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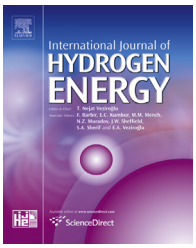

Three-dimensional numerical modeling on high pressure membrane reactors for high temperature water-gas shift reaction

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ABSTRACT

This study presents a three-dimensional numerical model that simulates the H_2 production from coal-derived syngas via a water-gas shift reaction in membrane reactors. The reactor was operated at a temperature of 900 °C, the typical syngas temperature at gasifier exit. The effects of membrane permeance, syngas composition, reactant residence time, sweep gas flow rate and steam-to-carbon (S/C) ratio on reactor performance were examined. Using CO conversion and H_2 recovery to characterize the reactor performance, it was found that the reactor performance can be enhanced using higher sweep gas flow rate, membrane permeance and S/C ratio. However, CO conversion and H_2 recovery limiting values were found when these parameters were further increased. The numerical results also indicated that the reactor performance degraded with increasing CO_2 content in the syngas composition.

Introduction

With the increasing demand for H_2 as an energy carrier in fuel cells and energy sources for combustion, H_2 production is one of the main topics in the energy research world. Due to its natural abundance, coal is expected to be one of the primary sources of H_2 production [1]. 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. For such coal-to-H_2 process, H_2 is produced mainly through the water-gas shift reaction (WGSR) currently used in many significant industrial applications [2].

The WGSR is a well-known and intensively studied reaction that can be theoretically expressed as $CO + H_2O \leftrightarrow H_2 + CO_2$. It is a mildly exothermic reaction with an equilibrium constant inversely proportional to temperature [3]. 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 (300–400 °C) for high throughput, then low temperature (200–250 °C) for increased

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Nomenclature

c_i	molar concentration of species i, mol m^{-3}
D	mass diffusivity, m^2 s^{-1}
E_m	membrane activation energy, J mol^{-1}
F	Correction factor for gas-phase reaction rate
I	unit tensor
J_{H_2}	hydrogen permeate flux, mol m^{-2} s^{-1}
k_f	forward water-gas shift reaction rate constant, $m^{1.5}$ $mol^{0.5}$ s^{-1}
K_{eq}	equilibrium constant
K_p	membrane permeance, mol m^{-2} s^{-1} $Pa^{-0.5}$
M	molecular weight, g mol^{-1}
m	species mass fraction
$\dot{n}$	species molar flow rate, mol s^{-1}
N_G	number of species in the gas mixture
p	pressure, Pa
Q_0	pre-exponential factor, mol m^{-1} s^{-1} $Pa^{-0.5}$
$Q_{in,P}$	sweep gas flow rate, sccm
$Q_{in,R}$	reaction side feed rate, sccm
r_i	molar generation rate of species i, mol m^{-3} s^{-1}
r_{CO}	water-gas shift reaction rate, mol m^{-3} s^{-1}
R_R	reaction side inlet port radius, m
R_P	permeation side inlet port radius, m
u_R	reactant averaged inlet velocity, m s^{-1}
w_P	sweep gas flow averaged inlet velocity, m s^{-1}
T	temperature, K
$\vec{V}$	velocity, m s^{-1}
x	molar fraction
Xco	CO conversion

Greek symbols

β	approaching to equilibrium factor
δ	membrane thickness, m
μ_m	gas mixture viscosity, kg m^{-1} s^{-1}
ρ	gas mixture density, kg m^{-3}
τ	residential time, s

Subscripts

0	reference state
i	ith species of the gas mixture
in	inlet
out	outlet
R	reaction side
P	permeation side

equilibrium CO conversion. Since syngas produced from a gasifier has high temperature (around 900 °C), a heat removal system must be incorporated in order to carry out WGSR. This leads to low thermal efficiency for the H_2 production from IGCC. Moreover, for zero CO_2 emission considerations, more work will be required for further CO_2 sequestration because of the low pressure involved in the two-stage WGSR.

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 zone shifts the reaction to the product side according to Le Chatelier's principle and 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 permeate stream that can be used in energy sources such as fuel cells or gas turbine cycle and a high pressure retentate stream containing CO_2 that could be sequestered after recovering heat and condensing water from the stream. With the high-pressure remaining CO_2, less compression work is needed for sequestration.

WGSR-MR has been studied extensively in the past using experimental and numerical approaches [4–8]. However, most of these studies focused on the low operating temperature ranges such as those for traditional two-stage reactors. Since syngas from a gasifier has a temperature around 900 °C and high pressure around 2000 kPa, it would be beneficial if the WGSR-MR could be integrated immediately after the gasifier [9]. Under such arrangement there would be no need for cooling the syngas and the overall thermal efficiency for the coal-to-H_2 system could be enhanced [10]. Because the permeance of most highly selective dense membranes increases with temperature, an increased H_2 flux could result in a high temperature environment. Moreover, a homogeneous reaction can take place at high temperatures and there is no need for using heterogeneous catalyst particles.

Based on the above advantages, Iyoha et al. [11,12] experimentally tested WGSR-MR performance using Pd-based membranes. They demonstrated that it is feasible to operate WGSR-MR at temperatures and pressures as high as 900 °C and 19 atm. Their experimental data showed that significantly higher CO conversion is possible compared with the equilibrium value and nearly complete H_2 recovery can be obtained when a pure Pd membrane was used. They pointed out the reasons for the enhanced CO conversion was due to the modest catalytic activity of the Pd membrane surface for the forward WGSR, the high rate of H_2 extraction through the Pd-based membranes and the long residence times. However, they also pointed out that the WGSR environment caused pinhole formation in the Pd membrane surface after long time operation. They also studied the H_2S effect on the WGSR-MR performance and found that the H_2S can deactivate the membrane surface, resulting in a precipitous drop in CO conversion. Membrane failure was found when the H_2S-to-H_2 ratio was higher than an equilibrium value at which Pd membrane sulfidization occurs.

Although challenges such as membrane stability and sulfide poison are present, efficient and cost-effective WGSR-MRs operated at high pressure and temperature would be desirable for future coal-to-H_2 development. Further understanding regarding high temperature WGSR-MR operation is needed. Numerical modeling has been recognized as an efficient approach for understanding engineering device design and physical details. Although several attempts have been made to model membrane reactors, very few three-