Ultra-pure hydrogen from natural gas

ULTRA-PURE HYDROGEN FROM NATURAL GAS

As hydrogen becomes more important as a product in the energy sector, a way to integrate CO_2 capture through novel processes and new reactor concepts becomes necessary

Hydrogen is becoming a very important product, not only as a chemical but also as an energy carrier, particularly in connection with pre-combustion CO_2 capture processes which allow boosting the energy efficiency of the conversion of conventional fossil fuels into electricity while integrating CO_2 capture and avoiding anthropogenic CO_2 emissions and associated environmental problems. Conventional hydrogen production technologies do not integrate CO_2 capture, and this calls for novel processes with new reactor concepts.

Membrane reactors – a process intensification story

A membrane reactor is a multifunctional reactor that integrates a reaction step and a separation step into a single apparatus, thus achieving a high degree of process intensification with associated improvements in energy efficiency and reactor performance. With palladium-based dense membranes, hydrogen can be selectively extracted almost entirely from a hydrogen-containing gas mixture. When membranes are used to extract hydrogen that is formed via an equilibrium limited reaction, the equilibrium can be shifted towards the products' side (Le Châtelier's principle). This enables full reactant conversion (avoiding reactant recycle streams) and simultaneous purification of the hydrogen product.

Traditionally, membrane reactors have been studied for dehydrogenation reactions because the reaction temperature of important dehydrogenations corresponds to the working temperature of the Pd-based membranes (300-600°C). Typical examples of more modern membrane reactor applications include the water gas shift reaction to convert CO and steam to hydrogen and CO_2, and methane steam reforming to convert methane with steam to hydrogen and CO_2. These membrane reactors can also be effectively used in pre-combustion CO_2 capture plants, where the hydrogen for the power production is recovered through the membranes, while the retentate of the reactor is CO_2 mixed with steam that can be easily purified and stored.

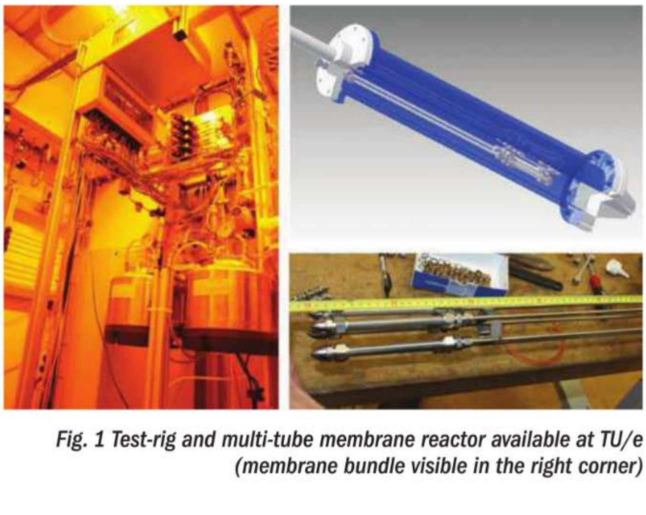

Fig. 1 Test-rig and multi-tube membrane reactor available at TU/e (membrane bundle visible in the right corner)

When compared with a conventional configuration, where a reactor is typically followed by a downstream separation unit, the use of membrane reactors can bring various potential advantages, such as reduced capital costs (due to the reduction of process unit and reactor volumes), improved yields and selectivities (due to the shift effect on the equilibrium reactions), and reduced downstream separation costs (separation is integrated).

The success of membrane reactors for hydrogen production is basically connected to: (i) advances in the membrane production methods which allow the production of thin membranes with high hydrogen fluxes and high hydrogen perm-selectivities; and (ii) the design of innovative reactor concepts which allow the integration of separation and energy exchange and the reduction of mass and heat transfer resistances.

Membrane reactors have been studied in different configurations, from packed-bed membrane reactors to membrane microreactors to fluidised-bed membrane reactors. While a packed-bed membrane reactor is simple to construct, the performance of these reactors is often decreased by the prevailing external mass transfer limitations (transport of hydrogen from the bulk of the catalyst bed to the membrane wall, also referred to as 'concentration polarisation') on the hydrogen flux through the membranes, and unavoidable and undesirable temperature gradients along the reactor that are detrimental to the stability of the membrane. To circumvent these limitations, membrane microreactors can be used as the decrease in scale decreases mass transfer limitations while also enormously increasing the available surface area for heat exchange, which allows for much better temperature control inside the reactor. However, microreactors need very active and stable catalysts as the amount of catalyst that can be installed per volume of reactor is very limited. Additionally, even for a small scale hydrogen production plant (few m^3/h hydrogen), the required number of micro-channels is huge, giving additional problems in achieving a proper gas distribution over all the channels and a very expensive maintenance cost of the reactor in case one or more channels fail (either because of catalyst deactivation or, even worse, because of membrane failure).

A good membrane deserves a good reactor concept: fluidised-bed membrane reactors

For these reasons our group is developing and demonstrating membrane-assisted fluidised-bed reactors for various applications. A typical fluidised-bed membrane reactor (FBMR) for hydrogen production consists of a bundle of hydrogen-selective membranes immersed in a fluidised catalytic bed operated in the bubbling regime. The use of FBMRs decreases the bed-to-wall mass transfer limitations but also allows a virtually isothermal reactor operation thanks to the intensive catalyst mixing. This opens up possibilities for autothermal reforming of hydrocarbons inside the membrane reactor, with large improvements in energy and carbon efficiencies. An example of our FBMR is reported in Fig. 1, where the membrane bundle is visible.

The main advantages of the FBMR can be listed as:

- Negligible pressure drop, which allows use of (very) small particle sizes, avoiding internal mass and heat transfer limitations;
- (Virtually) isothermal reactor operation;
- Flexibility in installment of membrane and heat transfer surface area and the arrangement of the membrane bundles; and
- Improved fluidisation behaviour as a result of:
  - Compartmentalisation, i.e. reduced axial gas back-mixing; and
  - Reduced average bubble size due to enhanced bubble breakage, resulting in improved bubble-to-emulsion mass transfer.

Along with the actual experimental demonstration of membrane reactor systems, an important research activity in our group is devoted to generating fundamental knowledge on the effect of fluidised-beds on the membranes and, *vice versa,* on the effect of

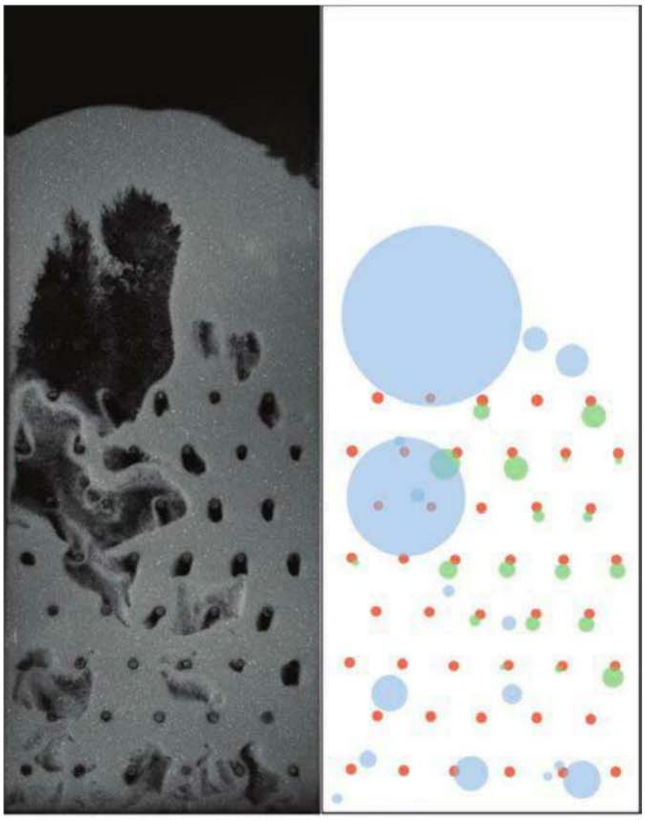

Fig. 2 Example of gas pockets detection, showing the membranes in red, the detected bubbles in blue and the detected gas pockets in green as the equivalent bubble diameter at the determined centre of mass position

the presence of, and permeation through, the membranes on the hydrodynamics and mass transfer of fluidised suspensions. This last aspect is often ignored and still largely uninvestigated, although we have shown that the presence of immersed membranes, and particularly the permeation of gas through the membranes, strongly affects the hydrodynamics in the bed and thereby the reactor performance. When not properly tuned, the reactor performance could significantly decrease due to the formation of densified particle zones near the membranes, but when optimally integrated, the performance could be even further improved due to enhanced bubble breakage and decreased gas back-mixing. Quantification of these effects, preferably in the form of advanced closure equations, allows the development of improved reactor models that can be used for the design and optimisation of larger scale FBMRs.

Modern tools to understand fundamentals of fluidised-bed membrane reactors

To study the hydrodynamics of FBMRs in great detail, we make use of advanced non-invasive optical techniques with high-resolution, high-speed charge-coupled device cameras, like particle image velocimetry (PIV) and digital image analysis (DIA). Our group has also recently developed new techniques that allow us to non-invasively measure the concentration profile inside a fluidised-bed with high temporal and spatial resolution using a high-speed infrared camera coupled with PIV/DIA (IR/PIV/DIA), and a new technique that extends the capability of PIV/DIA to high temperatures and reactive flows, making use of endoscopes for high temperature applications (ePIV/DIA).

An example of the usefulness of PIV/DIA to an FBMR is reported in Fig. 2, where we describe how internal horizontal membranes result in the formation of small gas pockets that can be detrimental for the mass transfer of gases to the membranes. The experimental findings on this effect are also well predicted by detailed computational fluid dynamics simulations carried out in parallel in our group.

In close collaboration with our research partners, among which is TECNALIA (Spain), we also investigate the effect of high temperature fluidisation on the performance of membranes, and design and develop new membranes for fluidised-beds with further improved longevity and yet the same excellent performance in terms of selectivity and permeability.

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