

Advanced Membrane Reactors in Energy Systems A Carbon-Free Conversion of Fossil Fuels

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Introduction

A sustainable use of fossil fuels in the future will undoubtedly make use of concepts, where the energy content of the fossil fuel is first transferred to hydrogen, followed by the conversion to the desired energy form. The driving force for these concepts is the possibility of capturing CO₂ elegantly, while using the favorable thermodynamics to increase the efficiencies of fossil fuel conversion. We, ECN and TU-Delft, have identified membrane reactors as a game changing technology for highly efficient conversion of fossil fuels to carbon free energy carriers.

The purpose of this project is to develop hydrogen and CO₂ membranes to allow combination of natural gas reforming with H₂ or CO₂ separation in separation enhanced reactors, i.e. membrane reactors, for carbon-free hydrogen production or electricity generation. These devices offer multiple advantages, such as eliminating the requirement of water gas shift reactors with associated costs reductions; offering higher conversion efficiencies at lower temperatures; and decreasing primary energy use for CO₂ separation/capture associated with electricity generation.

Background

The steam reforming and the water gas shift equilibriums are key reactions for the production of hydrogen from fossil fuels:



By removing either CO₂ or hydrogen from the reaction mixture, the equilibrium can be shifted to the product side. Effectively, this can lower the reaction temperature and improve the purity of the product. In conventional, hydrogen production from natural gas, the steam-reforming step is followed by two water gas shift (WGS) reactors. When

separating either CO₂ or hydrogen inside the reforming reactor, both the WGS steps can be eliminated. This implies that separation-enhanced techniques can also lead to investment costs reductions. Hydrogen or CO₂ separation is a flexible technique that can be used in hydrogen production from natural gas, but also can replace the WGS section of an IGCC or Biomass gasification plant. These techniques are especially suited for CO₂ capture, because the production of pure hydrogen and CO₂ streams is intrinsic to separation-enhanced reactors.

The combination of separation and reaction, as foreseen in membrane reactors, offers higher conversion of the reforming reactions at lower temperatures due to the removal of hydrogen or CO₂ from these equilibrium reactions, as shown in equations 1 and 2. For instance, in case natural gas reforming for carbon free hydrogen production, the use of membrane reactors will result in significantly lower operation temperatures (400 - 500°C) and higher efficiencies 85 - 90 instead of 75%.[1] In fact membrane reactors allow for low-irreversibility production and conversion of hydrogen to another energy form with integrated CO₂ capture.

Membrane reformers/reactors can be integrated in power generation systems but also in central heating devices. Our assessment studies clearly showed that in a more integrated approach of electricity production and CO₂ capture, using high-temperature membrane reactors will result in a substantially lower primary energy use for the CO₂ separation/capture [2]. Besides that, the low operation temperature of the membrane reactor creates possibilities for so-called chemical recuperation, compensating part of the CO₂ capture efficiency penalty.

The tasks defined within this project are:

Task 1	System analysis and thermodynamic evaluations	Executed by ECN
Task 2	Hydrogen membrane research and development	Executed by TUD
Task 3-a	Hydrotalcite CO ₂ membranes research and development	Executed by ECN
Task 3-b	Ionic liquids CO ₂ membranes research and development	Executed by TUD
Task 4	Catalyst screening	Executed by ECN
Task 5	Reactor modeling and design	Executed by ECN

Tasks 1, 4 and 5 pertain to both the hydrogen and carbon dioxide membrane cases.

Results

System and reactor analysis:

In the current project two types of membranes are under study: a H₂ selective and a CO₂ selective one. Prior to material development it should be clear whether application of the one is preferred to the other. Therefore we set out to make a fair comparison by assigning the same properties to a membrane black-box either fit for H₂ or CO₂ separation.

The present status as to the pros and cons for H₂ or CO₂ separation is the following:

- Separating CO₂ from Natural Gas Steam Reforming mixtures has the largest beneficial influence on conversion as compared to H₂, however, the driving force for

separation is close to zero in this case (Figure 1) due to the already low CO_2 partial pressure in the feed

- Application of membranes in combination with the Water Gas Shift reaction yields only a slight preference for H_2 separation
- Changing to low H_2/CO_2 ratio feedstock as from coal gasification (Figure 2) ensures the applicability of CO_2 separating membranes in all situations. Detailed overall system and exergy analyses are needed to discern between H_2 and CO_2 membranes in this case
- A sensitivity analysis on all important parameters involved indicate that there is no clear-cut optimum in parameter space

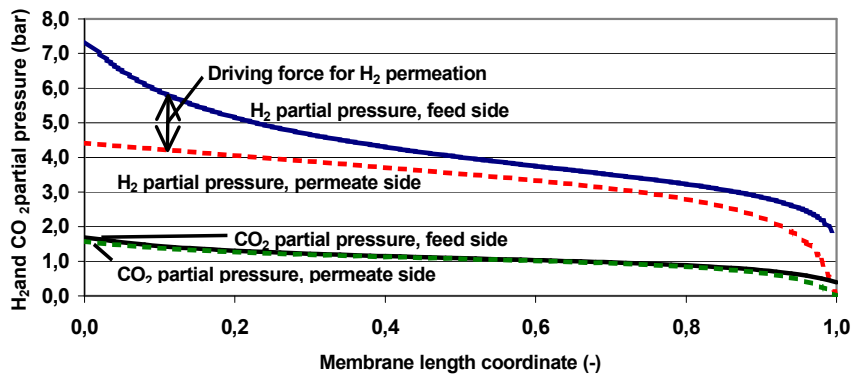


Figure 1 H_2 and CO_2 partial pressure profiles in a membrane reactor for natural gas steam reforming clearly showing that in this situation there is no driving force for CO_2 permeation

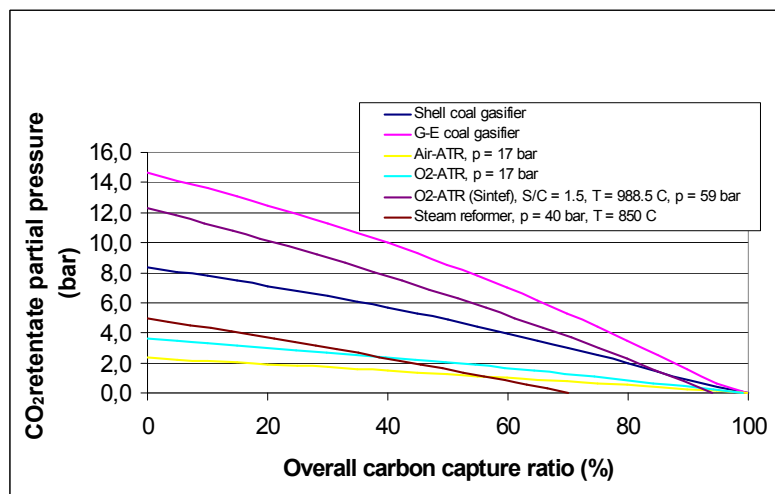


Figure 2 Carbon capture ratio versus CO_2 retentate partial pressure for different upstream processes: the General-Electric coal gasifier performs best, SR of natural gas worst.

- A short communication on this subject is currently being written; two conference papers have been submitted (GHTG-8 Trondheim Norway, Fifth Annual Conference on Carbon Capture & Sequestration Alexandria Virginia U.S.)

Two advanced membrane reactor configurations will be compared with respect to implementation in an Integrated Gasification Combined Cycle (IGCC) with carbon capture. The configurations enclose a water-gas-shift reactor for synthesis gas conversion, which is integrated with a hydrogen or carbon dioxide selective membrane. Each energy conversion system will be optimized on basis second law thermodynamic analysis, after which the conclusive assessment will take place by comparison of efficiency penalties and associated costs. The basic process flow schemes have been modeled in ASPEN+. For the modeling of the membrane reactors a water gas shift membrane reactor model written in FORTRAN is integrated in Aspen Plus. Finally, in order to perform the exergy analysis the dedicated subroutine "EXERCOM" is acquired and successfully coupled to the process flow simulator.

Membrane materials research

An inventory made on CO₂ membranes and membrane materials for CO₂ separation yields the following general conclusions:

- Existing polymer and polymer-hybrid materials are no options for CO₂ membranes due to loss of selectivity at operating temperatures higher than 100-200°C
- Porous or dense ceramic membranes with or without promoters like alkali carbonates, zirconates etc. are viable options that have to be explored further. They comprise among others porous or dense hydrotalcites and alumina impregnated with hydrotalcites
- Systems based on molten carbonate like concepts require too high an operating temperature to ensure reduction of energy use and CO₂ emissions
- Exotic new, scarcely investigated, compounds like calixarenes cannot *a priori* be excluded, but are too far out with respect to our established competences and skills. Production is still on the milligram scale and the possible use as a membrane material only speculative. Naturally any progress in the development of this kind of materials will be monitored.

The structural aspect of water and carbonate bearing layers in between sheets of magnesium-aluminium hydroxide in hydrotalcites leads to the assumption that both dense and porous membranes may be produced from this compound. They have already proven their applicability as CO₂ sorbent in sorption enhanced reaction processes [3]. As of October 1st 2005 a PhD student has started on the membrane materials development part. The first aim is to determine the stability window of hydrotalcites,

$M_6^{2+} M_2^{3+} (OH)_6 CO_3 \cdot 4H_2O$ with Mg²⁺ and Al³⁺ as cations, as to temperature, CO₂ and H₂O partial pressures and compositional differences between various commercial and in-house synthesized materials. To this end, *in-situ* XRPD (X-Ray Powder Diffraction) and DRIFT (Diffuse Reflectance Infrared Fourier Transform) as well as NPD (neutron powder diffraction), TGA-MS (Thermogravimetry-Mass Spectroscopy) and SEM-EDX (Scanning Electron Microscopy-Energy Dispersive X-ray analysis) measurements have been performed.

The present main conclusions can be formulated as follows. Commercial and homemade hydrotalcites seem to exist in a rather narrow phase width, where Mg/Al is about 65%. Large deviations invariably lead to the formation of impurity phases being either Mg or Al rich (Figure 3). Hydrothermal synthesis always gives more crystalline

materials than the Pural (Sasol) commercial ones. The often reported 'structural memory effect' could not be reproduced in using a humidified atmosphere (Figure 4). This does not mean that the sorption characteristics cannot be recovered. The active species are presumably just the hydroxyl groups and not the structure as such.

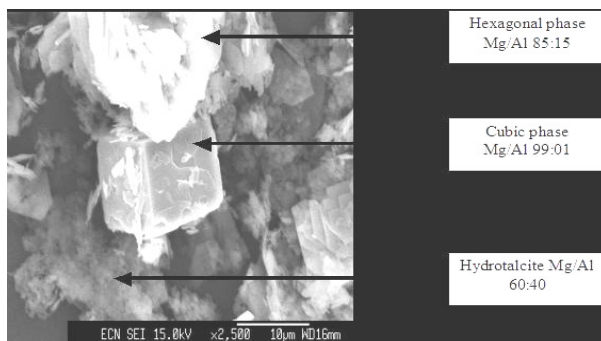


Figure 3 SEM-EDX result for hydrothermally synthesized 'Mg90' (Mg/Al=0.9, Mg rich)

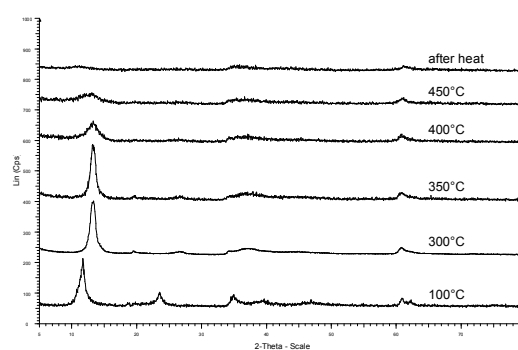


Figure 4 *In-situ* XRPD patterns of commercial MG50 (Mg/Al=0.5) as a function of temperature

The operational window for hydrotalcite as a membrane material is limited to 400°C. Since this is the target temperature for our membrane reactor (WGS) process this means that hydrotalcites are a viable option as a membrane material. It is still unknown whether hydrotalcites show bulk diffusion of CO₂, which opens the possibility of using dense membranes with high selectivity.

- One conference paper on this subject has been submitted (ICIM-9 Lillehammer, Norway)

Catalyst screening

The work planned for the first part of the catalyst task, is the screening of catalysts to assess the applicability of commercially available catalysts in either CO₂- or hydrogen-separating membrane reactors. In the reporting period four commercial Methane Steam Reforming (MSR) catalysts were tested. In Figure 5 the activity and stability of these catalysts at 400 °C is compared to three different non-commercial catalysts prepared by ECN. In between the data points showed in the graph, conditions were varied between hydrogen rich (to simulate conditions in a CO₂-separating membrane reactor) and carbon rich (to simulate a hydrogen-separating membrane reactor). Two of the ECN-catalysts and commercial catalysts B2 and C1 showed the highest initial activity. All catalysts apart from the B1 catalyst showed a similar initial deactivation, which resulted in stable operation after 100 hours at a lower methane conversion level. Interestingly, the commercial B1 catalyst, which did not show deactivation, has nickel as the active metal, while all other catalysts are noble-metal based.

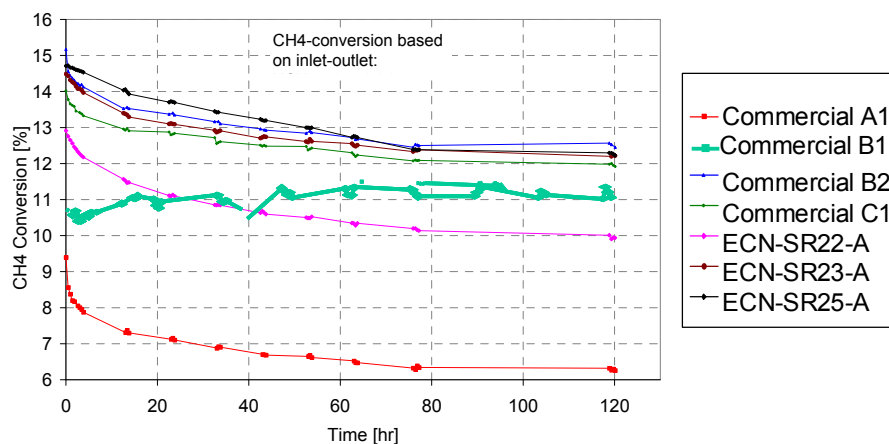


Figure 5 Methane conversion at 400°C and 3.5 bar(a) vs. time-on-stream. The catalysts were strongly diluted to exclude temperature effects and care was taken that the methane conversion was far from equilibrium.

Progress

- The necessary preliminary studies as to what knowledge is available on CO₂ separation materials and membranes (part of task 3) and the technical viability of H₂ and CO₂ separating membranes (part of task 1 and 5) have been performed. Both membranes are viable options albeit in their own field of application: H₂ membranes for high H/C and CO₂ membranes for low H/C ratios.
- Hydrotalcites have been characterized as to their decomposition behavior and their compositional and structural properties: the temperature window is limited to 400 °C, there is no structural memory effect. Hydrotalcites seem to exist only in a very limited phase width with an Mg/Al ratio of about 0.65.
- Both commercial and ECN made catalysts exist that after initial deactivation show a stable performance at T=400 °C under both carbon and hydrogen rich conditions.

Future Plans

Task 1 Exergy analyses will be done for different system configurations: fuels, applications, membranes etc. in order to further nail down the most viable options for the application of this kind of membranes in carbon capture technologies.

Task 3 Analyze neutron data in order to establish exact Mg/Al ratio. Establish transport mechanism on pure, crystalline, hydrotalcite membrane material. Determine isosteres for hydrotalcites both for water and for carbon dioxide

Task 4 In the next period, experimental work will continue with catalyst screening at higher temperatures. Also screening of water gas shift catalysts will be carried out, since results from tasks 1 and 5 show that especially for CO₂-separating membrane reactors this is a more viable option than steam reforming of methane.

Task 5 The next step will be to replace the black box one dimensional membrane reactor approach to a real reactor including all transport phenomena pressure drops etc. See also project plan and Statement of Work therein.

Publications

Kluiters, Steven C.A., Jan Wilco Dijkstra, Daniel Jansen, Wim G.Haije *Application of CO₂ selective membrane reactors in precombustion decarbonisation systems for power*

production, Abstract + paper for the 8th Greenhouse Gas Technologies Conference (GHGT-8) in Trondheim 2006, *submitted*

Feuillade, V.C., Haije, W.G., *Characterization of hydrotalcite materials for CO₂ selective membranes*, Abstract + paper for the 9th International Conference on Inorganic Membranes (ICIM) in Lillehammer 2006, *submitted*

Carbo, M.C., Jansen, D., Haije, W.G., Verkooijen, A.H.M., *Advanced Membrane Reactors for Fuel Decarbonisation in IGCC: H₂ or CO₂ separation?* Abstract for the Fifth Annual Conference on Carbon Capture & Sequestration, Alexandria, Virginia, 2006

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2. Lowe, C., CO₂ capture Project: Pre-combustion technology Overview. Third Annual conference on Carbon Capture and sequestration, May 3- 6, 2004, Alexandria, Virginia USA
3. Reijers, H.T.J., Valster-Schiermeier, S, Cobden, P.D., Van den Brink, R.W., Hydrotalcite as CO₂ Sorbent for Sorption-Enhanced Steam Reforming of Methane. *Industrial & Engineering Chemistry Research*; 45, 2522-3220, 2006.

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