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Process modelling, optimization & multiple operation points of post combustion CO_2 capture process, using aqueous monoethanolamine as solvent

Masterthesis

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Abstract

Absorption by means of chemical solvents, such as monoethanolamine (MEA) is acknowledged as the most commonly used process for CO_2 removal. Thus, any research aiming to improve the process efficiency, is gaining increasing attention. In this study, a rate based model describing the CO_2 capture process by MEA has been created in AspenPlus interface, using real data from an existing pilot plant. Afterwards, in order to perform the optimization, AspenPlus was connected to MATLAB and the genetic algorithm was used as optimization method. The objective function of the problem was to minimize the regeneration energy of the amine solvent, since the solvent regeneration dominates the total operating costs. The optimization reduces the regeneration energy from 3.80 to 3.40 GJ/ton CO_2. This represents about 11% energy savings to the process, just by varying the operating conditions. Finally, in the last part of this work, the variable electricity demand, in which the steam required for the operation of the stripper reboiler and consequently the whole capture plant is subjected to, is taken into consideration. Since seasonal changes in the electricity demands can have a more permanent character, they are confronted as alternative scenarios for unit operation. It is both essential and interesting to examine optimum operating conditions (multiple operation points) for the new data consisting the system every time. As starting point for the evaluations of this part is considered the optimized base case. The results indicate that in small steam limitations, the margins for improvements are not so wide since we are still operating near the optimum found for the base case, but as we proceed to examination of the scenarios with less steam available the optimization can achieve bigger and significant improvements.

Acknowledgement

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1. Introduction

In our days, one of the biggest environmental problems concerning our planet, with multiple and hazardous consequences for all, is global warming. Recent researches indicate that the majority of warming occurred last decades has been caused by human activities, and in the nearby future human influences are expected to continue contributing to the phenomenon in a vigorous way.

The size and impact of the increase of atmospheric concentration of greenhouse gases, such as carbon dioxide, methane, ozone, nitrous oxide and chlorofluorocarbons over the last century, has been an object of study for many researchers. According to the Intergovernmental Panel on Climate Changes (IPCC), carbon dioxide is the greenhouse gas, to which human activities have contributed the more, and is estimated to be responsible for about 60% of the total anthropogenic Greenhouse Gases (GHGs) (Metz *et al.*, 2005).

There is a number of sources from which CO_2 emissions arise, mainly fossil fuel combustion in the power generation, industrial, residential and transport sectors. Due to the large emission volumes that usually occur in power plants and other large-scale industrial processes, these sectors are the most compatible with the addition of CO_2 capture technology. On the contrary, large numbers of small point sources that characterize residential sector, as well as mobile sources in the case of transport sector, make them less amenable for capture at present.

Fossil fuel combustion provides more than 80% of the world's total energy demands and accounts for approximately 75% of current anthropogenic CO_2 emissions (Abu-Zahra *et al.*, 2007; Houghton *et al.*, 2001). Figure 1.1 indicates the total carbon emissions arising from the fossil fuels, which have experienced significant growth over the last century, as estimated from the Carbon Dioxide Information Analysis Center (CDIAC). Consequently, in order for greenhouses gases to be constrained in an agreeable level, the main research is focused in reducing CO_2 emissions from fossil fuels; and developing economically feasible technologies to do so is becoming more and more essential. The existing technological options for reducing net CO_2 emissions to the atmosphere include:

- reduction of energy consumption, through utilization and/or by improving the energy conversion efficiency
- shift to fuels with lower carbon content, like natural gas
- boost the usage of renewable energy sources or nuclear energy, since they emit little or no net CO_2
- sequester CO_2, by enhancing biological absorption capacity in forests and soils
- capture and storage of CO_2, either chemically or physically.

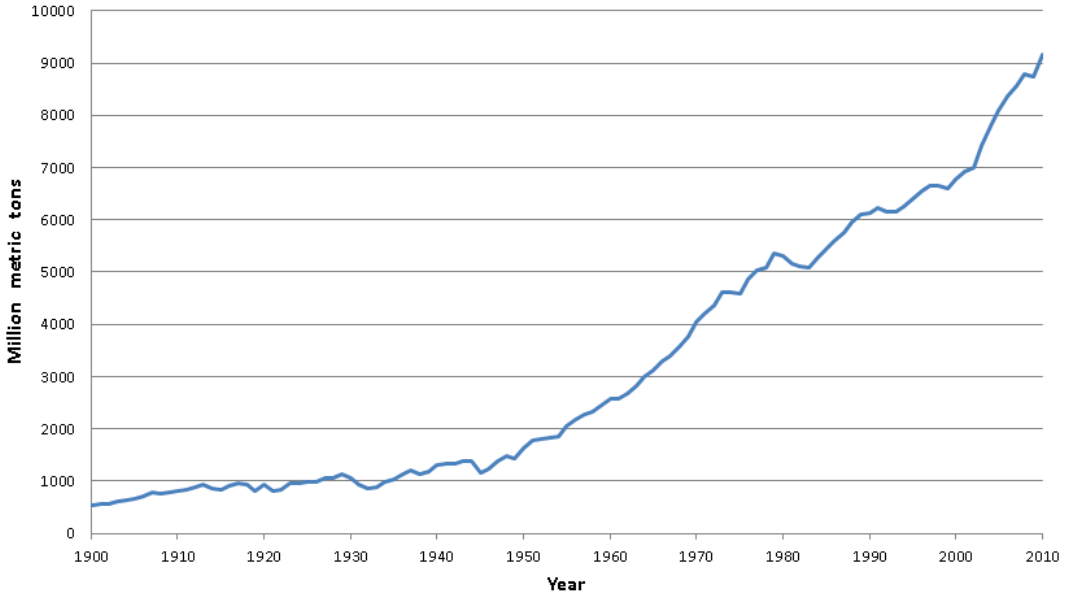

Figure 1.1.: *Total carbon emissions from fossil fuels (1900-2010). Source: CDIAC*

Since it is not only difficult to reduce the dependency on fossil fuels and switch to other energy sources, but also the conversion efficiency of other energy sources for power generation is in most cases not so high as the one of fossil fuels (Abu-Zahra *et al.*, 2007), a radical reduction of CO_2 emissions that results from fossil fuels combustion can principally be obtained by improving the efficiency of energy conversion in power plants and production processes, and/or by CO_2 capture and long term storage (CCS) .

In general, CCS is considered as a quite promising method, taking into account the ever increasing worldwide energy demand and the possibility of retrofitting existing plants with capture, transport and storage of CO_2. More specifically, by implementing CCS method, the

CO_2 arising from the combustion of fossil fuels or from processing industries, can be captured and stored away from the atmosphere for a long period of time.The captured CO_2 can either be used for enhanced oil recovery, in the chemical and food industries, or can be stored underground instead of being emitted to the atmosphere (Abu-Zahra *et al.*, 2007).

Although theoretically the whole stream that contains the low CO_2 concentrations could be directly transported and injected underground, the costs relating with this process make it rarely applicable in practice. Therefore, the CO_2 capture process is used, that aims to produce a nearly pure CO_2 stream, which can be easily transported and stored. Until now many applications separating CO_2 in large industrial plants are already in operation. In most cases though, the CO_2 is emitted to the atmosphere; and only in a few cases removal has been used for storage purposes. Currently, CO_2 capture processes are typically used to purify other industrial gas streams, or to obtain commercially useful amounts of CO_2 from flue gas streams generated by the combustion of coal or natural gas. (Metz *et al.*, 2005)

The three main techniques for CO_2 capture depending on the process or power plant application are:

- Post-combustion capture

Post-combustion systems are utilized to separate CO_2 from the flue gases generated by the combustion process of the primary fuel in air. These systems are usually used for capturing a low concentration of CO_2, typically about 3-15% by volume, and they normally acquire a liquid solvent. Currently, the most commonly post-combustion method for CO_2 capture is absorption with amine. The amine from the absorber is thermally regenerated and reused in the absorber. However, the major drawback of the amine based CO_2 capture process is the fact that solvent regeneration is energy intensive, and the whole process necessitates high capital and operating costs.

- Pre-combustion capture

The low concentration of CO_2 in flue gas implies large equipment sizes and high capital costs, since a large volume of gas has to be handled. An other drawback of the low CO_2 concentration, as already mentioned, is the use of powerful chemical solvents for capturing CO_2, the regeneration of which requires a large amount of energy. An hypothetical increase of the CO_2 concentration and pressure, would lead to a decrease of the CO_2 capture equipment, and the possibility for physical solvents to be used, with lower energy penalties for regeneration. This can be achieved by the pre-combustion capture. More accurately, pre-combustion systems

process the primary fuel in a reactor with steam and air or O_2 to produce synthesis gas, a mixture consisting mainly of CO and H_2. In a second reactor, called shift reactor, CO reacts with steam, and additional H_2 is produced, as well as CO_2. Afterwards, the resulting mixture of H_2 and CO_2 can be separated into a CO_2 stream that can be stored, and a stream of H_2 that can be combusted for power and/or heat generation. Despite the fact that the initial steps for fuel conversion are both more complex and costly than in post-combustion systems, the high concentrations of CO_2 produced by the shift reactor, typically 15-60% by volume on a dry basis, as well as the high pressures often encountered in these applications, are more desired for CO_2 separation. Pre-combustion would be used at power plants that employ integrated gasification combined cycle (IGCC) technology. However, the current challenges in IGCC are the high capital costs and the technology availability/reliability, since until now no IGCC plant incorporating CO_2 capture has yet been built. The absence of industrial experience employs a relative high number number of assumptions and increases the uncertainty, when referring to the potential of this method.

- Oxy-fuel combustion

An other way of increasing considerably the concentration of CO_2 in the flue gas stream is by using concentrated O_2, instead of air, for the combustion. In this case the O_2 can be produced by cryogenic air separation. Due to the fact that when the fuel is burnt in pure O_2, the flame temperature is excessively high, some CO_2 rich flue gas can be recycled to the combustor to make the flame temperature similar to the one appearing in a normal air-blown combustor. Oxyfuel combustion systems apply this technique; they use O_2 instead of air for combustion of the primary fuel to produce a flue gas that consist mainly water vapour and CO_2. This results in a flue gas with high CO_2 concentrations. The water vapour is then removed by cooling and compressing the gas stream. In most current designs for oxyfuel combustion, a purity of 95-99% for O_2, is assumed. An additional treatment of the flue gas may be needed in order to remove air pollutants and non-condensed gases, such as N_2, from the flue gas, before the CO_2 is sent to storage. The advantage of oxygen-blown combustion is the CO_2 concentration in flue gas around or above 80% by volume, so only simple CO_2 purification is required. Though, the major disadvantage of oxyfuel combustion, is the large quantity of oxygen that is required, which is quite expensive and high energy consuming. (Metz *et al.*, 2005; Hassan, 2005)

In Figure 1.2 the main technology options for CO_2 removal are represented in a schematic way. Each of them has different advantages that should be weighed against their costs and their overall effects on fuel efficiency. They all include a step concerning CO_2, H_2 or O_2

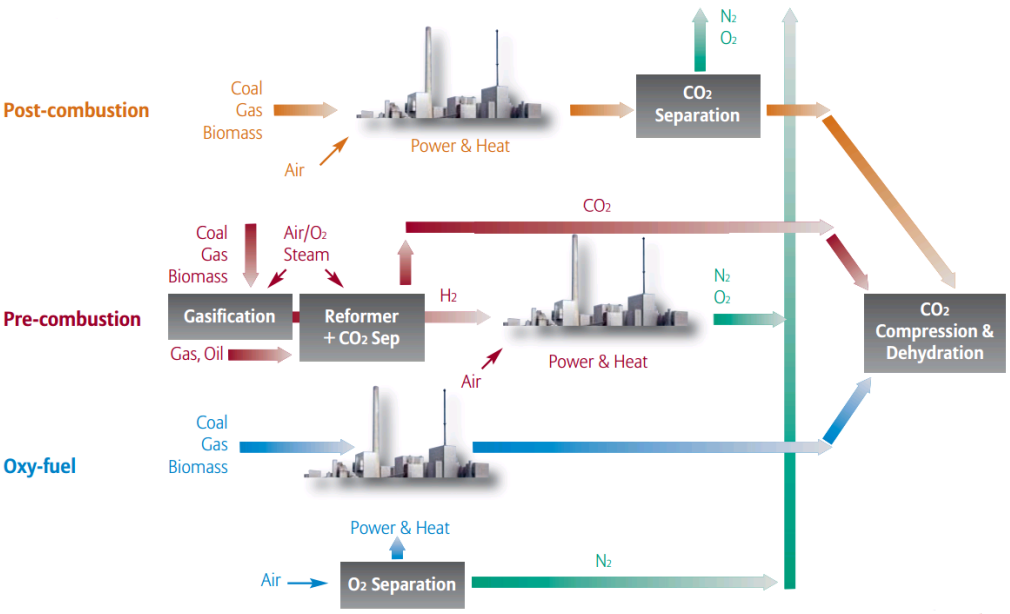

Figure 1.2.: *Technology options for CO_2 removal. Source: Bellona*

separation from a bulk gas stream, which can be either the flue gas, or the synthesis gas, or the air or raw natural gas, depending on the technology. These separation steps can be accomplished by means of physical or chemical solvents, membranes, solid sorbents, or by cryogenic separation. In general, the operating process conditions is a determinant factor for the selection of the capture technology. Current post- and pre- combustion systems for power plants are in principle capturing 85-95% of the CO_2 that is produced. Although higher capture efficiencies are possible, the required separation equipment becomes considerably larger in that case, the process more energy intensive, and consequently more costly. Capture and compression need roughly 10-40% more energy than the equivalent plant without capture, depending on the type of system. Due to the associated CO_2 emissions, the net amount of CO_2 captured is approximately 80-90%. As for the oxyfuel combustion systems, they are typically able to capture nearly all of the CO_2 produced. However, due to the need for additional gas treatment systems for removing pollutants such as sulphur and nitrogen oxides, the level of CO_2 captured is decreased to slightly more than 90% (Metz *et al.*, 2005; Inglese, 2011).

Among these three processes, which have been shown to be technically feasible for CO_2 capture from flue gas of fossil-fueled power plants, the post-combustion could be ascertained as the most promising one, regarding to its capacity to treat large volumes of flue gas and furthermore

the fact that is an end of the pipe treatment (Mores *et al.*, 2012). In general, post-combustion process, includes various technologies to separate CO_2 from flue gases, which are based on absorption, adsorption, membranes or other physical and biological separation methods, Figure 1.3. Each one of them has its own pros and cons. Among those technologies, the most mature ones are considered the ones based on absorption using liquid solvents.

Absorption by means of chemical solvents, such as monoethanolamine (MEA) is acknowledged as the most commonly used process for CO_2 removal. Generally, absorption processes acquire thermally regenerable solvents, which have a strong affinity for CO_2 and are regenerated at elevated temperatures. Thus, due to their demand on thermal energy for the regeneration of the solvent, many researchers are aiming to develop new solvent technologies to improve the efficiency of the CO_2 removal and reduce the total cost of the process. In this direction, a lot of studies about developing more efficient solvents have been held. For selecting new absorbent or absorbent mixtures (blends), some of them are focusing on solvent degradation, with higher stability, for the CO_2 process (Lepaumier *et al.*, 2009, 2010); others are more interested in achieving higher absorption rate and net cyclic capacity than the existing ones, reducing in that way the energy consumption of the removal process for example (Ma'mun *et al.*, 2007); and others try to consider and combine both effects of costs and performance (Dubois & Thomas, 2009). Another main field of studies, also aiming in maximizing the CO_2 capture efficiency and minimizing the process costs, is dealing with process simulation-evaluation and optimization. In this field, there are many different approaches and open research areas that include among others, process design optimization, operating conditions optimization, process flexibility and control. An important key decision when performing a simulation for CO_2 capture process, is the choice between rate based and equilibrium mathematical model. Moreover, in this large variety of studies, many different interfaces such us AspenPlus, Aspen Hysys, Matlab, gProms, GAMS and others, have been used to implement the models and perform the optimization. In order for a general idea about resent researches taking place in this area to be obtained, the works of (Abu-Zahra *et al.*, 2007) performing a parametric study using AspenPlus, as well as both the design and operating optimizations (Mores *et al.*, 2012, 2011) developed in GAMS targeting in minimizing both investment and operating costs and maximizing capture efficiency each time, are pointed out. In the field of dynamic management, (Kokossis *et al.*, 2006) have created an agent-enable environment taking into consideration the multiple savings that can be achieved by optimizing the utility system of the process. As for the dynamic modelling area, a recent study of (Rodriguez *et al.*, 2014) introduces a predictive framework, within the gCCS software, that can contribute a lot in understanding dynamic behavior of power plants.

Last but not least an other area of studies includes pilot-scale experimental works, which are important for validating models behavior. In this field, the need for dynamic pilot plant data for validation of models behavior during transient conditions has led to the dynamic absorber and process model of (Kvamsdal *et al.*, 2009; Flø *et al.*, 2015), respectively. All these areas are strongly connected and their combined results is expected to lead to significant process improvements.

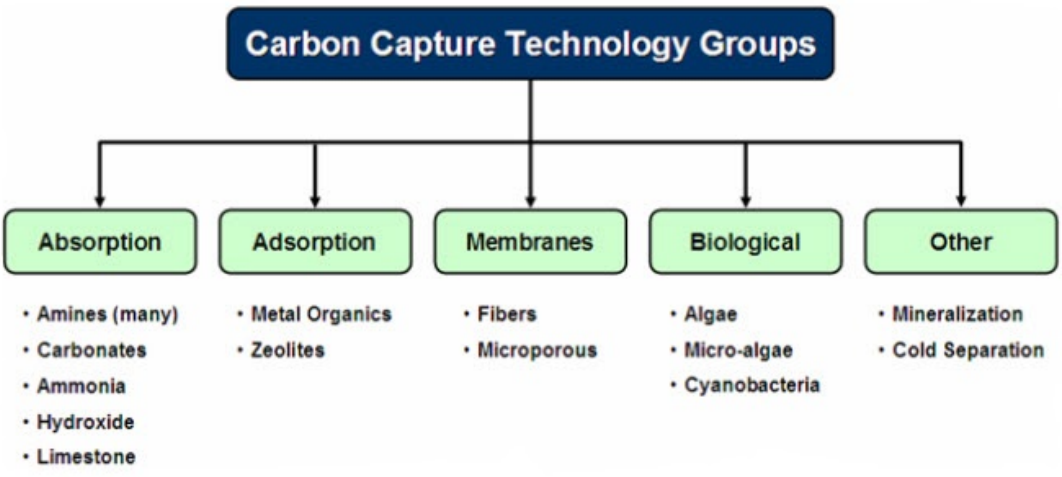

Figure 1.3.: *Post-Combustion CO_2 Capture Technology Groups. Source: EPRI 2009*

In this work the variable electricity demand, in which the steam required for the operation of the stripper reboiler and consequently the whole capture plant is subjected to, is taken into consideration. It is both essential and interesting to examine optimum operating conditions for the process when such a limitation is implied to the system. Avoiding the high complexity and challenging validation that a dynamic simulation requires, this work is constrained in a static confrontation that can be applied to more permanent or seasonal steam availability constraints; leaving although open the field for dynamic modelling in the near future.

The first part of this study refers to the process modelling. In order for the model to be built, real operating data have been used and implied to AspenPlus interface. The process modelling was based on aqueous MEA solution. It is of high importance that the built model represents in a good way the operation of the real unit. That means, that any changes applied to the model should be able to predict the unit's behavior, in case they were applied to the real system.

The second part is the optimization part. For this part AspenPlus was connected to MATLAB and the genetic algorithm was used to perform the optimization. A preliminary sensitivity analysis was used to detect the key performance variables, however, they were all included to the optimization part, because their synergistic effect was expected to give a larger effect on the overall process performance, compared to a variation of one single variable. The aim of this part was to find the values of the parameters that lead to the minimization of the regeneration energy of the solvent, and so to the minimization of the total costs of the process.

The third part focuses on generating some hypothetical scenarios and maximizing the unit performance, taking into account the restriction that can be applied to the system by lack of the required amount of steam. Also, at this point the aim was to optimize the process for the new data that consisted the system every time.

2. Simulation

2.1. Introduction

This part is dealing with the description of the CO_2 capture process model built in AspenPlus. It is a rate based model, that consists of the absorption/desorption process. Real operating data from test bed of Boryoung Power Plant in Republic of Korea were used for model validation, and in order to to specify feed conditions and some unit operation block specifications.

Thermophysical property models are based on the work of Austgen *et al.* (1989), and reaction kinetic models are based on the works of Pinsent *et al.* (1956) and Hikita *et al.* (1977). Electrolyte NRTL method for liquid and RK equation of state for vapor, are used to constitute the thermodynamics of the system. Rate-based model is chosen for the absorber and the stripper, where Onda correlations are included in transport properties model.

For the construction of the model, the AspenTech's existing rate based MEA model file was used as a starting point, to which all necessary changes were applied. (AspenPlus, 2008)

2.2. Modelling Approach

The main components used in the model to represent the chemical species that are present in the process are CO_2, MEA, H_2O, N_2 and O_2.

The CO_2 capture process with MEA is a reactive distillation process. This implies, that two main phenomena are involved: the mass transfer of CO_2 from the bulk vapour to the liquid solvent and the chemical reaction between CO_2 and the solvent.

In order for this behavior to be modeled, two different approaches that can be applied, are the equilibrium based approach versus the rate-based one. In the equilibrium stage models theoretical stages in which liquid and vapour phases attain equilibrium are assumed, as well

as perfect mixing. On the contrary, in the rate-based approach, actual rates for heat and mass transfer are taken into consideration. That is why, the last one is more appropriate in modelling reactive absorption processes, since phase equilibrium is hardly attained in practice (Lawal *et al.*, 2009).

2.3. Existing Plant

The model of the process is constructed based on operating data from the existing unit. The flow sheet of the unit is shown in Figure 2.1. As can be observed in the process diagram, the dry flue gas stream (2) enters the unit and interacts with water, in an absorber (ABS1), in order for SO_2 to be removed. Then, the top outlet stream (3), after cooled, enters the reactive distillation column (ABS2), where it reacts with the lean amine stream (14), in order for CO_2 to be absorbed. Finally, the rich amine stream coming out from the bottom of the column (10) recovers heat from lean amine stream (12)and then enters the stripper (STR), where the regeneration of the amine takes place. The lean amine outlet stream (12) is recycled back to the absorber, after cooled down to absorber level temperatures.

Subsequently, some basic characteristics about the absorber and the stripper are pointed out. The absorber is constituted by four IMTP packings, 4.2 meters height each. The total column height is 23.5 meters and the diameter 0.4 meter, the top pressure 1.017 atm, and the column pressure drop 0.013 atm. The stripper consists of three IMTP packings, 4.2, 4.2, and 2.85 meters height, respectively and a washing section on the top 1.75 meters height. The top pressure is 1.339 atm and a column pressure drop 0.010 atm. The column height is 17 meters and the column diameter 0.35 meters.

The feed conditions of the flue gas and the lean amine stream are presented in Table 2.1, and they both refer to the absorber inlet. In Table 2.1 the mole fractions in Flue Gas are utilized to unity, and the concentration in Lean in Stream refers to apparent components and represents the weight percent concentration of MEA in the aqueous MEA solution.

The regeneration energy of the unit is about 3.83 GJ/tonCO_2, which seems to be compatible with other existing units e.g. 3.7 GJ/tonCO_2 for CASTOR pilot plant in Esbjerg (Zero-Emission-Resource-Organisation, 2011), and other available data from the literature, 3.8 GJ/tonCO_2 (Singh *et al.*, 2003) and 4.1 GJ/tonCO_2 (Hamborg *et al.*, 2014). Finally,

a table with the main process indicators has been created Table 2.2, so that an adequate overview of the unit operation can be obtained.

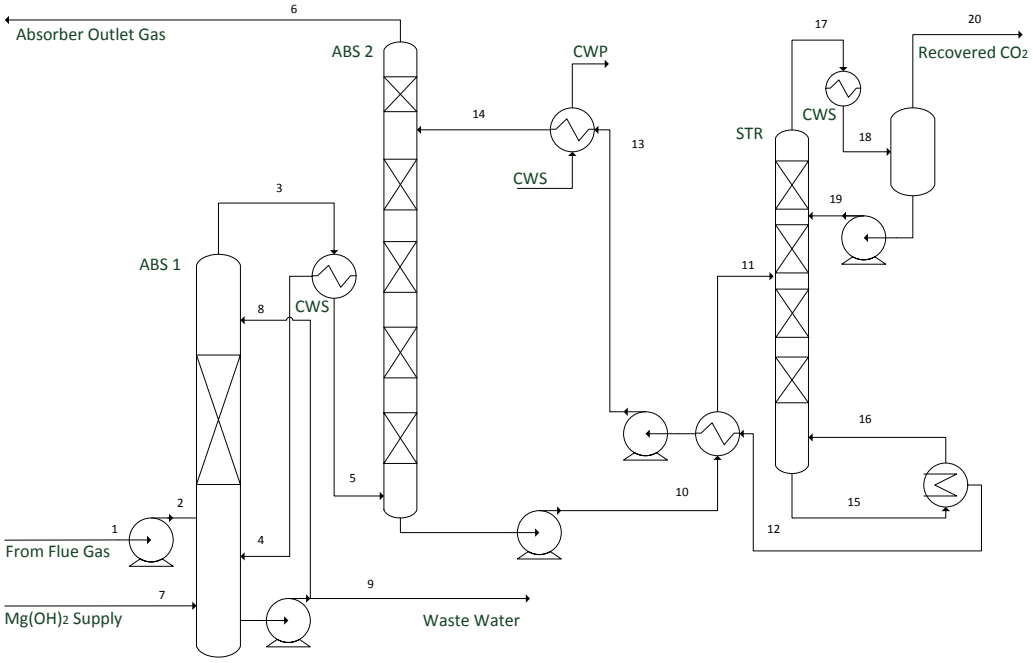

Figure 2.1.: *Process Diagram*

Table 2.1.: Feed Conditions

Stream ID	**Flue Gas**	**Stream ID**	**Lean in**
Temperature (K)	313.15	Temperature (K)	313.15
Pressure (atm)	1.032	Pressure (atm)	2.452
Total flow (l/min)	5994.8	Total flow (l/min)	20.6
Mole-Frac		Concentration (wt%)	31.2
H2O	0.07		
CO2	0.14		
N2	0.75		
O2	0.04		

Table 2.2.: Process Indicators

Item	Value	Unit
CO_2 removal	92.9	%
CO_2 amount	1.99	TPD
L/G ratio	3.73	kg/Sm^3
Regeneration Energy	3.83	GJ/tCO_2
Amount of amine	14.88	m^3/tCO_2

2.4. Physical properties

The electrolyte NRTL method is used to compute liquid properties, in this rate-based MEA model, because of the presence of charged species that make the solutions extremely non-ideal. The ELECNRTL property method is considered as one of the most versatile electrolyte property methods, since it can handle very low and very high concentrations, aqueous and mixed solvent systems (AspenPlus, 2001).

CO_2, N_2 and O_2 are selected as Henry-components (solutes) to which Henry's law is applied. Henry's constants are specified for these components with water and MEA Table 2.3.

The Redlich-Kwong equation of state is used to calculate vapor phase thermodynamic properties. It is appropriate for the examined system, due to the relative low operating pressures in the process (less than 10 atm) for which the vapor-phase non-ideality is small.

Mass transfer coefficients in the liquid and vapour films were determined by correlations given by Onda.

Table 2.3.: Henry Parameters

Component i	**CO2**	**CO2**	**N2**	**O2**
Component j	**H2O**	**MEA**	**H2O**	**H2O**
Temperature units:	K	K	K	K
Property units:	N/sqm	N/sqm	N/sqm	N/sqm
aij	-145.32	20.18	176.51	155.92
bij	765.9	-1138.5	-8432.8	-7775.1
cij	32.25	0	-21.56	-18.40
dij	-0.074	0	-0.008	-0.009
Tlower	0	0	273	274
Tupper	2000	2000	346	348
eij	0	0	0	0

2.5. Reactions

The following reactions may occur when CO_2 absorbs into and reacts with aqueous MEA. All species represented are in aqueous solution. All reactions are assumed to be in chemical equilibrium except those of CO_2 with OH^- and CO_2 with MEA.

Ionization of water:

$$2\,\mathrm{H_2O} \leftrightarrow\ OH^-\ +\ H_3O^+ \tag{2.1}$$

Dissociation of carbon dioxide:

$$\mathrm{CO_2} +\ 2\,\mathrm{H_2O} \leftrightarrow\ H_3O^+\ +\ HCO_3^- \tag{2.2}$$

Dissociation of bicarbonate:

$$\mathrm{HCO_3^-} +\ \mathrm{H_2O} \leftrightarrow\ CO_3^{2-}\ +\ H_3O^+ \tag{2.3}$$

Dissociation of protonated MEA:

$$\mathrm{MEAH^+ + \ H_2O \leftrightarrow \ } MEA \ + \ H_3O^+ \tag{2.4}$$

Carbamate reversion to bicarbonate:

$$\mathrm{MEACOO^- + \ H_2O \leftrightarrow \ } MEA \ + \ HCO_3^- \tag{2.5}$$

Bicarbonate formation and reversed reaction:

$$\mathrm{CO_2 + \ OH^- \rightarrow \ } HCO_3^- \tag{2.6}$$

$$\mathrm{HCO_3^- \rightarrow \ } CO_2 \ + \ OH^- \tag{2.7}$$

Reaction of dissolved CO2 with MEA and reversed reaction:

$$\mathrm{MEA + \ CO_2 \ ^+ H_2O \rightarrow \ } MEACOO^- \ + \ H_3O^+ \tag{2.8}$$

$$\mathrm{MEACOO^- + \ H_3O^+ \rightarrow \ } MEA \ + \ CO_2 \ + \ H_2O \tag{2.9}$$

The equilibrium constants for the reactions 2.1-2.5 are calculated from the standard Gibbs free energy change. The reduced power law expression is used for the rate-controlled reactions 2.6-2.9.

$$\mathrm{r = k \cdot \ T^n} \cdot \exp\left(\frac{-E}{R \cdot T}\right) \cdot \prod_{i=1}^{N} C_i^{a_i} \tag{2.10}$$

,where r is the reaction rate, k the pre-expodential factor, T the absolute temperature, n the temperature exponent (here considered as zero), E the activation energy, R the universal gas constant, N the number of components in the reaction, C_i the concentration of component, and a_i the stoichiometric coefficient of component i in the reaction equation.

The kinetic parameters for reaction 2.6 are taken from the work of Pinsent *et al.* (1956), and the kinetic parameters for reaction 2.7 are calculated by using the kinetic parameters of reaction 2.6 and the equilibrium constants of the reversible reactions 2.6 and 2.7. The kinetic parameters for reactions 2.8-2.9 in Table 2.4 are derived from the work of Hikita *et al.* (1977).

Table 2.4.: Parameters k and E in the reduced power law expression

Reaction No.	k	E (kcal/mol)
2.6	4.32e+13	13.25
2.7	2.38e+17	29.45
2.8	9.77e+10	9.86
2.9	3.23e+19	15.66

At this point should be noticed, that in order for kinetics parameters k, E to be decided, also other works have been examined, but the parameter values from kinetics of Pinsent and Hikita had the best fitting to the experimental temperature profiles of the absorber and stripper.

2.6. Simulation Approach

Simulation Flow Sheet

The simulation flow sheet is shown in Figure 2.2.

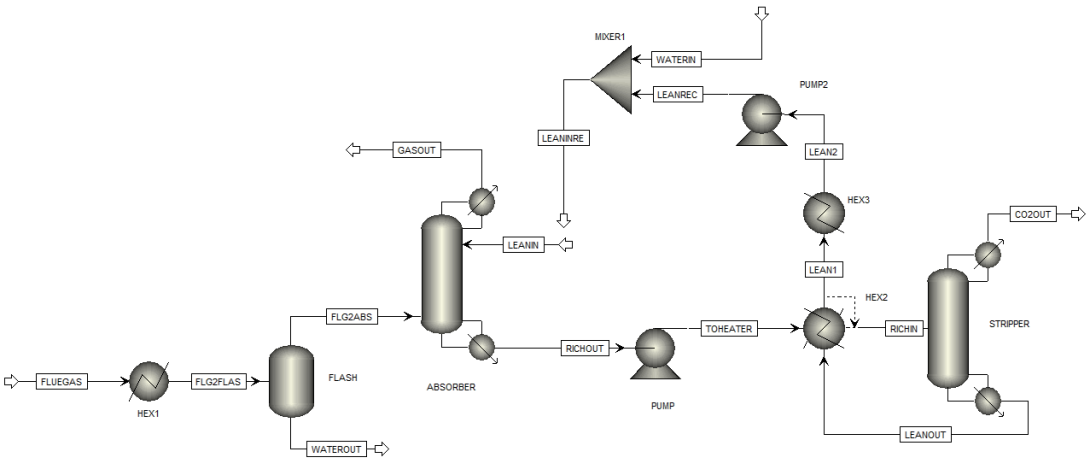

Figure 2.2.: *Rate-Based MEA Simulation Flow sheet in AspenPlus*

Process Description

The flue gases from the power plant, after treated for SO_2 removal, enter a cooler (HEX1), where they are cooled to 40^{o}C. Afterwards they enter a flash, operating also in the same temperature of 40^{o}C, in order to reassure the vapor phase for the absorber inlet. The gases flow through the packed bed absorber (ABS) counter currently with the absorbent (the aqueous MEA solution), in which the absorbent reacts chemically with the carbon dioxide. The rate based absorber model is simulated using AspenPlus Radfrac Block. The absorber consist of 113 stages and a partial-vapor condenser. The operating pressure is 1.017 atm with a column pressure drop of 0.013 atm. The column packing height is 16.8 m and the column diameter 0.4 m. A design spec has been created for fixing the Top Temperature to 41^{o}C, by varying the condenser duty. This enables cooling of the top outlet stream with water. The carbon dioxide treated gas, GASOUT, is vented to the atmosphere. The rich solvent coming out of the absorber, containing chemically bound CO_2, RICHOUT stream, is pumped to the stripper via a lean/rich cross heat exchanger (HEX2) in which the rich solvent, RICHIN, is heated to 93^{o}C, a temperature close to the stripper operating temperature; while the CO_2 lean solution, LEANOUT, is cooled. The chemical solvent is regenerated in the stripper (STRIPPER) at elevated temperatures and a pressure not much higher than atmospheric. More specifically, the stripper is also modeled with AspenPlus Radfrac Block. The calculation type of the stripper is rate based, with 40 stages, with a partial condenser and a Kettle reboiler. The top pressure is specified to 1.339 atm, with a column pressure drop and condenser pressure drop of 0.010 atm each. A design spec for fixing the CO_2 mole purity in the CO2OUT stream is set to 0.94. Reflux ratio is set to adjusted variable. The packing height is 11.25 m and there is also a washing section of 1.75 m height. The stripper diameter is 0.35 m. Heat is supplied to the reboiler using steam to maintain regeneration conditions. Steam is recovered in the condenser and fed back to the stripper, after which the produced CO_2 gas, CO2OUT, leaves the condenser. Finally, the lean solvent is pumped back to the absorber via the lean/rich heat exchanger (HEX2) and a cooler (HEX3) to bring its temperature down to the absorber level, about 40^{o}C. The WATERIN stream that is inserted to the model compensates for water and MEA loses. The mass flow of water and MEA in this stream is changing by a calculator, in order to reassure the conservation of water and MEA mass balances in the system. Respectively, the two pumps shown in the diagram compensate for pressure loses, and each one has a discharge pressure of 2.452 atm.

The feed conditions for the inlet streams of the process are specified by the existing unit inlet data.

Data fitting

However, the main goal of this part is to make sure that the created model is corresponding to the function of the existing unit, and the produced results represent in a good way what is happening to the real system. In order to do so, the values that are checked are the capture rate (CR) of the absorber, that it is wanted to be fixed at approximately 92.9%, and the regeneration energy of the stripper (RE), which is known for the process and is about 3.83 GJ/ton CO_2.

The parameters changing to fix the values that were mentioned above are the interfacial area factor and the moles of CO_2 in the LEANIN, which affects the loading of MEA. The parameters values that were chosen were found with trial and error and are shown in the Table 2.5.

Table 2.5.: Parameters Choice

Parameter	Value
Interfacial area factor	0.9
Moles of CO_2 in LEANIN	0.23

Results

The simulation was performed using AspenPlus. Key simulation results are presented in Table 2.6. The measured versus calculated absorber and stripper liquid temperature profiles are presented in Figure 2.3 and 2.4, respectively.

Table 2.6.: Key Simulation Results

Variable	Rate-Based MEA Model	Measurement
CO_2 loading of LEANIN ($MolCO_2$/MolMEA)	0.23	-
CO_2 loading of RICHIN ($MolCO_2$/MolMEA)	0.52	-
CO_2 removal level (%)	92.9	92.9
L/G ratio kg/Sm^3 kg/Sm^3 (kg/Sm^3)	3.76	3.73
Regeneration Energy (GJ/tonCO_2)	3.80	3.83

It is obvious that the built model represents in a really good way what is happening inside the columns of the absorber and the stripper.

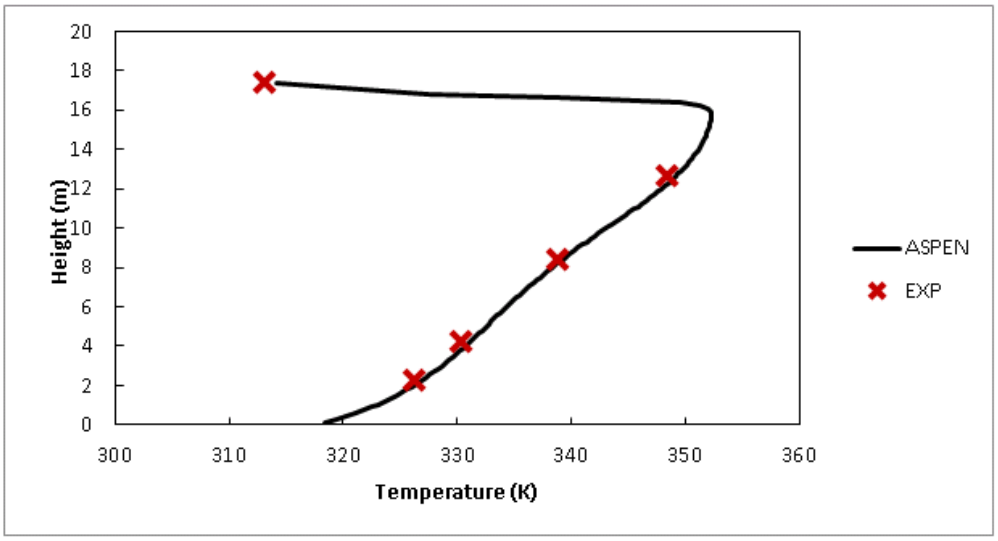

Figure 2.3.: *Temperature Profile Absorber*

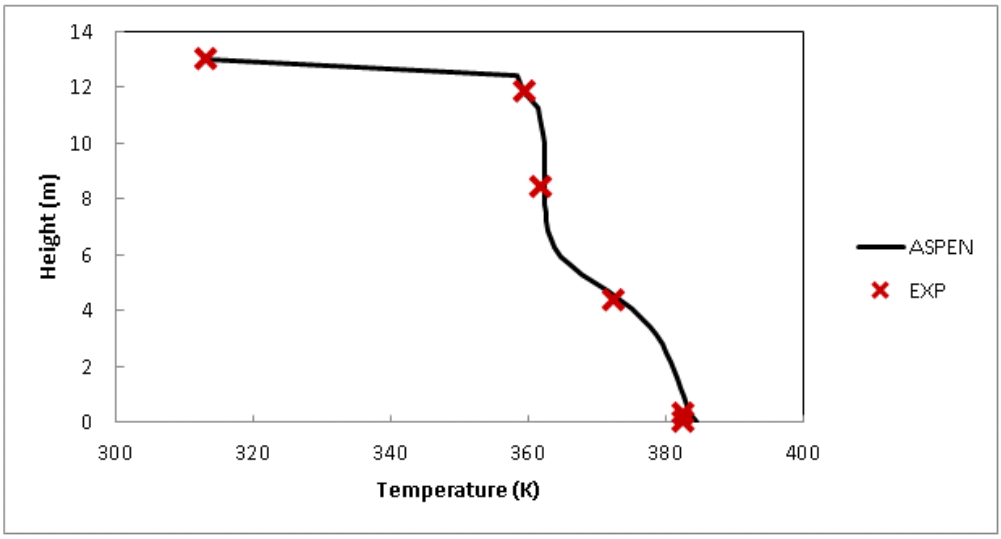

Figure 2.4.: *Temperature Profile Stripper*

Moreover the temperature difference between the two streams of the heat exchanger HEX2 is checked, to ensure that a minimum temperature difference that makes the heat transfer feasible is acquired.

Figure 2.5 shows a temperature difference at about 19 degrees, so the heat exchanger can

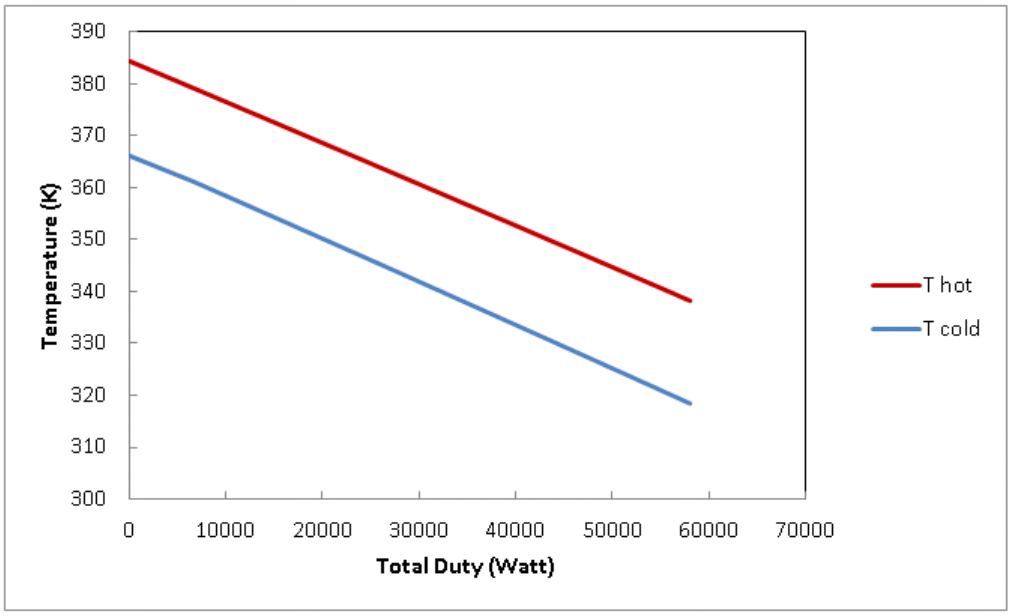

Figure 2.5.: *Temperature Difference HEX2*

work properly since a reasonable temperature is usually considered from 5 to 10 degrees.

In the created model (Figure 2.2) no recycle has been used for the LEANIN stream. This has happened in order to make the model more robust and the simulation easier to converge (taking also into account the next part of the study, which is the optimization part, so the model is going to run for many different values and it is important that the convergence is helped). Instead the matching of the streams LEANIN and LEANINRE is considered (results shown in Table 2.8), since actually both refer to the same stream.

Table 2.7.: Mass Balance Configuration

Stream	FLG2ABS	GASOUT	CO2OUT	WATERIN	Difference
Mass Flow (kg/hr)					
CO_2	89.314	6.351	82.964	-	0.001
MEA	-	10.692e-05	2.567e-12	9.223e-05	1.469e-05
H_2O	18.597	17.143	2.163	0.709	-

Table 2.8.: Lean In Stream Convergence

	LEANINRE	LEANIN	ABS(LEANIN-LEANINRE)
	LIQUID	LIQUID	
Mass Flow (kg/hr)			
MEA	207.353	207.349	0.004
H_2O	853.724	853.725	0.001
CO_2	3.87E-05	3.87E-05	0E-05
N_2	0	0	0
O_2	0	0	0
Total Flow (kg/hr)	1307.269	1307.270	0.001
Temperature (K)	313.15	313.15	0.00
Pressure (atm)	2.452	2.452	0.000
Liquid Frac	1	1	

3. Optimization

3.1. Introduction

After simulating the CO_2 capture process by MEA, it is of high importance that an attempt for optimizing the unit operation is made. Since the solvent regeneration is highly energy intensive, it affects the total operating costs significantly. That is why in order for the total costs of the unit to be minimized, the optimization is based on minimizing the regeneration energy of the stripper.

The absorption/ desorption processes that together constitute the examined CO_2 removal method are strongly coupled and main parameters from both influence the process operation. Consequently, simultaneous optimization of the whole CO_2 capture process is essential to determine the best operating conditions in order to minimize the total cost.

For this part AspenPlus Interface has been connected to MATLAB and the genetic algorithm has been used as an optimization method.

3.2. Optimization method

The genetic algorithms (GAs) are methods for solving optimization problems either constrained or unconstrained. They are based on a natural selection process that actually mimics biological evolution process. The way that these algorithms work, is repeatedly modifying a population of individual solutions. More specifically, at each iteration the genetic algorithms select individuals from the current population in a random way, and use them as parents in order to produce the children for the next generation. Over successive generations the genetic algorithms converge towards an optimal solution.

There are two main ways in which a genetic algorithm differs from a classical, derivative based, optimization algorithm. At first in the approach it uses to evolve to optimality, and then in the

selection of the next point. Particularly, in contradiction to a classical algorithm that generates a single point at each iteration and approaches an optimal solution through a sequence of points, the genetic algorithm generates a population of points in each iteration and the best point in the population approaches an optimal solution. Additionally, the genetic algorithm selects the next population by computation that uses random number generators, while a classical algorithm selects the next point in the sequence by a deterministic computation.

The genetic algorithm can be applied to solve a variety of optimization problems that are not well suited for standard optimization algorithms, including problems in which the objective function is discontinuous, non-differentiable, stochastic, or highly nonlinear.

The following outline summarize how a genetic algorithm works:

1. The algorithm begins by creating an initial population that can be random or implied to the system.
2. The algorithm then creates a sequence of new populations. At each step, the algorithm uses the individuals in the current generation to create the next population. To create the new population, the algorithm performs the following steps:
    a) Scores each member of the current population by computing its fitness value.
    b) Scales the raw fitness scores to convert them into a more usable range of values.
    c) Selects members, called parents, based on their fitness.
    d) Some of the individuals in the current population that have lower fitness are chosen as elite. These elite individuals are passed to the next population.
    e) Produces children from the parents. Children are produced either by making random changes to a single parent mutation or by combining the vector entries of a pair of parents crossover.
    f) Replaces the current population with the children to form the next generation.
3. The algorithm stops when one of the stopping criteria is met.

(The MathWorks, 2015a,b; Kunjur & Krishnamurty, 1997)

Through the operations of selection, crossover and mutation the population is evolving towards an optimum. These operations are constructing an useful, fast and robust technique, due to the combination of direction and chance in the search in an effective and efficient manner.

Since population implicitly contains much more information than simply individual fitness evaluations, the genetic algorithm combines the good information that is hidden in a solution with good information from another solution to produce new solutions with good information inherited from both parents, hopefully leading towards optimality.

The non linear nature of the optimization problem handled in this work, in combination with the many advantages mentioned above concerning the GA, led to its selection as optimization method. More accurately, since we are dealing with a rate based reaction model, with high complexity, the gradient and optimum for the optimization problem, are hard, if not impossible, to be found in a deterministic way. Among the variety of existing stochastic algorithms, the GA was chosen for its ability to explore and exploit simultaneously, a growing amount of theoretical justification, and its successful application to real-world problems.

3.3. Problem definition

A simplified formulation of the optimization problem, as inserted in the GA, could be:

$$\begin{aligned} & & min\ RE(x,h) \\ subject\ to & & crf(x,h) \\ & & con(x,h) = 0 \\ & & minimum\ (DT_{hot,HEX2}, DT_{cold,HEX2}) \geq 5 \\ & & T_{top,STRIPPER} \geq T_{ref} \end{aligned} \tag{3.1}$$

,where RE stands for regeneration energy and represents the objective function, crf the non linear constraint function about the fixation of the capture rate, con is a logical constraint referring to the convergence status of the simulation in AspenPlus, x the optimization variables, h the database of variables that arise from the simulation and constitute the connection between AspenPlus and MATLAB. The last two constraints are feasibility constrains. The first one refers to the feasibility of heat transfer in the HEX2, and the second to the necessary temperature of the CO2OUT stream, in order to be able to be cooled down with water. T_{ref} is set to 313.15 K. In the next sections a more detailed description of each component of the optimization is attempted.

At this point, it should be noticed that the connection between AspenPlus and MATLAB is achieved through the ActiveX server, which actually passes the whole Aspen Tree, with all the variables included to the simulation, to MATLAB through h.

As termination conditions/criteria for the GA are considered the generations, the stall generations and the function tolerance. As maximum generations number is considered the number of optimization variables multiplied by one hundred, so here 400 iterations, the amount of stall generations is set to 50 and the function tollerance is 1e-6. So the algorithm runs either until the average relative change in the fitness function value over stall genertions is less than function tollerance or until it reaches the maximum number of generations.

An attempt to describe GA's evolution flow in this study, incorporating the interaction with both AspenPlus and MATLAB is shown in Figure 3.1.

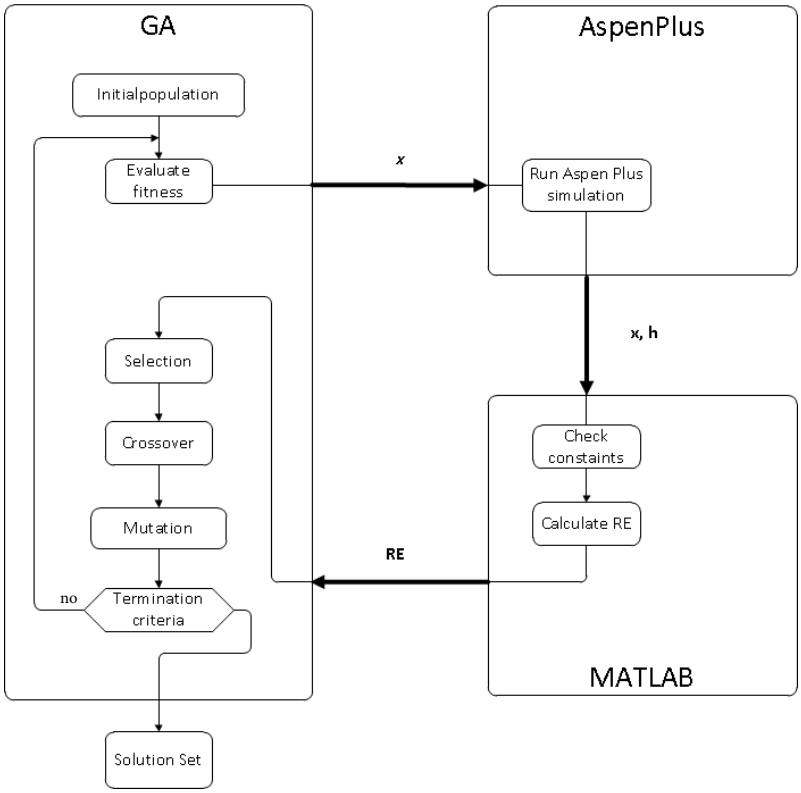

Figure 3.1.: *GA evolution flow*

3.4. Choice of variables

A crucial point for a successful optimization is the determination of the included variables. After a preliminary sensitivity analysis the optimization variables considered are the following:

- Temperature of flue gas coming into the absorber defined by FLASH operating temperature
- Operating temperature of HEX2
- Pressure of the stripper
- Pressure of the absorber.

As a starting point for the optimization, the initial values of the optimization variables from the base case scenario are implied to the system. Both the initial population and the ranges examined for each variable are shown in Table 3.1.

Table 3.1.: Optimization Variables

Variable	**Initilial Population**	**Range**
Temperature FLASH (K)	313.15	293.15-350.15
Temperature HEX2 (K)	366.15	350.15-390.15
Pressure STRIPPER (atm)	1.339	0.9-2.1
Pressure ABSORBER (atm)	1.017	0.9-2.1

3.5. Objective function

The objective or fitness function is the function that is to be optimized. The optimization algorithm tries to find the minimum of this function. This function is passed as input argument to the main genetic algorithm function.

The performance indicator used in the absorption/desorption process is the thermal energy required in the stripper (GJ energy/ton CO_2 removed). The thermal energy is expected to be a major contributor to the production cost and a change in the energy required will give a clear effect on the operating costs that is why it is chosen as the objective function for the optimization problem.

3.6. Nonlinear constraint

For a comprehensive analysis of the process operation, limitations and performance characteristics should be carefully taken into account when performing an optimization.

As a nonlinear constraint for the process is considered the fixation of the capture rate. Consequently, the nonlinear constraint function has been constructed in a way, so that the capture rate of the process for each set of the optimization variables values is kept fixed to 92.9%, by varying the amine flow in the LEAN IN stream. In order to do so, firstly an upper and lower bound for the amine flow are been created, so that the desired capture rate is achieved between this space, and subsequently by using a bisection method the exact value of the amine flow is calculated.

Another thing that is examined is the top temperature of the stripper. It is desired to be above 313.15 K, because under that temperature it will be hard for the outlet stream to be cooled with available cooling water. So, if the simulation converge for a top temperature of the stripper with lower value, this set of parameter values that lead to this result is automatically rejected.

Moreover the feasibility of heat exchange in the HEX2 is checked, Figure 3.2. A low minimum temperature difference is set to 5 degrees. After each iteration both temperature differences ($T_{LEANOUT}$ - T_{RICHIN} and $T_{TOHEATER}$ - T_{LEAN1}) are calculated and if they both are more than 5 degrees the exchange of heat is considered feasible, otherwise the examined set of values is again rejected.

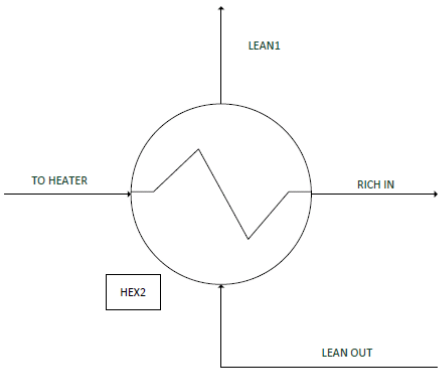

Figure 3.2.: *Heat Exchanger (HEX2)*

The genetic algorithm in order to solve nonlinear constraint problems uses the Augmented Lagrangian Genetic Algorithm (ALGA). This approach consists of the formulation of a subproblem by combining the fitness function and nonlinear constraint function using both the Lagrangian and the penalty parameters. Afterwards, the subproblem is approximately minimized using the genetic algorithm so that all the other constraints and bounds are satisfied.

It is also to be noticed, that after each run of the simulation the convergence of the process is checked. If the simulation converges and if the capture rate is able to be fixed to the desired value, the nonlinear constraint is satisfied and for this set of values the objective function evaluates the regeneration energy required, before another set of values is examined. Otherwise, in case that the capture rate was not able to be fixed or the simulation at some point didn't converge, the nonlinear constraint function is not satisfied and the genetic algorithm proceeds to the examination of a new set of values. A schematic description of the optimization process mentioned above can be pointed out in the Figure 3.3.

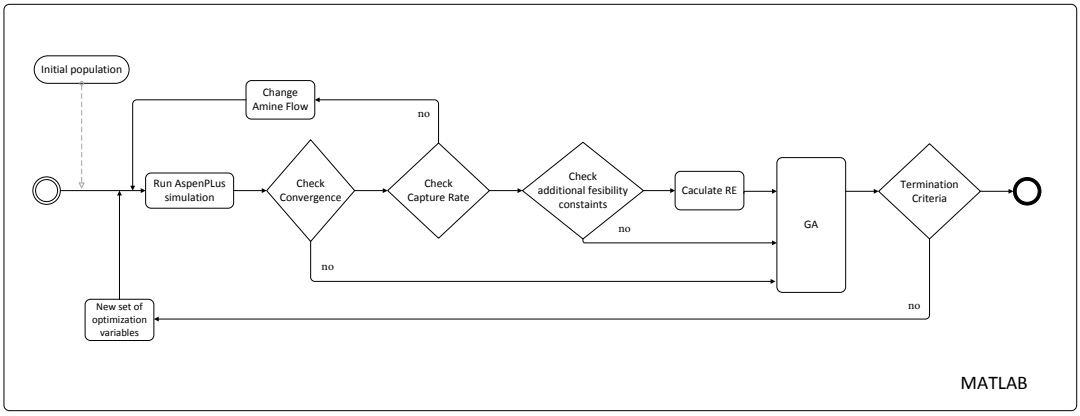

Figure 3.3.: *Optimization Process*

3.7. Results

The optimization managed to reduce the regeneration energy from 3.80 to 3.40 GJ/ton CO_2. This represents about 11% energy savings to the process. The optimized values of the optimization variables are shown in the Table 3.2. The capture rate is fixed to 92.9%, by adjusting the amine flow to 19.7 l/min. The top temperature of the stripper is approximately 314.71 K and the temperature differences to the heat exchanger are about 9.0 and 5.1 degrees.

Table 3.2.: Optimization Variables Results

T_{FLASH}	T_{HEX2}	$P_{STRIPPER}$	$P_{ABSORBER}$
300.82 K	375.69 K	1.345 atm	1.373 atm

As expected, the optimization tends to minimize the low temperature difference of the heat exchanger as much as possible, so that the thermal loading of the exchanger is maximized. This makes total sense. From the results can be concluded that a 7% of the savings occurs due to the optimized operation of the heat exchanger, and the rest 4% due to the other variables.

4. Steam limited scenarios

4.1. Introduction

Since electricity demands are changing by hour, on daily basis and also seasonally, it is expected that the amount of steam available for the process occasionally can be subjected to restrictions. The online adjustment of the CO_2 capture process per time of day or daily is considered as a transient state that can be described by dynamic modelling; for this reason is not going to be examined in the present work. On the other hand, seasonal changes in the electricity demands can have a more permanent character, and could be confronted as alternative scenarios for unit operation.

Therefore, the last part of this study is dealing with generating some scenarios, considering the restriction that can be applied to the system, by lack of enough steam for the stripper operation, resulting from variable electricity demand. Cases where 90%, 80%, 70% and 60% of the required stream is available are examined, and they represent Scenarios 1 to 4, respectively. These scenarios can be considered as multiple operating points for the unit process.

There are two possible approaches examined for dealing with this problem. Either reduce respectively the flow in the inlet streams such that the process operation does not alter at all, or treat the whole feed and adjust the amine flow, hoping to improve process operation. Both of these approaches are examined in this part.

4.2. The two approaches

As already mentioned, the available amount of steam can change, and consequently the operation of the unit should be adjusted to those changes. A reasonable way to deal with the new conditions, is by treating the same percentage of the inlet streams, as the percentage of available steam (100% each time represents the amounts specified in the base case). So in

case of 90% steam availability, it would make sense just to treat 90% of the flue gas stream and use 90% of the amine flow, without changing anything to the process. At this case, the regeneration energy of the unit remains the same, as well as the capture rate. Although, since now there is a 10% of flue gas that is emitted to the atmosphere without any treatment, the total capture rate of the flue gas coming out of the power plant is reduced to 90% of the one achieved when treating the whole feed.

In deed, by changing the input flue gas flow rate corresponding to the amount of steam the regeneration energy remains the same but the fact is that it could be improved by treating these cases all as changing operating points. This leads to the consideration of the second approach.

The second approach deals with the reduction to the available steam would be treating the whole feed and changing the amine flow. In this case, since the change in the steam flow is not combined with proportional change in the inlet streams flow the stripper operation changes and consequently the whole unit operation. For this reason the optimum conditions for the new case are expected to be different from the ones resulting from the optimization of the base case (100% steam and 100% feed), and an additional optimization might be needed.

4.3. Case study

A preliminary check for potential benefits of the second approach has been done, examining each time, if reducing the amount of feed to the percentage of the available amount of steam leads to better results than treating the whole feed. The study indicated that in all cases processing the whole feed was more promising. Since, as mentioned, in that case the unit operating conditions change, a new process optimization follows, in an effort to achieve some additional improvements/savings to the process. This new optimization aims this time to maximize the capture rate, since the energy consumed in the reboiler is now constrained by the available amount of steam.

As a base case file for this part, the optimized AspenPlus base case file has been used, with some additional changes. In particular, for the simulation of the second approach, the main challenge was the reduce in the reboiler duty (occurring since the change in the steam flow used in the reboiler can be translated to a proportional change in the reboiler duty) by fixing the amine flow; and has been implemented as design specification in the model.

For optimizing this approach again AspenPlus and MATLAB are used in combination, and the optimization method remained the genetic algorithm. The same optimization variables are taken into account and as constraints the convergence of the simulation, the feasibility of heat exchange in HEX2 with a respect to a minimum temperature difference of five degrees, and the top temperature of the stripper, are considered. The flow diagram of the optimization problems concerning this part can be summarized in Figure 4.1.

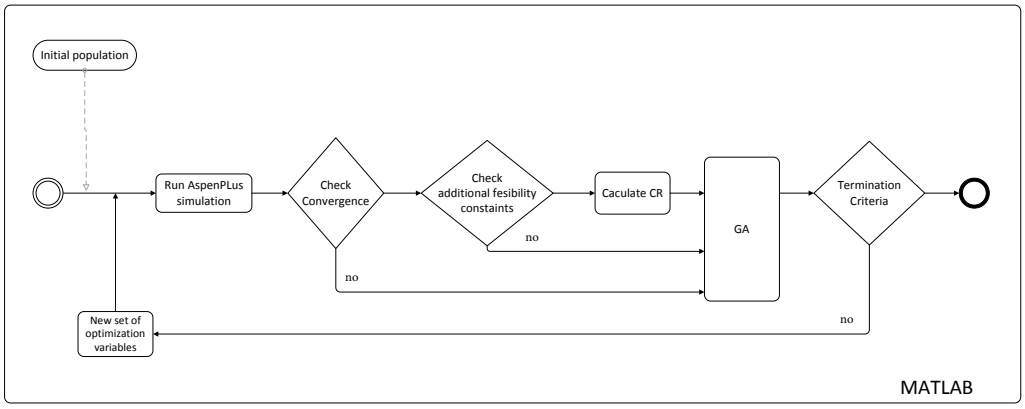

Figure 4.1.: *Optimization Process for Steam Limited Scenarios*

4.4. Results

The results of the initial comparison between the two approaches are shown for each scenario in the two first columns of Figure 4.2 and Figure 4.3, for the key indicators of capture rate and regeneration energy respectively. As already mentioned, it is clear that every time treating the whole feed leads to better results. However, this result no longer refers to the process optimum, since operating conditions has been changed. This is why a new optimization of the process is expected to give some improved results. The improved optimization results are shown each time in the last column of Figure 4.2 and Figure 4.3.

The optimized variables values for each case, composing the operation points for each scenario are summed up in Table 4.1.

Last but not least, for a better overview of the improvements achieved, two tables with the both capture rate (Table 4.2) and regeneration energy (Table 4.3) savings arising from the

application of the second approach and the optimization are created. It is to be noticed, that in the 90% scenario, the margins for improvements are not so wide since we are still operating near the optimum found for the base case, but as we proceed to examination of the scenarios with less steam available the optimization can achieve more significant improvements.

Table 4.1.: Multiple Operation Points- Variables Values

Scenario	Temp FLASH	Temp HEX2	Pres STR	Pres ABS	Amine Flow
1	374.79 K	299.79 K	1.345 atm	1.455 atm	17.75 l/min
2	374.57 K	295.35 K	1.470 atm	1.623 atm	15.74 l/min
3	376.27 K	301.32 K	1.595 atm	1.811 atm	13.59 l/min
4	376.75 K	300.82 K	1.717 atm	1.982 atm	11.57 l/min

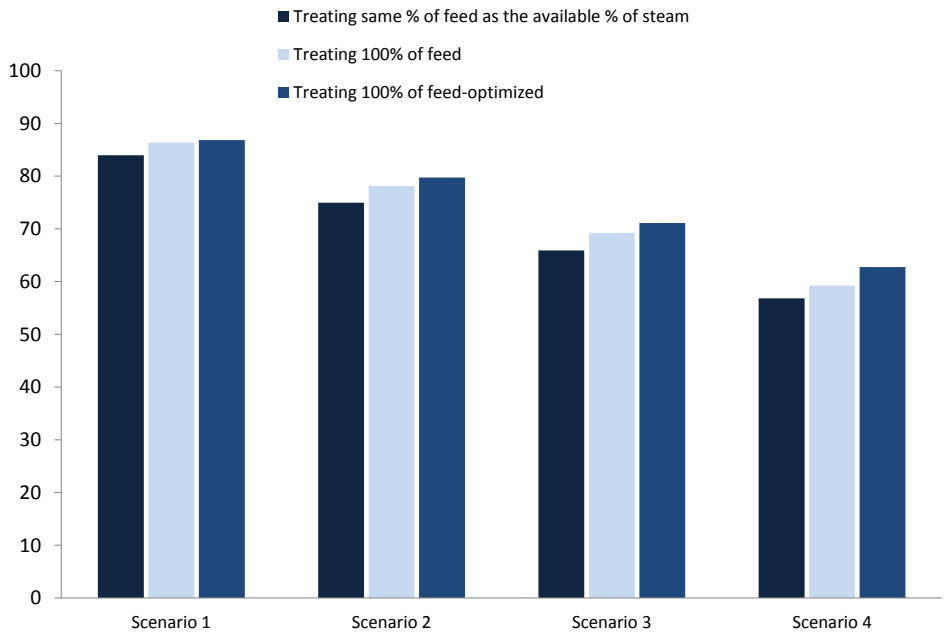

Figure 4.2.: *Multiple Operation Points CR (%)*

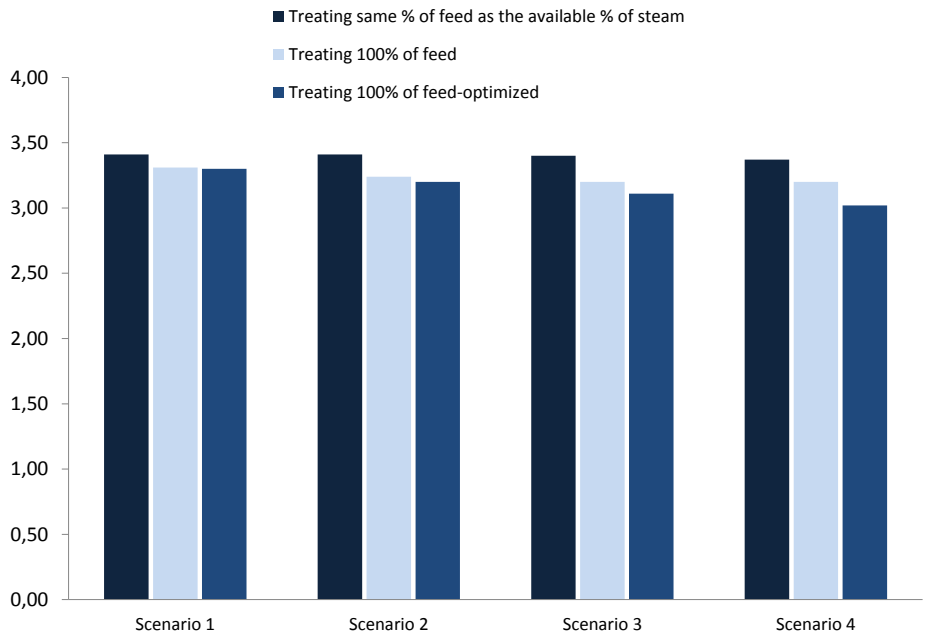

Figure 4.3.: *Multiple Operation Points RE (GJ/tonCO_2)*

Table 4.2.: Multiple Operation Points- CR Savings

Scenario	2nd Approach (%)	Optimization (%)	Total (%)
1	2.87	0.56	3.43
2	4.23	2.15	6.38
3	4.99	2.90	7.89
4	4.31	6.18	10.49

Table 4.3.: Multiple Operation Points- RE Savings

Scenario	2nd Approach (%)	Optimization (%)	Total (%)
1	2.93	0.29	3.23
2	4.99	1.17	6.16
3	5.88	2.65	8.53
4	5.04	5.34	10.39

5. Conclusions

This work dealt with CO_2 capture process by MEA. A rate based reactive distillation process model was constructed, based on real operating data. Consequently, an operating conditions optimization of the unit performance was attempted. This optimization managed to save up to 10% thermal energy in the process, just by adjusting the decision variables, without acquiring any retrofitting system for the process. The crossover heat exchanger HEX2 was found to have a major effect on the thermal energy requirement. That is why its optimized operation is crucial. Finally, by taking into consideration the limitation of steam, to which the whole process operation can be subjected, we ended up to the conclusion that the higher the steam limitation is, the bigger the need for optimization gets. This is expected, since as the steam availability decreases, the unit operation diverges more from the base case; and so more significant improvements by performing an optimization can occur.

Since steam availability affects a lot the unit operation it would be interesting in the future to examine the transient behavior from one condition to an other. This would acquire the extension of the steady state model to dynamic, and would provide an extra flexibility to the system.

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A. Abbreviations and Symbols

Abbreviations

$ALGA$	Augmented Lagrangian Genetic Algorithm
CCS	CO_2 Capture and Storage
$CDIAC$	Carbon Dioxide Information Analysis Center
CR	Capture Rate
$e.g.$	for example
GA	Genetic Algorithm
$GHGs$	Greenhouse Gases
$IGCC$	Integrated Gasification Combined Cycle
$IPCC$	Intergovernmental Panel on Climate Changes
MEA	Monoethanolamine
RE	Regeneration Energy