INTEGRATED ASSESSMENT OF WATER-GAS SHIFT Pd-MEMBRANE REACTOR FOR CO_2 CAPTURE

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Introduction

Applying CO_2 capture in power processes is to a large extent a question about integrating gas-separating process units. Regardless of technology (e.g. membranes, sorbents, solvents, cryogenic), it is important that an assessment is made of the performance of the overall CO_2 capture process with the novel capture-related process units operating under relevant conditions and with relevant parameters describing the unit performance. Within the BIGCCS centre, *integrated assessment* of CO_2 capture technology has therefore been made one of the research tasks. The studies on CO_2 capture within BIGCCS are conducted on three levels:

1) Fundamental research (e.g. membranes, sorbents, solvents)
2) Unit design and modeling (e.g. modeling of membrane reactors, sorption enhanced CO_2 capture or reforming, absorption and desorption with solvents)
3) Process design, modeling and simulations

We present work in progress on a 1D MATLAB code for a membrane reactor that has been linked to Aspen HYSYS through CAPE-OPEN. This enables process simulations where studies can be made of how changes in membrane reactor parameters affect overall process performance. The overall goal with this activity is to enable us to design new power cycles and obtain realistic process performance results which, will give useful feedback for further membrane development.

In the present work, varying expressions of the hydrogen flux for Pd-membranes in co-current Water-Gas Shift (WGS) reactors are employed to study the effects on hydrogen recovery and fuel production for Integrated Reforming Combined Cycle (IRCC) processes. The IRCC cycles studied in the literature typically consist of an air- or oxygen blown Auto Thermal Reformer (ATR), followed by high-temperature and low-temperature WGS reactors and CO_2 capture through absorption using MDEA. Typical energy penalty for such a process compared to an NGCC without capture amounts to 11-13 percentage points. In the membrane reactor, WGS and continuous H_2 separation occur simultaneously, thus eliminating the intermediate cooling and heating process steps and enabling a shift in reactor equilibrium, which permits the reactor to be operated at conditions expected to involve lower losses.

Membrane reactor model

A membrane reactor model with one-dimensional balance equations was implemented in MATLAB. The model is generic, meaning that it can be applied to both flat-plate and tubular geometries, and both for Water-Gas Shift and Steam-Methane Reforming [1] membrane reactors. Either Palladium-based (Pd-based) or dense ceramic membranes for H_2 separation

can be applied, through a change in the choice of flux model. For the current work, only Pd-based flux models were investigated, due to the relatively low flux of dense ceramic membranes at the investigated operating temperatures (300-600°C). The reaction kinetics were modeled by the equations proposed by Xu and Froment [2].

Modeling of H_2 flux through Pd -alloy membranes

Pd and many Pd-alloys have high solubility (S) and diffusivity (D) of H_2, and show great promise as membranes for medium to high temperature H_2 separation (~300-600°C). This type of membranes provides the best selectivity-flux combination of all the membrane classes. The H_2 flux through Pd membranes, F, ($mol \cdot m^{-2} \cdot s^{-1}$) may be given by

$$F_{H_2} = \frac{S \cdot D}{L} \cdot \left(\left(P_{H_2}^f \right)^n - \left(P_{H_2}^p \right)^n \right) = \frac{Q}{L} \cdot \left(\left(P_{H_2}^f \right)^n - \left(P_{H_2}^p \right)^n \right)$$

where L is the membrane thickness, and $P_{H_2}^f$ and $P_{H_2}^p$ are the H_2 pressure on the feed and permeate side, respectively. The product of the diffusivity, D, ($m^2 \cdot s^{-1}$) and solubility, S, ($mol \cdot m^{-3} \cdot Pa^{-n}$) is often referred to as the H_2 permeability, Q. When the H_2 flux is limited by diffusion through the membrane material, i.e. follows Sieverts' law, the H_2 pressure exponent, n, is ideally equal to 0.5. Variations in H_2 diffusivity and solubility with pressure, or surface contaminants like CO, however, can alter the *n*-value. For example, an *n*-value close to 1 is typical for a membrane where the H_2 flux is governed by surface rate limitations. In order to investigate the effect of the *n*-value on the outcome of the WGS reactor model we have applied the following values for *n*: 0.5, 0.63, and 1. A value of 0.63 is shown to provide the best fit describing the H_2 flux at a pressure between 2 and 26 bars, while 0.5 and 1 are the extreme values for diffusion and surface limiting cases, respectively.

Integration of membrane reactor model in Aspen HYSYS

The MATLAB membrane reactor model was integrated in Aspen HYSYS using CAPE-OPEN. The integrated model was employed for investigating hydrogen recovery rate and hydrogen flux through the membrane for fuel streams from oxygen-blown and air-blown AutoThermal Reformer (ATR) reactors. The n-value was varied as described above, for varying reactor tube length (from 8-20 meters). Since co-current and counter-current membrane reactor models give more or less the same CO conversion rate for the same membrane reactor input parameters, simulations were done with the less time-consuming co-current reactor model.

Results, conclusions and further work

The developed membrane reactor model, that was linked to Aspen HYSYS, enables studies on how changes in membrane parameters (e.g. *n*-value) affect the overall process results. The difference in H_2 recovery rate and flux for different *n*-values is significant for shorter reactor tubes, but negligible for longer tubes. As expected, the use of an air-blown ATR decreases the H_2 recovery due to decreased hydrogen partial pressure on the membrane feed side.
Further work will incorporate more extensive process simulations in order to highlight future research directions for membrane development, and useful applications for the membrane reactor will be investigated. The applications are foreseen to cover different aspects of hydrogen production with integrated CO_2 capture.

[1] Wilhelmsen, Ø., Anantharaman, R., Berstad, D., Jordal, K., 2011, "Multi-Scale modelling of a membrane reforming power cycle with CO_2 capture", Proceedings of 21st European Symposium on Computer-Aided Process Engineering (ESCAPE 21), May 30th -June 1st , Thessaloniki, Greece

[2] J. Xu and G.F. Froment, 1989, "Methane Steam Reforming, Methanation and Water-Gas Shift: I. Intrinsic Kinetics", AlChe, 35, 1, 97-103