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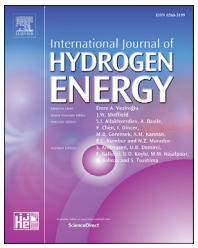

Hydrogen production by a Pd–Ag membrane reactor during glycerol steam reforming: ANN modeling study

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ABSTRACT

In the present work, an artificial neural networks (ANNs) model has been developed for investigation of glycerol steam reforming (GSR) process with Pd–Ag membrane reactor (MR) in the presence of Co/Al_2O_3 catalyst. Reaction pressure and sweep factor as independent variables (Inputs) and glycerol conversion, hydrogen recovery, hydrogen yield, H_2 selectivity, CO selectivity and CO_2 selectivity as dependent variables (outputs) are chosen for ANN modeling of GSR. The ANN model was developed by feed-forward back propagation network with *trainlm* algorithm and topology (2: 10: 6) and Sigmoid transfer function for hidden and output layers. A good agreement between predicted values using ANN with experimental results was observed (R^2 and MSE values were 0.9998 and 3.48×10^{-6} (based on normalized data), respectively). Modeling results indicated that all selected factors (reaction pressure and sweep factor) were effective on output variables. It was found that the reaction pressure with a relative importance of 59% was the most effective parameter in the GSR process with Pd–Ag MR in the presence of Co/Al_2O_3 catalyst.

Introduction

Nowadays, one of the main universal environmental challenges is devoted to the search for clean energy sources. Hydrogen is widely accepted as a clean energy carrier, particularly in fuel cell deployment, whereby its reaction with oxygen from air produces water, an environmentally benign emission [1].

Biodiesel is a renewable fuel, and it has been gaining much attention in the last few years. When biodiesel is produced through a process of *trans*-esterification of vegetable oils, glycerol is produced as a by-product. The use of glycerol for producing pure hydrogen or synthesis gas by steam reforming reaction could be particularly interesting.

A reaction kinetics study on the aqueous-phase glycerol steam reforming (GSR) reaction indicates that Pt and Pd catalysts are selective for producing hydrogen, with Pt showing high catalytic activity [2]. Huber et al. [2] used a heterogeneous catalyst based on Ni, Sn, and Al, active and selective for hydrogen production by aqueous-phase GSR reaction. Zhang et al. [3] studied the hydrogen production by the steam

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reforming reaction of ethanol and glycerol over Ir, Co, and Ni-based catalysts, determining that the Ir based catalyst is significantly more active and selective toward hydrogen production from GSR reaction.

According to the literature [4,5], three chemical reactions can be considered in the GSR process: one main reaction; namely, overall GSR reaction (SR, Eq. (1)), glycerol decomposition reaction (GD, Eq. (2)) and water gas shift (WGS, Eq. (3)):

$$C_3H_8O_3 + 3H_2O \leftrightarrows 3CO_2 + 7H_2 \quad \Delta H^0_{298} = +122.8 \text{ kJ/mol} \tag{1}$$

$$C_3H_8O_3 \rightarrow 3CO + 4H_2 \quad \Delta H^0_{298} = +246.1 \text{ kJ/mol} \tag{2}$$

$$CO + H_2O \leftrightarrows CO_2 + H_2 \quad \Delta H^0_{298} = -41.0 \text{ kJ/mol} \tag{3}$$

It should be noted that besides of the reaction products, namely hydrogen (desired product), carbon dioxide and carbon monoxide (undesired products), the non-reacted glycerol and water can be observed. Whereas to feed a proton exchange membrane fuel cells (PEMFCs), the high purity of hydrogen stream is needed, mostly because carbon monoxide poisons the palatine catalyst of the PEMFC and its concentration should be lower than 15 ppm [6]. This low content of carbon monoxide could be carried out by several strategies, namely using a permselective membrane. Combining in the same device both operations, reaction and separation, membrane reactors (MRs) present several advantages over traditional reactors (TRs). Besides reducing the number of chemical process units, at the same operating conditions, a MR could also achieve conversions higher than the ones obtained in a TR [7]. However, regarding the membrane kind to be housed in a MR, both MR cost and performance need to be taken into account. In particular, several studies have focused on the Pd-based MRs application [5,8–14].

Mathematical modeling represents an effective support to design and control industrial processes and, in particular, MRs aimed at performing GSR 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. Some modeling studies about MRs are currently available in the specialized literature [15–20].

In recent years, considerable attention has been given to the development of sophisticated techniques for exploring data sets. One such class of techniques is artificial neural networks (ANNs). The ANNs have many attractive theoretic properties, specifically, the ability to detect non-predefined relations such as nonlinear effects and/or interactions. These theoretic advantages come at the cost of reduced interpretability of the model output. Indeed, ANNs have been proposed as a supplement or alternative to common modeling techniques. However, ANNs are not without drawbacks. The primary disadvantage of an ANN is its "black box" quality, that is, without extra effort, it is difficult if not impossible to gain insight into a problem based on an ANN model.

In fact, a model based on ANNs does not apply any transport equation, which could help to indicate, based on the fundamental principles, the reciprocal relationships existing between the outputs and the inputs. Nevertheless, the number of studies conducted for ANN modeling of MRs is very limited. Only in a research work, Basile et al. [21] studied the ANN modeling of water gas shift (WGS) reaction in MRs.

According to the best of our knowledge, the ANNs analysis has been not yet utilized for modeling of GSR reaction in the MRs especially in the Pd–Ag MRs. Therefore, the main purpose of this work is the development of an ANN model able to forecast the behavior of GSR reaction.

Experimental procedure

Iulianelli et al. [5] investigated GSR in a Pd–Ag MR over Co–Al_2O_3 catalyst. In this research work, the experimental results of their work have been used for ANN modeling of Pd–Ag MR. The scheme of the plant for the experimental tests of MR is represented in Fig. 1. The reaction temperature is set at 400 °C, due to the maximum working temperature of the Pd–Ag membrane (around 450 °C), and the absolute reaction pressure range being between 1.0 and 4.0 bar (abs.), regulated by means of a back pressure controller. A sweep gas (N_2) stream is used in the permeate side of the MR, fed by means of a mass-flow controller. In all the experiments, the absolute pressure of MR permeates and the WHSV (calculated as the ratio between glycerol mass flow rate inlet and mass of catalyst) are kept constant at 1.0 bar and 1.01 h^{-1}, respectively. The MR was packed with 3 g of a Co–Al_2O_3 commercial catalyst in pellet form furnished by Johnson Matthey.

The following definitions were applied for describing the Pd–Ag MR performances:

$$\text{sweep factor} = \frac{Q_{\text{Sweep gas,in}}}{Q_{\text{Glycerol,in}}} \tag{4}$$

$$\text{Glycerol conversion}(\%) = \frac{\text{Glycerol}_{\text{in}} - \text{Glycerol}_{\text{out}}}{\text{Glycerol}_{\text{in}}} \times 100 \tag{5}$$

$$\text{Total hydrogen yield}(\%) = \frac{H_{2,\text{Permeate}} + H_{2,\text{Retentate}}}{7\text{Glycerol}_{\text{in}}} \times 100 \tag{6}$$

$$\text{Hydrogen recovery}(\%) = \frac{H_{2,\text{Permeate}}}{H_{2,\text{Permeate}} + H_{2,\text{Retentate}}} \times 100 \tag{7}$$

$$\text{Selectivity}(\%) = \frac{i_{\text{out}}}{\text{Total product}} \times 100 \quad i = H_2,\ CO_2 \text{ and } CO \tag{8}$$

Development of the ANNs model

Each ANN model consists of artificial neurons grouped into layers and put in relation to each other by parallel connections. As illustrated in Fig. 2, the simplest kind of neuron is identified by a scalar input (M), in reality multiplied by a scalar weight (W); the weighted input (M.W) is summed to a second scalar, known as the bias (B). The resulting neuron input (P = M.W + B) is then fed to a transfer function, which eventually produces a scalar output (O). Both W and B can be adjusted, during the so-called training step, to allow the network performing a particular task or exhibiting a desired behavior.