Modelling of an oxygen transport membrane for an IGCC process with CO_2 capture

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Abstract
Different models of IGCC processes are presented in this work. First, an IGCC process without CO_2 capture is described in detail; different types of gasifiers and performance data of existing power stations are presented. Second, a new concept of an IGCC process with an integrated oxygen transport membrane reactor and CO_2 capture is proposed. Process simulations of the stand-alone oxygen transport membrane reactor and the oxygen transport membrane reactor as part of the IGCC process were carried out. The results showed that the operating conditions of the membrane reactor affect the overall performance of the IGGC process tremendously; a change in pressure from 2 to 15 bar on the permeate side of the oxygen transport membrane reactor, e.g., increases the efficiency by 5%-points.

Keywords: Gasification, IGCC, OTM, CO_2 capture, membrane

Introduction

A variety of methods for CO_2 capture in fossil fuel power generation processes are proposed in the literature [1]. The concepts differ in the arrangement with respect to combustion. They can be differentiated into: pre-combustion, integrated (oxyfuel combustion), and post-combustion CO_2 capture. An Integrated Gasification Combined Cycle (IGCC) with CO_2 separation is an example of a coal-based cycle with pre-combustion capture. Semi-closed gas turbine combined cycles, oxyfuel-fired boiler and chemical looping combustion (CLC) processes belong to the cycles with integrated CO_2 capture [1]. Post-combustion capture is normally carried out by chemical absorption using either aqueous monoethanolamine (MEA), diethanolamine (DEA), or mixtures thereof as solvents
An important similarity between the processes with fuel decarbonisation and oxyfuel cycles is the requirement of oxygen enriched air or technically pure oxygen as an oxidant in the combustion process. Conventionally, the oxygen is produced by a cryogenic air separation unit (ASU). Due to a high demand of electrical or mechanical power, there is a need to develop new technologies for producing oxygen which can be utilised in power generation processes. High-temperature membranes seem to be a very promising option for this.
In this paper, the integration of membranes into an IGCC process is described. Results of computational simulations of an oxygen transport membrane (OTM) are presented; operating conditions of the membrane are reported and their impacts on membrane performance with respect to oxygen permeation flow as well as implications regarding the steam power cycle are discussed.

Gasification

Gasification processes at an elevated pressure can be classified by the type of reactor: (i) moving bed, (ii) fluidised bed, and (iii) entrained flow reactor. Another way of categorisation is reasonable [2]:

- allothermal or autothermal gasification
- oxygen- or air-blown gasification
- cooled or adiabatic gasifier
- pressure and temperature level of the gasification

Figure 1 shows the different types of gasifiers. The major differences are the operating conditions, residence time of the fuel in the gasification process and the gasification temperature. The residence time of the coal in the gasification process varies from a few seconds in entrained flow gasifiers up to one hour in a moving bed reactor. A high temperature in the gasification process is required to get a high carbon conversion rate. A low carbon conversion rate represents a loss of thermal efficiency because the non-converted carbon leaving the gasification can no longer be utilised [3]. In addition, a high gasification temperature favours a high carbon conversion rate. On this account, oxygen-blown gasifiers are favourable for IGCC processes.

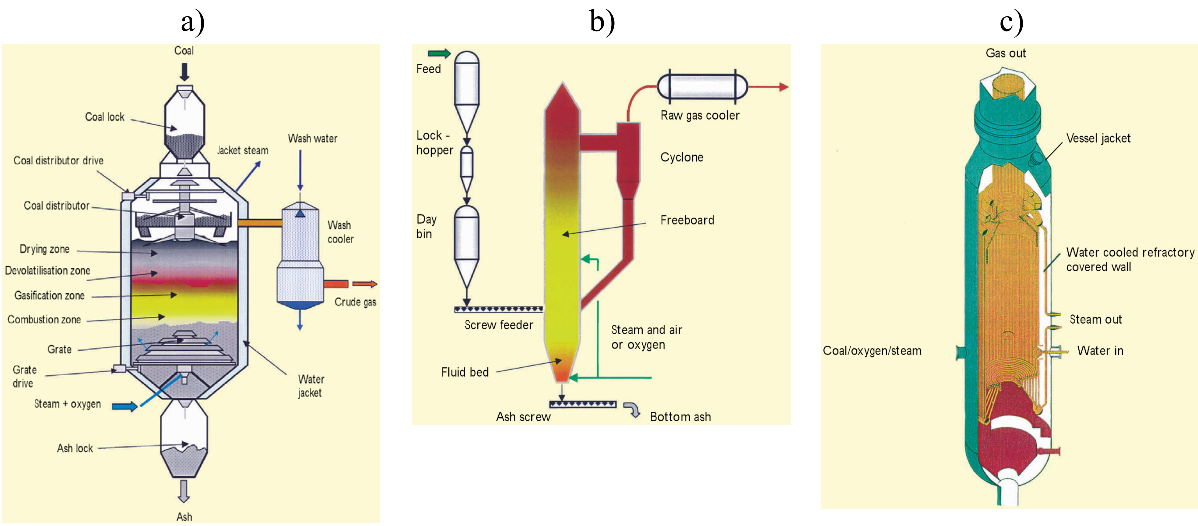

Figure 1 Different reactor types used in gasification:
a) moving bed gasifier b) fluidized bed gasifier c) entrained flow gasifier [4].

With regards to the occurring chemical reactions gasification of coal is a very complex process. The main chemical reactions determining the composition of the produced syngas contain the heterogeneous solid-gas reactions [5]:

Partial combustion	$C + \frac{1}{2} O_2$	⇔	CO	(exothermic)
Combustion	$C + O_2$	⇔	CO_2	(exothermic)
Gasification with hydrogen	$C + 2H_2$	⇔	CH_4	(exothermic)
Boudouard reaction	$C + CO_2$	⇔	$2\,CO$	(endothermic)
Gasification with steam	$C + H_2O$	⇔	$CO + H_2$	(endothermic)

and the homogeneous gas-gas reactions [5]:

Water-gas shift reaction	$CO+H_2O$	⇔	$CO_2 + H_2$	(exothermic)
Methanation	$CO+3H_2$	⇔	$CH_4 + H_2O$	(exothermic)

When modeling a gasification process using these main reactions chemical equilibrium is assumed without considering chemical kinetics. Although equilibrium is theoretically only reached after infinite time, the time of reaction in an entrained flow gasifier is so short that equilibrium can be assumed [2].Various authors [6, 7] apply this way of modeling the gasification by using commercial programs such as Aspen Plus.
Calculating the chemical kinetics for predicting the composition of the produced syngas [8, 9] is a more sophisticated approach. An in-house model for an entrained flow gasifier was developed at the University of Paderborn with co-operation with KTH, Stockholm [8, 10]. This model considers the chemical kinetics of 41 species. The equilibrium constants for each chemical reaction can be expressed as

$$k_i = \Lambda_i T^{\tau_i} e^{-\frac{E_{A_i}}{RT}} \qquad (1)$$

where Λ_i is the pre-exponential factor, T the temperature, E_{Ai} the activation energy and R the universal gas constant. For a broader explanations, see e.g. [11]. The chemical kinetics was modeled in MATLAB. The MATLAB functions were converted to MS Excel via a dynamic link library (dll).

IGCC process – general information and a new concept with an integrated OTMR

A simplified flow sheet of a conventional IGCC process is illustrated in Figure 2. Coal is gasified using steam (from the steam cycle) and technically pure oxygen (95 mol-%). The oxygen is produced by a cryogenic air separation unit (ASU). After gasification, particles are removed from the syngas, which is subsequently cleaned in various steps. Before combustion in a conventional gas turbine the syngas is saturated. The syngas contains mainly hydrogen and carbon monoxide as energy carriers. The exhaust gases from the gas turbine are led to a HSRG to drive a steam cycle. Some of the steam is produced in the gasifier by cooling the syngas after the gasification.

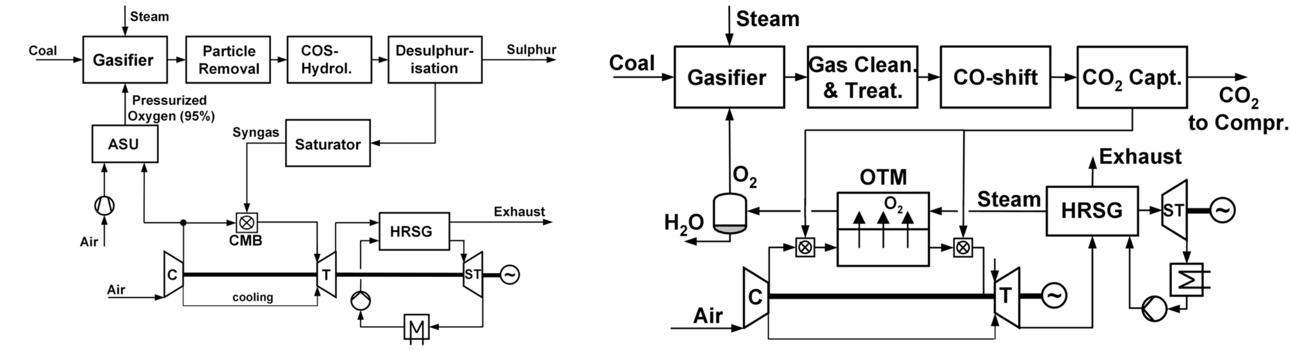

Figure 2 A simplified flow sheet of an IGCC process: w/o CO_2 capture on the left; with an integrated OTMR and CO_2 capture on the right.

In Europe, two IGCC power stations have demonstrated this technology in large scale applications: Nuon Power Buggenum (NL) and Elcogas Puertollano (E). Table 1 shows the performance data of both power stations:

	Nuon Power Buggenum (NL)	**Elcogas Puertollano (E)**
Feedstock	Coal (recently mixed with biomass)	Coal/ petroleum coke
Net Power Output	253MW	300MW
Net Efficency	43.2%	45.0%*
in operation since	1994/95	1998

Table 1 Performance data of IGCC power stations (* for high quality hard coal) [12].

The right flow sheet in Figure 2 shows a new concept for an IGCC with CO_2 capture . The feed stream of the OTMR is heated to about 900°C by combustion of hydrogen-rich syngas produced by the gasifier. Steam is used as a sweep stream for the OTMR; it is taken from the steam cycle. The retentate stream leaving the membrane is heated again to a conventional turbine inlet temperature (≈ 1425°C) before it is expanded in a gas turbine. The gas turbine and the cooling system are modelled according to [13].

Oxygen Transport Membranes (OTM) – Basics and description of the model

The importance of membranes for gas separation processes in general has increased in the last decades. Many studies about membranes and their practicability in power generation processes, including CO_2 capture, can be found in the open literature [1, 14, 15]. Inorganic membranes are considered the most promising membrane technology. For H_2, O_2, and CO_2 separation at high temperatures, the membranes are differentiated into: (a) dense Pd-based membranes for H_2 separation, (b) microporous membranes for H_2 and CO_2 separation, and (c) dense electrolytes and mixed conducting (ionic and electronic) membranes for O_2 and H_2 separation [14]. A common membrane design is an asymmetric structure. This type of membrane consists of a thin top layer determining the selective properties and a support structure providing mechanical strength.

Currently, the most promising membrane material for oxygen transport membranes is offered by the family of perovskites with the general formula $ABO_{3-\delta}$, where A is a mixture of alkaline and rare earth metals and B a mixture of Co and Fe [15]. However, membranes like this still show limited stability under large oxygen chemical potential gradients and high thermal expansion [16]. Recent experiments have shown that hollow fibre perovskite membranes of the chemical composition $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) [17] and $BaZr_xCo_yFe_zO_{3-\delta}$ (BZCF) [18] achieve high oxygen permeation fluxes and good mechanical stability. Therefore, Schiestel et al. [18] recommend perovskite hollow fibre membranes for industrial applications.

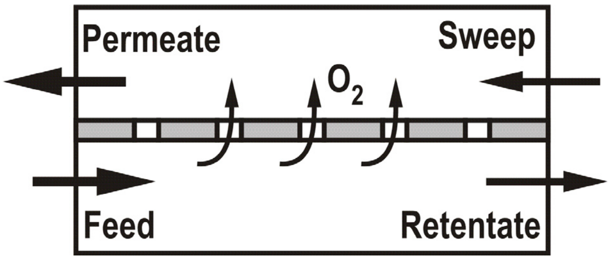

Figure 3 Schematic design of the OTMR.

In this paper, an oxygen transport membrane reactor (OTMR) is modelled as a counter current flow reactor. The design of the membrane reactor is schematically shown in Figure 3. For now, the model takes heat and mass transfer through the membrane and given pressure losses on the permeate and retentate side of the membrane into account. The reactor is modelled in MS Excel using the finite difference method. Pressure, partial pressure of oxygen, temperature, and specific heat capacity are calculated for each element. Property calculations are carried out in MS Excel via a plug-in from Aspen Properties 2004.1 using the PSRK equation of state.
The oxygen permeation flux N through the membrane can be expressed in terms of Fick's law [19]

$$N = \frac{D}{l_M} \ln\left(\frac{p_{O_2\,\mathrm{Ret}}}{p_{O_2\,Perm}}\right) \tag{2}$$

where D is the oxygen diffusivity, l_M the membrane thickness , and p_{O2} the partial pressure of oxygen. The diffusivity D can be described by the Arrhenius equation taking the temperature dependence into account

$$D = D_0 e^{-\frac{E_A}{R\,T}} . \tag{3}$$

In Eg. (3) E_A stands for apparent activation energy, R for the gas constant, and T for the thermodynamic temperature. Equation (2) and (3) lead to the oxygen permeation flux N in terms of temperature and partial pressure ratio

$$N = \frac{D_0}{l_M} e^{-\frac{E_A}{R\,T}} \ln\left(\frac{p_{O_2\,\mathrm{Ret}}}{p_{O_2\,Perm}}\right) \tag{4}$$

The eligible parameters were verified by experimental data from Shaula et al.[20]. They have been chosen as follows: $D_0 = 0.05$ mol min^{-1} s^{-1}, $l_M = 0.2$ mm, and $E_A = 50$ kJ/mol. The flux is calculated for each element for a given overall membrane surface. Heat and mass transfer are related to each other; heat transfer without mass transfer is calculated first to get a temperature profile along the membrane. The calculated temperatures are then used as starting values for the temperature profile considering mass transfer as well. The final results are calculated by iterative loops.

Results of Process Simulations

Calculations for the stand-alone OTMR and the OTMR as part of the IGCC process were carried out. The calculations of the stand-alone OTM reactor were performed to better understand the key parameters of the membrane.

The feed conditions. i.e. mass flow rate (150 kg/s), pressure (20 bar), and composition (O_2, N_2, H_2O, CO_2, Ar: 0.16, 0.76, 0.05, 0.02, 0.01 mol/mol) were kept constant for the OTMR calculations. The overall surface of the membrane was 30,000 m^2. Temperature of the feed stream, pressure and mass flow rate of the sweep stream were varied.

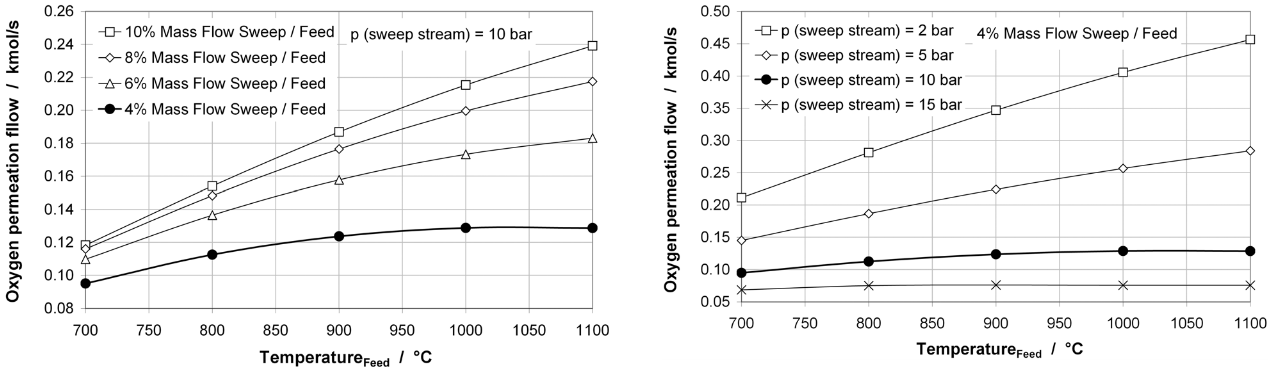

Figure 4 Oxygen permeation flow vs. feed temperature. Left: various sweep streams ($\Delta p_{Ret\text{-}Perm}$ = 10 bar). Right: different $\Delta p_{Ret\text{-}Perm}$ for a constant sweep stream.

The left chart of Figure 4 shows a strong dependence of oxygen permeation flow rate on the sweep stream mass flow rate; the pressure on the permeate side of the membrane is 10 bar. Parametric studies have shown that this effect increases with lower pressures on the permeate side. The right graph of Figure 4 illustrates the decrease in temperature dependence of the oxygen permeation flow at small total pressure differences between the retentate and the permeate side of the membrane; the sweep stream flow rate is set to 4% of the feed stream flow rate. Only at large total pressure differences between the permeate and retentate side of the membrane does a rise of the feed temperature lead to significantly increased oxygen permeation flow.

The implications of the performance of the OTM reactor for the IGCC process are representatively shown in Figure 5 by varying the pressure on the permeate side of the membrane. The results indicate that the operating conditions of the membranes have a tremendous effect on the overall efficiency of the power generation process with the integrated OTM reactor. An increase in the pressure of the sweep streams is associated with a rise in temperature because the steam is taken from the intermediate pressure steam turbine which lowers the steam section power output.

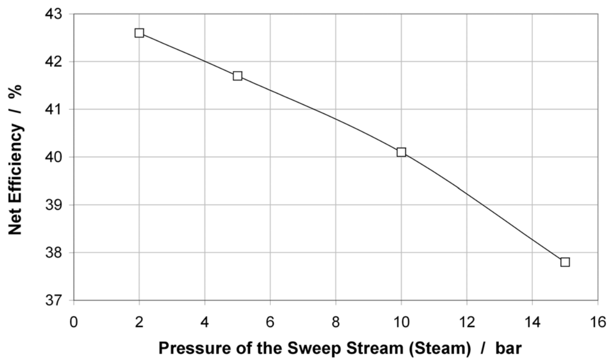

Figure 5 Net efficiency of the IGCC process vs. pressure of the sweep stream.

Conclusions

The IGCC power generation process is highly sensitive to the operating conditions of the membrane reactor. A key parameter is the total pressure difference between permeate and retentate in the OTMR. The partial pressure ratio, which is the driving for the mass transport through the membrane, can either be increased by a large sweep stream mass flow rate or by a high total pressure difference between permeate and retentate sides. Results of parametric studies of these operating conditions will be presented on the poster. Additional parameter variations such as the pressure loss on both sides of the membrane will be discussed in the poster session at the GHGT-8. Furthermore, the described models of the gasification process are to be compared.

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