

MODELLING AND SIMULATION OF A MEMBRANE FIXED-BED REACTOR FOR THE PRODUCTION OF HIGH PURITY HYDROGEN

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Summary

Membrane fixed-bed reactors are an important alternative to the conventional fixed-bed process for the production of high purity hydrogen through the water-gas shift reaction. The performance of this reactor has been studied, and compared to that of the conventional one, by means of computer simulations using a pseudo-homogeneous non-isothermal 2D model. The mayor benefits of membrane reactors are higher conversion and the production of high purity hydrogen directly in the shell side of the membrane, thus eliminating or reducing the need of further separation stages.

Keywords

Membrane reactors; hydrogen production; WGSR; reactor modelling.

Introduction

The need of high-purity hydrogen has increased largely in the last years, mainly for its use in fuel cells. The water-gas shift reaction (WGS) plays a key role in the synthesis of hydrogen from many raw materials (natural gas, biogas, oil fractions, coal, biomass, etc). According to this strategy, the organic raw material is transformed, through gasification or reforming operation, into a mixture of hydrogen and carbon monoxide (*syngas*). This carbon monoxide is subsequently transformed into carbon dioxide and hydrogen through the WGS reaction. As the WGS reaction is exothermic and equilibrium-limited, a multi-stage catalytic fixed-bed reactor with inter-stage cooling is normally used. Typically, the first bed operates at high temperature (300-400°C) with a $\text{Fe}_3\text{O}_4/\text{Cr}_2\text{O}_3$ catalyst, while the second-one operates at a lower temperature (200-250°C) with a $\text{CuZnO}/\text{Al}_2\text{O}_3$ catalyst.¹ The equilibrium reaction is shifted by working at low temperature in the second bed and with an important excess of steam ($\text{CO}/\text{H}_2\text{O}$ molar ratio 2 to 10). Despite this, the amount of catalyst and the size of the equipments are high, due to the low reaction rate and the high gas flow rates. Separator-type membrane reactors are an interesting alternative to the classical WGS process. In Fig. 1 the working principle of this membrane reactor is shown. The syngas mixture is fed to one side of the membrane, where the catalyst is arranged as a fixed-bed. The hydrogen generated in the reaction permeates through the selective membrane, thus shifting the equilibrium reaction. The purity of the hydrogen depends on the selectivity of the membrane, being the Pd-based membranes the most promising ones. These membranes are formed by a porous

metallic or ceramic support, an interphase, and a thin Pd layer. The high selectivity of the Pd layer allows to produce high purity hydrogen (> 99%), suitable for the use in fuel cells without additional purification.² The main drawbacks of Pd-based membranes are the low flux of hydrogen that permeates and the high cost of the membrane.

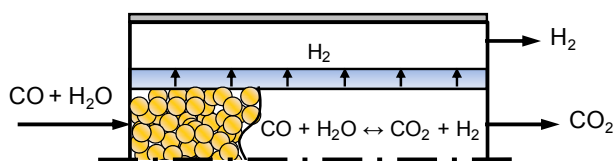


Fig.1 Working principle of the membrane fixed-bed reactor for the WGS reaction.

Methodology

In this work, the behavior of a fixed-bed membrane reactor for the WGS reaction has been modeled and simulated using a rigorous bidimensional model, which accounts for the mechanisms of hydrogen transport through the membrane. The considered membrane is cylindrical, with 0.01 m internal diameter, 0.003 m thick and 0.6 m of long, coated with a Pd layer of 20 μm at the outside. It is considered that only hydrogen permeates through the membrane, being the flux modeled by the law of Richardson.³ The membrane tube contains the catalytic fixed-bed, which consists in spherical $\text{Fe}_3\text{O}_4/\text{Cr}_2\text{O}_3$

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catalyst particles with 0.001 m diameter. In the conditions of the study, the intrinsic reaction is adequately modeled by power-law kinetics considering the reverse reaction.¹ The catalytic fixed-bed has been modeled using a pseudo-homogeneous non-isothermal 2D model with axial symmetry. The selection of a 2D model, more difficult to solve than 1D models which consider only variations in the axial direction, is justified by the presence of important concentration and temperature profiles in the radial direction. Mass transfer inside the catalyst particle has been taken into account using the effectiveness factor. The physical and transport properties for the catalyst bed have been calculated as a function of concentration and temperature at each point of the bed. The deviations from the ideal plug flow have been considered using axial and radial effective dispersion coefficients for packed beds in the mass and energy balances, and the momentum balance with radial porosity distribution. This way, the effect of channeling at the vicinity of the wall due to the increase in the porosity can be estimated. This mathematical model has been solved using the finite element method with the help of the software COMSOL Multiphysics 3.4.

Results

The mathematical model presented in the previous section was used to develop a detailed study on the performance of membrane reactors for the WGS reaction by means of computer simulations. The influence of the main operating conditions has been studied: space velocity ($GHSV$), hydrogen partial pressure at the shell side, and inlet gas temperature. The performance of the reactor is measured in terms of conversion and flow of hydrogen permeated through the membrane. It has been found that an increase in the space velocity ($GHSV$) reduces the outlet conversion for low inlet gas temperatures, but increases the amount of hydrogen permeated, particularly for high inlet gas temperatures (Fig. 2). Increasing the inlet gas temperature results in an increase in conversion at low temperatures, due to the increase in the reaction rate. At high temperatures (lower equilibrium constants) conversion decreases, but only slightly, since hydrogen permeation shifts the equilibrium. The hydrogen partial pressure at the shell side has a less marked effect than space velocity and temperature on both conversion and hydrogen permeated. Once the operating conditions of the membrane reactor have been optimized, the membrane reactor has been compared to the classical fixed-bed reactor process. The simulations show that, for the same operating conditions, conversion is higher for the membrane reactor. Therefore, and also considering that in the membrane reactor high-purity hydrogen is directly obtained from the shell-side of the reactor, membrane reactor seems a very promising technology for the synthesis of hydrogen by WGS reactions.

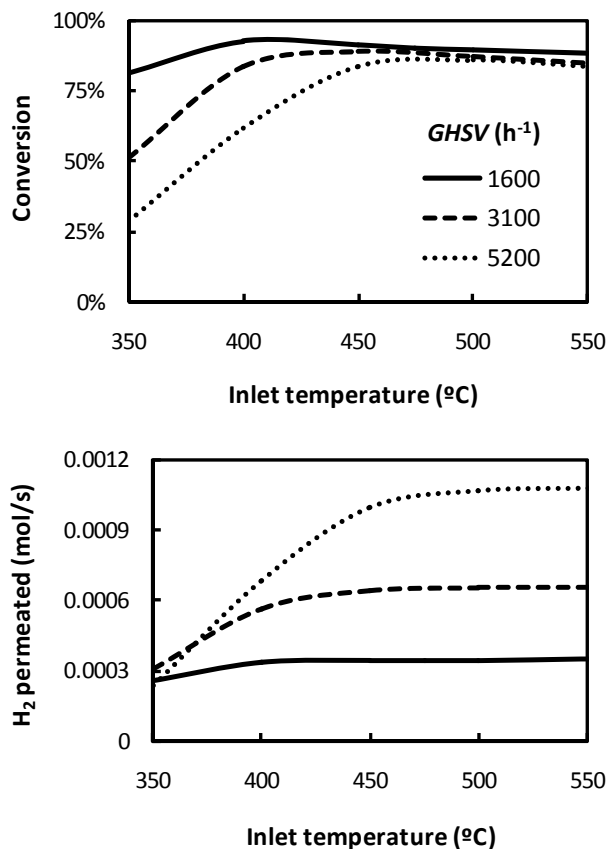


Fig. 2. Performance of the membrane reactor at different inlet temperatures and space velocities

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References

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