BABEŞ – BOLYAI UNIVERSITY
FACULTY OF CHEMISTRY AND CHEMICAL ENGINEERING
Department of Chemical Engineering
11 Arany János, Cluj – Napoca, Romania, 400028

Contributions to innovative carbon dioxide capture technologies applied to energy conversion systems

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PhD Thesis Summary

Ing. Anamaria Pădurean

Scientific supervisor
Prof. Ing. Dr. Paul Şerban Agachi

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Scientific supervisor:
Prof. Ing. Dr. Paul Şerban Agachi
Reviewers:
Dipl. Ing. Dr. Tobias Pröll, Vienna University of Technology
Prof. Ing. Dr. Teodor Todincă, Polytechnic University of Timişoara
Assoc. Prof. Ing. Dr. Radu Horațiu Barbu Mișca, Babeș – Bolyai University Cluj – Napoca

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Keywords: Carbon capture and storage (CCS), Post-Combustion Capture, Pre-Combustion Capture, Chemical - Looping Combustion Capture (CLC), Integrated Gasification Combined Cycle (IGCC) with and without CCS, Techno-economic evaluation

Part I – General Introduction

Chapter 1. Thesis overview

1.1. Motivation

Today, a large amount of worldwide primary energy consumption comes from fossil fuels like oil, coal and natural gas. According to International Energy Agency, about 40% of total primary energy is used for electricity generation and of this, coal is the fuel for 40%. Forecasts of future energy consumption predict a further increase of worldwide coal utilization in the coming 20 years. But the impact of energy production from fossil fuels on the environment is becoming a matter of growing concern. In addition to the risks for environment on a local scale, the mankind is now faced with danger of global warming caused by greenhouse gas emissions (mainly carbon dioxide). Therefore, fossil fuels are the major source of carbon dioxide emissions and they cause global warming with all its negative impacts. It is generally accepted today that huge efforts have to be undertaken to limit the greenhouse gas emissions and to reduce the impact of global warming. Mitigation scenarios indicate that this can only be achieved if all options for carbon dioxide reduction are followed.

An important reduction of greenhouse gas emissions resulting from fossil fuels utilization can be obtained by increasing the efficiency of power plants and industrial production processes, decreasing the energy demand and replacing fossil fuels by renewable energy sources or nuclear energy combined with carbon dioxide capture and long time storage. Unfortunately in practice, on a global scale, the alternative energy conversion processes cannot substitute rapidly the usage of fossil fuels, which will continue to represent a substantial share of the energy consumed for many years to come, the only feasible solution for now remaining these carbon capture and storages technologies (CCS). CCS involves three basic steps: carbon dioxide capture, transport to a suitable disposal site, and long – term storage. With respect to capture, attention is primarily directed at major point source emitters, particularly fossil fuel – fired power stations, but also other large industrial facilities, including those associated with the production of oil, gas, chemicals, steel and cement. For these reasons, it is important that there should be technology options that would allow continuous use of solid fuels, within these as mentioned above, without substantial CO_2 emissions.

Approaches to carbon dioxide capture technologies generated from fossil fuel energy conversion include post – combustion capture, pre-combustion capture, oxy – fuel combustion and chemical looping combustion. All these technologies can be achieved by several ways of carbon dioxide removal processes such as solid adsorption, absorption into a liquid solvent, membranes or other physical or biological separation methods etc. Among these techniques, carbon dioxide capture by gas – liquid absorption is one of the most common and commercially mature technologies today (e.g. carbon dioxide absorption process is applied in chemical processes like hydrogen and ammonia synthesis) and, in many cases, has been considered to be the most viable solution, compared to the other processes that are available.

1.2. Thesis objectives

CCS technologies are expected to play a significant role in the coming decades for reducing greenhouse gas emissions. Integrated Gasification Combined Cycle is one of the power generation technologies having the highest potential to capture carbon dioxide with the low penalties in term of plant energy efficiency and cost. The modification of the IGCC design for carbon capture can be done in various plant concepts considering the carbon capture method to be used (e.g. pre – and post – combustion capture, syngas chemical looping etc.).

Taking into account the previously mentioned challenges, this thesis aims to investigate various carbon dioxide capture methods suitable to be applied for an IGCC plant for power generation. The coal blended with biomass (sawdust) based IGCC case study investigated in the thesis produces around 350 – 450 MW net electricity with more than 90% carbon capture rate.

So, the main objectives of the thesis are as follows:

- A first objective is to assess and compare two of the most commercially mature CO_2 capture technologies today: post – combustion capture using chemical solvents and pre – combustion capture using physical and chemical solvents in order to integrate them into the IGCC power plant scheme. For this purpose the aim is to develop, for each investigated technology detailed flowsheet models in chemical engineering software Aspen Plus® which can be utilized then in future analysis for energy integration, costing, etc.

- The second objective is to find optimum operating points for the developed Aspen Plus® CO_2 capture process schemes, characterized by a minimum energy requirement for a given CO_2 removal and to understand how the design variables as columns heights, columns packed dimensions, solvent flowrate, stripper temperature and the operating bottom to feed ratio of the stripper affect each other at the level of the whole CO_2 capture process.
- Since it is necessary to explore the potential for energy integration between the power generation system and the capture system, the third objective is to identify possibilities for energy recovery in the system in order to reduce the energy penalty of CO_2 capture technologies. The modeling and simulation of the whole IGCC plant concept with different carbon dioxide capture methods produced the input data for quantitative evaluation of various plant schemes for analyzing the energy penalty involved by the carbon capture process. The investigated models are used to study the effects of the performance parameters (specific electricity, heating and cooling consumption for each kg of captured carbon dioxide, etc.) on the efficiency, emissions and costs of IGCC plant. A comparison in term of overall plant performance, energy consumption, CO_2 specific emissions, net electric power output, plant efficiency and costs of all IGCC based carbon capture technologies with conventional IGCC concept without CO_2 will be developed.
- The fourth objective is to investigate the chemical looping combustion CO_2 capture technology – the most innovative and attractive solution for CO_2 capture technology and to examine the feasibility and the performance of this technology for direct use of solid fuels.

1.3. Thesis structure and contribution

The thesis is divided in four parts: part I – General introduction, part II – Overall basis, part III – Evaluation of capture technologies and part IV – Comparison and recommendations. The short overview of the thesis is as follows.

Part I, entitled “General introduction” includes Chapter 1 where the thesis overview is presented.

Part II entitled “Overall basis” is divided in five Chapters.

Chapter 2, called “Introduction”, gives a brief presentation to the greenhouse gas effect, global warming and CO_2 mitigation problems; shows the relation between energy and climate; introduces the concept of carbon capture and storage (CCS) and motivates the need for a closer study of capture technologies.

Chapter 3, called “Theoretical background” presents a general description of the methodology that was applied for the comparative study of CO_2 capture technologies applied to Integrated Gasification Combined Cycle power plant. Three important CO_2 capture technologies are described in details: pre – combustion carbon dioxide capture by gas – liquid absorption using chemical and physical solvents, post – combustion carbon dioxide capture by gas – liquid absorption using chemical solvents and chemical looping combustion technology applied for solid fuels.

Chapter 4 entitled “Modeling of the process” presents the simulation models, which will be later applied in the studies. A large part of the thesis is focused on pre and post – combustion capture technologies using chemical and physical solvents by gas – liquid absorption. In order to compare these technologies it is necessary to perform on a consistent basis and to perform a process analysis of the system. Aspen Plus® software provides tools to achieve analysis of this type, reason why it was chosen as platform for the gas – liquid separation model. For chemical looping combustion model the equation oriented steady state simulation environmental IPSEpro has been applied for the model implementation. The dynamic behavior of the system, in the case of chemical looping combustion, was investigated using Matlab Simulink engineering platform.

Chapter 5 called “Base case scenario” gives a brief description of the technical background of the Integrated Gasification Combined Cycle power plant used in the models which the carbon dioxide capture technologies will be integrated in. An IGCC power plant, based on coal mixed with biomass (sawdust) in the ratio of 80 – 20 (% wt.), generating 350 – 450 MW net electricity was the basis for this study. The proposed specifications for investigated carbon dioxide capture technologies evaluated in this thesis are also listed in Chapter 5.

Part III entitled “Evaluation of capture technologies” is divided in three Chapters and together with Part IV represents the author’s original contribution of the thesis.

Chapter 6 describes an integrated methodology of assessing the pre – combustion carbon capture option using physical (dimethyl ethers of polyethylene glycol, methanol and N-Methyl-2-pyrolydone) and chemical solvents (methyldiethanolamine) suitable to be applied for IGCC – based power generation. The evaluation is based on modeling and simulation work (realized with the help of the engineering software Aspen Plus®), the most important design characteristics being evaluated in details like: selection of solvents, heat and power integration of the main plant sub – systems and quantification of carbon capture energy penalty. As an illustrative example, a full IGCC power plant with carbon capture system using the best solvent found is presented in details for giving example of what does it mean in term of key plant performance indicators, the application of pre – combustion CCS technologies in power generation sectors. This part of the thesis is based on papers I, II.

Chapter 7 evaluates carbon dioxide absorption, at low partial pressures, from flue gases by post – combustion capture process using aqueous solutions of various alkanolamines: monoethanolamine, diethanolamine, methyldiethanolamine, 2-amino-2methyl-1-propanol and their corresponding mixtures. At a constant capture rate of about 90%, the performance of these aqueous alkanolamine solutions are compared in terms of solvent loading and overall energy consumption. The evaluation is based on modeling and simulation work (realized with the help of the engineering software Aspen Plus®), the most important design characteristics being evaluated in details like: heat and power integration of the main plant sub – systems, selection of alkanolamines, quantification of carbon capture energy penalty, implications of environmental and operational criteria. An illustrative example of an IGCC scheme for power generation with and without post – combustion capture is presented to quantify the overall energy penalties involved by the capture process. This part of the thesis is based on papers I, III, IV, V and IX.

Chapter 8 presents the work realized during author's eight months research mobility at Vienna University of Technology where the feasibility and the performance of the chemical looping combustion technology for solid fuels was studied. A proposal for an appropriate and promising reactor design for direct use of solid fuel has been made based on the already successfully applied dual circulating fluidized bed system for gaseous fuel chemical looping combustion at TUV. In the design phase, a modeling tool for chemical looping processes needed for mass – and energy balance calculations of the solid fuel CLC system was created in the IPSEpro simulation environment. The dynamic behavior of the system was investigated for the cold flow model already existing at TUV using Matlab Simulink engineering platform. This part of the thesis is based on papers VI.

Part IV is entitled “Comparative and recommendations” and is divided in five Chapters.

Chapter 9 called “Comparative technico – economic assessments” presents a comparison of the current costs of CO_2 capture technologies in order to assess the relative rankings of the different technologies anticipated to meet the most of the future demand for electricity. An economic analysis and comparison was carried on for pre – combustion and post – combustion CO_2 capture technologies because these two technologies are the most common and commercially mature technologies today. The comparison is undertaken on an equivalent basis using cost metrics such as levelised cost of electricity, the cost of CO_2 avoided and the cost of CO_2 captured. This part of the thesis is based on paper I, VII, VIII and IX.

The “General Conclusions” Chapter 10 details the overall conclusions from the thesis and discusses further direction in which this study can be carried forth. The author’s main contribution and publications are also listed.

Abbreviations, nomenclatures, list of figures, list of tables and references used in the thesis can be found in Chapter 11, Chapter 12 and Chapter 13.

Part II – Overall Basis

Chapter 2. Introduction

Carbon capture and storage (CCS) is a modern technology approach trying to mitigate the contribution of carbon dioxide emissions and involves three basic steps: carbon dioxide capture, transport to a suitable disposal site, and long term storage. With respect to capture, attention is primarily directed at major point source emitters, particularly fossil fuel – fired power stations, but also other large industrial facilities including those associated with the production of oil, gas, chemicals, steel and cement.

Approaches to carbon dioxide capture technologies generated from the combustion of fossil fuels include post – combustion capture, pre – combustion capture, oxyfuel combustion and chemical looping combustion.

Pre–combustion capture technology involves separating CO_2 before the fuel is burned as it can be noticed in Figure 2.1. This technology process the fuel in a reactor with steam and air or oxygen to produce syngas – a mixture of H_2 and CO. Additional H_2, together with CO_2, is produced by reacting the CO with steam in a shift reactor. The resulting mixture of H_2 and CO_2 can then be separated into a CO_2 gas stream, and a stream of H_2. If the CO_2 is stored, the H_2 is a carbon – free energy carrier that can be combusted to generate power and/or heat (IPCC, 2005).

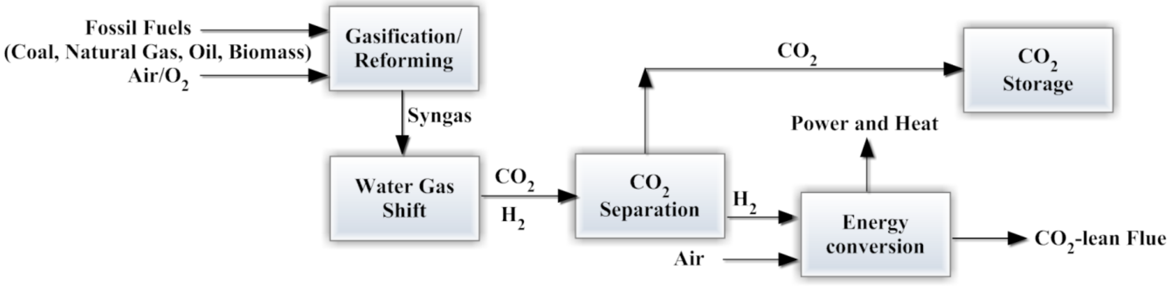


Figure 2.1. *Scheme of pre – combustion process (IPCC, 2005)*

Post–combustion capture technology involves separating CO_2 from flue gases produced by combustion (Figure 2.2), that contain 4 % to 8 % of CO_2 by volume for natural gas – fired power plants, and 12 % to 15 % by volume for coal – fired power plants.

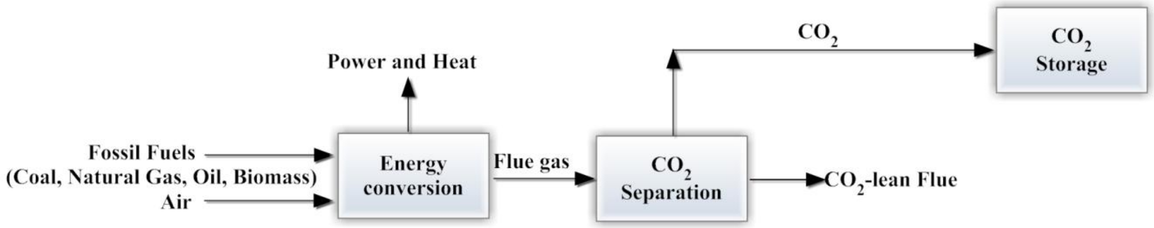


Figure 2.2. *Scheme of post – combustion process (IPCC, 2005)*

The CO_2 is captured typically through the use of solvents and successive solvent regeneration, sometimes in combination with membrane separation. The basic technology (using amine-based solvents) has been used on an industrial scale for decades, but the challenge is to recover the CO_2 with a minimum energy penalty and at an acceptable cost (IEA, 2008).

Chemical looping combustion technology (CLC) is a new combustion technology with inherent separation of the greenhouse gas CO_2. The technology involves the use of a metal oxide as an oxygen carrier which transfers oxygen from combustion air to fuel, and so a direct contact between air and fuel is avoided. So far oxides of iron, cooper, chrome, manganese and nickel have been investigated (Brandvoll et al., 2005; Ishida et al., 2002; Jin et al., 1999; Lyngfelt et al., 2001; Steeneveldt et al., 2006). The major components of a chemical looping process are: solid oxygen carrier, a chemical looping system, fuel and air supplies, heat utilization/recovery and CO_2 capture (Figure 2.3). The outlet gas from the fuel reactor consists of CO_2 and H_2O, which is easily removed by condensation (Steeneveldt et al., 2006).

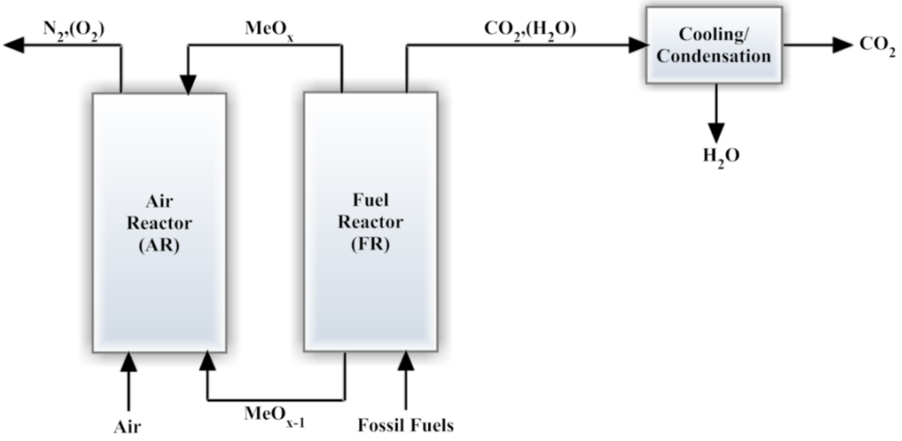
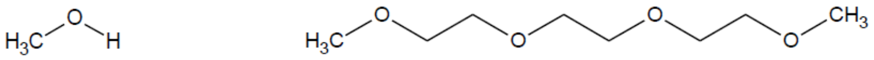


Figure 2.3. *Scheme of CLC combustion process (Lyngfelt et al., 2001)*

Chapter 3. Theoretical Background

3.1. Pre – Combustion Capture

In the case of pre – combustion capture technique (Figure 2.1), where carbon dioxide partial pressure is relatively high (about 10 – 12 bar) and its concentration is around 40 %, it is increasingly becoming normal practice to use physical solvents containing for instance methanol (Rectisol® technology), N-Methyl-2-pyrolydone (Purisol® technology) or mixture of dimethyl ethers of polyethylene glycol (Selexol® technology) (Cormos, 2008; Kohl and Nielsen, 1997) but chemical solvents could also be used. The structural formula of the physical solvents used for CO_2 capture in this present thesis are illustrated in Figure 3.1.



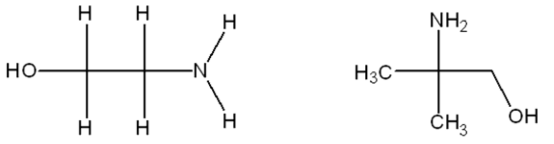
Rectisol (Methanol)   Selexol $CH_3(CH_2CH_2O)_3OCH_3$

Purisol (N-Methyl-2-pyrolydone)   Fuor Solvent (Popylene Carbonate)

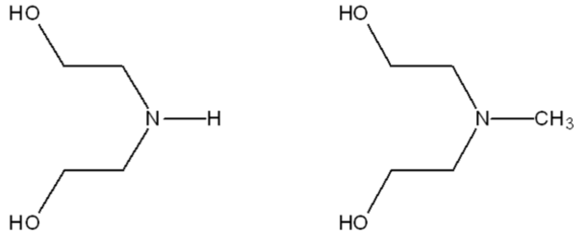
Figure 3.1. *Physical solvents structural formulas*

3.2. Post – Combustion Capture

The solvents used for post – combustion CO_2 capture can be physical, chemical or intermediate but chemical solvents, known as alkanolamines, are most likely to be used for post – combustion capture. This is because chemical solvents are less dependent on partial pressure (close to atmospheric) than physical solvents are, and carbon dioxide concentrations are relatively low e.g. 4 – 8 % vol. in natural gas – fired and 12 – 15 % vol. in coal – fired power plants. However, chemical solvents require more energy (as steam) to regenerate, that is, to break the relatively strong chemical link between CO_2 and the solvent. (IEA, 2007). Structural formulas for several alkanolamines used in carbon dioxide capture process are presented in Figure 3.2.



Mono-ethanol-amine **2-Amino-2-Methyl-1-Propanol**



Di-ethanol-amine **Methyl-di-ethanol-amine**

Figure 3.2. Alkanolamines structural formulas

3.4. Chemical – Looping Combustion

From environmental friendly characterization point of view, CLC has attracted wide attention and extensive investigation in the past a few years (Fang et al, 2009). A majority of the publications concerning CLC have used gaseous fuel such as methane or natural gas and the CLC concept using this type of fuels has already been successfully demonstrated at relevant operating conditions using oxygen carrier particles based on nickel (Pröll et al. 2010; Linderholm et al, 2009) at Vienna University of Technology. But, due to the low cost, the abundance and the intensive use of the solid fuels, it will be highly advantageous if the CLC process could be adapted for solid fuels. However, a satisfying solution for the use of solid fuels in this technology has not been proposed yet. One possibility of doing this is to undergo previous solid fuel gasification and afterwards to introduce the produced gas in the CLC system. Another strategy for the use of solid fuel in a CLC is the direct combustion in the CLC process, thus avoiding the need of gasifier.

When it comes to direct use of solid fuels in CLC several challenges additional to CLC using gaseous fuels have to be faced (Pröll et al. 2010). First, the solid fuel needs to be decomposed into its gaseous compounds.

Using single stage fluidized bed reactors, the char particles are expected to be well mixed with the oxygen carrier and sufficient residence time has to be achieved in the fuel reactor to minimize loss of char particles to the air reactor. Finally, ash and inert content of the fuel has to be discharged from the system. Here it is also expected, that in a single stage fluidized bed system, ash particles and oxygen carrier are well mixed. In order to minimize oxygen carrier renewal rates, it is desired to separate the ash from the oxygen carrier before removing it from the system. The definition of challenges for the direct use of solid fuels in CLC leads to two main tasks for research: finding a suitable oxygen carrier on one hand and finding a suitable reactor concept on the other hand (Fang et al., 2009; Lyngfelt, 2011; Hendersen 2010). The focus of this work was to find and evaluate a suitable reactor concept for the direct use of solid fuels in CLC. The concept proposed is based on the so called dual circulating fluidized bed reactor concept (DCFB) originally developed and successfully applied for gaseous fuels at Vienna University of Technology (Figure 3.3**,** a) (Pröll et al., 2009).

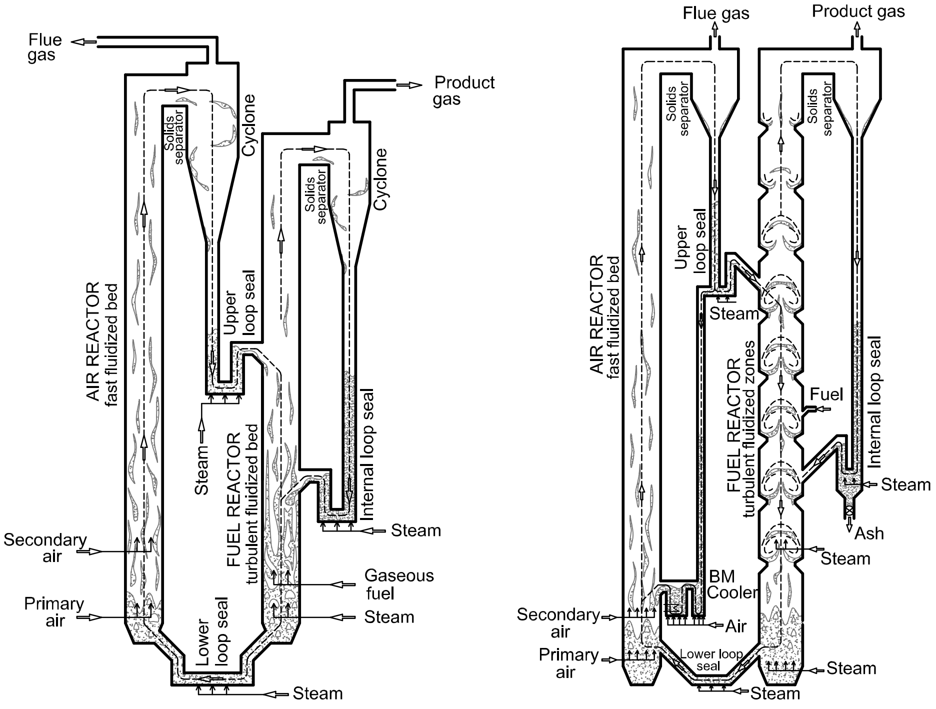


Figure 3.3 *a) Dual circulating fluidized bed system for gaseous fuel (Pröll et Hofbauer, 2010). b) Multistage circulating fluidized bed reactor concept with gas – solid counter – current flow*

Chapter 4. Modeling of the process

The ability to model power plant equipment and complete power plants is essential for optimizing the performance and consequently cutting down costs. For many years, computer models have been important tools for this area. In the beginning, the tendency was for companies to have large proprietary programs, implementing their specific design concepts. The rapid development of computing technology during recent years made maintenance of such programs difficult and costly. Nowadays, most of the companies including equipment manufacturers, plant operators, and engineering and consulting companies, prefer to use modeling environments that allow them to overcome the limits of purpose specific solutions. As a consequence, project's performance was improved and productivity increasing features, like graphic user interfaces and efficient data exchange with other programs, were made available to them (Dargam and Perz, 1998). Examples of software system with these capabilities are Aspen Plus® and SimTech's package IPSEpro - softwares which were used for simulation the processes in this present thesis.

Chapter 5. Base case scenario

An IGCC power plant, based on coal mixed with biomass (sawdust) in the ratio of 80 – 20 (% wt.), generating 350 – 450 MW net electricity was the basis for this study. The choice of sawdust as renewable energy sort and its characteristics takes into account the wide distribution of the biomass sort.

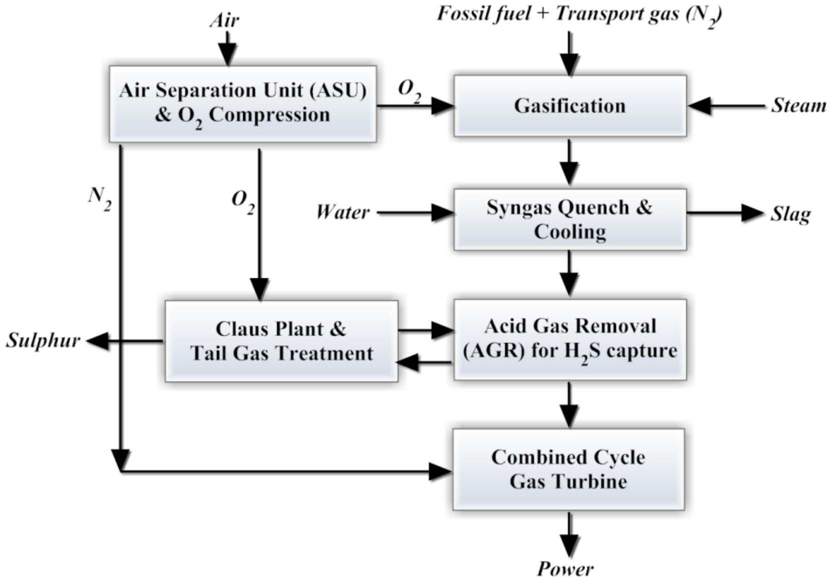


Figure 5.1. *IGCC Process flowsheet (Cormos et al., 2011)*

Since the purpose of this thesis was to investigate only the CO_2 capture technologies, in order to integrate them into IGCC power plant, other main sub – systems of the IGCC plant and their design assumptions used in the modeling and simulation can be found in open literature (Cormos 2008; Cormos et al., 2009; Higmann and van der Burgt, 2008; Maxim, 2011; Starr et al., 2007). Table 5.1 present the proposed specifications for investigated carbon dioxide capture technologies evaluated in the present thesis.

Table 5.1. *Proposed specifications for investigated carbon dioxide processes*

Electrical power output	IGCC with and without capture	350 – 450 MW_e
CO_2 capture percentage	IGCC with capture	90 %
Energy penalty	IGCC with capture	< 8%[*]
CO_2 avoidance cost	IGCC with capture	< 50 €/t_{CO_2}[*]
CO_2 removal cost	IGCC with capture	< 50 €/t_{CO_2}[*]
CO_2 captured stream	Compound	Concentration limit[**]
	H_2O	< 200 ppm
	CO_2	> 95 % vol.
	H_2S	< 200 ppm
	CO	< 2000 ppm
	O_2	< 10 ppm (EOR)
	Non-condensable gases (CH_4, N_2, Ar)	< 4 % vol.
	SO_x	< 50 ppm
	NO_x	< 50 ppm

[*] IEA, 2011; NETL, 2012

[**] Tohidi B, 2008

Part III – Evaluation of Capture Technologies

Chapter 6. Pre – Combustion Capture Systems

In this work a steady state process simulator Aspen Plus® was used to develop process models. Since the purpose of this thesis is to investigate carbon dioxide capture technologies, in order to be integrated afterwards in the power plant generation systems, only the AGR systems will be discussed in details. AGR parameters, specifications, assumptions and Aspen Plus® models will be discussed further.

The components specified in the simulation field, the syngas flowrate and compositions which have been used in the studies and other main sub – systems of the plants and their design assumptions used in the mathematical modeling and simulation are listed in Table 6.1 (Padurean et al., 2012).

Table 6.1. *Main design assumptions for pre – combustion carbon dioxide capture technology*

Syngas to AGR	Mass flow [t/h]	448.60
	Temperature [ºC]	37.00
	Pressure [atm]	32.30
	Gas composition	(% vol.)
	N_2	3.20
	CO_2	39.85
	CO	1.33
	H_2O	0.21
	H_2	54.66
	H_2S	0.14
	CH_4	0.01
	Ar	0.58
Absorption column	Solvent feed temperature [ºC]	0.10
	Solvent feed pressure[atm]	32.00
Solvent regeneration	Pressure levels [bar]	32.00; 13.00; 7.00; 2.00; 1.05
CO_2 compression	Delivery pressure [bar]	122.00
	Compressor efficiency [%]	85.00
CO_2 drying	Solvent	TEG
	Solvent feed pressure [atm]	4.95

The main unit operation blocks (absorption and desorption column) used in the equilibrium model are described in table below (Table 6.2). For the separation behavior of columns it was used the concept of equilibrium stages and the tray efficiencies for each of the stages it was incorporated. The method relates bulk vapour and liquid phase compositions and temperatures through the assumptions of physical, chemical and thermal equilibrium between the bulk phases.

Table 6.2. *Aspen Plus main unit operation blocks used in the equilibrium model*

Unit operation	Aspen Plus Block	Specifications
Absorber	RadFac	Column model: Equilibrium Number of stagews: 22 Column diameter: 0.8 m Number of sections: 4 Top stage pressure: 32 bar Packed type: IMTP Packed Dimension: 3 IN or 75 mm Section packed height: 5 m
Desorber	RadFac	Column model: Equilibrium Number of stages: 24 Column diameter: 0.8 m Number of sections: 4 Top stage pressure: 5 bar Kettle reboiler Ratio of liquid bottom flow rate to feed flow rate: 0.93 Packed type: FLEXIPAC Packed Dimension: 700 Y or 725 m^2/m^3 Section packed height: 5 m

For pre – combustion carbon dioxide capture technology, the CO_2 capture plant consist of absorption columns, desorption columns, drops separators, heat exchangers, pumps and stage compressors. A schematic diagram of the equipment used in this work is shown in Figure 6.1 for Selexol® solvent (Padurean et al., 2012).

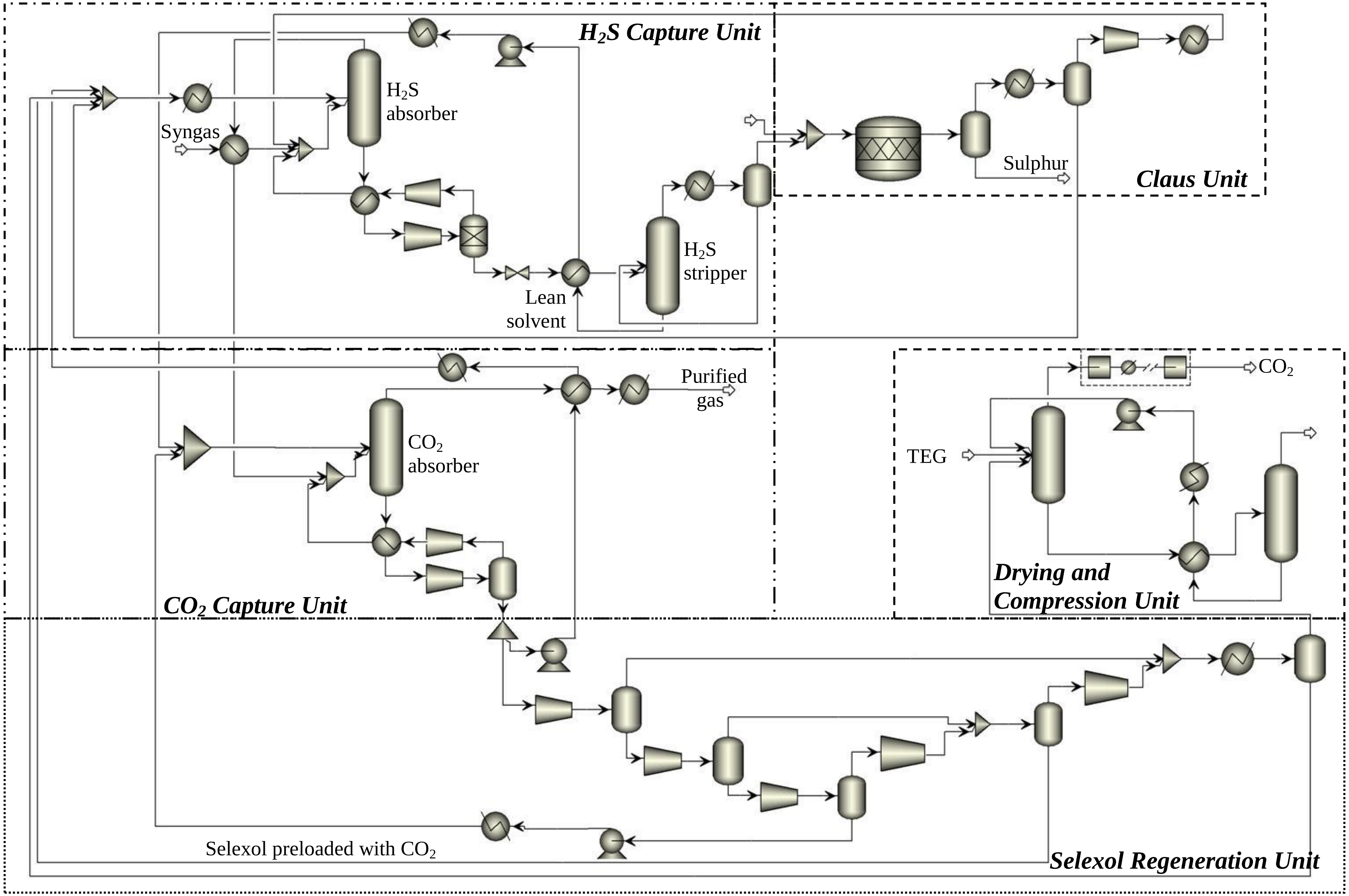


Figure 6.1. *Flowsheet for pre – combustion H_2S and CO_2 capture using Selexol®*

The AGR simulation results, regarding the hydrogen sulfide and carbon dioxide capture rates and energy related consumptions (ancillary power consumption, heating and cooling duties) using various solvents, are summarized in Table 6.3.

Table 6.3. *Energy related consumptions for AGR section*

Solvent	CO_2 capture rate [%]	H_2S capture rate [%]	Power duty [MW_e]	Cooling agent duty [MW_{th}]	Heating agent duty [MW_{th}]
Selexol®	91.44	95.96	14.12	6.81	34.05
Rectisol®	90.63	95.13	14.12	8.24	35.49
Purisol®	91.18	92.14	22.84	94.43	103.21
MDEA	92.41	96.63	8.93	210.29	369.68

A capture rate of around 90 % in case of CO_2 and around 95 % in case of H_2S in most of the cases was obtained, as it can be noticed from Table 6.3. Due to the fact that the IGCC power plant studied in this work uses a mixture of coal and biomass as fuel, the fossil carbon capture rate of the plant is higher than 90 %. For plant concept evaluated in this study, 88 % of the feedstock total carbon is coming from coal (fossil source) and 12 % from biomass (renewable source, non – fossil). Also from Table 6.3, it can be seen that the lowest consumption in all three energy – related ancillaries for carbon dioxide capture seems to be for the physical solvent Selexol®.

Having the results from Table 6.3 and using the equations below (Eqs 6.4 – 6.6), the technical coefficients for AGR removal were calculated and summarized in Table 6.4.

$$Power\ consumption\ (MW_e) = \left(\sum\left(Power_{pump}\right) + \sum\left(Power_{compressor}\right) + \sum\left(Power_{engine\ trbine}\right)\right)(MW_e)$$

Eq. 6.1

$$Heating\ agent\ consumption\ (MW_{th}) = \sum(Reboiler\ heating\ duty)\ (MW_{th}) \qquad \text{Eq. 6.2}$$

$$Cooling\ agent\ consumption\ (MW_{th})\ =\ \sum(Cooling\ duty)\ (MW_{th}) \qquad \text{Eq. 6.3}$$

$$Specific\ power\ consumption\ (MW_e h/kg) = \frac{Power\ consumption\ (MW_e)}{Final\ captured\ CO_2\ mass\ flow\ (kg/h)} \qquad \text{Eq. 6.4}$$

$$\text{Specific heating consumption } (MW_{th}h/kg) = \frac{\text{Heating agent consumption } (MW_{th})}{\text{Final captured } CO_2 \text{ mass flow (kg/h)}} \qquad \text{Eq. 6.5}$$

$$\text{Specific cooling consumption } (MW_{th}h/kg) = \frac{\text{Cooling agent consumption } (MW_{th})}{\text{Final captured } CO_2 \text{ mass flow (kg/h)}} \qquad \text{Eq. 6.6}$$

Table 6.4. *Technical coefficients for CO_2 capture by pre – combustion technology*

Solvent	Specific power consumption [MJ/kg$_{CO2}$]	Specific cooling consumption [MJ/kg$_{CO2}$]	Specific heating consumption [MJ/kg$_{CO2}$]
Selexol®	0.13	0.06	0.33
Rectisol®	0.14	0.08	0.35
Purisol®	0.22	0.93	1.01
MDEA	0.09	2.11	3.70

Table 6.4 shows that the best value in all three energy – related technical coefficients for carbon dioxide absorption are obtained for the physical solvent Selexol®. Selexol's vapor pressure is relatively low in normal process conditions. In comparison with the other physical solvent investigated that do require special recovery methods in order to prevent high solvent losses (eq. Rectisol®, who need deep refrigeration), Selexol® did not require special recovery methods. This implies that the overall energy consumption should be lower in the case of using Selexol® than in all the other physical solvent cases. Compared to chemical solvents (aklanolamines), Selexol® requires far less heat for regeneration due to the lack of chemical reaction resulting in much lower energy consumption. Other solvent comparisons can be found in the literature. In a technical report Doctor et al (Doctor et al., 1994) compared Selexol® and Rectisol® processes for an IGCC application and found that Selexol® process is less costly than Rectisol® process for fuel – cycle CO_2 sequestration. Burr and Lyddon (Burr and Lyddon, 2008) compared Selexol®, Purisol®, Rectisol® and Fluor Solvent and found that Selexol® has the advantage in applications involving both H_2S and CO_2 removal. They also found that all of the physical solvents can be used successfully for bulk removal of CO_2.

Having these results, the overall IGCC without and with CCS (pre – combustion carbon dioxide capture, using the best proved solvent Selexol®) plant performance indicators were calculated.

To evaluate the plant performance indicators parameters like cold gas efficiency (CGE), gross and net electrical efficiency (η_{gross} and η_{net}), energy penalty (EP) and specific CO_2 emissions (SE_{CO_2}) were calculated according to the following equations (Eqs 6.7 – 6.11) (Cormos, 2009):

$$CGE = \frac{Syngas\ thermal\ energy\ (MW)}{Feedstock\ thermal\ energy(MW)} \times 100 \qquad \text{Eq. 6.7}$$

$$\eta_{gross} = \frac{Gross\ power\ output\ (MW)}{Feedstock\ thermal\ energy(MW)} \times 100 \qquad \text{Eq. 6.8}$$

$$\eta_{net} = \frac{Net\ power\ output\ (MW)}{Feedstock\ thermal\ energy(MW)} \times 100 \qquad \text{Eq. 6.9}$$

$$EP = Efficiency\ without\ CCS\ (\%) - Efficiency\ without\ CCS\ (\%) \qquad \text{Eq. 6.10}$$

$$SE_{CO_2} = \frac{Emitted\ CO_2 mass\ flow\ [kg/h]}{Net\ power\ generated(MW)} \times 100 \qquad \text{Eq. 6.11}$$

Following modeling and simulation and heat and power integration, the key plant performance indicators for both investigated cases (without CO_2 capture and with pre – combustion CO_2 capture) were calculated. Table 6.5 presents overall IGCC plant performance indicator for evaluated cases.

Table 6.5. *Overall IGCC without and with pre – combustion CO_2 capture plant performance indicators*

Main Plant Data	Units	No capture	Pre –combustion capture
Solvent		-	Selexol®
Coal & sawdust flowrate (a.r.)	[t/h]	161.35	180.45
Coal / Swadust LHV (a.r.)	[MJ/kg]	25.353 / 16.057	
Feedstock thermal energy – LHV (A)	[MW_{th}]	1052.97	1177.66
Thermal energy of the syngas (B)	[MW_{th}]	835.37	934.27
Cold gas efficiency (B/A * 100)	[%]	79.33	79.33
Thermal energy of syngas exit AGR (C)	[MW_{th}]	832.00	834.58
Syngas treatment efficiency (C/B *100)	[%]	99.59	89.32
Gross electric power output (D)	[MW_e]	519.80	529.79
Total ancillary power consumption (E)	[MW_e]	75.08	104.82
Net electric power output (F = D - E)	]MW_e]	444.72	424.97
Gross electrical efficiency (D/A * 100)	[%]	49.36	44.98
Net electrical efficiency (F/A * 100)	[%]	42.23	36.08
Carbon capture rate	[%]	0.00	91.43
CO_2 specific emissions	[kg/MWh]	824.53	79.63

As it can be noticed from Table 6.5 the two investigated IGCC without and with CCS cases generate about 450 – 425 MW net electricity with a net electrical efficiency in range of 42 – 36%. Comparing IGCC scheme without carbon capture with the same technology but with pre – combustion capture using Selexol®, the overall plant energy efficiency penalty of the carbon capture process is about 6.15 %. The main reason of this fact is the significant increase in ancillary power consumption of the AGR system and captured CO_2 drying and compression step for the cases with pre – combustion capture compared with the case without capture. These results match with the reported results from the International Energy Agency (IEA, 2011) (which reports an average energy penalty of 8.2 % for 88 % pre – combustion CO_2 capture from an IGCC plant) and with Singh et al paper (Singh et al., 2011) (which reports a energy penalty of 6.5 % for 90 % pre – combustion carbon dioxide capture from an IGCC plant).

From greenhouse gas emission point of view, the implementation of pre – combustion carbon capture technology for an IGCC scheme is resulting in a substantial reduction of the specific carbon dioxide emission 79.63 kg_{CO_2}MWh for 90 % pre –

combustion capture vs. 824.53 kg_{CO_2}/MWh for the case without capture. The carbon capture rates were calculated considering the total feedstock carbon (coal + sawdust). For evaluated cases (coal to sawdust blending ratio = 80 % : 20 % wt.), 88 % of the feedstock carbon is fossil the rest being renewable. In this case the specific fossil CO_2 emissions are lower.

Chapter 7. Post – Combustion Capture Systems

The flue gas flowrate and compositions which have been used in the studies and other main sub – systems of the carbon dioxide capture plant and their design assumptions used in the mathematical modeling and simulation are listed in Table 7.1.

Table 7.1. *Main design assumptions for post – combustion carbon dioxide capture technology*

Flue gas	Mass flow [t/h]	2927.50
	Temperature [ºC]	40.00
	Pressure [atm]	1.05
	Gas composition	(% vol.)
	CO_2	8.40
	H_2O	4.52
	O_2	12.05
	N_2	74.13
	Ar	0.90
	SO_2	0.00
	NO_2	0.00
Absorption column	Solvent feed temperature [ºC]	40.00
	Solvent feed pressure [atm]	1.05
	Solvent feed concentration [wt. %]	≤ 30-50%
Heat exchangers	Minimum temperature difference [ºC]	10.00
Desorption column	Feed temperature [ºC]	95.00-115.00
	Pressure profile [atm]	2.00
	Regeneration temperature [ºC]	120
CO_2 compression	Delivery pressure [bar]	122.00
	Compressor efficiency [%]	85.00
CO_2 drying	Solvent	TEG

The developed mathematical model for carbon dioxide absorption and desorption was applied to the following aqueous alkanolamine systems (all below concentrations are reported in mass percentages) (Padurean et al., 2011):

1. Case 1: 30% MEA
2. Case 2: 30% DEA
3. Case 3: 50% MDEA
4. Case 4: 30% AMP
5. Case 5a: 10% MEA + 20% DEA
6. Case 5b: 20% MEA + 10% DEA
7. Case 6a: 10% MEA + 20% AMP
8. Case 6b: 20% MEA + 10% AMP
9. Case 7a: 10% DEA + 20% AMP
10. Case 7b: 20% DEA + 10% AMP
11. Case 8a: 10% MDEA + 20% AMP
12. Case 8b: 20% MDEA + 10% AMP
13. Case 9a: 10% MDEA + 20% MEA
14. Case 9b: 20% MDEA + 10% MEA
15. Case 10a: 10% DEA + 20% MDEA
16. Case 10b: 20% DEA + 10% MDEA

The main unit operation blocks (absorption and desorption column) used in the rate – based alkanolamine model are described in Table 7.2 and a schematic diagram of the equipment used in this work is shown in Figure 7.1.

Table 7.2. *Aspen Plus main unit operation blocks used in the rate – based amine model*

Unit operation	Aspen Plus Block	Specifications
Absorber	RadFac	Column model: Rate – based Number of stages: 20 Column diameter: 2 m Number of sections: 4 Top stage pressure: 1.05 bar Packed type: IMTP Packed Dimension: 3 IN or 75 mm Section packed height: 5 m Mass transfer coefficient method: Onda et al., (1968) Heat transfer coefficient method: Chilton and Colburn Interfacial area method: Onda et al., (1968) Flow model: Countercurrent Holdup: 0.003 m^3
Desorber	RadFac	Column model: Rate – based Number of stages: 20 Column diameter: 2 m Number of sections: 4 Top stage pressure: 2 bar Kettle reboiler Ratio of liquid bottom flow rate to feed flow rate: 0.965 Packed type: FLEXIPAC Packed Dimension: 2 Y or 225 m^2/m^3 Section packed height: 5 m Mass transfer coefficient method: Bravo et al., (1985) Heat transfer coefficient method: Chilton and Colburn Interfacial area method: Bravo et al., (1985) Flow model: Mixed Holdup: 0.003 m^3

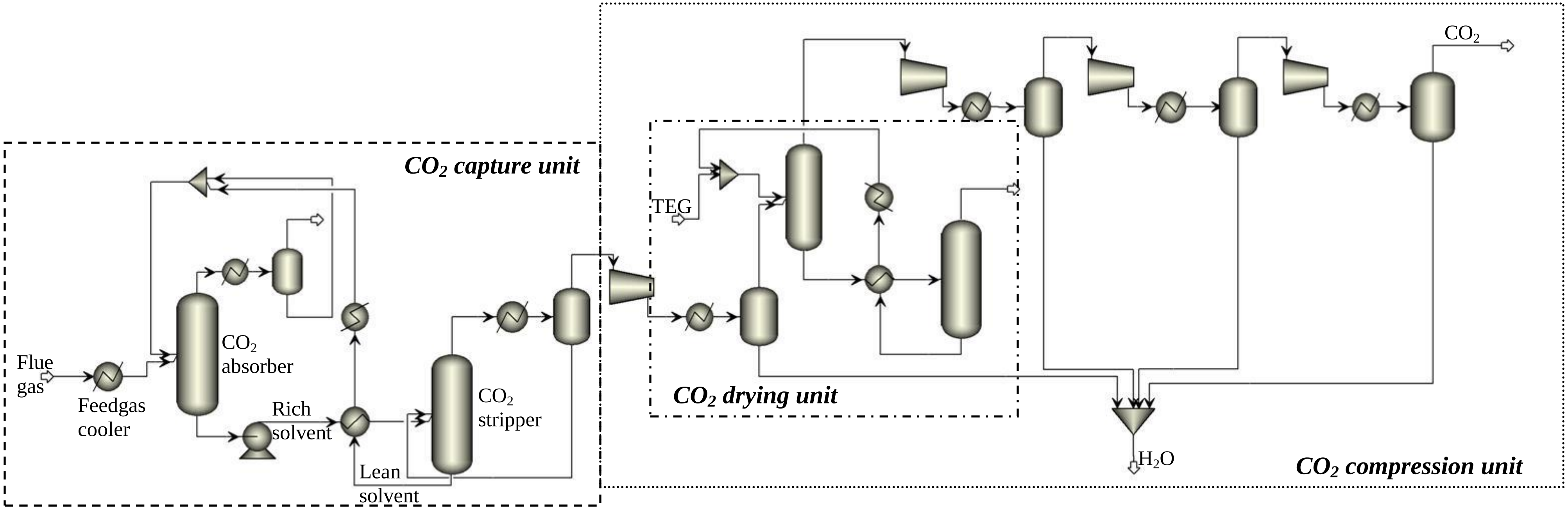


Figure 7.1. *Flowsheet for post – combustion CO_2 capture using alkanolamine*

The CO_2 post – combustion capture technology simulation results, regarding the carbon dioxide capture rates, solution viscosity and energy related consumptions (ancillary power consumption, heating and cooling duties) using various alkanolamines, are presented in Table 7.3.

Table 7.3. *CO_2 post – combustion capture simulation results*

Solvent	CO_2 capture rate [%]	Solution viscosity [cP]	Power duty [MW_e]	Heating agent duty [MW_{th}]	Cooling agent duty [MW_{th}]
Case 1	89.31	0.80	0.17	297.81	291.61
Case 2	93.40	0.89	0.27	310.78	292.91
Case 3	89.31	1.02	0.47	344.30	336.17
Case 4	93.815	2.19	0.17	268.90	242.88
Case 5a	90.08	0.85	0.27	323.26	313.42
Case 5b	98.84	0.83	0.27	372.54	346.30
Case 6a	90.51	1.56	0.16	289.77	260.58
Case 6b	96.24	1.12	0.16	292.45	266.79
Case 7a	91.11	1.51	0.18	262.28	234.10
Case 7b	95.39	1.16	0.28	324.21	302.27
Case 8a	97.84	1.44	0.26	297.99	268.50
Case 8b	90.55	1.06	0.26	282.31	250.77
Case 9a	92.57	0.79	0.21	309.52	280.26
Case 9b	90.40	0.78	0.30	340.17	310.61
Case 10a	91.39	0.81	0.33	323.11	293.61
Case 10b	95.85	0.83	0.28	301.89	269.42

A capture rate of around 90 % in most alkanolamines was obtained, as it can be noticed from Table 7.3. This capture rate was calculated reporting the final mass flow of captured CO_2 to the initial mass flow CO_2. Having the results from Table 7.3 and using the equations described in previous subchapter (Eqs. 6.4 – 6.6), the technical coefficients for CO_2 absorption in alkanolamines solution were calculated. (see Figure 7.2).

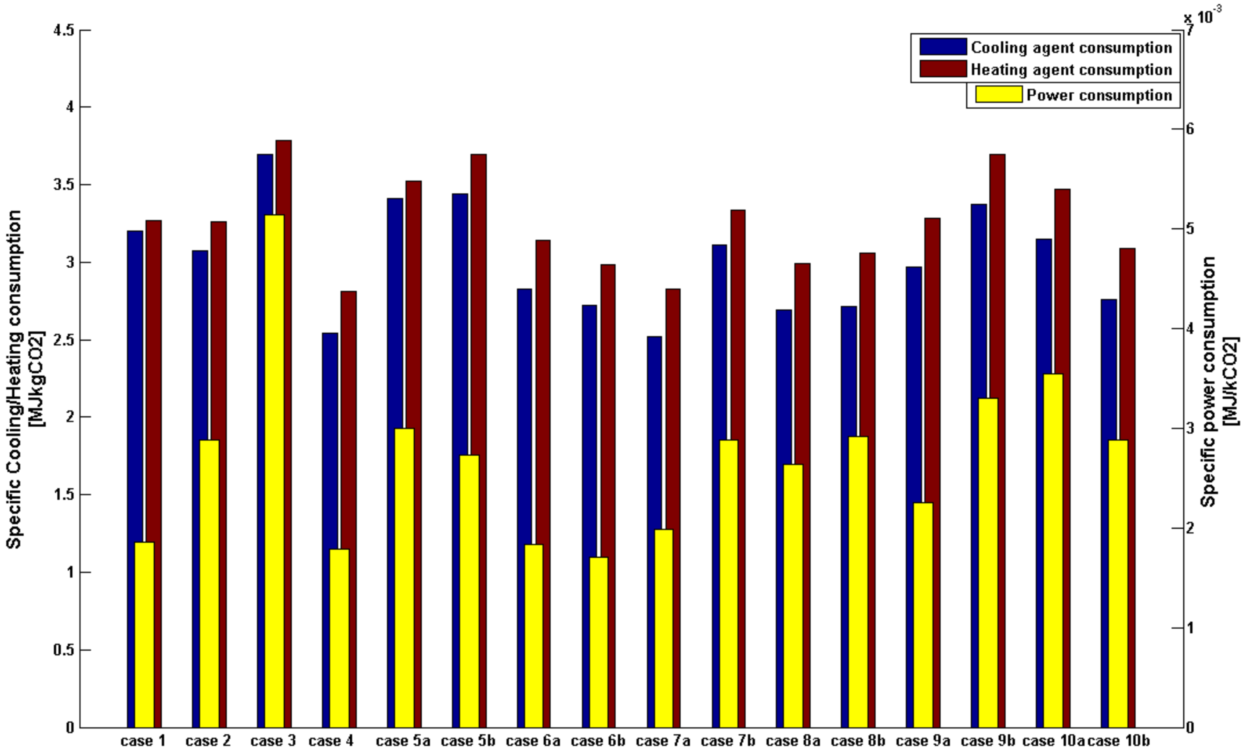


Figure 7.2. *Technical coefficients for CO_2 absorption in various alkanolamines solutions*

Figure 7.2 shows that the best value in all three energy – related technical coefficients for carbon dioxide absorption seems to be the case 1 (primary alkanolamine MEA) and the case 4 (sterically alkanolamine AMP) and their corresponding mixture cases 6a (10% MEA + 20% AMP) and 6b (20% MEA + 10% AMP).

Having the results from Table 7.3, the overall IGCC without and with CCS (post – combustion carbon dioxide capture, using the best proved solvent primary alkanolamine MEA) plant performance indicators were calculated. It must be mentioned here that the case without CCS (used for comparison purposes) uses Selexol® as AGR solvent to capture H_2S from the syngas stream before being sent to the gas turbine for power generation.

To evaluate the plant performance indicators parameters like cold gas efficiency (CGE), gross and net electrical efficiency (η_{gross} and η_{net}), energy penalty (EP) and specific CO_2 emissions (SE_{CO_2}) were calculated according to the following equations (Eqs 6.7 – 6.11), (see Chapter 6).

Table 7.4 presents overall IGCC plant performance indicator of the investigated cases without CO_2 capture and with post – combustion CO_2 capture using MEA chemical solvent.

Table 7.4. *Overall IGCC without and with post – combustion CO_2 capture plant performance indicators*

Main Plant Data	Units	IGCC No Capture	IGCC Post-combustion
Solvent		-	MEA
Coal & sawdust flowrate (a.r.)	[t/h]	161.35	161.35
Coal / Swadust LHV (a.r.)	[MJ/kg]	25.353 / 16.057	
Feedstock thermal energy – LHV (A)	[MW_{th}]	1052.97	1052.97
Thermal energy of the syngas (B)	[MW_{th}]	835.37	835.37
Cold gas efficiency (B/A * 100)	[%]	79.33	79.33
Thermal energy of syngas exit AGR (C)	[MW_{th}]	832.00	832.00
Syngas treatment efficiency (C/B *100)	[%]	99.59	99.59
Gross electric power output (D)	[MW_e]	519.80	460.35
Total ancillary power consumption (E)	[MW_e]	75.08	101.11
Net electric power output (F = D - E)	[MW_e	444.72	359.24
Gross electrical efficiency (D/A * 100)	[%]	49.36	43.72
Net electrical efficiency (F/A * 100)	[%]	42.23	34.11
Carbon capture rate	[%]	0.00	90.88
CO_2 specific emissions	[kg/MWh]	824.53	95.44

As can be noticed from the Table 7.4, comparing IGCC scheme without carbon capture with the same technology but with post – combustion capture using MEA, the penalty in overall plant energy efficiency of the carbon capture process is about 8.12 %. The main reason of this fact is the significant increase in ancillary power consumption of the AGR system and captured CO_2 drying and compression step for IGCC with CCS case compared with IGCC without CCS case (in this case AGR system only separate the hydrogen sulphide form the syngas).

From greenhouse gas emissions point of view, the implementation of carbon capture technology for an IGCC scheme is resulting in a substantial reduction of the specific carbon dioxide emission (95.44 kg_{CO_2}/MWh for post – combustion capture vs. 824.53 kg_{CO_2}/MWh for the case without capture). IGCC technology has also other important benefits from environmental point of view: very low SO_x and NO_x emissions, possibility to process lower grade coals which are difficult to handle by conventional steam plant (see Table 7.1).

Chapter 8. Chemical – Looping Combustion Systems

In chemical looping with solid fuels, the fuel can be directly introduced into the fuel reactor of gasified in a primary, separate step, in which case the second step becomes CLC with gaseous fuels. The chemical looping combustor used in this present study is design for direct fuel introduction.

A proposal for an appropriate and promising reactor design has been made by Pröll and Hofbauer (see Figure 3.3) at Vienna University of Technology. This multistage circulating fluidized bed riser approach is based on the already successfully applied dual circulating fluidized bed (DCFB) system for gaseous fuel CLC (Pröll et al. 2009). Figure 8.1 illustrated the existing cold flow model of a DCFB pilot plant equipped with three flow obstacles and operated with air and bronze powder.

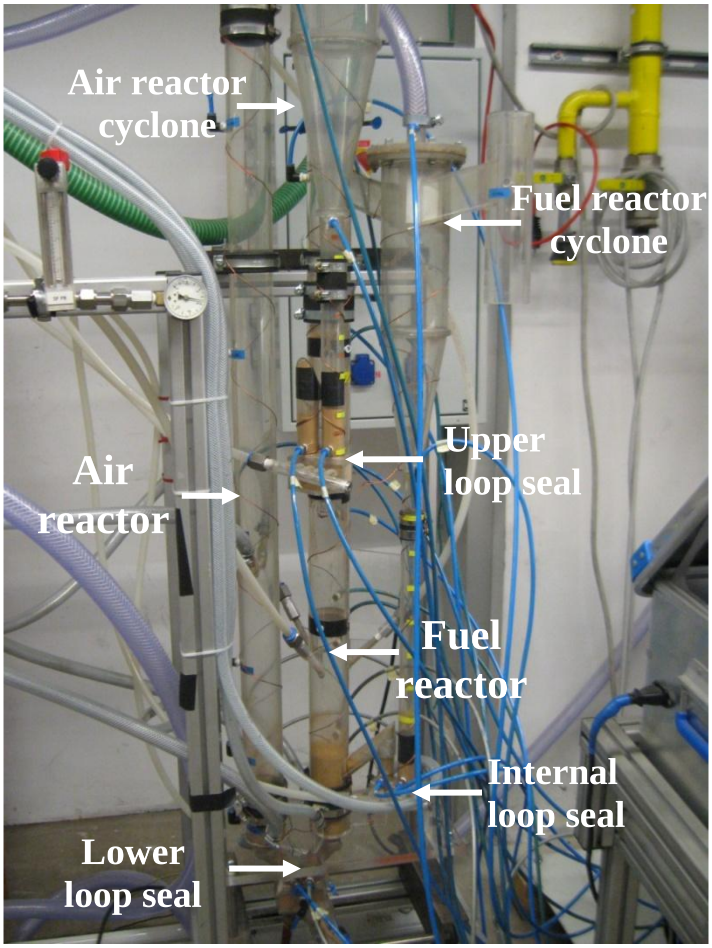


Figure 8.1. *TUV cold flow model for solid fuel CLC*

In order to be able to discuss the behavior of the new implemented reactor system, a reference case is defined. From this reference case, parameter variations are performed. Table 8.1 summarizes the main operating parameters for the FR.

Table 8.1. *Fuel reactor design specifications*

Parameter	Value
Oxygen Carrier	Ilmenite
Fuel type	Biomass
Fuel thermal power	1 MW
Split condition number	
φ_{OC}	0.18
φ_{char}	0.25
φ_{ash}	0.4
Solid residence time	7-20 s
LLS temperature	950 ºC
Air-fuel ratio	1.2

Table 8.2 presents few preliminary results of IPSEpro modeling on solid fuel CLC concept.

Table 8.2. *CLC simulations results*

Parameter	Value	Unit
CO_2 separation efficiency	91.20	[%]
Char loss	23.39	[%]
ILS ash content	37.60	[wt%]
LLS ash content	15.50	[wt%]
ULS Temperature	1017	[ºC]

The LLS temperature of 950 °C leads to an AR temperature of 1015 °C. The calculated temperature profile can be seen in Figure 8.2. The decrease between zone 5 and 6 is due to the decompositions of the fuel. 25% of the char is lost to the AR resulting in a CO_2 separation efficiency of 92 %. Regarding the segregation of ash, in the LLS (bottom of FR) the ash content is about 13 wt% and where the ash is leaving the reactor its content is about 37%.

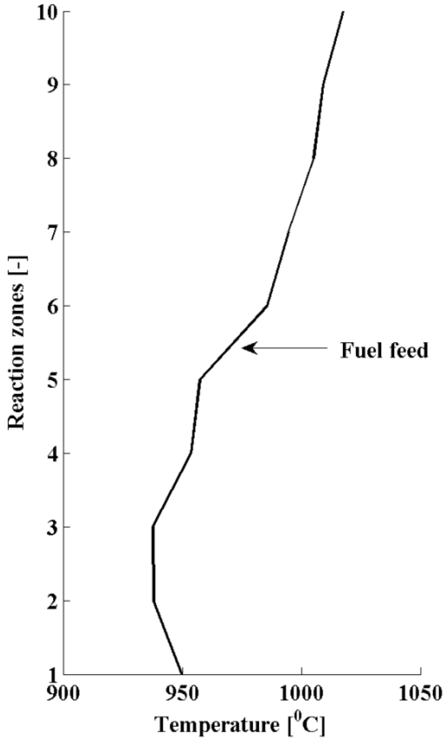


Figure 8.2. *Fuel reactor temperature profile*

A sensitivity analysis was studied to observe the effect of the fuel reactor temperature variation on the CO_2 separation efficiency. In the simulation analysis model, the FR temperature was varied from 900 to 1000 ºC. All other operating conditions remained the same as the base case model. The results from this sensitivity analysis are illustrated in Figure 8.3.

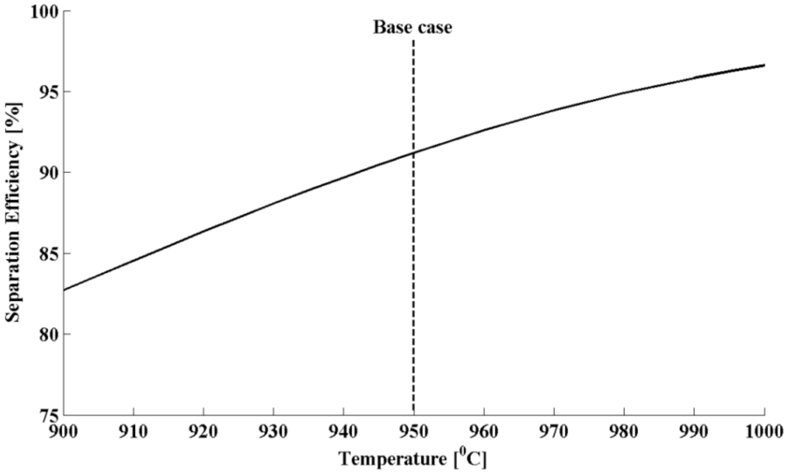


Figure 8.3. *Fuel reactor temperature sensitivity analysis*

As it can be seen from Figure 8.3, at a higher temperature higher char conversion and lower char loss to the AR is obtained which leads to a higher CO_2 separation efficiency.

Another sensitivity analysis was conducted to observe the effect of ash split condition number Φ_{ash} (at 2 different renewable rate of OC) variation on the ash content on the ILS and LLS. In the simulation analysis model, the split condition number Φ_{ash} was varied from 0.2 to 0.6. All other operating conditions remained the same as the base case model (see Subchapters **Error! Reference source not found.**). The results from this sensitivity analysis are illustrated in Figure 8.4.

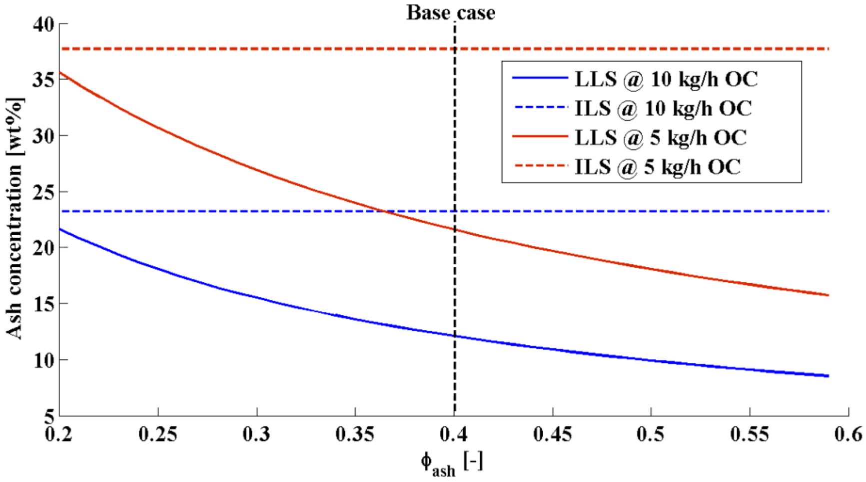


Figure 8.4. *FR ash content sensitivity analysis*

As it can be noticed from Figure 8.4 the ash content in the ILS depends only on the OC renewable rate and the ash content in the LLS, the one who goes to the AR, depends on this split condition number Φ_{ash}. As higher the split condition number Φ_{ash} as lower the ash content through the AR.

In order to describe the process talking place in the fuel rector, it is also important to describe the phase flow inside the reactor. The so – called residence time distribution (RTD) of fluid elements is used to assess the mixing behavior of a phase passing the reactor. A mathematical model was used to describe the dynamic behavior of the fuel reactor from the TUV cold flow model design for the solid fuel CLC.

The inputs into the model are the reactor geometry, particles proprieties, solids mass flows and the total pressure drop across the reactor. The bed material is assumed to be represented by spherical particles of an average particle size. The inputs used in the reactor model can be seen in Table 8.3 (Guío-Pérez et al., 2011; Schmid et al., 2011).

Table 8.3. *Fuel reactor Matlab model inputs*

Parameter	Value	Unit
Reactor geometry	$H_{total} = 0.7$	m
	$D = 0.054$	m
Global circulation rate	$m_{ILS} = 177.77$	kg/h
Particle properties	$\rho_p = 8730$	kg/m^3
	$d_p = 68$	μm
	$\Phi = 1$	-
Operating pressure	$p=1.013$	bar
Volume fraction solids	$\varepsilon_S = 0.05$	-
Segregation term	$\varphi = 0.1802$	-

Three main cases were investigates:

Case 1: FR with one RZ (no ring type flow obstacles)

Case 2: FR with 3 RZ (2 ring type flow obstacles corresponding to the TUV cold flow model for the solid fuel CLC)

Case 3: FR with 10 RZ (corresponding to IPSE model)

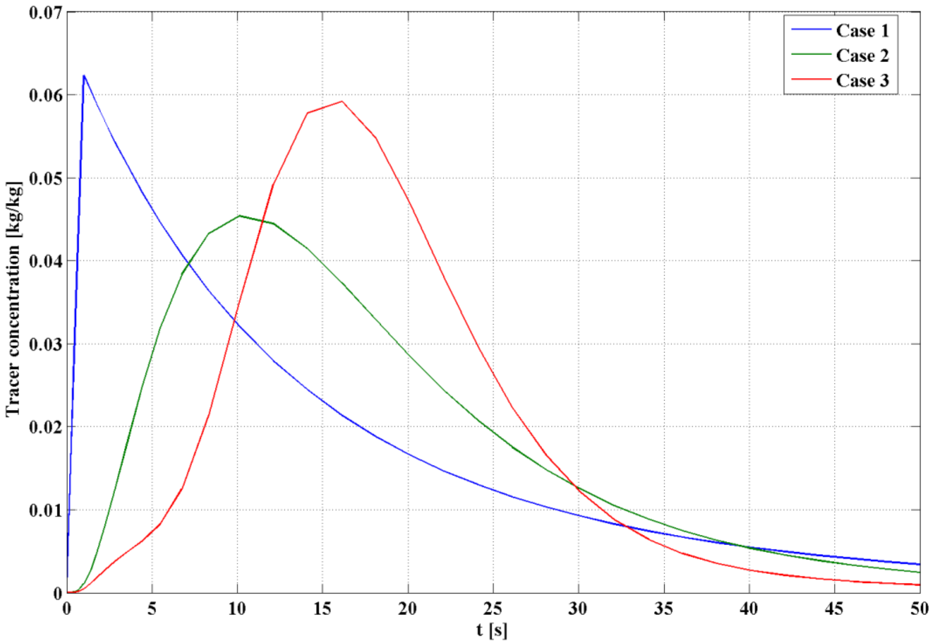


Figure 8.5. *The residence time distribution of the investigated cases*

As it can be seen in Table 8.4, since the same quantity of the solid bed material is used in all the previous mention cases the mean passing time through reactors is the same in all the investigated cases. What it will change it is only the signal shape (the signal response) (see Figure 8.13).

Table 8.4. *Matlab model outputs*

Parameter	Value	Unit
$\tau_{\text{case 1}}$	19.6	s
$\tau_{\text{case 2}}$	19.4	s
$\tau_{\text{case 3}}$	19.3	s

Part IV – Comparison and Recommendations

Chapter 9. Comparative Techno – Economic Assessment

9.1. Performance in Base Case Scenario

Because of growing worldwide interest in CO_2 capture and storage as a potential option for climate change mitigation, the expected future cost of CCS technologies also is of significant interest. The present chapter presents a comparison of the current costs of CO_2 capture technologies in order to assess the relative rankings of the different technologies anticipated to meet the most of the future demand for electricity.

An economic analysis and comparison will be carried on only for pre – combustion and post – combustion CO_2 capture technologies because these two are the most common and commercially mature technologies today.

The comparison is undertaken on an equivalent basis using cost metrics such as levelised cost of electricity (LCOE), the cost of CO_2 avoided and the cost of CO_2 captured. The levelised cost of electricity is a metric used to represent the average cost generating electricity for the duration of the power plant's economic lifetime. Table 9.1 and Table 9.2 present overall plant capital costs estimation and operating and maintenance (O&M) costs estimation of analyzed case studied (IGCC with no carbon capture, IGCC with pre – combustion CO_2 capture process using Selexol® as solvent and post – combustion CO_2 capture process using MEA as solvent).

Table 9.1. *Overall IGCC plant capital cost estimation*

Main Plant Data	Unit	No CO_2 capture	Pre-Combustion	Post-Combustion
Solvent		-	Selexol®	MEA
Gasification Island	t_{coal}/h	169.53	185.40	169.53
Power Island	$MW_{el\ gross}$	243.60	247.11	222.39
Total Installed Cost (excl.contingency)	MM €	761.00	932.72	1036.08
Total Investment Cost	MM €	913.26	1119.26	1243.30
Gross Power Production	$MW_{el\ (gross)}$	519.80	529.79	460.35
Net Power Production	$MW_{el\ (net)}$	444.72	424.97	359.24
Total Investment Cost per kW_{el} (gross)	€/$kW_{el\ (gross)}$	1756.95	2112.65	2700.77
Total Investment Cost per kW_{el} (net)	€/$kW_{el\ (net)}$	2053.57	2633.74	3460.92

Table 9.2. *Operating and Maintenance (O&M) overall plant costs estimation*

Fixed O&M	Without capture		Pre-Combustion		Post-Combustion	
	(MM€/year)	(10^3€/kWh)	(MM€/year)	(10^3€/kWh)	(MM€/year)	(10^3€/kWh)
Annual Maintenance Cost	27.07	8.11	31.47	9.87	32.98	12.24
Direct Labor Cost	4.76	1.42	5.60	1.75	5.60	2.07
Administrative, Support & Overhead Cost	1.43	0.42	1.68	0.52	1.68	0.62
Total	33.26	9.97	38.75	12.16	40.26	14.94
Variable O&M	Without capture		Pre-Combustion		Post-Combustion	
	(MM€/year)	(10^3€/kWh)	(MM€/year)	(10^3€/kWh)	(MM€/year)	(10^3€/kWh)
Fuel	58.60	17.56	65.53	20.56	58.60	21.74
Auxiliary Fuel	2.13	0.63	2.13	0.66	2.13	0.79
Make Up Water	0.17	0.04	0.17	0.05	0.17	0.05
Catalysts	0.50	0.15	1.50	0.47	1.50	0.55
Solvents	0.00	0.00	0.96	0.30	0.99	0.36
Chemicals	1.69	0.51	1.70	0.53	1.73	0.64
Waste Disposal	3.09	0.92	3.51	1.10	3.48	1.29
Total	66.17	19.84	75.49	23.69	68.59	25.46

After extracting the underlying capital and operating costs that reflect the performance characteristics of each technology, levelised costs of electricity (LCOE) is calculated. The best methods of assessing the profitability of all the investigated cases (IGCC with no carbon capture, IGCC with pre – combustion CO_2 capture process using Selexol® as solvent and post combustion CO_2 capture process using MEA as solvent) are based on projections of the cash flows during the plant life. Figure 9.1 shows the cash flow curves for these investigated processes.

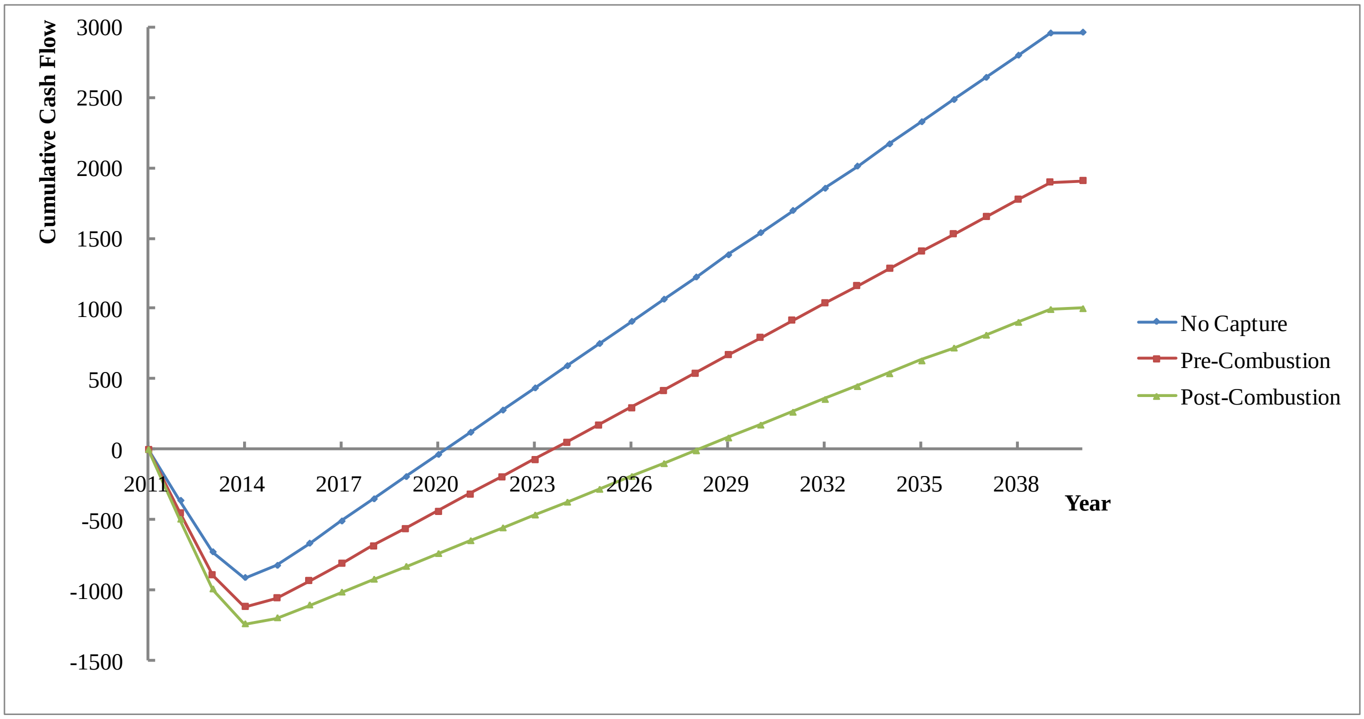


Figure 9.1. *Cash flow curves for IGCC plant without and with (pre – and post – combustion) CO_2 capture*

The figure plots the NPV as a function of time from the present day through 2021 in the case of the plant without CCS, 2024 in the case of pre – combustion capture process and in 2029 in the case of post – combustion capture process, when a retrofit is assume to take place, through to 2040 when the plant has been operational. The curves shown in Figure 9.1 illustrate similar features. The cost of construction is extend over a number of years (7 years for the plant without CCS scenario, 10 years for the plant with pre – combustion capture technology scenario and 15 years for the plant with post –combustion capture technology scenario) leading to a significantly negative initial NPV, and then as the plant comes online and starts to generate electricity, the NPV rises according to the amount of power produced and the operational costs of the plant.

Additional to the levelised cost of electricity, there are other metrics used for comparing CCS technologies such as cost per tonne of CO_2 avoided or emitted relative to the plant without CCS and cost of CO_2 captured (IPCC, 2005).

Table 9.3 shows the electricity production costs, costs of CO_2 avoided and captured, for all the investigated cases IGCC without CO_2 capture and with CO_2 capture (pre – and post – combustion).

Table 9.3. *Summary results of the economic assessment of CCS technologies*

Description	Units	Without Capture	Pre-combustion	Post-combustion
Solvent	-	-	Selexol®	MEA
LCOE	¢/kWh	5.92	7.61	9.25
Cost of CO_2 Avoided	€/t_{CO_2}	-	21.40	46.11
Cost of CO_2 Captured	€/t_{CO_2}	-	19.58	37.24

9.2. Variation of Relevant Boundary Conditions

The present chapter reports an investigation of how does all these plant performance parameters, mentioned above, changes if the CO_2 capture performance changes. The bellow cases were investigated and compared:

Case A: IGCC with no carbon capture

Case B: IGCC with 70% carbon dioxide pre – combustion capture using Selexol®

Case C: IGCC with 80% carbon dioxide pre – combustion capture using Selexol®

Case D: IGCC with 90% carbon dioxide pre – combustion capture using Selexol®

Case E: IGCC with 70% carbon dioxide post – combustion capture using MEA

Case F: IGCC with 80% carbon dioxide post – combustion capture using MEA

Case G: IGCC with 90% carbon dioxide post – combustion capture using MEA

Comparing these three post – combustion IGCC capture cases (Case E, Case F and Case G) with the pre – combustion IGCC capture cases (Case B, Case C and Case D) can be concluded that net electrical efficiencies are lower in the case of using post – combustion capture technique. This fact can be explained that in the case of pre – combustion less heat for regeneration is required (due to the lack of chemical reaction) resulting in much lower energy consumption than in the case of using post – combustion capture technique for capturing CO_2. If the heat consumption would decrease, no steam extraction from the ST to the capture sub – system would be necessary and the ST output would increase. This would increase the net plant efficiency when capturing CO_2 by pre – combustion process then by post – combustion process. The decrease in energy efficiencies for IGCC plants with CCS can be observed from Figure 9.2.

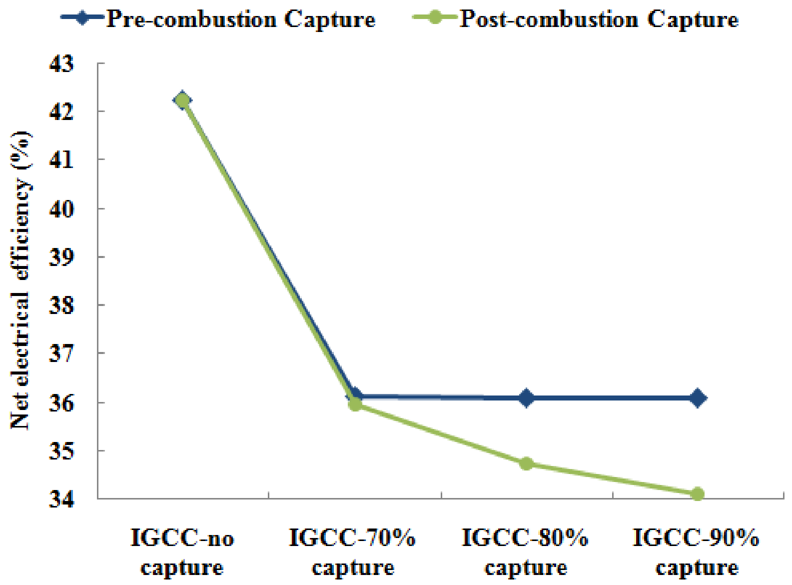


Figure 9.2. *Energy efficiencies for the investigated IGCC plant cases*

Also. comparing these three post – combustion IGCC capture cases (Case E, Case F, Case G) with the pre – combustion IGCC capture cases (Case B, Case C, Case D) can be observed that capital investment costs are much higher in the case of using post – combustion capture technique. The incremental cost due to CO_2 capture for the CCS IGCC investigated cases can be observed as well in Figure 9.3. Almost published studies give competitive position of IGCC pre – combustion relatively to post-combustion applied for pulverized coal technology (IPCC, 20005; Global CCS Institute, 2011; Zero emission platform, 2011; NETL 2011). The originality of this thesis is that it investigates post – combustion capture for IGCC, which has not been extensively studied to date, in comparison with pre – combustion capture. When comparing IGCC without CCS power generation technology with conventional Pulverized Coal (PC) without CCS, the favorite in term of capital cost investments are the PC plants (1300-1500 €/kW net vs. 1900-2100 €/kW net (Cormos 2010; IEA, 2007; NETL, 2011)) but the introduction of CCS stage bring very close the capital investments (in the range of 2400 – 2600 €/kW net for both technologies).

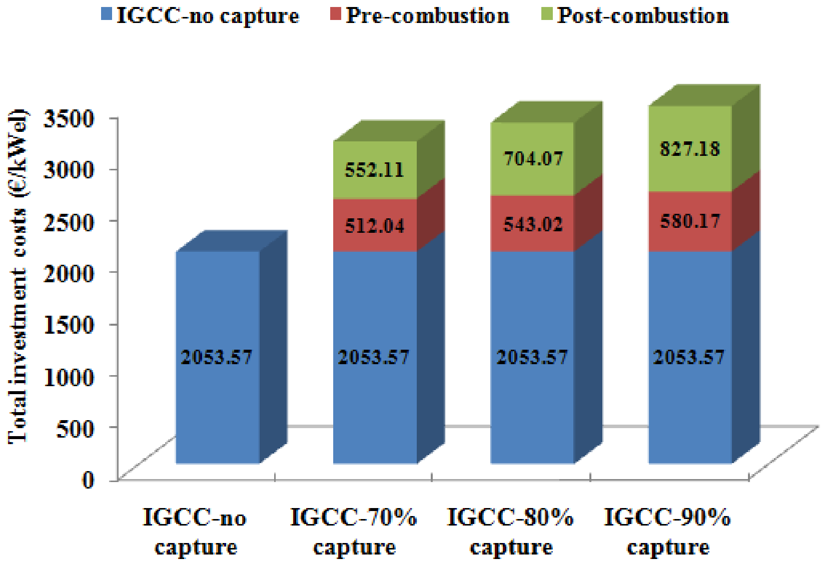


Figure 9.3. *The incremental cost due to pre – and post – combustion CO_2 capture*

Figure 9.4 illustrates the CO_2 capture and avoided costs for all the investigated cases (IGCC with different percentage of CO_2 pre and post – combustion capture).

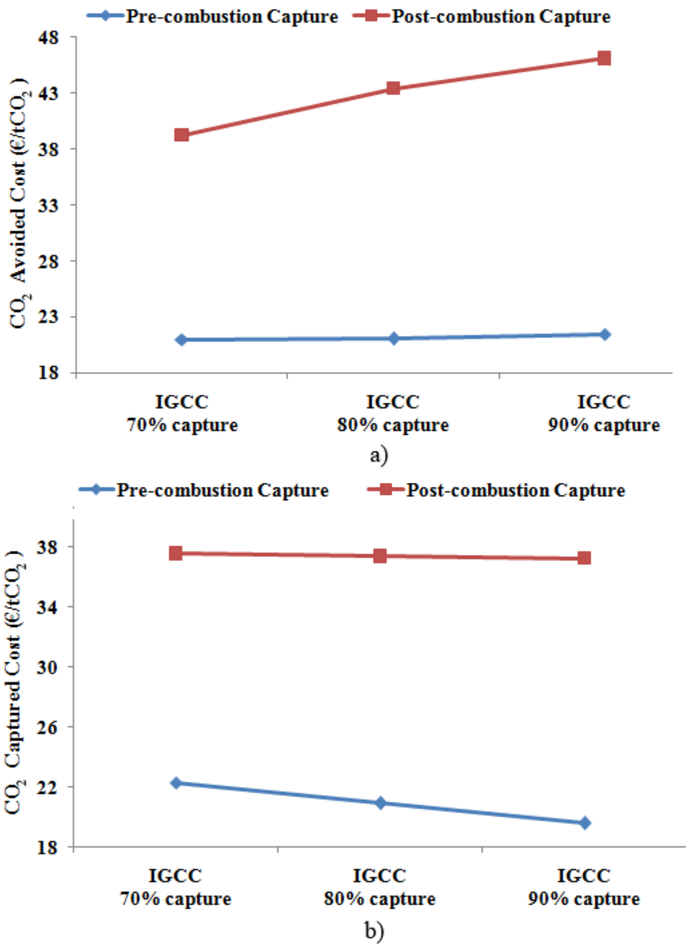


Figure 9.4. *CO_2 avoided (a) and captured (b) costs for the IGCC CCS investigated cases*

CO_2 avoided costs and CO_2 captured costs are important and useful metrics for comparing economics of a specific CO_2 capture process against alternative CO_2 capture technologies. Comparing investigated technologies: post – combustion IGCC capture cases (Case E, Case F, Case G) with the pre – combustion IGCC capture cases (Case B, Case C, Case D) can be observed that both CO_2 captured and CO_2 avoided costs are much higher in the case of using post – combustion capture technique (by a factor of 1.87 higher for 70% capture, by a factor of 2.06 higher for 80% capture and by a factor of 2.15 higher for 90% capture for avoided costs and by a factor of 1.68 higher for 70% capture, by a factor of 1.83 for 80% capture and by a factor of 1.90 for 90% capture for captured costs). These results match with the reported results from the International Energy Agency report (IEA, 2011) (which reports that CO_2 avoided costs vary between 40 $\$/t_{CO_2}$ and 74 $\$/t_{CO_2}$ for case studies across OECD regions) and with National Energy Technology Laboratory recent report (NETL, 2012) (which reports a value of 83.06 $\$/t_{CO_2}$ for an IGCC power plant which uses as fuel 76% coal and 26% biomass – switchgrass).

Chapter 10. General conclusions

Integration of carbon dioxide capture technologies based on gas – liquid process in a complete coal mixed with biomass IGCC power station simulation model has been studied in order to calculate the plant performance parameters, net power output, efficiency, overall CO_2 emissions, capital investment, cost of electricity and CO_2 removal and avoidance costs. The results show that this research got the same order of magnitude as other published references for similar absorption processes, but the resulted efficiency decrease is lower in the present work than compared to others work.

In the case of the pre – combustion CO_2 capture technology four different physical (Selexol®, Rectisol® and Purisol®) and chemical (MDEA) solvents have been investigated and simulations in Aspen Plus® were developed. As main conclusion concerning the evaluated solvents for pre – combustion CO_2 capture is that physical solvent, Selexol® is more energy efficient that the other physical and chemical solvents investigated. Selexol's vapor pressure is relatively low in normal process conditions. In comparison with other physical solvents investigated that do require special recovery methods in order to prevent high solvent losses (eq. Rectisol®, who need deep refrigeration), Selexol® did not require special recovery methods. This implies that the overall energy consumption should be lower in the case of using Selexol® than in all the other physical solvent cases. Compared to chemical solvent MDEA, Selexol® requires less heat for regeneration due to the lack of chemical reaction resulting in much lower energy consumption. A sensitivity analysis was performed for the simulation by varying the Selexol® solvent flow rate, H_2S stripper bottom to feed ratio and hygroscopic solvent (TEG) flow rate in order to study the behavior of different model parameters and to establish dependencies among them.

For the post – combustion CO_2 capture technology, energy – related consumption coefficients (power consumption, heating agent consumption and cooling agent consumption), the environmental impact and the performance of four different alkanolamines (monoethanolamine, diethanolamine, methyldiethanolamine and 2 – amino – 2 – methyl – 1 – propanol) and their corresponding mixtures using Aspen Plus® software were analyzed.

The simulations show that, regarding the hydrodynamic characteristics, viscosity of blended solutions has a lower value than the simple alkanolamine solutions. Accordingly the use of mixed amines is an interesting and promising approach since it may bring about improvement in gas absorption, in solution viscosity and in reducing energy requirement for solvent regeneration. Regarding the energy consumptions, the simulation results show that, the 30% MEA, 30% AMP and their corresponding mixture 10% MEA with 20% AMP and 20% MEA with 10% AMP give the best results in the carbon capture process.

In order to have a final way to decide which technology is the best, an economical evaluation was conducted. The economic analysis and comparison was achieved only for pre – combustion and post – combustion CO_2 capture technologies because these two are the most common and commercially mature technologies today.

Another important part of the present thesis was focused on the investigation of the most innovative and attractive solution for CO_2 capture technology which is chemical looping combustion capture. Based on the already successfully applied dual circulating fluidized bed system for gaseous fuel CLC, a proposal for an appropriate and promising reactor design for direct use of solid fuel has been made. By applying ring – type flow obstacles along the height of a CFB reactor, the gas solid contact is increased and the formation of a core – annulus profile is prohibited. Combining this approach with the DCFB concept, the re – oxidized bed material from the air reactor can enter the fuel reactor close to the top and establish a counter – current flow of the particles and the gas. Additionally, a segregation effect is expected by selectively transporting smaller ash particles to the top of the reactor so that it can be dispose in the internal loop seal. Thus, a relatively small geometrical change may be a key to make dual bed systems significantly more efficient in fuel conversion.

10.1. Author’s contribution

The author’s personal contributions to this present thesis were detailed presented in the third and the fourth part of the thesis. In these parts, two of the most commercially mature CO_2 capture technologies today: post – combustion capture using chemical solvents and pre –

combustion capture using physical and chemical solvents in order to integrate them into the IGCC power plant scheme were assessed and compared. For each investigated technology detailed flowsheet models were developed in chemical engineering software Aspen Plus® which were utilized then in future analysis for energy integration, costing, etc. The optimum operating points for the developed Aspen Plus® CO_2 capture process schemes, characterized by a minimum energy requirement for a given CO_2 removal were also investigated and found. A detailed examination of how the design variables as columns heights, columns packed dimensions, solvent flowrate, stripper temperature and the operating bottom to feed ratio of the stripper affect each other at the level of the whole CO_2 capture process was presented.

A comparison in term of overall plant performance, energy consumption, CO_2 specific emissions, net electric power output, plant efficiency, electricity costs and CO_2 captured and avoided costs of all IGCC based carbon capture mature technologies with conventional IGCC concept without CO_2 was also developed in the present thesis.

Regarding the most innovative and attractive CO_2 capture technology – chemical looping combustion capture, the author’s contribution was to examine the feasibility and the performance of this technology for direct use of solid fuels. For this fact a fuel reactor design (from Vienna University of Technology) was proposed and a comprehensive model for this fuel reactor concept design, based on mass and energy balances was developed using the equation – oriented steady state simulation environment IPSEpro. As an important part of this work, the dynamic behavior of the system was investigated for the cold flow model already existing at TUV using Matlab Simulink engineering plantform.

10.2. List of publications

The present thesis is based on the work published in the following articles:

I. **Anamaria Padurean**, Calin-Cristian Cormos, Paul Serban Agachi, Technico-economical evaluation of post- and pre – combustion carbon dioxide methods applied for an IGCC plant for power generation, *Environmental Engineering and Management Journal*, article in press, Impact factor 1.435

II. **Anamaria Padurean**, Calin-Cristian Cormos, Paul Serban Agachi, Pre-combustion carbon dioxide capture by gas – liquid absorption for Integrated Gasification

Combined Cycle power plants, *International Journal of Greenhouse Gas Control*, 1 – 11, 2012, Impact factor 5.111

III. **Anamaria Padurean**, Calin-Cristian Cormos, Ana-Maria Cormos, Paul Serban Agachi, Multicriterial analysis of post – combustion carbon dioxide capture using alkanolamine, *International Journal of Greenhouse Gas Control*, 676 – 685, 2011, Impact factor 5.111

IV. **Anamaria Padurean**, Calin-Cristian Cormos, Ana-Maria Cormos, Paul Serban Agachi, Technical assessment of CO_2 capture using alkanolamines solutions, *Studia Universitatis Babes – Bolyai, Chemia*, LV,1, 55 – 64, Romania, 2010, Impact factor 0.231

V. Ana-Maria Cormos, Jozsef Gaspar, **Anamaria Padurean**, Modelling and simulation of carbon dioxide absorption in monoethanolamine in packed absorption columns, *Studia Universitatis Babes – Bolyai, Chemia*, LIV, 3, 37 – 48, Romania, 2009, Impact factor 0.231

VI. Stefan Penthor, **Anamaria Padurean**, Johannes Schmid, Tobias Pröll, Paul Serban Agachi, Hermann Hofbauer, Direct solid fuel CLC using biomass, *3rd IEAGHG Network Meeting and Technical Workshop on High Temperature Solid Looping Cycles*, Vienna University of Technology, Vienna 30 – 31 August 2011

VII. Calin-Cristian Cormos, **Anamaria Padurean**, Ana-Maria Cormos, Paul Serban Agachi, Power generation based on coal and low – grade fuels co – gasification with carbon capture and storage, *Clean Coal Conference – CCT2011*, Zaragoza, Spain, 2011

VIII. Calin Cristian Cormos, **Anamaria Padurean**, Paul Serban Agachi, Technical evaluations of carbon capture options for power generation from coal and biomass based on integrated gasification combined cycle scheme, International Conference on Greenhouse Gas Technologies (GHGT-10 – 19 – 23 September 2010 RAI Amsterdam, The Netherlands), *Energy Procedia*, 4, 1861–1868, 2011

IX. Ana-Maria Cormos, Jozsef Gaspar, **Anamaria Padurean**, Calin –Cristian Cormos, Paul Serban Agachi, Techno – economical analysis of carbon dioxide absorption in mono – ethanolamine by mathematical modeling and simulation, *20th European Symposium on computer aided process engineering (ESCAPE – 20)*, 1691 – 1698, 2010

Chapter 11. Selected References

[1] Bravo J.L., Rocha J.A., Fair J.R., Mass transfer in gauze packings, *Hydrocarbon Processing*, 1985, 91-95

[2] Burr B., Lyddon L., A comparison of physical solvents for acid gas removal, Bryan Research and Engineering, Inc, Bryan, Texas, U.S.A, 2008

[3] C.C. Cormos, Conceptual design of typical power plant configurations for the estimation of reference capital costs including material, Report IE/2010/07/23 107058, 2010

[4] Cormos C.C., Decarbonizarea combustibililor fosili solizi prin gazeificare, Presa universitară Clujeană , Cluj Napoca, 2008. (Written in Romanian)

[5] Dargam F C.C, Perz E. W., A decision support system for power plant design, *European Journal of Operational Research*, 109, 1998, 310-320

[6] Doctor R.D., Molburg J.C., Thimmapuram P.R., Berry G.F., Livengood C.D., Gasification combined cycle: carbon dioxide recovery, transport and disposal. Technical Report No ANL/ESD-24, 1994

[7] Global CCS Institute, CO_2 Capture Technologies. Pre Combustion Capture, 2012

[8] Global CCS Institute, Economic assessment of carbon capture and storage technologies, WorleyParsons, 2011

[9] Grace J.R., Contacting modes and behavior classification of gas-solids and other two-phase suspentions, Canadian Journal of Chemical Engineering, 64, 1986

[10] Guío-Pérez, D. C., Marx, K., Pröll, T., Hofbauer, H., Fluid Dynamic effects of ring-type internals in a dual circulating fluidized bed system, *Proceedings of the 10th International Conference on Circulating Fluidized Beds*, Mai 2011, Oregon, USA

[11] Higman C., van der Burg M., Gasification, Second Edition, Elsevier, 2008

[12] IEA Greenhouse Gas R&D Programme (IEA GHG), “Development of Storage Coefficients for CO_2 Storage in Deep Saline Formations”, 2009/13, October 2009

[13] IEA Greenhouse Gas R&D Programme (IEA GHG), “Safety in Carbon Dioxide Capture, Transport and Storage”, 2009/06, June 2009

[14] IEA, International Energy Agency, “World energy outlook”, 2010

[15] IEA, International Energy Agency, “Cost and Performance of Carbon Dioxide Capture from Power Generation”, 2011

[16] IPCC, 2005: Metz, B., Davidson O., de Coninck H. C., Loos M., Meyer L. A. (eds.). IPCC Special Report on Carbon Dioxide Capture and Storage. Prepared by Working Group III of the Intergovernmental Panel on Climate Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 442 pp.

[17] IPCC, 2007, Solomon S., Qin D., Manning M., Chen Z., Marquis M., Averyt K.B., Tignor M., Miller H.L., Fourth Assessment Report of the Intergovernmental Panel on Climate Change: The Physical Science Basis.

[18] IPCC, Climate change 2007: Synthesis Report, Valencia, Spain, 2007

[19] Kohl A., Nielsen R., Gas purification, 5th Edition, Golf Publishing Company, 1997.

[20] Leion, H., Mattisson, T., Lyngfelt, A., Use of ores and industrial products as oxygen carriers in chemical-looping combustion, *Energy and Fuels*, 23, 2009, 2307-2315

[21] Lewis W.K., Gilliland E.R., Sweeney W.P., Gasification of carbon: metal oxides in a fluidized powder bed, *Chemical Engineering Progress*, 47, 1951, 521-256

[22] Linderholm C., Mattisson T., Lyngfelt A., Long-term integrity testing of spray-dried particles in a 10-kW chemical-looping combustor using natural gas as fuel, *Fuel* 88, 2009, 2083-2096

[23] Lyngfelt A., Leckner B., Mattisson T., A fluidized bed combustion process with inherent CO_2 separation, application of chemical lopping combustion, *Chemical Engineering Science*, 56, 2001, 3101-3113

[24] Lyngfelt, A., Oxygen carriers for chemical looping combustion – 4000 h of operational experience, *Oil & Gas Science and Technologies*, 66, 2011, 161-172

[25] NETL, Greenhouse Gas Reduction in the Power Industry Using Domestic Coal and Biomass, Volume 1: IGCC, DOE/NETL-2012/1546, 2012

[26] Onda K., Takeuchi H., Okumoto Y., Mass transfer coefficients between gas and liquid phased in packed columns, *Journal of Chemical Engineering of Japan*, 1968, 1, 56

[27] Perz E., A computer method for thermal power cycle calculation. ASME-Paper IGTI GT-351, 1990

[28] Pröll T., Applied modeling in process engineering and energy technology, Lecture notes, LVA 166.198, 2010

[29] Pröll T., Hofbauer H., A dual fluidized bed system for chemical looping combustion of solid fuels, *Proceedings of the AIChE Annual Meeting* 2010, Salt Lake City, Utah, U.S.A., November 7-12

[30] Pröll T., Mayer K., Bolhà-Nordenkampf J., Kolbitsch P., Mattisson T., Lyngfelt A., Hofbauer H., Natural minerals as oxygen carriers for chemical looping combustion in a dual circulating fluidized bed system, *Energy Procedia*, 1, 2009, 27-34

[31] Pröll, T., Rupanovits, K., Kolbitsch, P., Bolhàr-Nordenkampf J., Hofbauer, H., Cold flow model study on a dual circulating fluidized bed (DCFB) system for chemical looping processes, Werther, J., et al. (Eds.), *Circulating Fluidized Bed Technology IX*, TuTech, Hamburg, 2008, 783-788

[32] Schmid, J. C., Pfeifer, C., Kitzler, H., Pröll, T., Hofbauer, H., A new dual fluidized bed gasifier design for improved in situ conversion of hydrocarbons, *Proceedings of the 3rd international conference on Polygeneration Strategies*, August 2011, Vienna, Austria

[33] Seider W.D., Seader J.D., Lewin D.R., Product and Process Design Principles. Synthesis Analysis and Evaluation, John Wiley & Sons, Inc, 2003

[34] Smith R., Chemical Process Design and Integration, John Wiley & Sons Ltd., 2005

[35] Starr F., Tzimas E., Cormos C.C., Peteves S., IGCC: coal-based processing technology for the future, *Hydrocarbon Process*, 5, 2007, 10-12

[36] Tohidi B., Risk of hydrate formation in low water content CO_2 and rich CO_2 systems, Hydrafact for Progressive Energy, Carried out Under the EC Dynamis Project, 2008

[37] U.S. Greenhouse Gas Inventory Report. Climate Change – Greenhouse Gas Emissions, 11 April 2011

[38] Zero Emission Platform (ZEP) Report, The cost of CO_2 storage. Post-demonstration CCS in the UE, 2011