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Development of pilot WGS/multi-layer membrane for CO_2 capture

See Hoon Lee [a], Jung Nam Kim [b], Won Hyun Eom [b], Shin-Kun Ryi [c], Jong-Soo Park [c], Il Hyun Baek [b,*]

[a] Department of Resources and Energy Engineering, Chonbuk National University, 71-2 Jang-dong, Yuseong-gu, Daejeon 305-343, Republic of Korea
[b] High Efficiency and Clean Energy Research Division, Korea Institute of Energy Research, 71-2 Jang-dong, Yuseong-gu, Daejeon 305-343, Republic of Korea
[c] Energy Materials and Convergence Research Department, Korea Institute of Energy Research, 71-2 Jang-dong, Yuseong-gu, Daejeon 305-343, Republic of Korea

HIGHLIGHTS

- A pilot scale water gas shift with multi-layer Pd–Cu membrane module has been developed.
- The pressure of the hybrid system enhances hydrogen permeation and results in concentrating CO_2 in retentate flow.
- The CO_2 concentration of retentate flow reached over 80 vol.% from 5 vol.% of original syngas.
- We conclude the WGS/membrane hybrid system is a promising way to achieve 90 vol.% of CO_2 in IGCC plants.

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ABSTRACT

For pre-combustion CO_2 capture processes, a 1 Nm^3/h water gas shift (WGS)/multi-layer membrane system has been developed. Simulated syngas (H_2: 25–35, CO: 60–65, CO_2: 5–15 vol.%) was used in these experiments. The 1 Nm^3/h WGS/multi-layer membrane system consisted of mass flow controllers, water gas shift reactors, gas/steam separators, five layer Pd–Cu membrane module, back pressure regulator, gas chromatograph (GC) analyzers and nondispersive infrared (ND-IR) gas analyzers. The operation conditions of WGS/multi-layer membrane system were 200–400 °C, 10–20 bar and steam/carbon ratios in WGS were between 2.0 and 5.0. In the experiments of WGS/multi-layer membrane system, the average gas concentration before membrane module was H_2: 57–58, CO_2: 42–43, CO: 0.2–0.3 vol.%. The CO_2 concentration of retentate flow reached up to 80 vol.% and the H_2 concentration of permeate flow was over 99 vol.%.

1. Introduction

As a need for clean energy usage has increased in the world, integrated gasification combined cycle (IGCC) with pre-combustion CO_2 capture and storage has been developed as a means for maximizing energy efficiency and minimizing climate change. Pre-combustion CO_2 capture, a technology for reducing CO_2 is a highly economical and efficient process that involves the exhausted heat and the use of microequipment in combination with several technologies [1,2]. Also, the demand for hydrogen is expected to grow rapidly in coming years with the uptake of low-emission transport and power generation technologies. Though steam methane reforming to produce syngas accounts for most of the global H_2 production, coal gasification may increasingly replace steam methane reforming to meet the world's growing demand for H_2 with coal's abundance and low-cost [3].

In gasification processes with pre-combustion CO_2 capture coal is converted into environmentally more friendly syngas which is composed of CO, H_2, and CO_2. Especially, the concentration of CO in gasification processes can be in the range of 35–65 vol.%. This is much larger than that is produced in the reforming processes of natural gas, which is about 10 vol.%. In order to capture CO_2 economically in gasification processes, CO in syngas must be converted into CO_2 and H_2 by the water gas shift reaction and then CO_2 must be separated from the H_2 mixture. This approach makes the CO_2 capture process techno-economically viable and maximizes the H_2 yield. Furthermore a novel process such as hydrogen membrane can be conducive to capturing CO_2 and producing efficiently H_2 at relatively lower costs and lower energy consumption than conventional pre-combustion CO_2 capture technologies with absorption units [4,5].

Taking into account the exothermic nature of the WGS reaction, higher CO conversions are favored at lower temperature. But kinetics is almost instantaneous at very high temperatures. Because of the inherent temperature increase during the reaction, synthesis gas generation is typically conducted in adiabatic CO-shift reactors

* Corresponding author. Tel.: +82 42 860 3648; fax: +82 42 860 3641.
E-mail address: ihbaek@kier.re.kr (I.H. Baek).

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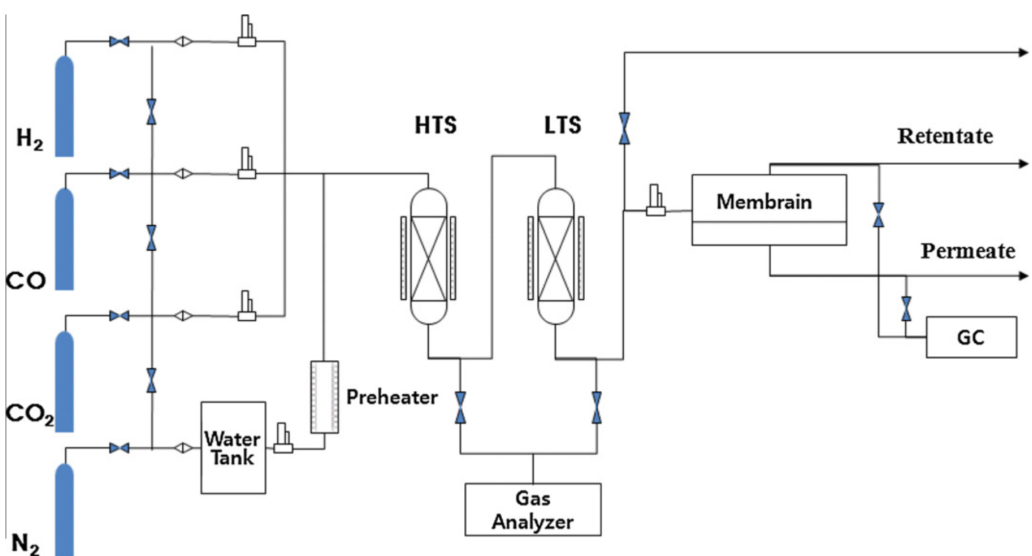
to avoid catalyst overheating and improve the reaction conversion [6]. Conventional two stage process for WGS is generally carried out in two adiabatic reactors, which are a low temperature shift reactor (LTS: 200–220 °C) and a high temperature shift reactor (HTS: 300–450 °C). The extent of the shift conversion determines the final CO concentration in the fuel gas and thus the maximum level of CO_2 control [7].

The separation of hydrogen from shifted syngas increases the concentration of CO_2 stream and results in CO_2 capture cost in coal gasification processes. Therefore many countries like USA, Canada, Japan and Europe is developing pre-combustion CO_2 capture technologies with WGS. To separate hydrogen and CO_2, some researchers suggested hydrogen membrane which allow for the selective permeation of hydrogen to the permeate side, while the high-pressurized retentate stream consists primarily of CO_2. Thus, subsequent CO_2 compression for transport and storage requires low energy [3,5,6,8–10]. Generally palladium alloys have been studied as hydrogen-separating membranes in applications that include hydrogenation and dehydrogenation reactions, H_2 recovery from plant streams, and coal gasification because of the capability to separate hydrogen from gaseous mixtures and stability of Pd and Pd alloy membrane [11–13]. Many studies for Pd or Pd alloy membranes have focused on reducing the thickness of Pd-based membranes because of its obvious connection with hydrogen permeation flux [5].

In this study, a hybrid system composed of two step water gas shift reactors and a five layer Pd–Cu membrane module were used for generating CO_2 rich stream and hydrogen production. The goal was to study the feasibility of WGS reactors with membrane module for pre-combustion CO_2 capture and prove the possibility of a hybrid system to be applied in coal gasifiers. The gas composition of shifted syngas, permeate flow, retentate flow were analyzed to confirm CO_2 enrichment and the purity of H_2.

2. Experimental

In this work, a pilot scale system has been used to facilitate carbon capture based on pre-combustion technologies shown in Fig. 1. This system consisted of water gas shift reactors and a Pd–Cu membrane module operated in a hybrid mode. In the initial stage, the typical syngas is emulated by adjusting the gas composition- CO, H_2, CO_2, N_2. This was achieved by mass flow controllers (MFCs, Brooks Co, 5850) connected to relevant gas cylinders. To inject high temperature steam to the WGS reactors, a pressurized water tank, liquid flow controller (Bronkhorst co., L3O) and steam generator were used. To mix simulated syngas with steam and heat gas



(a) Schematic diagram of WGS/multi-layer membrane system

(b) Picture of WGS/multi-layer membrane system

Fig. 1. Pilot scale WGS/multi membrane system (a) schematic diagram (b) picture of pilot unit.