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# Sweep gas flow effect on membrane reactor performance for hydrogen production from high-temperature water-gas shift reaction

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ABSTRACT

The sweep gas flow effect on hydrogen production via water-gas shift reaction (WGSR) using a membrane reactor (MR) was studied numerically in this work. The sweep gas flow rate was used as the primary parameter while the effects of flow pattern, inlet temperature, size, and gas type in the permeation side on MR performance were examined in detail. Using CO conversion and $H_2$ recovery to characterize the MR performance, it was found that the sweep gas flow with inlet/outlet ports arranged on the same side (parallel flow mode) is the optimal design providing higher CO conversion, $H_2$ recovery and lower reaction temperature compared with the other examined flow pattern designs. By varying the sweep gas flow inlet temperature the sweep gas flow can serve as cooling or heating fluid in the reactor. For both cooling and heating cases reactor performance could be degraded due to lower catalyst activity and reversed WGSR, respectively. For the $H_2$-selective MR, the sweep gas type does not affect the MR performance under the same operating conditions. By changing the size of the permeation side it was found that $H_2$ recovery could be improved by permeation side reduction without significantly affecting the CO conversion.



## 1. Introduction

Hydrogen is currently being widely examined as a possible energy carrier because of its high energy content and environmental compatibility. It can be produced from a wide range of primary energy sources. Among them, coal-derived syngas produced from Integrated Gasification Combined Cycle (IGCC) plants represents an attractive pathway for $H_2$ production combined with electricity generation and the synthesis of valuable chemicals. In the coal-to-$H_2$ process $H_2$ is produced mainly through the water-gas shift reaction (WGSR) currently used in many important industrial applications [1].

The WGSR is a well-known and intensively studied reaction. It is a mildly exothermic reaction with an equilibrium constant inversely proportional to temperature [2]. This implies that the reaction is thermodynamically favored at lower temperatures. However, a faster reaction rate can be reached at higher temperatures because of higher chemical kinetics. Therefore, the traditional WGSR is carried out in two steps; first high temperature (300–500 °C) for high throughput, then low temperature (200–250 °C) for increased CO conversion. To enhance the overall coal-to-$H_2$ thermal efficiency and cost-effective design, efforts have been devoted to carrying out the WGSR in membrane reactors (WGSR-MR). In WGSR-MR, WGSR and $H_2$ separation take place simultaneously. The continuous removal of $H_2$ from the reaction side shifts the reaction to the product side according to Le Chatelier's principle. As a result, significantly higher CO conversion and $H_2$ recovery can be achieved. The WGSR-MR produces two gas streams: a high-purity $H_2$ permeated stream that can be used in energy sources such as fuel cells or gas turbine cycles and a high pressure retentate stream containing $CO_2$ that could be sequestered after recovering heat and condensing the water from the stream. With the high-pressure remaining $CO_2$, less compression work is needed for sequestration [3,4].

WGSR-MR has been studied extensively over the past from both experimental study and numerical simulation. In most cases, $H_2$ selective materials such as pure Pd and Pd-based alloys were used as membrane material [5,6]. The general conclusion from the experimental studies is that optimal CO conversion could be achieved using high $H_2$ permeation membrane, low feed rate, high reaction pressure and high sweep gas flow rate [7–11]. Note that most of these experimental works focused on temperatures in the 200–350 °C range, which is the typical temperature range for conventional two-stage WGSR reactors. Since coal-derived syngas is usually produced at high pressure and temperature, it would be desirable that WGSR-MR be operated under high pressure and temperature conditions.

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Under such operating conditions the cooling load can be reduced and the hydrogen permeation can be increased. Augustine et al. [12] recently experimentally studied WGSR-MR at temperatures in the 400–500 °C range with an operating pressure of 14.4 bars. They indicated that for WGSR-MR operated in this range, optimum CO conversion was found at 450 °C. Catalano et al. [13] carried out experiments for WGSR-MR at temperatures in the 420–440 °C range and pressures of 7–20 bars using large surface area composite Pd-based membranes. At low reactant flow rate, 98.1% CO conversion and 81.5% hydrogen recovery at 440 °C was reported. Iyoha et al. [14] experimentally tested WGSR-MR performance using pure Pd and Pd-Cu membranes. They pointed out that it is feasible to operate WGSR-MR at temperatures and pressures as high as 900 °C and 19 atm.

In addition to the experimental work, MR performance can also be realized through the aid of modeling. Mendes et al. [15] recently provided a review on WGSR-MR modeling. Because of mathematical simplicity 1-D modeling is the most commonly used model in studying reactor performance [16–18]. The 1-D model results may under- or over-estimate the reactor performance because $H_2$ permeation through the membrane and heat transfer between reaction and permeation sides are truly a two-dimensional effect. For example, $H_2$ permeates through the membrane in the radial direction while the reactant flow is in the axial direction in typical tubular reactors. This implies that 2-D or 3-D modeling should be considered in describing the actual physical phenomena in the MR [19–24].

The most common MR design is the tube-and-shell type which is similar to the traditional heat exchanger. In this design the reaction side is usually the tube side while the permeation side is the shell side. In order to increase the $H_2$ permeation through the membrane in WGSR-MR, a sweep gas flow is usually introduced in the permeation side. The sweep gas flow serves as an inert gas that carries the $H_2$ away and also serves as a cooling or heating fluid to the reaction from the heat transfer point of view. Over the past most works focused on membrane fabrication aimed at high permeance and reliability, paying little attention to the sweep gas flow effect on the overall MR performance. In the study by Basile et al. [25] the flow direction effect on MR performance was examined. Based on their results more uniform driving force for $H_2$ permeation and higher $H_2$ recovery can be obtained when the flows in the reaction and permeation sides occur in counter-current flow mode. In the study by Barbieria et al. [26] the reaction side was designed on the shell side while the tube was the permeation side. They claimed that under such design the reactor volume could be reduced while the reactor performance remained unchanged compared with the traditional MR design. Without introducing sweep gas flow, Adrover et al. [27] demonstrated that the co-current flow mode could attenuate the thermal effects in the MR by minimizing the temperature increase in the catalyst bed. That is, sweep gas flow acts as a cooling medium along the reactor length.

Numerical modeling has become a powerful tool to predict physical phenomena and can be used in guiding reactor design [28,29]. Using an axisymmetric geometry, a parametric study on the MR performance at high pressure and high temperature was carried out in our previous study [30]. Extending from this study, the present study aims to explore the effect of permeation side design on MR performance using a three-dimensional numerical model. Flow pattern, flow rate, temperature and sweep gas flow type effects on the WGSR-MR performance are discussed in detail.

## 2. Physical and mathematical models

### 2.1. Physical model

The MR studied is shown in Fig. 1. The studied reactor is similar to many experimental studies reported in the literature [31–33]. The tube is treated as the reaction side while the shell side is regarded as the permeation side. On the reaction side the tube is divided into inlet section, membrane-coated section (denoted as membrane tube in the following discussion), and outlet section. In the membrane tube section, Fe-Cr catalyst particles were filled to form a catalyst bed. The syngas is introduced to the reaction side from the inlet section of the reaction side as shown in Fig. 1(a). To focus on the permeation side effect, the reactant flow considered in this study is a mixture of CO and steam with a specified carbon to steam ratio (denoted as S/C). The inlet/outlet ports for the sweep flow are attached vertically to the outer surface of the shell side. The sweep gas flow is introduced into the permeation side through an inlet port to carry the permeated $H_2$ out of the permeation side. The flow directions shown in Fig. 1(a) are denoted as a counter flow mode in which the reactant flows at a direction opposite to that of the sweep gas flow. Detailed reactor geometric dimensions are depicted in Fig. 1(b). The membrane tube has a length of 150 mm and radius (denoted as $R_R$) of 5 mm taken from the study of Chiappetta et al. [34]. All other dimensions are specified to complete the reactor design.

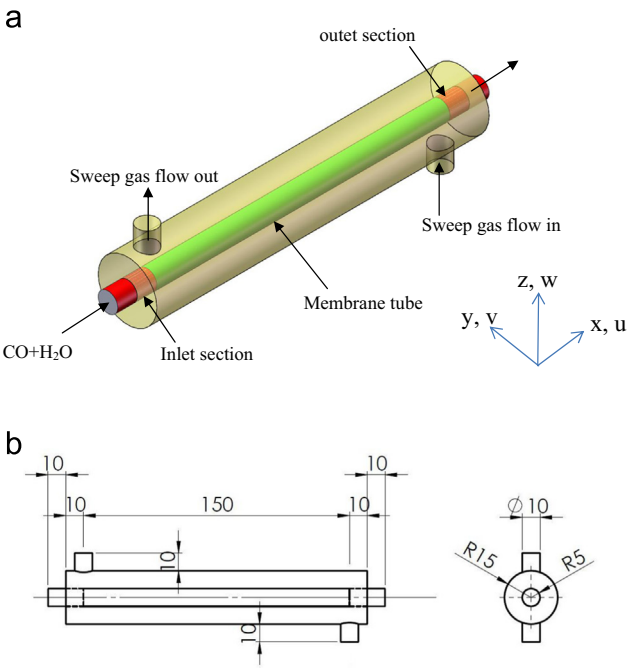


**Fig. 1.** Physical model of MR. (a) Flow configuration with sweep gas flow in counter flow mode, and (b) detail geometric dimensions. Unit: mm.

### 2.2. Mathematical model

The assumptions and mathematical models for the momentum, energy transport, species transport, chemical reaction and hydrogen permeation have been described in detail in our previous study [30]. Because the physical model is in three-dimensional, the boundary conditions need to be modified accordingly. Referring to Fig. 1, the boundary conditions for both reaction and permeation sides are specified as follows:

(1) reaction side inlet

$$u = 2\overline{u}_R[1-(r/R_R)^2], v = w = 0, \dot{n}_{CO} = \dot{n}_{CO,in,R}, \dot{n}_{H_2O} = \dot{n}_{H_2O,in,R}, T = T_{in,R} \quad (1a)$$

(2) permeation side inlet

$$u = 0, v = 0, w = 2\overline{w}_P[1-(r/R_P)^2], \dot{n}_{H_2} = 0, \dot{n}_{SW} = \dot{n}_{SW,in,P}, T = T_{in,P} \quad (1b)$$