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Water gas shift reaction in membrane reactors: Theoretical investigation by artificial neural networks model and experimental validation

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ABSTRACT

In this work, a theoretical approach via artificial neural networks model has been followed for studying the water gas shift reaction in hydrogen selective membrane reactors, based on an experimental campaign useful for training the aforementioned model. In particular, such parameters as the reaction pressure (from 150 to 300 kPa), reaction temperature (from 300 to 360 °C), gas hourly space velocity (GHSV) between 2000 and 6000 h^{-1}, sweep gas flow rate (between 35.75 and 130.42 mL/min of N_2), H_2O/CO feed molar ratio (from 1/1to 4.5/1) and feed configuration (co–or counter-current mode with respect to the sweep gas) have been considered from both a modeling and an experimental point of view in order to analyze their influence on the water gas shift performance (in terms of CO conversion, hydrogen recovery, hydrogen permeate purity) in two membrane reactors, allocating dense Pd–Ag membranes, having different active membrane surface areas. As best experimental results, by using a Cu–Zn based catalyst, at GHSV = 3340 h^{-1}, T = 350 °C, H_2O/CO feed molar ratio = 2/1 and co-current configuration of sweep gas, CO conversion around 100% and H_2 recovery of about 70% were reached. Meanwhile, the artificial neural networks model has been validated by using part of the experimental tests as training values and, then, it was used for optimizing the system to achieve as much as possible high hydrogen recovery. The model predicted the experimental performance of the water gas shift membrane reactors with an error on CO conversion lower than 0.5% and around 10% for the H_2 recovery over the experimental tests not used during the model training.

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Introduction

The water gas shift (WGS) reaction is a well-known process used industrially to increase the amount of H_2 from a syngas stream by decreasing the amount of CO according to the following reaction:

$$CO + H_2O \leftrightarrow H_2 + CO_2 \quad \Delta H^\circ = -41.1\ kJ/mol \tag{1}$$

This reaction is slightly exothermic, thus favored by low temperatures, while not dependent of the reaction pressure because there is no variation of the moles number from the reactants towards the products. Furthermore, it is limited by thermodynamic equilibrium.

Industrially, WGS reaction is performed in a two-stages adiabatic reactors with intermediate cooling, after a reforming process. The first reactor is characterized by high temperature (HT), between 400 and 450 °C, in the presence of Fe–Cr oxides as catalyst, while the second reactor operates at low temperature (LT) 200–250 °C, using as catalyst Cu–Zn oxides. The output stream from the second reactor is, then, directed to some hydrogen separation unit (for example, the pressure swing adsorption) for its purification [1].

A valid alternative to the WGS reaction performed in traditional reactors (TRs) is represented by the utilization of inorganic membrane reactors (MRs), which - according to the IUPAC definition [2] - are equipments combining the separation characteristics of the inorganic membranes with the typical properties of the chemical reaction in a single unit. In particular, the membrane not only plays the role of a separator, but it integrates the reactor itself, making possible to achieve higher conversion than a traditional WGS process at the same operating conditions. In the current specialized literature, there is a great number of scientific studies concerning WGS reaction in MRs [3–13]. Among them, Mendes et al. [3] reviewed in a detailed study the state of the art on WGS reaction, particularly addressing on new catalysts and recent developments about MR technology. However, the high cost of Pd makes economically unfavorable the utilization of Pd-based membranes in MRs, particularly at larger scale [8]. More recently, the need of depleting the palladium content in the membranes utilized in WGS MRs has been reflected in several studies in which composite Pd-based membranes were used in MRs for performing WGS reaction. For example, Liguori et al. [9] studied from an experimental point of view this reaction by using an MR housing a composite Pd-based membrane. The composite membrane was constituted of a dense Pd-layer of around 20 μm deposited on porous stainless steel tubular support. As best results, the authors reached a CO conversion of 80% and a H_2 recovery equal to 60%, with a correspondent 95% of H_2 purity at 1100 kPa, 390 °C and GHSV of around 3500 h^{-1}. In the same field, Catalano et al. [10] used an MR adopting a composite membrane with a Pd-layer of ~8 μm supported also on porous stainless steel, obtaining a maximum CO conversion of 98%, 92% of H_2 recovery with 99.5% of H_2 purity.

Mathematical modeling represents an effective support to design and control industrial processes and, in particular, MRs aimed at performing WGS reaction. Different approaches can be used to develop reliable models aimed at investigating how MR responses may change under the influence of both external and manipulated variables.

A large number of theoretical studies regarding WGS reaction are currently available in the specialized literature. Indeed, many 1D models have been proposed to simulate the performance of WGS reaction in MRs. Meanwhile, a lower number of studies have been focused on 2D and or 3D mathematical models [14–18]. In the latter case, more rigorous analyses were realized, also considering the angular component of the space, for asymmetric reactors. As compared to other theoretical approaches, a model based on Artificial Neural Networks (ANNs) does not use any transport equation, which could help to determine, on the basis of fundamental principles, the mutual relationships existing between the inputs and the outputs. ANNs are composed of several simple interconnected computational elements called neurons, which operate in parallel. These elements are inspired to biological nervous system whose functions they try somehow to reproduce. Then, ANNs are a data-driven method capable to learn from examples, capturing the functional relationships existing between the input(s) and the output(s). Even though the prediction of each single neuron could be imperfect and bias-affected, the outcome of the interconnection(s) among neurons is a computational tool capable to learn from examples and to provide accurate predictions even with examples never seen before [19]. This feature makes ANNs a particularly useful tool to model phenomena difficult to be described by an equation-based approach, since no a priori knowledge about the system under study is actually required.

To the best of our knowledge, the artificial neural networks analysis has been not yet utilized for modeling WGS reaction in MRs. Then, the aim of this work is the pioneeristic development of an ANNs model able to predict the behavior of WGS reaction performed in a dense Pd–Ag MR by changing the operating conditions, with subsequent experimental validation.

Experimental

The experimental plant is schematically reported in Fig. 1. In particular, the feed mixture flowed to the MR is controlled by means of Brooks mass flow controllers (MF-100, MF-101 and MF-102) for CO, N_2 and H_2, while liquid water is fed by a Dionex P680 HPLC pump (P-100) and vaporized by a heater (E-100). The mixture of reactants is, thus, fed to the MR, which is exercised in the temperature range between 300 and 360 °C, while the reaction pressure was varied from 100 to 300 kPa through a backpressure (BP-100) controller, placed on the outlet of the retentate stream. The latter stream, representing one of the two the outputs of the MR, before being analyzed is made anhydrous, by condensing the steam in an ice trap (V-100). Successively, both retentate and permeate streams are analyzed by an HP 6890 Series GC system gas chromatograph, containing two columns, Porapack R 50/80 - 8 ft × 1/8 inch and CarboxenTM 1000-15 ft × 1/8 inch, connected in series, followed by a molecular sieve. The start-up of the plant consists of an MR heating up with a temperature increase of 1 °C/min, flowing a N_2 stream (~17 mL/min) at atmospheric pressure. Subsequently, at the set reaction temperature, the catalyst