



# **DECAFF: ECN'S IN-HOUSE R&D PROGRAMME ON DE- CARBONISATION OF FOSSIL FUELS**

D. Jansen

*The Seventh International Conference on Greenhouse Gas Control Technologies  
(GHGT-7) in Vancouver, Canada 5th -9th September, 2004*

DECEMBER 2004

# DECAFF: ECN'S IN-HOUSE R&D PROGRAMME ON DE-CARBONISATION OF FOSSIL FUELS

Daniel Jansen\*

Energy Research Centre of the Netherlands ECN, P.O. Box 1, 1755 ZG Petten, The Netherlands

## Abstract

This paper gives an overview of the results of the first phase of ECN's in-house R&D programme on de-carbonisation of fossil fuels. More detailed results are given in other papers and posters also presented at this GHGT-7 conference.

## Introduction

Since 2002 ECN develops, as part of the long-term, in-house R&D programme "DeCaFF", CO<sub>2</sub> capture technologies for electricity and hydrogen production systems. The objective of the programme is to develop integrated CO<sub>2</sub> capture technologies for electricity and hydrogen production systems resulting in CO<sub>2</sub> capture cost of 20- 25 €/per tonne. Within DeCaFF two system approaches are developed for CO<sub>2</sub> capture i.e. 1) Pre-Combustion De-Carbonisation (PCDC) of fossil fuels and 2) oxygen firing or nitrogen-free conversion of fossil fuels. These two approaches are substantially supported with system and technology assessments. Finally, several options for mineral CO<sub>2</sub> sequestration using waste materials or soil components are explored.

## Pre-Combustion Carbonisation i.e. hydrogen production

In this approach CO<sub>2</sub> is captured from the fuel (primarily natural gas or coal) before combustion. The fossil fuel is first transferred (via gasification or reforming) to hydrogen and CO<sub>2</sub> for CO<sub>2</sub> capture. For this purpose ECN develops high efficient hydrogen production systems with integrated CO<sub>2</sub> removal on basis of 1) Pd-alloy membranes and 2) CO<sub>2</sub> adsorbents. The removal of either hydrogen or CO<sub>2</sub> in a methane steam reforming or water-gas shift reactor favours the thermodynamics of the process. This opens new options for milder process conditions, increased efficiency and better integration of the fuel conversion into power generation systems such as gas turbine combined cycles.

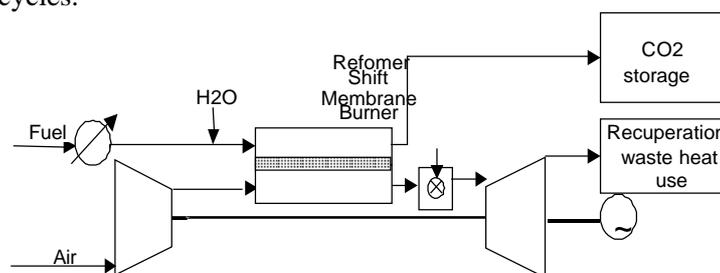
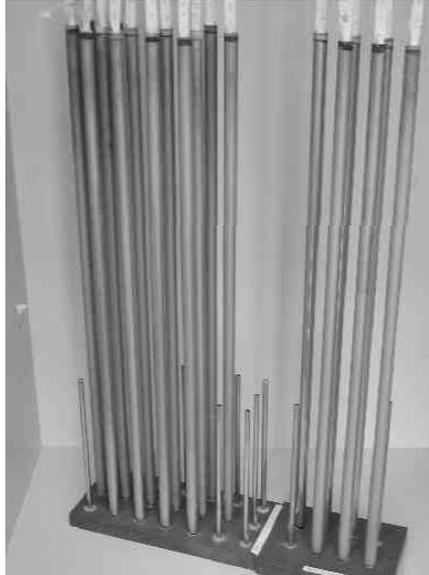


Figure 1. Simplified scheme of an integrated reformer PCDC natural gas combined cycle.

## H<sub>2</sub> selective Pd/alloy membranes for steam reforming reaction and simultaneous recovery of CO<sub>2</sub>

The objective of this project is the development of hydrogen Pd-alloy membrane reactor technology operating at 400-600°C, which is cost-effective in capturing a CO<sub>2</sub> rich gas stream and delivering a hydrogen rich gas stream, that can be used directly in appropriate hydrogen utilisation technologies. The general feature of the reactor is that hydrogen is separated from the reaction zone where it is produced via the reforming reaction.



*Figure 2. Set of 24 membrane tubes with a length of 0.8 meter for the bench scale unit*

In order to guarantee a proper evaluation the aim is to have a bench-scale membrane reactor of relevant size operational by the end of 2005. Although very challenging based on the existing state of the art, currently the relevant size is estimated to be 10 kW, which equals about 1 m<sup>2</sup> of membrane surface area.

#### Results

- System assessment studies showed that integration of the Pd-alloy reformer membrane reactor in a natural gas combined cycle reduce the efficiency penalty associated with the CO<sub>2</sub> capture. The investment costs for the CO<sub>2</sub> capture plant can also be reduced. Overall result is that CO<sub>2</sub> avoidance costs could be in the range of 25 €/tonne as long as the additional specific investment costs are < 280 €/kW.
- Performance targets for the Pd/Ag membranes in PCDC natural gas combined cycles have been determined i.e. flux up to 100 kWh/m<sup>2</sup>, membrane costs < 1400 €/m<sup>2</sup> and membrane lifetime > 16,000 hours.
- By optimising the electroless plating technique it was possible to manufacture membrane layers (Pd/23% Ag) with a total thickness of 3 to 5 µm on ceramic supports (see figure 2). Prototype membranes are available now with lengths up to 1 meter. Permeation tests show high hydrogen fluxes equivalent to 100 kWh/m<sup>2</sup>.

#### *Sorbent enhanced reforming for hydrogen production*

ECN identified SERP as a promising PCDC technique for the production of fuel grade hydrogen combined with CO<sub>2</sub>-capture.

#### Results

- There are three main challenges in the development of this technology: 1) CH<sub>4</sub> conversion >98% is needed, 2) reduction of CO<sub>2</sub> stripping steam to < 3 moles steam / mole CO<sub>2</sub> and 3) CO<sub>2</sub> capture efficiency >85%.
- ECN's catalyst/sorbent combination showed 98% CH<sub>4</sub> conversion at 400 °C until breakthrough of CO<sub>2</sub> (see figure 3), 85% CO<sub>2</sub> capture efficiency, however with a steam/CO<sub>2</sub> ratio > 10.
- Promising new hydrotalcites and promoters have been found.

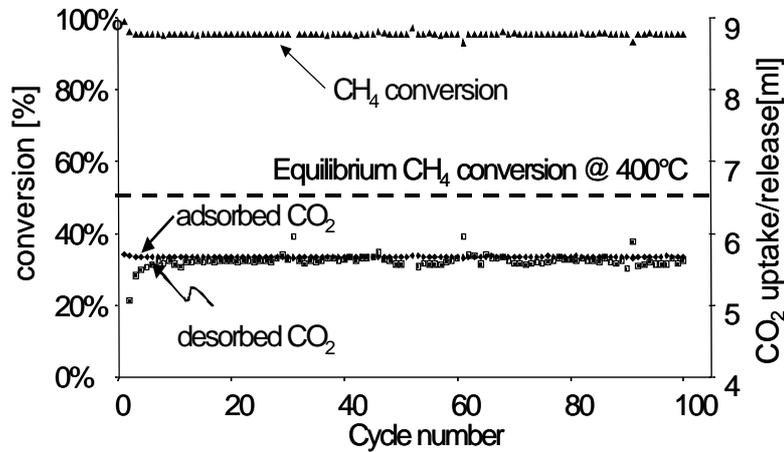


Figure 3. Methane conversion of ECN,s catalyst/sorbent combination.

### Oxy-fuel firing or nitrogen-free conversion in SOFC/GT systems

Conventional techniques for CO<sub>2</sub> capture in power plants suffer from large efficiency and financial penalties as a result of the low concentration CO<sub>2</sub> in the flue gasses. An approach to overcome this problem is to use Solid Oxide Fuel Cells (SOFC) that intrinsically separate oxygen and nitrogen whilst producing power. In SOFC systems 85% of the fuel conversion is already nitrogen free. Complete nitrogen free conversion is possible through de-nitrogenated conversion of the not converted fuel. Hydrogen or oxygen transport membranes can be used in this afterburner. ECN activities in this area involves proof of principle of a novel concept that has been developed for CO<sub>2</sub> capture in SOFC and SOFC hybrid systems (patent pending). The concept uses a water gas shift membrane reactor afterburner (WGSMR-afterburner). Besides that, dedicated oxygen transport membranes are developed for CO<sub>2</sub> free electricity production in gas turbine cycles and (hybrid) SOFC systems.

#### Water gas shift membrane afterburner

This project involves proof of principle of a novel concept that has been developed for CO<sub>2</sub> capture in SOFC and SOFC hybrid systems (patent pending). The concept uses a water gas shift membrane reactor afterburner (WGSMR-afterburner). The working principle is depicted in the figure 4 below.

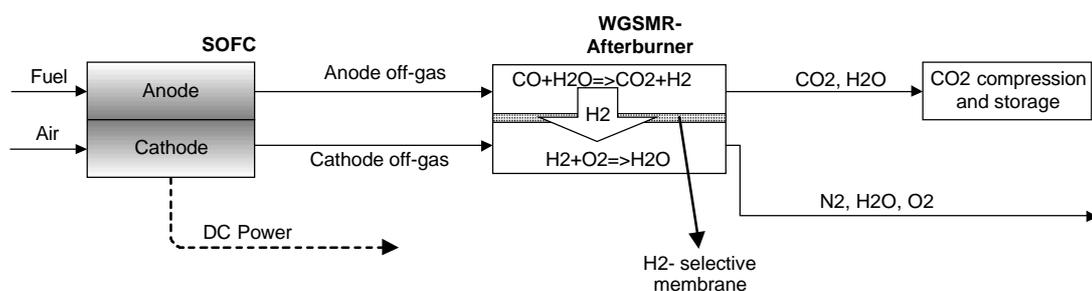


Figure 4: Working principle of the WGMS-burner

- Detailed system assessment studies have shown that if the system is combined with a gas turbine (GT) it is possible to generate electricity with 60.7% efficiency, higher than that of conventional (combined cycle) systems. The energy penalty associated with CO<sub>2</sub> capture is less than 50% of that of conventional MEA based CO<sub>2</sub> capture systems
- A patent application has been granted for the concept of combining SOFC with the WGSMR-afterburner, and possible implementation schemes.
- For assessment of the membrane reactor concentration and temperature profiles a membrane reactor model has been developed. The membrane reactor model is implemented as a user-model in Aspen Plus. The model consists of partial differential equations describing the mass-and heat balances along the membrane length. The model can describe both co-current as counter-current operation of the membrane

reactor. Each of the features mentioned can be switched off, so the model is also suitable for describing e.g. a membrane module without reactions. The output of the model will be both permeate and retentate stream data, as well as the concentration and temperature profiles along the membrane length.

- A proof of principle experiment has been conducted. The experiment demonstrated feasibility of the WGSMR-burner concept.

### **Mineral CO<sub>2</sub> sequestration**

CO<sub>2</sub> sequestration by mineral carbonation has been recognised as a promising route for permanent and safe storage of CO<sub>2</sub>. As feedstock, typically, calcium or magnesium containing primary minerals are used (e.g. wollastonite (CaSiO<sub>3</sub>) and forsterite (Mg<sub>2</sub>SiO<sub>4</sub>)). A possibly attractive alternative is the use of suitable alkaline solid residues, such as ashes from waste incineration, demolition waste and slags from steel production. Although their total sequestration capacity may be relatively limited compared to primary minerals, the use of alkaline solid residues could make the first mineral sequestration plants economically feasible because of their widespread availability in industrial areas at low costs. For steel slag we have found that calcium conversions of over 70 % are possible at relatively mild process conditions (d < 106 µm, 200°C, 10 bar CO<sub>2</sub>, 15 min.) without any further pre-treatment or an extra addition of chemicals. At ECN the influence of various process parameters on the carbonation process has been determined and the rate-determining step has been identified. Currently, process optimisation and cost evaluation of a mineral CO<sub>2</sub> sequestration plant based on steel slag carbonation is carried out.

#### **Acknowledgements**

The contributions of my colleagues Jan Wilco Dijkstra, Paul Pex, Ruud van den Brink and Wouter Huijgen and the financial support of the Dutch Ministry of Economic Affairs are gratefully acknowledged.