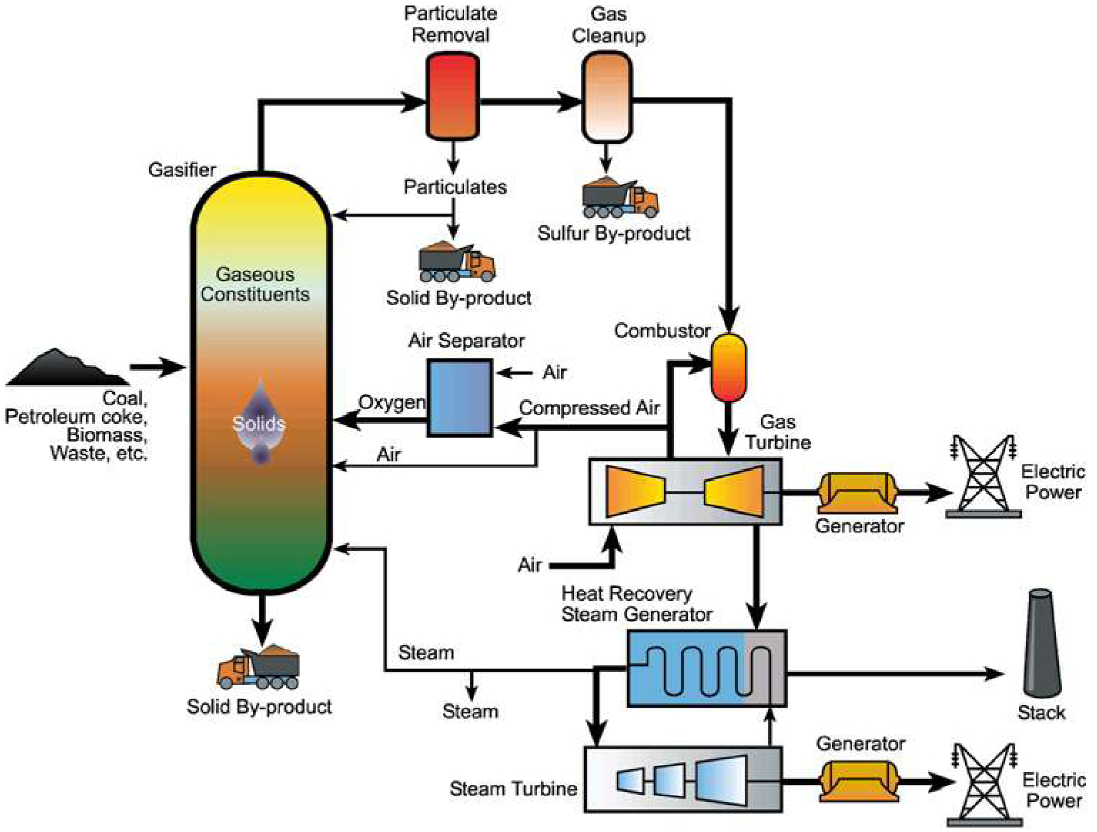

# System analysis of chemical and carbonate looping processes in IGCC power plants for $CO_2$ separation

*Master's Thesis within the Master's programme Sustainable Energy Systems*

TUONG-VAN NGUYEN

Department of Energy and Environment
*Division of Energy Technology*
CHALMERS UNIVERSITY OF TECHNOLOGY
Göteborg, Sweden 2011

MASTER'S THESIS T2011:357

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Supervisor at Forschungszentrum Jülich: Sebastian Schiebahn
Supervisor at Chalmers University of Technology: David Pallarès
Examiner at Chalmers University of Technology: Anders Lyngfelt

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Department of Energy and Environment
Division of Energy Technology
Chalmers University of Technology
SE-41296 Göteborg
Sweden

Tel. +46-(0)31 772 1000

Cover:
Process flow diagram of an integrated gasification combined cycle (IGCC) power plant

Reproservice / Department of Energy and Environment
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I, Tuong-Van Nguyen, hereby declare that the work presented in this research report has been performed solely by myself except where explicitly identified to the contrary: all the ideas and figures of others, whether published or unpublished, have been properly referenced. This thesis has been submitted specifically for the degrees of Master of Science at Chalmers University of Technology, Göteborg, Sweden and of Engineer at École des Mines, Albi-Carmaux, France.

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System analysis of chemical and carbonate looping processes in IGCC power plants for $CO_2$ separation

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# Abstract

Chemical and carbonate looping cycles have a strong potential for efficient $CO_2$ capture with limited energy penalty. The main objective of this thesis is to assess the feasibility and to evaluate the potential of these solid looping cycles in integrated gasification combined cycles (IGCC) power plants.

Chemical looping combustion (CLC) can replace the combustion chamber of the conventional gas turbine cycle. The integration of this process can result in nearly 100% carbon capture efficiency and around 5% electrical efficiency penalty of the combined cycle. The sensitivity analysis reveals the strong impact of the oxidation reactor temperature and of the pressure ratio. Several configurations of the combined cycles with, for example, $CO_2$-turbine and top firing have thus been proposed and can all achieve close to 100% $CO_2$-capture.

Chemical looping gasification (CLG) does not have the potential of capturing carbon dioxide but eliminates the need for a cryogenic distillation unit and ease the generation of synthesis gas. However, the type of oxygen carrier, the solids flow rate and the oxygen-to-fuel ratios are critical design factors for a successful integration of CLG.

Carbonate looping ex situ allows the capture of carbon dioxide by moving the equilibrium of the water-gas shift reaction towards the generation of hydrogen. The capture of carbon dioxide can reach up to 93% and its purity up to 97%.

This thesis suggests therefore that both chemical and carbonate looping cycles have a high potential for efficient power generation, with or without carbon dioxide capture. The easiest process to integrate, from a technological aspect, may nevertheless be chemical looping combustion of synthesis gas.

**Keywords:** Integrated Gasification Combined Cycle (IGCC), $CO_2$ capture, chemical looping, carbonate looping, synthesis gas combustion, gasification, water-gas shift reaction, hydrogen production, fluidised bed

Systemanalys av chemical- och carbonate looping-processer för koldioxidavskijning i förgasning integrerad med gaskombikraftverk

Examensarbete inom Masterprogram i Sustainable Energy Systems
TUONG-VAN NGUYEN
Institutionen för Energi och Miljö
Avdelningen för Energiteknik
Chalmers Tekniska Högskola

# Sammanfattning

Chemical- och carbonate looping-processer har stor potential för infångning av koldioxid med små energiförluster. Målsättningen med detta examensarbete är att utvärdera dessa tekniker utifrån genomförbarhet, verkningsgrad och komplexitet vid integrering med IGCC-kraftverk.

Brännkammaren i en gasturbin skulle kunna ersättas med ett tvåstegsförbränningssystem (chemical looping combustion): detta alternativ ger en koldioxidavskiljning på cirka 100% och leder till en förlust i elektrisk verkningsgrad på mindre än 5% för kombicykeln. Simuleringarna visar att högre elektrisk verkningsgrad kan erhållas om oxidationsreaktorns utgångstemperatur höjs eller tryckförhållandet över turbinen varieras. Flera olika konfigurationer av IGCC-kraftverk, med till exempel en extra $CO_2$-turbin och top-firing, har undersökts: generellt ändras inte infångningsgraden av $CO_2$ fastän den elektriska effektiviteten varierar med några få procent.

Chemical looping gasification är en metod som kan minska koldioxidutsläppen per se. Fördelen med tekniken är att den underlättar syntesgasproduktionen och att IGCC-kraftverk med den processen inte kräver energislukande kryodestillation. Typen av metalloxidpartiklar-, samt material- och syre-flöden är kritiska designparameterar för att höja bränsleomvandlingen och förbättra förgasningsprocessen.

Carbonate looping ex situ kan vara ett intressant alternativ till de huvudtekniker som erbjuds för $CO_2$-avskiljning före förbränningsprocessen. Den kemiska jämvikten i vatten-gas skiftreaktionen drivs mot ökad $CO_2$- och $H_2$-produktion, vilket kan resultera i upp till 93% $CO_2$-infångning.

Detta examensarbete bekräftar att chemical- och carbonate looping-tekniker kan kombineras med IGCC-kraftverk och medföra hög elektrisk verkningsgrad, med eller utan $CO_2$-avskiljning. Den process som mest sannolikt kan bli implementerad är antagligen tvåstegsförbränningen då den når ett genombrott i minskade energiförluster för $CO_2$-infångning.

**Nyckelord:** Förgasning integrerad med gaskombikraftverk, koldioxidavskiljning, chemical looping, carbonate looping, syntesgasförbränning, förgasning, vatten-gas skiftreaktion, vätgasproduktion, fluidiserad bädd

Analyse systémique des procédés de boucle chimique et cycle calcique dans les centrales CCGI pour le captage du $CO_2$

Travail de Fin d'Etudes (TFE) en Génie Énergétique
TUONG-VAN NGUYEN
Centre de Recherche d'Albi en Génie des Procédés des Solides Divisés, de l'Énergie et de l'Environnement (RAPSODEE)
Groupe Énergétique et Environnement
École des Mines d'Albi-Carmaux

# Résumé

Le captage du $CO_2$ consiste à capturer le dioxyde de carbone produit, entre autres, dans les centrales énergétiques, afin d'éviter son rejet dans l'atmosphère. Les voies les plus répandues sont néanmoins coûteuses et gourmandes en énergie. Certaines techniques, comme les boucles chimiques et les cycles calciques, présentent, en théorie, de plus faibles pénalités énergétiques. Cette thèse consiste en une étude de faisabilité de ces procédés dans les centrales à cycle combiné et gazéification intégrée.

Le système de combustion en boucle chimique peut remplacer la chambre de combustion des turbines à gaz. Le rendement de capture du $CO_2$ s'élève alors à près de 100% et l'efficacité électrique du cycle combiné décroît de 5 points comparé à un cycle combiné conventionnel. La température du réacteur d'oxidation et le rapport de pression des turbines à gaz ont une forte influence sur ces résultats et doivent être optimisés en conséquence. Plusieurs configurations possibles du cycle combiné ont été testées et toutes permettent d'atteindre un rendement de capture du $CO_2$ proche de 100%.

Le système de gazéification en boucle chimique ne permet pas de séparer le dioxide de carbone du reste des fumées. Il évite en revanche le recours à une installation de séparation d'air et réduit donc la consommation d'énergie associée à la production du gaz de synthèse. Le choix de l'oxyde métallique, le rapport oxygène-carburant et la quantité de solides circulant entre les deux réacteurs sont des paramètres critiques à prendre en compte lors de la conception du système.

L'alternance des réactions de carbonatation et calcination, ou cycle calcique, permet de capturer le dioxyde de carbone dans les courants de gaz brûlés en déplaçant l'équilibre chimique de la réaction de gaz à l'eau dans le sens de la génération d'hydrogène. Le rendement de capture du $CO_2$ peut atteindre 93% pour une pureté de 97 %.

Les études et simulations réalisées montrent que les procédés de boucle chimique et cycle calcique ont un fort potentiel pour piéger efficacement le dioxyde de carbone tout en ayant un faible impact sur l'efficacité énergétique des centrales CCGI. Cependant, au vu des recherches actuellement menées, la technique de combustion en boucle chimique semble la plus adaptée à un développement à échelle industrielle.

**Mots-clés:** Cycle Combiné à Gazéification Intégrée (CCGI), capture du $CO_2$, boucle chimique, cycle calcique, combustion de gaz de synthèse, gazéification, réaction du gaz à l'eau, production d'hydrogène, lit fluidisé

# Preface

This manuscript presents the results of my research project for obtaining the Master's degree in Sustainable Energy Systems at Chalmers University of Technology (Göteborg, Sweden) and the Engineer's degree at École des Mines (Albi-Carmaux, France). This Master's Thesis was performed from November 2010 to April 2011 at the Institut für Energie- und Klimaforschung - Brennstoffzellen (IEK-3) at the Forschungszentrum Jülich - Helmholtz-Gemeinschaft with Dipl.-Ing Sebastian Schiebahn as supervisor. The centre leads researches on energy systems and this work focuses on the integration of novel processes into IGCC power plants for carbon capture and storage.

The report describes the methods used at a level of details high enough to make possible to reconduct the several analyses. The structure is both thematic and chronological: the first parts correspond to the literature study carried on at the beginning of the project, the second ones to the numerical simulations built in the middle and the third ones to the conclusions drawn during the last months. However, the plan is articulated around the two major processes evaluated: chemical and carbonate looping. It is thus possible to read almost independently each part and to focus exclusively on the concluding sub-chapters.

The edition of this manuscript is actually the second one, as submitted at Chalmers University of Technology in October 2011 and is slightly different from the one available at the Forschungszentrum Jülich. It takes into account the feedbacks obtained from every person involved in the development process of this report and addresses several issues that were neglected during the redaction of the first version. The structure and content of some chapters have been improved, some basic corrections have been provided and more information has been covered.

Aachen, October 2011,

Tuong-Van Nguyen.

# Acknowledgements

It would not have been possible to achieve this Master's Thesis without the time and help of all the kind people involved in my graduate studies, to, unfortunately, only some of whom it is possible to give particular mention here. The responsibility for any oversights is entirely my own and I apologize in advance that I could not mention all of them one by one.

First of all, I would like to express my gratitude to my supervisor at the Forschungszentrum Jülich, Sebastian Schiebahn, who gave me the opportunity to work with this exciting topic and followed my progresses with great interest. His advice has been invaluable on both a professional and personal level: I believe that I have strongly benefited of his involvement in my work and of his experience as a process engineer and as a researcher. I consider myself as fortunate to have him as a supervisor who let me proceed in my own way and gave me assistance when needed.

My gratefulness also goes to David Pallarès, my supervisor at Chalmers University of Technology, for his availability and guidance since the beginning of my Master's studies in 2009. Although it was not so easy to work on a distance, the several discussions we had contributed to the improvement of this work and continue to inspire me for my career prospective.

It was particularly appreciable to get valuable insights from my examiner Anders Lyngfelt as well. Aside from his critics to make my work better, the publications of his research group represent a non-negligible part of my literature study on chemical looping.

I have learnt a great deal from my former classmates who studied with me over these last two years. Among them, my two opponents, Diane and Nicolas, who were the first readers of the several report drafts, made precious and thoughtful comments that helped me to revise this work. Besides this task of reviewing, Nicolas provided me great help with the LaTeX edition of this manuscript and I feel very much indebted to him.

This thesis would not have been possible without the financial and technical support of the Forschungszentrum Jülich and its staff: the library and computer facilities were essential to carry out this work towards its successful realization.

These first thanks were dedicated to those who directly assisted me in the preparation and development of this Master's Thesis, but my time spent in Germany would not have been as nice and productive without the efforts made by my office mates in promoting a welcoming and friendly environment. In this regard, I have the chance to personally acknowledge those who supported me at the Institut für Energie- und Klimaforschung and who are mentioned as follows.

Two other students were working on their diploma thesis during my whole stay at the research centre and I had the pleasure to get to know them. I address therefore a particular word of thanks to Thomas for being such an open-minded co-worker who took

care of all of us. As the saying goes, coffee makes the world go round, and the numerous and refreshing coffee breaks he organized helped me to get the most out of myself. A special thought to Hassan too, who started and finished his work exactly at the same times and under the supervision of Sebastian as well. It was really enjoyable to work together and to have several constructive discussions in and out of the Forschungszentrum.

Though they had only joined us a couple of months later, they definitely left their mark on the ambience at the institute. It would most probably not have been as funny without the presence of the witty Henning who tried to convert all of us to the religion of tea and without the warm-hearted Freddy who tried to teach me German and teased me a bit too often, with unfortunately better success. I remember their encouragements and I am really thankful for the fact that there were persons like Carsten and them who cheered me up at hard times, when, for instance, I was looking for a PhD position.

A simple paragraph fails to express my big and sincere gratitude to Daniel, for his friendship, his presence and moral support during my studies in Göteborg and my Master's Thesis in Aachen. I feel extremely lucky in having a friend like him whose kindness and confidence in me definitely helped me to make good personal and career choices.

Finally, I have the honour to conclude by a special acknowledgement to my family. They raised me with love and took several times a load off my shoulders. I cannot be grateful enough for their encouragements and support during my peregrinations in Europe these last six years.

# Contents

# List of Figures

# List of Tables

# Nomenclature

### Abbreviations upper case

| | |
|---|---|
| ASPEN | Advanced system for process engineering |
| ASU | Air separation unit |
| CC | Combined cycle |
| CCR | Carbon capture rate |
| CCS | Carbon capture and storage |
| CLAS | Chemical looping air separation |
| CLC | Chemical looping combustion |
| CLG | Chemical looping gasification |
| CLH | Chemical looping hydrogen |
| CLOU | Chemical looping oxygen uncoupling |
| CSR | Continuously stirred reactor |
| EBSILON | Energy balance and simulation of the load response of power generating or process controlling network structures |
| GT | Gas turbine |
| HeatX | Heat exchanger |
| HRSG | Heat recovery steam generator |
| IGCC | Integrated gasification combined cycle |
| MEA | Monoethanolamine |
| NGCC | Natural gas-fired combined cycle |
| PSA | Pressure swing adsorption |
| PFR | Plug flow reactor |
| RGIBBS | Gibbs reactor |
| TIT | Turbine inlet temperature |
| Syngas | Synthesis gas |

### Abbreviations lower case

| | |
|---|---|
| ar | As received |
| atm | Atmosphere |
| maf | Moisture- and ash-free |
| ppb | Parts-per-billion |
| ppm | Parts-per-million |
| vppm | Volumetric parts-per-million |
| wt | Weight |

## Indices

| | |
|---|---|
| air | Air |
| ar | Air reactor |
| coal | Coal |
| da | Depleted-air |
| e | Electric |
| exh | Exhaust gases |
| ext | External |
| fg | Flue gases |
| fr | Fuel reactor |
| fuel | Fuel |
| g | Gaseous |
| in | Inlet |
| is | Isentropic |
| losses | Heat losses |
| mec | Mechanical |
| out | Outlet |
| ox | Oxidised state |
| pol | Polytropic |
| react | Reaction |
| red | Reduced state |
| s | Solid |
| sr | Steam reactor |
| stm | Steam |
| syn | Synthesis gas |
| th | Thermal |

## Chemical compounds

| | |
|---|---|
| $ABO_3$ | Perovskite-structured materials |
| $Al_2O_3$ | Aluminium(III) oxide - Alumina |
| Ar | Argon |
| C | Carbon - Char |
| $C_nH_m$ | Hydrocarbon |
| $Ca(OH)_2$ | Calcium hydroxide |
| $CaC_2$ | Calcium carbide |
| $CaCO_3$ | Calcium carbonate |
| CaO | Calcium oxide - Quicklime |
| CaS | Calcium sulphide |
| $CaSO_4$ | Calcium sulphate - Gypsum |
| $CaTiO_3$ | Calcium titanium oxide |
| $CH_4$ | Methane |
| CO | Carbon monoxide |
| $Cl_2$ | Chlorine |
| $CO_2$ | Carbon dioxide |

| | |
|---|---|
| $COS$ | Carbonyl sulphide |
| $Co$ | Cobalt |
| $CoO$ | Cobalt(II) oxide |
| $Cu$ | Copper |
| $CuO$ | Copper(II) oxide - Cupric oxide |
| $Fe$ | Iron |
| $Fe_3C$ | Iron carbide |
| $Fe_2O_3$ | Iron(III) oxide - Hematite |
| $Fe_3O_4$ | Iron(II, III) oxide - Magnetite |
| $FeCO_3$ | Iron carbonate |
| $FeO$ | Iron(II) oxide - Wüstite |
| $FeS$ | Iron sulphide |
| $FeTiO_3$ | Ilmenite |
| $H_2$ | Hydrogen |
| $H_2O$ | Water |
| $H_2S$ | Hydrogen sulphide |
| $HCl$ | Hydrogen chloride |
| $HCN$ | Hydrogen cyanide |
| $HCOOH$ | Formic acid |
| $Hg$ | Mercury |
| $Li_2CO_3$ | Lithium carbonate |
| $Li_2O$ | Lithium oxide |
| $Me_xCO_3$ | Metal carbonate |
| $Me_xO_y$ | Metal oxide (oxidised state) |
| $Me_xO_{y-1}$ | Metal oxide (reduced state) |
| $Me_x(OH)_2$ | Metal hydrate |
| $MgCO_3$ | Magnesium carbonate |
| $MgO$ | Magnesium oxide |
| $Mn$ | Manganese |
| $Mn_2O_3$ | Manganese(III) oxide |
| $Mn_3C$ | Manganese carbide |
| $Mn_2O_4$ | Manganese(II, III) oxide - Hausmannite |
| $MnCO_3$ | Manganese(II) carbonate |
| $MnO$ | Manganese(II) oxide |
| $MnS$ | Manganese(II) sulphide |
| $MnS_2$ | Manganese(IV) sulphide |
| $MnSO_4$ | Manganese(II) sulphate |
| $N_2$ | Nitrogen |
| $N_2O$ | Nitrous oxide |
| $N_2O_3$ | Nitrogen trioxide |
| $N_2O_4$ | Nitrogen tetra-oxide |
| $NH_3$ | Ammonia |
| $NH_4Cl$ | Ammonium chloride |
| $Ni$ | Nickel |
| $NiAl_2O_4$ | Nickel alumina tetra-oxide |
| $Ni_3C$ | Nickel carbide |

| | |
|---|---|
| $Ni_3S_2$ | Tri-nickel disulphide |
| $NiO$ | Nickel(II) oxide |
| $NiS$ | Nickel sulphide |
| $NiS_2$ | Nickel disulphide |
| $NO$ | Nitric oxide |
| $NiSO_4$ | Nickel sulphate |
| $NO_2$ | Nitrogen dioxide |
| $O_2$ | Oxygen |
| $PbCO_3$ | Lead carbonate |
| $PbO$ | Lead oxide |
| $SO_2$ | Sulphur dioxide |
| $SO_3$ | Sulphur trioxide |
| $Sr$ | Strontium |
| $SrCO_3$ | Strontium carbonate |
| $ZnCO_3$ | Zinc carbonate - Smithsonite |
| $ZnO$ | Zinc oxide |
| $ZrO_2$ | Zirconium oxide |

### Greek upper case letters

| | | |
|---|---|---|
| $\Delta_r\mathrm{H}$ | Reaction enthalpy | [kJ/mol] |
| $\Delta\mathrm{P}$ | Pressure drop | [bar] |
| $\Delta\mathrm{T}$ | Temperature difference | [°C, K] |

### Greek lower case letters

| | |
|---|---|
| $\eta$ | Efficiency |
| $\gamma$ | Gas yield |

### Latin upper case letters

| | | |
|---|---|---|
| $\mathrm{H}$ | Enthalpy | [MJ] |
| $\dot{\mathrm{H}}$ | Enthalpy rate | [MW] |
| $\mathrm{M}$ | Molar mass | [kg/mol] |
| $\mathrm{P}$ | Pressure | [bar] |
| $\mathrm{Q}$ | Heat | [MJ] |
| $\dot{\mathrm{Q}}$ | Heat rate | [MW] |
| $\mathrm{R}_o$ | Oxygen-carrying capacity | |
| $\mathrm{T}$ | Temperature | [°C, K] |
| $\mathrm{W}$ | Work | [MJ] |
| $\dot{\mathrm{W}}$ | Work rate | [MW] |

### Latin lower case letters

|  |  |  |
|---|---|---|
| $\dot{m}$ | Mass flow rate | [kg/s] |
| $\dot{n}$ | Molar flow rate | [kmol/s] |

# Chapter 1

# Introduction

## 1.1 Motivation

$CO_2$-capture by the conventional separation technologies is an energy-intensive step and results thus in a reduction in the overall energy efficiency of the power generation process. Novel power plant concepts and alternative technologies give the chance to decrease these efficiency penalties and to make the capture of carbon dioxide commercially and technically more attractive. Chemical and carbonate looping belong to this new class of processes of which the interest has grown these last years because of their expected lower energy penalties and their high $CO_2$-capture efficiencies. In parallel, the interest for integrated gasification combined cycles has risen since this type of power plants combines well-known technologies and offers possible applications for both chemical and carbonate looping. It is therefore of strong interest to investigate the possibility of integrating solid looping processes in an IGCC power plant to reach high-energy and $CO_2$-capture efficiencies to face the global warming challenge.

## 1.2 Aim and scope

The objective of this thesis is to estimate the potential for $CO_2$-mitigation of chemical and carbonate looping processes in Integrated Gasification Combined Cycle (IGCC) power plants. The reference power plant considered here is a $CO_2$-capture ready IGCC based on water-gas shift reactor technology. This work is structured around two main goals. The first goal is to provide to the reader a deep understanding of the chemical and carbonate looping processes, their technical achievements and their state of the art. The second goal is to investigate the most promising concepts when these processes are implemented in an IGCC power plant in terms of energy and $CO_2$-capture efficiencies.

## 1.3 Methodology

The work in this thesis mainly consisted of two different phases: first, a familiarisation with the concepts of chemical and carbonate looping by literature research, then, a modelling and simulation of the most promising processes with the software ASPEN Plus and EBSILON Professional.

## 1.4 Delimitations

This master's thesis deals exclusively with static modelling of solid looping cycles in IGCC power plants where combustion and gasification phenomena take place. A process-scale approach is used to model the different systems involved: the insights of the reactors are not investigated and the kinetics of the reactions occurring are not taken into account. The full IGCC power plant is not modelled and only the gasification and combined cycle steps are considered.

## 1.5 Thesis outline

This thesis consists of 10 chapters from the general background of this work to the outcomes and recommendations. A short description of each follows:

- The introductory Chapter 1 draws a global picture of this project and presents the overall methodology. The following Chapter 2 depicts the energy and environmental issues nowadays and gives a brief overview of the current $CO_2$-capture techniques.
- Chapters 3 and 4 respectively describe the chemical and carbonate processes with a strong focus on the materials used, the reactors design, the process integration and the challenges to face in the near future.
- Chapter 5 presents the possible designs of IGCC power plants with solid looping processes, their advantages and their drawbacks. Chapter 6 introduces the modelling basis in ASPEN Plus and EBSILON Professional for the simulations of the most promising power plant concepts.
- Chapter 7 assesses the first design evaluated: an IGCC power plant with synthesis gas chemical-looping combustion and inherent $CO_2$-capture. Chapter 8 concerns another category of IGCC with the implementation of solid looping in situ for production of synthesis gas and possible capture of carbon dioxide. Chapter 9 deals with the implementation of carbonate looping in the water-gas shift reactor for removal of carbon dioxide whereas the processes evaluated in these two last chapters present the integration of chemical looping processes.
- Finally, this report ends up with Chapter 10 that contains a summary and a discussion of the different processes evaluated and gives some ideas for future work.

# Chapter 2

# Sustainable energy futures

## 2.1 Energy outlook

Energy has become a key in the development of our modern society. A sufficient, cheap and clean energy supply is essential to meet the human needs and to drive towards a sustainable and prosper society. With the significant increase of the world population, expected to reach the 10 billion by the end of the $21^{st}$ century, and the strong economic growth of developing countries in Asia and in Africa, the total world energy demand is projected to increase by 49% from 2007 to 2035. Nowadays, more than 80% of the primary energy supply comes from fossil fuels such as coal, natural gas and oil and this dependency of energy and electricity generation on these fuels will probably continue within the next decades [1]:

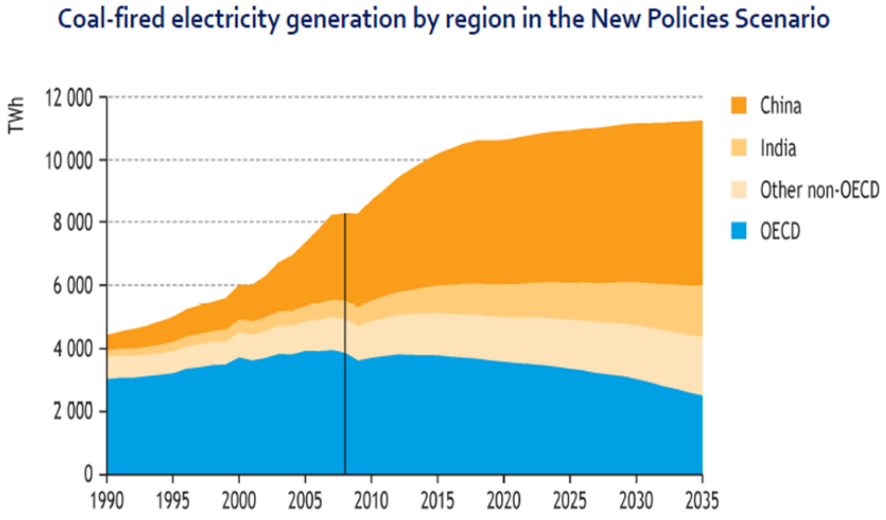

Figure 2.1: Probable scenario for electricity generation from coal [1]

However, these resources are relatively limited and their conversion to useful forms of energy like heat and electricity is responsible for large emissions of greenhouse gases with mainly carbon dioxide $CO_2$. Other factors including deforestation and land use have also contributed to this increase of the greenhouse gases emissions but to a lower extent [2].

## 2.2 $CO_2$ emissions and mitigation strategies

Since the early beginning of the $20^{th}$ century with the industrial age to the current decade, the $CO_2$ level in the atmosphere has increased from around 300 ppm to 385 ppm and the global average temperature of about 0.74°C [3]. At present, there is a global scientific consensus that these rises are strongly correlated. Human activities have leaded to dangerous interferences with the climate and global warming has become the most infamous one [2]. Our current energy system is based on an extensive use of coal, oil and gas that are $CO_2$-emitting and finite energy resources and there is so a need for a long-term energy strategy that answers to the following challenges [2]:

- Climate challenge: how is it possible to reduce the environmental impact of energy production and use?
- Resource challenge: how is it possible to build an energy system that does not depend on finite energy resources on the long term?
- Development challenge: how is it possible to supply enough energy to ensure to everybody satisfying standards of living?

Most of the scientific community claims that emitting greenhouse gases to the atmosphere has a positive feedback effect on the mean global temperature. Consequently, solutions to control and cut the anthropogenic emissions of greenhouse gases worldwide need to be found. A reasonable way to reach this goal is to lower the atmospheric emissions of carbon dioxide. Several approaches are possible and the most logical one is to decrease sharply the global energy consumption per capita by changing our habits.

However, it is unlikely to become a long-term solution to answer to the greenhouse gases emission problem for the following reasons. On the one hand, people living in the developed countries want to preserve their current lifestyles that are quite energy-intensive. On the other hand, people living in developing countries need to use the cheapest and available resources like coal to develop their industries and to reach higher standards of living [4]. The most reasonable ways to mitigate the $CO_2$ emissions are so to [5]:

- Decrease the energy intensity of human activities
- Substitute high $CO_2$-emitting energy resources for low ones
- Capture and store the $CO_2$ produced in the power and process sectors

Decreasing the energy consumption for the same quality of service can be achieved by, for instance [5]:

- Increasing the energy efficiency of power generation processes to minimize the fuel consumption
- Reducing the energy requirements of buildings while keeping the same quality of indoor climate

- Improving the industrial processes (for example cement industry) to lower their energy expenditures

Replacing high $CO_2$-emitting energy resources by low ones can be accomplished by, for example [5]:

- Using natural gas instead of coal which has a lower carbon-to-hydrogen ratio and emits less carbon dioxide per unit of primary energy
- Shifting from fossil fuels to nuclear or renewable energies such as wind, hydro, solar, biomass, etc., which do not emit $CO_2$ while they are used

Finally, a solution that can be considered is to capture directly the carbon dioxide from power plants and process industries and to store it into geological formations, aquifers, oceans, etc [5; 6]. Regional aspects such as technical feasibility (geological storage) and public acceptance have to be taken into account [7]. Environmental policy instruments and political incentives are often needed in local, regional and worldwide scale to encourage investments from privates and industries in these relatively new technologies. It is possible to split climate policies into two different types [8; 9]:

- Rigorous policies such as prices on $CO_2$ emissions (carbon taxes) or efficiency levels to reach (efficiency standards) or technology supports (subsidies)
- Soft policies such as agenda and information buildings (information meetings, climate summits and protocols, etc.)

## 2.3 Carbon capture strategies

There are three main strategies to capture carbon dioxide from power plants [10; 11]:

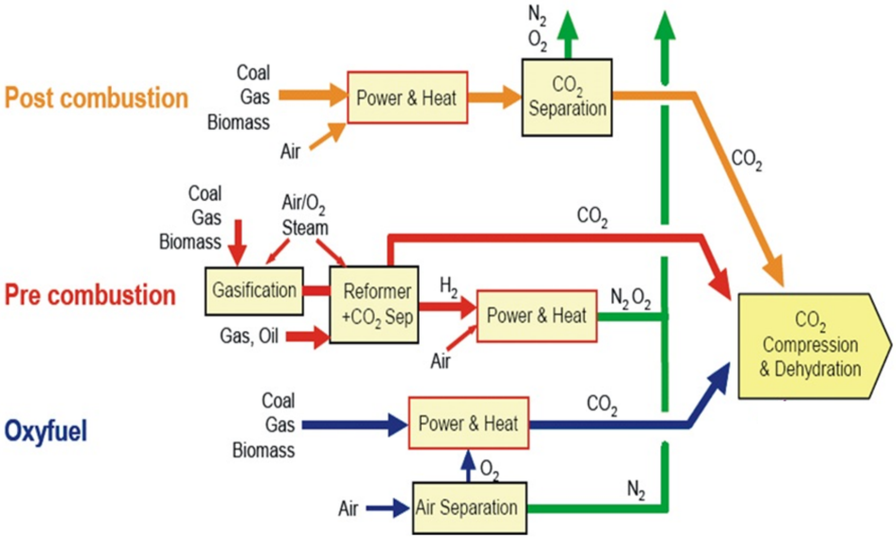

Figure 2.2: Carbon capture routes [12]

### 2.3.1 Pre-combustion

Pre-combustion capture involves removal of the carbon dioxide prior to the combustion step [11; 13; 14]. The primary fuel is converted into a synthesis gas with mainly carbon monoxide and hydrogen via gasification and these four main reaction routes [15]:

- Partial oxidation: Heavy hydrocarbons (including coal) are partially combusted with pure oxygen in sub-stoichiometric conditions.

  $$\mathrm{C}_n\mathrm{H}_m + \frac{n}{2}\mathrm{O}_2 \longrightarrow \mathrm{nCO} + \frac{m}{2}\mathrm{H}_2 \tag{2.1}$$

  This reaction is exothermic, which implies the generation of heat. The requirement of pure oxygen involves air separation prior to the partial oxidation step, usually by cryogenic distillation.

- Steam reforming: Light hydrocarbons react with steam in strong fuel-lean conditions.

  $$\mathrm{C}_n\mathrm{H}_m + \mathrm{nH}_2\mathrm{O} \longrightarrow \mathrm{nCO} + (\mathrm{n} + \frac{m}{2})\mathrm{H}_2 \tag{2.2}$$

  This reaction is endothermic, which implies the need for heat supply, by, for instance, burning a part of the primary fuel.

- Auto-thermal reforming can be considered as a combination of the both reactions presented above. The heat needed to sustain the steam reforming reaction is provided by the partial oxidation one.

- Cracking - Methanation: Heavy hydrocarbons are decomposed into light ones and later into hydrogen and carbon:

  $$\mathrm{CH}_4 \longrightarrow \mathrm{C} + 2\,\mathrm{H}_2 \tag{2.3}$$

  $$\Delta_r\mathrm{H} = 75\ \frac{MJ}{kmol}$$

  The synthesis gas is then cooled down, cleaned and sent to a water-gas shift reactor where carbon monoxide reacts with steam, yielding carbon dioxide and hydrogen:

  $$\mathrm{CO} + \mathrm{H}_2\mathrm{O} \longrightarrow \mathrm{CO}_2 + \mathrm{H}_2 \tag{2.4}$$

  $$\Delta_r\mathrm{H} = \text{-}41\ \frac{MJ}{kmol}$$

Finally, the carbon dioxide is removed by physical or chemical absorption processes [11], leading to a $H_2$-rich fuel gas that is thereby fuelled in a combined cycle. The high partial pressure of carbon dioxide in the synthesis gas compared to the flue gases in post-combustion capture processes makes the separation process less energy intensive.

A major advantage of pre-combustion capture processes is their maturity: they have been proven and used in an industrial scale like in IGCC-CCS power plants [16]. Another advantage is the generation of hydrogen for gas turbines or fuel cells [17]. However, a major drawback is the requirement of a water-gas shift reactor, responsible for high auxiliary steam consumption and thus high-energy penalty.

### 2.3.2 Oxy-fuel combustion

Oxy-fuel combustion is a novel technique that consists of burning the fuel in pure oxygen in nearly stoichiometric conditions instead of air as in conventional power plants. The oxygen comes from an air separation unit and leads to the production of fuel gases mainly composed of carbon dioxide and steam. It becomes then possible to get a high $CO_2$-purity gas stream by cooling down the flue gases under the condensation temperature of the water [10; 12; 18].

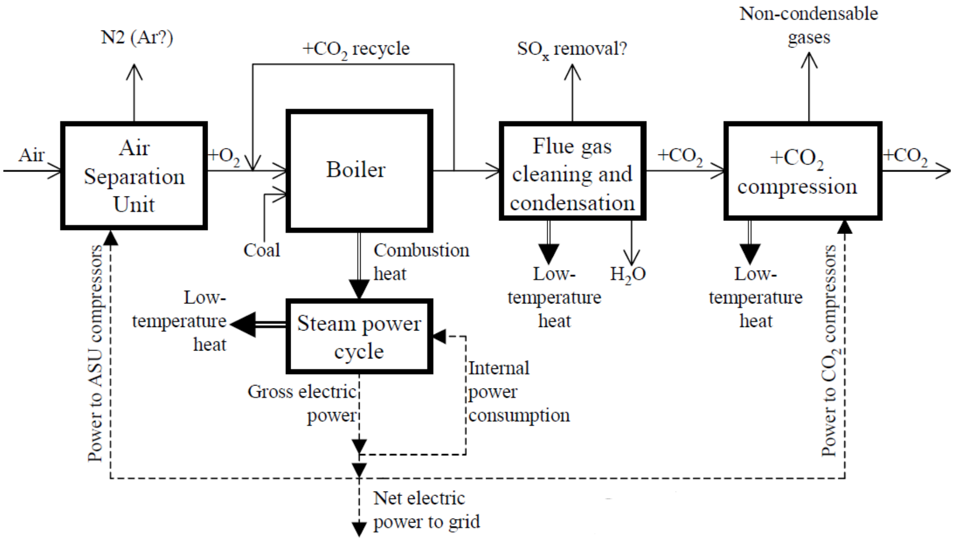

Figure 2.3: Oxy-fuel power plant flowchart [12]

Operating a combustion reactor with only pure oxygen in stoichiometric conditions would lead to rather high flame temperatures and high radiative heat transfer that commonly used materials cannot endure. There are at present two main ways to control the process temperature, either by steam injection, or by recirculation of the flue gases [19]. Oxy-fuel combustion has appeared as a promising direction for new power plants based on combustion of solid and gaseous fuels and presents several benefits [12; 18].

Regarding the pollutants' issues, oxy-fuel power plants have the potential to reach a 100% efficiency of capture of $CO_2$ ready for sequestration. Moreover, the production of nitrous oxides is greatly diminished because the only nitrogen present in the process comes from the fuel and the temperature levels in the combustion chamber are rigorously controlled. From a design perspective, oxy-fuel power plants need lower area and space than conventional power plants because the masses and volumes of the flue gases and of the other flows to handle are much smaller [12; 18].

Finally, oxy-fuel processes are based on relatively conventional technologies and there are ongoing studies on potential retrofit. Besides that, oxy-fuel power plants have been commercially demonstrated through few of them has been operated so far [12]. Oxy-fuel combustion plants present the same disadvantage as IGCC systems. The major issue with oxy-fuel plants is the need for an oxygen supplier in front of the overall process, i.e. a cryogenic air separation unit.

### 2.3.3 Post-combustion

Post-combustion capture is a technique for removing carbon dioxide from the flue gases after having burnt the fuel. Several technologies to achieve this goal have been developed and some are similar to the techniques employed as pre-combustion capture processes (such as absorption and adsorption ones):

- Chemical absorption-based techniques [20]: carbon dioxide is selectively absorbed in an aqueous amine-based solution with for instance monoethanolamine (MEA). MEA reacts with carbon dioxide in a low-temperature absorber, giving an unstable acid-base complex, which decomposes later in a high-temperature regenerator. This technique requires high-energy consumption to bring heat to the regenerator and high solvent flow rates to reach a high $CO_2$-capture efficiency and is well suited for low-pressure applications.

- Physical absorption-based techniques [21]: at the difference of the first technique presented above, there is no reaction between the solvent such as methanol or carbonates and the carbon dioxide. The absorption of $CO_2$ is driven by the solubility differences between the two chemical species and is mostly limited by the vapour-liquid equilibrium of the mixture. This technique is preferable to the chemical absorption based one when flue gases have a high $CO_2$ content, i.e. a molar concentration above 35% and for high-pressure applications.

- Adsorption-based techniques: materials such as zeolites or active carbon, which have strong adsorption affinities with carbon dioxide, attract and attach carbon dioxide from the flue gas stream. An example of this kind of technique is pressure-swing adsorption.

- Membrane contactors-based techniques: the flue gases circulate through a microporous membrane whereas the solvent circulates outside it: the contact between both phases is so indirect and only carbon dioxide, in theory, diffuses through the membrane from the flue gases to the aqueous solution. The main issues are that the membranes may be polluted by impurities present in the flue gas stream and that this technique has not been proven yet in a large scale.

- Solid looping techniques [22]: chemical specie in its solid phase such as limestone reacts with carbon dioxide in the flue gases, producing carbonates that are thereby regenerated into oxides in an auxiliary reactor. This technique is similar, in principle, to the chemical absorption-based techniques.

- Chemical looping combustion: this technique is sometimes considered as a post-combustion process because of its inherent carbon separation feature.

The absorption techniques have been widely demonstrated and are already used in thermal power plants and in process industries. Some are currently in a state of development and researches are led to improve their heat integration and the sorbent recovery [20]. A strong advantage of this category of techniques is its suitability for retrofit of existing power plants though the energy penalty and running costs of amine scrubbing processes are higher than pre-combustion and oxy-fuel combustion [23].

### 2.3.4 Alternative concepts (solid looping cycles)

Solid looping cycles are a new approach to the capture of carbon dioxide in the conventional combustion and gasification processes. Chemical looping refers to $O_2$-looping: a metal carrier captures oxygen from air or steam and releases it to oxidise a fuel, avoiding direct contact and mixing of the reactants. On the opposite, carbonate looping, also known as $CO_2$-looping, uses a sorbent that captures carbon dioxide by carbonation in flue gases and releases it by calcination in a separate reactor [22; 24; 25].

This thesis will exclusively focus on chemical and carbonate looping processes since they are the most relevant in the context of carbon capture and storage. Iodine, sulphur, brome, zinc, hydroxide peroxide and other types are not considered here.

The interest for chemical and carbonate looping in the context of carbon capture and storage is relatively recent. The possible applications of solid looping cycles in power plants are multiple, though none of them has been demonstrated in an industrial scale yet. Some examples of these applications are:

- Chemical looping combustion: a combustion technique with inherent separation of carbon dioxide from nitrogen and other chemicals [26]
- Chemical looping reforming/gasification: a reforming technique with inherent generation of synthesis gas without the need of an air separation unit [27]
- Carbonate looping as a pre-combustion technique to replace the chemical absorption processes such as SELEXOL to capture carbon dioxide [22; 24; 25]

# Chapter 3

# Chemical looping processes

## 3.1 Chemical looping principle and reactions

### 3.1.1 General principle

Chemical looping is a process in which a solid, usually a metal, carries oxygen from air or steam to a fuel gas and converts it, avoiding a direct contact between the both reactants. This oxygen carrier is usually bound with an inert material that does not participate to the reactions. The conversion of the fuel is driven by two intermediary reactions [27; 28]:

- Metal oxidation and air depletion in an air reactor, also called oxidation reactor
- Metal oxide reduction and fuel oxidation in a fuel reactor, also called reduction reactor

Figure 3.1 illustrates the principle of chemical looping:

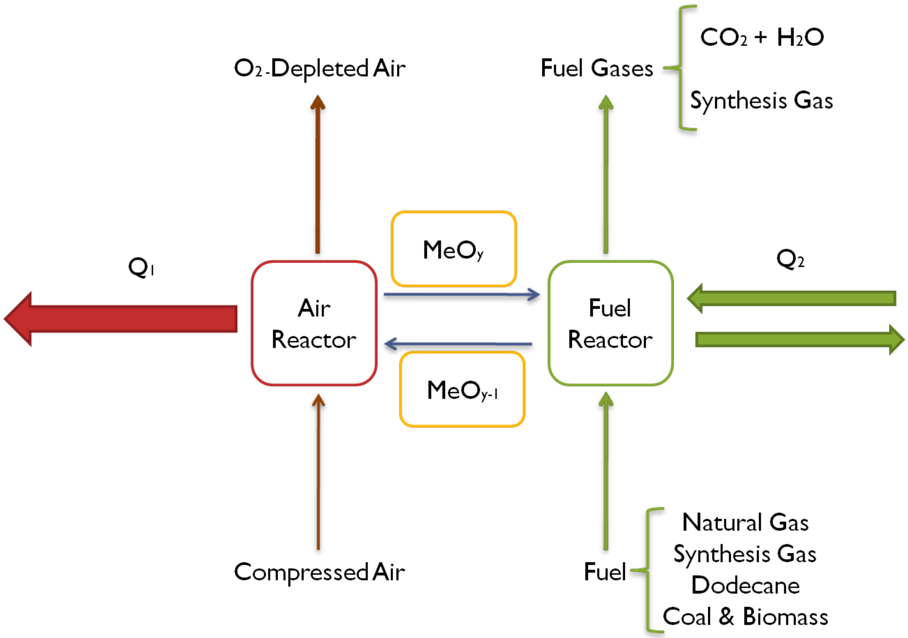

Figure 3.1: Chemical looping principle

Whereas the oxidation reaction occurring in the air reactor is usually exothermic and fast, the reduction reaction of the metal oxide in the fuel reactor can be either endothermic or exothermic depending on the oxygen carrier and fuel processed and is slower than the oxidation reaction. The total amount of heat generated or absorbed in the chemical looping process is though always the same as in a normal system where the reactants are directly mixed together [27].

The fact that the reactants do not directly interact have raised two main interests for the chemical looping technologies. On the one hand, the chemical exergy destruction in the overall reaction is lower than in the base case [29]. On the other hand, nitrogen is not mixed with the fuel, making possible to sequestrate carbon dioxide more easily [30]. Though the general feature of chemical looping is the splitting of one reaction in at least two sub-reactions, there are different types of chemical looping depending on the applications considered [31].

Most of the researches have been performed on chemical looping combustion. This technique presents the advantage that carbon dioxide is not mixed with nitrogen from air but with steam only. Chemical-looping combustion is therefore a combustion technique with inherent separation of carbon dioxide [30].

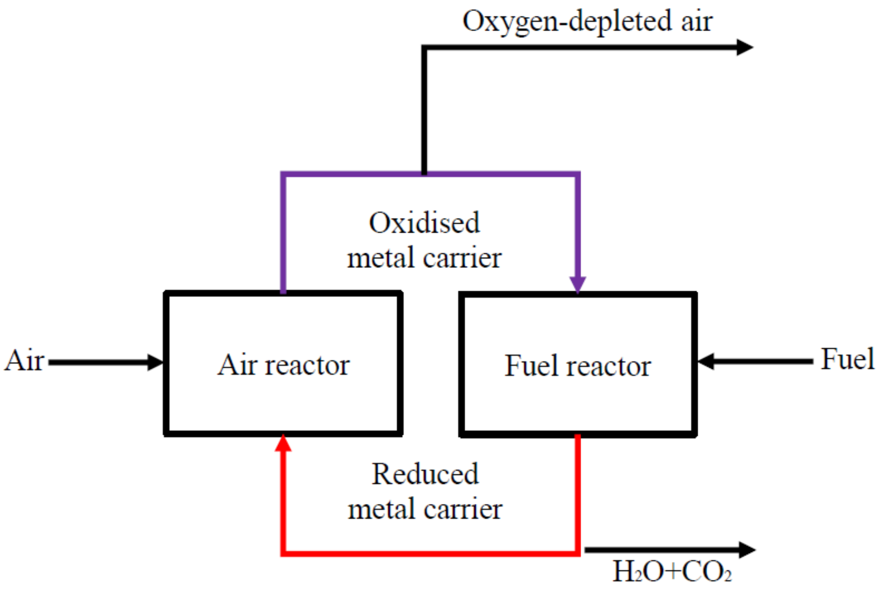

Figure 3.2: Chemical looping combustion (adapted from [32])

The work done so far in this field can be divided in three main parts:

- Development of chemical-looping materials
- Investigation of the possible reactor designs and pilot studies
- Study of cycle performances and applications in industrial scale

The different chemical looping reactions relevant to this thesis are presented in the following chapters.

### 3.1.2 Chemical looping combustion of gaseous fuels

Two main types of gaseous fuels have been investigated in chemical looping combustion: natural gas, which contains mostly methane and hydrocarbons [33], and synthesis gas, which contains mostly carbon monoxide and hydrogen. Most of the researches have been carried out on the first fuel but since this thesis deals with the integration of chemical looping in IGCC power plants, the examples presented as follows consider synthesis gas. The general global reaction for complete combustion of synthesis gas in air is the following [34; 35]:

$$\begin{aligned} CO + \frac{1}{2}O_2 &\longrightarrow CO_2 \\ H_2 + \frac{1}{2}O_2 &\longrightarrow H_2O \end{aligned} \tag{3.1}$$

A classic chemical looping combustion system is composed of two reactors with reactions occurring continuously [30; 32], as illustrated with Figure 3.3:

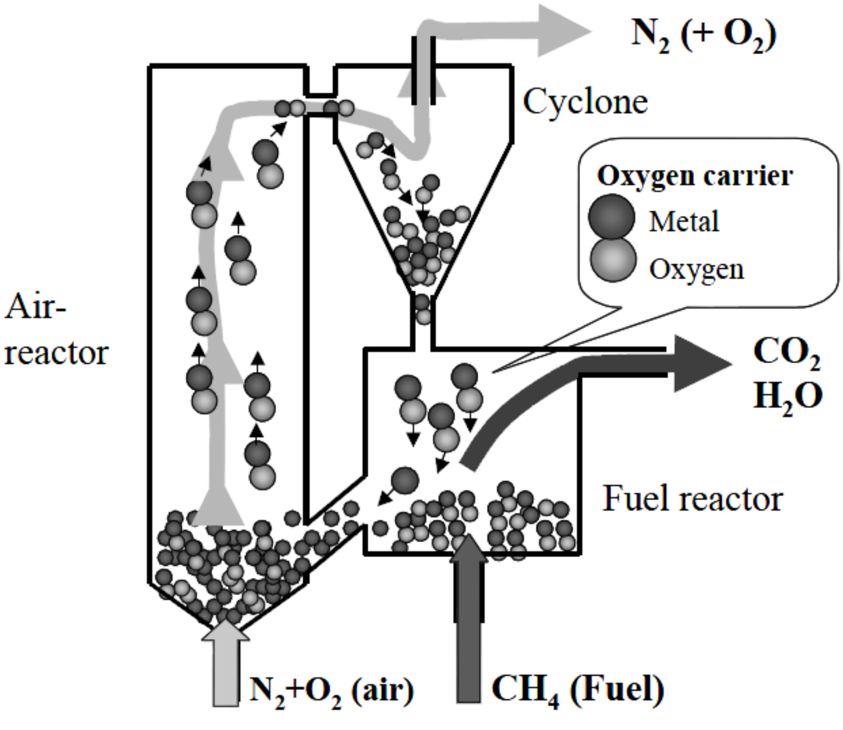

Figure 3.3: Chemical looping combustion applied to natural gas [36]

The system is based on the two following reactors:

- An air reactor in which the metal is oxidised by air, yielding metal oxides and oxygen-depleted air

- A fuel reactor in which the metal oxide is reduced and the synthesis gas oxidized, yielding metal particles, carbon dioxide and hydrogen

In the reduction reactor, carbon monoxide and hydrogen reacts with metal oxide, yielding carbon dioxide and water:

$$\begin{aligned} CO + Me_xO_y &\longrightarrow CO_2 + Me_xO_{y-1} \\ H_2 + Me_xO_y &\longrightarrow H_2O + Me_xO_{y-1} \end{aligned} \tag{3.2}$$

The outlet stream from the fuel reactor is composed of a solid phase containing reduced metal oxide and of a gaseous phase containing carbon dioxide and steam. In real combustion conditions, the solid phase contains reduced and unconverted metal oxides and the gaseous phase contains to some extent unburned hydrocarbons such as methane and other chemical species such as hydrogen, sulphur and nitrous oxides, etc. The solid phase stream circulates thereby into the air reactor where it reacts with air, usually in fuel-lean conditions, following this reaction:

$$Me_xO_{y-1} + \frac{1}{2}O_2 \longrightarrow Me_xO_y \tag{3.3}$$

The outlet stream from the air reactor is composed of solid phase containing metal oxide and of gaseous phase containing nitrogen and traces of oxygen. The mechanisms involved are relatively well known and the challenges to tackle at present are related to the implementation of chemical looping in the process and power industries.

### 3.1.3 Chemical looping combustion of solid fuels

More and more attention has been paid to CLC applied to solid fuels such as coal and petroleum coke [37; 38]. The general principle is the same than chemical looping combustion of gaseous fuels. However, combustion of solid fuels by chemical looping is more problematic because of the difficulty to handle solid-solid reactions fast enough. The main difference lies so in the reactions occurring in the fuel reactor [31; 39; 40]. Even if chemical looping combustion of solid fuels is not directly related to the main subject of this thesis, it is briefly presented in this chapter because the issues to handle are similar to the ones met in chemical looping gasification.

Combustion of char in solid fuels is a complex process: the reactions occurring are different depending on the size of the particles and some other factors. The usual steps are, if the particles are small enough: first, drying, with evaporation of the moisture content; then, de-volatilization, with release of the volatiles; finally, combustion of the char with the oxygen present in the surroundings [41]. Chemical-looping combustion of solid fuels needs to address the following issue: both reactants, i.e. char and oxygen carrier, are in solid phases and the reaction rate in the fuel reactor is unlikely to be high enough. Char undergoes a two-steps process: first, a gasification step where char reacts with steam to form carbon monoxide and secondly an oxidation step where gasification products react with the metal oxides to form carbon dioxide and steam [39]:

$$\begin{aligned} C + H_2O &\longrightarrow CO + H_2 \\ CO + Me_xO_y &\longrightarrow CO_2 + Me_xO_{y-1} \\ H_2 + Me_xO_y &\longrightarrow H_2O + Me_xO_{y-1} \end{aligned} \tag{3.4}$$

Chemical-looping combustion of solid fuels is a hard challenge to tackle because solid-solid reactions and char gasification are slow compared to gas-solid ones.

The residence time in the fuel reactor should be high enough to achieve full char conversion [42]. Another issue is the conversion of hydrogen and carbon monoxide, which should be oxidized before leaving the fuel reactor. The oxygen carrier used should so have a high reactivity with these chemical compounds and the reactor considered should allow a high solid-gas contact to ensure a full conversion of the gasification products.

Finally, the last major concern is the $CO_2$-capture efficiency. All the carbon dioxide produced by char combustion should be entrained in the flue gases from the fuel reactor, i.e. transfer of unconverted char from one reactor to another should be avoided to avoid its combustion in the air reactor. There are two main ways to solve this problem. The first one is to use a carbon stripper that avoids re-circulation of char; the second one is to increase the residence time in the fuel reactor to ensure complete char conversion.

### 3.1.4 Chemical looping reforming and gasification

Another application of chemical looping is chemical-looping reforming whose the principle is similar to chemical-looping combustion [43]. Chemical looping gasification is a name used for the particular case of chemical-looping reforming applied to solid fuels such as coal or biomass [44; 45]. The main difference is that the fuel is not burnt but partially oxidized instead to produce a synthesis gas stream from a fuel such as natural gas or coal [46]. The general global reaction for partial oxidation in air and steam is the following [15]:

$$\mathrm{C_nH_m} + \frac{n}{2}\mathrm{O_2} \longrightarrow \mathrm{nCO} + \frac{m}{2}\mathrm{H_2} \tag{3.5}$$

The two main reactions which follow, respectively called steam reforming and $CO_2$ reforming, help to regulate the ratio of hydrogen and carbon monoxide in the synthesis gas [47]:

$$\begin{aligned} \mathrm{C_nH_m} + \mathrm{nH_2O} &\longrightarrow \mathrm{nCO} + (\mathrm{n} + \frac{m}{2})\mathrm{H_2} \\ \mathrm{C_nH_m} + \mathrm{nCO_2} &\longrightarrow 2\,\mathrm{nCO} + \frac{m}{2}\mathrm{H_2} \end{aligned} \tag{3.6}$$

A classic chemical looping reforming system is composed of two reactors, an air reactor where the metal is oxidised and a fuel one where the metal oxide is reduced and the fuel oxidized in presence of steam and, in some cases, of carbon dioxide. A part of the fuel will be fully burnt, following the reaction path but most of it will react with the metal oxide [15].

$$\mathrm{C_nH_{2m}} + \mathrm{nMe_xO_y} \longrightarrow \mathrm{nCO} + \mathrm{mH_2} + \mathrm{nMe_xO_{y-1}} \tag{3.7}$$

The outlet stream from the fuel reactor is composed of a solid phase containing reduced metal oxide and of a synthesis gas containing mostly carbon monoxide and hydrogen. It is further processed in a water-gas shift reactor to increase the hydrogen and carbon dioxide contents and then to separate the carbon dioxide out of the synthesis gas [27]. The main advantage of this process is the generation of synthesis gas that is not diluted with nitrogen from air and that does not require the use of a costly and energy-intensive air separation unit [27].

### 3.1.5 Chemical looping hydrogen

Chemical looping hydrogen refers to the applications of chemical looping with hydrogen generation [48; 49]. Metal particles react with steam instead of air, yielding a mixture of steam and hydrogen [50; 51; 52]. The reaction taking place in the oxidation reactor is:

$$\mathrm{H_2O + Me_xO_{y-1} \longrightarrow H_2 + Me_xO_y} \tag{3.8}$$

If chemical looping hydrogen is applied in reforming/gasification processes, the reaction occurring in the fuel reactor is then:

$$\mathrm{C_nH_{2m} + nMe_xO_y \longrightarrow nCO + mH_2 + nMe_xO_{y-1}} \tag{3.9}$$

If chemical looping hydrogen is applied in combustion processes, the reaction occurring in the fuel reactor is then:

$$\mathrm{C_nH_{2m}} + (2n + \mathrm{m})\mathrm{Me_xO_y \longrightarrow nCO_2 + mH_2O} + (2n + \mathrm{m})\mathrm{Me_xO_{y-1}} \tag{3.10}$$

The choice of the oxygen carrier material is critical: it should be able to react with steam to carry enough oxygen without having to process too large material flow rates and it should be able to convert steam to hydrogen in a high yield [50; 51; 52]. The most interesting materials may be iron oxides because of their high capacity to split water [53; 54].

### 3.1.6 Chemical looping oxygen uncoupling

Chemical looping oxygen uncoupling is a particular case of chemical looping that enables gas-solid reactions like oxygen with a solid fuel instead of solid-solid ones like metal oxides with coal or biomass [55]. The solid metal oxide does not directly react with the fuel but decomposes itself to a lower oxidation state metal and oxygen [56; 57; 58].

$$\begin{gathered}\mathrm{Me_xO_{y-1}} + \frac{1}{2}\mathrm{O_2 \longrightarrow Me_xO_y} \\ \mathrm{Me_xO_y \longrightarrow Me_xO_{y-1}} + \frac{1}{2}\mathrm{O_2}\end{gathered} \tag{3.11}$$

The oxygen stream generated by the decomposition reaction of the metal oxide can thereby be used for burning or reforming the solid fuel (usually combustion of solid fuels and other applications such as air separation [58]).

The oxygen carrier should have the ability to react reversibly with gaseous oxygen at the conventional operating temperatures of chemical looping reactors. This thermodynamic constraint involves that the equilibrium partial pressure of the oxygen for the oxidation reaction should be high at the air reactor temperature and low at the fuel reactor temperature [55; 56; 59].

The only oxygen carrier systems suitable for these applications are copper, manganese and cobalt [55; 56] although mixtures of different oxides might be relevant too [60]. The equilibrium diagrams reveal that the manganese and cobalt are more interesting than copper because their equilibrium temperatures are lower, which implies that the air separation could occur at lower temperatures, thus reducing the energy consumption of a low-temperature air separation unit [58].

## 3.2 Chemical looping materials

### 3.2.1 Requirements

The research on chemical looping has first been focused on the development of oxygen carrier: it is a key factor to understand the mechanisms of chemical looping. Several aspects concerning the physical, chemical and thermal properties of these materials need reflection. The desired characteristics are [22; 27; 32]:

- High oxygen transport capacity
- High yield of the incoming fuel to the desired products
- High reaction rates with both fuel and air or steam
- Appropriate melting points
- Appropriate heat of reactions
- High mechanical strength
- Inhibition of carbon formation
- High resistance to contamination
- Low cost
- Low health and environmental impacts

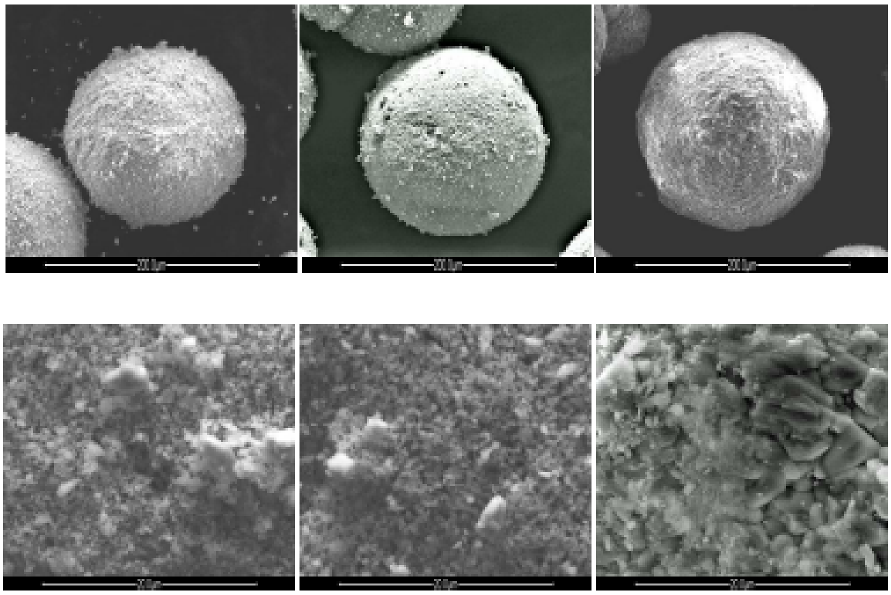

Figure 3.4: SEM-images of chemical looping particles [78]

### 3.2.2 Oxygen carrying capacity

The oxygen carrying capacity, i.e. the maximum transported amount of oxygen for a given mass flow of oxygen carrier, depends mainly on the type of oxygen carrier processed and on the amount of inert support added to the material [27; 32]. There are different variables expressing the oxygen carrying capacity, such as the oxygen-carrying ratio defined as:

$$R_0 = \frac{M_{ox} - M_{red}}{M_{ox}} \tag{3.12}$$

The oxygen-carrying capacity expresses the weight change of the oxygen carrier particle between its oxidised and reduced forms and shows thus the amount of oxygen that can be carried by the metal considered, as presented in Table 3.1.

Table 3.1: Oxygen ratio and conversion extent of various oxygen carriers [22;27]

| **Oxygen carrier pair** | **Oxygen ratio $R_o$** [%] | **Maximum conversion extent** [%] |
|---|---|---|
| **Ni/NiO** | 21.42 | 100 |
| **$MnO/Mn_3O_4$** | 6.13 | 16.67 |
| **$Fe_3O_4/Fe_2O_3$** | 3.34 | 11.11 |
| **$Fe_2O_3/FeO$** | 10.02 | 33.33 |
| **$Fe_2O_3/Fe$** | 30.06 | 100 |
| **Co/CoO** | 21.35 | - |
| **Cu/CuO** | 20.11 | 100 |

The materials with the highest oxygen-carrying ratio are nickel, cobalt and copper. The system $Fe/Fe_2O_3$ has a high oxygen-carrying ratio too but, in real chemical looping systems, the most likely oxidations states of iron are FeO, $Fe_2O_3$ and $Fe_3O_4$, and not pure iron. It is therefore considered that, in general, iron oxides have a low oxygen-carrying ratio compared to the other metal oxides. Some other materials, not presented here, such as calcium, strontium and beryllium sulphates have a much higher oxygen ratio than nickel or cobalt.

Increasing the proportion of inert material leads to a decrease of the oxygen-carrying capacity: the proportion of metal oxides in their pure form in the composite particle goes down and the weight change between the oxidation and reduction reactors decreases in consequence. Higher oxygen carrying capacity results in lower circulation solid flows and therefore in smaller reactors, reducing the overall investment cost of the chemical looping system.

Higher inert material proportion may have benefits from an economical point of view since nickel is, for instance, much more expensive than alumina, and from a thermal point of view because it usually has a high thermal capacity and can therefore carry more heat from the air to the fuel reactor. Lower inert material proportion results in smaller solids flow rates, which has, as enhanced before, the benefit of reducing the size of the reactors.

### 3.2.3 Thermodynamic and equilibrium constraints

The chosen oxygen carrier should be able to convert a high fraction of the processed fuel to the desired products at thermodynamic equilibrium. A low conversion implies the formation of other chemical compounds, resulting in losses of the fuel heating value into useless exit products from the fuel reactor. The degree of conversion is limited by thermodynamic constraints: an ideal oxygen carrier should be able to convert close to 100% the fuel processed to reach high-energy efficiency [22; 30; 61].

Every single chemical reaction actually consists of two reverse reactions, called forward and backward, and the concentrations of the chemical species in presence drive it in one direction or another. There is a dynamic state called chemical equilibrium where the rates of the forward and backward reactions are equal. The concentrations of the reactants and products will not change over time. The extent of the forward and backward reactions depends on conditions such as temperature, pressure, etc. The equilibrium diagrams show the variations of the equilibrium constant with the temperature for a given reaction.

Since there is a large amount of possible oxygen carrier and fuels, only the thermodynamic properties of the most conventional ones (nickel, copper, iron, manganese, cobalt) with synthesis and natural gas are presented. Metals such as iron and cobalt have several stable oxidation forms while undergoing oxidation and reduction cycles, at the difference of nickel that usually has only one [61]. It is thus of importance to investigate which are the reactions to consider.

The gas yields express the maximum possible extent of fuel conversion in the cases of methane, carbon monoxide and hydrogen at a temperature of 1000°C.

Table 3.2: Gas yields for various oxygen carriers [27]

| **Oxygen carrier pair** | $\gamma_{CH_4}$ [%] | $\gamma_{CO}$ [%] | $\gamma_{H_2}$ [%] |
|---|---|---|---|
| **Ni/NiO** | 98.83 | 98.83 | 99.31 |
| **$MnO/Mn_3O_4$** | 99.99 | 99.99 | 99.99 |
| **$Fe_3O_4/Fe_2O_3$** | 100 | 100 | 100 |
| **$Fe_2O_3/FeO$** | - | - | - |
| **$Fe_2O_3/Fe$** | - | - | - |
| **Co/CoO** | 92.99 | 92.99 | 95.74 |
| **Cu/CuO** | 100 | 100 | 100 |

It can be seen that iron, copper and manganese oxides allow the complete conversion of methane, carbon monoxide and hydrogen, which is of particular interest when processing natural or synthesis gas. On the opposite, nickel and cobalt cannot fully convert these fuels and it is thus expected that the carbon capture efficiencies are lower. In general, increasing temperature leads to lower gas yields whereas increasing pressure does not affect the yields of carbon monoxide and hydrogen but affects negatively the yield of methane [27].

### 3.2.4 Reactivity and kinetic constraints

It is desired to have high reaction rates in both chemical looping reactors to ensure high fuel conversion in the fuel reactor and high regeneration of the oxygen carrier in the air reactor over a relatively short lap of time [22; 27; 62]. While reactivity is correlated to the reactions kinetics in chemical looping, the degree of conversion is determined by thermodynamics and equilibrium states. The reactivity of the oxygen carrier directly affects the minimum solids flow rate to circulate and has therefore an impact on the design of chemical-looping reactors. The kinetics of the reduction and oxidation reactions of the oxygen carriers depend in theory on the nature of the reactants processed (fuel and regenerator), their physical state (solid, liquid, gas), their concentrations and the temperature and pressure of the system [32].

In practice, other factors related to the hydrodynamics of the chemical-looping reactor such as gas-solid contacts need to be considered to make a proper estimation of the solids inventories [22; 32]. Mass transfer resistances in the gas film and in the product layer are actually of importance and models relating chemical kinetics to the geometry of the oxygen carrier particle have been developed [63; 64]. In the case of chemical-looping combustion, the calculations of the minimum solids flow rate to proceed are based on calculations on the fuel reactor. It is indeed critical to achieve a high fuel conversion and the oxidation reaction of the metal material is generally much faster. On the opposite, in the case of chemical-looping hydrogen, the solid inventory estimations are based both on calculations on fuel and steam reactors: it is indeed essential to achieve a fast and high steam to hydrogen conversion as well [22; 65].

Only few studies have been done on the pressure effect on oxygen carrier behaviour. It is nevertheless an important issue when integrating chemical looping in pressurised systems such as combined cycles [66]. It is expected that increasing the operating pressure of the chemical looping system leads to a higher thermal process efficiency because less energy would be needed to compress and sequestrate the carbon dioxide stream. Experiments carried out in pressurised thermogravimetric analysers revealed that an increase of the total pressure of the system is unfavourable to the kinetics of the oxidation and reduction reactions. A possible explanation is that the internal structure of the oxygen carrier particles is modified. This negative effect has an influence on the design of pressurised chemical looping systems: since the reaction rates are lower then the amount of oxygen carrier present in the system has to be increased [66].

### 3.2.5 Melting point and heat of reaction

Chemical looping reactors may be applied in high-temperature processes lie combined cycles. It is thus essential to use an oxygen carrier that could endure these operating conditions without melting since the particles would otherwise lose in chemical reactivity. Another point is that, when using a fluidized bed, it is critical to avoid softening and agglomeration of the oxygen carrier particles since they play the role of fluidizing particles as well.

A common point between all the metal oxides experimented is that the oxidation reaction is strongly exothermic. The main issue is thus to control the air reactor temperature to avoid reaching excessive temperatures and softening of the oxygen carrier particles. The heat generated from this combustion reaction can be either carried out by circulation of oxygen carrier to the fuel reactor or removed by external cooling, generating steam or electricity. The metal oxide does play a role of heat carrier besides being an oxygen carrier. Moreover, the inert material, which is used as a support to the metal oxide, also takes part in the heat transfer between both reactors.

Regarding the melting temperatures, copper may not be suitable for use in chemical looping system because its melting temperature is relatively low and it would therefore be problematic to process it in combined cycles. Some other metal oxides, not discussed here, such as cadmium, zinc or caesium, are not suitable either: zinc is usually at a liquid state at these high temperatures and it opened prospectives for using liquid oxygen carriers.

Table 3.3 presents the melting points of the main oxygen carrier systems investigated in chemical looping with the reaction enthalpies of oxidation at 1000°C and 1 atmosphere.

Table 3.3: Thermal properties of various oxygen carriers in oxidation reactions [27]

| **Oxidation reaction** | **Melting point of the oxidised metal form** [°C] | **Melting point of the reduced metal form** [°C] | $\Delta_r$**H** [kJ/mol$O_2$] |
|---|---|---|---|
| $\mathbf{Ni + \frac{1}{2}O_2 \rightarrow NiO}$ | 1955 | 1455 | -468.5 |
| $\mathbf{MnO + \frac{1}{6}O_2 \rightarrow \frac{1}{3}Mn_3O_4}$ | 1562 | 1842 | -449.4 |
| $\mathbf{Fe_3O_4 + \frac{1}{4}O_2 \rightarrow \frac{3}{2}Fe_2O_3}$ | 1565 | 1597 | -478.8 |
| $\mathbf{FeO + \frac{1}{4}O_2 \rightarrow \frac{1}{2}Fe_2O_3}$ | 1565 | 1420 | -553.6 |
| $\mathbf{Fe + \frac{3}{4}O_2 \rightarrow \frac{1}{2}Fe_2O_3}$ | 1565 | 1538 | -539.4 |
| $\mathbf{Co + \frac{1}{2}O_2 \rightarrow CoO}$ | 1830 | 1495 | -466.9 |
| $\mathbf{Cu + \frac{1}{2}O_2 \rightarrow CuO}$ | 1446 | 1085 | -295.9 |

Table 3.4 shows the reaction enthalpies of reduction with methane, carbon monoxide and hydrogen at 1000°C and 1 atm.

Table 3.4: Thermal properties of various oxygen carriers in reduction reactions [22]

| **Oxidation carrier pair** | $\Delta_r$**H(**$CH_4$**)** [kJ/mol] | $\Delta_r$**H(CO)** [kJ/mol] | $\Delta_r$**H(**$H_2$**)** [kJ/mol] |
|---|---|---|---|
| **Ni/NiO** | 133.5 | -47.2 | -15.0 |
| $\mathbf{MnO/Mn_3O_4}$ | 95.4 | -56.8 | -24.6 |
| $\mathbf{Fe_3O_4/Fe_2O_3}$ | 154.2 | -42.0 | -9.9 |
| $\mathbf{Fe_2O_3/FeO}$ | 303.7 | -4.7 | 27.5 |
| $\mathbf{Fe_2O_3/Fe}$ | 274.5 | -12.0 | 20.2 |
| **Co/CoO** | 741.8 | -48.0 | -15.8 |
| **Cu/CuO** | -211.6 | -133.5 | -101.3 |

The reduction reaction of the metal oxide is either endothermic or exothermic, depending on the fuel processed and on the oxygen carrier used. At the exception of the copper oxide, all the reactions between metal oxides and methane are endothermic. The reduction reactions of metal oxides with carbon monoxide are mildly exothermic whereas they are either endothermic or exothermic with hydrogen. Reduction reactions of the metal oxides with synthesis gas are therefore either mildly exothermic or endothermic, depending on the composition of the synthesis gas. The main exception to this rule is copper oxide, with both exothermic oxidation and reduction reactions in any case.

On the one hand, an endothermic reaction will cause a temperature drop and heat needs to be provided to sustain the reactor temperature. It is usually provided by the solids circulation between both reactors since the oxidation reaction is exothermic. On the other hand, if the reduction reaction is exothermic too, the amount of solids to circulate between both reactors is not critical to sustain the fuel reactor temperature. In that case, the temperature is sustained by either external cooling or larger airflow rates.

### 3.2.6 Mechanical and thermal stabilities

Oxygen carrier particles should be able to withstand mechanical and thermal stresses to avoid attrition, sintering and fragmentation and have a low tendency for agglomeration. It would otherwise lead to reactivity losses and a need for large particle make-ups to compensate the wasted particles [27].

High mechanical strength is usually correlated to low porosity, which means that resistant particles have a low reactivity surface and thus a low reactivity. On the opposite, high thermal stability is usually associated with high reactivity because thermally stable particles do not decompose at high temperatures and thus do not lose reactivity [27].

The particle size has a direct impact on the mechanical and thermal stabilities of the oxygen carrier and on its capture in the cyclone separation process. The oxygen carrier particles usually have a diameter in the range of hundreds of micrometers, with the exception of some experiments led on nanoparticles [67].

There are two main ways to increase the mechanical strength of the particle. Both can be used to improve the chemical and carbonate looping particles:

- Addition of support and inert materials
- Use of proper preparation methods

The advantage with the addition of a support material is that it stabilises the mechanical structure of the oxygen carrier particle, improves its thermal stability and increases its porosity and thus its reactivity [27]. A classic example of inert material used is alumina $Al_2O_3$ for nickel-based oxygen carriers [68; 69] but other more uncommon supports such as titanium for iron or zirconium oxide $ZrO_2$ for manganese have been experimented too [70; 71; 72].

The proportion of inert material in the oxygen carrier particle has a strong impact on the mass and heat balances in the system [27]. It is desirable that the oxygen carrier particle can undergo a large number of chemical looping cycles without high reactivity losses to avoid frequent wastes and large make-ups, which would be costly. The durability of the composite particle (oxygen carrier and inert) depends strongly on the syntheses techniques used, such as sol-gel, wet impregnation or freeze granulation [22].

### 3.2.7 Inhibition of carbon formation

Solid carbon may be formed for instance by methane decomposition, coke formation or reverse Boudouard reaction, especially in low oxygen partial pressure conditions [15; 73]:

$$\begin{aligned} \mathrm{CH_4} &\longrightarrow \mathrm{C} + 2\,\mathrm{H_2} \\ \mathrm{CO} + \mathrm{H_2} &\longrightarrow \mathrm{C} + \mathrm{H_2O} \\ 2\,\mathrm{CO} &\longrightarrow \mathrm{C} + \mathrm{CO_2} \end{aligned} \tag{3.13}$$

Whereas the methane decomposition and reverse Boudouard reactions are favoured at low temperatures, the coke formation becomes problematic only at high temperatures. The formation of carbon and carbides (NiC, FeC, MnC...) in general is detrimental to the performance of the chemical-looping system [74]. First, solid carbon can be transported away of the fuel reactor and form carbon oxides in the air one, hence contaminating the depleted air gases.

$$\begin{aligned} \mathrm{C} + \frac{1}{2}\mathrm{O_2} &\longrightarrow \mathrm{CO} \\ \mathrm{C} + \mathrm{O_2} &\longrightarrow \mathrm{CO_2} \end{aligned} \tag{3.14}$$

Moreover, the presence of solid carbon may decrease the reactivity of the metal oxides, either by accumulation on the particles or by formation of metal carbides and carbonyls, though these last reactions are unlikely to occur [65]. Finally, when using a circulating fluidized bed, the insertion of solid carbon in the interstitial spaces between the fluidizing particles can lead to an increase of the pressure drop across the reactors, causing operational problems [22].

There are two main ways to reduce the carbon formation in the fuel reactor: either by injecting steam, which shifts the equilibrium of the coke formation, or by operating at higher temperatures, which inhibits the reverse Boudouard reaction [15; 22]. In the first case, only a small amount of steam should be injected since otherwise it will hinder the conversion of synthesis gas when using it as a fuel. In the second case, it is necessary to use a metal oxide that has a high melting temperature and to use a fuel with low tendency to coke formation [74; 75].

### 3.2.8 Resistance to sulphur poisoning

The amount of sulphur contained in the fuel ranges, in gaseous fuels, from 20 vppm in natural gas to 8000 vppm in raw syngas, and, in solid fuels, ranges from 0.5 to 5% on a mass basis depending on the type of coal (anthracite, bituminous, etc). Thermodynamic studies and laboratory-scale experiments have investigated the oxygen carrier behaviour in presence of sulphur impurities and have proven that sulphur poisoning may become a big issue [76; 77].

First, the sulphur present in the fuel can react with metal oxides, producing solid metal sulphides at equilibrium conditions. Secondly, it can eventually be released as sulphur dioxide $SO_2$ and trioxide $SO_3$ or as hydrogen sulphide $H_2S$ and carbonyl sulphide COS. The possible effects are so reactivity decrease of the oxygen carrier and thus reduction of fuel conversion [76; 77].

Researches on sulphur fate have mainly been carried out on nickel, copper, iron, cobalt and manganese oxides though there are some studies on beryllium, calcium and strontium ones. The main conclusion was that the rate of sulphur contamination depends strongly on the operating conditions of the chemical looping reactors such as temperature, pressure, air ratio and on the type of oxygen carrier processed [27; 75]. The thermodynamic analysis demonstrated the general following results [27; 76; 77]:

- Sulphur oxides can contaminate the exit gases from both air and fuel reactors because sulphur is transported by oxygen carriers from one reactor to another.
- Formation of solid sulphides and sulphates occurs at all temperatures but is significant only if nickel or cobalt-based oxides are used.
- Oxidation of hydrogen sulphide to sulphur dioxide is favoured at high temperatures and low pressures and the degree of conversion can reach 100% with copper and iron oxides.
- Oxygen carrier particles can recover their initial reactivity because reactions with sulphur are fully reversible, though it leads to the generation of sulphur oxides in fuel and air reactors [78].

### 3.2.9 Health and environmental effects

The oxygen carrier chosen should preferably be environmentally sound to be easily disposed since large flows of these materials are used in chemical looping systems. It should as well have a low impact on human health and, regarding the safety tables, the most problematic oxygen carrier is nickel because of its irritation properties and cancer hazards. All other ones are relatively safe and have been extensively used in experiments and pilot studies [61].

### 3.2.10 Cost issue

Chemical looping is a relatively new technique and there is already a large panel of mature strategies to mitigate the $CO_2$-emissions such as amine scrubbing. Though the efficiency penalty is lower and the $CO_2$-capture efficiency higher, it is still a challenge to make chemical looping an economically viable alternative.

A clear advantage of the chemical looping technology is, as it will be discussed in a further part, the use of either moving or fluidised bed reactors, which are well-known and already used technologies. It is so relatively easy to estimate the investment costs of the chemical looping reactors regarding their specifications. The major running cost of the chemical looping processes is therefore the oxygen carrier cost that depends on [61]:

- Raw material cost (supply)
- Production cost (synthesis, granulation, thermal treatment, etc.)
- Make-up cost (replacement of the deactivated particles)
- Environmental cost (waste)

### 3.2.11 Comparison of the different oxygen carriers

Table 3.5 summarizes the advantages and drawbacks of the various oxygen carrier systems presented in this study.

Table 3.5: Comparison of various oxygen carriers

| **Oxygen carrier pair** | **Ni/NiO** | **MnO/$Mn_3O_4$** | **$Fe_3O_4$/$Fe_2O_3$** | **Co/CoO** | **Cu/CuO** |
|---|---|---|---|---|---|
| **Oxygen-carrying capacity** | + | - | - | + | + |
| **Fuel conversion** | $\sim$ | + | + | - | + |
| **Reactivity** | + | + | - | + | + |
| **Melting point** | $\sim$ | + | + | + | - |
| **Mechanical strength** | - | $\sim$ | + | $\sim$ | $\sim$ |
| **Resistance to sulphur** | - | $\sim$ | + | - | + |
| **Carbon formation** | - | $\sim$ | - | $\sim$ | + |
| **Cost** | - | $\sim$ | + | $\sim$ | $\sim$ |
| **Environmental and health impact** | - | $\sim$ | + | $\sim$ | $\sim$ |

There is so far no metal oxide displaying all the desired characteristics [79]. The choice of one metal oxide rather than another depends on the application and reactions considered (combustion, reforming, etc).

Nickel-based oxygen carriers present the highest oxidation and reduction rates in chemical-looping combustion, have a high oxygen carrying capacity and are suitable in the operating temperature and pressure ranges in chemical looping. However, they cannot fully convert methane, catalyse solid carbon formation, are highly sensible to sulphur poisoning, are expensive and present environmental and human hazards [61; 80; 81].

Manganese-based oxygen carriers can achieve as well a full conversion of methane. They are usable at high temperatures, are quite cheap and safe, but have a low oxygen transport capacity and a lower reactivity than nickel and copper-based oxygen carriers [61; 80; 81].

Iron-based oxygen carriers are the cheapest oxygen carriers but have a low oxygen carrying capacity [82] and the lowest reactivity with fuels such as methane [61; 80; 81]. However, they are the only suitable oxygen carriers in chemical-looping hydrogen because of their high capacity to convert steam to hydrogen [83; 84].

Cobalt-based oxygen carriers have a high oxygen carrying capacity, a high reactivity with every type of fuel, are suitable for use at high temperatures but have a severe thermodynamic limit regarding fuel conversion [27].

Copper-based oxygen carriers have the highest oxygen carrier capacity, can achieve a full conversion of methane, present high reactivity, inhibit carbon formation, are relatively cheap and are safe [85; 86]. They are also the only oxygen carriers to have both exothermic oxidation and reduction reactions. They have nevertheless a high tendency for softening and agglomeration under high temperature conditions [61; 80; 81]. They might be suitable for applications in gasification because of the lower temperatures than in combustion processes [87; 88].

### 3.2.12 Innovations

An idea raised recently is to process an artificial mixed metal oxide to combine the advantages of different metal oxides and to compensate their eventual drawbacks. Several composites were tested, such as iron and nickel-based oxygen carrier with spinel [89; 90].

The idea behind this combination is that nickel oxide has high reactivity towards methane and hydrocarbons, at the difference of iron oxides, but is more expensive. The addition of nickel oxides to hematite has presented positive effects: the reaction rate of this mixed metal oxide is higher than of usual iron-based oxygen carrier and this mixture is cheaper to get than the normal nickel-based oxygen carrier [89; 90]. However, some issues have been pointed up such as an induction time before the composite particle oxidises [91].

Another new possibility for oxygen carriers is perovskite-structured materials: they have the same crystal structure as calcium titanium oxide $CaTiO_3$ and their general formula is $ABO_3$ with both A and B cations. Studies led on these materials showed that they display a high thermal stability, a high reactivity with methane and a decent mechanical resistance. However, they have a high tendency for agglomeration and cannot inhibit carbon formation [90].

The system calcium sulphide CaS and sulphate $CaSO_4$ is sometimes considered as a breakthrough for oxygen carrier development. Calcium sulphide has a higher oxygen carrier capacity than other metal oxides, is widely available, has a high melting point, is inexpensive and is environmentally friendly [92; 93; 94]. However, thermodynamic analysis showed that solid carbon deposition is possible under usual operating conditions. These materials also have low reaction rates compared to metal oxides and gradually lose reactivity over cycles [95; 96] for the following reasons.

First, calcium sulphate has a higher molar volume than calcium sulphide and blocks access of oxygen to the reactive surfaces. Secondly, calcium sulphate has a high tendency for attrition and decomposition at high temperatures, which limits its use in chemical looping combustion systems. A solution recently proposed is to add binders like silicon dioxide to increase the mechanical strength and the reactivity of calcium sulphate [97].

Attention has recently been paid to ilmenite, a titanium and iron natural oxide mineral with the general formula $FeTiO_3$ that presents the great advantages of being inexpensive and environmental-friendly [98; 99; 100].

Although this material has an initial low reactivity compared to nickel or copper oxides, its reactivity increases through cycles before stabilizing at a maximum. It becomes around five times higher for hydrogen and carbon monoxide and around fifteen times for methane. This increase of reactivity has been explained by the morphological changes of the ilmenite particles: the surface shape smoothly evolves from a sharp-edged to a granular one and the porosity rises. However, a drawback with ilmenite is its losses of oxygen carrying capacity over the red-ox cycles [98; 99; 100].

Innovations on chemical looping materials do not consist only of innovations on different materials but on different synthesis methods too. Preparation processes of the oxygen carrier like screening or impregnation have a strong impact on its shape and structure and thus on the mechanical stability of the particle and the reaction kinetics [101; 102; 103]. An example is the manufacturing of metal oxide nanoparticles that display better oxidation and reduction kinetics and larger conversion of sulphides [67].

## 3.3 Chemical looping reactor technology

### 3.3.1 Choice of reactor system

For most purposes in combustion and gasification processes, the reactor types can be classified into three main categories [15; 104]:

- Moving-bed
- Fluidised-bed
- Entrained-flow

They differ from each other by the temperature and pressure operating range, the oxygen and steam demand, the residence time and the fuel and bed material processed.

A moving bed reactor consists of a bed in which the fuel moves downward under gravity effects while the gaseous reactant such as air, steam or pure oxygen usually moves upwards. Whereas the gaseous products generated by the reactions leave at the top of reactor, solid inert such as ash and slag are extracted at the bottom. The reactions occurring in this type of reactor do not take place in the whole chamber. The reactor can be divided in several zones where different processes take place and the temperature and gas composition profiles vary strongly with the height of the bed [15]. Moving beds behave like plug-flow reactors.

Fluidised beds in general are characterised by a higher exit temperature than moving beds. The basic and general principle of a fluidised bed, either bubbling or circulating is as follows. A fluid substrate, air or carbon dioxide, goes from the bottom of the reactor through a granular material at high enough velocities to suspend the solid particles and to fluidise them. The substrate has thus two main functions: it acts as a reactant with the solid material and acts as a fluidising medium material for the bed [15].

The main difference between the bubbling and circulating fluidised beds lies on the mean gas and solid velocities that are higher in the second type. Whereas in a bubbling reactor, the solid phase is stationary and the reaction takes place only in the bed, in a circulating reactor, the solid particles are carried with the gas, allowing the reaction to take place in the entire reactor device [15; 41]. The advantage of bubbling fluidised beds over riser ones is the lower attrition rate due to the lower velocity of the solid particles and the better heat transfer between the solid and gaseous phases. On the opposite, the advantage of risers over bubbling reactors is the lower pressure drop when using fine solid particles and the higher conversion rate when proceeding fast reactions [105]. A circulating fluidised bed consists of three main parts [41]:

- The riser: the gas substrate enters at the bottom and fluidises the solid material. The high velocities of the gases lead to solids entrainment and both phases flow co-currently upward in the entire riser
- The integrated cyclone: both phases coming from the top of the riser are introduced in a cylinder container and are separated by centrifugal forces
- The down-comer: the solid flow is carried back to the riser

In practice, there is some additional equipment [41]:

- A succession of cyclones instead of a single one is generally used to achieve the desired separation efficiency between the gaseous and solid phases
- Heat exchangers, where a heat carrier circulates, are placed inside the riser to control the reactor temperature
- Loop seals are positioned between the cyclone and the down-comer to prevent gas leakages

This type of reactor behaves as a continuously stirred reactor, though circulating fluidised beds behave in between co-current plug flow and perfectly mixed reactors. The efficiency of this kind of reactor is thus lower than a moving bed because, first, a part of the fuel is constantly removed with the ash and slug and, secondly, fuel solid particles may be entrained with the gaseous products and may not be recovered in the integrated cyclone. However, the methane and tars contents of the synthesis gas generated by means of a fluidised bed are generally lower than in syngas from moving bed reactors due to the higher outlet temperature [15].

Entrained-flow reactors are characterised by a higher exit temperature than fluidised and moving bed reactors: the operating temperature is above the ash melting point, ensuring the transformation of ash into slag. The feed and blast circulate co-currently from the top of the reactor and the gas and slag exit at the bottom [15]. This type of reactors is not suitable in chemical-looping applications. The residence time, which is usually of some seconds, is too short to achieve high reduction and oxidation rates, thus leading to low fuel conversion and low efficiency. Another issue is that the bed material particles processed in entrained-flow reactors have a diameter lower than 100 $\mu$m: this size may be too small in the case of oxygen carrier particles because they would have a low mechanical strength and a high tendency for attrition and agglomeration. Finally, since the operating temperature is usually above the ash melting point, there are strong risks of metal oxide softening and ash agglomeration on the oxygen carrier particles.

The choice of either moving or fluidised beds depends then on the applications considered but extensive studies have been done on fluidised bed reactors for chemical-looping combustion of gaseous fuels [25]. An ideal reactor system in chemical looping should satisfy the following criteria [32]:

- Excellent gas-solid mass transfer to achieve high fuel and oxygen carrier conversion
- Excellent gas-solid heat transfer to promote heat exchanges and to allow a temperature control in situ
- Continuous oxygen carrier transportation between the two reactors to ensure oxygen carrier oxidation and reduction reactions and to promote high oxygen carrier conversion
- No gas leakages between the two reactors to avoid losses in carbon capture efficiency
- No solid leakages to the rest of the process to avoid losses in process energy efficiency

Thus, an ideal reactor for chemical looping applications may be a dual fluidised bed, i.e. two fluidised beds connected to each other. There are several different types of dual fluidised bed reactors in chemical looping with, for instance [106]:

- Dual bubbling fluidised bed
- Dual high-velocity fluidised bed
- Bubbling bed as air reactor and high-velocity bed as fuel one
- Bubbling bed as fuel reactor and high-velocity bed as air one
- Dual circulating fluidised bed

A bubbling fluidised bed reactor enhances the gas-solid contact and is more suitable for slow reactions limited by thermodynamic equilibrium, such as fuel reduction. The greater mass and heat transfers are favourable to endothermic reactions. On the opposite, a high-velocity fluidised bed reactor is more suitable for fast and complete reactions, such as metal oxidation [106].

The first historically proposed and most popular reactor design for chemical looping applications is thus a dual fluidised bed with a high-velocity bed as air reactor and a bubbling fluidised bed as fuel reactor [32]. Combustion of natural and synthesis gas has been studied in these types of reactors with the example of a 300 W unit at Chalmers University of Technology [107].

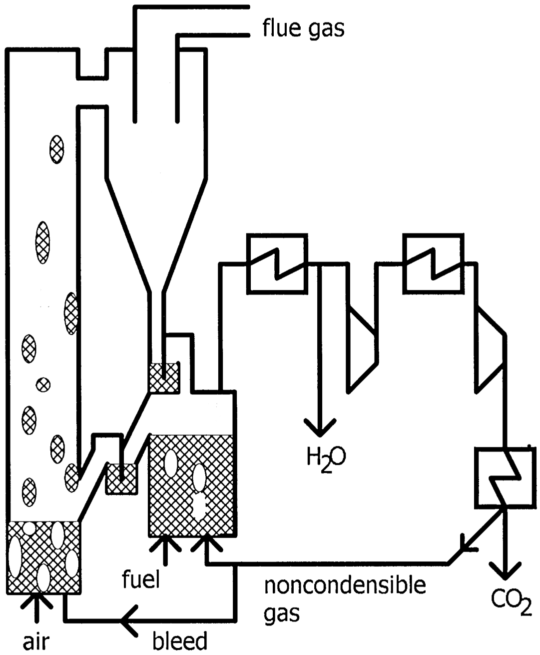

Figure 3.5: Interconnected fluidised beds for chemical looping combustion [32]

This kind of reactor can thus be assimilated to a circulating fluidised bed with a bubbling bed incorporated between the down comer and the riser. The popularity of fluidised bed technology among the chemical looping applications is justified by [24; 32]:

- Fluid-like behaviour of the solid particles (and so, oxygen carrier) reduces the radial and axial concentration gradients

- Perfect mixing of the different phases in presence reduces the presence of temperature gradients inside the reactors

- Integration of cyclones and loop seals prevents gas leakages between the different parts of the circulating fluidised bed

- The continuous solid circulation through the entire reactor (riser, cyclone and downcomer) enhances the reaction rates

However, the fluidised bed presents the inherent advantage and default of excellent axial and radial mixing: all the gaseous and solid phases are thus perfectly mixed together, at the difference of moving beds. In chemical-looping gasification, it entails that the final gaseous product lean in hydrogen and carbon monoxide dilutes the newly generated syngas rich in hydrogen and carbon monoxide: the conversion efficiency is therefore limited in fluidised bed reactors [22].

In a moving bed, the unconverted solid phase reacts with highly converted gaseous phase, and vice-versa. The fresh produced synthesis gas rich in hydrogen and carbon monoxide is thus not mixed with the final gaseous product and reacts mainly with oxygen carrier particles at low oxidation states. On the opposite, the converted synthesis gas lean in hydrogen and carbon monoxide reacts mainly with oxygen carrier particles at high oxidation states. The conversion efficiency can therefore be much higher in moving beds than in fluidised beds [22; 108].

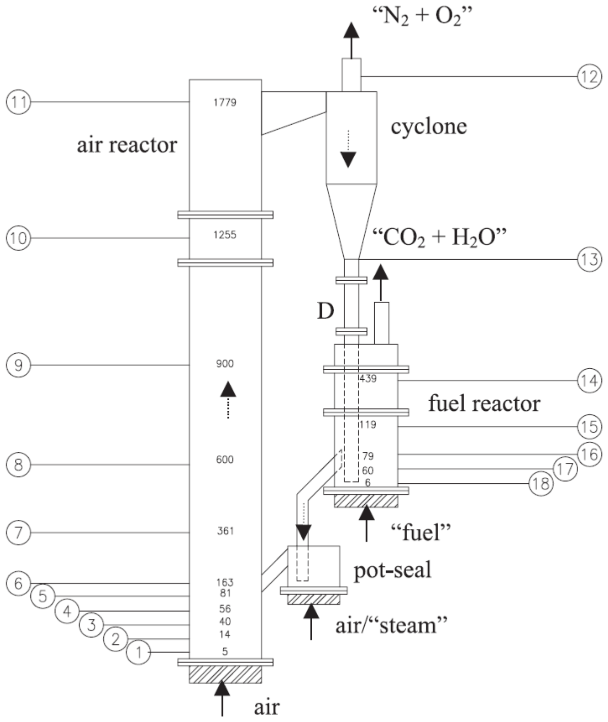

Figure 3.6: Layout of interconnected fluidised beds [32]

### 3.3.2 Relations between oxygen carrier and reactor operation

One of the key criteria in the design of chemical looping reactors is the amount of oxygen carrier in the system and therefore the solids circulation rate between the oxidation and reduction reactors [32; 109]. The values of these design parameters depend on several factors such as the oxygen carrier properties and the type of reactor: the general procedure for designing a chemical looping reactor is described in Figure 3.7 and the relevant criteria in Appendix B.

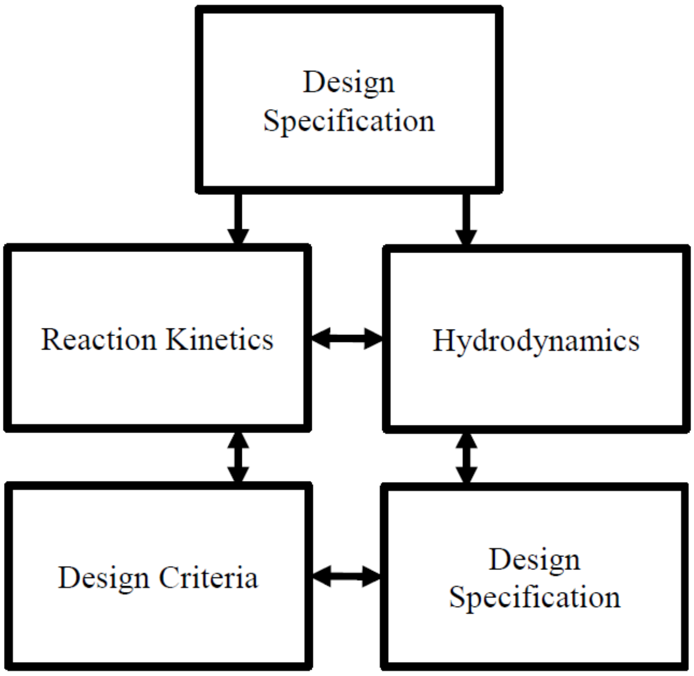

Figure 3.7: Design procedure of a chemical looping reactor [32, 63]

The term of conversion difference refers to the mass difference of the oxygen carrier particle between the oxidation and reduction reactors. In other terms, it expresses the amount of oxygen carried from the air to the fuel reactor and depends therefore on the oxygen carrying capacity and on the extent of conversion of the metal oxide, as seen in Table 3.1.

A high conversion difference means that the oxygen carrier particle carries a large quantity of oxygen from the air to the fuel reactor and therefore the minimum solids circulation rate required is low. The solids circulation rate is thus inversely proportional to the conversion difference [22; 32]. The conversion rate is a kinetic parameter and measures the variation of the oxygen carrier conversion in response to changes in time. Fast reaction kinetics implies high conversion rates: the necessary residence time for transferring the required amount of oxygen is lower and the bed mass is thus lower too [22; 32].

There are two main parameters influencing the conversion rate: the size of the oxygen carrier particle and the concentration of the reactants. The conversion rate is inversely proportional to the size of the oxygen carrier particle and proportional to the concentration of the reactants [22; 32].

The gas yield illustrates the maximum thermodynamically allowed amount of fuel that can be converted. A gas yield of 100% means that all the fuel is converted and there is therefore no need to re-circulate the exhaust gases to promote fuel conversion. The air ratio depends on the maximum amount of oxygen that can be transferred from the oxidation to the reduction reactors and on the fuel consumption [22; 32].

Accurate calculations need nevertheless a deep knowledge of the reactor geometry and hydrodynamics but these simple mass balances can lead to rough estimations of these design parameters [110]. In addition, it should be realized that the metal oxide particle carries heat, thus changing the heat balance of the system and influencing the temperature control.

### 3.3.3 Reactor design parameters

Designing and scaling-up a circulating fluidised bed is a complex task that should consider, among other parameters, the solids circulation rate, the bed mass and the air and gas flow rates [22; 32]. The three most relevant design parameters for a fluidised bed are [41]:

- Cross-sectional area: the cross-sectional area of the bed is related to the airflow rate and to the superficial gas velocity. It should be high enough to ensure fluidisation but relatively low to avoid erosion of the bed walls.
- Fluidisation velocity: the fluidising velocity is linked to the mean particle size of the oxygen carrier particle. It should be relatively low to reduce the attrition risk of the oxygen carrier particles but high enough to ensure fluidisation.
- Height: the height of the fluidised bed is correlated to the heat transfer inside the reactor and the kinetics of the reactions taking place. It should be high enough so that the volume heat load is within an acceptable range to avoid excessive thermal stress and to allow a sufficient residence time for the oxidation and reduction of the oxygen carrier.

Since the aim of this thesis is not to investigate the integration of chemical and carbonate looping at a reactor level, the detailed hydrodynamics of the circulating fluidised bed is neither presented nor considered in the rest of the study.

### 3.3.4 Reactor system arrangement

*Cyclone separation*

Cyclones are gas-solid separators: the ones integrated in the chemical-looping system are critical to remove the solid particles from the gaseous streams, such as metal oxides from oxygen-depleted air or metal particles from carbon dioxide and steam mixture. In general, the heterogeneous mixture flows in a spiral pattern from the top of the cyclone, which corresponds to the outlet of the riser, and is entrained along the main body towards the conical part. The difference of density coupled to the rotational and gravity effects exercised on the solid particles lead to their separation from the gaseous stream [41].

Cyclones have been widely applied in the circulating fluidised bed technology and are preferred to other types of gas-solid separators such as fabric filters because of their relatively low cost, low-pressure drop and suitability in these kinds of operations. However, it is interesting to point out that in some chemical looping pilot systems, cyclones were coupled to filters to reach higher separation efficiency [41]. The particle size is generally not a critical issue because most of the cyclones used in industry have a high efficiency for particles larger than 10 $\mu m$ and the general size of an oxygen carrier particle in chemical-looping applications is generally above 50 $\mu m$ [22; 41].

Two types of cyclones have mainly been used in industry: uni-flow and reverse-flow. The main difference is the position of the gas stream outlet that is located at the top in a reverse-flow cyclone and at the bottom in a uni-flow one. The second type is the most efficient type and is often coupled to a loop seal to reach an even higher efficiency [22; 41].

### *Loop seals*

The solids flowing down from the cyclone are fed back into the riser: they usually run through a standpipe, react, in case of a chemical-looping application, in an additional reactor and pass a valve before their injection at the bottom of the riser [41; 111]. The two major types of standpipes developed so far are the overflow and underflow: the difference lies in the position of the outlet of the standpipe and thus in the pressure distribution. The underflow type is particularly appropriate when the standpipe makes the connection between the cyclone and a bubbling fluidised bed [41; 111].

A valve either mechanical or non-mechanical controls the solids flow rate and controls the gas leakages between the low-pressure standpipe and the high-pressure riser. Mechanical valves present the advantage of being simple and well known but are less efficient than non-mechanical ones for preventing gas leakages. Several combinations such as loop seal, L-, J- and H-valve exist and the choice of one in particular depends on the solids circulation rate and on the operation regime [41; 111]. So far, the most common valve used in the experiments in chemical-looping combustion is a loop seal.

Air runs through the loop seal by means of aeration or supply chamber at a relatively low velocity: fluidisation should be limited to avoid large pressure drops in the standpipe. The aeration divided in several parts involves that a part of the air stream flows into the standpipe while the rest goes through the other parts of the loop seal. The standpipe compensates the differences of pressure between the bubbling fluidised bed reactor and the loop seal: the solids flow rate introduced in the riser are at a higher pressure than the air stream at the bottom. The gas velocity, the passage length, the division of flow, the spread and repose angles are critical factors of the design of the loop seal [41; 111; 112].

### *Carbon stripper*

It is of importance to avoid circulation of unconverted char between the air and fuel reactors since it would lead to losses in carbon capture efficiency. Cyclones and loop seals aim to reduce the solid leakages but the use of a carbon stripper complements these technologies and help achieving a higher carbon capture rate [113].

## 3.4 Chemical looping processes in power plants

### 3.4.1 Thermodynamic potential

The development and incorporation of chemical looping into the power industry depends partly on its potential to produce energy at a high efficiency. Research has been led on the possible integration of these processes in existing power plants and on novel power ones. Most of the power generation processes currently used in the energy industry are based on the combustion of gaseous fuels such as natural gas, which explains the interest for chemical-looping combustion at first [114; 115]. The particular interest for the development of chemical looping systems primarily emerged from the potential of chemical looping combustion systems to achieve higher thermal efficiency than conventional power plants. They are expected to attain higher energy and exergy efficiency for two reasons.

First, the conventional combustion reaction is non-reversible and leads to a decrease of the total efficiency of the thermal power plants. Chemical-looping combustion is based on the idea that the combustion reaction can be carried out in two different reactors: by avoiding direct contact between fuel and air it is possible to reduce the exergy destruction of the combustion process [116; 117]. It means in practice that chemical looping combustion approaches the behaviour of a reversible internal combustion engine without excessively high temperatures. The type of heat engine applicable to recover the excess heat from the oxidation reactor and to provide heat to the reduction one could be based on a Rankine cycle to generate work and increase the overall process efficiency [118].

The second reason for an increase of net power efficiency is that since the carbon dioxide generated is inherently separated from nitrogen and is only mixed with steam, only a simple condensation step is needed, avoiding the usual energy-intensive $CO_2$ separation or cryogenic air separation unit [116; 117]. Chemical-looping combustion processes were so examined by exergy analysis tools such as energy-utilisation graphs [116; 119], Sankey exergy diagrams [120] and Grassmann entropy diagrams [29]. Exergy studies are often applicable in chemical industries and help to find out improvement possibilities in power processes [121; 122]. The different studies led confirmed this theory and revealed that the exergetic power efficiency varies with different metal oxides but stays higher than in conventional combustion processes [29].

The integration of chemical looping combustion in combined cycles may therefore become of great interest compared to the other carbon dioxide capture options [123; 124], with the example of natural-gas fired power plants [125; 126] or gasification ones [127]. Though no exergetic studies have been led so far on chemical looping reforming and gasification, these applications may reach higher exergetic efficiency because the reactants are not directly mixed and the reaction is split into sub-reactions. Moreover, according to the different exergy analysis of carbon gasification, the highest exergy efficiency in gasification processes is around 1200 to 1300 K for a pressure of 10 bars [128], which corresponds roughly to the temperature ranges in chemical looping gasification.

Finally, an intrinsic advantage of chemical looping reforming is the avoidance of an air separation unit, reducing thus the energy penalty [27]. Chemical looping gasification is not related to carbon dioxide capture and there is still a need for, first, a water-gas shift reactor that enhances the formation of hydrogen and converts the carbon monoxide to carbon dioxide, and, secondly, a $CO_2$-capture unit.

### 3.4.2 Carbon capture potential

The interest of this new technique for $CO_2$-capture has only risen recently with a particular focus on chemical looping on its applications in combustion. The arrangement of the chemical-looping reactors implies that fuel and air are never mixed. It results thus in one stream of depleted-oxygen air from the air reactor and in one of fuel gases consisting of carbon dioxide and steam from the fuel reactor in combustion processes. A further condensation leads to the generation of a highly pure carbon dioxide stream ready for sequestration. One of the main features of chemical-looping combustion is so the inherent $CO_2$-capture without direct losses in efficiency since there is no need to provide additional energy to separate carbon dioxide from the flue gases.

### 3.4.3 Hydrogen generation potential

Hydrogen is a promising energy carrier and its production is growing year after year. Nowadays, it is mainly produced from fossil raw materials though, for instance, hydrocarbons reforming and coal gasification. Fossil fuels are expected to continue to be the main energy source within the next decades: the development of a hydrogen economy in parallel of carbon capture and storage may help increasing the social acceptance and driving towards a more sustainable economy [129; 130].

Chemical looping was originally a technique for hydrogen generation though the steam iron scheme where liquid iron split steam in hydrogen and was used in industrial scale at the beginning of the $20^{th}$ century until it became not economically interesting anymore [31; 120]. The application of chemical looping for hydrogen generation is thus technically feasible and is thermodynamically more interesting with iron-based oxygen carriers [83; 120] and moving-bed reactors [51; 131; 132]. Using chemical looping for both carbon sequestration and hydrogen generation is therefore a possibility and its technical feasibility has been assessed in different studies [133; 134; 135].

### 3.4.4 Integration in power cycles

Chemical looping is applicable in power cycles in many different ways. Most of the chemical looping integrations in conventional power cycles have focused on the chemical looping combustion of natural or synthesis gas as fuel in combined cycles like in NGCC and IGCC and some on the chemical looping gasification of solid fuels such as coal. There are nevertheless several other options to implement chemical looping such as [36]:

- Reforming for solid oxide fuel cells (SOFC)
- Air saturation cycle
- Steam injected gas turbine
- Steam cycle
- Hot air turbine

The different possible implementations of chemical looping in IGCC power plants are developed further in Chapter 5.

### 3.4.5 Process simulation

Studies have been undertaken on process engineering software to get a deeper knowledge about the integration of chemical looping in power cycles, with the following objectives [136; 137]:

- Modelling a chemical looping system in a realistic power cycle
- Exploiting new integration concepts
- Estimating the performances of chemical looping processes
- Investigating the influences of different fuel choices or oxygen carriers
- Identifying suitable operating regimes (temperatures, pressures, etc)
- Discovering possible design and process issues (aside reactions, etc)

Achieving simulations may provide highly relevant information about operating conditions and thus fills the gap between oxygen carrier development and pilot scale studies. However, outcomes are not observed in a real environment: the simulation results depend strongly on the assumptions made and may be unrealistic, especially when it comes to studies on dynamic behaviour and transient state of power cycles [138; 139].

Process simulations showed that even if chemical looping exhibits a higher exergetic efficiency, the comparison between conventional gas turbine cycles and with integrated chemical looping combustion have sensibly the same energy efficiencies, with variations depending on the oxygen carrier and fuel processed [29; 136; 140]. The reason for these similar net energy efficiencies is the following: chemical looping combustion reduces the exergy destruction in the combustion process but most of the exergy savings are in form of chemical exergy [29], which is not usable for power generation, at the difference of physical exergy [141; 142; 143].

Though the net energy efficiencies of gas turbine cycles are similar, with or without integrated chemical looping combustion, the energy efficiency of a power plant with chemical looping combustion is higher than a power plant with conventional carbon capture processes such as pre-combustion decarbonisation [144] or physical absorption [145].

Process simulations of chemical looping combustion in power plants demonstrated that the carbon capture efficiency could reach up to 100%: the efficiency losses are due to eventual gas leakages between the air and fuel reactors. The purity of the carbon dioxide ready to sequestration is usually around 98 to 99% after condensation. This feature of inherent carbon capture is only characteristic of chemical-looping combustion and not of, for instance, chemical-looping gasification. In this last case, the gases from the fuel reactor mainly consist of carbon monoxide and hydrogen, the aim is to separate the hydrogen for use in a combined cycle from the carbon species by use of a water-gas shift reactor followed by a $CO_2$-absorption unit.

They also confirmed that it is possible to generate a high-purity hydrogen stream and to capture the carbon dioxide but that there is a trade-off between $CO_2$ emissions and process efficiency [146]. When applied to the combustion of synthesis gas, the energy conversion efficiency from coal to hydrogen based on the higher heating value can go up to 73-75% with a steam conversion of 60% and a carbon capture efficiency of 100% [131].

### 3.4.6 Large-scale development

Four main European projects have contributed so far to the development of chemical looping:

- GRACE (2002-2008) on gaseous fuels combustion
- ENCAP (2004-2007) on solid fuels combustion
- CLC Gaspower (2006-2008) on chemical looping combustion scaling-up
- ECLAIR (2008-2012) on industrial design of chemical looping power cycles [147]

Out of Europe, there is for instance the Ohio State University (OSU) research group that has developed other concepts and processes axed on chemical looping gasification: the researches were validated with pilot units based on interconnected moving beds but have not yet been extended to a demonstration scale.

At present, the only concept of chemical looping applicable in IGCC processes with $CO_2$ capture and developed further than a pilot scale is the ALSTOM flexible power plant concept [148; 149]. The main feature of this new concept is that both chemical and carbonate looping are implemented in the gasifier. The oxygen carrier used is the system calcium sulphide CaS - calcium sulphate $CaSO_4$ and the carbon carrier is the system calcium oxide CaO - calcium carbonate $CaCO_3$.

The type of chemical looping in this process is thus chemical-looping gasification: chemical looping drives the reactions to the generation of a synthesis gas with a high content of hydrogen and a low content of carbon dioxide and steam. The carbon dioxide is then captured by means of carbonate looping, shifting the equilibrium of the water-gas shift reaction towards the carbon dioxide side. The generated synthesis gas has therefore a high content in hydrogen [148].

The calcium carbonate produced in the gasifier is thereby sent to a calcination reactor in which it is burnt: it decomposes thus into gaseous carbon dioxide at relatively high temperatures (of at least 900°C) and calcium oxide that is re-processed into the gasifier.

This process has two main advantages. First, the produced synthesis gas has a high hydrogen content because the chemical and carbonate looping drive the water-gas shift reaction towards the generation of hydrogen and carbon dioxide. Secondly, the capture of carbon dioxide takes place upstream and eliminates the need for a water-gas shift reactor and an absorption unit [148].

The major drawback of this option is its complexity [22; 148]. The integration of chemical looping in the gasifier is a difficult task because of the slow kinetics of solid-solid reactions and of the risks of contamination by sulphur, halides and ash. The implementation of carbonate looping is a big issue as well because of the affinity of limestone with sulphur species. More generally, handling two solid looping cycles in the same reactor is a great challenge to face.

Regarding the schedule given by ALSTOM on the development of chemical looping, a prototype was already manufactured [150] and the development of demonstration plants is likely to occur after 2012 and of commercial plants after 2017 [151; 152; 153].

### 3.4.7 Economic assessment

The main running cost of chemical looping power cycles may be the oxygen carrier particle cost (supply and synthesis): a way to decrease this cost is to use minerals from the industry, such as ores from the steel plants for example. There may thus be a trade-off between required quality and cost, but the few studies led demonstrated that these industrial products show good reactivity and could be suitable [154].

The economic viability of chemical looping among the carbon capture options and in the current power plants is to demonstrate. It is expected that the investment costs of such technologies may be high and operations of power plants with chemical looping may result in increases of the electricity cost [155; 156]. The use of incentives may thus be necessary to implement chemical looping on the market. However, regarding the fact that all $CO_2$-capture technologies need tax measures for their successful integration, it is more relevant to compare chemical looping to the other capture options. It seems that power plants with chemical looping are more economically interesting because of the lower $CO_2$-allowance price [148; 156].

ALSTOM has actually led a study on the economics of chemical looping with the following assumptions [148] and results:

- Plant size: 400 $MW_e$
- Cost basis: 2006, American dollars
- Coal cost: 1.5 $\$/MMB_{tu}$
- Levelised capital charge: 13.8%
- Capacity factor of the power plant: 85%

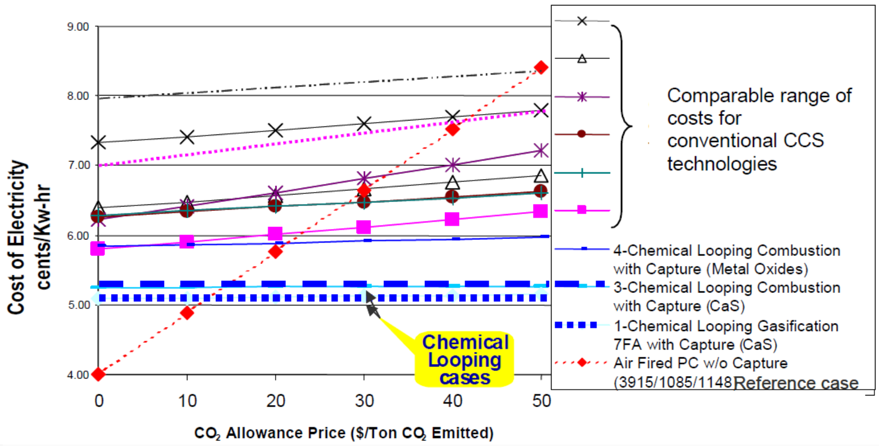

Figure 3.8: Electricity cost for conventional capture technologies and chemical looping [148]

Even if the value of the electricity cost strongly differs depending on assumptions such as the geographical frame and time, the main conclusion is that chemical looping can achieve a lower carbon dioxide avoidance price than the technologies currently present on the market.

## 3.5 Challenges and prospective

Most of the researches have been undertaken on the development of suitable oxygen carriers and experiments partially demonstrated the relevancy and feasibility of chemical looping in a practical scale. Unfortunately, it seems that the most reactive metal oxides that are nickel-based are among the most expensive and most harmful ones. Other oxygen carrier particles have been investigated: iron oxides and new materials such as ilmenite look promising, though less reactive.

Most of the pilot studies are nevertheless limited to chemical looping combustion of gaseous fuels. Extension of this concept to liquid and solid fuels needs further investigations and innovative processes such as chemical looping oxygen uncoupling have been developed to palliate these issues. Chemical looping gasification is a relatively new concept.

Process simulations increased the interest for chemical looping because of its inherent carbon dioxide capture and higher overall energy efficiency than conventional processes. However, chemical looping is still an immature technology. There is almost no real experimental data on long-term operation of continuous chemical looping systems and on off-design behaviour.

Another important point is the difficulty of practical integration of chemical looping in conventional power plants. The currently used gas turbines are manufactured for given operating conditions that may be very different from the optimal operating conditions of chemical looping. For instance, the gas turbine in a conventional gas cycle is designed for combustion flue gases, which have a strongly different composition than oxygen-depleted air [105]. Another issue related to the gas turbines is that the compressor, the combustion chamber and the turbine are generally arranged in a single unit. In chemical looping combustion of synthesis gas, as presented later, the combustion takes place in two reactors independent of the turbine unit. It may thus be a major issue to adapt chemical looping to the conventional mechanical equipments and power plants.

A few pilot plants were designed and built by several laboratories in Europe, America and Asia but there is no large-scale application, though it is expected to arise with the ALSTOM research program [148]. There are economy issues to deal with before it becomes competitive among the carbon capture options and the current power plants. Though the integration of chemical looping avoids the construction of a costly post-combustion unit, the costs related to the oxygen carrier material may be particularly high, especially if metal oxides such as nickel are used.

Chemical looping is thus in the agenda towards a sustainable $CO_2$-free economy although it is hard to foresee when it will become suitable for commercial applications.

# Chapter 4

# Carbonate looping processes

## 4.1 Carbonate looping principle

Chemical and carbonate looping are based on two different fundamental concepts. Chemical looping uses oxygen carriers to avoid a direct contact between the reactants and, in the case of combustion, to avoid the mixing of carbon dioxide with other species. On the opposite, carbonate looping uses solid carriers to remove in situ the carbon dioxide produced in the power processes or ex situ in the flue gases. The capture of carbon dioxide is driven by two intermediary reactions:

- Carbonation of the metal oxide in a given process reactor
- Calcination of the metal carbonate in a regeneration reactor

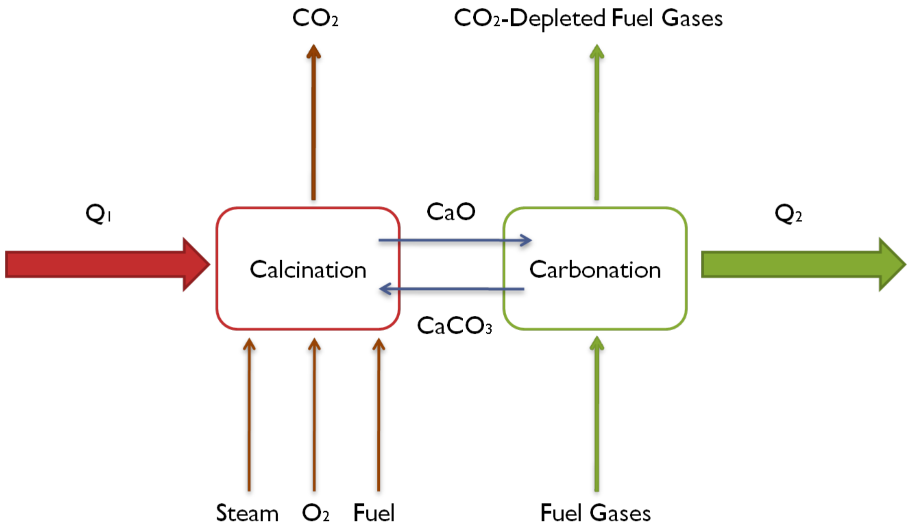

Figure 4.1: Carbonate looping principle

Whereas the carbonation reaction is exothermic, the reverse reaction, i.e. calcination reaction of the metal carbonate in the regeneration reactor is endothermic. It is therefore critical to achieve an efficient heat integration of this process to reduce the energy penalties due to the high operating temperatures needed in the regeneration reactor.

The fact that carbon dioxide is removed in situ and is not inherently separated from the flue gases involves that metal oxides with high sorption capacity are needed in the carbonation reactor to capture carbon dioxide and to reach a high purity for further sequestration.

Various possible applications of carbonate looping in power and cement processes have been investigated and it appears that it is feasible to implement this carbon capture technique as a pre- or as a post-combustion step. In general, a typical carbonate looping cycle of gaseous fuel follows this reaction scheme. The metal oxide reacts with carbon dioxide, producing a metal carbonate.

$$\mathrm{Me_xO + CO_2 \rightleftharpoons Me_xCO_3} \tag{4.1}$$

The outlet stream is biphasic and contains a solid phase with metal carbonate and unconverted metal oxide. In practice, the solid phase contains some metal sulphides and chlorides as well because of the contamination of the metal oxide by sulphur and halides and, in the case of carbon dioxide removal in situ, some metal oxide particles covered by a layer of ash.

These degradations of the sorbents lead further to reactivity losses and to necessary make-ups. The metal carbonate formed is thereby sent to the calcination reactor where the reverse reaction occurs:

$$\mathrm{Me_xCO_3 \rightleftharpoons Me_xO + CO_2} \tag{4.2}$$

However, for practical issues such as sintering and reactivity losses through several cycles, steam is often introduced in the carbonate looping system and thus an intermediate hydration-dehydration step should be considered:

$$\begin{aligned} \mathrm{Me_xO + H_2O} &\rightleftharpoons \mathrm{Me_x(OH)_2} \\ \mathrm{Me_x(OH)_2 + CO_2} &\rightleftharpoons \mathrm{Me_xCO_3 + H_2O} \end{aligned} \tag{4.3}$$

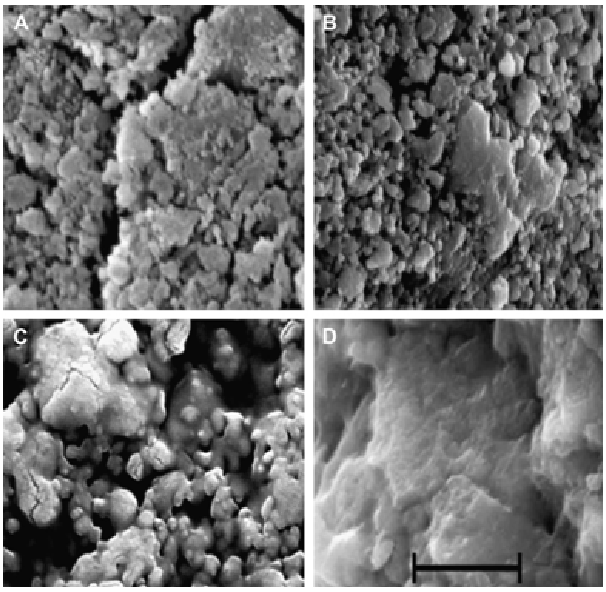

Figure 4.2: SEM-images of carbonate looping particles (limestone)

## 4.2 Carbonate looping materials

### 4.2.1 Requirements

At the difference of chemical looping, the choice of metal oxides is rather limited. The most known metal oxides that have the capacity of absorbing carbon dioxide are zinc, manganese, magnesium, calcium, lithium, strontium and lead. The criteria to satisfy for a metal oxide used in $CO_2$-capture are [22; 157]:

- Suitable calcination temperature
- High reactivity with $CO_2$ in the process temperature range
- Low decay in reactivity over cycles
- Resistance to sintering
- Resistance to poisoning
- Low cost
- Low environmental impact

A compromise has to be found between the heat quality and the heat needed for the calcination reaction. Carbonate looping has two limitations regarding the $CO_2$-capture efficiency. The first one is a thermodynamic-equilibrium constraint: at a given temperature, the maximum amount of carbon dioxide reacting with oxides is limited by the equilibrium of the carbonation reaction. The second one is more related to kinetics and reactor issues: for a given conversion one wants to achieve, the carbon dioxide carrier has to be reactive enough to avoid huge solid flow rates and large reactor designs. The work carried out on carbonate looping has not focused on the development of carbon dioxide carriers but more on the research of suitable kinds of calcium carbonates (limestone, dolomite, synthetic sorbents...) and proper preparation methods (synthesis...).

### 4.2.2 Decomposition temperature and reaction enthalpy

The thermal properties of several carbon carriers are presented in Table 4.1.

Table 4.1: Decomposition temperature & reaction enthalpy of various carbonates [22]

| **Reaction** | **Decomposition temperature** [°C] | **Reaction enthalpy $\Delta_r H$** [kJ/mol] |
|---|---|---|
| $\mathbf{ZnO + CO_2 \rightarrow ZnCO_3}$ | ~ 300 | ~ -70 |
| $\mathbf{MnO + CO_2 \rightarrow MnCO_3}$ | ~ 300 | ~ -110 |
| $\mathbf{PbO + CO_2 \rightarrow PbCO_3}$ | 315 | ~ -95 |
| $\mathbf{MgO + CO_2 \rightarrow MgCO_3}$ | 540 | -118 |
| $\mathbf{CaO + CO_2 \rightarrow CaCO_3}$ | 850 | -178 |
| $\mathbf{Li_2O + CO_2 \rightarrow Li_2CO_3}$ | 1310 | ~ -230 |
| $\mathbf{Sr + CO_2 \rightarrow SrCO_3}$ | ~ 1350 | ~ -240 |

Metal oxides with a low decomposition temperature are not suitable because they may capture and release carbon dioxide in the same reactor [157]. Moreover, a low decomposition temperature implies that carbonation occurs at even lower temperatures: it is thereby kinetically unfavoured and energy generated by this exothermic reaction is low-grade heat, which makes it less interesting in the overall process [22]. Sodium, manganese, copper, magnesium, zinc and lead carbonates have calcination temperatures between 150 and 550°C [22] and are thus not suitable.

However, metal carbonates that start decomposing at high temperatures such as lithium and strontium carbonates are not desired since more heat needs then to be provided. This high-grade heat usually comes from combustion of fuel in pure oxygen to produce a pure carbon dioxide stream, which means that the energy demand of the air separation unit increases and so does the energy consumption of the process [22].

Calcium carbonate has a decomposition temperature around 850-900°C, the exact value depending on the partial pressure of carbon dioxide in the atmosphere considered [22]. It has therefore been the most studied and employed metal oxide for carbonation cycle applications. The main reactions involved are then:

$$\begin{aligned} \mathrm{CaCO_3} &\rightleftharpoons \mathrm{CaO} + \mathrm{CO_2} \\ \mathrm{Ca(OH)_2} &\rightleftharpoons \mathrm{CaO} + \mathrm{H_2O} \\ \mathrm{Me_x(OH)_2} + \mathrm{CO_2} &\rightleftharpoons \mathrm{Me_xCO_3} + \mathrm{H_2O} \end{aligned} \tag{4.4}$$

### 4.2.3 Thermodynamic and equilibrium constraints

A key issue in carbonate looping is to maximise the removal of carbon dioxide in the carbonation reactor. The phase equilibrium diagrams illustrate the relationship between the partial pressures of the chemical species present in the system and the reaction equilibrium temperatures.

The carbonation reaction, in carbonate looping cycles for pre-combustion $CO_2$ capture, usually takes place in parallel of the water-gas shift reaction. The main reason is that the first reaction leads to a decrease of the partial pressure of carbon dioxide in the WGS reactor, the equilibrium constant of this system is thus much higher in the usual operating range of temperatures and pressures and this process has therefore a higher hydrogen yield.

The calcination reaction occurs only if the carbon dioxide partial pressure is lower than the equilibrium partial pressure. In the cases of carbonation and hydration, the partial pressures that should be considered in the thermodynamic analysis are so steam and carbon dioxide ones. Low temperatures favour hydration and carbonation and high ones favour the reverse reactions.

The reactor design is of importance because it has a direct influence on the partial pressures of carbon dioxide and steam and thus on the equilibrium temperatures of carbonation and hydration reactions. For instance, the equilibrium partial pressure of carbon dioxide in a synthesis gas from a slagging moving bed gasifier is usually much lower than from a slurry entrained flow reactor, which means that the operating temperature in the carbonation reactor should be lower in the second case to drive the reaction towards the generation of calcium carbonates.

### 4.2.4 Decay in reactivity over cycles

The reactivity of calcium sorbents over repeated cycles of calcination and carbonation is a key issue. Kinetic studies of these reactions showed that the carbon dioxide carrying capacity decreases strongly with the number of cycles to around 10% of its initial value. These losses in reactivity have been the main point of investigation of carbonate looping research [158]. A full understanding of this phenomenon needs comprehension of the mechanisms implied in the reactions. The carbonation reaction, i.e. the reaction between calcium oxide and carbon dioxide, can be divided in two stages:

- Fast carbonation stage kinetically controlled
- Slow carbonation stage diffusion controlled

Calcination is a relatively fast reaction: for instance, the calcination of a 0.5 mm particle lasts around 50 seconds whereas sulphation reactions last around 1200 seconds [41]. Experiments showed that the decay of calcium oxide conversion over carbonation and calcination cycles is mainly due to a decay of calcium oxide conversion over the first stage [158].

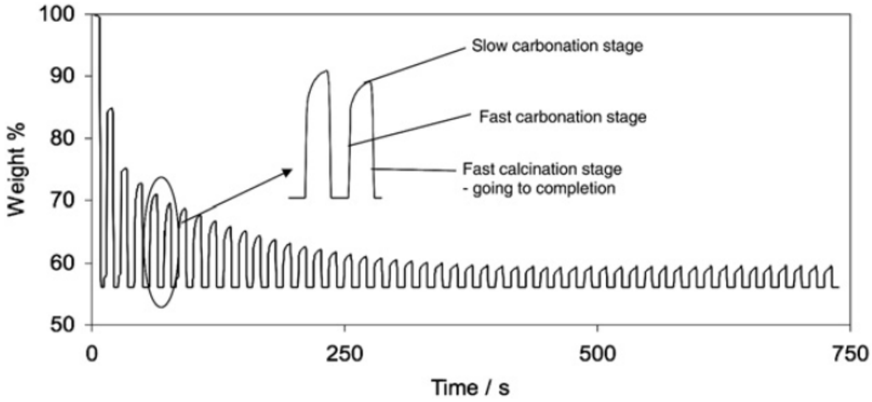

Figure 4.3: Kinetics of carbonation and calcination [158]

Calcium carbonate is three times bigger in volume than calcium oxide; therefore, the formation of a calcium carbonate layer on the calcium oxide particles reduces the reactive surface area and impedes the diffusion of carbon dioxide. It explains then the transition from a fast kinetically controlled stage to a slow diffusion-controlled one. This obstruction of pores is only reversible to some extent, which means that the particle porosity will continue decreasing with operations, leading to a reactivity drop-off [158; 159]. The sharp reactivity over the cycles decay is also due to a decrease of porosity during calcination. The high temperature required to drive this reaction favours sintering, i.e. pore shrinkage and grain growth. There is so an increase in meso-porosity and a decrease in micro-porosity [160].

The temperature conditions during calcination and carbonation have thus a strong impact on the regeneration of the sorbent particle and on its reactivity. However, other factors such as sintering and poisoning explain these losses in reactivity [161].

It is desirable that the sorbent particle can undergo a large number of carbonate looping cycles without high reactivity losses to avoid frequent wastes and large make-ups, which would be costly.

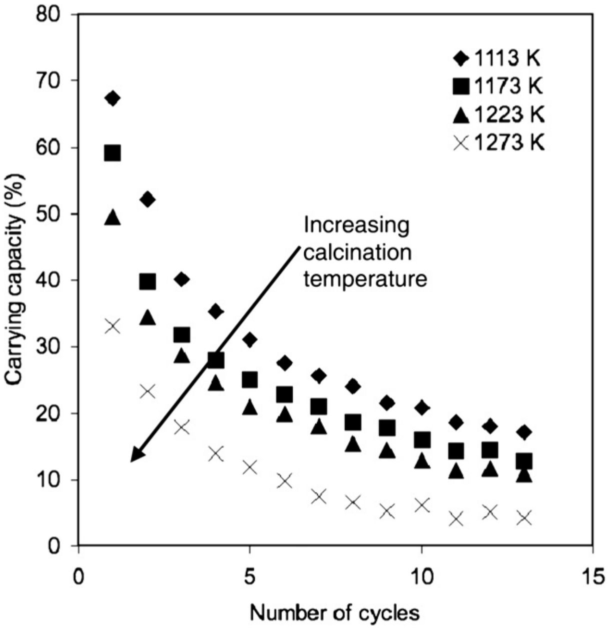

Figure 4.4: Impact of calcination temperature on calcium oxide carrying capacity [158]

The durability of the carbon carrier particle depends strongly on the syntheses and preparation techniques used [22] such as thermal pre-treatment and doping [162]. Another way to restore sorbent reactivity is to hydrate the calcium oxide particles into calcium hydroxide $Ca(OH)_2$ in a separate and thus third reactor [163].

### 4.2.5 Attrition and sintering

Other factors that amplify the sintering effect are high calcination durations, high steam and carbon dioxide partial pressures and presence of impurities. The duration of the calcination is usually not a big issue because the rate of this stage is usually high and the addition of steam is in fact beneficial for the overall system. Though sintering is favoured at high steam partial pressures, the introduction of steam during calcination decreases the temperature and the partial pressure of carbon dioxide, resulting globally in a lower sintering effect. The decrease of carbon dioxide partial pressure has also a positive effect in the sense that the calcination rate is therefore higher when the carbon dioxide partial pressure is much lower than the equilibrium vapour pressure [22; 158].

Another suggestion to decrease the sintering impact is to operate calcination in a vacuum, so at lower pressure and temperatures [22]. Finally, another option is to operate calcination in nitrogen to reduce the partial pressure of steam and carbon dioxide, but it leads to surface area losses. Even if sintering is reduced by operating at lower temperatures and pressures, or with steam, the sorption capacity of the calcium sorbent is expected to decrease. Researches on synthetic sorbents and on activation pre-treatment like sorbent doping [162] have been led to study how to counter this effect [164; 165].

### 4.2.6 Poisoning issues

Contamination of calcium oxides is one of the main issues in carbonate looping because it leads to reactivity losses and lower carbon dioxide capture efficiency. Carbonation and hydration reactions usually compete with reactions involving sulphur compounds.

$$\mathrm{CaO + 2\,HCl \rightleftharpoons CaCl_2 + H_2O} \tag{4.5}$$

The affinity with sulphur has been exploited for capture of sulphur in situ with fluidised beds of limestone [166]. An idea that has been raised is to capture both carbon dioxide and sulphur in the same reactor to reduce the requirements for a sulphur-cleaning unit and to produce a pure hydrogen stream. However, sulphur poisoning leads to a sharp decrease of the carbon dioxide carrying capacity of calcium oxides and so to a degradation of the sorbent. Several sulphur species present in flue gases from combustion such as sulphur dioxide and in synthesis gases from gasification such as hydrogen sulphide can react with the calcium-looping particle. The reaction of sulphur dioxide with calcium oxide, called indirect sulphation, occurs when the partial pressure of carbon dioxide is higher than the equilibrium vapour pressure of carbon dioxide.

$$\mathrm{CaO + SO_2 + \frac{1}{2}O_2 \rightleftharpoons CaSO_4} \tag{4.6}$$

On the opposite, the reaction of sulphur dioxide with calcium carbonate, called direct sulphation, occurs when the partial pressure of carbon dioxide is lower than the equilibrium vapour pressure of carbon dioxide.

$$\mathrm{CaCO_3 + SO_2 + \frac{1}{2}O_2 \rightleftharpoons CaSO_4 + CO_2} \tag{4.7}$$

The reaction of calcium oxide with hydrogen sulphide is favoured at higher temperatures and lower steam partial pressures:

$$\begin{gathered}\mathrm{CaO + H_2S \rightleftharpoons CaS + H_2O}\\ \mathrm{CaCO_3 + H_2S \rightleftharpoons CaS + H_2O + CO_2}\end{gathered} \tag{4.8}$$

The reaction of calcium oxide with carbonyl sulphide is favoured at higher temperatures and higher carbon dioxide partial pressures as highlighted here:

$$\mathrm{CaO + H_2S \rightleftharpoons CaS + H_2O} \tag{4.9}$$

The formation of calcium sulphate is detrimental for the carbonate looping cycle for two reasons. First, the sulphation reactions compete with the carbonation and calcination ones, leading to sorbent losses. Secondly, the calcium sulphate has a higher molar volume than calcium oxide and carbonate, which results in the formation of this layer on the calcium looping particles and lowers the porosity. In theory, the calcium sulphate can be converted to calcium oxide but the operating temperature needed is far above the optimum calcination temperatures and is thus considered as detrimental for the carbonate looping system. Formation of calcium sulphate is thereby considered as sorbent losses and make-up need so to be done to replace it.

Several ways to avoid reactions with sulphur and the generation of calcium sulphides have been investigated. One way is to use spent sorbent to capture the sulphur before using the calcium looping particle. Another way is to hydrate the calcium oxide particles with steam to improve the reversibility of the carbonation and calcination reactions. The presence of a desulphurisation unit before the carbonate looping one may also present beneficial effects because it would reduce the fate of sulphur.

Contamination by halides is an issue as well which has been less studied because of the small amount of chlorine compounds in flue and synthesis gases. As with hydrogen sulphides, this reaction is favoured at high temperatures and high steam partial pressures.

$$\mathrm{CaO} + 2\,\mathrm{HCl} \rightleftharpoons \mathrm{CaCl_2} + \mathrm{H_2O} \tag{4.10}$$

Poisoning of calcium oxides by solid carbon is unlikely to happen because of the high temperature around 2000°C usually required.

$$\mathrm{CaO} + 3\,\mathrm{C} \rightleftharpoons \mathrm{CaC_2} + \mathrm{CO} \tag{4.11}$$

### 4.2.7 Cost issue

The overall sorbent cost for carbonate looping depends strongly on which kind of calcium oxide is used. Natural sorbents such as limestone are widely available and have low costs whereas synthetic ones have high preparation cost. However, these last have a higher reactivity and there is a need to achieve studies to investigate which option is the most promising.

Synthesis of the most interesting sorbents may be based on precipitation preparation methods and cheap simple materials, which might be a driving force towards the use of synthetic sorbents. Finally, carbonate looping needs to be competitive against commercially proven technologies such as absorption or adsorption techniques in pre-combustion [157] and monoethanolamine absorption in post-combustion [167].

### 4.2.8 Comparison of the sorbents

Calcium carbonate is widely available on natural state in the form of limestone, which has therefore been the most employed sorbent for carbonate looping cycles. Other sorbents such as dolomite and lithium orthosilicate have also been considered for carbonate looping [168].

Dolomite is a natural sorbent with both calcium and magnesium oxides and has a higher initial porosity and thus reactivity than limestone. Moreover, magnesium oxide has a higher melting point than calcium oxide, reducing thus the sintering effect during calcination and therefore the reactivity decay. Finally, magnesium oxides are believed to stabilize the structure of dolomite compared to limestone, having thus a higher thermal and mechanical stability over the cycles [168]. However, regarding the equilibrium phase diagram of magnesium oxide, carbonation, at atmospheric pressure, takes place at around 385°C while it takes place at around 650°C for calcium oxides. Magnesium oxides do therefore not contribute to the absorption of carbon dioxide [168].

The development of synthetic sorbents that do not present the drawbacks of natural ones has become an issue recently, with for instance works on lithium orthosilicate. Its reaction rate towards carbon dioxide is high and its long-term reactivity is about four times higher than natural limestone [168].

## 4.3 Carbonate looping reactor technology

The development of carbonate looping benefits from the returns of experience gained with the development of sulphur removal by limestone. The use of calcium sorbent for the absorption of sulphur in fluidised beds is a mature technique already applied in current power plants [41]. As in chemical looping applications, the fluidised bed technology is often considered as the most suitable type of reactor for carbonate looping applications [169; 170; 171]. Only a few studies have been carried out on the applications of carbonate looping in pre-combustion capture but the ones done suggest the use of a circulating fluidised bed as well [22; 158].

The inherent advantage of excellent gas-solid mixing which enhance the reactivity of calcium oxide towards carbon dioxide and which ease the temperature control in the reactor has been a decisive factor towards this choice. Moreover, the carbon dioxide sorbent, i.e. the calcium oxide, is circulating between the carbonation and the calcination reactors: since both reactors are fluidised beds, the choice of a dual fluidised bed seems therefore reasonable [171]. There are several different types of dual fluidised bed reactors suitable for carbonate looping [171]:

- Dual bubbling fluidised bed
- Dual high-velocity fluidised bed
- Bubbling bed as carbonator and high velocity bed as calcination reactor
- Bubbling bed as calcination reactor and high velocity bed as carbonator

Bubbling and high-velocity beds present both great advantages that would make them suitable for carbonate looping applications. The gas-solid contact and therefore the mass transfer are better in a bubbling fluidised bed reactor. Since the carbonation and calcination reactions are limited by a thermodynamic equilibrium, the choice of a bubbling fluidised bed seems judicious because this type of reactor has higher conversion efficiency. Moreover, the better heat transfer due to the higher heat capacity of bubbling beds is favourable to calcination since this reaction is strongly endothermic and thus requires a large amount of heat. However, the high-velocity fluidised bed reactors are more appropriate when processing large gas flow rates, which is usually the case in an industrial scale with the current power plants. It is thus critical to design properly the risers to reach high conversion efficiency and to process carbon-looping particles highly resistant to attrition.

Since the most appropriate reactors for carbonate looping applications are circulating fluidised beds, as it is the case as well for chemical looping, the theory behind such as design parameters is the same. There are small-scale pilot plants operating at the following places [173]:

- University of Stuttgart with sponsoring of EnBW [174]
- Spanish Research Council [170]
- University of Darmstadt [172]
- CANMET Energy Technology Centre, where carbonate looping has been experimented on synthesis gas with success [175]

## 4.4 Carbonate looping power cycles development

### 4.4.1 Energy efficiency

Carbonate looping involves an energy penalty due to the strong endothermic feature of the calcination reaction. The arrangement of the carbonation and calcination reactors in the overall process is thus critical to reduce the heat demand of the calcination reaction. A part of the heat needed comes from the circulation of the calcium particle between both reactors but most of it generally comes from the combustion of fuel in pure oxygen, which implies a higher demand for the cryogenic air separation unit.

### 4.4.2 Carbon capture potential

The carbonate looping processes are limited in carbon dioxide capture efficiency by the thermodynamic equilibrium of the carbonation reaction and by the reactivity of the sorbent. It is thus not theoretically possible to reach 100% capture of carbon dioxide, at the opposite of chemical looping processes that are characterised by inherent carbon dioxide sequestration.

### 4.4.3 Hydrogen generation potential

Carbonate looping, when integrated as a pre-combustion process only, has a high potential for high-purity hydrogen. This hydrogen stream can be, depending on the case, be sent to a combined cycle in which it would be burnt, expanded and cooled. Another possibility is to send the hydrogen stream to a fuel cell and there would so not be co-generation but tri-generation instead with electricity, heat and hydrogen as process products [158].

### 4.4.4 Process integration in power plants

Carbonate looping may be either implemented as a pre- or a post-combustion process in coal-fired power plants [24]. Carbonate looping in pre-combustion processes, and thus, in gasification systems, aims to remove the carbon dioxide from the synthesis gas. It shifts the equilibrium of the water-gas reaction towards the products side (i.e. carbon dioxide and hydrogen), leading to the production of a hydrogen rich synthesis gas when it is applied before or during the shift reaction [158] and captures carbon dioxide when it is applied after.

Several ways have been investigated to promote thus the generation of hydrogen: carbonation can either take place in situ, i.e. in the gasification reactor itself or in the water-gas shift reactor [157; 158]. It may be more difficult to handle the carbonation reaction directly in the gasifier reactor since it will increase the complexity of the system with several parallel reactions and ash and sulphur fates will become of importance [176].

Carbonate looping in post-combustion processes actually consists of flue gas cleaning. The product gases from the combustion reaction go through a bubbling fluidised bed of calcium oxide where carbon dioxide is removed by carbonation [169; 177]. Post-combustion is also applicable in IGCC power plants: it is the case when carbonate looping aims to remove carbon dioxide from the flue gases after they run through the gas turbine cycle.

### 4.4.5 Process simulation

The studies carried out on process engineering software have as objectives:

- Modelling a carbonate looping system in a realistic power cycle
- Exploiting new integration concepts
- Estimating the energy penalties of carbonate looping processes
- Estimating the potential for $CO_2$ capture
- Identifying suitable operating regimes (temperatures, pressures, etc)

Most of the simulations achieved on carbonate looping processes focused on their integration for flue gas treatment and so on post-combustion capture [178]. However, the ones led on their integration as a pre-combustion capture process showed that carbonate looping has a high potential in efficiently removing carbon dioxide for a limited energy penalty [158].

The estimations of the energy penalty for carbonate looping have been only achieved on simulations of post-combustion capture but are expected to be in the same range when applied as a pre-combustion capture method. The main energy penalty of this process is due to the need for pure oxygen or, at least, high-temperature steam, to provide the heat necessary to drive the calcination reaction. It is higher than in chemical looping systems but is lower than conventional post-combustion capture processes such as amine scrubbing. Rough estimations of the efficiency drop are usually 3 to 8% without considering the energy penalty for the carbon dioxide compression, compared to amine scrubbing with an efficiency penalty of 8 to 10% [167; 179].

The carbon capture efficiency cannot reach 100% because of thermodynamic and equilibrium limitations of the carbonation/calcination reaction and of the water gas shift reaction. It is estimated to around 90-92% but the purity of the carbon dioxide stream ready for sequestration can reach 98-99% after condensation [158; 172]. Process simulations confirmed as well that carbonation enhances in parallel the generation of hydrogen by shifting the equilibrium of the water gas shift reaction. It seems therefore possible to generate a hydrogen stream with a steam-to-hydrogen conversion up to 65% and a purity of 90% [22; 158].

### 4.4.6 Large-scale development

There is so far no large-scale development or industrial application of carbonate looping in power plants: the only use of calcium oxide as sorbent in power plants is for sulphur removal present in flue gases. Projects such as CaOling that are funded by the European Community's program have as final aim the development of a demonstration plant by 2012 [180]. It should nevertheless be pointed up that, at present, these researches and development programs deal exclusively with post-combustion carbonate looping because of its ease of retrofit [181]. It seems thus that carbonate looping would more probably be integrated this manner [158; 179].

However, one of the key points for a successful integration of carbonate looping technology at a large scale, independent of the fact that it is integrated as pre- or post-combustion capture, is its potential synergy with cement industry [158; 182].

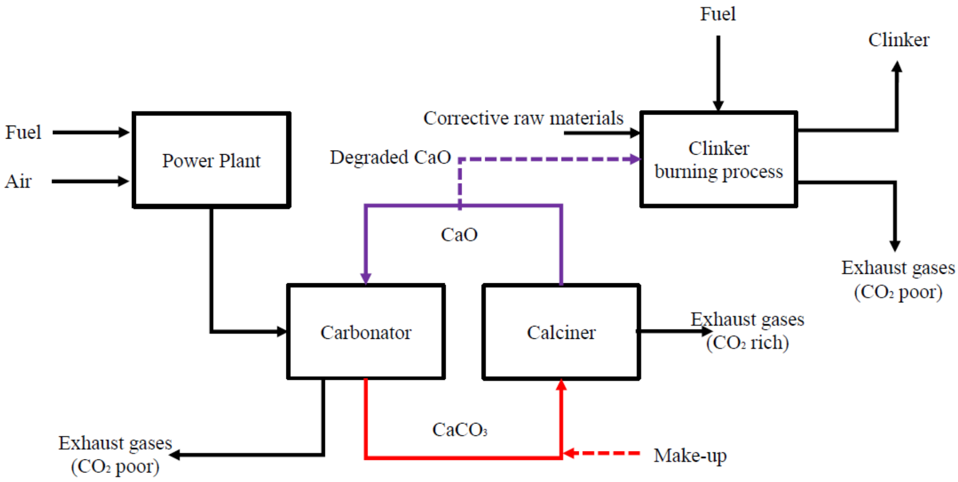

Figure 4.5: Synergy of carbonate looping process with power plant and cement industry (adapted from [183])

This synergy between power plants and cement industries has been mostly investigated for applications of post-combustion carbonate looping but the idea stays similar for pre-combustion [148; 182]. This type of process industry requires large amounts of calcium oxide to produce cement: integrating carbonate looping in a power plant in parallel of cement manufacturing would therefore decrease the carbon dioxide emissions from both industries and reduce the carbonate looping costs [158; 179]. Carbonate looping as a pre-combustion capture process is theoretically applicable in a power plant with synergy with cement industry but is not compatible with existing clinker burning processes and requires [184]:

- New burner for hydrogen combustion
- Adequate recovery system to provide heat to the gasification reactions

However, the produced cement may have a lower quality and be expensive, and, in pre-combustion, only the carbon dioxide emissions from the fuel are reduced, not the ones from the processes [184].

### 4.4.7 Economic viability

The calculation of the $CO_2$-abatement cost in carbonate looping processes is a difficult task. An economic evaluation of carbonate looping for post-combustion capture gave a rough estimation of 10-15 euros per tonne of carbon dioxide avoided [179; 185]. None was done on pre-combustion capture though it was estimated that combining pre-combustion carbonate looping and cement industry would increase the cement production costs of 4-55 euros per tonne of carbon dioxide avoided [184].

## 4.5 Challenges and prospective

Most of the researches carried out on carbonate looping have focused on the improvement of the carbonate looping particle with a particular matter to reactivity losses. Unfortunately, the most available and cheapest calcium-based sorbents are the most concerned by the deactivation and degradation issues over the looping cycles. The ideal type of reactor for carbonate looping applications is a dual fluidised bed, as it is the case in chemical-looping applications too. This technology is well known and the injection of calcium sorbent into fluidised beds has already been used as a sulphur capture process. The different possible applications were investigated, with a strong focus on flue gases cleaning in post-combustion process. Using carbonate looping as a pre-combustion method, for instance, has been less investigated and meets the problems of direct contact with contaminants and difficult synergies with cement industry.

Only laboratory and pilot experiments were led, carbonate looping processes have not been applied in demonstration plants or in an industrial scale. Carbonate looping may become a decisive technology in the field of carbon capture and a step further in the development of carbonate looping may be the ALSTOM process. At the difference of chemical looping, carbonate looping does not present the advantage of inherent carbon dioxide sequestration. Another drawback is the strong endothermic feature of the calcination reaction, which requires thus heat usually provided by fuel combustion in pure oxygen. The overall process and carbon capture efficiencies are thus lower. The great advantages of carbonate looping compared to the other carbon capture options in pre-combustion are nevertheless the ease of hydrogen production, the lower energy penalty and the availability and cost of the sorbents.

Regarding the economics of carbonate looping, the costs related to the carbon dioxide carrier material may be the highest ones, especially if synthetic materials are used. It is thus of importance to develop suitable sorbents with cheap preparation methods. Moreover, a possible solution is the sale of spent sorbents to the cement industry, which would thus be favourable to the economy of the carbonate looping systems.

Carbonate looping is an immature technology: more and more solutions are investigated so that it can compete with mature technologies, especially when paying attention to pre-combustion capture.

# Chapter 5

# Solid looping cycles in IGCC power plants

## 5.1 Reference system: IGCC with $CO_2$ capture

The Integrated Gasification Combined Cycle (IGCC) is a technology based on gasification processes and combined cycles: solid fuels such as coal or biomass are converted into a synthesis gas that feeds a combined cycle, generating electricity by running through a gas turbine and recovering waste heat by passing a heat recovery steam generator. In general, an intermediate gas cleaning step is implemented between the gasification and combined cycle to decrease the concentration of harmful pollutants. A conventional IGCC with $CO_2$ capture has the process configuration shown in Figure 5.1.

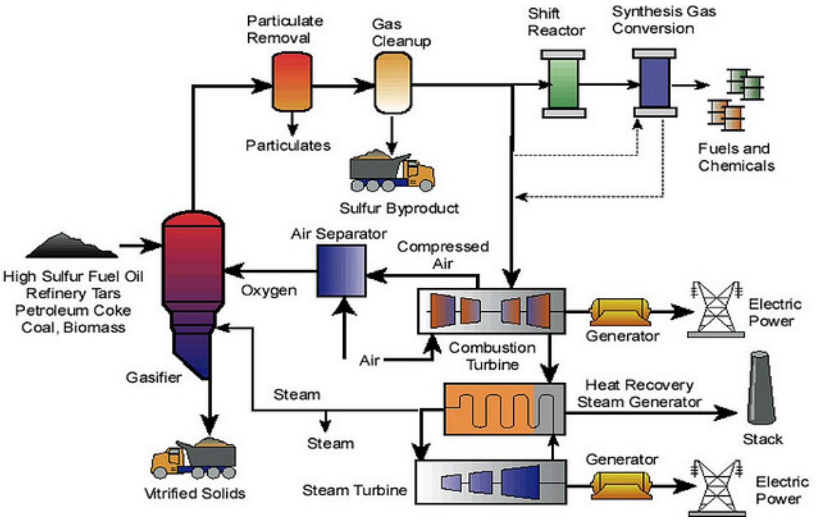

Figure 5.1: Conventional IGCC power plant

The main features of IGCC power plants compared to conventional power generation processes are:

- Higher overall process efficiency
- Higher capital cost

- Lower emissions of pollutants such as sulphur dioxide
- Potential for a low-cost carbon dioxide capture

Integrated gasification combined cycle power plants have the potential to achieve a relatively cheap and efficient carbon capture compared to the conventional power plants. However, their complexity and the issues with their flexibility have been an impediment to their expansion on the power plants market. The choice of the different technologies and their successful operation depend strongly on their integration and synergy between each other [186; 187]. It is therefore necessary to use optimization tools to achieve efficient energy integration and therefore improve the overall energy efficiency. Process simulation studies revealed that there are trade-off between efficiency and $CO_2$ capture and that pinch analysis is a proper way to find an optimum design [188].

An air separation unit separates by cryogenic distillation atmospheric or compressed air into oxygen and nitrogen. The gasifier uses then this oxygen stream to oxidise partially the solid fuel at high pressures (30-80 bars) and at high temperatures (500-1500°C). The hot raw synthesis gas, mainly composed of carbon monoxide and hydrogen, runs through a cooler such as a water quench unit or a heat recovery system: the temperature drops to around 300-500°C and the alkali compounds condense to a solid phase. This cold raw synthesis gas passes the cleaning system that includes a candle filter or a water scrubber to remove ash and particulates and the absorption and Claus treatment systems to remove the sulphur compounds.

There are several variants in the configuration of this part of the IGCC process regarding the type of cleaning unit that is used. However, it is particularly essential to achieve the removal of the different impurities present in the hot raw synthesis gas. Since only pure oxygen and not air enters the gasifier for the partial oxidation reaction, the nitrogen compounds, usually hydrogen cyanide HCN and ammonia $NH_3$, that are present in the synthesis gas, originally come from the solid fuel fed and are thus in relatively low quantities.

The water-scrubbing unit usually removes efficiently these compounds because of their very high solubility in water. Considering the chlorine compounds such as hydrogen chloride HCl and ammonium chloride $NH_4Cl$, the water-scrubbing unit has as well the potential to remove most of these pollutants. In general, the Claus treatment, also called acid gas removal process, has the potential to remove up to 99.8% of the sulphur compounds present in the synthesis gas as hydrogen sulphide $H_2S$ and carbonyl sulphide. Finally, the other pollutants such as lead, mercury and arsenic, which are present in varying amounts depending on the solid fuel processed, generally deposit as solids in the candle filter.

The clean and cold synthesis gas resulting of the cleaning system usually has a low temperature around 50-300°C and burns in compressed air in the gas turbine system. The exhaust gases produced with a temperature of at least 600°C run though a heat recovery steam generator. The hot steam generated at different pressure levels enters a steam turbine cycle, generating extra-electricity and heat.

The design of the IGCC power plant with $CO_2$-capture is sensibly the same, with the presence of a gasifier, a synthesis gas cleaning process and a combined cycle. The main difference lies in the addition of two components that are the water-gas shift reactor, where extra-steam converts carbon monoxide into carbon dioxide and hydrogen, and a

$CO_2$-capture unit, based on chemical or physical absorption to remove the carbon dioxide from the synthesis gas. Usually, the integration of carbon dioxide capture leads to lower electrical efficiency and higher cost. The estimations depend strongly on the considered base case and on the assumptions done. However, based on the Puertollano power plant and on methanol absorption, the losses in efficiency are about 4 to 5% [15] and the increases in electricity cost by 25 to 40% [189].

The reference system considered in this thesis is an IGCC with carbon dioxide capture initially integrated with the following features:

- Conventional gasification system: air separation unit and gasifier
- Water quench and water-gas shift reactor
- Selective catalytic reduction and Claus treatment
- Combined cycle
- $CO_2$ drying and compression system

The main point of this thesis is to check the possibilities of integrating chemical and carbonate looping cycles into this type of power plants, to evaluate the potential for $CO_2$-capture and to estimate the induced losses in energy efficiency. There are several possible combinations as presented in the next sections but only some of them have been developed further than at a process simulation scale. The different possibilities are thus examined and compared at the end of this chapter regarding their current level of technology, their technological interest, etc.

## 5.2 IGCC with chemical-looping for oxygen uncoupling (ASU)

In conventional IGCC power plants, whether their design includes a $CO_2$ capture unit or not, an air separation unit, usually a cryogenic distillation device, provides the oxygen needed in the gasification step. Air is liquefied in different steps at a pressure about 5-10 bars to very low temperatures and oxygen is separated from other components such as nitrogen and argon by distillation.

This process component is one of the most costly and energy-intensive part of the gasification power plants. The power required to drive the unit varies between 5 and 7% of the gross generator output of an IGCC power plant and the overall energy efficiency penalty induced is around 10-15%. Economic evaluations of IGCC power plants estimate the initial cost of the air separation device to between 10 and 15% of the total capital cost of the power plant and this unit notably contributes to the overall running costs [58; 104].

The other air separation methods are membrane separation (ion-transport) and water electrolysis but most of them are still immature and present the drawback of either being costly or energy-intensive. Chemical looping is still an immature technique but has the potential to separate oxygen out of air and thus to replace the conventional cryogenic distillation process at a lower economic and energetic cost.

It is therefore possible, in theory, to replace the air separation unit by a chemical looping one, as shown in Figure 5.2. The type of chemical looping that is of interest in this case is chemical looping uncoupling.

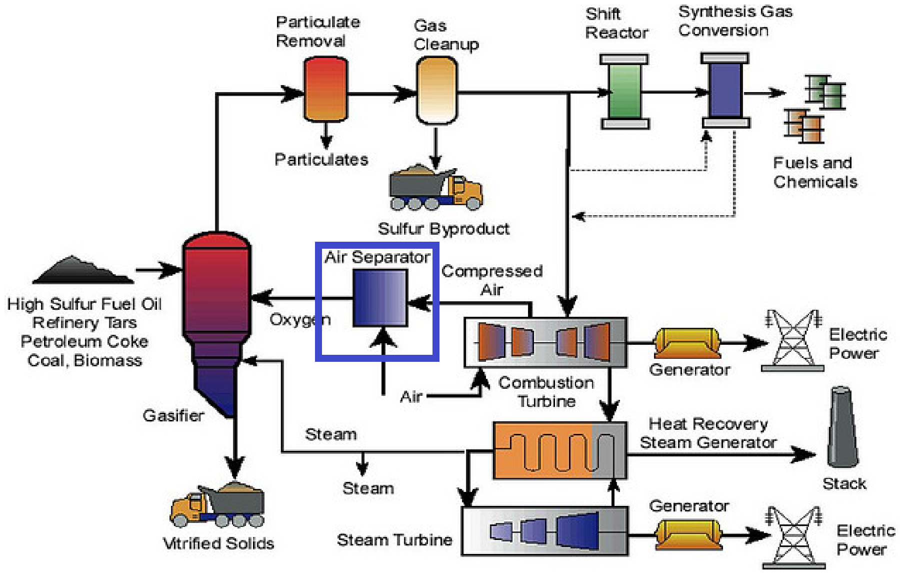

Figure 5.2: Integration of chemical looping air separation in IGCC

The metal oxide captures oxygen in the air reactor and releases it in the fuel reactor, generating pure oxygen, as presented in Figure 5.3. Fresh air runs through several heat exchangers and enters the air reactor of the chemical looping system in which it oxidises the metal used as oxygen carrier. The metal oxide enters then fuel reactor and releases oxygen in a superheated steam before being sent back to the oxidation reactor. The mixture of steam and oxygen is cooled under the condensation temperature of water to obtain a high-purity oxygen stream that is suitable for use in the gasification reactor [58].

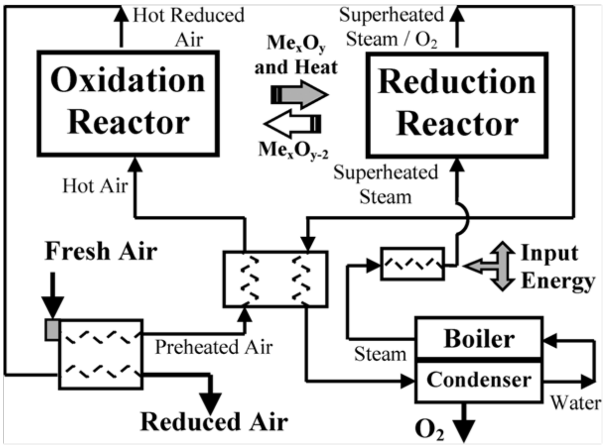

Figure 5.3: Chemical looping air separation [58]

Experiments demonstrated the feasibility of applying chemical looping uncoupling for air separation, though the economic viability is still to demonstrate [58].

## 5.3 IGCC with chemical-looping gasification

The gasification reactor is one of the key components of an IGCC power plant: steam, oxygen and solid fuel react to produce a synthesis gas directly used on the site. The studied power generation system is an IGCC power plant where an integrated chemical-looping gasification unit replaces the usual gasifier and eliminates the need for a cryogenic air separation unit, as illustrated by Figure 5.4. The main difference of this type of IGCC power plant compared to the conventional one is that chemical looping is integrated in situ and can achieve different purposes.

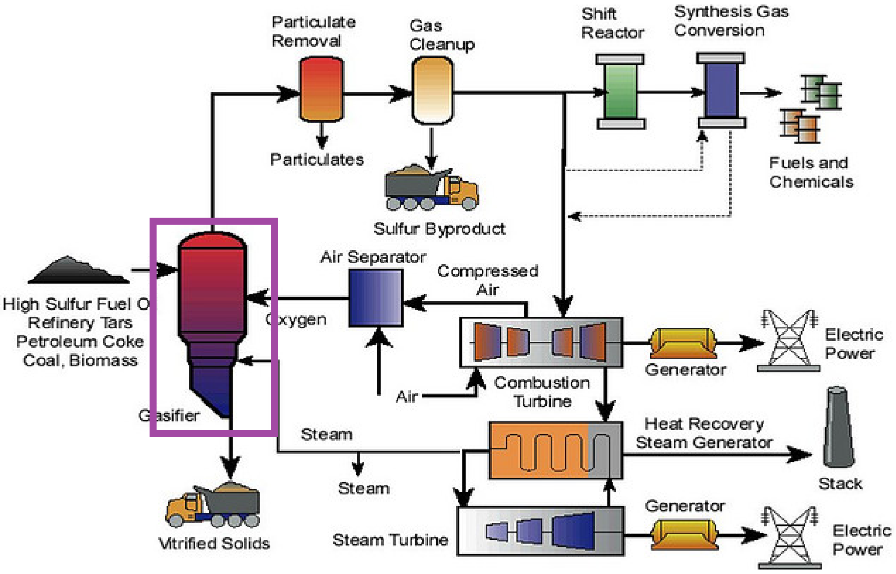

Figure 5.4: Integration of chemical looping gasification in IGCC

A main feature of the chemical-looping gasification is the high fuel-to-air ratio: the operation in fuel-rich conditions leads to generation of synthesis gas by reforming/gasification instead of combustion as it is the case in chemical-looping combustion. Gasification of solid fuels occurs by using air indirectly with metal oxide particles. Fresh air is pressurised in a compressor to the same operating pressure of the gasifier, enters the air reactor of the chemical looping gasification system and oxidises the metal particles.

The oxygen carrier particles enter the gasifier, in which they react with the solid fuel in fuel-rich conditions, producing a synthesis gas with a high content of carbon monoxide and hydrogen and returning then to the air reactor. In case of CCS, the synthesis gas goes through the cleaning step and the water-gas shift reactor where carbon monoxide yields to carbon dioxide. A $CO_2$-capture adsorption unit removes the carbon dioxide and leads to the generation of a hydrogen rich syngas.

As in a conventional IGCC power plant, compressed air and synthesis gas run through a combined cycle and generate heat and power. The oxygen carrier selected should have a high selectivity towards carbon monoxide and hydrogen, a high reactivity with solid fuels such as coal and high conversion efficiency of pollutants such as methane and tars, generally undesirable in a synthesis gas.

A flow sheet of a possible configuration of an IGCC power plant with chemical looping gasification is presented in Appendix F.

## 5.4 IGCC with chemical-looping combustion

In all types of IGCC power plants, the synthesis gas produced in the gasification step and cleaned in the gas treating process runs through a gas turbine cycle in which it burns with air in the combustion chamber. The studied power generation system is an IGCC power plant where an integrated chemical-looping combustion unit replaces the usual combustion chamber of the gas turbine.

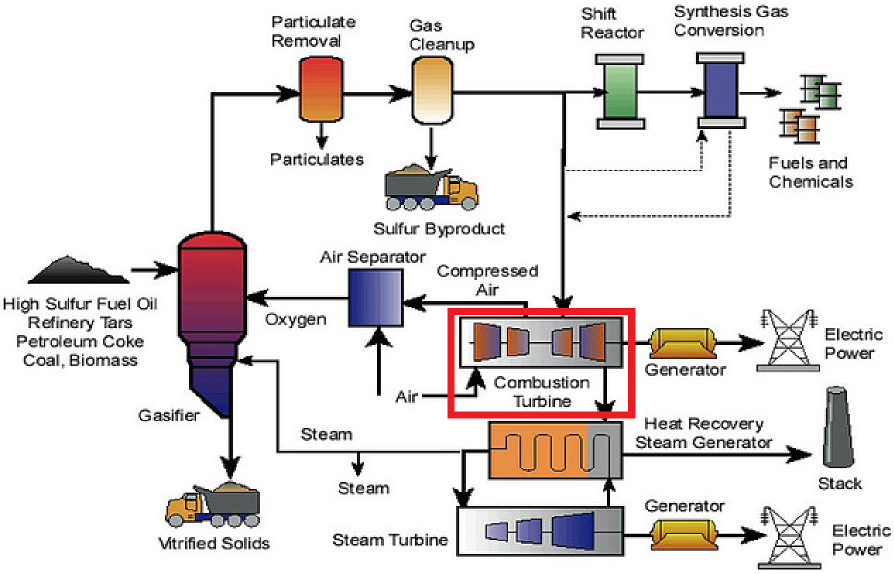

Figure 5.5: Integration of chemical looping combustion of synthesis gas in IGCC

Chemical-looping combustion presents the feature of inherent carbon capture and dispenses thus the need for a water-gas shift and a $CO_2$-capture adsorption unit. Fresh air is first pressurised in a compressor to the same pressure of the synthesis gas and enters the air reactor of the chemical looping system in which it oxidises the metal used as oxygen carrier. The oxygen-depleted air expands then in a gas turbine, generating power, and enters the HRSG, exchanging heat and producing steam. The nitrogen stream is usually mixed with the pressurised air stream.

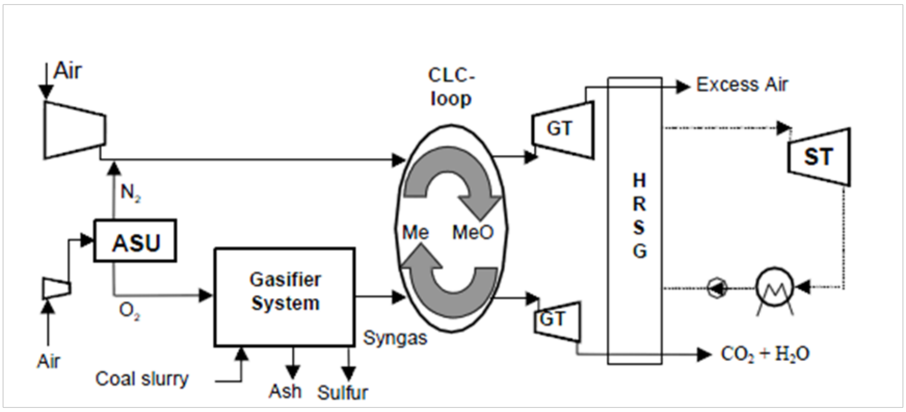

Figure 5.6: Chemical looping combustion of synthesis gas in IGCC [136]

The metal oxide at a high oxidation state enters the fuel reactor and reacts with the synthesis gas generated in the gasification process at the same pressure as in the air reactor, leading to the production of carbon dioxide and steam. The exhaust mixture passes eventually a $CO_2$-turbine, generating power, and goes as well through the HRSG. The oxygen-depleted air stream has a higher temperature than the mixture of carbon dioxide and steam stream because of the strong exothermic feature of the metal oxidation and the mild endothermic or exothermic feature of the fuel oxidation.

Regarding the materials used, the oxygen carrier particle should have a high reactivity towards carbon monoxide and hydrogen to convert them into carbon dioxide and steam. The most suitable oxygen carriers regarding their reactivity are nickel, cobalt and manganese, though several studies consider iron oxides instead because of their low cost and large availability. It is possible to adapt this process to produce hydrogen in parallel, by regenerating the metal oxide by steam instead of air, which thus yields hydrogen [131]. In this case, the most appropriate oxygen carrier is iron because of its favourable thermodynamics [65; 83; 190].

A flow sheet of a possible configuration of an IGCC power plant with chemical looping combustion is presented in Appendix E.

## 5.5 IGCC with carbonate looping in situ

In conventional IGCC power plants, gasification occurs only in presence of the solid fuel and oxygen and with steam that acts as reaction enhancer: the generated syngas has a high content of carbon monoxide and hydrogen. Carbonate looping is integrated in the gasifier in situ, as shown in Figure 5.7.

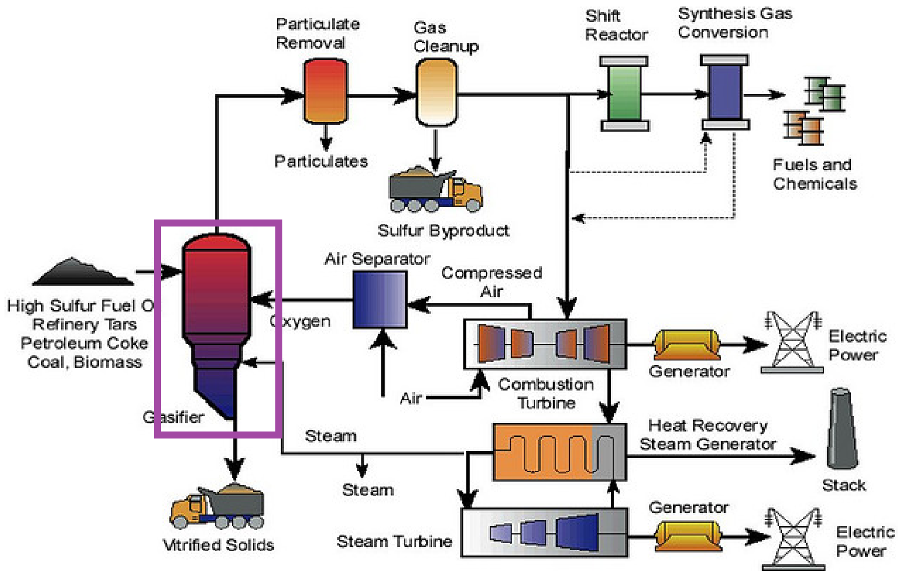

Figure 5.7: Integration of carbonate looping in situ in IGCC

A carbonate looping particle circulates between the gasifier and the regeneration reactor, as presented in Figure 5.8. Two main overall reactions take place in the gasifier: normal gasification and carbonation.

The solid calcium sorbent absorbs the carbon dioxide contained in the synthesis gas via carbonation in a temperature range of 500-700°C and releases it in the regeneration reactor where calcination occurs at around 900-1000°C.

The absorption of carbon dioxide shifts the equilibrium of the water-gas shift reaction towards the product side, leading to the generation of a rich hydrogen synthesis gas: there is thus no need for a water-gas shift reactor and an adsorption-based $CO_2$-capture unit. Another interesting feature of this integration of carbonate looping lies on the heat requirements of a conventional gasifier. Whereas the gasification is generally an endothermic process, carbonation is a mild-exothermic reaction. The heat released during the carbonation reaction can provide a part of the heat needed to run the steam reforming reaction, decreasing the need for other kinds of heating. In general, combustion of char provides the extra-heat required. Finally, calcium oxides and carbonates catalyse the decomposition of tars and contribute thus to a higher purity of the hydrogen stream.

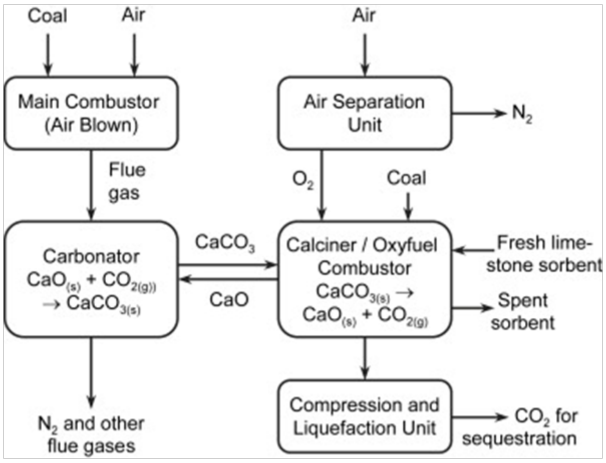

Figure 5.8: Carbonate looping in gasification in situ [158]

However, handling carbonation and gasification reactions is a complex challenge because calcium oxides have the tendency to react with sulphur compounds rather than with carbon dioxide, leading to lower reactivity and carbon capture efficiency. Another issue is the integration of the regeneration reactor in the IGCC process. Calcination is an endothermic reaction: the heat needed is generally provided by combustion of the solid fuel in oxy-fuel conditions: it implies thus higher costs and energy efficiency penalty.

Carbonate looping is suitable to apply directly in the gasifier of an IGCC power plant when processing low-sulphur and low-ash fuels in moving or fluidised beds because of their appropriate operating temperature ranges. Examples of processes are:

- HyPr-Ring process [191; 192]
- Fuel-Flexible GE process [193]
- ZECA process [194]

The main difference between these processes is the way to handle the regeneration of the calcium oxide particle, for instance by direct calcination or by an intermediate hydration step, and to integrate the regenerator in the overall power plant.

## 5.6 IGCC with carbonate looping in the water-gas shift (WGS) reactor

In conventional IGCC power plants with $CO_2$ capture, the synthesis gas runs through a cleaning process that generally includes a water-gas shift reactor and a $CO_2$-absorption step. Absorption by chemical sorbents or physical processes allows thereby the removal of carbon dioxide, leading to a $CO_2$ stream ready for sequestration.

Carbonate looping uses the system calcium oxide - calcium carbonate for the capture of carbon dioxide in the synthesis gas. The carbon dioxide content of the syngas is usually low and between 5 and 25% in volume after sulphur and halides cleaning. In the IGCC system proposed in this sub-chapter, carbonate looping is integrated as a pre-combustion capture system, but ex situ, i.e. not in the gasifier.

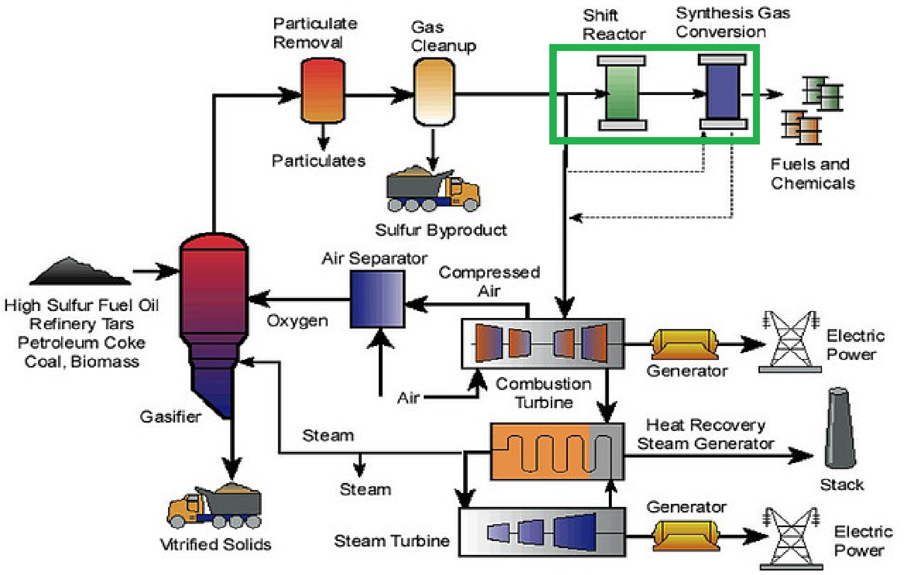

Figure 5.9: Integration of carbonate looping water-gas shift in IGCC

Carbonation takes place in the water-gas shift reactor and shifts the equilibrium to the product side, promoting the generation of a rich hydrogen synthesis gas and an efficient removal of carbon dioxide [176; 195]. Carbonate looping allows therefore combining the water-gas shift reaction and the $CO_2$ absorption in a single reactor instead of two like in conventional IGCC power plants with $CO_2$ capture. Another advantage of operating carbonate looping ex situ is the lower risks of poisoning from sulphur and deactivation by ash, at the difference of carbonate looping in situ.

When comparing with conventional $CO_2$-capture options such as MEA-scrubbing, carbonate looping ex situ is believed to present a lower energy penalty because the amount of heat required to drive the regeneration reaction is smaller. Moreover, it is expected that carbonate looping ex situ may be more competitive because the calcium sorbent is naturally abundant and cheap. An example of this type of processes with carbonation ex situ is the OHIO Calcium Looping Process [22].

A flow sheet of a possible configuration of an IGCC power plant with carbonate looping is presented in Appendix G.

## 5.7 IGCC with carbonate looping post-combustion

The primary way of integrating carbonate looping system was its implementation in thermal power plants for post-combustion capture. It has not been studied extensively but it is in theory feasible to integrate it as a post-combustion capture system in IGCC power plants too: the carbonate looping system is added after the water-gas shift reactor and the combustion step in the gas turbine system.

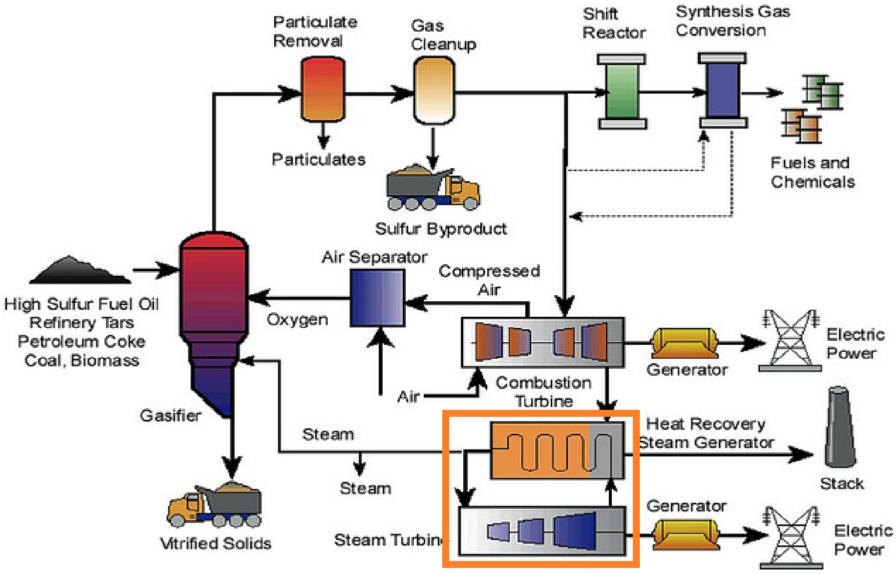

Figure 5.10: Integration of carbonate looping post-combustion in IGCC

## 5.8 IGCC with advanced solid looping cycles

Different configurations of how to integrate chemical looping processes in IGCC have been presented but there are more advanced and complex ones [196]. An example of a complex chemical looping process is the hybrid combustion-gasification process proposed by ALSTOM, as shown in Figure 5.11.

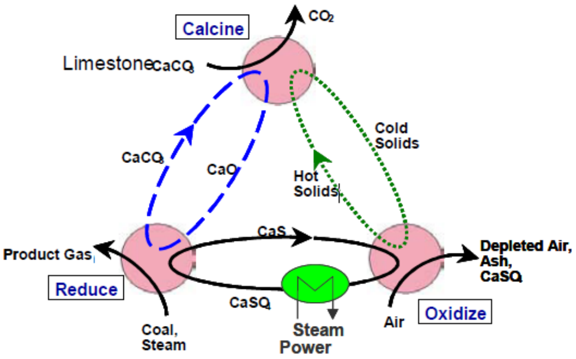

Figure 5.11: ALSTOM chemical-carbonate looping process [148]

## 5.9 Comparison and discussion

Not all these processes have been investigated in this study. This sub-chapter aims to present a short comparison between these different configurations and to justify the choice of the processes studied later.

Table 5.1: Comparison of different IGCC-configurations (chemical looping)

| **Process** | **IGCC chemical-looping ASU** | **IGCC chemical-looping gasification** | **IGCC chemical-looping combustion** |
|---|---|---|---|
| **Potential for high energy efficiency** | Lower energy penalty | Lower energy penalty | Higher exergy efficiency |
| **$CO_2$-capture** | Possible (if oxy-fuel IGCC) | No | Yes |
| **Hydrogen generation** | No | Possible | Possible |
| **Scientific research** | Few | Relatively known | Well-known |
| **Technical issues** | Limited choice of oxygen carriers | | |
| **Economic viability** | Controversy | Unknown | Probable |
| **Large-scale development** | Unknown | Expected | Expected |

CLAS is a novel application of chemical looping only developed these last years: the idea of building a chemical looping unit for air separation in IGCC is therefore even more recent and its viability is still to demonstrate. Chemical-looping gasification, like CLAS, abolishes the requirement of an energy-intensive air separation unit and leads therefore to an increase of the energy efficiency of the overall process. It can moreover be used for hydrogen production. Chemical looping combustion presents the feature of inherent $CO_2$ separation and benefits from the researches conducted on solid looping cycles since they mostly deal with CLC: this process is thus more technologically advanced than the others.

Table 5.2: Comparison of different IGCC-configurations (carbonate looping)

| **Process** | **IGCC carbonate-looping in situ** | **IGCC carbonate-looping ex situ** |
|---|---|---|
| **Potential for high energy efficiency** | Lower energy penalty | Lower energy penalty |
| **$CO_2$-capture** | Yes | Yes |
| **Hydrogen generation** | Possible | Possible |
| **Scientific research** | Few | Relatively known |
| **Technical issues** | Fate of pollutants & solids handling | Fate of pollutants & solids handling |
| **Economic viability** | Unknown | Possible |
| **Large-scale development** | Expected | Expected |

Carbonate looping in situ may become an interesting alternative for $CO_2$-capture since it shifts the equilibrium of the water-gas reaction, but the slow kinetics, the contamination by sulphur and deactivation by ash and the heat integration are tricky issues to consider. Carbonate looping ex situ in IGCC power plants is a promising technique because it combines the advantages of carbonate looping in situ but the contamination and deactivation risks are less problematic.

Finally, most of the researches carried out on solids looping cycle are based on the integration of chemical looping combustion of synthesis gas. This technique has a high potential for $CO_2$-capture, lower exergy destruction and is the most well known. To conclude, the processes investigated further in this thesis are chemical looping gasification, carbonate looping ex situ and chemical looping combustion.

# Chapter 6

# Methodology and modelling basis

This chapter introduces the general methods and models used in the works carried out in the thesis. The specific assumptions related to each individual simulation are presented in the related chapter for more clarity. The main components of each model are the reactors of the looping process: both carbonation and calcination in carbonate looping or oxidation and reduction in chemical looping. The other unit operators such as, for instance, compressor and turbine, are assumed state-of-the-art and the assumptions made are common to every simulation. The methodology used to carry out this thesis and the simulations associated is presented and justified in parallel of the descriptions of the models. The specific details related to each individual simulation are shown in the corresponding chapter.

## 6.1 ASPEN Plus general model set-up

The different chemical species taken into consideration are the conventional components of coal, synthesis gas, steam and air, the metal oxide and carbonate, the different carbides, sulphates and chlorines possibly formed under operating conditions. The databanks chosen for the properties of the components are INORGANIC, SOLID, COMBUST and PURE22 because they are the most relevant regarding the process, the chemical species and reactions involved. The thermodynamic property methods suggested in power processes are based either on the Redlich-Kwong equation of state with Soave modification or on the Peng-Robinson one. The simulation uses the first one although the second one is valid as well: a quick sensitivity analysis has shown that there is no significant difference between both when simulating chemical looping combustion systems.

## 6.2 Chemical and carbonate looping reactors

The key components of the chemical and carbonate looping processes are respectively, the oxidation and reduction reactors and the carbonation and calcination ones. Their modelling and the assumptions made are of particular importance in quality and relevancy of the simulations' results. Among all the assumptions necessary to carry out the simulations, the ones related to mass and heat balances, thermodynamic and equilibrium issues are essential and are therefore presented in the following sub-chapters.

### 6.2.1 Mass balance

The principle of mass conservation specifies that the mass of a closed system, i.e. isolated with known boundaries, remains constant over the time and is thus completely independent of the processes taking place inside this system. It implies that for any reactor, the mass of the reactants is strictly equal to the mass of the products. By considering every single reactor as a closed system, the different mass balances are thus possible to deduce. The examples given as follows are valid for a chemical-looping combustion system but can be applied to other systems if the inlets and outlets of the reactors investigated are known.

The mass balance over the air reactor in which combustion of the metal oxide takes place is:

$$\dot{m}_{air,in} + \dot{m}_{Me_xO_{y-1}} = \dot{m}_{air,out} + \dot{m}_{Me_xO_y} \tag{6.1}$$

With:

- $\dot{m}_{air,in}$ the mass flow rate of air introduced in the air reactor
- $\dot{m}_{air,out}$ the mass flow rate of oxygen-depleted air at the outlet of the air reactor
- $\dot{m}_{Me_xO_{y-1}}$ the mass flow rate of metal oxide and inert at a low oxidation state
- $\dot{m}_{Me_xO_y}$ the mass flow rate of metal oxide and inert at a high oxidation state

Since the conversion of the oxygen carrier does not usually reach 100%, the mass flow rates of oxygen carrier actually include both unconverted and converted metal oxides.

The mass balance over the fuel reactor in which the reduction of the metal oxide and the combustion of the fuel take place is:

$$\dot{m}_{fuel} + \dot{m}_{Me_xO_y} = \dot{m}_{exh} + \dot{m}_{Me_xO_{y-1}} \tag{6.2}$$

With:

- $\dot{m}_{fuel}$ the mass flow rate of synthesis gas introduced in the reactor
- $\dot{m}_{exh}$ the mass flow rate of the exhaust gases produced
- $\dot{m}_{Me_xO_{y-1}}$ the mass flow rate of metal oxide and inert at a low oxidation state
- $\dot{m}_{Me_xO_y}$ the mass flow rate of metal oxide and inert at a high oxidation state

The exhaust gases contain the combustion products, so carbon dioxide and steam, but unconverted fuel and pollutants such as sulphur oxides as well. These mass balances are valid for all basic chemical looping reactors where only two streams flow into and out of the oxidation and reduction reactors. The mass balance over the overall chemical-looping system is thus:

$$\dot{m}_{air,in} + \dot{m}_{fuel} = \dot{m}_{air,out} + \dot{m}_{exh} \tag{6.3}$$

ASPEN Plus handles the mass balances issues by iterative method: given initial estimates, the software, based on several resolution algorithms, solves the mass balances by iterations.

### 6.2.2 Heat balance

There are several approaches when modelling the heat balance of a reactor. The first approach considers that no heat crosses the boundaries of the reactor: the system is adiabatic. In this case, ASPEN Plus calculates by itself the temperature over the reactor. The second approach considers that heat crosses the boundaries of the reactor: there is either external cooling or heating and the system is not adiabatic. In this case, the user specifies the amount of heat exchanged with the surroundings or the temperature of the reactor. ASPEN Plus then calculates the missing data. The simulations carried out take into account either the first or the second approach for each single reactor depending on the specifications made. They are individually presented in the corresponding subchapters. The examples given as follows are valid for a chemical-looping combustion system but can be applied to other systems as well. The heat balance over the air reactor is:

$$\dot{H}_{air,in} + \dot{H}_{Me_xO_y} + \dot{Q}_{react,1} = \dot{H}_{air,out} + \dot{H}_{Me_xO_{y-1}} - \dot{Q}_{losses,1} - \dot{Q}_{ext} \tag{6.4}$$

With:

- $\dot{H}_{air,in}$ the enthalpy of the air stream at the inlet of the reactor
- $\dot{H}_{air,out}$ the enthalpy of the air stream at the outlet of the reactor
- $\dot{H}_{Me_xO_y}$the enthalpy of the metal oxide stream at a high oxidation state
- $\dot{H}_{Me_xO_{y-1}}$ the enthalpy of the metal oxide stream at a low oxidation state
- $\dot{Q}_{losses,1}$ the heat losses to the surroundings (defined as positive, equal to 0 in adiabatic conditions)
- $\dot{Q}_{react,1}$ the heat generated by the oxidation reaction (defined as positive)
- $\dot{Q}_{ext}$ the heat removed by external cooling (defined as positive)

The heat balance over the fuel reactor is:

$$\dot{H}_{fuel} + \dot{H}_{Me_xO_{y-1}} + \dot{Q}_{react,2} = \dot{H}_{exh} + \dot{H}_{Me_xO_y} - \dot{Q}_{losses,2} \tag{6.5}$$

With:

- $\dot{H}_{fuel}$ the enthalpy of the fuel stream
- $\dot{H}_{exh}$ the enthalpy of the exhaust stream
- $\dot{H}_{Me_xO_y}$the enthalpy of the metal oxide stream at a high oxidation state
- $\dot{H}_{Me_xO_{y-1}}$ the enthalpy of the metal oxide stream at a low oxidation state
- $\dot{Q}_{react,2}$ the heat generated or consumed by the reduction reaction
- $\dot{Q}_{losses,2}$ the heat losses to the surroundings (defined as positive)

In the simulations presented in this thesis, the heat losses to the surroundings and not the heat removed by external cooling or added by external heating are always assumed null. The chemical species in presence are in thermal equilibrium at the outlet of the reactor, which means that they leave the system at the same temperature. ASPEN Plus handles the energy balances by iterative method as well.

### 6.2.3 Reactor geometry

The preferable type of reactor for either chemical- or carbonate-looping is an interconnected fluidised bed. For instance, in the case of chemical looping applications, one of the beds is high-velocity fluidised and the second one is bubbling fluidised.

A detailed investigation of the kinetics and an accurate modelling of this type of reactor are not the purposes of the study. A bubbling fluidised bed behaves as a continuously stirred reactor with perfect axial and radial mixing whereas a high-velocity fluidised bed behaves as in between CSR and PFR. This study does not take into account the geometry of the reactor, the fluidisation issues and the velocities of the different streams. However, the simulations carried out take into consideration the pressure drops and further discussions include comments about the heat loads of the fluidised beds.

In the simulations, a pressure drop of 1 bar occurs over the fluidised and moving beds. In the particular case of chemical-looping hydrogen, the oxidation reactor is a moving bed. The behaviour of this kind is more similar to a plug-flow reactor with no axial mixing.

### 6.2.4 Thermodynamics and equilibrium

Among the different assumptions made in the models used in ASPEN Plus, the main one is to consider that thermodynamic equilibrium between the different chemical species in presence is reached: the Gibbs free energy is minimised and equilibrium is reached. This assumption is reasonable when the residence time in the fluidised beds is high enough [197].

The stoichiometry of the different reactions in the chemical looping reactors is known and it is thus possible to use RSTOIC modules. However, because of the high degree of complexity of the system, it is more convenient to use a reactor module that handles these thermodynamic and equilibrium calculations by itself, such as a RGIBBS module.

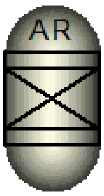

Figure 6.1: RGIBBS module in ASPEN Plus

There is no need to specify the reactions taking place in each reactor: ASPEN Plus estimates by itself which reactions are likely to occur and to which extent, given the operating conditions. The equilibriums are both chemical and phase equilibrium: ASPEN Plus calculates the amounts of chemical species present at the outlet of the reactor and the phases (gaseous, liquid and solid) in which they are. However, to improve the modelling of the reactors, the possible products and phases were specified in the model instead of letting ASPEN Plus iterating it.

A simple RGIBBS unit simulates the behaviour of a continuously stirred reactor with chemical and phase equilibrium at the outlet: this module is thus suitable for the modelling of a fluidised bed. In practice, using the basic RGIBBS module does not allow an understanding at a reactor level of the circulating fluidised bed. A more rigorous model implies that the circulating fluidised bed should be schematized by a succession of different ASPEN modules to simulate each region [198; 199; 200] and different models for emissions and reaction kinetics [201; 202].

However, a counter-current moving bed behaves like a plug-flow reactor where the reactants enter on different sides. Since a plug-flow reactor behaves like an infinite succession of continuously stirred reactors, a sequence of RGIBBS modules with counter-current fluid and solid phases is thus suitable for the modelling of this kind of reactor [203]. In the simulations, a sequence of three RGIBBS reactors models a counter-current reactor.

## 6.3 Pressure changers

### 6.3.1 Compressors

Compressors are mechanical devices that increase the pressure of a gas by reducing its volume: the fluid temperature usually increases. The model used in ASPEN Plus is a basic polytropic compressor module, without inter-staging or inter-cooling.

Figure 6.2: Compressor module in ASPEN Plus

The assumptions made are:

- Compressor polytropic efficiency $\eta_{pol}$: 92%
- Compressor mechanical efficiency $\eta_{mec}$: 97%
- Air compressor outlet pressure $P_{out}$: 17 bars (CLC)

### 6.3.2 $CO_2$ compressor

Gas compression usually generates heat and increases its temperature. $CO_2$-compression is a particular case in the sense that the final pressure has to be above 100 bars, which exceeds by far the pressures usually met in combined cycles. The temperature is therefore expected to increase significantly, which implies that a large amount of energy is needed to run the compressor. A way to decrease the required work is to make the compression step less adiabatic and more isothermal, which can be achieved by staged compression with inter-cooling. The model used in ASPEN Plus for $CO_2$-compression is a multi-stage compressor.

Figure 6.3: Multistage compressor module in ASPEN Plus

The assumptions made are:

- Compressor stage polytropic efficiency $\eta_{pol}$: 88%
- Compressor stage mechanical efficiency $\eta_{mec}$: 97%
- $CO_2$ compressor outlet pressure $P_{out}$: 110 bars
- Number of stages: 4
- Cooler outlet temperature: 30°C
- Cooler pressure drop: 0.05 bar

The same efficiencies are set for all compressors and the same temperatures and pressure drops are set for all coolers.

### 6.3.3 Turbines

Turbines are mechanical devices that decrease the pressure of a gas by expanding it, i.e. increasing its volume, at the opposite of compressors and pumps that increase the pressure of a fluid. The model used in ASPEN Plus is an isentropic turbine module, which is the same as a compressor module, with different outlet conditions and parameters.

Figure 6.4: Turbine module in ASPEN Plus

In all the process simulations, the turbines have been represented by a single stage turbine, which means that there is neither multi-staging nor inter-cooling. The assumptions made are:

- Turbine isentropic efficiency $\eta_{is}$: 90%
- Turbine mechanical efficiency $\eta_{mec}$: 95%
- Turbine inlet temperature (TIT): 1200°C
- Gas turbine outlet pressure $P_{out}$: 1.5 bars
- Air cooling flow $\dot{m}_{air}$: 0 kg/s

There are two points to highlight. First, the turbine materials can usually withstand a maximum temperature of 850-900°C, which is lower than the usual temperature at the outlet of the chemical looping combustion system, for example. Increases in temperatures may cause thermal fatigue of the turbine materials and raise corrosion issues: it is thus necessary either to use thermally resistant materials or to cool the turbine by supplying cold air. Secondly, in the particular case that the gas processed is steam or a mixture with high steam content, there are risks of erosion if the temperature at the outlet of the turbine is below the dew point of the mixture. Water droplets may form inside the turbine and erode the blades. The pressure ratio or outlet pressure has thus to be controlled.

## 6.4 Temperature changers

### 6.4.1 Basic coolers and heaters

Heaters and coolers are basic thermal devices that respectively increase or decrease the temperature of a gas, fluid or solid by supplying or removing heat. The heat generation can come from the burning of a fuel and the heat removal can come from the circulation of cold water. The model used in ASPEN Plus is a Heater/Cooler with either outlet temperature or heat exchanged specified.

Figure 6.5: Heater module in ASPEN Plus

The assumptions made are case by case and are detailed in the relevant chapters. In the processes simulated in this study, heat exchangers model the heat recovery from the exhaust gases and the solid streams like ash. Basic heater and cooler modules had only been used when starting to model the different solid looping processes to get a rough estimation of the amount of heat exchanged with the environment. These simplified modules were later replaced by HeatX modules when improving the simulations.

### 6.4.2 Heat exchangers

In the case that the heat exchange to cool or to heat a given stream happens between two streams present in the process, a heat exchanger models more realistically the process. The model used in ASPEN Plus is a HeatX that can simulate either co-current or counter-current heat exchangers. However, in this work, only counter-current ones were modelled to simulate the heat transfer between fluids/fluids, fluids/solids and solids/solids.

Figure 6.6: Heat exchanger HeatX module in ASPEN Plus

The heat recovery steam generator was designed at first with this kind of modules to get some valuable insights of the process but, as presented in the next sub-section, was more rigorously modelled using EBSILON Professional.

### 6.4.3 Heat recovery steam generator

The heat recovery steam generator, commonly abbreviated HRSG, includes several heat exchangers to recover heat from hot fluid streams (carbon dioxide or stream, for example) by generating steam. This steam runs through a steam turbine, producing electricity, and returns later to the HRSG system.

The design of this system is critical in the design of the power plant to reach high-energy efficiency. The steam cycle evaporation temperature and pressure levels are critical factors that should be chosen adequately to optimise the production of high and medium pressure steams [15]. However, designing HRSG is more complex when implementing chemical looping because of the larger number of streams to consider. The high temperature level expected in the chemical looping system due to the strong exothermic feature of some reactions involves that generation of low-, medium- and high-pressure steam is feasible [144]. Moreover, external cooling may be provided in the circulating fluidised bed since it is necessary to regulate the temperature levels. There is so room for optimising the heat generation processes.

In a first step, a simple heater module models the HRSG in ASPEN Plus to estimate the maximum amount of heat that can be extracted from the different streams and thus the maximum amount of electricity that can be generated. In a further step, an EPSILON flowchart based on the results of the ASPEN Plus simulates the behaviour of the HRSG and estimates the amounts of energy reasonably recovered as heat and power. It should be pointed out that the model used in this Master's Thesis is idealized and returns thus optimistic results compared to one could actually expect.

The EBSILON model used for the heat recovery steam generator is based on the own work of the supervisor of this Master's Thesis Sebastian Schiebahn.

## 6.5 Separators

### 6.5.1 Solid-liquid/gas separators

The cyclones integrated in the chemical and carbonate looping systems are necessary to separate the solid particles out of the gaseous streams. The efficiency of the cyclones decreases with the size of the particles [41]. However, it is not a critical issue in chemical looping applications: the diameter of the oxygen carrier particle is in the range of millimetres whereas the critical diameter for cyclone separation is in the range of micrometres [22]. The cyclone separation efficiency is therefore set to 100%.

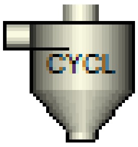

Figure 6.7: Cyclone module in ASPEN Plus

### 6.5.2 Ash removal

Ash present in the fuel may be problematic in combustion and gasification processes. The temperatures of the fluidised beds are usually set to avoid softening and melting: ash particles would otherwise agglomerate on the fluidised bed particles, and so on the oxygen carrier ones, and lead to reactivity losses. Ash extraction is thus an issue of importance when designing the chemical looping reactors. Coarse ash is drained by opening a valve at the bottom of the reactor whereas fly ash is entrained with the flue gases and is collected in an electrostatic precipitator [41].

Figure 6.8: Solid separator module in ASPEN Plus

For ease of modelling the separation efficiency of ash, coarse and fly, is set to 100%. The ash solid streams from the separation unit pass an air heat exchanger for heat recovery with hot water, steam or so.

## 6.6 EBSILON general model set-up

A HRSG is a complex system composed of feed water heaters, boilers, super-heaters, re-heaters, de-aerators and steam turbines. The main idea is to utilise the energy contained in the hot gases from the gas turbine cycle in a steam cycle to recover heat and generate extra-electricity. The design of this system like the arrangement of the heat exchangers has to be optimised to maximise the heat recovery and to reach high combined cycle efficiency. Optimising the steam cycle is equivalent to, according to the second law of thermodynamics, minimizing the entropy generation. The overall aim is to maximise the power generation from the steam turbines, by recovering high-grade heat, i.e. heat at high temperatures, reducing the temperature difference in the heat exchangers and rejecting the flue gases at the lowest temperature possible.

The EBSILON model used but not developed within the frame of this thesis is based on the following assumptions and data issued from Kloster [204]. The model is adapted for HRSG with three-temperature levels and is thus not perfectly suitable for heat recovery from streams at high temperatures and pressures. The interactions between the gas turbine cycle and the HRSG system are idealized and the results obtained are therefore optimistic.

### 6.6.1 Steam cycle pressure and temperature levels

It is obvious that the production of high-pressure steam is more interesting for power production than medium- or low-pressure and therefore the aim is to generate it as much as possible. Designing this heat system with three different levels of pressure and temperatures allows nevertheless maximising the heat recovery at low temperatures of the flue gases. The EBSILON model consists of a three-pressure-level power cycle with the following operating parameters:

Table 6.1: EBSILON steam cycle temperature & pressure levels

| **Steam** | **Temperature** [°C] | **Pressure** [bar] |
|---|---|---|
| **High-pressure** | 550 | 170 |
| **Medium-pressure** | 550 | 35 |
| **Low-pressure** | 240 | 5.5 |
| **Condensed** | 24.08 | 0.03 |

No optimization of the steam cycle parameters has been done within the frame of this Master's thesis unless it was necessary to run the simulations and there are therefore possibilities for improving the interactions between the gas turbine and the steam cycle. For instance, in a chemical looping combustion system, it is possible to process directly the $CO_2$/H2O stream into the heat recovery system without previous expansion. In this case, the temperature is above than 1000°C and a steam cycle with the parameters set in this model is not adequate: a super-critical steam cycle should be designed instead.

### 6.6.2 Heat exchangers

Steam generation takes place in three sections. The first one is the economiser or pre-heater, which is used to increase the feed-water temperature near the boiling point. It is possible to control the flue gases outlet temperature by changing the feed-water inlet one. The second section is the evaporator in which water is vaporised at constant temperature and pressure. The aim is to minimize the temperature difference at the pinch point, i.e. the temperature difference between the steam and flue gas outlets, to recover as much heat as possible. The third and last section is the super-heater, which is used to dry the saturated vapour by rising its temperature and its thermal energy content. The different parameters are presented in Table 6.2.

Table 6.2: EBSILON temperature differences & pressure drops

| | | **Temperature difference at pinch point ΔT** [°C] | **Pressure drop ΔP** [bar] |
|---|---|---|---|
| **High-pressure** | Super-heater | - | 5 |
| | Evaporator | 10 | 8 |
| | Pre-heater | - | 2 |
| **Medium-pressure** | Super-heater | - | 0.5 |
| | Evaporator | 10 | 3 |
| | Pre-heater | - | 2 |
| **Low-pressure** | Super-heater | - | 0 |
| | Evaporator | 10 | 3 |
| | Pre-heater | - | 1 |
| **Condensed** | Condenser | 5 | 1 |

### 6.6.3 Pressure changers

The other general assumptions that are related to the water pumps and steam turbines are listed as follows:

- Pump isentropic efficiency $\eta_{is}$: 80%
- Pump mechanical efficiency $\eta_{mec}$: 99.8%
- High-pressure turbine isentropic efficiency $\eta_{is}$: 89%
- High-pressure turbine mechanical efficiency $\eta_{mec}$: 99.8%
- Medium-pressure turbine isentropic efficiency $\eta_{is}$: 92.5%
- Medium-pressure turbine mechanical efficiency $\eta_{mec}$: 99.8%
- Low-pressure turbine isentropic efficiency $\eta_{is}$: 88%
- Low-pressure turbine mechanical efficiency $\eta_{mec}$: 99.8%

# Chapter 7

# IGCC with synthesis gas chemical looping combustion

## 7.1 Description

### 7.1.1 Principle

The principle of this proposed system is detailed in Chapter 5.4. The oxygen carrier considered in this simulation is nickel oxide with nickel alumina as inert support with a ratio of 60-40 on a mass basis. The nickel is oxidised in the air reactor following this path:

$$\mathrm{Ni} + \frac{1}{2}\mathrm{O_2} \longrightarrow \mathrm{NiO} \tag{7.1}$$

The nickel oxide burns synthesis gas in the fuel reactor following these paths:

$$\begin{aligned} \mathrm{NiO} + \mathrm{CO} &\longrightarrow \mathrm{Ni} + \mathrm{CO_2} \\ \mathrm{NiO} + \mathrm{H_2} &\longrightarrow \mathrm{Ni} + \mathrm{H_2O} \end{aligned} \tag{7.2}$$

Several other chemical reactions usually take place in the fuel reactor, nickel can be contaminated by sulphur, carbon and halide, which involves the generation of solid nickel sulphides, carbides and halides and reactivity losses over chemical looping cycles. These potential reactions have been presented in a previous chapter on chemical looping and are taken into account in the ASPEN Plus simulations with the use of RGIBBS modules.

Whereas in a conventional combined power plant only one gas stream exits the cycle, two gas streams, an oxygen-depleted air one and a carbon dioxide and steam one are produced in IGCC with chemical-looping combustion. So far, this application is the most probable and known way to integrate chemical looping in IGCC power plants.

Several research groups on chemical looping carried out studies on synthesis gas chemical looping combustion and on the choice of suitable materials. Moreover, the researches on the integration of this process in IGCC processes benefit from the extensive studies on chemical looping combustion of methane in NGCC power plants. The conclusions drawn for NGCC power plants are valid for IGCC power plants as well since they deal with the efficiency of the combined cycle.

### 7.1.2 Assumptions

The input data for the calculations in the process simulation is presented in Table 7.1 and in Table 7.2 and is based on scientific literature on chemical looping combustion of synthesis gas.

The amount of nickel circulating between the two reactors is the minimum flow rate required to reach the highest capture of carbon dioxide and thus the highest purity of the carbon dioxide stream after condensation. Since the reactions of combustion between the synthesis gas and the nickel oxide are limited by a relatively severe chemical equilibrium, it is not possible to fully burn the fuel, which implies that there are some small amounts of carbon monoxide left in the flue gases.

Some additional assumptions such as the temperature and pressure of the syngas that are respectively around 300°C and 22.5 bars were done. They are nevertheless reasonable because synthesis gas produced in IGCC power plants usually has a pressure in between 20 and 30 bars and a relatively low temperature because of the water quenching and the flue gas cleaning steps that are usually optimal at temperatures around 300-500°.

Table 7.1: Process streams of IGCC-CLC

| | | | **Baseline case** |
|---|---|---|---|
| **Synthesis gas** | Flow rate $\dot{m}_{syn}$ | $[\frac{kg}{s}]$ | 1 |
| | Temperature | [°C] | 300 |
| | Pressure | [bar] | 22.5 |
| **Air** | Temperature | [°C] | 15 |
| | Pressure | [atm] | 1 |
| **Circulating solids** | Ni | [% wt] | 60 |
| | $Al_2O_3$ | [% wt] | 40 |
| | Flow rate $\dot{m}_s$ | $[\frac{kg}{s}]$ | 4 |

The temperature of 1200°C in the air reactor is an acceptable temperature in chemical-looping combustion processes to avoid sintering and melting of the oxygen carrier particles. The temperature of 1084°C is the temperature of the fuel reactor when operated in adiabatic conditions (no heat is either added or removed from the reactor). The pressure drop over the chemical looping combustion unit depends on the type of fluidised bed: it is however set to 1 bar over the whole system without any distinction between air and fuel reactors.

Table 7.2: Reactors of IGCC-CLC

| **Chemical-looping system** | | **Baseline case** |
|---|---|---|
| **Air reactor temperature $T_{ar}$** | [°C] | 1200 |
| **Fuel reactor temperature $T_{fr}$** | [°C] | 1084 |
| **Pressure drop $\Delta P$** | [bar] | 1 |
| **Heat losses $\dot{Q}_{losses}$** | [MW] | 0 |

The composition of the synthesis gas varies with the power plant considered. However, the main components of this mixture in an IGCC power plant without $CO_2$-capture are always carbon monoxide and hydrogen and usually represent more than 65-70% in volume of the synthesis gas. The concentrations of steam, carbon dioxide, methane and nitrogen vary depending on the type of synthesis gas cooling and gasification unit. For instance, the proportions of carbon dioxide and steam range from 5 to 15% each depending on the type of fuel gasified and on the type of gasifier. They have therefore a large impact on the heating value of the synthesis gas: the higher the concentrations of carbon dioxide and water, the lower will be the heating value.

The assumptions made regarding the composition of the fuel are presented in Table 7.3. For simplicity, the simulations do not take into account sulphur, mercury, halides, carbonyls and arsenic because of their low concentrations after the flue gas cleaning system.

Table 7.3: Synthesis gas composition in IGCC-CLC

| **Synthesis gas** | | **IGCC-CLC** |
|---|---|---|
| **CO** | [% mol] | 46.6 |
| **$CO_2$** | [% mol] | 13.3 |
| **$H_2$** | [% mol] | 37.2 |
| **$N_2$** | [% mol] | 2.5 |
| **$CH_4$** | [% mol] | 0.1 |
| **$H_2O$** | [% mol] | 0.3 |
| **$H_2S$ + COS** | [ppm] | 12 |

The assumptions for the performance study of the proposed system are:

- The airflow rate is calculated so that the temperature in the air reactor, which is adiabatically operated, is equal to 1200°C.
- The air separation unit is not integrated in the system: the nitrogen stream produced does not run through the gas turbine.
- The cooling for the gas turbine is neglected.
- The pressure of the system is the same in both chemical looping reactors to avoid gas leakages between both.
- The heat losses in the chemical looping reactors are negligible in regard to the ones in the overall IGCC system.
- The pressure drops over the heaters and condensers are negligible compared to the high pressures involved in the system and the pressure drop in the chemical looping reactors.
- The net calorific value is equal to 10.835 MJ/kg, considering the composition of the synthesis gas shown in Table 7.3.

The model created has been evaluated by comparison with three other models issued of literature.

## 7.2 Validation of the model

### 7.2.1 Comparison with the study of Anheden and Svendberg

Anheden and Svendberg [140] carried out a performance study of an IGCC power plant with integrated chemical looping combustion of synthesis gas. The model proposed uses nickel-, manganese- and iron-based oxygen carriers but the parametric study presented in this chapter considers only the results with nickel oxides. The full IGCC power plant was modelled with several simplifications presented in their study.

The inputs of the simulation were the amount and composition of coal processed in the power plant (Illinois no.6) but this comparison study is based on the synthesis gas composition after gas cleaning: 50.72% CO, 29.21% $H_2$, 12.64% $H_2O$, 6.92% $CO_2$, 0.45% $N_2$, 0.03% $CH_4$ in molar proportions. Parameters such as temperature and pressure at the inlet of the chemical looping system are fixed and were based on the assumptions done by Anheden and Svendberg in their simulations.

The models used to simulate the mechanical devices were isentropic compressors and turbines with an isentropic efficiency of 85% and a mechanical one of 100%. The conversion of mechanical power to electric one was assumed ideal, i.e. the efficiency of the generator is equal to 100%.

A particularity of the design of the chemical looping combustion system proposed by Anheden and Svendberg was the inclusion of a heat exchanger between both reactors. The flue gases mainly containing $CO_2$ and $H_2O$ at the outlet of the fuel reactor exchange heat with the hot solids stream at the outlet of the air reactor: the temperature of the flue gases increases, allowing larger power generation in the $CO_2/H_2O$ turbine and in the heat recovery steam generator. The minimum temperature difference is set to 50°C.

The comparison between the proposed model of this thesis and the one submitted in the corresponding paper returns:

Table 7.4: Comparison with the study of Anheden & Svendberg

| | | | **Personal model** | **Anheden model** | **Relative error** |
|---|---|---|---|---|---|
| **Oxygen-depleted air** | Flow rate $\dot{m}_{da}$ | $[\frac{kg}{s}]$ | 258.2 | 259 | -0.31% |
| | Temperature | [°C] | 1259 | 1280 | -1.65% |
| **Flue gases** | Flow rate $\dot{m}_{fg}$ | $[\frac{kg}{s}]$ | 48.8 | 49 | -0.41% |
| | Temperature | [°C] | 904 | 893 | +1.23% |
| **Work** | Gas turbine | [MW] | 200 | 202 | -1% |
| | $CO_2$ turbine | [MW] | 35.6 | 36 | -1.11% |
| | Compressor | [MW] | -100.9 | -99 | +1.92% |
| **Heat** | Steam cycle | [MW] | 234.7 | 229 | +2.49% |

The relative errors between both simulations are all under +/- 2.5%, which is considered as acceptable to validate the model proposed.

### 7.2.2 Comparison with the study of Erlach and al.

The study carried out by Erlach and her research group deals with the performance of different IGCC configurations with chemical looping combustion based on nickel oxides and with possible integration of a $CO_2$-turbine [144]. The model proposed includes all the IGCC process with a black box representing the chemical looping combustion unit. There is no information about the internal working of the chemical looping unit: the fuel conversion efficiency is estimated to 98% with a nickel conversion rate of 98% in the air reactor and a nickel oxide conversion rate of 77% in the fuel reactor.

The inputs of the simulation are for instance coal composition and mass flow: the composition of the synthesis gas, the pressure and the temperature levels in the chemical looping system are thus results of the simulation and not input parameters, at the difference of the model proposed in this thesis. A way to check the validity of this model is to use the results returned by Erlach simulation such as fuel composition and inlet flow rates of the chemical looping system and to compare the results such as outlet flow rates, temperatures, pressures of the chemical-looping reactors. Some of the results from their model were thus used as input in this model.

The airflow rate at the inlet of the chemical looping combustion system is about 1737.43 kg/s with a temperature of 15°C at atmospheric pressure. The synthesis gas enters the combustion unit at a flow rate of 140.61 kg/s with a temperature of 41°C at a pressure of 33.3 bars and has the following composition: 63.2% CO, 29.7% $H_2$, 0.2% $H_2O$, 1.6% $CO_2$ and 5.4% $N_2$ in molar proportions. As a first attempt to run the ASPEN Plus model, the solids flow rate was at first set to 750 kg/s so that the fuel conversion efficiency was about 98%.

The models used to simulate the mechanical devices were polytropic compressors and turbines with a polytropic efficiency of 92% for the compressor and of 91% for the gas turbine. The conversion of mechanical power to electric one was not assumed ideal and the efficiency of the generator is equal to 98.5%.

The comparison between the proposed model of this thesis and the one submitted in the corresponding paper of Erlach returns:

Table 7.5: Comparison with the study of Erlach & al.

| | | | **Personal model** | **Erlach model** | **Relative error** |
|---|---|---|---|---|---|
| **Oxygen-depleted air** | Flow rate $\dot{m}_{da}$ | $[\frac{kg}{s}]$ | 1517.12 | 1518.41 | -0.08% |
| **Flue gases** | Flow rate $\dot{m}_{fg}$ | $[\frac{kg}{s}]$ | 241.72 | 240.36 | +0.57% |
| **Captured $CO_2$** | Flow rate $\dot{m}_{CO_2}$ | $[\frac{kg}{s}]$ | 205.07 | 204.42 | +0.32% |
| | $CO_2$ | [% mol] | 91.3 | 89.5 | +2.01% |
| | $N_2$ | [% mol] | 7.53 | 7.7 | -2.21% |
| **Power** | Gas turbine | [MW] | 500.9 | 503.3 | -0.48% |

The relative errors are all under +/- 2.5%, which is acceptable to validate the model proposed.

### 7.2.3 Comparison with the study of Rezvani and al.

The study carried out by Rezvani and his research group deals with the performance and economic assessment of IGCC configurations with different carbon dioxide capture systems. Some data such is not available and is thus extrapolated and marked by an asterisk (*). The model proposed in this study with the same inputs and assumptions returns the following results, the temperatures given for the oxygen-depleted air and flue gases streams are after expansion:

Table 7.6: Comparison with the study of Rezvani & al.

| | | | **Personal model** | **Rezvani model** | **Relative error** |
|---|---|---|---|---|---|
| **Oxygen-depleted air** | Flow rate $\dot{m}_{da}$ | $[\frac{kg}{s}]$ | 657.6 | 650 | +1.17% |
| | Temperature | [°C] | 465.6 | 462 | +0.78% |
| **Flue gases** | Flow rate $\dot{m}_{fg}$ | $[\frac{kg}{s}]$ | 116.5 | 124.1 | -6.12% |
| | Temperature | [°C] | 653.4 | 667 | -2.04% |
| **Captured $CO_2$** | Flow rate $\dot{m}_{CO_2}$ | $[\frac{kg}{s}]$ | 104.9 | 97.23 | +7.89% |
| **Power** | Gas turbine | [MW] | 540.1 | 551.7 | -2.10% |
| | $CO_2$ turbine | [MW] | 298.3 | 286.2 | +4.23% |

The relative errors are all under +/- 7.5%, the bigger relative errors compared to the other parametric studies are due to the uncertainties and additional assumptions made about synthesis gas composition, air temperature, etc.

## 7.3 Comparison of a conventional GT to a GT with integrated chemical looping combustion

### 7.3.1 Motivation and method

The interest of comparing a conventional gas turbine cycle and a chemical looping combustion unit lies in the estimations of efficiencies: is it possible to achieve lower exergy destruction and lower energy losses when integrating chemical looping? This power process study considers as a first trial two-baseline cases:

- IGCC without $CO_2$ capture, in which the synthesis gas fuelled to the gas turbine did not run through a $CO_2$-cleaning system and has thus relatively high carbon monoxide and dioxide contents.

- IGCC with chemical-looping combustion of synthesis gas, in which the syngas fuelled to the system has the same composition of the clean and cold syngas after Claus treatment in an IGCC power plant without $CO_2$ capture.

### 7.3.2 Results of the ASPEN Plus simulation

The simulation of the gas turbine cycle with integrated chemical looping combustion of synthesis gas returns the following results, for the set of temperatures defined in the assumptions. In the case of a conventional IGCC power plant with a gas turbine with an inlet temperature of 1200°C, there are three main streams of importance: the air running through the combined cycle system and the flue gases, at the inlet and at the outlet of the gas turbine.

Table 7.7: Properties of key streams of IGCC

| **Stream** | **Mass flowrate** $[\frac{kg}{s}]$ | **Temperature** [°C] | **Pressure** [bar] |
|---|---|---|---|
| **Air (gas turbine inlet)** | 10.235 | 15 | 1.013 |
| **Flue gases (reactor outlet)** | 11.235 | 1200 | 16 |
| **Flue gases (gas turbine outlet)** | 11.235 | 586.5 | 1.1 |

On the opposite, in a combined cycle with integrated chemical looping combustion, there are the solids and the $CO_2/H_2O$ mixture streams to consider:

Table 7.8: Properties of key streams of IGCC-CLC

| **Stream** | **Mass flowrate** $[\frac{kg}{s}]$ | **Temperature** [°C] | **Pressure** [bar] |
|---|---|---|---|
| **Air (gas turbine inlet)** | 10.464 | 15 | 1.013 |
| **Oxygen-depleted air (air reactor outlet)** | 9.810 | 1200 | 16 |
| **Oxygen-depleted air (air turbine outlet)** | 9.810 | 558 | 1.1 |
| **Circulating solids (air reactor outlet)** | 4.65 | 1200 | 16 |
| **Circulating solids (fuel reactor outlet)** | 4 | 1084 | 16 |
| **$CO_2$ /$H_2O$ (gas turbine outlet)** | 1.654 | 645.5 | 1.1 |
| **$CO_2$ (ready to sequestration)** | 1.330 | 30 | 110 |

The simulations show that the amount of air required to sustain a temperature of 1200°C in the combustion system is slightly higher when integrating chemical looping, which involves higher compression work and turbine power.

Table 7.9: Gaseous streams compositions of IGCC-CLC

| | | **Oxygen-depleted air (air reactor outlet)** | **$CO_2/H_2O$ (gas turbine outlet)** | **$CO_2$ (ready to sequestration)** |
|---|---|---|---|---|
| **$N_2$** | [% mol] | 80.7 | 2.5 | 3.9 |
| **$O_2$** | [% mol] | 19.2 | - | - |
| **CO** | [% mol] | - | 0.5 | 0.8 |
| **$CO_2$** | [% mol] | - | 59.4 | 93.7 |
| **$H_2O$** | [% mol] | - | 37.5 | 1.3 |
| **$H_2$** | [% mol] | - | 0.2 | 0.3 |
| **NO** | [% mol] | 1000 | 0.003 | 5000 |
| **$NO_2$** | [% mol] | 34 | - | - |
| **$N_2O$** | [% mol] | 367 | - | - |
| **$NH_3$** | [% mol] | - | 17 | 26 |

The investigation of the compositions of the different streams at the outlet of the chemical looping system reveals several important points:

- The airflow rate is in strong excess compared to the amount of solids and the oxygen-depleted air still contains a non-negligible amount of oxygen.
- The amounts of carbon monoxide and hydrogen in the $CO_2/H_2O$ mixture are negligible compared to the proportions of carbon dioxide and steam.
- It is possible to produce a $CO_2$-rich stream, with a molar concentration of about 60% at the outlet of the fuel reactor and a purity of more than 90% after condensation.

The comparison of a normal gas turbine cycle and a gas turbine cycle with $CO_2$-capture by means of chemical looping returns the following results:

Table 7.10: Power generation in conventional and CLC gas turbine cycles

| **Power** $[MW]$ | **Conventional gas turbine cycle** | **Gas turbine cycle with CLC** | **Absolute difference** |
|---|---|---|---|
| **GT compressor** | -4.264 | -4.360 | -0.096 |
| **GT turbine** | 8.030 | 7.042 | - |
| **$CO_2$ turbine** | | 1.026 | |
| **Net GT** | 3.766 | 3.709 | -0.057 |
| **$CO_2$ compressor** | - | -0.446 | - |
| **Total (without $CO_2$ compression)** | 6.165 | 6.160 | -0.005 |
| **Total (with $CO_2$ compression)** | - | 5.714 | - |

The results from the simulations show that a gas turbine cycle with chemical looping system instead of the conventional combustion chamber exhibits slightly lower net power generation, for the same fuel and operating conditions. The electrical efficiency of a gas turbine cycle fuelled with synthesis gas and with conventional combustion is thus slightly higher than in a gas turbine cycle with chemical-looping combustion based on nickel oxides as oxygen carrier. However, these results show only the specific power generation from the gas turbine system: power production in combined cycles also occurs in bottoming cycle with heat energy recovery from the exhaust gases.

### 7.3.3 Results of the EBSILON simulation

The ASPEN Plus simulation only shows the power production from the gas turbine system, the simulation of the steam cycle with EBSILON Professional completes these first results by calculating the power production from the bottoming cycle (heat recovery steam generator):

Table 7.11: Steam power generation in conventional and CLC combined cycles

| **Power** $[MW]$ | **Conventional gas turbine cycle** | **Gas turbine cycle with CLC** | **Absolute difference** |
|---|---|---|---|
| **Steam pump** | -0.071 | -0.072 | -0.001 |
| **Steam turbine** | 2.470 | 2.564 | 0.096 |
| **Net HRSG** | 2.399 | 2.451 | 0.052 |

It is thus possible to calculate the net power production of the combined cycle and its efficiency.

Table 7.12: Energy balance of the conventional and CLC combined cycles

| **Power** $[MW]$ | | Conventional combined cycle | Combined cycle with CLC | Absolute difference |
|---|---|---|---|---|
| **Energy content** | Synthesis gas | 10.835 | 10.835 | 0 |
| **Power generation** | Gas turbine cycle | 8.030 | 8.068 | 0.038 |
| | HRSG | 2.470 | 2.564 | 0.096 |
| **Power consumption** | Gas turbine cycle | -4.264 | -4.360 | -0.096 |
| | HRSG | -0.071 | -0.072 | -0.001 |
| **Net power** | | 6.165 | 6.160 | -0.005 |
| **Efficiencies** | $\eta_{cc}$ (LHV basis) | 56.9% | 56.86% | 0.04% point |
| | $\eta_{cc}$ (with $CO_2$ compression) | - | 52.74% | - |

### 7.3.4 Discussion

The present simulation aims to give hints about how to compare chemical looping combustion system with conventional ones in the case of integrated gasification combined cycle power plants (IGCC). When focusing on the combined cycle step, it can be seen from the ASPEN Plus and EBSILON Professional simulations that the electrical efficiencies of both combined cycles are sensibly the same with a slight advantage for conventional ones. The results may look contradictory to what is expected and to the studies led on this field: the interest for chemical looping primarily emerged from the fact that it causes lower thermodynamic irreversibility and is thus favoured.

Several reasons can explain this difference between chemical looping combustion of synthesis gas and conventional combustion. Chemical looping causes, in theory, lower exergy destruction in the combustion process and thus may have higher potential for electricity generation. However, a thermodynamic system consists of several types of exergy. Amongst them are the physical exergy, which is related to the differences of temperature and pressure from the environment; the chemical exergy, linked to the differences of chemical composition from the environment; the kinetic exergy, correlated to the velocity differences, and the potential one, associated with the height of the overall system [141].

A detailed exergy analysis on chemical looping systems demonstrates that the exergy savings in the combustion process are mainly in the form of chemical exergy, which is not usable for power generation in gas turbine and steam cycles, at the difference of physical exergy, which actually decreases. Assuming that the differences of kinetic and the potential exergies between the two types of system are negligible compared to the amounts of physical and chemical exergies, it appears that the total exergy content of the exhaust streams is larger in chemical looping combustion because the gains in chemical exergy overcome the losses in physical exergy of the system.

In practice, combined cycles without chemical looping would have a higher electrical efficiency because the inlet temperature of the gas turbine may exceed 1200°C, which is hardly possible in chemical looping because the solid particles used in the process may melt. Another point is the temperature at the exit of the fuel reactor, which may be lower than at the air reactor outlet. It involves therefore lower heat recovery in the HRSG system compared to a conventional combined cycle.

The Carnot efficiency, i.e. the maximum theoretical efficiency, which depends on the temperature ratio between the studied system and the environment, is thus higher in conventional combined cycles than in combined cycles with integrated chemical looping. The development of oxygen carrier particles for applications at high temperatures is thus critical to be able to reach a Carnot efficiency as high as in usual combined cycles.

It is nevertheless interesting to promote chemical looping processes because of their inherent $CO_2$ capture feature: a gas turbine equipped with chemical looping combustion has the potential to capture almost 100% of the carbon dioxide generated in the process while absorption based on MEA has a carbon capture efficiency of only up to 90%.

The energy efficiency of chemical looping systems integrated in IGCC is so lower than conventional IGCC power plants without $CO_2$-capture but much higher than IGCC power plants with classical $CO_2$-capture processes. Chemical looping is thus a promising alternative to other $CO_2$-capture options in IGCC.

## 7.4 Sensitivity analysis on oxygen carrier

### 7.4.1 Impact of the inert-to-carrier ratio

Using a pure metal oxide without any material support in chemical looping is not recommended since the oxygen carrier particle will show a low mechanical and thermal stability. The addition of an inert material, though it does not contribute to the reactions involves, leads to higher reactivity of the oxygen carrier particle by increasing its porosity and improving its stability. It may too increase the chemical resistance to parasite reactions with sulphur or halide species present in the synthesis gas. There are several types of inert material but the one used in the simulations is alumina $Al_2O_3$. Other studies are usually based on this specific material when added to nickel.

An increase in the inert-to-carrier ratio means that, for the same amount of active material, the amount of inert material and thus the total solid flow increase, affecting several variables like the temperature of the fuel reactor and the fuel conversion efficiency. Figure 7.1 exposes the correlation between inert-to-carrier ratio and fuel reactor temperature.

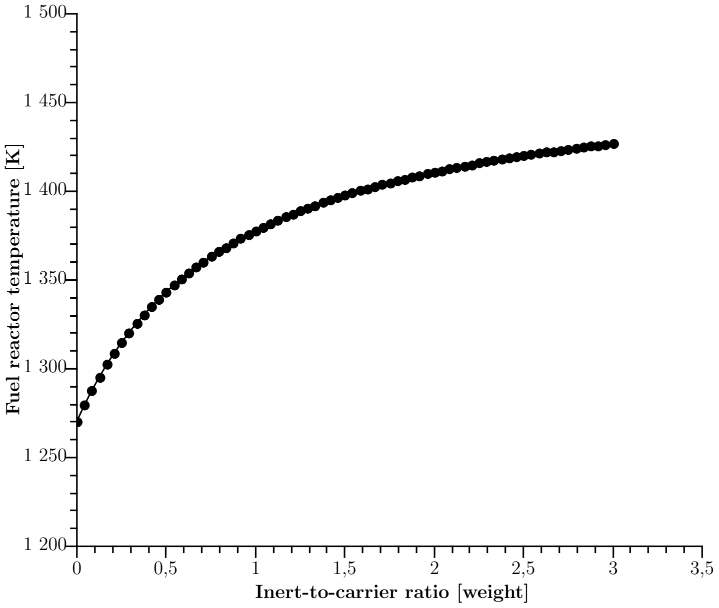

Figure 7.1: Impact of inert-to-carrier ratio on fuel reactor temperature

It can be deduced from Figure 7.1 that an increase of the inert-to-carrier ratio leads to a sharp increase of the fuel reactor temperature until a peak of around 1430-1450°C when it exceeds the value of 3-3.5. The solids flow carries more heat from the oxidation to the reduction reactor but the amount of oxygen transported does not change.

The temperature increase of the fuel reactor implies a better kinetics and thermodynamics for the reaction between the oxygen carrier and the synthesis gas: this reaction is endothermic and is thus favoured at more elevated temperatures. Consequently, the conversion of carbon monoxide to carbon dioxide is enhanced and the carbon capture rate of the overall system is higher. The inert-to-carrier ratio has therefore a direct effect on the fuel reactor temperature and an indirect one on the fuel conversion efficiency.

### 7.4.2 Impact of solid circulation rate

An increase in the solids circulation flow rate means that, for the same inert-to-carrier ratio, the amount of reactive material and of support increases, changing the heat balance of the system. The larger the solids flow rate is, the higher is the fuel reactor temperature.

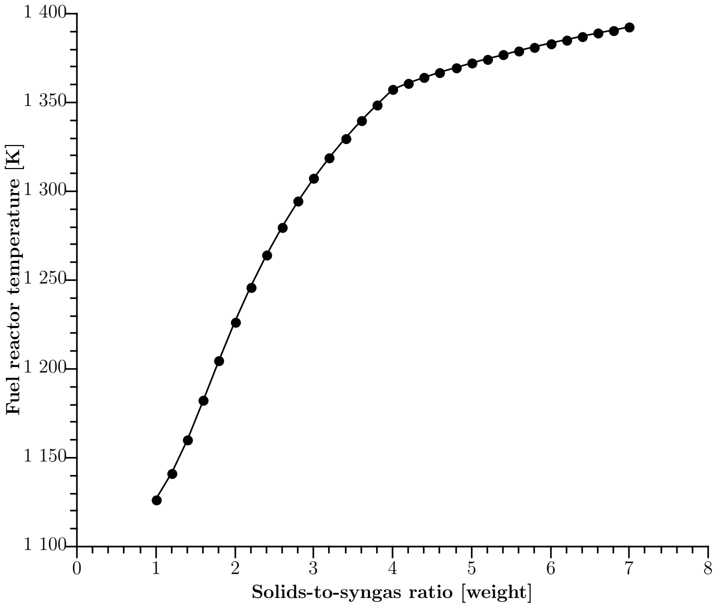

Figure 7.2: Impact of solids-to-syngas ratio on fuel reactor temperature

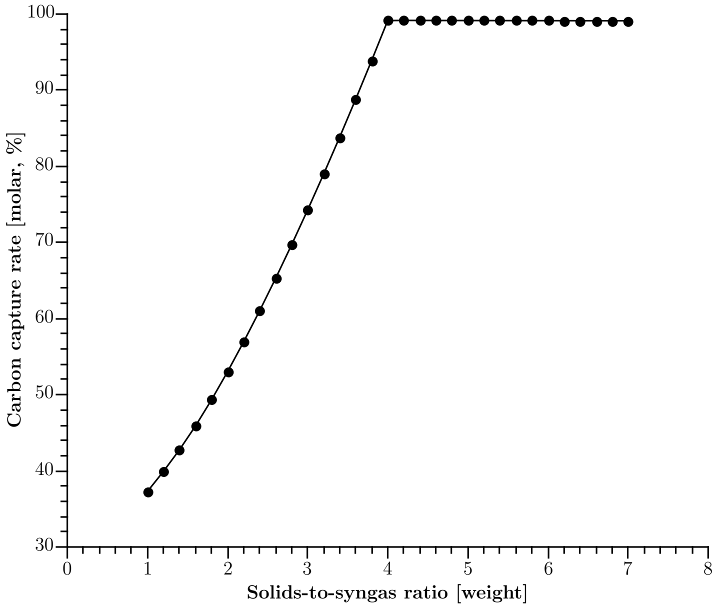

Figure 7.3: Impact of solids-to-syngas ratio on carbon capture rate

As expected, the carbon capture rate increases with larger solids flow rate but reaches a maximum around 99.1% because of equilibrium limitations.

# 7.5 Comparison of oxygen carriers

## 7.5.1 Motivation and method

Nickel-based metal oxides are the most investigated oxygen carrier materials because of their high reactivity towards methane, their high oxygen carrying capacity and their high melting temperatures. They however have the drawbacks of high price and toxicity issues. On the opposite, metal oxides such as manganese and iron are cheaper and environmental-friendly but have a lower oxygen carrying capacity and narrower operating range.

Manganese can swing between more than four oxidation states but only two are likely to form in the chemical combustion process: manganese (II) oxide MnO and hausmannite $Mn_3O_4$. The reactions involved in the fuel reactor are:

$$\begin{aligned} Mn_3O_4 + CO &\longrightarrow 3\,MnO + CO_2 \\ Mn_3O_4 + H_2 &\longrightarrow 3\,MnO + H_2O \end{aligned} \tag{7.3}$$

In addition, the one in the air reactor is:

$$6\,MnO + O_2 \longrightarrow 2\,Mn_3O_4 \tag{7.4}$$

Iron can swing between more than four oxidation states but only four are likely to form in the chemical combustion process: iron Fe, wüstite FeO, hematite $Fe_2O_3$ and magnetite $Fe_3O_4$. The reactions involved in the fuel reactor are:

$$\begin{aligned} Fe_2O_3 + CO &\longrightarrow 2\,FeO + CO_2 \\ FeO + CO &\longrightarrow Fe + CO_2 \\ Fe_2O_3 + H_2 &\longrightarrow 2\,FeO + H_2O \\ FeO + H_2 &\longrightarrow Fe + H_2O \end{aligned} \tag{7.5}$$

In addition, the ones in the air reactor are:

$$\begin{aligned} Fe + \frac{1}{2}O_2 &\longrightarrow FeO \\ 3\,FeO + \frac{1}{2}O_2 &\longrightarrow Fe_3O_4 \\ Fe_3O_4 + O_2 &\longrightarrow 6\,Fe_2O_3 \end{aligned} \tag{7.6}$$

It is obvious that nickel, manganese and iron have different thermodynamic features (the oxygen carrying capacity of nickel is for instance higher than of manganese), kinetic ones (the equilibrium constant of the combustion reaction between manganese and carbon monoxide is higher than with nickel), thermal ones (different heats of reaction...).

Regarding Table 3.1, Table 3.2, Table 3.3 and Table 3.4 it is possible to predict qualitatively the differences between the several oxygen carriers. For instance, nickel has the highest oxygen carrying capacity, followed by manganese and iron: the required flow rates to achieve the same fuel conversion are thus the smallest with nickel and the largest with iron.

The simulation aims to check if it is possible to reach the same carbon capture efficiencies with manganese and iron instead of nickel and what are the mass flow rates and temperatures related, with the same assumptions used in the nickel case.

### 7.5.2 Results and discussion

Different solids inventory of various oxygen carriers, and thus different solids-to-fuel ratios, have an impact on the carbon capture efficiency.

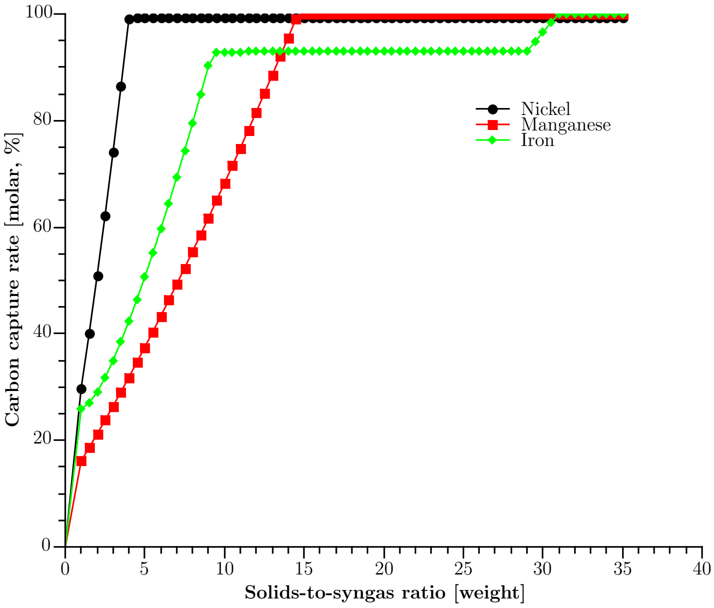

Figure 7.4: Impact of different oxygen carriers on carbon capture rate

There are strong differences between the three systems. In the case of nickel-based oxygen carrier, the required solids-to-syngas ratio to reach 99.1% of $CO_2$-capture efficiency, which is the maximum value thermodynamically allowed for nickel, is around 4. In the case of manganese-based, the solids-to-syngas ratio has to increase by more than three times to around 14.5. The extreme case is iron with a needed solids-to-syngas ratio of around 31.

Table 7.13 presents the exact results (mass flow rates, proportions of oxidised and reduced oxygen carrier, inert material) obtained by the simulation for a carbon capture efficiency of 99.1%. The reason for these differences is that nickel has a much higher oxygen carrying capacity than manganese and iron and thus, for the same amount of oxygen transported, the flow rates of nickel are much smaller. Using nickel-based oxygen carrier is thus advantageous considering the design of the circulating fluidised bed because the amount of bed material needed is much smaller.

Table 7.13: Required solids flow rate for 99.1% carbon capture rate

| | | | **Nickel** | **Manganese** | **Iron** |
|---|---|---|---|---|---|
| **Circulating solids** | Flow rate $\dot{m}_s$ | $[\frac{kg}{s}]$ | 4 | 14.50 | 30.69 |
| **(fuel reactor outlet)** | Proportions oxide/inert | [%wt] | 60/40 | 60/40 | 60/40 |
| **Circulating solids** | Flow rate $\dot{m}_s$ | $[\frac{kg}{s}]$ | 4.65 | 15.15 | 31.34 |
| **(air reactor outlet)** | Proportions reduced/inert | [%wt] | 72.9/27.1 | 61.72/38.28 | 62.49/37.51 |

However, it can be seen from Figure 7.4 that the reactions between nickel and synthesis gas have a more severe equilibrium restriction than the ones with manganese or iron, which has an impact on the maximum carbon capture rate. Table 7.14 presents the composition of the carbon dioxide stream with the maximum attainable carbon capture efficiency and the associated flow rate.

Table 7.14: Features of different oxygen carrier systems for maximum carbon capture rate

| | | | **Nickel** | **Manganese** | **Iron** |
|---|---|---|---|---|---|
| **Circulating solids (fuel reactor outlet)** | Flow rate | $[\frac{kg}{s}]$ | 4 | ~14.8 | ~35.1 |
| **$CO_2$ ready to sequestration** | Flow rate | $[\frac{kg}{s}]$ | 1.33 | 1.33 | 1.33 |
| | $CO_2$ | [% mol] | 94.12 | 95.15 | 95.15 |
| | $N_2$ | [% mol] | 3.95 | 3.97 | 3.97 |
| | $H_2O$ | [% mol] | 0.87 | 0.87 | 0.87 |
| | CO | [% mol] | 0.08 | 0.08 | 0.07 |
| | $H_2$ | [% mol] | 0.27 | 0.003 | 0.002 |
| **Carbon capture rate** | CCR | [% mol] | 99.22 | 99.98 | 99.95 |

The carbon capture rate is the highest with almost 100% with manganese, followed by iron and nickel behind. It means that iron and manganese oxides can convert close to 100% carbon species (carbon monoxide and methane) to carbon dioxide as shown by the low content in carbon monoxide in the flue gases. Figure 7.5 shows the impact of the choice of different oxygen carriers on the temperature in the fuel reactor.

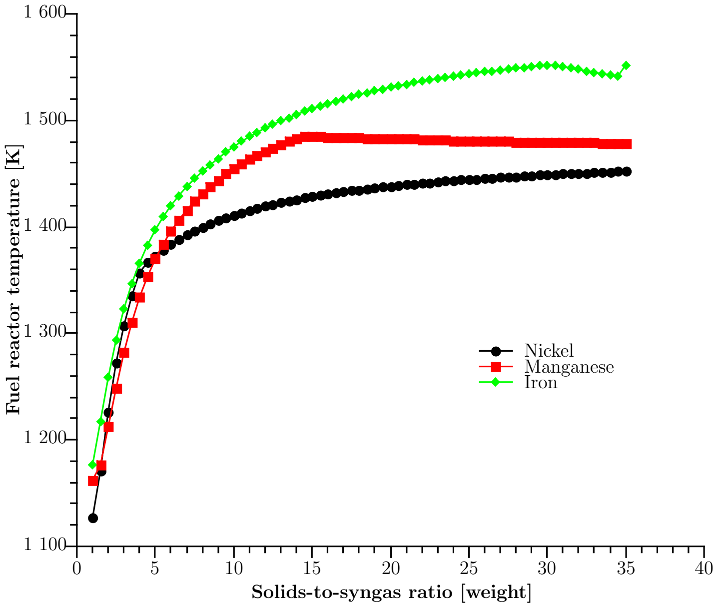

Figure 7.5: Impact of different oxygen carriers on fuel reactor temperature

The temperature in the fuel reactor is always the highest with iron-based oxygen carrier, followed by manganese and finally by nickel. The two main reasons that justify these differences are the different heat capacities of these three chemical species and the different heats of reaction in the air and fuel reactors.

The value of the outlet temperature of the fuel reactor depends strongly on the composition of the synthesis gas. A syngas rich in methane would lead to lower fuel reactor temperatures because of the endothermic characteristic of the reactions of manganese and iron with methane.

The temperatures reached when processing manganese are acceptable whereas they may be problematic when using iron because of the attrition and sintering risks. For the maximum carbon capture rate and the corresponding mass flow rate, the temperature in the fuel reactor is 1212°C for manganese and 1279°C for iron.

## 7.6 Sensitivity analysis on the temperature levels

Several process parameters have a strong impact on the performance of the integrated chemical looping combustion process in the combined cycle power plant. The process parameters related to temperatures considered as critical depend on the studies, but there is a consensus that the following ones are the most important [205; 206]:

- Air reactor outlet or turbine inlet temperature
- Pressure of the chemical-looping combustion system

The air reactor outlet temperature is a key parameter because it is usually equal to the turbine inlet temperature: it has thus a direct and great impact on the maximum power generation of the gas turbine system. The pressure of the overall combustion system is another key parameter because it is equal (after taking into account the pressure drops) to the inlet pressure of the turbine and therefore directly affects the maximum power generation too.

Other variables, which have an effect, but less significant, on the maximum power production and therefore on the overall efficiency of these power generation systems are [205; 206]:

- Air reactor inlet temperature
- Fuel reactor inlet temperature
- Fuel reactor outlet temperature
- Steam cycle temperature and pressure evaporation levels

The impacts of the process parameters that are believed to have a strong effect on the combined cycle efficiency are quantified and presented in the following sub-sections, whereas the impacts of the secondary ones are just qualified.

### 7.6.1 Impact of the air reactor temperature

Since the oxidation of the metal particle is a strongly exothermic reaction, there is a need for reducing the temperature in the air reactor, which depends on several factors such as:

- Heat released during the combustion process
- Air flow rate
- External cooling

The simulations carried out consider the regulation of the airflow rate for sustaining the temperature of the air reactor to the desired value.

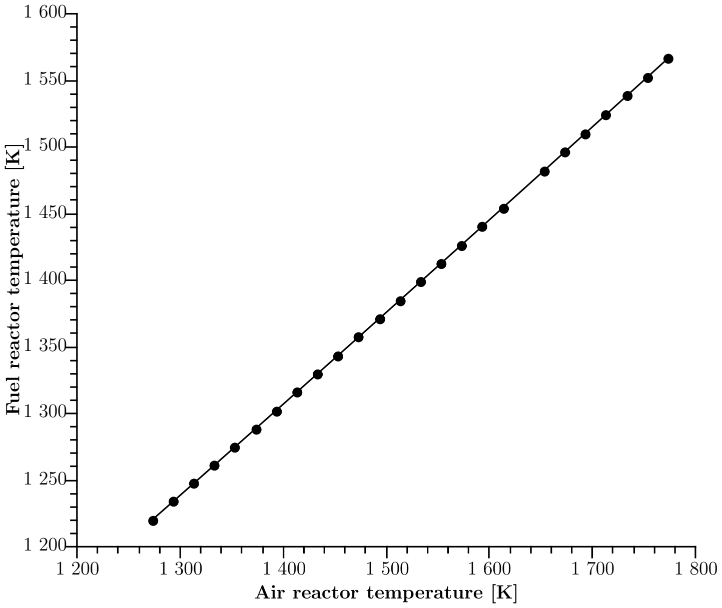

Figure 7.6: Impact of air reactor temperature on fuel reactor temperature

The higher is the air reactor temperature, the higher is the fuel reactor temperature, because the solids flow circulating in the chemical looping system transports heat. The relation between both temperatures in the chemical looping combustion system is linear, which implies that it is relatively easy to control the temperature in the fuel reactor by adjusting the airflow rate, the external cooling or the recirculation of the exhaust gases in the air reactor.

In conventional combined cycles, the main limitation is the maximum temperature that the materials composing the turbine can withstand. In combined cycles with integrated chemical looping combustion, the main restriction is the maximum allowable temperature without melting of the oxygen carrier particles.

Softening of the bed particles may cause problems to run the interconnected fluidised bed because of agglomeration and reactivity losses. It is therefore unlikely that metal oxides such as copper with a melting temperature under 1000°C become interesting. In case that the melting temperature of the oxygen carrier system considered is very high, the limiting factor is the maximum temperature the cyclone materials can endure.

At low values, an increase in the total airflow rate leads to an increase of the air reactor temperature: nickel reacts with oxygen, producing heat and causing thereby a temperature rise that is larger than the temperature drop due to the air cooling effect. However, at high values, the oxygen carrier is completely oxidised and no more nickel reacts with oxygen: larger air circulation results thus in lower air reactor temperatures.

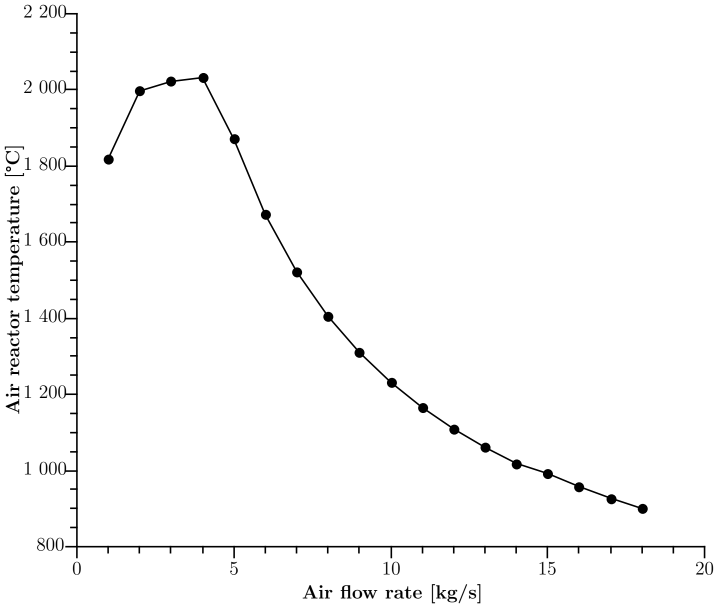

Figure 7.7: Impact of airflow rate on air reactor temperature

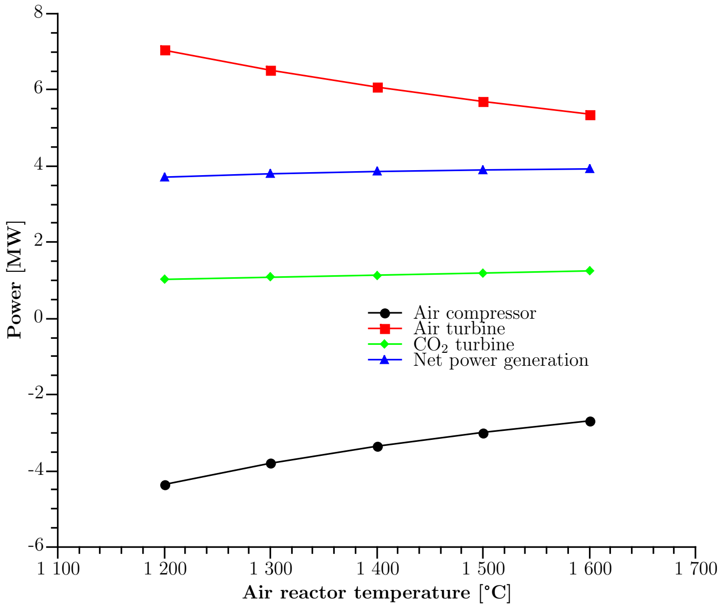

Figure 7.8: Impact of air reactor temperature on gas turbine net power generation

As expected, the higher is the temperature in the air reactor, the more power is generated.

### 7.6.2 Impact of the fuel reactor temperature

The temperature in the fuel reactor depends mainly on the solids inventories: the larger is the flow rate of the oxygen carrier, the more heat is carried from the oxidation to the reaction reactor. The direct benefit of a high temperature in the fuel reactor is a better kinetics and a more favourable thermodynamics because of the endothermic feature of the syngas oxidation reaction when processing nickel. The fuel reactor is therefore operated in adiabatic conditions.

When processing iron or manganese, the syngas oxidation is likely exothermic too, in that case, it is possible to control it by external cooling or exhaust gas recirculation as well. The temperature of the reduction reactor controls the temperature level of the recoverable exhaust heat since the fuel gases run through the heat recovery steam generator.

### 7.6.3 Impact of the air stream temperature

The air stream temperature depends on the use of an air pre-heater located upstream of the chemical looping system. If no air pre-heater is present in the power plant, the air temperature is equal to the outlet temperature of the air compressor of the gas turbine cycle. A possibility for pre-heating the air stream without burning additional fuel is to recover heat from the air or fuel reactor or from the combined cycle [105].

The higher the air temperature, the larger is the enthalpy of the air stream entering the chemical looping system and therefore the amount of heat available. In order to control the temperature in the air reactor, it is needed to regulate the amount of heat generated and therefore, for example, the airflow rate. In this case, increasing the airflow rate leads to an increase in compressor and turbine work, but to a larger volume of the air reactor or higher gas velocities, that may have an influence on the fluidisation conditions and pressure drops over the reactors.

### 7.6.4 Impact of the fuel stream temperature

The fuel stream temperature depends on the use of a fuel pre-heater located upstream of the chemical looping system. If no fuel pre-heater is present in the power plant, the fuel stream temperature is equal to the outlet temperature of the gas cleaning system of the IGCC power plant. A possibility for pre-heating the fuel stream without burning additional fuel is to recover heat from the air or fuel reactor or from the combined cycle, as suggested for the air stream too [105].

### 7.6.5 Multi-reactor

The mildly exothermic feature of the syngas reaction with metal oxides in chemical looping combustion leads to relatively high temperature levels in the system. A possibility is to split this combustion system into two sub-chemical looping combustion ones: the temperatures reached in the reactors are thus lower and the risks of sintering and melting of the oxygen carrier particles are thereby minimised. The obvious drawback is the higher equipment cost because of the increased number of reactors, pipes, turbines and so [145].

## 7.7 Integration of supplementary firing (air reactor)

### 7.7.1 Motivation and method

An option to increase the inlet temperature of the air turbine without changing the operating temperature in the oxidation reactor is to burn a part of the fuel in a secondary combustion chamber. Since the most common oxygen carrier particles cannot withstand too high temperatures because of melting and sintering risks, the advantageous feature of supplementary firing is to increase the exhaust temperature of the oxygen-depleted air without increasing the temperature inside the air reactor [205].

If the fuel reacts with air, it is then necessary to bring extra energy to separate the carbon dioxide from the flue gases or it leads to $CO_2$ penalty otherwise. On the other hand, if the fuel burns in pure oxygen the demand for a cryogenic air separation unit will increase. Both possibilities involve higher energy or $CO_2$ penalties. In general, top firing for increasing the temperature of the oxygen-depleted air stream consists of fuel burning in presence of air and involves larger carbon dioxide emissions to the atmosphere.

Since the air stream entering the chemical looping combustion system is in excess to regulate the temperature in the air reactor, the oxygen-depleted air still contains some oxygen. It is therefore possible to increase the exhaust temperature by mixing it with some fuel and without compressing extra air. The system simulated consists therefore of an additional combustor in which oxygen-depleted air and synthesis gas react.

The assumptions made are:

- The additional combustor is operated adiabatically.
- The pressure drop over the combustor is equal to 1 bar.
- The amount of synthesis gas introduced in this system is adjusted so to increase the temperature of the oxygen-depleted air by 100°C.

### 7.7.2 Results and discussion

The simulations carried out with ASPEN Plus return the following results: around 0.132 kg/s of synthesis gas, so 11.7% of the total amount needs to be processed in the top firing to increase the temperature of the oxygen-depleted air by 100°C.

Table 7.15: Properties of key streams in supplementary firing for air reactor

| **Stream** | **Mass flow rate** $[\frac{kg}{s}]$ | **Temperature** [°C] | **Pressure** [bar] |
|---|---|---|---|
| **Oxygen-depleted air (combustor inlet)** | 9.810 | 1200 | 16 |
| **Synthesis gas (combustor inlet)** | 0.132 | 300 | 16 |
| **Flue gases (combustor outlet)** | 9.942 | 1300 | 15 |

Table 7.16: Composition of key streams in supplementary firing for air reactor

| | | **Syngas** | **Oxygen-depleted air** | **Flue gases** |
|---|---|---|---|---|
| $\mathbf{N_2}$ | [% mol] | - | 80.7 | 81.8 |
| $\mathbf{O_2}$ | [% mol] | - | 19.2 | 16.2 |
| **CO** | [% mol] | 46.6 | - | - |
| $\mathbf{CO_2}$ | [% mol] | 13.3 | - | 1.1 |
| $\mathbf{H_2O}$ | [% mol] | 0.3 | - | 0.7 |
| $\mathbf{H_2}$ | [% mol] | 37.2 | - | - |
| **NO** | [ppm] | - | 1000 | 1656 |
| $\mathbf{NO_2}$ | [ppm] | - | 34 | 23 |
| $\mathbf{N_2O}$ | [ppb] | - | 367 | 348 |

As illustrated by Table 7.16 the amount of oxygen decreases in parallel of an increase of carbon dioxide and steam because of the additional burning.

Table 7.17: Additional simulation results for supplementary firing - air reactor

| **Additional results** | | |
|---|---|---|
| $\mathbf{CO_2}$ **emissions** | $[\frac{kg}{s}]$ | 0.171 |
| **Flue gases turbine power** | [MW] | 7.514 |
| **Net GT power gain** | [MW] | 0.472 |
| **HRSG steam pump** | [MW] | 0.090 |
| **HRSG steam turbine** | [MW] | 3.050 |
| **Net HRSG power gain** | [MW] | 0.509 |
| **Total net combined cycle gain** | [MW] | 0.981 |
| **Extra-emitted** $\mathbf{CO_2}$ | $[\frac{kg}{MJ}]$ | 0.174 |

Additional air firing, as seen in Table 7.17, leads to an increase of the power generation in both gas turbine and steam cycles.

Table 7.18: Combined cycle efficiencies for supplementary firing - air reactor

| **Combined cycle efficiency** | |
|---|---|
| **CC efficiency** | 58.2% |
| **CC efficiency (with** $\mathbf{CO_2}$ **compression)** | 54.6% |
| **CC efficiency gain** | 1.9% point |

Supplementary firing by 100°C leads to an increase of the power generation, of the net energy efficiency and of the $CO_2$ emissions. Top firing does usually not lead to such a strong increase of the net energy efficiency but brings the advantage of more flexible power generation, better transient behaviour and higher part-load efficiencies [138; 139] and the drawback of a need for high-temperature resistant materials or additional cooling [205].

## 7.8 Integration of supplementary firing (fuel reactor)

### 7.8.1 Motivation and method

Increasing the inlet temperature of the $CO_2/H_2O$ turbine without changing the operating temperature in the reduction reactor can be achieved by top firing. Since the $CO_2/H_2O$ stream contains only few amounts of carbon monoxide and hydrogen, it is therefore not possible to burn it and to increase its temperature as it was the case with air top firing. Regarding the fact that the $CO_2/H_2O$ mixture has already a relatively high temperature, increasing it by indirect heating with heat exchangers is not technologically feasible.

Supplementary firing for increasing the temperature of the carbon dioxide stream consists of fuel burning in presence of pure oxygen to avoid an excessive dilution of carbon dioxide by nitrogen. The three streams are directly mixed together to promote heat transfer, leading therefore to a higher oxygen and carbon monoxide content of the $CO_2/H_2O$ stream.

The assumptions made in the process simulations are:

- The additional combustor is operated in adiabatic conditions.
- The pressure drop over the combustor is equal to 1 bar.

Since an increased demand of the air separation unit and a lower conversion efficiency leads to an increase of the overall energy penalty, the aims are both to minimize the oxygen demand and to avoid high concentrations in carbon monoxide and hydrogen in the $CO_2/H_2O$ mixture.

The amounts of synthesis gas and oxygen introduced in this additional system are adjusted to respect the following constraints:

- Less than 1% mol of carbon monoxide in the $CO_2/H_2O$ mixture
- Less than 1% mol of hydrogen in the $CO_2/H_2O$ mixture

### 7.8.2 Results and discussion

The simulations carried out with ASPEN Plus return the following results:

Table 7.19: Properties of key streams in supplementary firing for fuel reactor

| **Stream** | **Mass flowrate** $[\frac{kg}{s}]$ | **Temperature** [°C] | **Pressure** [bar] |
|---|---|---|---|
| **$CO_2/H_2O$ (combustor inlet)** | 1.654 | 1085 | 16 |
| **Synthesis gas (combustor inlet)** | 0.044 | 300 | 16 |
| **Oxygen (combustor inlet)** | 0.055 | 30 | 16 |
| **Flue gases (combustor outlet)** | 1.753 | 1185 | 15 |

Table 7.20: Composition of key streams in supplementary firing for fuel reactor

| | | **Syngas (combustor inlet)** | **Oxygen-depleted air (combustor inlet)** | **Flue gases (combustor outlet)** |
|---|---|---|---|---|
| **$N_2$** | [% mol] | - | 2.5 | 2.4 |
| **$O_2$** | [% mol] | - | - | 1.8 |
| **CO** | [% mol] | 46.6 | 0.5 | 1 |
| **$CO_2$** | [% mol] | 13.3 | 59.4 | 57.8 |
| **$H_2O$** | [% mol] | 0.3 | 37.5 | 36.7 |
| **$H_2$** | [% mol] | 37.2 | 0.2 | 0.2 |
| **NO** | [ppm] | - | 3117 | 573 |
| **$NO_2$** | [ppm] | - | - | 1 |
| **$N_2O$** | [ppb] | - | - | 13 |
| **$NH_3$** | [ppb] | - | 17 | 16 |

Around 0.04 kg/s of synthesis gas, so 4.2% of the total amount of syngas in the chemical looping system, needs to be processed in the top firing to increase the temperature of the $CO_2/H_2O$ mixture by 100°C. From the different process simulations, it is therefore possible to calculate the gains in net power generation and in $CO_2$-compression.

Table 7.21: Additional simulation results for supplementary firing - fuel reactor

| **Additional results** | | |
|---|---|---|
| **Flue gases turbine power** | [MW] | 1.151 |
| **Net GT power gain** | [MW] | 0.125 |
| **$CO_2$-compressor** | [MW] | -0.483 |
| **Losses** | [MW] | -0.037 |

As expected, the power generated in the $CO_2$-turbine is higher because of the larger flue gases flow rate and for the most part because of the higher temperature of the $CO_2/H_2O$ mixture.

## 7.9 Sensitivity analysis on the pressure levels

The pressure levels should be considered as well because changes in pressure have an influence on the particles reactivity and thus on the solids inventories. It is a big issue in combined cycle power plants since the fuel and air pressures in a chemical looping system would usually be above 15 bars. The process parameters related to pressures considered as critical depend on the studies, but the following ones are the most critical [205; 206]:

- Gas turbine pressure ratio
- Pressure of the carbon dioxide stream before sequestration

### 7.9.1 Gas turbine pressure ratio

The pressures in the oxidation and reduction reactors are the same in order to avoid gas leakages. The simulations show that increasing the system pressure results in a negligible decrease in $CO_2$ capture efficiency, as confirmed by few studies and experiments carried out [66]. Changing the pressure of the chemical looping combustion system has however a strong impact on the net power generation of the gas turbine cycle. Lower pressure results in lower power consumption in the compressors and in lower power generation in the depleted oxygen air turbine.

The higher is the pressure ratio, the larger is the amount of work generated in the $CO_2$-turbine and the lower is the outlet temperature of the $CO_2$-steam mixture. However, this value should not be below the dew point of the $CO_2$-water mixture: the formation of water droplets inside the turbine would then be possible and liquid water causes turbine blade erosion and reduces the life use of the device. The pressure ratio over the turbine or, equivalently, the outlet pressure of the gas turbine cycle is an important design factor and is subject to optimization. Low-pressure ratios imply low work generation and high-pressure ratios imply high work generation but low outlet turbine temperatures.

In theory, higher-pressure ratios lead to higher turbine power generation and thus higher net plant efficiency. In practice, there is an optimum value of pressure ratio for a maximum turbine power generation and another one to maximise the net plant efficiency [205; 206].

The reason is that there is an efficiency drop due to the air turbine cooling. Turbine materials cannot withstand too high temperatures and cold air goes through the gas turbines to lower the turbines inlet temperatures. The airflow rate therefore increases in order to provide the cooling needed, which implies larger compressor work and turbine power. However, the extra compressor work may be higher than the extra turbine power, and the net power generation decreases.

### 7.9.2 Pressure of the $CO_2/H_2O$ stream

The pressure of the $CO_2/H_2O$ stream at the outlet of the fuel reactor is equal to the overall pressure of the chemical-looping system, so around 15-25 bars, depending on the pressure drops in the overall system and the operating pressure of the gasifier. There are two main possibilities:

- The first possibility is to send directly the $CO_2/H_2O$ stream to the steam cycle: the high temperature associated with the chemical-looping combustion system allows therefore the generation of almost exclusively high-pressure steam and the power production in the steam cycle will thus be high. A three-level pressure steam cycle may thus not be appropriate and a critical one may be preferable.

- The second possibility is to integrate a $CO_2$-turbine before the steam cycle: the power produced in the gas turbine cycle increases but the temperature of the $CO_2/H_2O$ mixture decreases. The lower temperature of the stream when running through the HRSG unit implies that less high-pressure steam and more low-pressure steam will be produced. The direct consequence is a lower power production in the steam cycle.

## 7.10 Integration of $CO_2$-turbine

### 7.10.1 Motivation and method

In an IGCC power plant without $CO_2$-turbine, the $CO_2/H_2O$ mixture has a temperature in the range 1000-1200°C, which is the outlet temperature of the fuel reactor, and a pressure in the range 15-25 bars, which is the overall pressure of the chemical-looping system. Since the temperature and pressure of this stream are that high it is therefore possible to generate high temperature and pressure steam.

Moreover, the dew point of the $CO_2/H_2O$ mixture at a pressure over 10 bars is above 180°C. Cooling down this stream below its dew point leads to water condensation and release of its latent heat. This heat is usable for evaporating water upstream of the steam cycle because, at conventional pressures, the boiling point of water is below the dew point of the $CO_2/H_2O$ mixture.

The implementation of the turbine has a strong impact on the design of the overall process. First, the expansion of the $CO_2/H_2O$ stream to atmospheric pressure involves a decrease in temperature and pressure. These lower temperature and pressure of the $CO_2/H_2O$ mixture involve changes in the HRSG design.

Secondly, the dew point of a $CO_2/H_2O$ mixture at atmospheric pressure is around 90°C, which is below the boiling point of the water at the different pressures of the steam cycle. The latent heat from this stream is therefore not recoverable for evaporating water in the steam cycle.

Finally, the expansion of the $CO_2/H_2O$ stream to lower pressure involves larger power consumption in the $CO_2$-compressor for carbon dioxide sequestration. It is thus interesting to evaluate the integration of the $CO_2$-steam turbine in the overall power plant process, i.e. to check if it is profitable expanding this stream before re-compressing the carbon dioxide for sequestration after the HRSG.

### 7.10.2 Results and discussion

Integrating a $CO_2$-turbine has a detrimental effect on the bottoming steam cycle because of the temperature drop of about 400-450°C over the expander. When integrating the $CO_2$-turbine, the generation of high-pressure steam is smaller whereas the production of medium- and lower-pressure one is larger.

The comparison of both cycles reveals that the net power generation of the combined cycle is much higher when integrating a $CO_2$-turbine but these benefits are partly lost when taking into consideration the extra-work needed to compress the carbon dioxide stream. The total net power production of the cycle is larger when implementing a $CO_2$-turbine, which leads to an increase of the cycle efficiency of nearly 3%.

In practice, this difference will be smaller because the model used in this Master's work to simulate the static behaviour of the HRSG without $CO_2$ turbine is not appropriate. The choice of integrating an additional turbine is thus open to discussions, regarding the cost of a $CO_2/H_2O$ turbine and its dynamic behaviour. Researches within this field suggest that, depending on the considered cases, different configurations of the whole system may be optimum.

Table 7.22: Energy balance of CLC combined cycle w/o $CO_2$-turbine

| **Power** $[MW]$ | | **CLC with $CO_2$ turbine** | **CLC without $CO_2$ turbine** | **Absolute difference** |
|---|---|---|---|---|
| **Energy content** | Synthesis gas | 10.835 | 10.835 | 0 |
| **Power generation** | Gas turbine cycle | 8.068 | 7.042 | -1.026 |
| | HRSG | 2.564 | 2.952 | 0.388 |
| **Power consumption** | Gas turbine cycle | -4.360 | -4.360 | 0 |
| | HRSG | -0.072 | -0.088 | -0.016 |
| **Net power** | | 6.160 | 5.547 | -0.613 |
| **Efficiencies** | $\eta_{cc}$ (LHV basis) | 56.9% | 51.2% | -5.7% point |
| **$CO_2$ compression** | | -0.446 | -0.145 | 0.301 |
| **Net power** | | 5.714 | 5.402 | -0.312 |
| **Efficiencies** | $\eta_{cc}$ (LHV basis) | 52.7% | 49.9% | -2.8% point |

## 7.11 Integration of $H_2$-production

### 7.11.1 Motivation and method

The interest for integrating hydrogen production in parallel of $CO_2$-capture raised these last years and it is so interesting to investigate if chemical looping hydrogen is applicable in parallel of chemical looping combustion of synthesis gas. The process considered is therefore a variant of the process proposed earlier. The main difference lies in the design of the oxidation reactor where regeneration of the metal oxide particles takes place in two steps and thus in two reactors:

- Oxidation with steam which leads to the production of a $H_2/H_2O$ mixture and to an oxidation of the metal particles
- Oxidation with air which leads to a higher conversion of metal oxides or a conversion to a further oxidation state

The most suitable oxygen carrier system for this type of application is iron oxides because of their thermodynamic properties and their several oxidation states. Iron can swing between four oxidation states: iron Fe, wüstite FeO, hematite $Fe_2O_3$ and magnetite $Fe_3O_4$. The amounts of steam injected and of air affect directly the proportions of the different iron oxides and the reactions involved are:

- In the steam reactor

$$\begin{aligned} \mathrm{Fe} + \mathrm{H_2O} &\longrightarrow \mathrm{FeO} + \mathrm{H_2} \\ 3\,\mathrm{FeO} + \mathrm{H_2O} &\longrightarrow \mathrm{Fe_3O_4} + \mathrm{H_2} \end{aligned} \tag{7.7}$$

- In the air reactor

$$4\,\mathrm{Fe_3O_4} + \mathrm{O_2} \longrightarrow 6\,\mathrm{Fe_2O_3} \tag{7.8}$$

- In the fuel reactor (synthesis gas combustion)

$$\begin{aligned} \mathrm{Fe_2O_3} + \mathrm{CO} &\longrightarrow 2\,\mathrm{FeO} + \mathrm{CO_2} \\ \mathrm{FeO} + \mathrm{CO} &\longrightarrow \mathrm{Fe} + \mathrm{CO_2} \\ \mathrm{Fe_2O_3} + \mathrm{H_2} &\longrightarrow 2\,\mathrm{FeO} + \mathrm{H_2O} \\ \mathrm{FeO} + \mathrm{H_2} &\longrightarrow \mathrm{Fe} + \mathrm{H_2O} \end{aligned} \tag{7.9}$$

There are two main possibilities for the hydrogen stream: either it passes a combined cycle to produce electricity and heat or it runs through a PSA unit to increase its purity for further use.

The same data for the gas turbine cycle as in the rest of the study is taken and the additional assumptions regarding the steam reactor are based on literature studies [25]:

Table 7.23: Additional process input of IGCC-CLC/CLH

| **Chemical-looping system** | | **Baseline case** |
|---|---|---|
| **Steam flowrate $\dot{\mathbf{m}}_{sr}$** | $[\frac{kg}{s}]$ | 6 |
| **Steam reactor temperature $\mathbf{T}_{sr}$** | [°C] | 400 |
| **Pressure drop $\Delta$P** | [bar] | 1 |
| **Heat losses $\dot{\mathbf{Q}}_{losses}$ [MW]** | | 0 |

### 7.11.2 Results and discussion

The simulation of this coupled chemical looping combustion of synthesis gas and chemical looping hydrogen returns the following results.

Table 7.24: $H_2/H_2O$ mixture composition in IGCC-CLC/CLH

| **$H_2/H_2O$ mixture** | | **IGCC-CLC/CLH** |
|---|---|---|
| **CO** | [% mol] | - |
| **$CO_2$** | [% mol] | - |
| **$H_2$** | [% mol] | 55.46 |
| **$N_2$** | [% mol] | - |
| **$CH_4$** | [% mol] | - |
| **$H_2O$** | [% mol] | 44.54 |
| **$H_2S$ + COS** | [ppm] | - |

It can be deduced that the generation of hydrogen is feasible when processing iron oxides with a relatively high yield of steam to hydrogen.

## 7.12 Concluding remarks

The present Master's Thesis explores the possibility of integrating chemical looping combustion in an IGCC power plant by replacing the combustion chamber of the gas turbine. The simulations demonstrated the feasibility of this customized process and emphasized the following results:

1. The integration of $CO_2$-capture in the gas turbine system is possible with a carbon capture rate higher than 99% when there are no leakages between the air and fuel reactor.
2. It is possible to produce a $CO_2$-stream ready for sequestration with purity higher than 93% after condensation and compression to 110 bars.
3. For the same turbine inlet temperature (TIT), a conventional combined cycle without $CO_2$ capture has a higher electrical efficiency than an integrated chemical looping combustion system with $CO_2$-turbine by 4% points (LHV basis and $CO_2$-compression included).
4. Nickel-, manganese- and iron-based metal particles are suitable oxygen carriers for chemical looping combustion. The solids flow rates to process are larger with manganese and iron because of their smaller oxygen carrying capacity but the conversion of carbon species is higher than with nickel.
5. The electrical efficiency of the chemical looping system is highly dependent on the turbine inlet temperature, and thus on the maximum temperature allowable in the air reactor. An increase of 100°C of the temperature of the oxygen-depleted air by supplementary firing results in larger power generation and higher electrical efficiency by 2% points (LHV basis and $CO_2$-compression included).
6. The gas turbine pressure ratio and thus the pressure at the outlet of the gas turbine cycle have a large impact on the total power generation and electrical efficiency. The expansion of the $CO_2/H_2O$ mixture results in a gain in 3% points electrical efficiency (LHV basis and $CO_2$-compression included) of the combined cycle.
7. Hydrogen production in parallel of $CO_2$-capture is feasible only with iron-based oxygen carriers with a limited conversion of steam of about 55%.

# Chapter 8

# IGCC power plant with chemical looping gasification

## 8.1 Description

### 8.1.1 General principle

The principle of this proposed system is detailed in Chapter 5.3. The oxygen carrier considered in this simulation is nickel oxide with nickel alumina as inert support. The nickel is oxidised in the air reactor following this path:

$$\mathrm{Ni} + \frac{1}{2}\mathrm{O_2} \longrightarrow \mathrm{NiO} \tag{8.1}$$

Gasification involves several chemical reactions with carbon, carbon monoxide, carbon dioxide, hydrogen, steam and methane. The reactions occurring in the reactors and that involve nickel oxides are thus:

- Combustion reactions

$$\begin{aligned} \mathrm{NiO} + \mathrm{C} &\longrightarrow \mathrm{Ni} + \mathrm{CO} \\ \mathrm{NiO} + \mathrm{CO} &\longrightarrow \mathrm{Ni} + \mathrm{CO_2} \\ \mathrm{NiO} + \mathrm{H_2} &\longrightarrow \mathrm{Ni} + \mathrm{H_2O} \end{aligned} \tag{8.2}$$

The other reactions involved are:

- Boudouard Reaction

$$\mathrm{C} + \mathrm{CO_2} \longrightarrow 2\,\mathrm{CO} \tag{8.3}$$

- Water-gas reaction

$$\begin{aligned} \mathrm{C} + \mathrm{H_2O} &\longrightarrow \mathrm{CO} + \mathrm{H_2} \\ \mathrm{CO} + \mathrm{H_2O} &\longrightarrow \mathrm{CO_2} + \mathrm{H_2} \end{aligned} \tag{8.4}$$

- Methanation reaction

$$C + 2\,H_2 \longrightarrow CH_4 \tag{8.5}$$

It is however possible to summarize these reactions into this overall reaction:

$$C_nH_m + nNiO \longrightarrow nCO + \frac{m}{2}H_2 + nNi \tag{8.6}$$

Whereas in a conventional combined power plant only one gas stream exits the cycle, two gas streams, an oxygen-depleted air one and a synthesis gas stream are produced in IGCC with chemical-looping gasification.

### 8.1.2 Assumptions

The general assumptions used to run the IGCC-CLG models are as follows in Table 8.1 and in Table 8.2. The amounts of oxygen and steam introduced in the gasification system and the operating parameters are based on data from previous studies in literature. Sensitivity analysis on the oxygen- and steam-to-fuel ratios are presented later in this study.

Table 8.1: Process streams of IGCC-CLG

| | | | **Baseline case** |
|---|---|---|---|
| **Coal** | Flow rate $\dot{m}_{coal}$ | $[\frac{kg}{s}]$ | 1 |
| | Temperature | [°C] | 25 |
| | Pressure | [bar] | 30 |
| **Air** | Oxygen-to-fuel ratio | [wt] | 0.84 |
| | Flow rate $\dot{m}_{air}$ | $[\frac{kg}{s}]$ | 3.4 |
| | Temperature | [°C] | 15 |
| | Pressure | [atm] | 1 |
| **Circulating solids** | Ni | [% wt] | 60 |
| | $Al_2O_3$ | [% wt] | 40 |
| | Solid-to-fuel ratio | [wt] | 18 |
| **Steam** | Steam-to-fuel ratio | [wt] | 0.06 |
| | Temperature | [°C] | 300 |
| | Pressure | [bar] | 30 |

Coal is pumped at an ambient temperature of 25°C and dried before being introduced in the gasifier. Air enters the power plant at ambient conditions but is heated and compressed before running through the gasifier. Steam is generated in the heat recovery steam generator and injected at a temperature of 300°C. The temperature of 1200°C in the air reactor is a reasonable limit for chemical looping applications and the one of 930°C in the fuel reactor is the adiabatic temperature for this amount of nickel oxide processed, which means that there are no heat losses to the environment. Heat is nevertheless carried from one reactor to the other by the solids flow (oxygen carrier and inert particles).

The pressure drop is considered as negligible compared to the pressure losses in the overall IGCC system and the chemical looping system is assumed adiabatic.

Table 8.2: Reactors of IGCC-CLG

| **Chemical-looping system** | | **Baseline case** |
|---|---|---|
| **Air reactor temperature $\mathbf{T}_{ar}$** | [°C] | 1200 |
| **Fuel reactor temperature $\mathbf{T}_{fr}$** | [°C] | 930 |
| **Pressure drop $\Delta$P** | [bar] | 1 |
| **Heat losses $\dot{\mathbf{Q}}_{losses}$ [MW]** | | 0 |

The exact composition of the fuel can strongly vary depending on the type of coal or biomass processed. Whereas, on a mass basis, anthracite contains more than 85% of carbon, less than 15% of moisture and has a higher heating value of more than 32.5 MJ/kg, brown coals contain less than 35% of carbon, up to 65% of moisture and has a higher heating value as received of less than 17 MJ/kg. Several types of coal are investigated in this study but the type of coal considered here is a sub-bituminous coal with the following composition:

Table 8.3: Coal composition

| | **Proximate analysis** [% wt ar] | | | | **Ultimate analysis** [% wt maf] | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Fixed carbon | Volatile matter | Water | Ash | C | H | O | N | S |
| **Sub-bituminous coal** | 33.8 | 34.3 | 25 | 6.9 | 73.9 | 5.3 | 18.1 | 1.2 | 1.4 |

For simplifications, the baseline cases assume that:

- The pressure of the system is the same in both chemical looping reactors to avoid gas leakages between both.
- The heat losses in the chemical looping reactors are negligible.
- The pressure drops over the heaters and condensers are negligible compared to the high pressures involved in the system.
- The amount of metal oxide set is the minimum amount of metal oxide and inert material that should circulate to capture the total amount of oxygen flowing through the air reactor.
- The coal is dried and has a moisture content of 10% at the gasifier inlet. The lower heating value of the coal moisture and ash free is equal to 28.91 MJ/kg and the net calorific value of the coal as received in the gasifier is therefore equal to 23.62 MJ/kg.

## 8.2 Comparison of a conventional gasifier to a gasifier with integrated chemical looping

### 8.2.1 Motivation and method

The interest of comparing a conventional gasifier to a gasifier with integrated chemical looping is to evaluate the feasibility of the implementation of this new type of process in conventional power plants. Chemical looping gasification eliminates the need for a cryogenic distillation unit and thus reduces the energy penalty for air separation. Moreover, devising the gasification routes in several reaction schemes is thermodynamically advantageous because it would decrease the exergy destruction over the overall process. This power process study considers therefore a two-baseline case:

- IGCC with chemical-looping gasification, in which the coal fuelled to the system reacts with oxygen and steam in fuel-rich proportions and indirect contact
- IGCC without chemical-looping gasification, in which the coal fuelled to the system directly reacts with steam and oxygen from the cryogenic air separation unit

In a conventional gasifier, there is only a stream of synthesis gas exiting the system whereas, in an integrated chemical looping gasifier, there is an additional stream of oxygen-depleted air. It is thus possible to generate power by expanding this stream and by recovering heat in HRSG system. Since the synthesis gas has to be cooled before entering the gas cleaning system, it is attractive to heat the oxygen-depleted air before entering the HRSG system.

### 8.2.2 Results and discussion

The air reactor temperature is always higher than the fuel reactor one because of the exothermic feature of the oxidation of metal materials and the endothermic feature of the gasification process. For this reason, it is of interest to operate the gasifier in adiabatic conditions so that the temperature is as high as possible, which shifts the equilibrium to the desired products.

Table 8.4: Properties of key streams of IGCC with conventional gasifier

| **Stream** | **Mass flow rate** $[\frac{kg}{s}]$ | **Temperature** [°C] | **Pressure** [bar] |
|---|---|---|---|
| **Air** | 2.130 | 15 | 1.013 |
| **Steam** | 0.450 | 300 | 30 |
| **Synthesis gas** | 1.864 | 980.3 | 29 |

In the case of IGCC with integrated chemical looping gasification and with the same amounts of oxygen and steam at the inlet of the system, ASPEN Plus returns the following results.

Table 8.5: Properties of key streams of IGCC-CLG

| **Stream** | **Mass flow rate** $[\frac{kg}{s}]$ | **Temperature** [°C] | **Pressure** [bar] |
|---|---|---|---|
| **Air (gas turbine inlet)** | 10.464 | 15 | 1.013 |
| **Oxygen-depleted air (air reactor outlet)** | 9.810 | 1200 | 16 |
| **Oxygen-depleted air (air turbine outlet)** | 9.810 | 558 | 1.1 |
| **Circulating solids (air reactor outlet)** | 4.65 | 1200 | 16 |
| **Circulating solids (fuel reactor outlet)** | 4 | 1084 | 16 |
| **$CO_2$/$H_2O$ (gas turbine outlet)** | 1.654 | 645.5 | 1.1 |
| **$CO_2$ (ready to sequestration)** | 1.330 | 30 | 110 |

It can be seen that the temperature at the gasifier outlet is higher in the conventional case than in chemical looping gasification and that the amount of synthesis gas generated is slightly higher.

Table 8.6: Comparison between conventional and integrated chemical looping gasifier

| | | IGCC | IGCC-CLG |
|---|---|---|---|
| **$N_2$** | [% mol] | 0.4 | 0.4 |
| **CO** | [% mol] | 39.8 | 36.3 |
| **$CO_2$** | [% mol] | 9.0 | 12.6 |
| **$H_2O$** | [% mol] | 12.8 | 13.9 |
| **$H_2$** | [% mol] | 35.8 | 31.7 |
| **$CH_4$** | [% mol] | 1.9 | 5.1 |
| **$SO_2$** | [% mol] | 0.4 | - |
| **HCl** | [ppm] | 256 | 273 |
| **LHV** | $[\frac{MJ}{kg}]$ | 10.8 | 9.5 |

The synthesis gas generated by a conventional gasifier has a larger content in carbon monoxide and a small one in carbon dioxide, whereas the contents in steam and hydrogen are similar. The lower heating value of the first synthesis gas is roughly equal to 10.8 MJ/kg and the second to 9.5 MJ/kg. The cold gas efficiencies are therefore 85.2% for the conventional gasifier and 74% for the integrated one. These losses are mainly due to the relatively high temperature of the oxygen-depleted air stream after the combined cycle and, for every gasifier system, to the presence of ash and slag.

Regarding the energy balance of the overall system, power is generated in the gas turbine and heat recovery steam generator systems in which oxygen-depleted air runs through and amounts for around 3.6% of the coal lower heating value.

Table 8.7: Energy balance of the oxygen-depleted air

| **Power** $[MW]$ | **Oxygen-depleted air** |
|---|---|
| **Air compressor** | -1.178 |
| **Air turbine** | 1.382 |
| **Steam pump** | -0.02 |
| **Steam turbine** | 0.668 |
| **Net generation** | 0.852 |

## 8.3 Sensitivity analysis on the operating conditions

### 8.3.1 Impact of the gasifier temperature

To investigate the exact impact of the gasifier temperature on the synthesis gas composition and on carbon conversion, the air, steam and solids flow rates are kept constant and the temperature is varied by changing the heat supplied or extracted from the gasifier. Figure 8.1 shows that the carbon monoxide and hydrogen contents of the synthesis gas sharply increase with increasing temperature in the gasifier, because of the endothermic feature of the Boudouard and water gas shift reactions and the exothermic feature of the combustion ones.

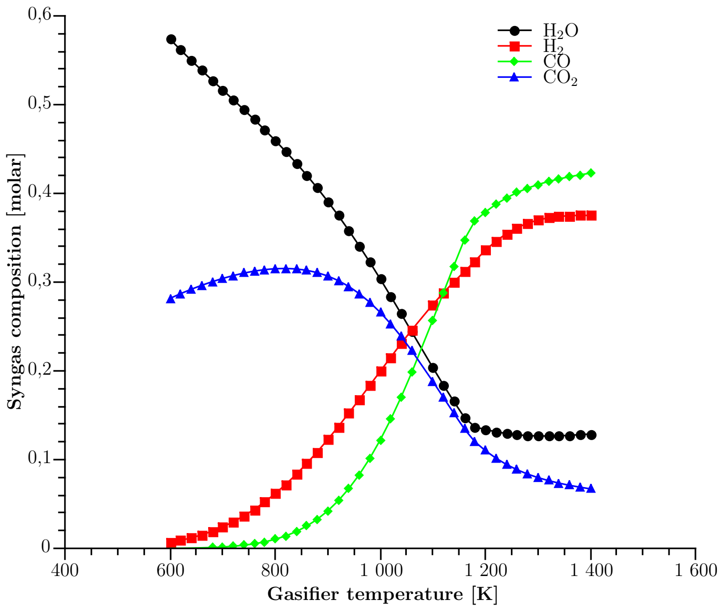

Figure 8.1: Impact of gasifier temperature on syngas composition

Figure 8.2 demonstrates that the hydrogen and carbon monoxide yield reaches its maximum at around 1500 K.

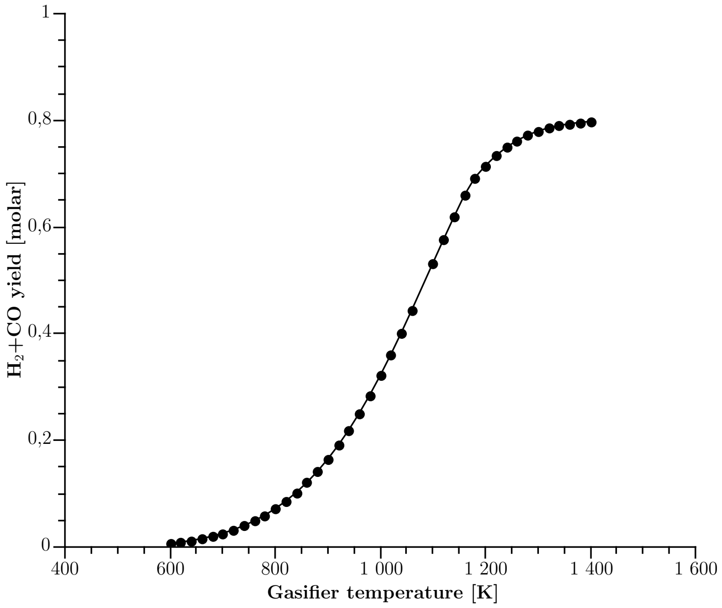

Figure 8.2: Impact of gasifier temperature on $H_2$+CO yield

The temperature of the gasifier has a direct impact on the thermodynamics of the reactions occurring and thus on the char conversion, as presented in Figure 8.3. The fuel conversion is complete for temperatures higher than 1200 K: it is thus not attractive to operate the process at temperatures higher than 1500 K because of the higher oxygen consumption and the detrimental effect on the overall economics of the plant.

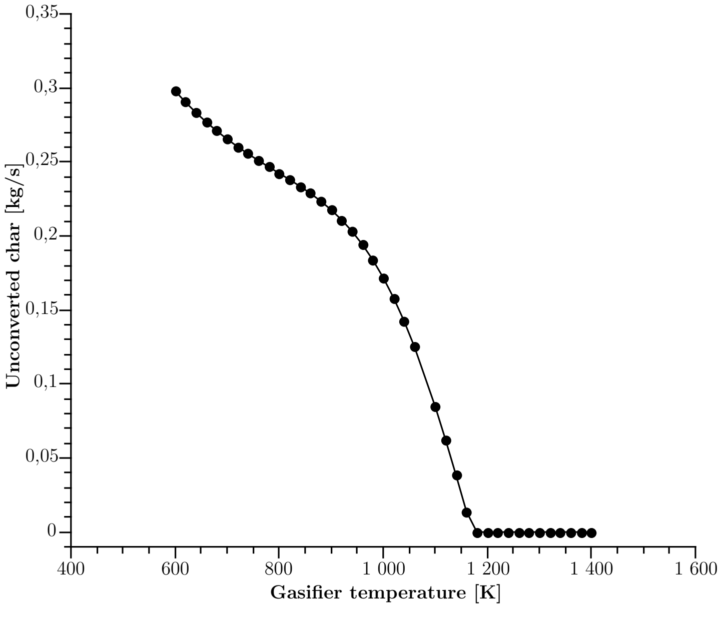

Figure 8.3: Impact of gasifier temperature on char conversion

### 8.3.2 Impact of the pressure level

The selection of a gasifier pressure depends mostly on the process requirements but is usually above 15-20 bars in an IGCC power plant. The effect of pressure on the synthesis gas composition is highlighted in Figure 8.4.

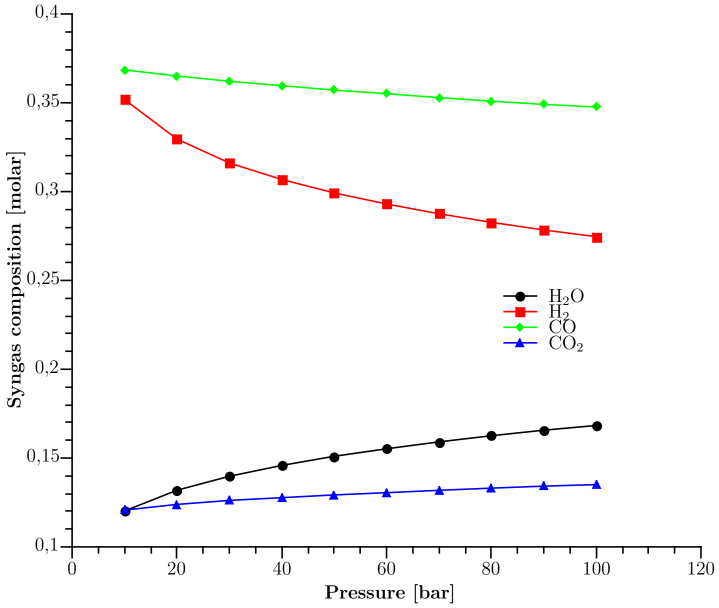

Figure 8.4: Impact of pressure on syngas composition

The steam and carbon dioxide concentrations strongly increase with increasing pressure. The pressure level has also an impact on the thermodynamics of the reactions taking place in the gasifier and thus on the char conversion, as illustrated by Figure 8.5.

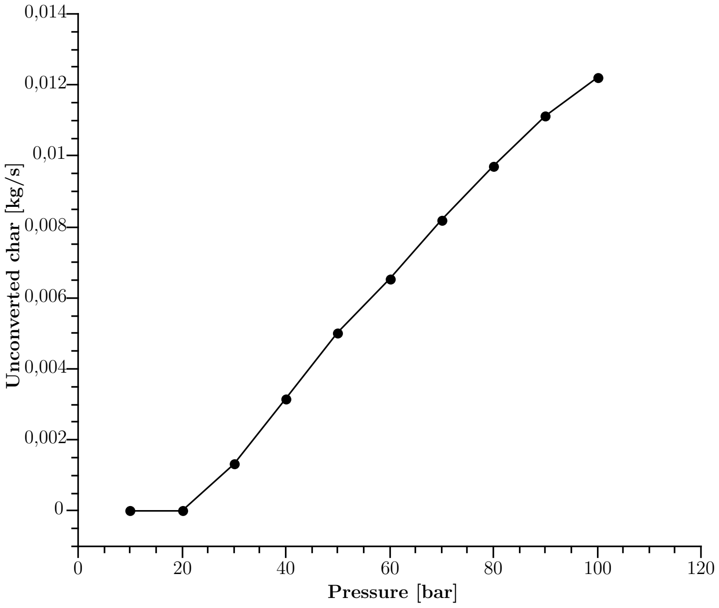

Figure 8.5: Impact of pressure on char conversion

### 8.3.3 Impact of the steam-to-carbon ratio

Steam acts as a moderator and influences the $H_2$/CO ratio via the reforming and WGS reactions: it is essential to gasify the fuel and to avoid the presence of solid carbon. A higher steam-to-fuel ratio enhances the fuel conversion to synthesis gas via the reforming reaction.

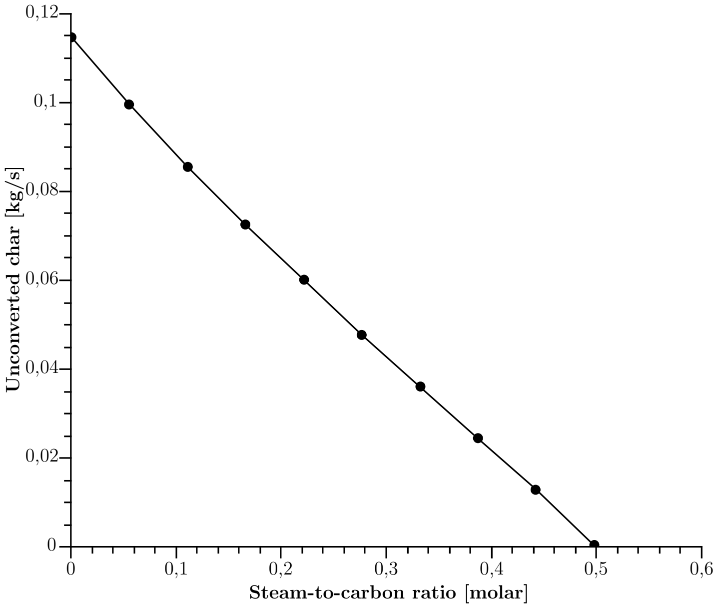

Figure 8.6: Impact of steam-to-carbon ratio on char conversion

Figure 8.7 presents the syngas composition variations with steam to-carbon ratio: higher steam-to-carbon ratio involves a lower CO-concentration and a higher $H_2O$ one because of the water-gas-shift reaction.

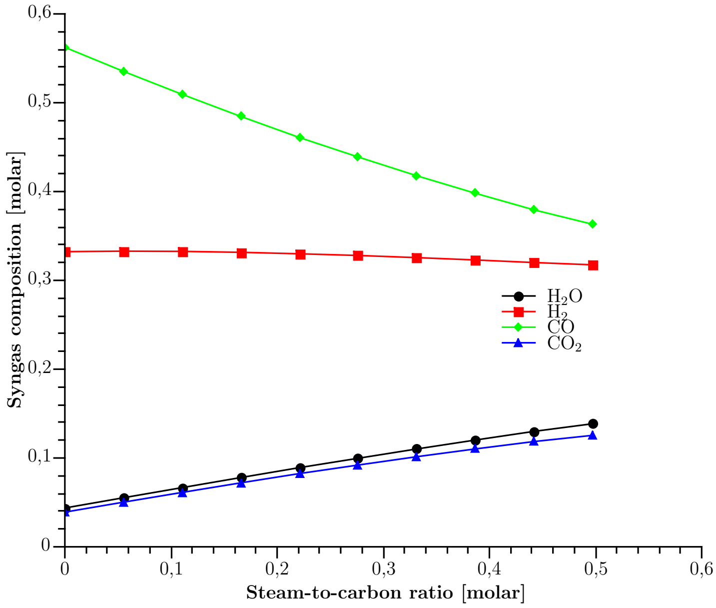

Figure 8.7: Impact of steam-to-carbon ratio on syngas composition

### 8.3.4 Impact of the oxygen-to-carbon ratio

The amount of oxygen introduced in the chemical looping gasification system has also an influence on the conversion of char, as presented in Figure 8.8.

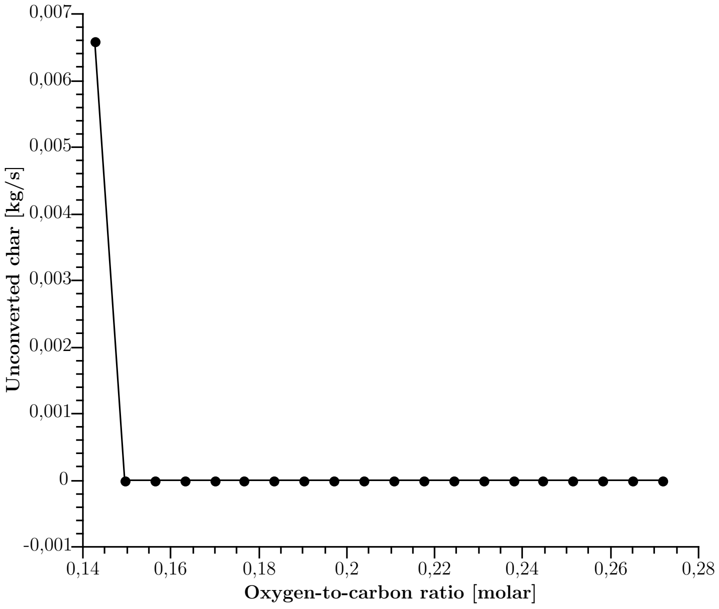

Figure 8.8: Impact of oxygen-to-carbon ratio on char conversion

Higher oxygen-to-fuel ratio results in enhanced char conversion and also has a direct effect on the syngas composition, as shown in Figure 8.9. The concentrations of carbon monoxide and hydrogen in the synthesis gas will decrease with an increasing oxygen flow because the combustion reactions become predominant.

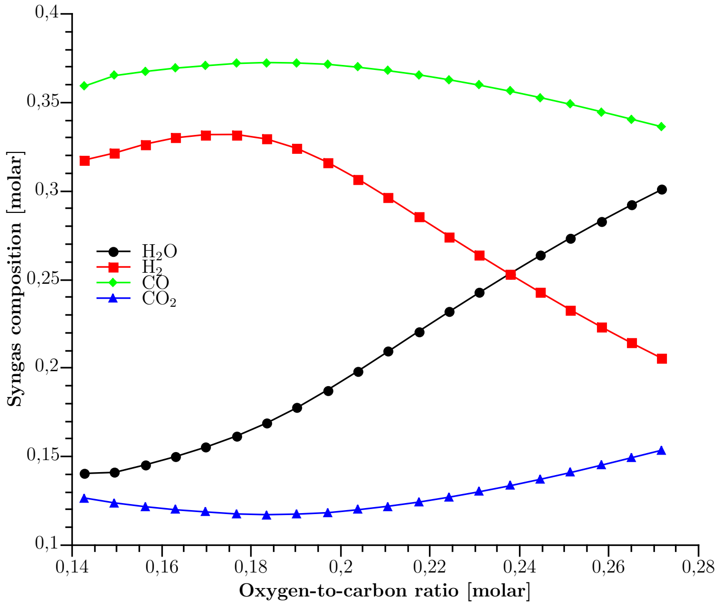

Figure 8.9: Impact of oxygen-to-carbon ratio on syngas composition

## 8.4 Sensitivity analysis on the oxygen carrier

### 8.4.1 Impact of the inert-to-carrier ratio

Increasing the inert flow rate changes the whole heat balance but the impact is minor:

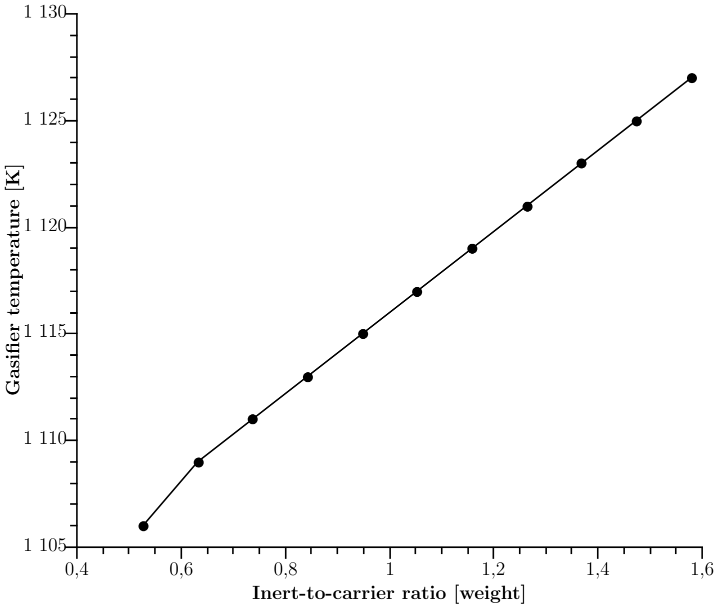

Figure 8.10: Impact of inert-to-carrier ratio on gasifier temperature

### 8.4.2 Impact of the solids flow rate with nickel

Increasing the circulating solids flow rate has, on the opposite, a strong impact:

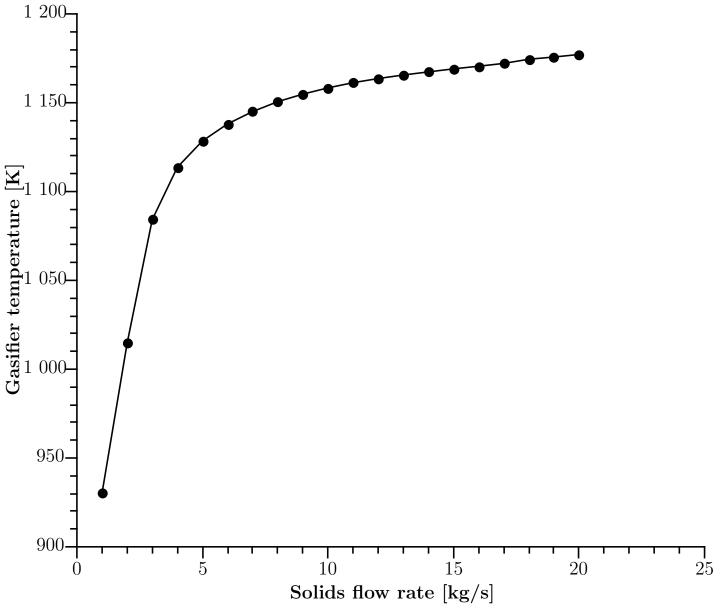

Figure 8.11: Impact of solids flow rate on gasifier temperature

Increasing the solids flow rate has a double effect: first, the amount of oxygen carried from the air to fuel reactor increases; secondly, the amount of heat transported by the circulating solids increases too, contributing to the temperature rise in the gasifier, as illustrated with Figure 8.11. These results suggest that processing a larger flow of solids has thus a strong impact on the char conversion and on the composition of the synthesis gas produced in the gasifier, as shown respectively with Figure 8.12 and Figure 8.13.

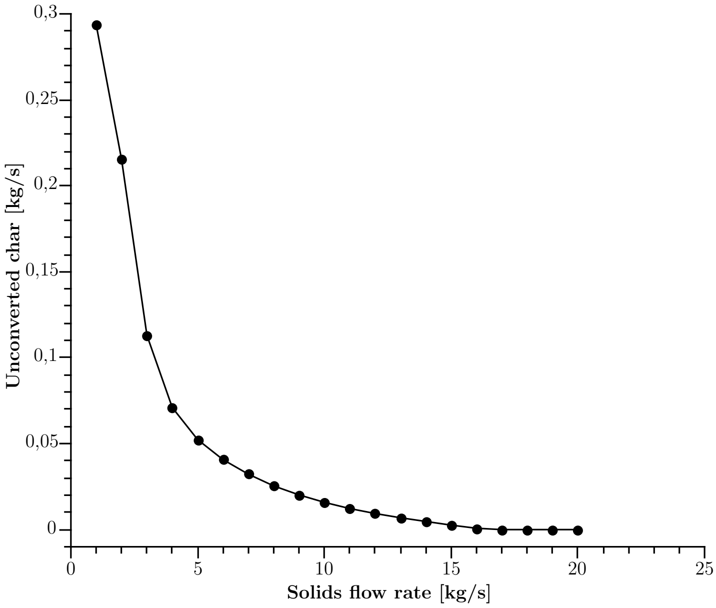

Figure 8.12: Impact of solids flow rate on char conversion

The amount of char unconverted decreases with increasing solids flow rate and the variation is almost linear.

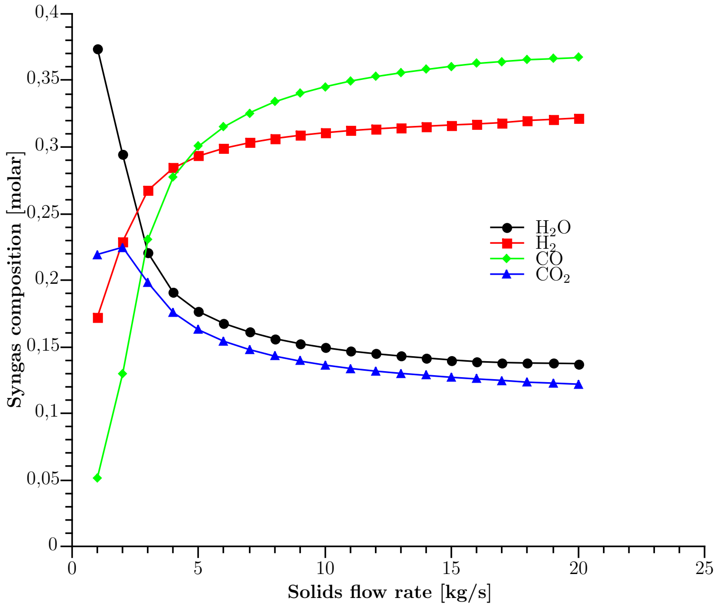

Figure 8.13: Impact of solids flow rate on syngas composition

Additional simulations on ASPEN Plus demonstrated that the higher char conversion is mainly due to the increasing oxygen flow in the gasifier whereas the variations in syngas composition are for the most part due to the effect of temperature. The oxygen impact on syngas composition is significant only at solids flow rate lower than 5 kg/s and account for variations of about 3 to 5% of the concentration of each chemical species. It does not have a major effect at large solids flow rate since most of the oxygen contained in the air processed in the chemical looping gasification system has already been transported to the gasifier. The fuel conversion into synthesis gas is an endothermic process: high temperatures shift the equilibrium of the reaction to the generation of carbon monoxide and hydrogen.

### 8.4.3 Impact of the solids flow rate with iron

Iron swings between several different oxidation states: the solid flow circulating between the air and fuel reactors consists in fact of several iron oxides with proportions varying in function of different factors such as the solids inventory.

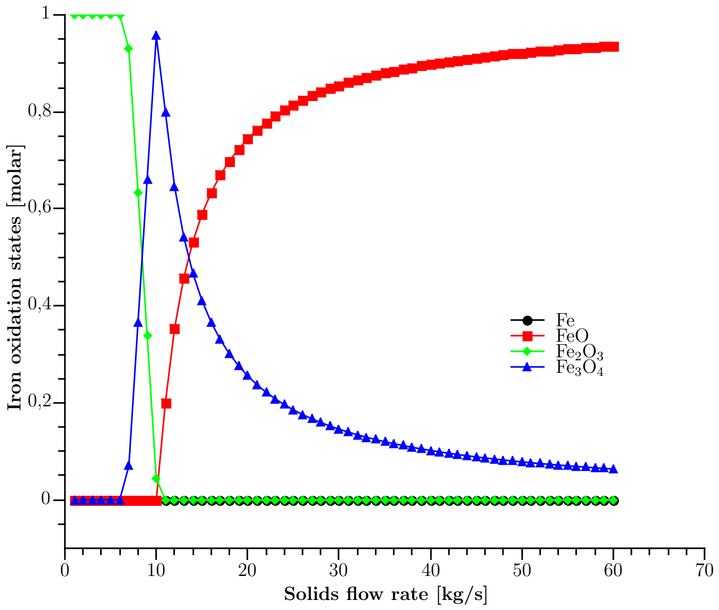

Figure 8.14: Impact of solids flow rate on iron oxidation states

For solids flow rate between 0 and 8 kg/s, all the iron present as wüstite FeO is oxidised to hematite $Fe_2O_3$. For solids flow rate between 8 and 12 kg/s the hematite is further oxidised to magnetite $Fe_3O_4$, which explains the decrease of the concentration of hematite in parallel of the concentration of magnetite. For solids inventory larger than 12 kg/s, there is no oxygen enough to oxidise fully the ferrous oxide introduced in excess, and thus the concentration of magnetite decreases in profit of wüstite.

The increase of the solids flow rate, besides affecting the overall heat balance, has an impact on the amount of oxygen introduced in the gasifier, especially regarding the fact that iron in different oxidation states circulates between both reactors. The amount of unconverted char and syngas composition will therefore vary due to the differences of oxygen amount.

The amount of unconverted char decreases with increasing solids flow rate. There are nevertheless local variations for solids flow rate around 8 and 11-12 kg/s.

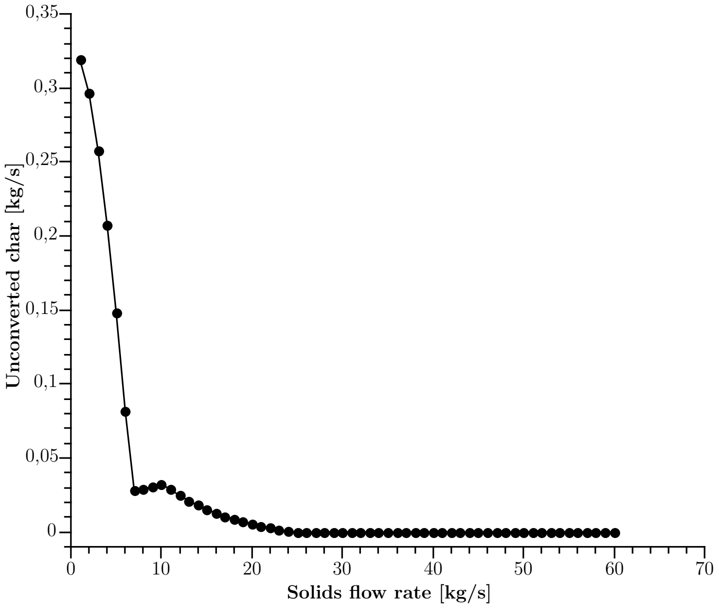

Figure 8.15: Impact of solids flow rate on char conversion with iron

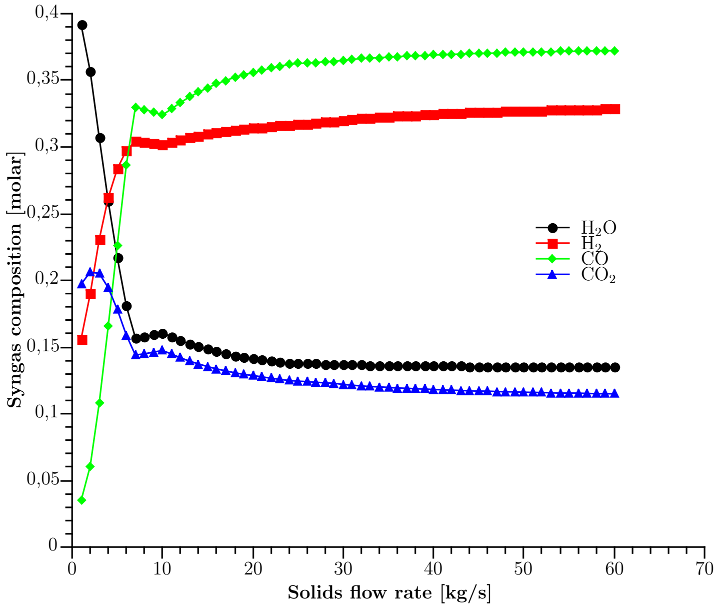

Figure 8.16: Impact of solids flow rate on syngas composition with iron

In general, the CO- and $H_2$- contents of the syngas tend to increase, with local variations around 8 kg/s and 11-12 kg/s. On the opposite, the $CO_2$- and $H_2O$- concentrations tend to decrease. The fact that iron reacts in several steps with oxygen explains the different changes in variations of unconverted char and syngas content.

## 8.5 Comparison of oxygen carriers

### 8.5.1 Motivation and method

Nickel-based metal oxides are the most investigated oxygen carrier materials but several studies were led on the processing of manganese and iron. The comparison below aims to investigate if manganese- and iron-based oxygen carriers are suitable for chemical-looping gasification. The same assumptions are used for the comparison of the three different metal oxides: the mass flow rate is set to 18 kg/s.

### 8.5.2 Results and discussion

Considering the same solid flow rates, the same oxygen- and steam-to-carbon ratios, the composition of the syngas generated and the temperature in the air and fuel reactors are:

Table 8.8: Reactor temperatures in CLG

| | | **Nickel** | **Manganese** | **Iron** |
|---|---|---|---|---|
| $\mathbf{T}_{ar}$ | [°C] | 1200 | 1191 | 1307 |
| $\mathbf{T}_{fr}$ | [°C] | 897 | 898 | 888 |

Table 8.9: Features of different oxygen carrier systems in CLG

| | | | **Nickel** | **Manganese** | **Iron** |
|---|---|---|---|---|---|
| **Circulating solids (fuel reactor outlet)** | Flow rate | $[\frac{kg}{s}]$ | 4 | ∼14.8 | ∼35.1 |
| **$CO_2$ ready to sequestration** | Flow rate | $[\frac{kg}{s}]$ | 1.33 | 1.33 | 1.33 |
| | $CO_2$ | [% mol] | 12.6 | 12.5 | 13.3 |
| | $N_2$ | [% mol] | 0.4 | 0.4 | 0.4 |
| | $H_2O$ | [% mol] | 13.9 | 13.8 | 14.6 |
| | CO | [% mol] | 36.3 | 36.2 | 34.8 |
| | $H_2$ | [% mol] | 31.7 | 31.7 | 31.1 |
| | $CH_4$ | [% mol] | 5.1 | 5.1 | 5.3 |

Two main factors can explain these differences in synthesis gas composition. First, manganese, nickel and iron do not show the same discrimination on the different chemical species in presence. They do not have the same selectivity and reactivity with char. Secondly, the heat capacity of these oxides is different, being the highest for manganese and the lowest for iron. The amount of heat carried is thus larger in the manganese case and the temperature in the fuel reactor is, as expected, the highest. Since a low temperature favours the exothermic reactions and penalises the endothermic ones, the formation of carbon dioxide and water over carbon monoxide and hydrogen is larger in the case of iron.

## 8.6 Comparison of different types of feedstock

### 8.6.1 Motivation and method

As underlined in Chapter 8.1, the composition of the coal feedstock strongly differs depending on the type considered. Coals are generally classified regarding their carbon content and heating value into four main types: anthracite, bituminous, sub-bituminous and brown coal. At the difference of clean synthesis gas, the sulphur and ash contents can be relatively high and therefore metal oxide contamination is a more critical issue.

Biomass feedstock was not studied quantitatively because the main focus of this thesis was on IGCC power plants based on coal. It is nevertheless interesting to remark that biomass is in fact a generic name for several different types of fuel (wood chips, straw, wood pellets, sugar canes, etc) with compositions that may strongly differ.

However, they usually have a larger content in water, sulphur, halides and mercury than coal and the lower heating value of the fuel as received is often around 10-12 MJ/kg. The first issue is thereby that the drying and cleaning steps are more critical and more energy-intensive. The second one is that there are higher contamination risks of the oxygen-carrying particles.

The aim of this part of the study is thus to investigate the impact of processing different coals in the chemical-looping gasification system. Different parameters such as composition of the synthesis gas and solids inventory are considered. The different fuels studied are lignite and anthracite with the following compositions:

Table 8.10: Coals composition for different feedstock

| | **Proximate analysis** [% wt ar] | | | | **Ultimate analysis** [% wt maf] | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Fixed carbon | Volatile matter | Water | Ash | C | H | O | N | S |
| **Lignite** | 27.8 | 24.9 | 36.9 | 10.4 | 71 | 4.3 | 23.2 | 1.1 | 0.4 |
| **Anthracite** | 81.8 | 7.7 | 4.5 | 6.0 | 91.8 | 3.6 | 2.5 | 1.4 | 0.7 |

The interest of investigating anthracite is that this fuel contains much more carbon than the other types of carbon whereas the interest of investigating lignite lies down in the fact that the water content is much higher. The proportion of volatiles depends on their origins but lignite usually contains more volatile matter than anthracite.

### 8.6.2 Results and discussion

As mentioned before, anthracite has a much higher carbon content than the other ranks of coals and, on the opposite, lignite has a higher water content, which implies that the char and so the burnable part of the fuel is smaller.

Table 8.11 and Table 8.12 show that the amounts of air and solids needed to sustain the temperature of the air reactor to 1200°C and to convert all char are much larger with anthracite.

Table 8.11: Properties of key streams of IGCC-CLG (lignite case)

| **Stream** | **Mass flowrate** $[\frac{kg}{s}]$ | **Temperature** [°C] | **Pressure** [bar] |
|---|---|---|---|
| **Air (gas turbine inlet)** | 1.456 | 15 | 1.013 |
| **Steam** | 0.450 | 300 | 30 |
| **Synthesis gas** | 1.698 | 984 | 29 |
| **Oxygen-depleted air (air reactor outlet)** | 1.123 | 1200 | 29 |
| **Circulating solids (air reactor outlet)** | 15.336 | 1200 | 29 |
| **Circulating solids (fuel reactor outlet)** | 15.003 | 984 | 29 |

Table 8.12: Properties of key streams of IGCC-CLG (anthracite case)

| **Stream** | **Mass flowrate** $[\frac{kg}{s}]$ | **Temperature** [°C] | **Pressure** [bar] |
|---|---|---|---|
| **Air (gas turbine inlet)** | 4.60 | 15 | 1.013 |
| **Steam** | 0.450 | 300 | 30 |
| **Synthesis gas** | 2.42 | 845.8 | 29 |
| **Oxygen-depleted air (air reactor outlet)** | 3.54 | 1200 | 29 |
| **Circulating solids (air reactor outlet)** | 31.06 | 1200 | 29 |
| **Circulating solids (fuel reactor outlet)** | 30 | 845.8 | 29 |

The gasifier temperature increases with solids flow rate but is higher with lignite than with anthracite because char combustion occurs to a lower extent.

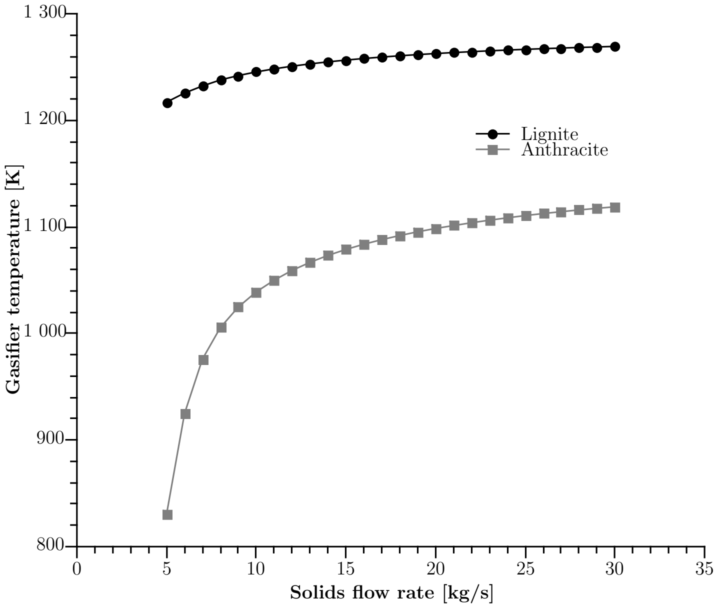

Figure 8.17: Impact of solids flow rate on gasifier temperature

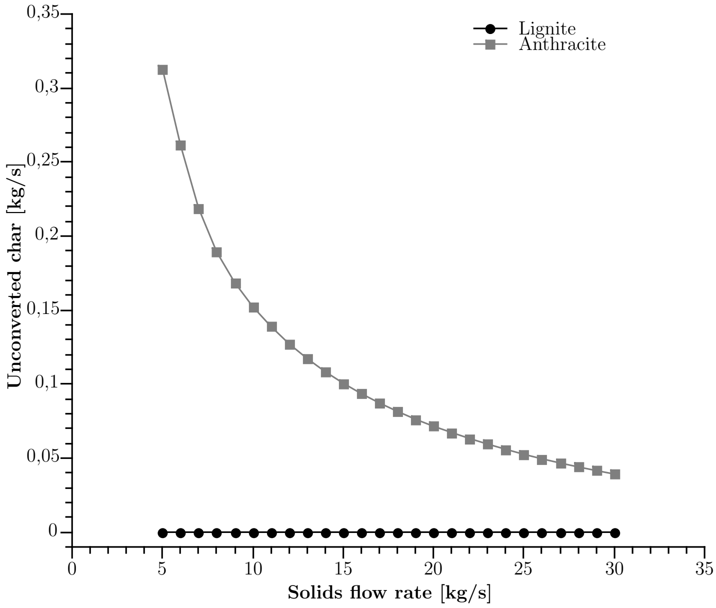

Figure 8.18: Impact of solids flow rate on char conversion

The amount of unconverted char is larger with anthracite than with lignite because, first, anthracite has a larger carbon content than lignite and thus the oxygen demand and the required solids flow rate are higher, and, secondly, for the same solids flow rate, the gasifier temperature is higher with lignite than with anthracite, promoting the endothermic reactions.

The variations in syngas composition with solids flow rate are mainly due to the increasing temperature whereas the higher char conversion is due to the increasing amount of oxygen transported.

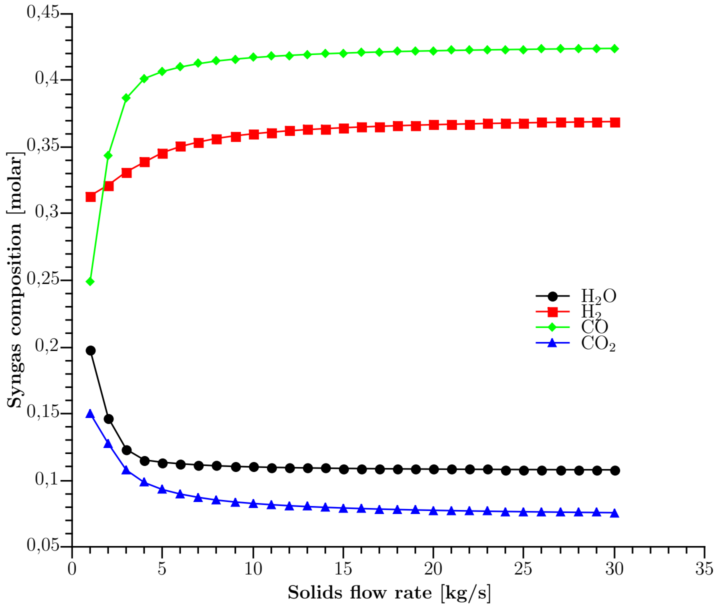

Figure 8.19: Impact of solids flow rate on syngas composition (lignite)

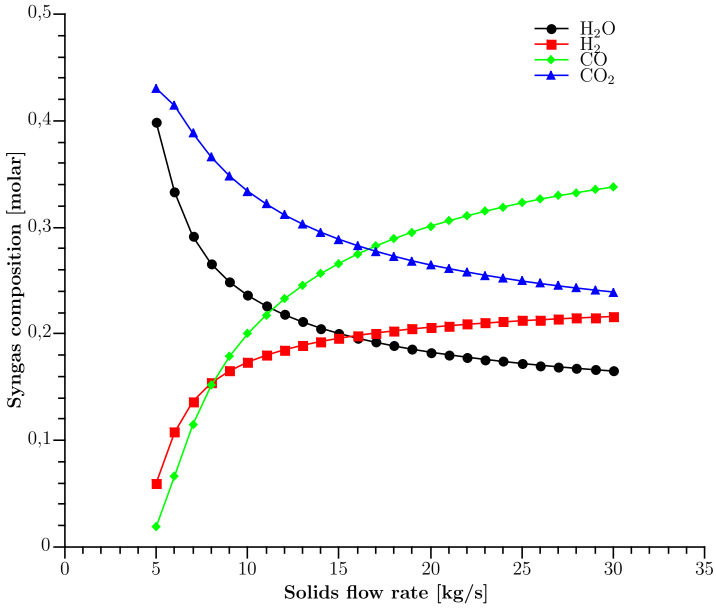

Figure 8.20: Impact of solids flow rate on syngas composition (anthracite)

Syngas generated from lignite is more CO- and $H_2$- rich: the reason is that the gasifier temperature is always higher, promoting therefore the endothermic reactions. In conclusion, for high-rank coals, it is needed to increase the oxygen flow rate to convert all carbon into carbon monoxide and, in parallel, to increase the solids flow rate to carry more heat.

## 8.7 Comparison of moving and fluidised bed designs

### 8.7.1 Motivation and method

So far, the simulations achieved with ASPEN Plus consider the use of interconnected fluidised bed reactor for chemical and carbonate looping. It is nevertheless of great interest to investigate the influence of using an interconnected moving bed reactor system instead, i.e two moving bed reactors connected to each other. The way of how to model a moving bed reactor in ASPEN Plus was discussed in Chapter 5.

A moving-bed consists of a bed in which the gaseous reactants generally move upwards whereas the solid ones move downwards. This type of reactor does not present the feature of perfect axial mixing, at the difference of fluidised bed. A particular advantage of moving beds compared to fluidised beds is the higher fuel conversion due to the poor axial mixing, which allows fresh synthesis gas to react with highly converted solids and highly converted syngas to react with fresh solids. Moving beds are therefore appropriate for slow or equilibrium-limited reactions such as the generation of hydrogen.

The aim of this part of the study is to investigate the differences between the fluidised and moving bed reactors in terms of fuel conversion and oxygen carrier conversion. Regarding the different several sensitivity analyses carried out previously, it seems more advantageous to process a low airflow rate and a high solids circulation flow rate to promote the gasification reactors.

The assumptions done are:

- Nickel-based oxygen carrier
- Oxygen-to-fuel ratio: 0.21
- Steam-to-fuel ratio: 0.06
- Solids-to-fuel ratio: 10
- Adiabatic moving-bed reactor

The same solids-, oxygen- and steam-to-fuel ratios were taken in the simulations carried out with moving and fluidised bed reactors to make relevant comparisons. The overall moving bed reactor system is also assumed adiabatic, with no exchanged heat with the environment: only the solids flows carry heat from the oxidation to the gasification reactor.

It is expected that, regarding the inherent features of fluidised and moving bed reactors, hydrogen generation is enhanced with the second mode rather than with the first one. A question that can thus be raised is how the synthesis gas composition changes in a moving bed reactor in function of the airflow rate and of the oxygen-to-fuel ratio and if these variations are similar to the ones seen when using fluidised bed reactors.

### 8.7.2 Results and discussion

The comparison of both designs returns the results presented in Figure 8.21, Figure 8.22, Figure 8.23 and Table 8.13 for the composition of the synthesis gas at the outlet of the gasifier.

It can be seen that the moving bed reactor enhances the generation of hydrogen and leads to a slightly higher yield to hydrogen and carbon monoxide than the fluidised bed. A moving bed reactor can achieve an hydrogen concentration of nearly 60% whereas a fluidised bed one cannot achieve more than 50%.

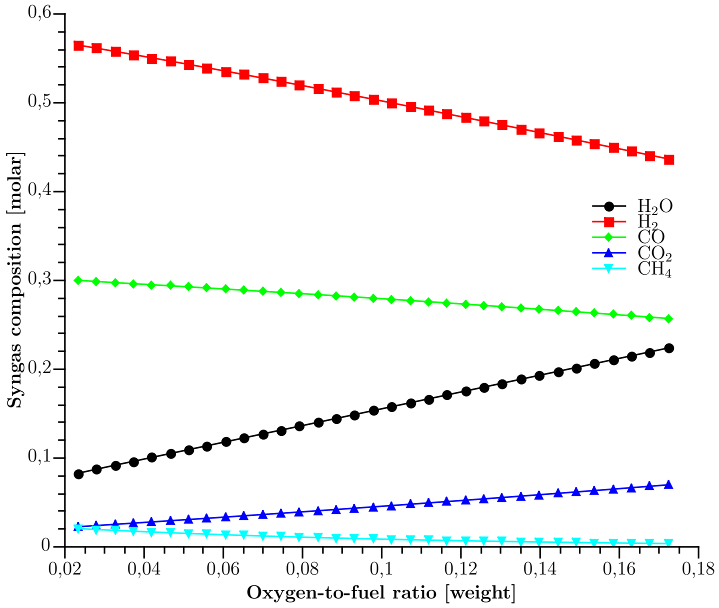

Figure 8.21: Impact of oxygen-to-fuel ratio on syngas composition in a moving bed reactor

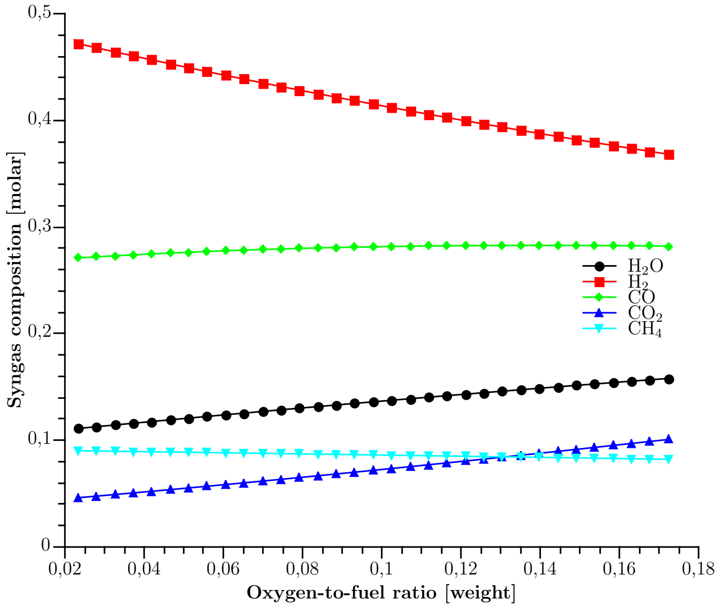

Figure 8.22: Impact of oxygen-to-fuel ratio on syngas composition in a fluidised bed reactor

It appears that the syngas composition follows the same variations in fluidised and moving bed reactors. The steam and carbon dioxide contents increase whereas the carbon monoxide and hydrogen ones decrease.

The main difference lies in the higher hydrogen content in a syngas generated in a moving bed reactor. Another difference is the larger content in methane due to the lower temperature of the fluidised bed reactor with the assumptions done to compare both modes. In practice, the steam-to-fuel ratio would be increased to lower the amounts of unconverted char and methane. It should be remarked that, the temperature in a fluidised bed reactor is usually higher than of a moving bed, on average, and that the concentration of methane is thus lower.

Table 8.13: Comparison of the fluidised and moving bed designs for chemical looping gasification

| **Synthesis gas** | | **Fluidised bed** | **Moving bed** |
|---|---|---|---|
| **CO** | [% mol] | 30.68 | 26.15 |
| **$CO_2$** | [% mol] | 9.77 | 7.38 |
| **$H_2$** | [% mol] | 36.78 | 41.71 |
| **$N_2$** | [% mol] | 0.77 | 0.77 |
| **$CH_4$** | [% mol] | 6.64 | 0.19 |
| **$H_2O$** | [% mol] | 14.63 | 23.75 |
| **$N_2$** | [% mol] | 0.77 | 0.77 |
| **$H_2$ + CO yield** | [% mol] | 67.46 | 67.86 |

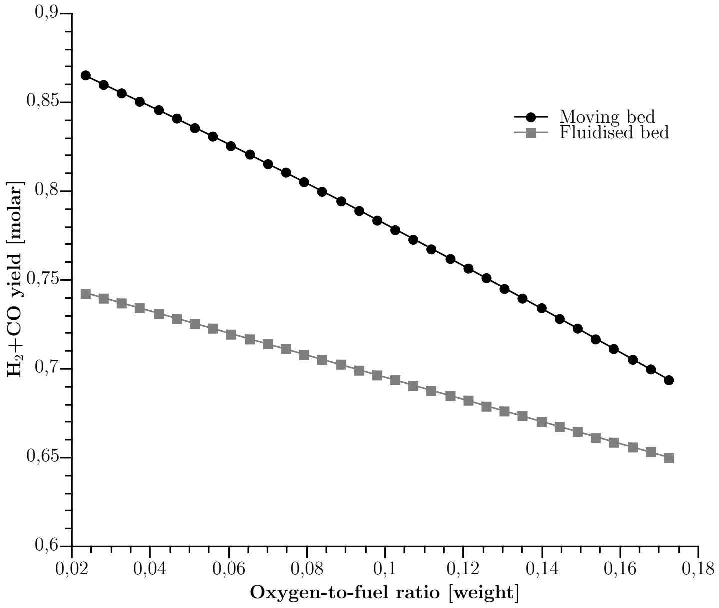

Figure 8.23: Impact of reactor design and oxygen-to-fuel ratio on $H_2$+CO yield

When paying attention to the total yield to hydrogen and carbon monoxide, as shown in Figure 8.23, it is clear that the moving bed is more interesting than the fluidised mode because of its plug-flow behaviour, which justifies the use of this type of reactor in chemical looping gasification, and in other applications such as chemical looping hydrogen. However, this advantage of moving beds over fluidised ones is only valid at relatively low oxygen-to-fuel ratios, when gasification reactions are predominant over combustion ones.

## 8.8 Concluding remarks

The present study reveals the following facts on integrated chemical looping gasification:

1. For the same amount of coal, air and steam processed, the temperature at the outlet of a conventional gasifier is higher than with direct gasification using chemical looping and the synthesis gas generated has a larger content in carbon monoxide and hydrogen and thus a higher heating value.

2. The cold gas efficiency decreases from around 85% to around 75% when changing from a conventional gasifier to a chemical looping gasifier. However, chemical looping gasification involves in parallel power generation because the air stream introduced in the system expands in a gas turbine cycle and runs through a heat recovery steam generator.

3. The circulating solids flow rate has a double effect in the gasifier. It brings oxygen from the air to the fuel reactor, enhancing char conversion, and carries heat produced by the exothermic oxidation of metal particles, rising gasifier temperature and promoting endothermic reactions.

4. The oxygen- and steam-to-carbon ratios are important operating parameters of the chemical looping gasification system: high values lead to high char conversion but to high generation of steam and carbon dioxide, which results in lower heating value of the synthesis gas.

5. Nickel, manganese and iron metal particles are suitable oxygen carriers for chemical looping gasification but the $H_2$+CO yield is the highest in the case of manganese.

6. Chemical looping gasification can be applied to different types of coal. However, processing coals with high ranks such as anthracite results in larger airflow rate and solids circulation.

7. Moving and fluidised bed reactors have different behaviours: the syngas compositions are different, with a higher $H_2$+CO yield with a moving bed than with a fluidised one.

# Chapter 9

# IGCC power plant with carbonate looping ex situ

## 9.1 Description

### 9.1.1 General principle

The principle of this type of IGCC power plant is detailed in Chapter 5.6. Capture of carbon dioxide occurs by carbonation based on calcium oxide. Calcium oxide reacts with carbon dioxide and generates calcium carbonate and heat. This reaction is exothermic and is thus favoured at low temperatures.

$$\mathrm{CaO} + \mathrm{CO_2} \longrightarrow \mathrm{CaCO_3} \tag{9.1}$$

Capturing carbon dioxide moves thus the equilibrium of the water-gas shift reaction towards the products side and enhances the yield of hydrogen and the conversion of carbon monoxide:

$$\mathrm{CO} + \mathrm{H_2O} \longrightarrow \mathrm{CO_2} + \mathrm{H_2} \tag{9.2}$$

The addition of steam is thus critical to ensure a high conversion of methane and carbon monoxide to carbon dioxide and hydrogen. The synthesis gas at the outlet of the carbonation reactor is thus rich in hydrogen and steam and a further condensation step allows the separation of both species.

$$\mathrm{CaO} + \mathrm{H_2O} \longrightarrow \mathrm{Ca(OH)_2} \tag{9.3}$$

The calcium carbonate particles enter the regenerator, in which they release carbon dioxide in presence of steam. Steam indeed acts as a moderator and enhances the calcination reaction by hydration. This reaction is endothermic and is thus favoured at high temperatures.

$$\begin{aligned} \mathrm{CaCo_3} &\longrightarrow \mathrm{CaO} + \mathrm{CO_2} \\ \mathrm{Ca(OH)_2} &\longrightarrow \mathrm{CaO} + \mathrm{H_2O} \end{aligned} \tag{9.4}$$

### 9.1.2 Assumptions

The choices of the ratios steam to syngas and calcium to syngas are based on literature studies [22]. For more clarity, the ratios are presented on a mass and on a molar basis because most of the researches carried out on carbonate looping use molar ratios to present their assumptions. In general, it is recommended to keep relatively low steam- and solids-to-fuel ratio because steam production is energy-intensive and large solid flow rates are difficult to handle. The temperature and pressure of the system are chosen regarding the usual features of a typical IGCC power plant.

Table 9.1: Process streams of IGCC-carbonate looping

| | | | **Baseline case** |
|---|---|---|---|
| **Synthesis gas** | Molar flow rate $\dot{n}_{syn}$ | $[\frac{mol}{s}]$ | 1 |
| | Mass flow rate $\dot{m}_{syn}$ | $[\frac{kg}{s}]$ | 20.43 |
| | Temperature | [°C] | 300 |
| | Pressure | [bar] | 22.5 |
| **Steam** | Molar flow rate $\dot{n}_{stm}$ | $[\frac{mol}{s}]$ | 3 |
| | Mass flow rate $\dot{m}_{stm}$ | $[\frac{kg}{s}]$ | 54.05 |
| | Temperature | [°C] | 300 |
| | Pressure | [bar] | 22.5 |
| **Carbon carrier** | Molar flow rate | $[\frac{mol}{s}]$ | 1.35 |
| | Mass flow rate | $[\frac{kg}{s}]$ | 75.70 |

The choice of the calcination temperature of 1000°C and the carbonation temperature of 600°C are based on the thermodynamic data of the system calcium oxide CaO - calcium carbonate $CaCO_3$. It should be pointed up that a calcination temperature above 900°C is a sine qua non to shift the equilibrium of the calcination reaction. This limit value depends, amongst several thermodynamic factors, on the steam partial pressure of the system.

Table 9.2: Reactors of IGCC-carbonate looping

| **Carbonate-looping system** | | **Baseline case** |
|---|---|---|
| **Carbonation reactor temperature $T_{ar}$** | [°C] | 600 |
| **Calcination reactor temperature $T_{fr}$** | [°C] | 1000 |
| **Pressure drop $\Delta P$** | [bar] | 1 |
| **Heat losses $\dot{Q}_{losses}$ [MW]** | | 0 |

The carbonation and calcination reactors are assumed fully adiabatic: heat is carried from the calcination to the carbonation reactor with the circulating solids flow but there is no thermal exchange with the environment in the baseline case, at the difference of the cases considered later on. The pressure drop over the carbonate looping cycle is estimated to 1 bar, as done in the simulations about chemical looping presented in Chapters 7 and 8.

For simplifications, the baseline cases assume that:

- The air separation unit is not integrated in the system: the nitrogen stream produced does not run through the gas turbine
- The gas turbine does not need any cooling by air flow
- The pressure of the system is the same in both chemical looping reactors to avoid gas leakages between both
- The heat losses in the carbonate looping reactors are negligible The pressure drops over the heaters and condensers are negligible compared to the high pressures involved in the system
- At the beginning, the process is not energy integrated, discussions about these issues follow the sensitivity analysis part
- The syngas went through a cleaning step before the calcium looping cycle and so the sulphur and halides contents of the syngas are negligible

Table 9.3: Syngas composition of IGCC-carbonate looping

| **Synthesis gas** | | **IGCC-CLC** |
|---|---|---|
| **CO** | [% mol] | 46.6 |
| $\mathbf{CO_2}$ | [% mol] | 13.3 |
| $\mathbf{H_2}$ | [% mol] | 37.2 |
| $\mathbf{N_2}$ | [% mol] | 2.5 |
| $\mathbf{CH_4}$ | [% mol] | 0.1 |
| $\mathbf{H_2O}$ | [% mol] | 0.3 |
| $\mathbf{H_2S + COS}$ | [ppm] | 12 |

There is margin for integrating this carbonate looping process into a conventional IGCC power plant. The waste heat recovered in the carbonation reactor is low-grade and is thus not usable for the heat supply needed in the calcination one. The calcination reaction in the regenerator reactor is indeed endothermic and it implies thus a need for heating, either by direct heating or indirect one. Both options for the design of the calcination reactor and thus for the regeneration of the calcium oxide particle follow.

Most of the studies led on carbonate looping raised the idea of oxy-fuel combustion: coal or synthesis gas burns in pure oxygen in the regeneration reactor, generating the heat needed to drive the calcination reaction. The products of this reaction are thus combustion products that are mostly carbon dioxide and steam. The steam generated during the combustion process can be separated out of the products stream by a further condensation step, leading thus to the generation of a $CO_2$-rich stream.

The aim is to provide as close as possible the exact amount of oxygen needed for the oxy-fuel combustion process. The oxygen supplied comes from the air separation unit and so an extra use of oxygen leads to a detrimental energy extra demand, which implies losses in energy efficiency and larger operating costs. The oxygen coming from the air separation unit is at a temperature of 30°C and a pressure of 22.5 bars.

### 9.1.3 Results and discussion

Table 9.4 presents the results of the simulation of the base case.

Table 9.4: Gaseous streams of IGCC-carbonate looping

| | | $CO_2$ ready to sequestration | $H_2$ ready to use |
|---|---|---|---|
| **Molar flow rate** | $[\frac{mol}{s}]$ | 0.586 | 0.826 |
| **Mass flow rate** | $[\frac{kg}{s}]$ | 25.65 | 2.77 |
| $N_2$ | [% mol] | - | 2.94 |
| $O_2$ | [% mol] | - | - |
| **CO** | [% mol] | - | 0.05 |
| $CO_2$ | [% mol] | 99.17 | 0.31 |
| $H_2O$ | [% mol] | 0.83 | 0.82 |
| $H_2$ | [% mol] | - | 93.78 |
| **NO** | [% mol] | - | - |
| $NO_2$ | [% mol] | - | - |
| $N_2O$ | [% mol] | - | - |
| $NH_3$ | [% mol] | - | 0.16 |
| **Carbon capture rate** | [% mol] | 96.83 | |

It can be seen that it is possible to reach a high carbon capture rate and to generate a synthesis gas with a high purity in hydrogen. The limiting factors that prevent from reaching a carbon capture rate of 100% are the equilibrium limit of the carbonation and water gas shift reactions: there are few amounts of unconverted carbon monoxide and methane in the synthesis gas, which involves losses in carbon capture efficiency.

## 9.2 Sensitivity analysis on the operating conditions

### 9.2.1 Impact of the calcium-to-carbon ratio

The amount of calcium oxide introduced in the carbonate looping system has a direct impact on the carbon capture efficiency: the higher is the calcium-to-carbon ratio, the higher is the carbonation conversion. However, larger solid flows require larger reactors and lead thus to an increase of the process cost.

Another impact of increasing the calcium-to-carbon ratio is the changes of the $H_2$-rich synthesis gas composition. One aim of the design of the carbonate looping process is to calculate the optimum calcium-to-carbon ratio in order to maximise the carbon capture rate, minimise the cost of the overall system and maximise the generation of hydrogen.

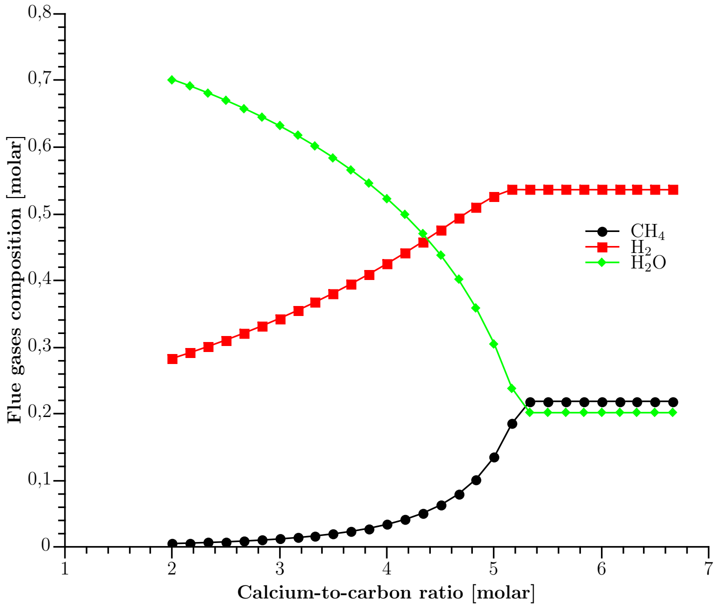

Figure 9.1: Impact of calcium-to-carbon ratio on flue gas composition

Increasing the amount of calcium oxide circulating implies larger $CO_2$ removal and $H_2$ production until an equilibrium from a calcium-to-carbon ratio of about 5.2.

### 9.2.2 Impact of the calcination reactor temperature

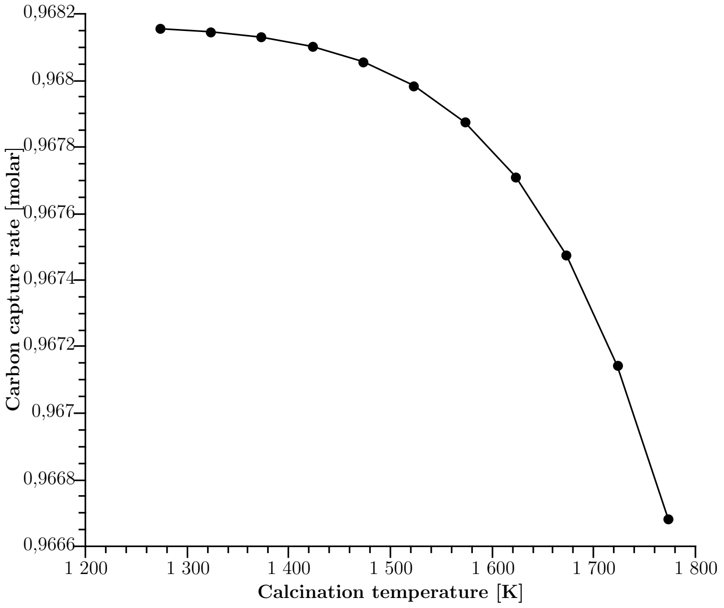

Figure 9.2: Impact of calcination temperature on carbon capture rate

The carbon capture rate is constant around 96.6-96.8%: it is thus more interesting to operate the calcination reactor around the equilibrium temperature to minimize the amount of heat provided to the regeneration reactor and the oxygen demand.

### 9.2.3 Impact of the carbonation reactor temperature

The carbonation reaction that mainly takes place in the carbonation reactor is exothermic and thus generates heat. Regulating the carbonation reactor temperature actually implies regulating the external cooling of this reactor.

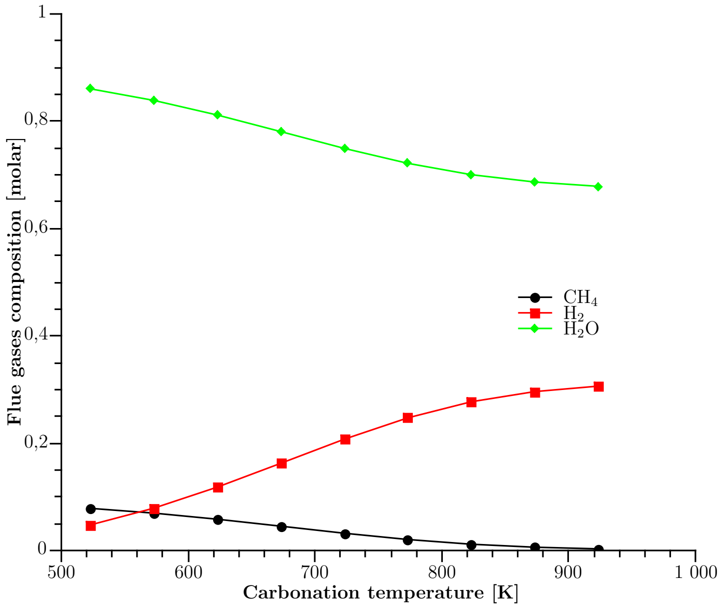

Figure 9.3: Impact of carbonation temperature on flue gas composition

The methane and water contents decrease with increasing the carbon temperature, the reason being that high temperatures favour endothermic reactions such as the steam methane reforming reaction.

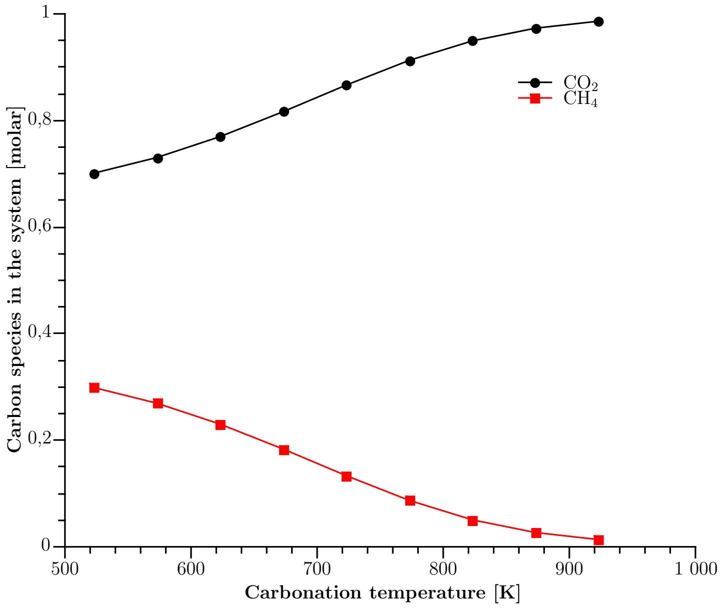

Figure 9.4: Impact of carbonation temperature on carbon conversion

More methane and water yield to hydrogen and carbon monoxide, though this last compound directly yields carbon dioxide through the water-gas shift reaction. The carbon present in the carbonate looping system is thus mostly methane or carbon dioxide. The carbonation temperature has an impact on the carbon conversion into carbon dioxide or methane, and thus on the repartition of carbon on methane or carbon dioxide flows.

As said previously a higher carbonation temperature, though it moves the equilibrium of the carbonation reaction, leads to higher conversion of methane to carbon monoxide and further dioxide. The amount of carbon dioxide capture removed increases in parallel of the decreasing of the methane flows in the carbonate looping system.

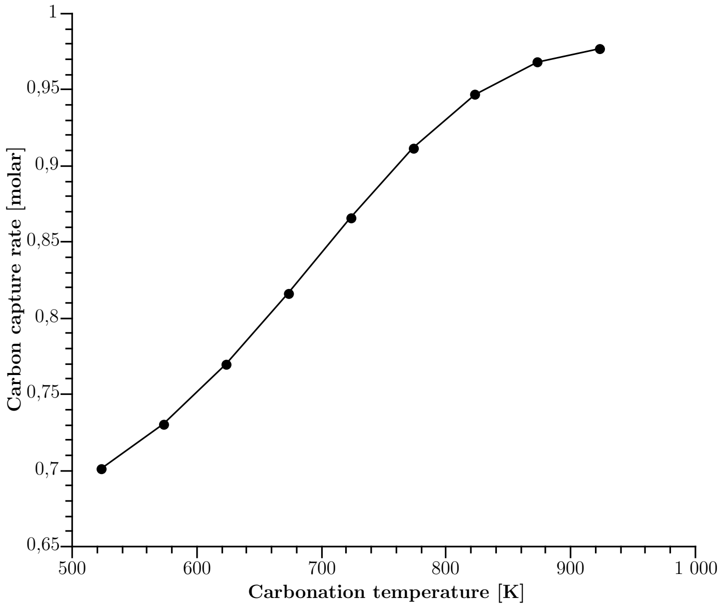

Figure 9.5: Impact of carbonation temperature on carbon capture rate

The carbon capture rate strongly varies with the carbonation temperature from around 70% to 97%. This result may look surprising considering that carbonation is an exothermic reaction and is therefore favoured at low temperatures. The reason is highlighted by investigating the composition of the solid flow at the outlet of the carbonation reactor.

Upon the addition of stream in the carbonate looping system to reduce the sintering effect and to enhance the recyclability of the carbonate looping particle, calcium oxide will react with steam by hydration to form calcium hydrates. This reaction is nevertheless predominant mostly at low temperatures, which explains the low carbon capture rate associated.

The equilibrium temperatures corresponding to the partial pressures that are typical of the synthesis gases after sulphur cleaning are usually above 600°C, which explains why the formation of calcium carbonate is favoured at these temperatures rather than at low temperatures where it competes with hydration.

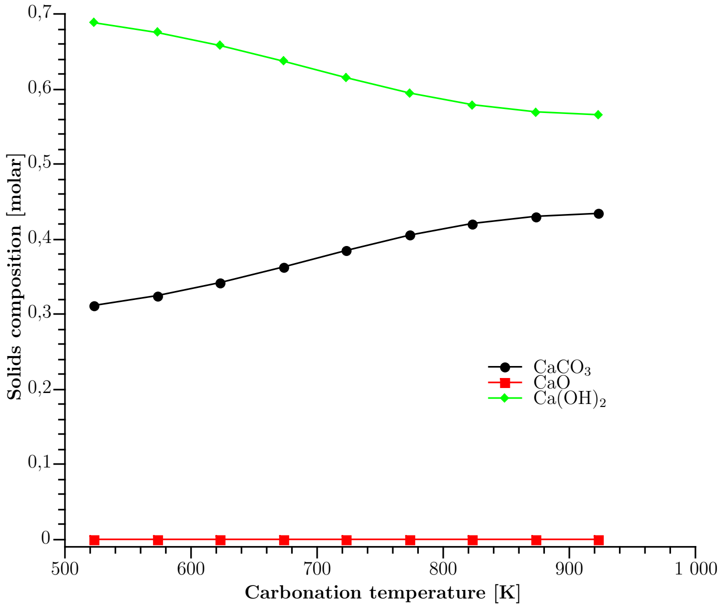

Figure 9.6: Impact of carbonation temperature on solid flow composition

### 9.2.4 Impact of the pressure level

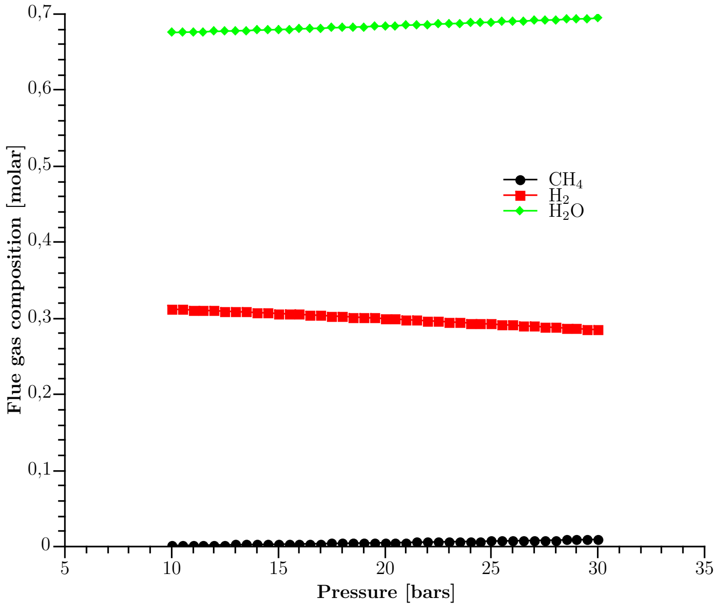

Figure 9.7: Impact of pressure on flue gas composition

The pressure level has a relatively small impact on the synthesis gas composition after the carbonation reactor: the steam and methane contents increase in the synthesis gas with increasing pressure whereas the hydrogen content decrease. It is thus more interesting to operate at low pressures if possible.

### 9.2.5 Impact of the steam-to-carbon ratio

The amount of steam introduced in the carbonate looping system has a direct impact on the synthesis gas composition after the carbonation reactor. The higher is the amount of steam introduced, the higher is the amount of hydrogen generated. However, the amount of steam yielding to hydrogen is limited by thermodynamic equilibrium and thus the purity of the synthesis gas in hydrogen decreases with increasing steam. The steam-to-carbon ratio has however a low impact on the purity of the hydrogen stream after condensation, which stays around 93-95%. The carbon capture rate is constant and stays around 96.8-97.8%.

In practice, the major benefit of introducing steam, which is not possible to foresee by simulations based on equilibrium assumptions, is the positive impact of hydration on the reactivity of calcium looping particles. According to the different studies carried out, processing a small steam flow is more interesting since it lowers the energy consumption due to the production of steam and leads to higher reactivation of the carbonate looping particles [207].

## 9.3 Comparison of the different heat integration options

### 9.3.1 Motivation and method

Whereas the carbonation reaction is exothermic and generates heat at low temperatures (600-700°C), the calcination one is endothermic and requires heat at relatively high temperatures (900-1000°C).

There is a need for providing heat to the calcination reactor. First, all the heat generated in the carbonation process is not suitable for use in the calcination reactor because of its low-grade feature. Secondly, the amount of heat necessary in the calcination reactor is larger than the amount of heat produced in the carbonation one. There are different options to integrate efficiently the calcination reactor in the overall process: either with direct calcination by oxy-fuel combustion or by hot solids recirculation or with indirect calcination by internal heat exchanger. The different possibilities are presented and discussed as follows.

### 9.3.2 Direct calcination by oxy-fuel combustion of coal

A possibility to provide the heat needed in the calcination reactor is to burn coal or char directly in the calcination reactor with pure oxygen. The advantage is to promote a direct heat exchange between the different reactants. The main drawbacks are the processing of pure oxygen, which leads to a higher demand of the air separation unit, and the possible large amounts of impurities present in the coal, which lead to a contamination of the $CO_2$-rich stream and of the calcium oxide particles. The use of coal directly in the calcination reactor presents several major drawbacks as discussed: it has therefore not been simulated within the framework of this study on carbonate looping processes.

### 9.3.3 Direct calcination by oxy-fuel combustion of syngas

Burning synthesis gas directly in the calcination reactor with pure oxygen leads to a direct heat exchange between the calcium carbonate and the exhaust gases and therefore to a better calcination efficiency. The advantage of processing clean synthesis gas instead of coal is the lower amount of impurities like sulphur, nitrogen or halides. However, the common drawback is that the demand of pure oxygen involves an increase of the energy penalty associated with the use of an air separation unit. The simulations showed that 0.375 kmol/s of synthesis gas, which corresponds to around 27% of the total amount, and 0.16 kmol/s of oxygen should run through the regenerator to sustain a temperature of 1000°C. The composition of the $CO_2$-rich stream is in this case:

Table 9.5: Composition of the $CO_2$-stream ready to sequestration

| **$CO_2$ before condensation** | | **IGCC-carbonate looping** |
|---|---|---|
| **CO** | [% mol] | 0.14 |
| **$CO_2$** | [% mol] | 59.74 |
| **$H_2$** | [% mol] | 0.05 |
| **$N_2$** | [% mol] | 2.5 |
| **$CH_4$** | [% mol] | - |
| **$H_2O$** | [% mol] | 37.57 |
| **$H_2S$ + COS** | [ppm] | - |

It can be seen that the contents in carbon monoxide, methane and nitrogen are negligible compared to the contents in water and carbon dioxide. The carbon dioxide stream after condensation can thus reach a high $CO_2$-purity.

### 9.3.4 Direct calcination by hot solids recirculation

The calcium looping particles have the function of heat carrier besides carrying carbon dioxide from the carbonation to the calcination reactor. A part of the heat generated in carbonation supplies thus a part of the heat required in calcination. A way to provide the missing heat is to use an inert material such as bauxite that carries heat from a high-temperature reactor to the calcination one. An example is the ALSTOM hybrid combustion-gasification process where chemical and carbonate looping processes take place. Bauxite carries heat from the air reactor where oxidation of chemical looping particles takes place at temperatures around 1200°C to the calcination reactor where carbon dioxide is released at temperatures around 900-1000°C [148].

### 9.3.5 Indirect calcination by internal heat exchanger

Another way to maintain the required temperature of the calcination process is to provide heat by internal heat exchanger tubes in the regenerator. The direct advantage is that there is no extra supply of fuel such as coal or synthesis gas: the composition of the bed and the dimensions of the reactor stay unchanged. The direct disadvantage is the relatively low efficiency of transferring heat through tubes in the reactor compared to direct fuel burning.

## 9.4 Integration of sulphur capture

### 9.4.1 Motivation and method

The presence of sulphur in the synthesis gas impedes the capture of carbon dioxide because of the strong affinity with calcium particles. This part of the study aims to provide a more accurate idea of the impact of the sulphur content of the synthesis gas on the carbonate looping cycle. The assumptions made are:

- Carbonation temperature of 600°C
- Regeneration temperature of 1200°C
- Direct calcination by oxy-fuel combustion of syngas
- Sulphur present as hydrogen sulphide $H_2S$
- Same calcium- and steam-to-carbon ratios as the baseline case

### 9.4.2 Results and discussion

Sulphidation and carbonation reactions compete in the carbonation reactor. Contamination of calcium oxides by sulphur species involves the generation of calcium sulphides instead of calcium carbonates, decreasing thus the carbon capture rate.

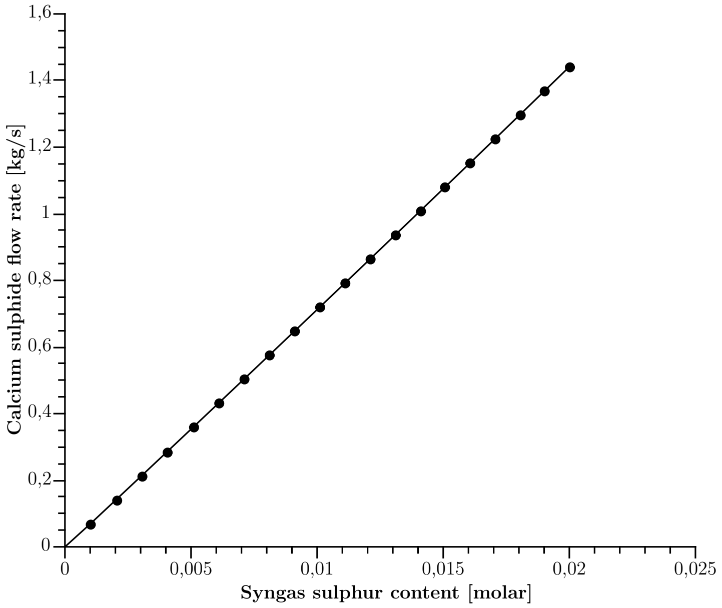

Figure 9.8: Impact of syngas sulphur content on calcium sulphide generation

It can be deduced that the generation of calcium sulphides is a linear function of the sulphur content of the synthesis gas and does not reach a maximum. The presence of sulphur is therefore particularly detrimental to the carbonate looping cycle since the calcium sulphide produced is particularly stable in this range of temperatures and calcium oxide particles are wasted.

## 9.5 Concluding remarks

The present work allows drawing the following conclusions on integrated carbonate looping ex situ, i.e. in the water-gas shift reactor:

1. The integration of carbonate looping ex situ is possible and, as expected, enhances fuel conversion to hydrogen by removal of carbon dioxide and moving the equilibrium of the water-gas shift reaction. The carbon capture rate can reach up to 96% and the purity of the $CO_2$-rich stream generated can exceed 97%.

2. High calcium-to-carbon ratios enhance the removal of carbon dioxide and increase the fuel conversion to hydrogen. There is nevertheless an equilibrium point that corresponds to a calcium-to-carbon ratio of 5, on a molar basis, where no more hydrogen can be further generated.

3. The introduction of steam is beneficial, in theory, to the regeneration of the calcium sorbent particle since it decreases the overall sintering effect and increases its reactivity. The simulations carried out showed that the addition of steam is beneficial to the conversion of methane. It should be kept as low as possible since steam is expensive and since it has a low impact on the carbon capture rate that stays around 96-97%.

4. The regeneration of the calcium oxide particle in the calcination reactor requires heat since it is an endothermic reaction and the temperature should be as high as 900-1000°C. There are several possibilities to integrate this step and the most probable option is the direct burning of synthesis gas with pure oxygen. Around 27% of the total amount of syngas needs to be burnt in the calcination reactor to sustain the desired temperature.

5. Calcium oxide particles can react with pollutants such as the sulphur compounds present in the synthesis gas, which results therefore in the generation of calcium sulphide and logically to a decrease of the carbon capture rate.

# Chapter 10

# Conclusion

## 10.1 Outcomes

The integration of solid looping cycles in integrated gasification combined cycles is a complex topic, due to a lack of knowledge about chemical and carbonate looping and the limitations and inaccuracies of process-level modelling. This thesis has aimed to check what the benefits of chemical and carbonate looping are and whether these processes have the potential to become competitive for carbon dioxide capture and for higher process efficiency in IGCC power plants. Chemical looping combustion of synthesis gas is a promising process to integrate in IGCC. Its feature of inherent carbon dioxide separation and its lower energy penalty compared to conventional $CO_2$ capture processes make this process highly promising.

1. The study of the baseline case with nickel as oxygen carrier and a turbine inlet temperature of 1200°C revealed that the capture of carbon dioxide from the IGCC power plant is feasible and has the potential to reach more than 99% carbon capture rate.

2. The efficiency of the overall plant could not be calculated but the electrical efficiency of the combined cycle is around 52% which is slightly less than a combined cycle without $CO_2$-capture, but higher than a combined cycle with $CO_2$-capture. This value is highly sensible to the air reactor temperature and to the gas turbine pressure ratio.

3. Critical design factors for the reactor are the inert-to-carrier ratio and the solids circulation mass flow rate because they have both an impact on the mass and heat balances of the chemical looping system and thus on the overall combined cycle.

4. When paying attention to the metal oxide, it turns out that nickel has a higher oxygen carrying capacity than manganese and iron. The circulation of solids is thus smaller in the first case, which allows the construction of a smaller and cheaper reactor and eases the solids handling. However, it appears too that nickel cannot fully convert carbon compounds, at the opposite of manganese, and the capture of carbon dioxide is not complete. Another remark is that only iron oxides are suitable for generation of hydrogen thanks to their favourable thermodynamics.

5. The integration of a $CO_2$-turbine is a problematic question since it enables larger power production in the gas turbine cycle but leads to lower quality of steam generation in the bottoming steam cycle. The net power efficiency of the combined cycle, including $CO_2$-compression, is slightly higher and other considerations should therefore be taken into account.

6. At present, the turbine inlet temperature at the outlet of the chemical looping system is limited to around 1200°C due to material issues. This process has nevertheless the potential to achieve a capture of close to 100%.

Chemical looping gasification is an interesting alternative to the classic air separation and gasifier units: it does not have a potential to ease $CO_2$-capture but to reach higher overall efficiency of the IGCC power plant.

1. The integration of chemical looping gasification is feasible, whether the metal processed is nickel, manganese or iron, and can lead to the same composition of synthesis gas at the outlet of the gasification unit.

2. The choice of air and solids flow rates are critical parameters in the design of chemical looping gasification because they are related to the amounts of oxygen and heat carried from one reactor to another. There is therefore margin to optimise the system to operate the gasifier in fuel-rich and high-temperature conditions.

3. The feedstock composition has a strong impact on the operating conditions of the CLG unit: it is essential to adapt the air, steam and solids flow rates in function of the carbon and moisture contents.

4. Moving bed reactors present other features than circulating fluidised beds: it turns out that they allow, for the same operating conditions, a higher hydrogen and carbon monoxide yield, and, for a given synthesis gas composition, require lower solids circulation and airflow rate.

Carbonate looping ex situ is a promising technique for capturing carbon dioxide after the gasifier and before the combined cycle: it enables the generation of a hydrogen-rich synthesis gas by moving the equilibrium of the water-gas shift reaction.

1. The assessment led in this thesis has proven that carbonate looping has relevant features for $CO_2$ capture and is proper for integration in IGCC power plants with a carbon capture rate higher than 93% and hydrogen purity higher than 90% after condensation. The efficiency of the overall plant could not be calculated but it is expected that, carbonate looping cycles have a lower energy penalty than conventional pre-combustion $CO_2$-capture processes.

2. Critical design parameters for an efficient carbon dioxide capture are carbonation/-calcination temperatures and steam-to-fuel ratio since they have an impact on the equilibrium of the different reactions involved and thus on the carbon capture rate.

3. Optimising the heat integration is the key point to achieve successful development of carbonate looping in IGCC power plants: oxy-fuel combustion of coal or syngas leads to higher energy penalty whereas indirect calcination by heat exchangers is less thermal efficient.

4. Capturing sulphur in parallel of carbon dioxide is feasible: the most suitable option is therefore to purge the solids flow rate and to provide a make-up of calcium oxides.

## 10.2 Suggestions

There are different areas where there is room for improvement and further work. Regarding the way this thesis has been carried out, the recommendations are to:

1. Pursue literature research on the topics of chemical and carbonate looping cycles. These processes are under development and different ideas will come up within the next months with the different research groups and companies working on this topic.

2. Extend the study from system analysis to reactor investigation. Though the main aim has been to assess solid looping cycles on a process scale, it is interesting to check their feasibility and their limitations when coming to a reactor model, especially since the RGIBBS module used in this study idealises the behaviour of the chemical looping reactors.

3. Assess the dynamic behaviour of chemical and carbonate looping cycles in IGCC power plants. Only a few researches on dynamic modelling have been carried out so far and there is a strong lack of knowledge about these processes on this aspect.

Apart from these points, there are several possibilities for improving the models presented in this work. Hence, the suggestions are to:

1. Improve their robustness. There is margin to optimise the ASPEN Plus models and the processes simulated on themselves. For example, customised and ordered databanks would allow for more realistic and less sensitive results.

2. Extend them to a power plant scale. The chemical looping combustion and carbonate looping ex situ models are limited to the combined cycle process whereas the chemical looping gasification is restricted to the gasification step. Assessing all the power plant would allow deeper understanding of the interactions between the different units and relatively accurate calculations of efficiencies and energy demands.

3. Continue the evaluation of solid looping cycles by modelling and simulating the unconsidered processes and the new advanced ones that will be developed in the following years.

Finally, in the long-term, it would be relevant to compare the estimations and results from this thesis and to validate them by comparison with experiments and real-case power plants.

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# Appendix A

# Preparation and synthesis methods

There are several preparation and synthesis methods to prepare the composite oxygen carrier particle [22]:

- Mechanical mixing: powders of the metal oxide and the support material desired are directly mixed together and are then fixed by binding agents before being shaped to achieve the desired particle morphology.
- Freeze granulation: both metal oxide and support are mixed together in distilled water with a dispersant to improve the homogeneity of the mixture. The powder slurry obtained is treated by binding agents, dried and sintered to achieve spherical particles.
- Dry impregnation: metal nitrate solution is treated with powder of the support material and is calcined to achieve the desired ratio of oxygen carrier and support and to increase its stability.
- Wet impregnation: wet and dry impregnation methods are similar in principle, with variations in quantities and operating conditions.
- Dissolution method: solutions of metal salt and support material are directly mixed together and precipitated to a powder state by addition of water and alcohol. The liquid phase is therefore dried by successive calcinations.
- Sol-Gel process: a chemical solution composed of the metal oxide and inert material evolves towards a diphasic liquid-solid material.
- Solution combustion: metal nitrates and support material are mixed in a water-glycine solution that is first heated and then ignited to produce the desired particle.

Each of these methods presents advantages and drawbacks: the choice of one technique rather than another depends on the materials processed (oxygen carrier and inert) and on the habits of the laboratories.

# Appendix B

# Design procedure

There are several criteria to consider while designing a chemical looping reactor. The properties of the chemical looping particles, the involved reactions, the heat transfer and the hydrodynamics inside the reactors may all have an impact on the process performance:

*Reaction kinetics*

- Temperature
- Carrier reactivity
- Gas conversion
- Carrier capacity

*Hydrodynamics*

- Bed operating regime
- Solid entrainment rates
- Gas leakage
- Residence time

*Design criteria*

- Fuel mass flow
- Air to fuel ratio
- Solid circulation rate

# Appendix C

# Pre-treatment and doping

There are several methods to improve the chemical and carbonate looping particles reactivity over cycles [22]:

- Thermal pre-activation: different limestone-based sorbents are pre-treated in a nitrogen rich atmosphere under various different temperature conditions. Whereas the initial carrying capacity is lower than non pre-treated limestone sorbents, the residual one is about twice higher. An unexpected result is the increase of carrying capacity of thermal pre-treated sorbents during the first cycles.

- Doping: doping in sorbent preparation methods refers to the use of chemical additives or supports in aqueous or in solid forms to improve the calcium oxide properties. Common aqueous solutions are acetic acid $CH_3COOH$, ethanol $C_2H_5OH$, water, sodium chlorine NaCl and sodium carbonate $NaCO_3$. Potential solids are alumina, titanium dioxide $TiO_2$, silica $SiO_2$, magnesium sulphate $MgSO_4$ and lithium carbonate $LiCO_3$. The effects of these additives are open to criticism. Experiments in a laboratory scale with a TGA showed an increase of reactivity whereas pilot studies in realistic conditions did not show any positive effect. However, no doping methods tested are proved to improve largely the long-term reactivity.

- Synthesis by precipitation: a new kind of calcium-based sorbents has been developed recently by precipitation synthesis. The aim has been to create a synthetic sorbent with high reactive area and so high reactivity. The calcium carbonate differs from natural limestone because of its high meso-porosity (i.e. pores with a diameter higher than 10 nm). Large pores are less likely than micro-pores to be fully obstructed by calcium carbonate layers or by sintering effect, leading thus to a higher reactivity. There are a few differences between natural and synthetic sorbents prepared by precipitation regarding the reaction mechanisms. The diffusion-controlled phase in carbonation, i.e. the first stage, is much faster in the case of synthetic sorbents and is probably due to a solid-state diffusion mechanism.

- Synthesis by dispersion and matrix: cyclic studies and experiments on synthetic sorbents show that the porosity stays constant over the cycles and thus their performance do not decrease. Another difference is the relation between partial pressures and reactivity: whereas a lower partial pressure is favourable to the kinetics of calcination reaction for natural sorbents, it is the opposite with synthetic ones.

# Appendix D

# Components lists in ASPEN Plus

The different species used in ASPEN Plus for the simulations are:

Table D.1: General components list in ASPEN Plus

| Component ID | Type | Component name | Formula |
|---|---|---|---|
| CARBON | SOLID | CARBON-GRAPHITE | C |
| CO | CONV | CARBON-MONOXIDE | CO |
| CO2 | CONV | CARBON-DIOXIDE | CO2 |
| CH4 | CONV | METHANE | CH4 |
| H2O | CONV | WATER | H2O |
| N2 | CONV | NITROGEN | N2 |
| O2 | CONV | OXYGEN | O2 |
| H2 | CONV | HYDROGEN | H2 |
| S | CONV | SULFUR | S |
| H2S | CONV | HYDROGEN-SULFIDE | H2S |
| SO2 | CONV | SULFUR-DIOXIDE | O2S |
| SO3 | CONV | SULFUR-TRIOXIDE | O3S |
| COS | CONV | CARBONYL-SULFIDE | COS |
| HCL | CONV | HYDROGEN-CHLORIDE | HCL |
| CL2 | CONV | CHLORINE | CL2 |
| NO | CONV | NITRIC-OXIDE | NO |
| NO2 | CONV | NITROGEN-DIOXIDE | NO2 |
| N2O | CONV | NITROUS-OXIDE | N2O |
| N2O3 | CONV | NITROGEN-TRIOXIDE | N2O3 |
| N2O4 | CONV | NITROGEN-TETROXIDE | N2O4 |
| NH3 | CONV | AMMONIA | H3N |
| AL2O3 | SOLID | ALUMINIUM-OXIDE-ALPHA-CORUNDUM | AL2O3 |
| AR | CONV | ARGON | AR |
| HG | CONV | MERCURY | HG |
| NH4CL | CONV | AMMONIUM-CHLORIDE | NH4CL |
| HCOOH | CONV | FORMIC-ACID | CH2O2 |

Table D.2: Components list in ASPEN Plus (nickel case)

| Component ID | Type | Component name | Formula |
|---|---|---|---|
| NI | SOLID | NICKEL | NI |
| NIO | SOLID | NICKEL-OXIDE-BUNSENITE | NIO-B |
| NI3C | SOLID | TRINICKEL-CARBIDE | NI3C |
| NIAL2O4 | SOLID | NICKEL-DIALUMINIUM-TETRAOXIDE | NIAL2O4 |
| NIS0:-01 | SOLID | NICKEL-0.84-SULFIDE | NIS0.84 |
| NIS | SOLID | NICKEL-SULFIDE | NIS |
| NIS2 | SOLID | NICKEL-DISULFIDE | NIS2 |
| NI3S2 | SOLID | TRINICKEL-DISULFIDE | NI3S2 |
| NISO4 | SOLID | NICKEL-SULFATE | NISO4 |

Table D.3: Components list in ASPEN Plus (manganese case)

| Component ID | Type | Component name | Formula |
|---|---|---|---|
| MN | SOLID | MANGANESE | MN |
| MNO | SOLID | MANGANESE-OXIDE | MNO |
| MN2O3 | SOLID | DIMANGANESE-TRIOXIDE | MN2O3 |
| MN3O4 | SOLID | TRIMANGANESE-TETRAOXIDE | MN3O4 |
| MNO2 | SOLID | MANGANESE-DIOXIDE | MNO2 |
| MNCO3 | SOLID | MANGANESE-CARBONATE | MNCO3 |
| MN3C | SOLID | TRIMANGANESE-CARBIDE | MN3C |
| MNS2 | SOLID | MANGANESE-DISULFIDE | MNS2 |
| MNS | SOLID | MANGANESE-MONOSULFIDE-GREEN | MNS |

Table D.4: Components list in ASPEN Plus (iron case)

| Component ID | Type | Component name | Formula |
|---|---|---|---|
| FE | SOLID | IRON | FE |
| FEO | SOLID | FERROUS OXIDE | FEO |
| FE2O3 | SOLID | HEMATITE | FE2O3 |
| FE3O4 | SOLID | MAGNETITE | FE3O4 |
| FES | SOLID | IRON-MONOSULFIDE | FES |
| FE3C | SOLID | TRIIRON-CARBIDE | FE3C |
| FECO3 | SOLID | IRON-CARBONATE | FECO3 |
| FE0.947O | SOLID | WUESTITE | FE0.947O |

Table D.5: Components list in ASPEN Plus (calcium case)

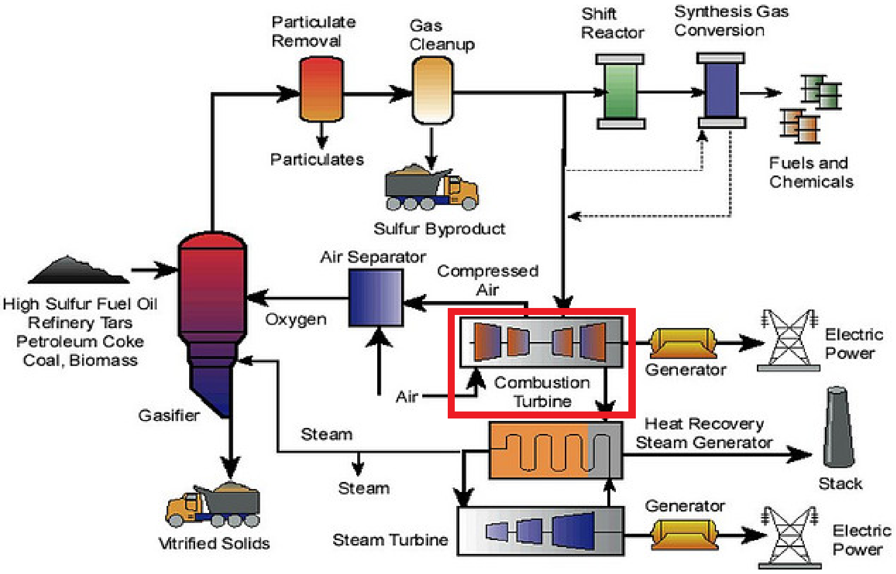
| Component ID | Type | Component name | Formula |
|---|---|---|---|
| CAO | SOLID | CALCIUM-OXIDE | CAO |
| CACO3 | SOLID | CALCIUM-CARBONATE-ARAGONITE | CACO3-A |
| CACL2 | SOLID | CALCIUM-CHLORIDE | CACL2 |
| CAC2 | SOLID | CALCIUM-DICARBIDE | CAC2 |
| CAS | SOLID | CALCIUM-SULFIDE | CAS |
| CASO3 | SOLID | CALCIUM-SULFITE | CASO3 |
| CA(OH)2 | SOLID | CALCIUM-HYDROXIDE | CA(OH)2 |
| CASO4 | SOLID | CALCIUM-SULFATE | CASO4 |

# Appendix E

# Chemical looping combustion: flow sheet and models

The following items are included in this appendix:

- Schematics of an IGCC power plant with chemical looping combustion of synthesis gas (1 page)
- Flow diagram of an IGCC power plant with chemical looping combustion of synthesis gas (1 page)
- ASPEN flow sheet of chemical looping combustion of synthesis gas with $CO_2$-turbine (1 page)
- ASPEN flow sheet of chemical looping combustion of synthesis gas without $CO_2$-turbine (1 page)
- ASPEN flow sheet of chemical looping combustion of synthesis gas with air top-firing (1 page)
- ASPEN flow sheet of chemical looping combustion of synthesis gas with fuel top-firing (1 page)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Refinery Tars
Petroleum Coke
Coal, Biomass
Oxygen
Combustion Turbine
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Heat Recovery Steam Generator
Stack
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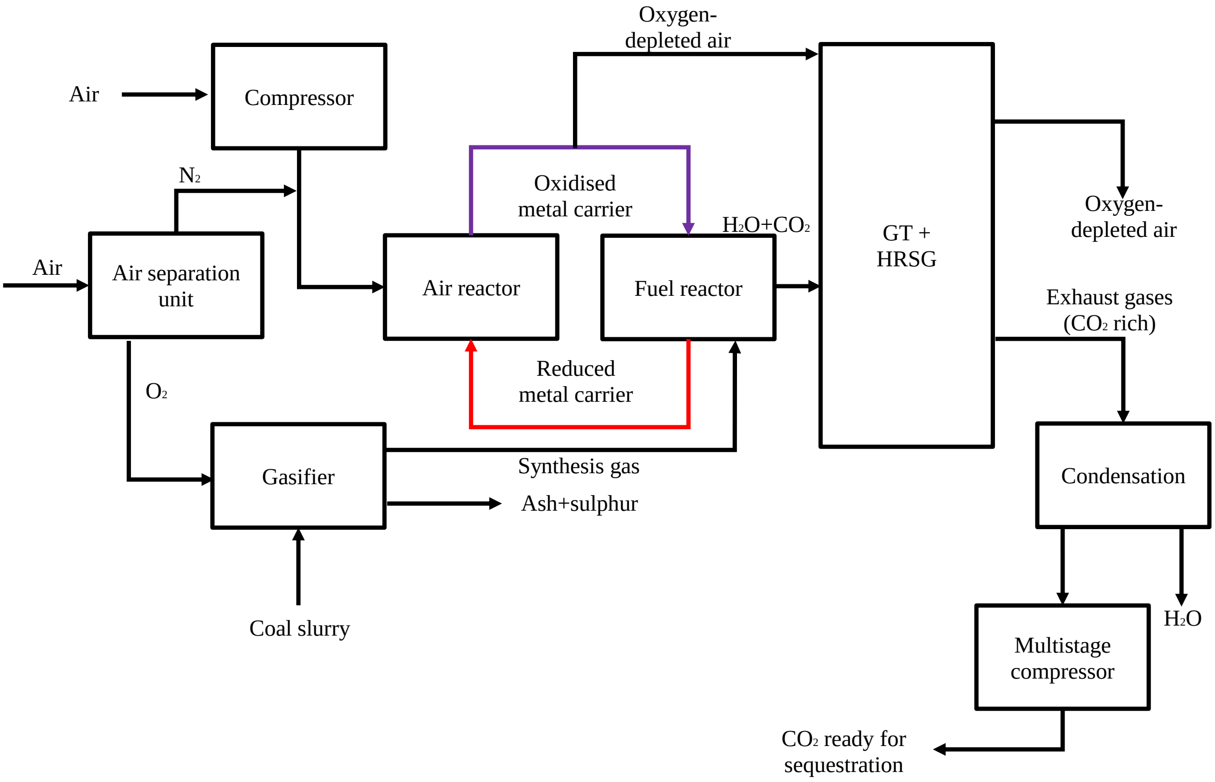
Electric Power
Vitrified Solids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Oxidised metal carrier
$H_2O+CO_2$
GT + HRSG
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Air separation unit
Air reactor
Fuel reactor
Exhaust gases ($CO_2$ rich)
$O_2$
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Gasifier
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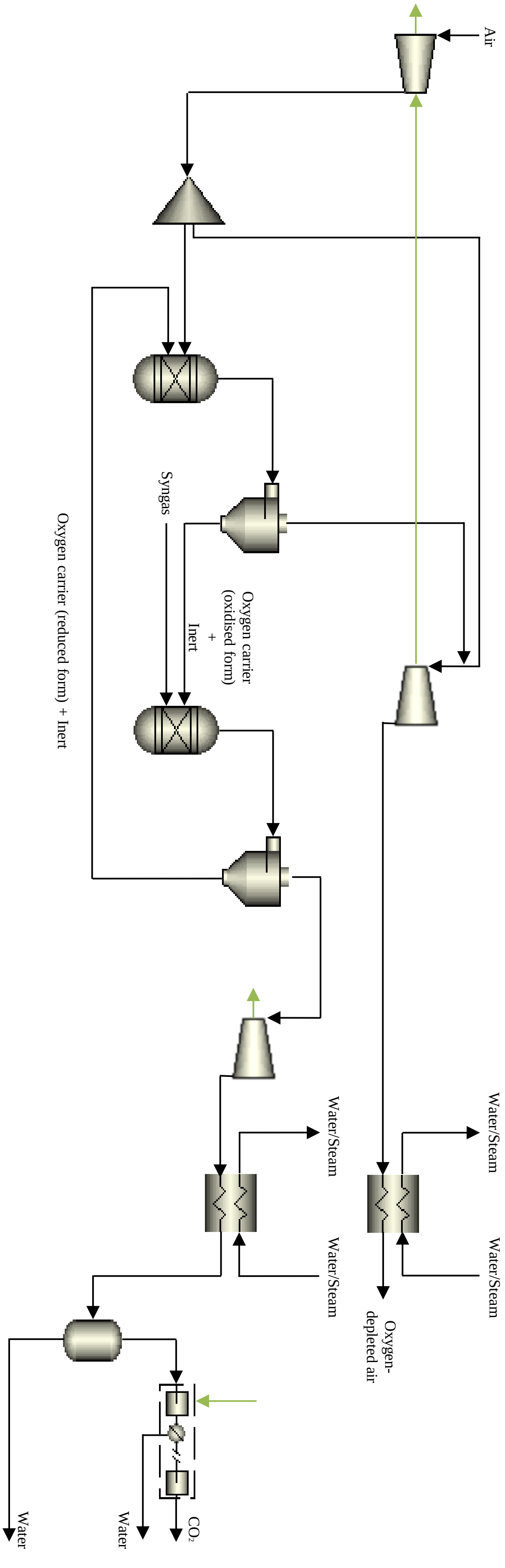
Condensation
Coal slurry
Multistage compressor
$H_2O$
$CO_2$ ready for sequestration


Air
Syngas
Oxygen carrier (oxidised form) + Inert
Oxygen carrier (reduced form) + Inert
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Water/Steam
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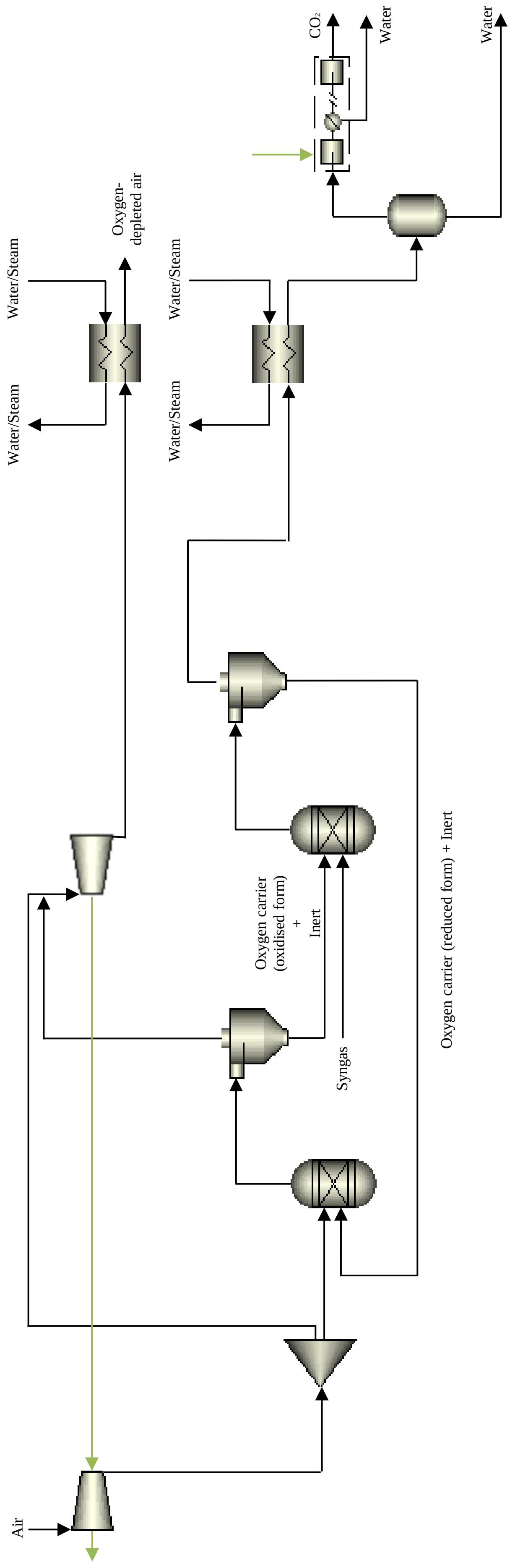
Water
Water
$CO_2$


Air
Oxygen carrier (reduced form) + Inert
Syngas
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Water/Steam
Water/Steam
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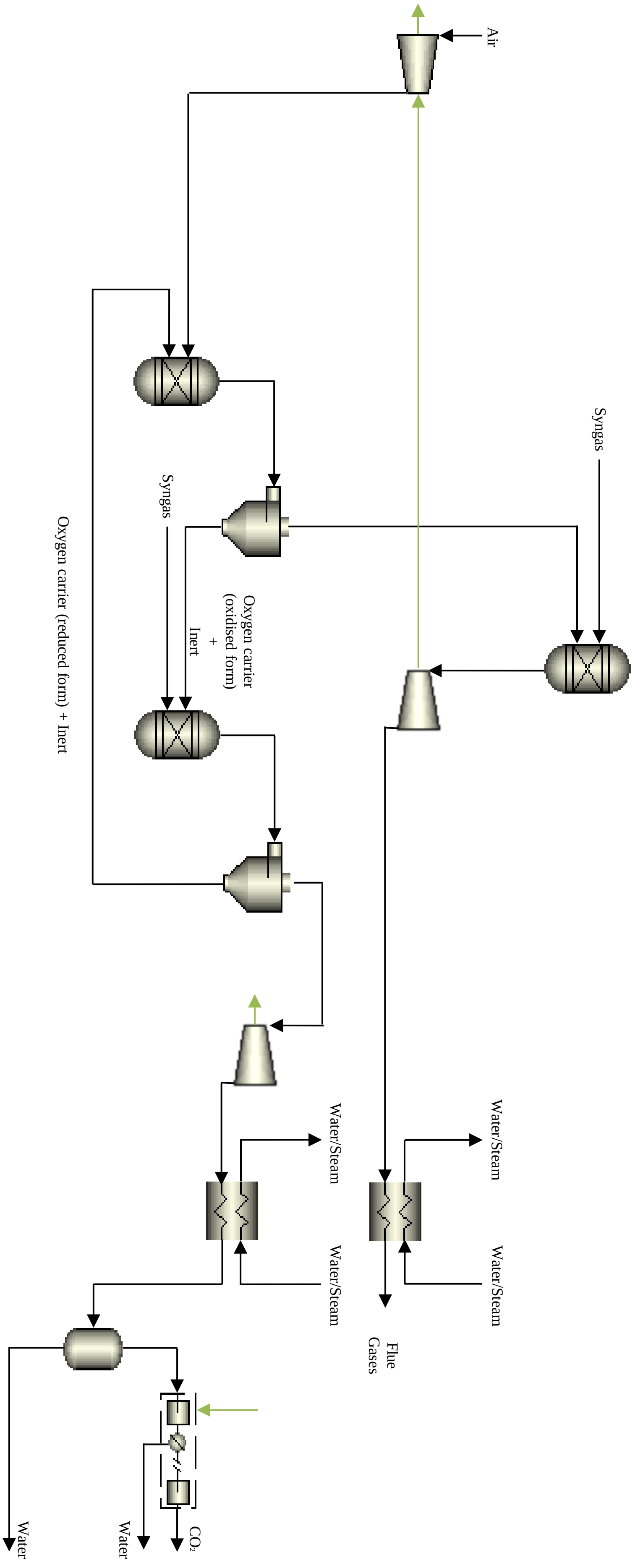
Water
Water
$CO_2$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Syngas
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Oxygen carrier (oxidised form) + Inert
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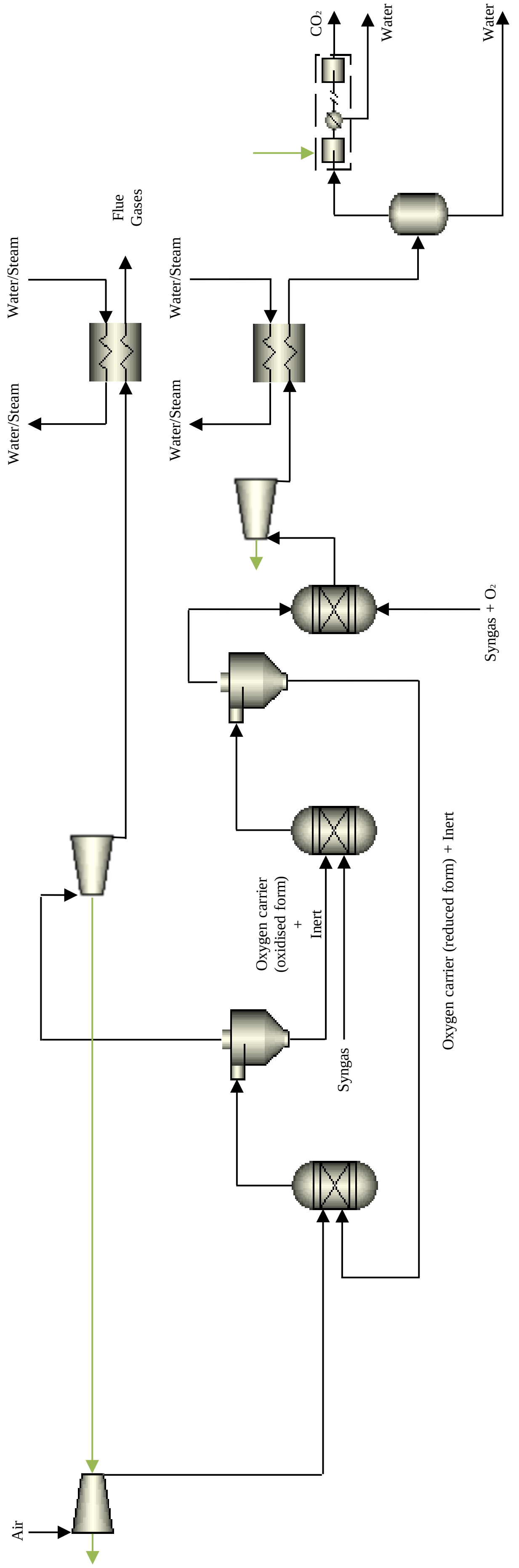
CO2

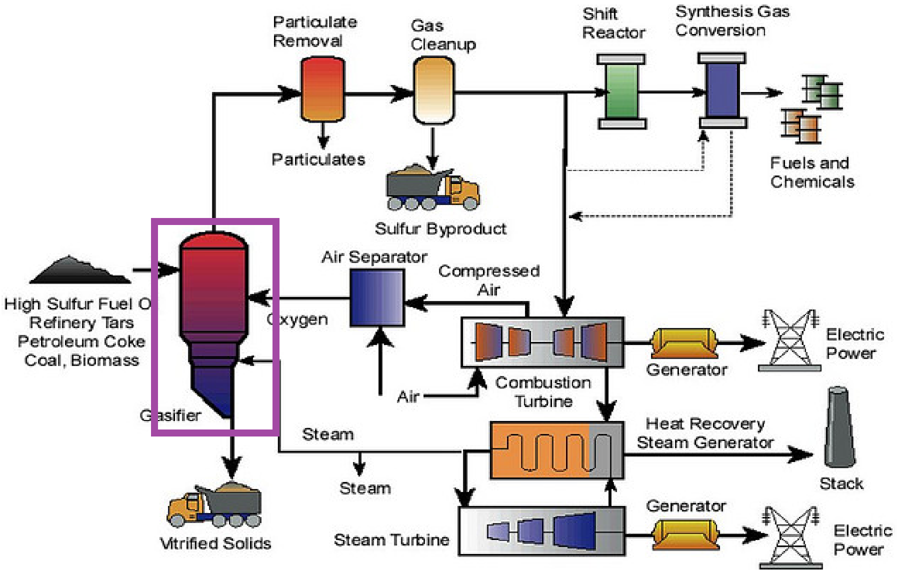

Air
Oxygen carrier (reduced form) + Inert
Syngas
Oxygen carrier (oxidised form) + Inert
Syngas + O₂
Water/Steam
Water/Steam
Flue Gases
Water/Steam
Water/Steam
Water
CO₂
Water

# Appendix F

# Chemical looping gasification: flow sheet and models

The following items are included in this appendix:

- Schematics of an IGCC power plant with chemical looping gasification (1 page)
- Flow diagram of an IGCC power plant with chemical looping gasification (1 page)
- ASPEN flow sheet of chemical looping combustion of synthesis gas without energy recovery (1 page)
- ASPEN flow sheet of chemical looping combustion of synthesis gas with energy recovery (1 page)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Fuels and Chemicals
Sulfur Byproduct
Air Separator
Compressed Air
High Sulfur Fuel O
Refinery Tars
Petroleum Coke
Coal, Biomass
Oxygen
Electric Power
Generator
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Combustion Turbine
Gasifier
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Steam
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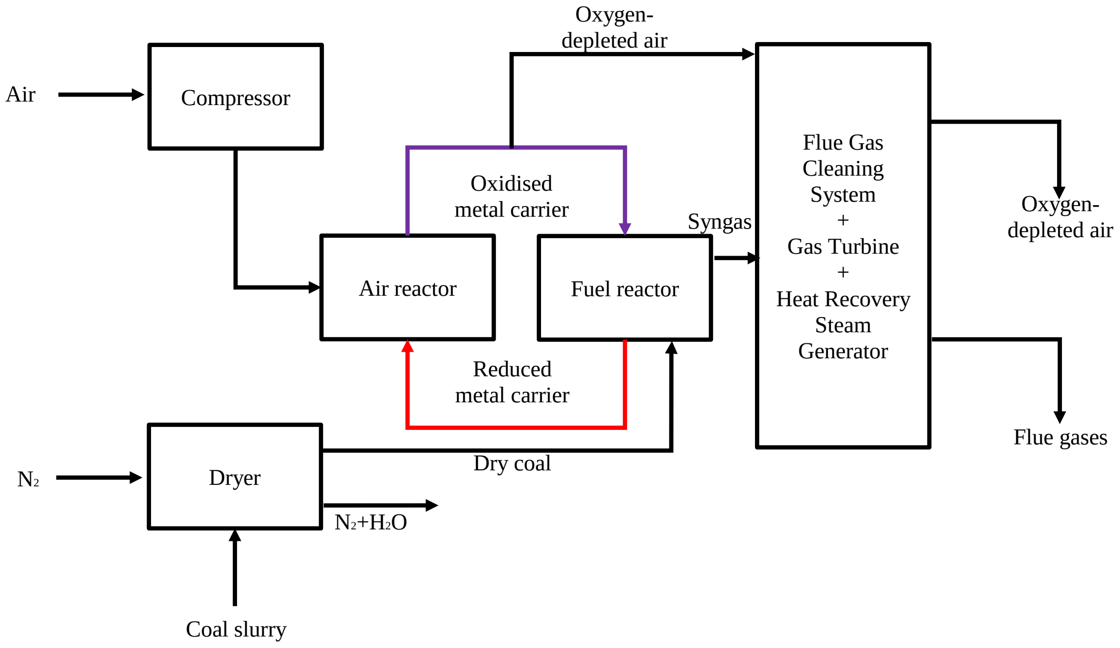
Generator
Steam Turbine
Electric Power
Vitrified Solids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Compressor
Oxygen-depleted air
Oxidised metal carrier
Air reactor
Fuel reactor
Syngas
Flue Gas Cleaning System + Gas Turbine + Heat Recovery Steam Generator
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Reduced metal carrier
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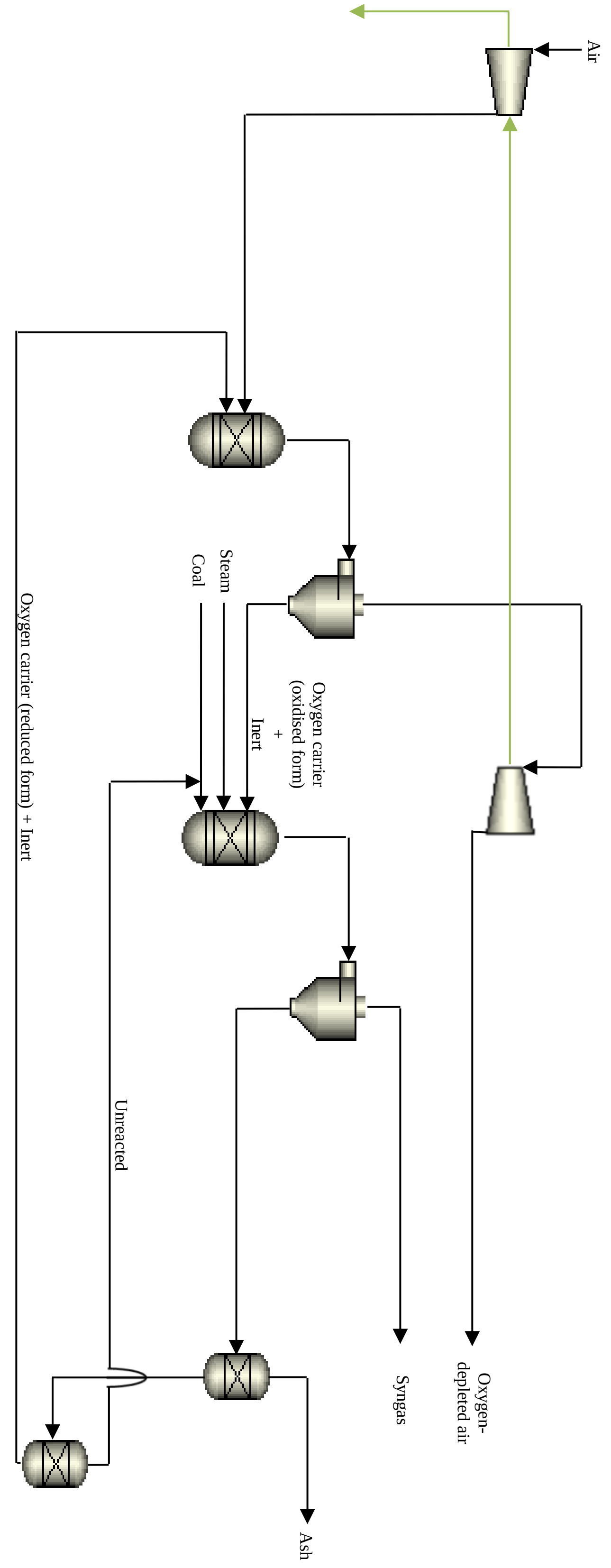
Dryer
Dry coal
N₂+H₂O
Coal slurry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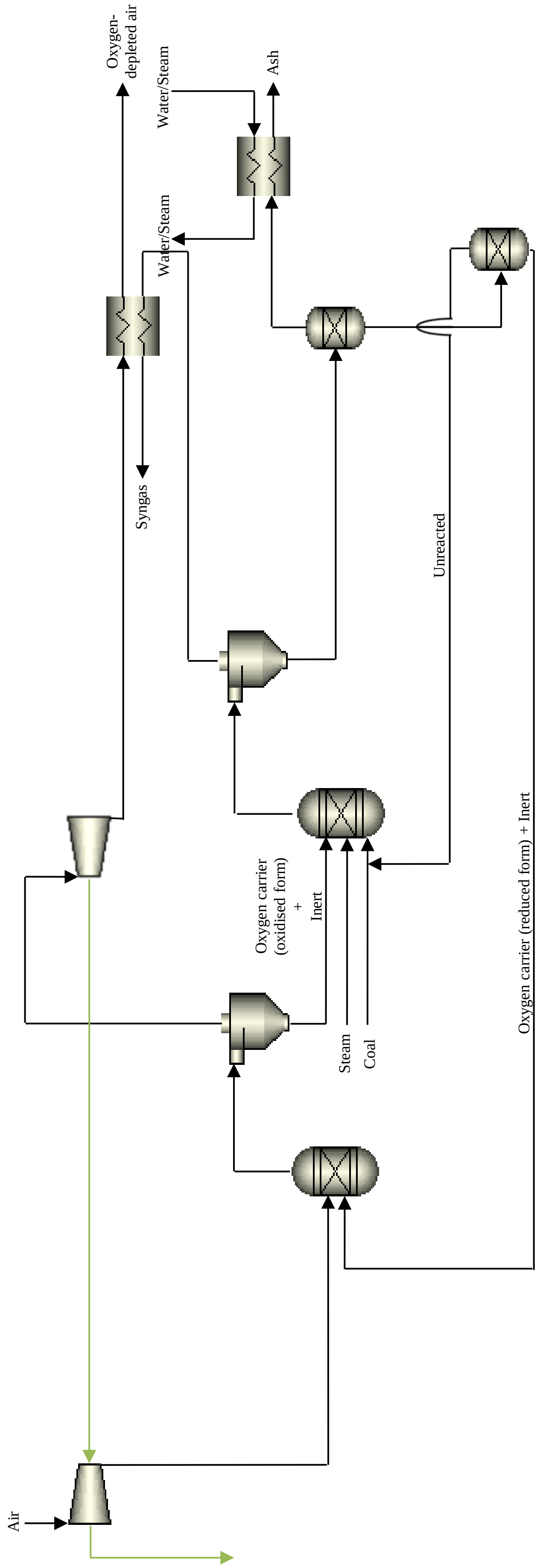
Steam
Coal
Oxygen carrier (oxidised form) + Inert
Unreacted
Syngas
Oxygen-depleted air
Ash

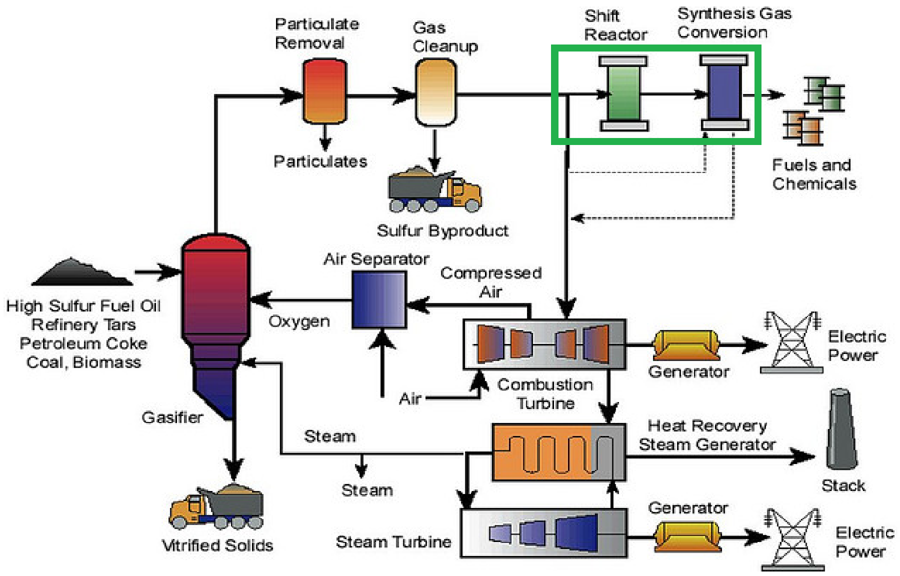

Oxygen-
depleted air
Water/Steam
Ash
Water/Steam
Syngas
Unreacted
Oxygen carrier
(oxidised form)
+
Inert
Steam
Coal
Oxygen carrier (reduced form) + Inert
Air

# Appendix G

# Carbonate looping: flow sheet and models

The following items are included in this appendix:

- Schematics of an IGCC power plant with carbonate looping - WGS (1 page)
- Flow diagram of an IGCC power plant with carbonate looping (1 page)
- ASPEN flow sheet of carbonate looping (1 page)
- ASPEN flow sheet of carbonate looping with hydration reactor (1 page)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Removal
Gas
Cleanup
Shift
Reactor
Synthesis Gas
Conversion
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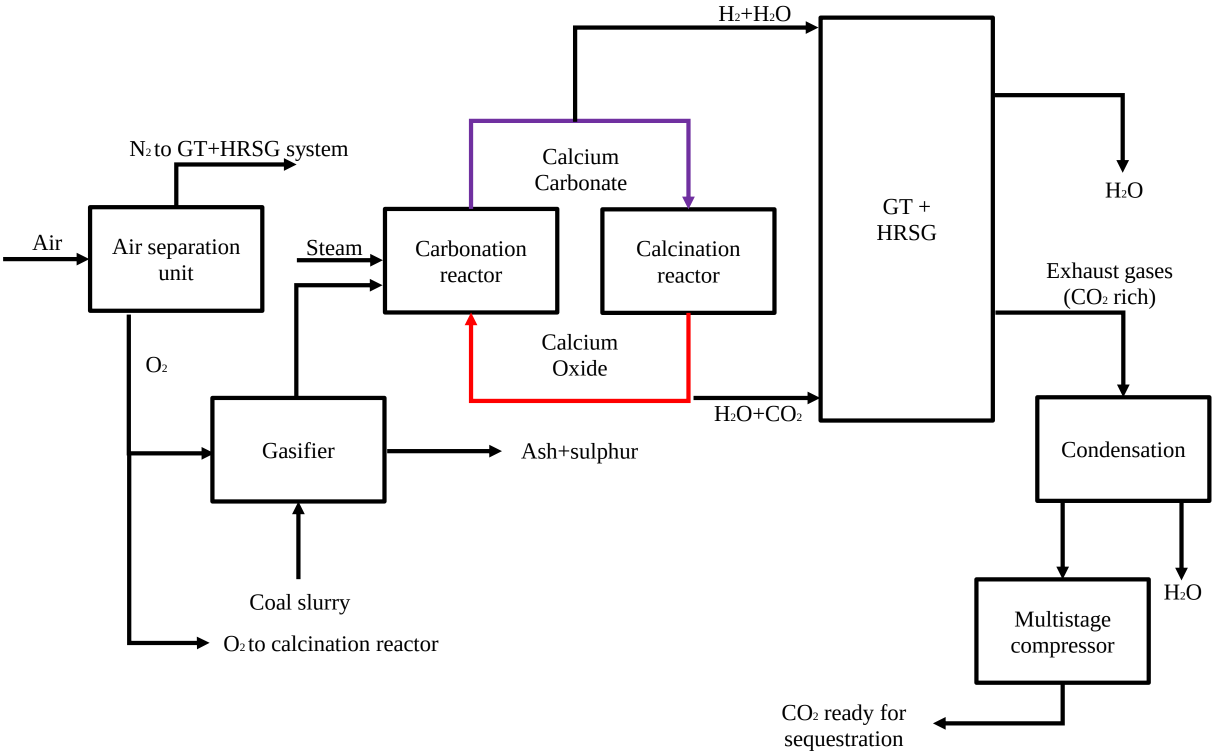
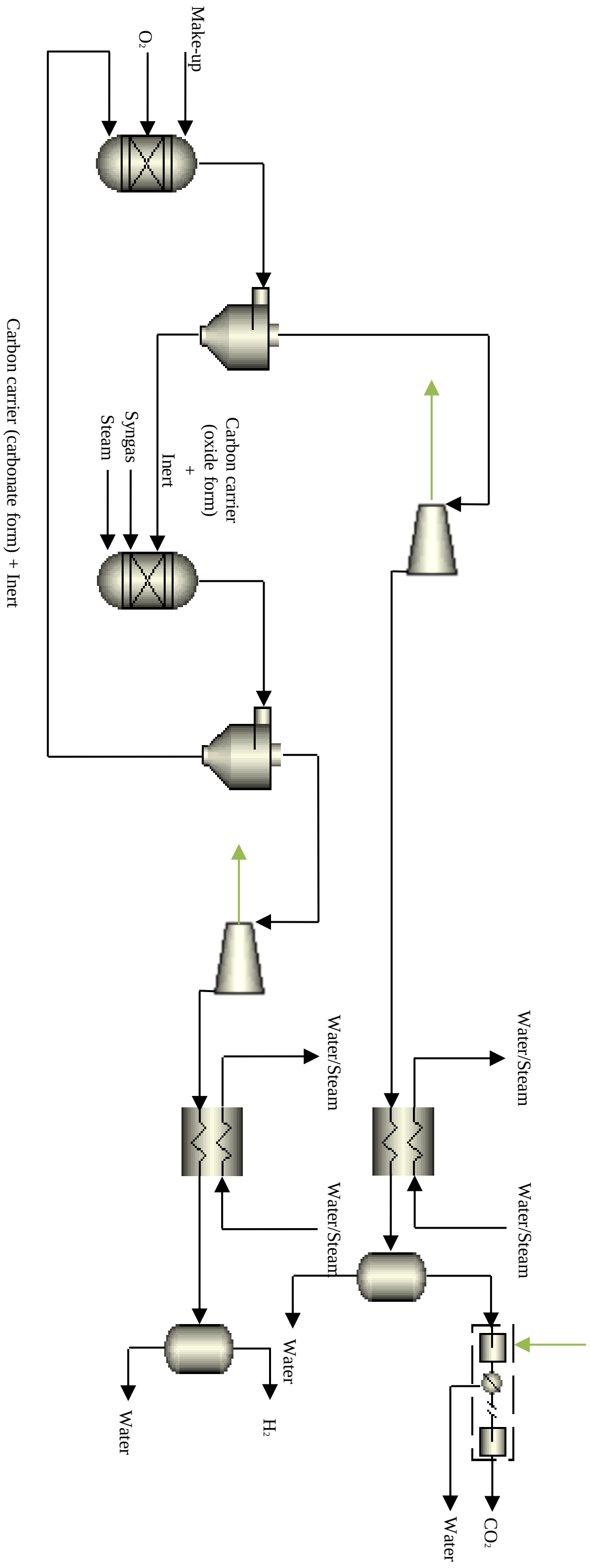
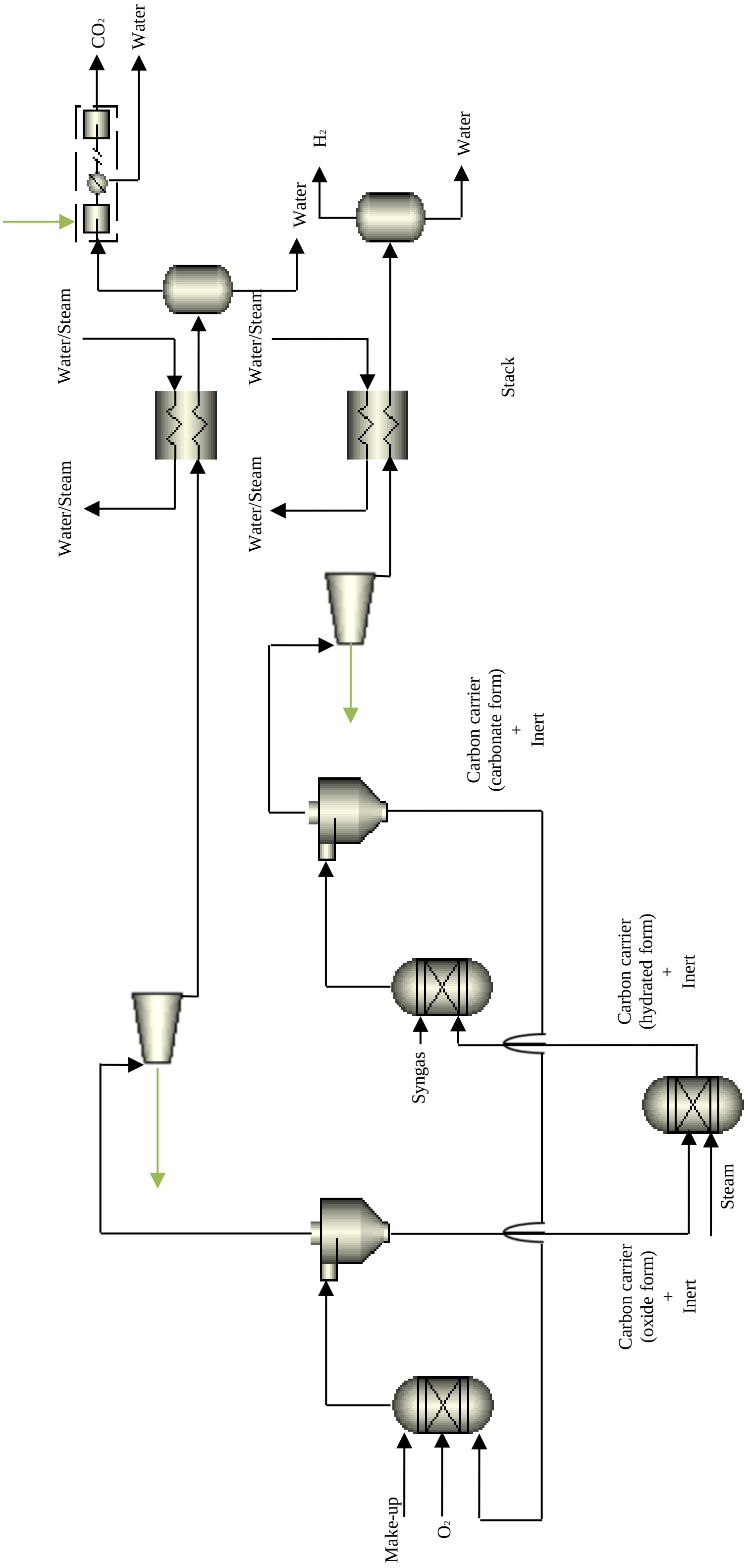
Fuels and
Chemicals
Air Separator
Compressed
Air
Oxygen
High Sulfur Fuel Oil
Refinery Tars
Petroleum Coke
Coal, Biomass
Gasifier
Air
Combustion
Turbine
Generator
Electric
Power
Steam
Steam
Heat Recovery
Steam Generator
Stack
Vitrified Solids
Steam Turbine
Generator
Electric
Power


H2+H2O
N2 to GT+HRSG system
Calcium Carbonate
H2O
Air
Air separation unit
Steam
Carbonation reactor
Calcination reactor
GT + HRSG
Exhaust gases (CO2 rich)
O2
Calcium Oxide
H2O+CO2
Gasifier
Ash+sulphur
Condensation
Coal slurry
H2O
Multistage compressor
O2 to calcination reactor
CO2 ready for sequestration


Make-up
O₂
Carbon carrier (oxide form) + Inert
Syngas
Steam
Carbon carrier (carbonate form) + Inert
Water/Steam
Water/Steam
Water/Steam
Water/Steam
Water
H₂
Water
CO₂
Water


CO$_2$
Water
Water
H$_2$
Water
Water/Steam
Water/Steam
Water/Steam
Water/Steam
Stack
Carbon carrier
(carbonate form)
+
Inert
Carbon carrier
(hydrated form)
+
Inert
Syngas
Steam
Carbon carrier
(oxide form)
+
Inert
Make-up
O$_2$