Dynamic Modelling of CO_2-removal units for an IGCC power plant

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Abstract

This article describes dynamic models of the carbon dioxide (CO_2) -removal units which are coupled with conventional models to form a complete model of an IGCC power plant with CO_2 capture.

Therefore some components of the Modelica_Fluid 1.0 library and packages of the Modelica.Media library from Modelica 3.0 were used. Not yet available components were developed.

The results obtained with Dymola 7.1 were compared with steady state simulations calculated with other tools (ChemCAD and Aspen Plus) and a very good agreement was found.

Keywords: IGCC, Rectisol Wash, CO Shift, CO_2-removal

1 Introduction

The object of interest is an Integrated Gasification Combined Cycle (IGCC) Carbon Capture & Storage (CCS) power plant with Siemens Fuel Gasifier Technology (SFGT). This is a climate-friendly power plant where a gas island consisting of gasification and a gas treatment is connected with a Combined Cycle (gas and steam turbine) to generate electricity.

The interactions between the several plant units are very complex and require a dynamic analysis to predict bottlenecks, to react to planned revisions (e.g. load changes), unplanned outages (gasifier trip, gas turbine trip, etc.) and to ensure the correct and safe operation behaviour of the plant. Furthermore the dynamic model is the basis for the development of an optimised control system. The overall object of the research is to raise the availability of IGCC power plants (Figure 1) because this is inevitably connected with the operating and therefore economic efficiency of the plant.
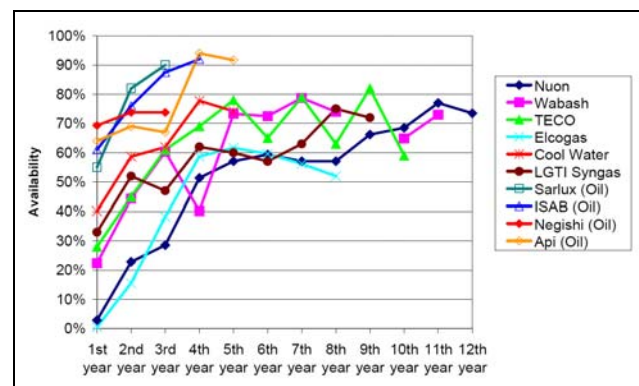

Figure 1: Availability statistics for IGCC first-of-a kind plant [1]

As illustrated in Figure 1 the availability rises over the years of operation. The aim is to start already with a higher availability and of course to operate the plant with a high availability. This demands an exact process knowledge which can be gained with dynamic modelling.

Making use of dynamic modelling for analysing IGCC processes gets more and more relevant.

Schoen for example used a dynamic model to control the performance of the Buggenum IGCC [2]. The U.S. Department of Energy's (DOE) of the National Energy Technology Laboratory (NETL) works on an IGCC dynamic plant simulator for a research and training center [3].

This contribution deals with the simplified modelling of the transient behaviour of an IGCC power plant with Modelica and Dymola with the focus on the gas path of the plant.

The introduction provides a short review of the IGCC power plant with CCS technology and the interaction of the sub-units.

The main part of the article describes the dynamic modelling of the CO_2-removal units: CO shift and Rectisol wash.

In the last part of the paper results of the modelled sub-units are demonstrated and an outlook of further challenges is given.

2 IGCC power plant

In Figure 2 the sub-units of an IGCC power plant and their main interaction flows are shown.
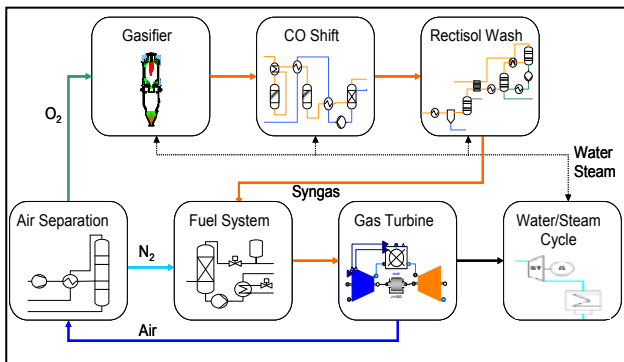

Figure 2: Simplified scheme of an IGCC power plant

In the gasifier the coal is gasified with oxygen (O_2) to produce a synthesis gas (syngas). The main components of the syngas are carbon monoxide (CO) and hydrogen (H_2).

In the next step the CO of the syngas is converted in the CO shift together with steam into CO_2 and H_2.

The formed CO_2, sulphur compounds like hydrogen sulphide (H_2S) and carbonyl sulphide (COS) and other impurities like nitrogen compounds are removed from the syngas by means of a physical wash, e.g. Rectisol or Selexol. In the presented contribution

the Rectisol wash is chosen which uses methanol (CH_3OH) as solvent. This physical scrubbing process separates highly purified CO_2 which allows the application of CCS technologies.

In the fuel system the cleaned syngas is diluted with nitrogen (N_2) to produce an utilisable fuel for the gas turbine to generate electricity.

Parts of the compressed air from the gas turbine compressor can be routed to the air separation unit. There the air is separated into O_2 for the gasification process and N_2 as fuel diluting agent.

The gasifier und gas turbine waste heat is used to generate steam. This steam is routed to a steam turbine for electrical power generation.

3 Developed Models

The motivation of using Modelica for this application is based on its multi-purposed, object-oriented background, which allows the user an equation-based approach. In contrast, tools like Aspen Dynamics offer already most of the required components and also more detailed media models, but are not that flexible for user specific developments.

For the implementation some models from the Modelica.Media and the Modelica_Fluid library were used. These libraries provide components to model thermo-hydraulic systems, but do not focus on gas dynamic problems [4]. Consequently components which are not yet available in the Modelica libraries, like the shift reactors or the absorber columns, were modelled. Further physical properties of methanol as physical solvent of the Rectisol wash and its mixture with CO_2 or water (H_2O) were defined as incompressible media.

Because of the complexity of the process many assumptions and simplifications were necessary to ensure a simulation in real time. For example the chemical water gas shift reaction and the sour gas absorption are approximated by interpolation functions depending on temperature. The developed models are based on the equations obtained from thermodynamic literature and assume equilibrium conditions with ideal behaviour in liquid phase and vapour phase.

Generally only the gas path is modelled and the water / steam cycle is neglected. The gas vector consists of the following 8 components:

$$N_2, H_2, CO, CO_2, CH_4, H_2S, COS, H_2O.$$

3.1 CO Shift

The CO shift is an equilibrium-limited reaction. *CO* reacts exothermally with steam at elevated temperatures according to:

$$CO + H_2O \rightarrow CO_2 + H_2. \quad (\Delta H_{298} = -41 \text{ kJ/mole}) \quad (1)$$
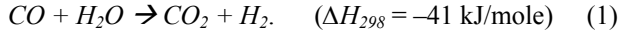
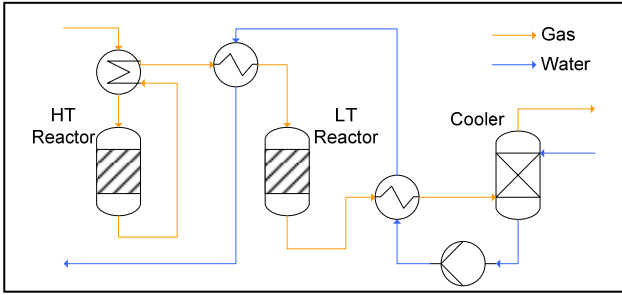Figure 3 shows a simplified process flow diagram for this application.

Figure 3: Process flow diagram of a CO shift

In the presented example the CO shift is carried out in two adiabatic reactors in series with intercooling.

Because of the already adequate moisture content after the gasifier with quench there is no saturation step necessary after the gasification island.

The heat of the exit gas from the first reactor (high temperature CO shift, HT) is recovered as high-pressure superheated steam. The steam produced after the second reactor (low temperature CO shift, LT) is recovered by further heat integration [5].

The *CO* concentration in the exit gas depends on the temperature and the mixture composition of the syngas which is provided by the gasifier.

In the first reactor the bulk of *CO* is converted. The LT reactor, which is installed downstream of the HT shift realises a *CO*-conversion down to parts per million (ppm) levels at the reactor outlet.

The reactors include a catalyst bed to promote the CO shift reaction. This catalyst is capable for the conversion of *CO* in sour gas. This means it is active in the presence of sulphur compounds. The positive side effect of this catalyst is the simultaneously executed COS hydrolysis with the following chemical reaction:

$$COS + H_2O \rightarrow CO_2 + H_2S. \quad (\Delta H_{298} = -35 \text{ kJ/mole}) \quad (2)$$
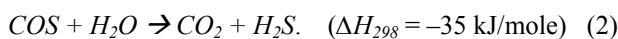
Down-stream of the CO shift reactors the shifted syngas is cooled down and the condensed water is separated and used for the intercooling.

3.1.1 CO Shift Reactor

In the reactor model the mass, component mass, energy and momentum equations have to be considered.

The balance equations were all effected by the CO shift and the COS hydrolysis. These chemical reactions can be considered as instantaneous that means that the chemical equilibrium is attained. The reactions are modelled with the help of conversion rates for *CO* and *COS* which are calculated by linear equations depending on the temperature T in a predefined interval as described as follow:

$$conversionrate(T) = a + bT. \quad (3)$$

The values for these linear equations were obtained by a sensitivity analysis of a CO shift reactor in Aspen Plus by varying the temperature in the corresponding interval. With these conversion rates the component mass balances are calculated. Based on this knowledge the energy balance can be specified with the exothermal heat of the CO shift and COS hydrolysis reaction. Therefore the heat values of the gas at the inlet and outlet are used. The energy balance also includes the reactor mass as heat storage.

The pressure drop depends on the mass flow. For the design case default parameters for both reactors are given. The following relation is used [6]:

$$\frac{\dot{m}^2}{\Delta p} = \frac{\dot{m}_0^2}{\Delta p_0}, \quad (4)$$

where $\dot{m}_0$ is the mass flow and Δp_0 the pressure drop in the design case.

Important for the design and the dynamic behaviour is also the space velocity, which has to be between 1,000 h^{-1} and 3,000 h^{-1} for this application [7]. In this example the space velocity is set to 2,600 h^{-1}.

3.1.2 Heat Exchanger

The heat exchanger is built on several heat nodes to realise more than one heat transmission point.

Every heat node consists of two vessels called ClosedVolume taken from the Modelica_Fluid library. They are connected by their heat ports with a given heat transfer coefficient. With the valves between the heat nodes the pressure drop, given as a constant parameter, is taken into account.
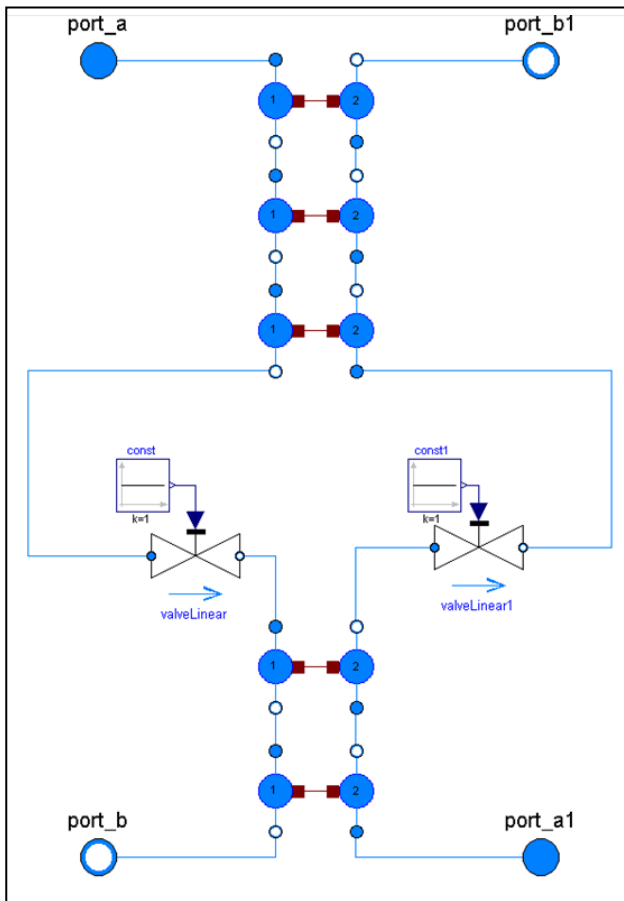
Figure 4: Schematic of the heat exchanger with 5 heat nodes in Dymola

3.1.3 Cooler

The cooler is located between the CO shift and the Rectisol wash.

In the cooler the gas is cooled down and the condensed water leaves the column.

To account for the temperature and moisture gradient the column is divided into theoretical stages, where the conservation laws are derived for each theoretical stage. The mass balance includes the gas and the water flows. For the water content in the gas the saturation state is calculated. The heat of condensation is considered in the energy balance. The pressure drop is assumed as constant for the complete column.

3.1.4 Specific challenges

The process flow diagram of the complete CO shift diagram in Dymola is shown in Figure 5.

The validation of the dynamic model is another challenge, because relevant dynamic data (T, X, p) from existing plants is not yet available. Nevertheless, steady state performance was validated with the help of simulation result in Aspen Plus and ChemCAD.

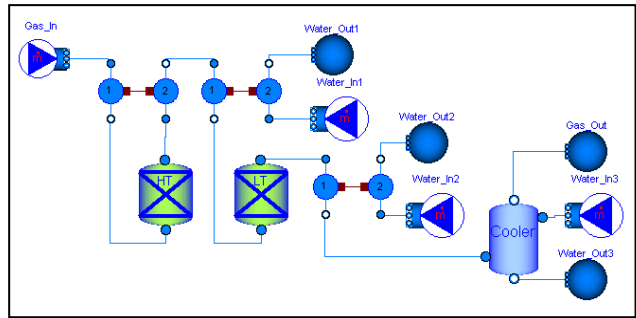The dynamic behaviour could only be validated via plausibility check.

Figure 5: Process flow diagram of the CO shift diagram in Dymola

3.2 Rectisol Wash

The Rectisol process is a physical wash process which uses cold methanol as physical solvent. The undesired components of the raw gas, that are produced in gasification with coal, such as CO_2, H_2S, COS, HCN, NH_3 and other traces are physically absorbed by methanol. In the regeneration part these components are desorbed by reducing the pressure of the solvent, stripping or reboiling the solvent.

The different solubilities of the components allow a selective removal of H_2S and CO_2 dependent on the temperature. Also the solubility of the trace components, which is much higher than those of H_2S, allows removing them separately in the prewash stage. This gives the ability to achieve very high gas purity with H_2S concentration of typically 0.1 ppm and CO_2 concentrations in the range of $2 - 4$ Vol.-% down to few ppm [7].

In Figure 6 the process flow diagram of the Rectisol plant in Dymola is presented. The process flow diagram shows a selective two-step design. This means that H_2S is removed in the first step followed by the CO_2-removal in the second step.

The raw gas entering the plant in the prewash stage is cooled. There trace components are removed at a very small cold solvent rate. The gas is first chilled by heat exchange with process off-gas and then by refrigeration.

Thereafter, in the H_2S absorber the sulphur is removed from the gas using a relatively small flow of CO_2-rich solvent to a residual sulphur content of below 0.1 ppm.

The CO_2 is removed in a two-stage CO_2 absorber with the main methanol flow. In the lower section, the CO_2 content of the gas is reduced to about 5 % using flash-regenerated methanol. The remaining

CO_2 is removed using regenerated, cold methanol in the upper section.

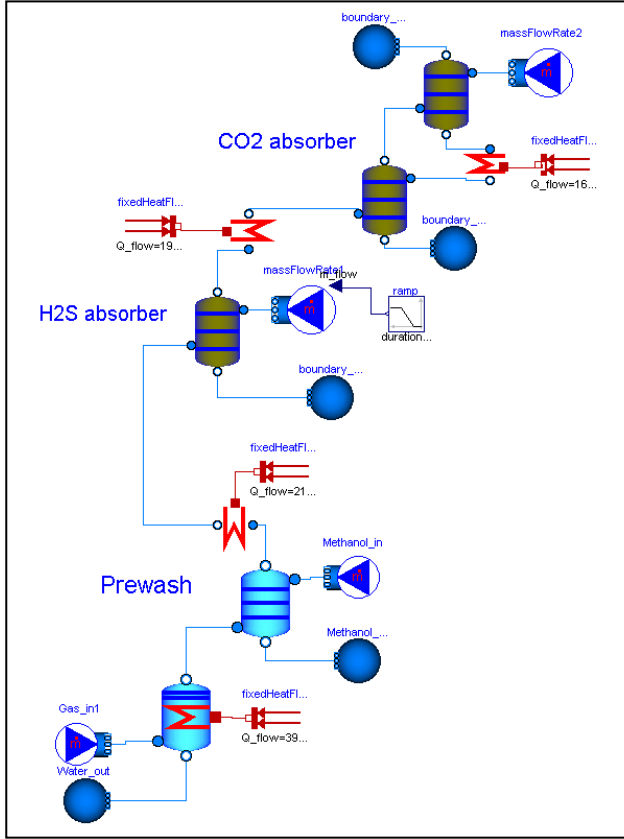The refrigeration balance of the system is maintained by an ammonia refrigeration plant.

Figure 6: Process flow diagram of the modelled Rectisol plant in Dymola

For the simulation of the Rectisol plant only the gas path is modelled. The regeneration of the methanol solvent and the interaction with the water steam cycle are neglected. Furthermore only the absorption of CO_2 into methanol is taken into account. There is no transfer of H_2S and other trace components considered.

3.2.1 Mixture of Methanol and CO_2

For the modelling of the Rectisol plant the solvent methanol and its mixtures with CO_2 or water are necessary. These media are not yet available in the Modelica.Media library. Therefore they were created as incompressible media with the help of tables. The minimal data set needed to describe the thermodynamic states is tables of the density ρ and the specific heat capacity c_p as functions of the temperature. For these values data from the NIST Chemistry WebBook was included [8].

For the mixture M of CO_2 and methanol ideal properties were assumed. This leads to the following equations, where the properties of the mixture follows from the properties of the components in respect of there mass fraction X:

$$\rho_M = 1 / \left(\frac{X_{CH_3OH}}{\rho_{CH_3OH}} + \frac{X_{CO_2}}{\rho_{CO_2}} \right), \tag{5}$$

$$c_{p,M} = X_{CH_3OH} \cdot c_{p,CH_3OH} + X_{CO_2} \cdot c_{p,CO_2}. \tag{6}$$

The same relations are used for the mixture of CH_3OH and H_2O needed in the prewash section.

3.2.2 Prewash

The Prewash consists of a cooler and a prewash column. In the cooler with condensate trap a predefined heat flow is released. In the prewash column a small methanol flow cools the gas down again and is derived together with the condensed water flow.

For the calculation of the saturated gas properties the same equations like in the cooler are used.

3.2.3 CO_2 Absorber

The raw gas enters the absorber column at the bottom section and is contacted with the scrubbing methanol introduced at the top of the column. The methanol leaves the column at the bottom together with the absorbed CO_2.

The modelling of the absorber column is based on the equilibrium stage model, which divides the column into theoretical stages and calculates the balance equations for each several stage (Figure 7).
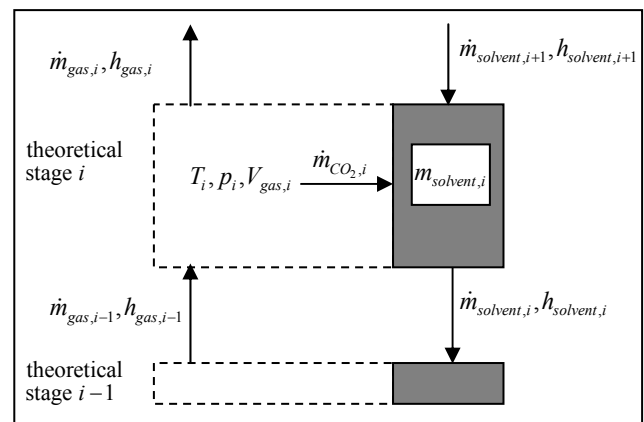

Figure 7: Schematically illustration of in- and output streams of a theoretical stage

In the CO_2 absorber there are two different media: the gas and the solvent. For each medium a mass balance is considered but only one energy balance is implemented.

The following modelling assumptions are used:

1) Each column theoretic stage is considered as an adiabatic system.

2) In the energy balance the wall material is regarded as a heat storage system and the exothermic process heat of the CO_2 absorption in the polar solvent is implemented.

3) On the liquid side methanol does not vaporise and hence does not go into the gas phase. Against on the gas side only CO_2 is transferred into the liquid phase.

4) This solubility of CO_2 in CH_3OH is a function of temperature at a partial pressure of one atmosphere.

5) For the gas / liquid equilibrium the ideal Henry law is used, even though this is completely reliable only at low molar fraction and at moderate pressure where no real gas behaviour is to be considered. The Henry law can be described with the following equation [9]:

$$Y_{gas,i} \cdot p = HK \cdot Y_{solvent,i}, \qquad (7)$$

where $Y_{gas,i}$ is the molar fraction of the component i in the gas, $Y_{solvent,i}$ the molar fraction of the component i in the solvent, p the pressure and HK the Henry coefficient. In this case CO_2 is meant by the component i.

6) To calculate the Henry coefficient experimentally investigated values [10] were interpolated and expressed as polynomial of the temperature T in a predefined interval:

$$HK(T) = a + bT + cT^2. \qquad (8)$$

7) For the pressure loss Δp only the hydrostatic part is considered [11]. Therefore it depends only on the solvent level h_{CH_3OH} on the theoretical stages:

$$\Delta p = \rho_{CH_3OH} \cdot g \cdot h_{CH_3OH}, \qquad (9)$$

where ρ_{CH_3OH} is the density of methanol and g the standard gravity.

3.2.4 Validation of the CO_2 absorber

The steady state results of the models were validated with calculations simulated with tools like Aspen Plus and ChemCAD. Therefore the CO_2 absorber is connected with sources and sinks of gas or solvent to compare the results for several cases between Dymola, Aspen Plus and ChemCAD (Figure 8).
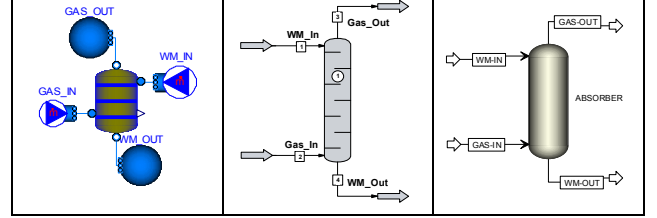

Figure 8: CO_2 absorber in Dymola (left), ChemCAD (middle) and Aspen Plus (right)

For the reference case the following input values are used.

	solvent_in	gas_in
$\dot{m}$ [kg/s]	568.07	225.80
T [K]	223.15	238.85
p [bar]	24.25	24.35
X_{N_2} [−]	0	0.090626
X_{H_2} [−]	0	0.058889
X_{CO} [−]	0	0.047220
X_{CO_2} [−]	0	0.803203
X_{CH_4} [−]	0	0.000062
X_{H_2S} [−]	0	0
X_{COS} [−]	0	0
X_{H_2O} [−]	0	0
X_{CH_3OH} [−]	1	0

Table 1: Input values in the CO_2 absorber for the reference case

In this table $\dot{m}$ is the mass flow, T the temperature, p the pressure and X the mass fraction.

The CO_2 absorber was simulated with 8 theoretical stages and the input values listed in Table 1 in ChemCAD, Dymola and Aspen Plus.
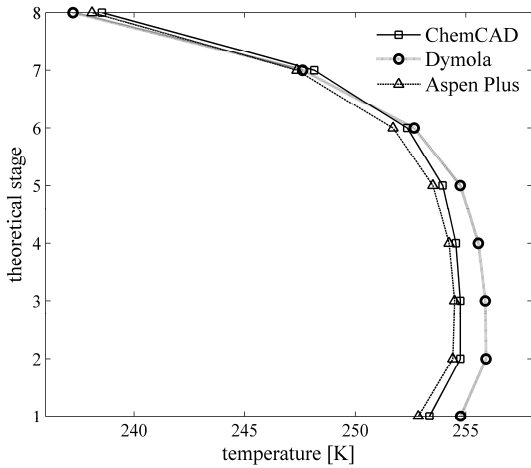
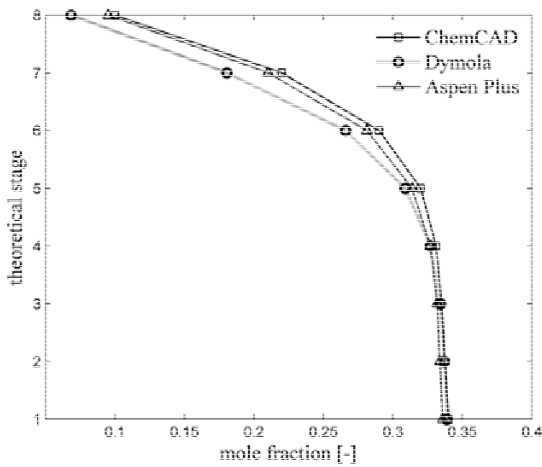Figure 9: Temperature profile of CO_2 absorber

Figure 10: CO_2 content profile in the gas of the CO_2 absorber

case 1	Reference case (Table 1)
case 2	$T_{gas\_in} = 228.85\,K$
case 3	$\dot{m}_{gas\_in} = 425.8\,kg/s$
case 4	$X_{CO_2,gas\_in} = 0.603203$ $X_{N_2,gas\_in} = 0.290626$
case 5	$\dot{m}_{solvent\_in} = 368.0345\,kg/s$
case 6	$T_{solvent\_in} = 243.15\,K$
case 7	$X_{CO_2,solvent\_in} = 0.15$ $X_{N_2,solvent\_in} = 0.85$
case 8	$p_{gas\_in} = 34.35\,bar$ $p_{solvent\_in} = 34.25\,bar$

Table 2: Variation of the input values of the CO_2 absorber

Figure 9 and Figure 10 show the absorber profiles of the temperature and the CO_2 content of the gas. The theoretical stage 8 is the head and stage 1 is the sump of the column. The profiles correlate very well with each other.

As shown in Table 2 the input values were varied for 8 cases.

Figure 11 to Figure 14 show the results of comparing the CO_2 content in the outlet gas and in the solvent and the associated temperatures of the gas and the solvent from the simulation in Dymola with the steady state results calculated in ChemCAD and Aspen Plus.
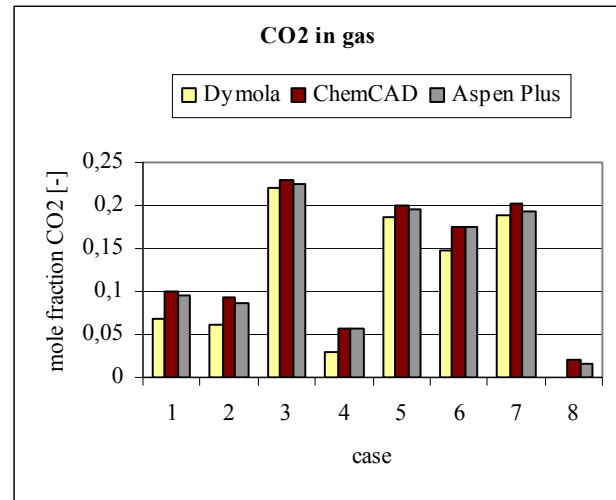

Figure 11: Mole fraction of CO_2 in outlet gas of CO_2 absorber compared between Dymola, ChemCAD and Aspen Plus
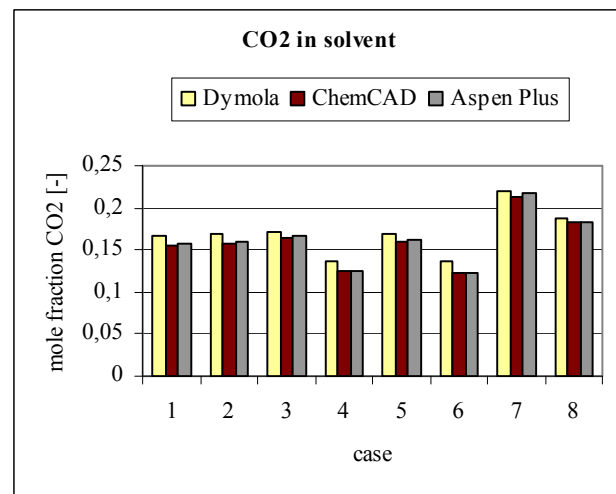

Figure 12: Mole fraction of CO_2 in solvent after CO_2 absorber compared between Dymola, ChemCAD and Aspen Plus
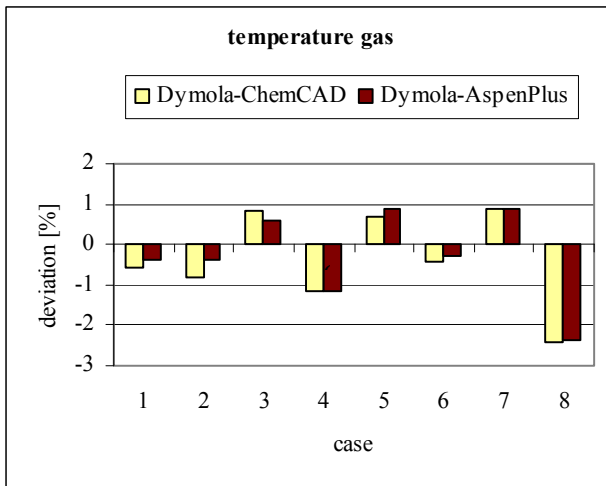
Figure 13: Deviation of temperature of the outlet gas of CO_2 absorber compared between Dymola and ChemCAD and between Dymola and Aspen Plus
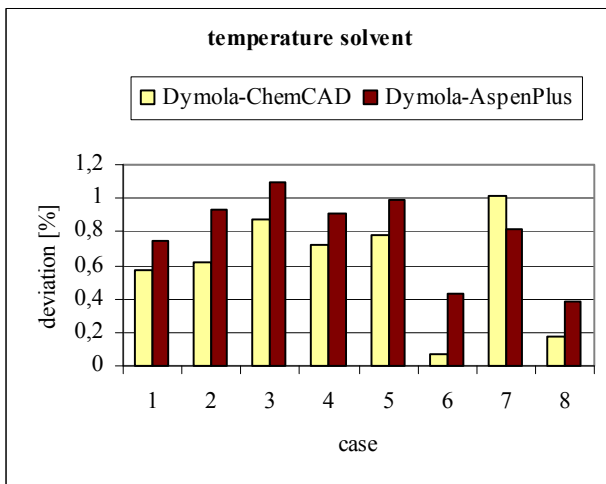

Figure 14: Deviation of temperature of the solvent after CO_2 absorber compared between Dymola and ChemCAD and between Dymola and Aspen Plus

As physical property model in ChemCAD the extended Soave-Redlich-Kwong method and in Aspen Plus the Predicted Redlich Kwong-Soave method were used. The results obtained in the Dymola model show similar results compared to the other simulation tools.

The main differences appear in the CO_2-fraction in gas in case 1 and 2 with 3.2 mole-% between Dymola and ChemCAD (Figure 11) and for the temperature in gas in case 8 with a deviation of 2.4 % between Dymola and ChemCAD as well as between Dymola and Aspen Plus (Figure 13).

4   Conclusions and Outlook

Dynamic models for the CO_2 removal were presented. Because of the ambition to guarantee a computing time faster than real time the resulting DAE systems were solved by the variable time step solver DASSL in Dymola.

The developed simulation models of the CO shift and the Rectisol wash have proven their capability to simulate complex power plant components.

A good agreement was observed for the steady state results of Dymola simulations compared to Chem-CAD and Aspen Plus calculations.

Future work will concentrate on power block models, a model for the air separation unit and the gasifier. At the end the overall ambition is to couple the dynamic models with each other in order to build a complete model of an IGCC with CO_2 capture. When all developed models have been sufficiently validated and connected various process studies of control concepts can be performed.

References

[1]   Holt, N.: Gasification Technology Status. Electric Power Research Institute EPRI, California USA, 2006

[2]   Schoen, P.: Dynamic Modeling and Control of Integrated Coal Gasification Combined Cycle Units. PhD thesis, Faculty of Mechanical Engineering and Marine Technology, Technical University Delft, 1993

[3]   Provost, G. T.; Erbes, M. R.; Zitney, S. E.; Phillips, J. N.; McClintock, M.; Stone, H. P.; Turton, R.; Quintrell, M.; Marasigan, J.: Generic Process Design and Control Strategies Used to Develop a Dynamic Model and Training Software for an IGCC Plant with CO_2 Sequestration. International Pittsburgh Coal Conference, Pittsburgh, USA, 2008

[4]   Casella, F.; Otter, M.; Proelss, K.; Richter, Ch.; Tummescheit, H.: The Modelica Fluid and Media library for modeling of incompressible and compressible thermo-fluid pipe networks. Proceedings of the 5th International Modelica Conference, Wien, 2006

[5]   Haldor Topsoe: Sulphur resistant water-gas shift/sour shift, www.topsoe.com, 2009

[6]   Perez, A. A. G.: Modelling of a Gas Turbine with Modelica. Department of Automatic Control, Lund Institute of Technology, 2001

[7]   Kohl, A.; Nielsen, R.: Gas Purification: 5th Edition, Gulf Publishing Company, Houston, Texas, 1997

[8]   National Institute of Standards and Technology (NIST) Chemistry WebBook, http://webbook.nist.gov/chemistry/form-ser.html (call date: 11-08-09)

[9]   Felli, V.: Appendix C: Analysis and simulation of a rectisol-based acid gas purification process. In: A cost-benefit Assessment of Gasification-Based Biorefining in the Kraft Pulp and Paper Industry, 2006

[10] Schroedter, F.; Melzer, W.-M.; Knapp, H.: Investigation of phase equilibria in multi-component mixtures consisting of propane, carbon dioxide, water and various organic solvents. Gas Separation and Purification, Vol. 5, 1991

[11] Sattler, K.: Thermische Trennverfahren, Grundlagen, Auslegung, Apparate. 3. Auflage, WILEY-VCH, Weinheim, 2001