

## Hydrogen recovery in a combined natural gas-hydrogen distribution network using carbon molecular sieve membranes

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### Abstract

In the EU 6<sup>th</sup> FWP, NaturalHy, the use of existing natural gas networks to distribute hydrogen is being investigated. Hydrogen would be injected into the network at the source and be recovered from the natural gas mixture at the site of use. Membranes have been identified as a promising means of separating the hydrogen and are under development by several partners in the project. The Membrane Research Group at NTNU is developing carbon molecular sieve membranes, which are based on abundant and cheap wood pulp, for this application. These membranes can, when properly prepared, achieve good separation of hydrogen from the network with low energy consumption, feasible fluxes and a relatively pure product (greater than 90 vol% hydrogen).

**Keywords:** H<sub>2</sub>, membranes, carbon, natural, gas

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### Introduction

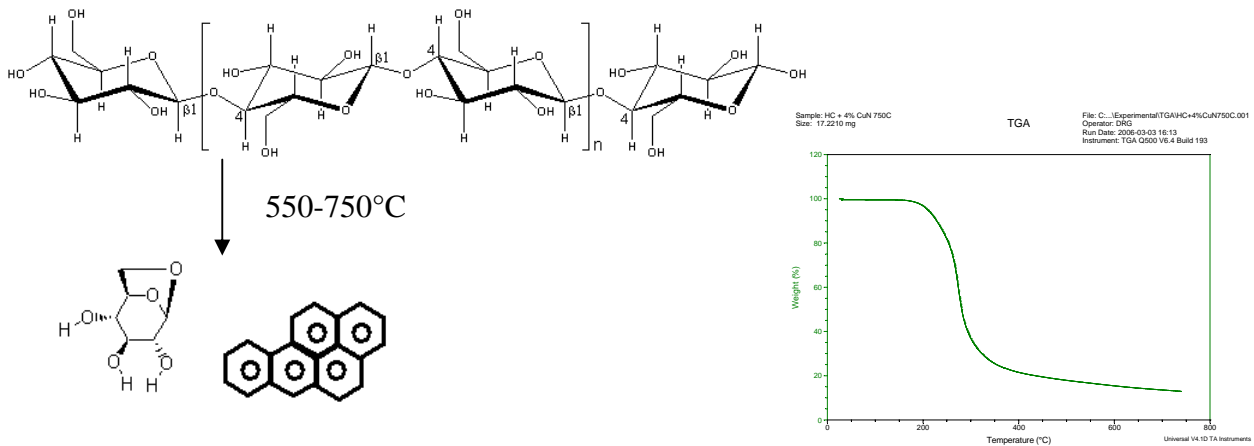
The transition to a full hydrogen distribution system may be a lengthy and costly exercise; hence a transitional approach using existing natural gas (NG) networks in Europe to transmit mixtures of hydrogen and NG is being investigated. In a EU 6<sup>th</sup> FWP project, NaturalHy, consisting of 39 European partners, the aims are to test all critical components in a mixed network by adding hydrogen to existing natural gas networks. This consortium includes network operators, hydrogen producers, specialist practitioners and academic researchers. The effect of hydrogen on technical components of the pipeline, reliability, safety and pipeline integrity as well as the possibility to separate out hydrogen for the end user, are being tested.

Critical to the success of the project is the feasible separation of the hydrogen for end-use components requiring relatively pure hydrogen, such as fuel cells. Palladium membranes are commonly seen as the bench mark membrane technology for the recovery of hydrogen from feed streams with a low (<30 vol%) hydrogen concentration. In order for these membranes to function efficiently, the entire gas feed stream must be heated to temperatures higher than 350°C, incurring a capital and energy penalty.

A promising alternative membrane material, under development at the Membrane Research Group (MEMFO) at NTNU, is the carbon molecular sieve (CMS). This is produced by the carbonisation of cellulose (wood pulp) at temperatures of 550-750°C to produce a nanoporous carbon film, capable of discriminating between the smaller hydrogen molecules and the remaining molecules in the gas stream. Carbon membranes are highly chemical stable and tolerate high temperatures, making them well suited to many hydrogen applications. However, in the context of NaturalHy, their main benefit is that they can achieve high separation productivity at ambient to moderate temperatures. The starting material for construction, wood pulp, is also cheap and abundant. Carbon membranes at MEMFO are at the bench scale testing stage.

### Carbon molecular sieve formation and fabrication

Carbon molecular sieves are formed by the carbonisation (or pyrolysis) of a polymeric precursor at temperatures between 400 and 800°C. This is usually performed under vacuum or an inert gas such as nitrogen. The focus at the Membrane Research Group (MEMFO) has been on the use of cellulose, derived from plentiful wood pulp, as a precursor for carbonisation. During the heating program, which proceeds in several steps, the cellulose structure decomposes, releasing mass as CO<sub>2</sub>, CO, H<sub>2</sub>, N<sub>2</sub>, NO<sub>x</sub> and H<sub>2</sub>O. This change is shown in Figure 1.



**Figure 1 Evolution of a CMS from cellulose to levoglucosan and benzopyrene [1]. The TGA graph on the right depicts weight loss of the precursor as temperature increases**

The final structure consists of graphite layers interspersed with amorphous regions. These regions contain nanopores on the order of 3-10 Å which offer a transport route to gases. The gases may diffuse through the pores or may adsorb on the walls and travel through the pores by a mechanism known as surface flow. The size of the pore constrictions influences the ability of the molecules to pass through the material; small or linear molecules diffuse more easily than relatively larger, bulkier molecules [2]. This is the principle behind molecular sieving, which allows hydrogen to permeate through the carbon membrane while methane, nitrogen and higher hydrocarbons in natural gas are largely retained. Further details on the preparation and performance of these membranes may be found in the work of Lie [3,4].

The governing equation for transport through a carbon molecular sieve is shown in Equation 1.

$$dQ_i = dA \cdot \frac{P_i}{l} \cdot (p_{i,f} - p_{i,p}) \quad (1)$$

Where subscript  $i$  refers to a specific component,  $Q_i$  is the volumetric flux of  $i$  ( $\text{m}^3(\text{STP})/\text{h}$ ),  $P_i$  is the permeability constant in the membrane for  $i$  ( $\text{m}^3(\text{STP}) \cdot \text{m}/\text{m}^2 \cdot \text{bar} \cdot \text{h}$ ),  $l$  is the thickness of the membrane (m),  $p$  is the partial pressure (bar) and subscripts  $f$  and  $p$  refer to the feed and permeate sides, respectively.

The driving force for permeation is the partial pressure difference and will benefit from higher hydrogen concentrations and feed pressures. The ratio of the permeabilities of two gases,  $P_1/P_2$ , is referred to as the selectivity of the membrane.

The addition of a dissolved metal salt or oxide to the precursor affects the final configuration of the pores, as the compound ends up in a solid state in the carbon matrix. This metal additive may disrupt the packing of the graphite regions, exhibit an affinity for the gases that are permeating the membrane and/or increase the conductivity of the membrane material. The latter point is important for regeneration, which is discussed in the next section.

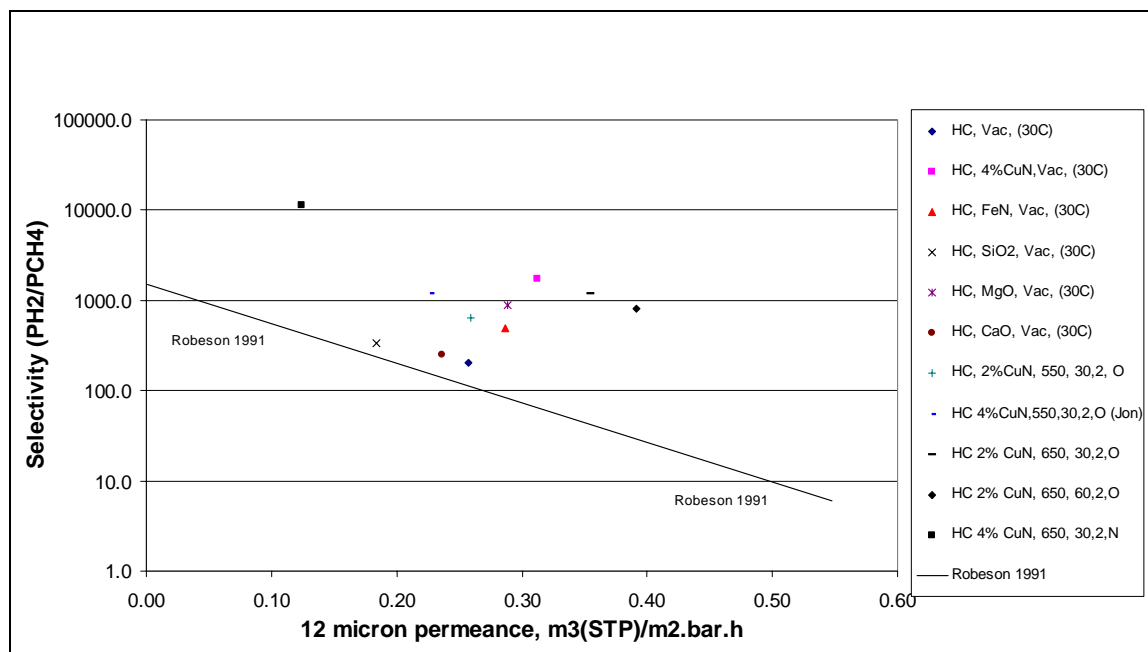
### Regeneration

When carbon membranes are applied at low temperatures (e.g. 0-50°C), the long-term permeance is often found to decrease slowly, because forces of attraction in the nanopores lead to strong gas sorption. Hence, a periodical regeneration is beneficial. Traditional regeneration techniques, like external heating of the membrane, have suffered from low regeneration efficiency. To restore membrane capacity, MEMFO has developed an electrothermal technique, where low voltage current is passed through the carbon, causing efficient desorption of strongly sorbed gas from the pore walls. The technique often recovers more than 100% of the permeance, and can be applied on-stream while the membrane is in operation. Permeation enhancement is believed to be caused by ohmic heating and electrostatic repulsion. Other mechanisms, like molecular orientation at the pore entrances, may also be active. The high efficiency of this regeneration method may be explained by the fact that both heat and mass transfer have the same direction (i.e. from the inner parts of the carbon to the surrounding fluids).

**Membrane performance**

Many carbonisation protocols have been screened at MEMFO, with an effort to increase the rate of hydrogen permeation while maintaining the high selectivity over methane. The addition of variable amounts of metal salts has also been investigated. The resulting membranes are characterised by single gas tests, where the transport rate of a pure gas is measured over the membrane, and mixed gas tests, where the feed is a gas mixture representing the intended application. The first test offers a quick means of characterising a membranes performance. The second test provides a more realistic result because it reflects competition between gases in the pores and at the membrane surface. Other important variables are the temperature and pressure at which the membrane operates.

A summary of the more promising single gas results at MEMFO is presented in Figure 2.



**Figure 2 Single gas results for different carbon membranes developed at MEMFO. Permeance values are normalised with a thickness of 12 microns. HC = hemicellulose-cellulose, CuN = copper nitrate**

The permeance, or pressure normalised flux, of hydrogen is shown on the abscissa and plotted against the selectivity of hydrogen over methane. The line on the graph represents the Robeson upper bound, which is considered to be the performance limit for traditional polymeric membranes. Carbon molecular sieves clearly exceed this boundary.

The mixed gas results for the family of cellulose with copper (II) nitrate addition, which has consistently performed well, are shown in Table 1.

**Table 1 Mixed gas results for copper nitrate**

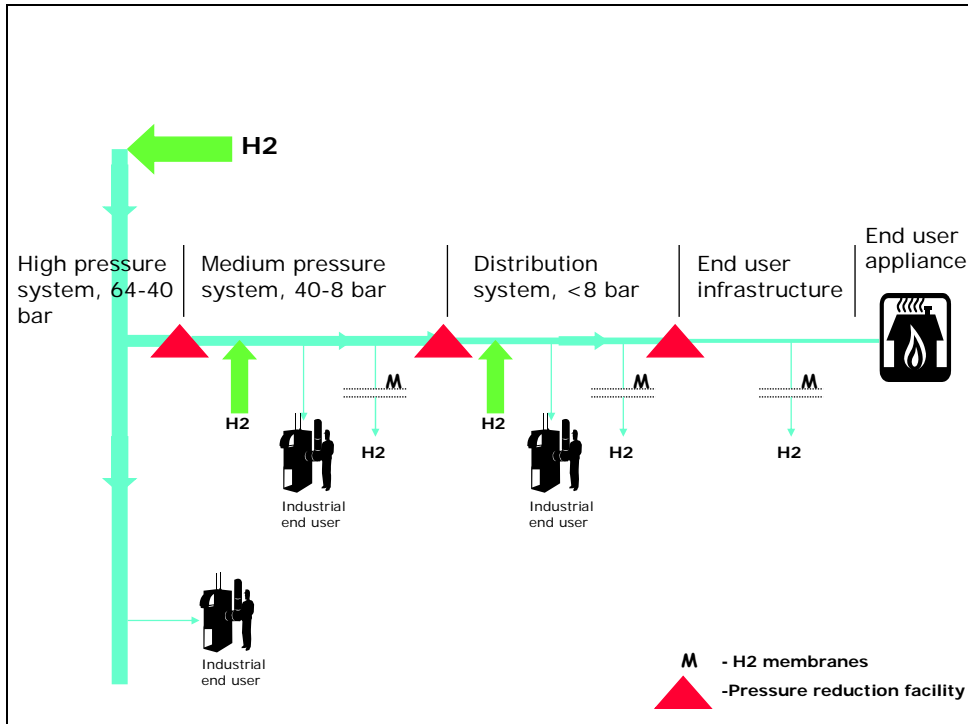
| Material         | Test Temp., °C | Test Feed Pressure, bar | H <sub>2</sub> permeability, m <sup>3</sup> (STP).m/m <sup>2</sup> .bar.h * 10 <sup>6</sup> | Selectivity | H <sub>2</sub> permeance, m <sup>3</sup> (STP)/m <sup>2</sup> .bar.h (l = 12 microns) |
|------------------|----------------|-------------------------|---|-------------|---|
| HC, 4% CuN, 550C | 90             | 4                       | 4   | 679         | 0.34  |
| HC, 2%CuN, 650C  | 30             | 2                       | 2   | 181         | 0.16  |
| HC, 2%CuN, 650C  | 30             | 6                       | 2   | 541         | 0.15  |
| HC, 2%CuN, 650C  | 80             | 2                       | 3   | 218         | 0.28  |
| HC, 2%CuN, 650C  | 80             | 6                       | 3   | 532         | 0.26  |

It can be seen from the table that higher operating temperatures significantly increase the permeation of hydrogen. On the other hand, the permeation rate was relatively insensitive to pressure in the range tested, which represents that available in a residential application. The implication of these results in the recovery of hydrogen from a natural gas pipeline is discussed in the next section.

**Simulation results**

The mixed gas performance of the carbon membrane with 2 wt% copper (II) nitrate was used in the simulations, which were performed in Hysys using an integrated in-house membrane model.

The recovery of hydrogen from a pipeline is influenced by the partial pressure of the hydrogen in that pipeline. Thus, the simulation results differed significantly for the different pipeline segments shown in Figure 3.



**Figure 3 NaturalHy network**

One of the advantages of the carbon membrane is that the feed gas need not be heated for the membrane to function. Although heating improves performance and reduces the required membrane area, energy consumption increases.

The results of the simulations are shown in Table 2, where the permeate pressure was adjusted so that hydrogen would be recovered in significant amounts at a purity of 90% or greater. A simplified original NG composition was assumed of 95 vol% CH<sub>4</sub> and 5 vol% higher hydrocarbons for all of the cases. The hydrogen product (permeate) was compressed to 1.5 bar(abs).

**Table 2 Carbon membrane application in NaturalHy**

| Performance   | Case 1)<br>40 bar<br>30 vol% H <sub>2</sub> | Case 2)<br>40 bar<br>10 vol% H <sub>2</sub> | Case 3)<br>6 bar<br>30 vol% H <sub>2</sub> | Case 4)<br>6 bar<br>10 vol% H <sub>2</sub> |
|---|---|---|--|--|
| H <sub>2</sub> Recovery, %                            | 80  | 80  | 80   | 75   |
| H <sub>2</sub> Purity, vol%                           | 97  | 90  | 92   | 90   |
| Permeate pressure, kPa                                | 150   | 30  | 50   | 5  |
| Membrane area, m <sup>2</sup> /(kg H <sub>2</sub> /h) | 13  | 38  | 200  | 235  |
| Energy cost, MJ/kg H <sub>2</sub>                     | 0   | 3.7   | 2.3  | 10.2                                       |

These results are for a single stage membrane system, for which there is a trade-off between hydrogen recovery and purity. Higher hydrogen partial pressures in the above cases produce cleaner and more energy efficient separations. For Case 1, a fuel cell requiring 100 m<sup>3</sup>(STP) H<sub>2</sub>/h could be serviced by a membrane unit with an area of 110 m<sup>2</sup> which would not incur any energy costs. For Cases 2, 3 and 4, vacuum is drawn on the permeate side which results in energy consumption; the lower the vacuum the higher the energy cost.

Recoveries and purities can be increased by use of several stages, lower vacuums and the use of sweep, although at higher energy and capital costs.

### **Conclusion**

Carbon molecular sieves are an advanced membrane technology that could effectively recover hydrogen from hybrid hydrogen-natural gas networks. The starting material, wood pulp, is abundant and cheap and the energy cost of operating such membranes would be relatively low. The development of these membranes is ongoing at the Norwegian University of Science and Technology, involving the screening of carbon membrane variations, production of larger scale membrane modules and eventual lifetime testing.

### **Acknowledgment**

The authors wish to acknowledge the EU 6<sup>th</sup> FWP, NaturalHy, for funding and the interesting opportunity created in the project.

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