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Design aspects of the cyclic hybrid adsorbent-membrane reactor (HAMR) system for hydrogen production

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ABSTRACT

As a result of stricter environmental regulations worldwide, hydrogen is becoming an important clean energy source. For it to replace fossil fuels in mobile applications, however, it will require the creation of a production and delivery infrastructure equivalent to the one that currently exists for fossil fuels, which is an immense task. As an alternative and interim step towards the new hydrogen economy, various groups are currently studying steam reforming of methane (SRM) for the on-board generation of hydrogen, or for on site production, in order to alleviate the need for compressed or liquid hydrogen storage. One such technology is the hybrid adsorbent-membrane reactor (HAMR) system, which couples reaction and membrane separation steps with adsorption on the reactor and/or membrane permeate side. Our early studies involved the development of a mathematical model for the HAMR system applied to hydrogen production through SRM. Recently, experimental investigations with the water-gas shift reaction, using microporous membranes and hydrotalcite-type CO_2 adsorbents, were carried out in order to validate the HAMR design model. In this paper, we focus on the practical process design aspects of the HAMR hydrogen production process. A continuous, four-bed HAMR process scheme is proposed and investigated both experimentally and through modeling studies.

1. Introduction

With the growing global population, the number of vehicles and the energy demand for transportation are both projected to grow (Ogden, 2001). Continued reliance on fossil fuels, however, poses challenges with respect to air pollution and energy supply security. Combustion of liquid fuels is responsible for about two thirds of all greenhouse gas emissions. Even with gains in energy efficiency, it is likely that low- or zero-carbon fuels will still be needed to meet future carbon emission reduction goals (Gregory and Pangborn, 1976; Philcox and Fenner, 1996; Yacobucci, 2004; McHugh, 2005; Shoko et al., 2006). PEM fuel cells are a viable alternative to conventional technologies for clean power generation, and their market will expand significantly, if key technical barriers are overcome. A key such barrier is the economic production of pure H_2, the principal fuel used. The current technology for H_2 production is the conventional steam reforming of methane (SRM) and of other hydrocarbons, which is practiced commonly at large-scale for NH_3 and methanol synthesis; it is, however, a complicated capital- and energy-intensive operation, which is difficult to scale-down for fuel cell applications. In addition to its use in fuel cells, H_2 is also being considered as a fuel in power generation, as it is known to improve the burning characteristics of commonly utilized fuels like coal and natural gas. Production costs are again the key barrier for the more widespread use of H_2 in this emerging application.

A unique hybrid adsorbent-membrane reactor (HAMR) system, which combines *in situ* preferential H_2 permeation and simultaneous CO_2 adsorption, has been previously proposed by our group (Park and Tsotsis, 2004; Fayyaz et al., 2005; Harale et al., 2007) for pure H_2 production through the SRM. With the aid of a membrane, and until the adsorbent is saturated, this reactor produces pure H_2. Once saturated, the adsorbent is regenerated via a pressure-swing adsorption (PSA) operation. The HAMR system can be viewed as a membrane reactor (MR) under a PSA operation, potentially suitable for using in a scaled-down version of the SRM process. Conventional MR (Liu et al., 2002; Sanchez and Tsotsis, 2002; Karnik et al., 2003; Ma and Lund, 2003; Tosti et al., 2003; Basile et al., 2003; Drioli, 2004) and sorption-enhanced reactor (SER) technologies (Balasubramanian et al., 1999; Hufton et al., 1999; Waldron and Sircar, 2000; Ding and Alpay, 2000a, 2000b,2001; Ortiz and Harrison, 2001; Xiu et al., 2002a, 2002b, 2003a, 2003b, 2004; Lee et al., 2007a, 2007b; Lee et al., 2008a,

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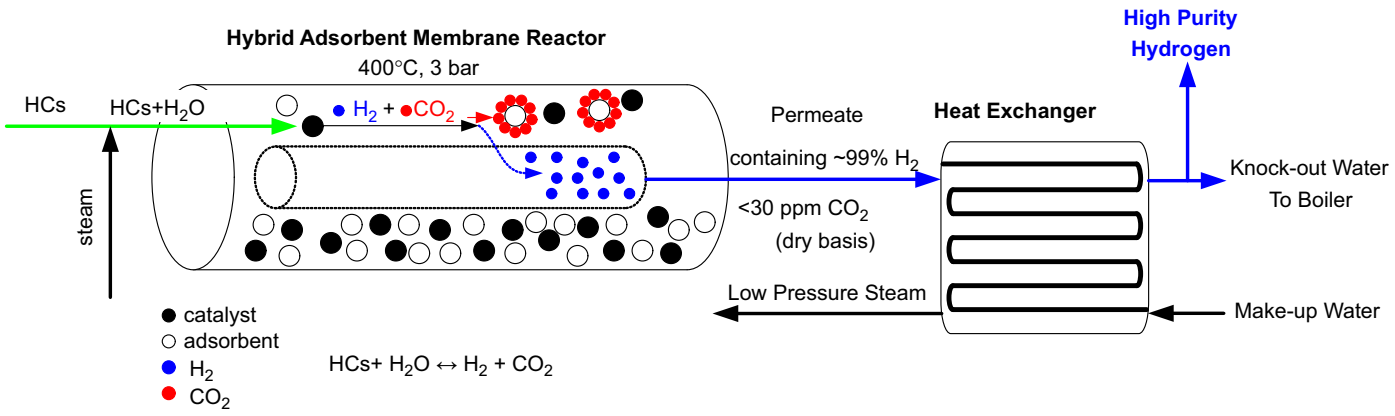

Fig. 1. The HAMR-hydrogen production process.

2008b) proposed in the literature, allow only one of the two SRM products (H_2 for the MR or CO_2 for the SER) to be removed. The ability of the HAMR to remove both products offers additional synergies, both in terms of reaction rate enhancement and product purification. Use of dual adsorbents can, in principle, achieve a similar result; however, separate adsorbent regeneration and product collection are complex operations, in addition to the fact that appropriate high-temperature H_2 adsorbents are lacking.

The HAMR concept, as originally proposed by Park (2001) and Park and Tsotsis (2004), involved a pervaporation MR system, and coupled the reaction and pervaporation steps through a membrane with water adsorption. Coupling reaction, pervaporation, and adsorption significantly improved the performance. Elnashaie and co-workers (Prasad and Elnashaie, 2002, 2003, 2004; Chen and Elnashaie, 2004) analyzed mathematically the behavior of a circulating fluidized-bed HAMR system utilizing Pd membranes. Their reactor was assumed to operate at steady state by continuously re-circulating the catalyst and adsorbent for regeneration through a second reactor. The ability of Pd membranes to withstand the extreme conditions of the fluidized-bed SRM environment and of the adsorbents to undergo continuous recirculation and regeneration still remain to be validated experimentally, however.

Fayyaz et al. (2005) presented a detailed model of a HAMR system, for H_2 production (see Fig. 1) involving a catalytic packed-bed MR, coupling the SRM reaction through a porous SiC membrane with CO_2 adsorption. The HAMR characteristics were investigated for a range of temperatures and pressures relevant to the SRM application. The HAMR system exhibited enhanced CH_4 conversion, H_2 yield, and product purity (when compared to conventional MR and SER processes), which confirmed its promise for reducing the hostile operating conditions of conventional methane-steam reformers, and for meeting H_2 product purity for PEM fuel cells.

Harale et al. (2007) subsequently validated experimentally the HAMR model by studying the catalytic water-gas shift (WGS) reaction, using a commercial layered double hydroxide (LDH) as adsorbent for the CO_2, and nanoporous H_2-selective carbon molecular sieve (CMS) membranes. The reactor was investigated for a range of temperatures and pressures, and the experiments were shown to compare well with the predictions of the mathematical model.

2. The continuous HAMR system

In the proposed HAMR process, the reactants, steam and CH_4 (for the SRM reaction) or CO (for the WGS reaction), are fed into a reactor containing a catalyst, a CO_2 adsorbent, and a hydrogen-permselective porous membrane. During this step a hydrogen-rich product is obtained on the permeate side. Once the adsorbent is saturated with CO_2, however, it must be regenerated. The spent adsorbent can be regenerated using a PSA process, which involves reducing the operating pressure at constant temperature. The HAMR process, similar to the SER, is cyclic, and for its implementation, in order to continuously produce a hydrogen-rich product, at least two reactors must be utilized, each undergoing repetitive reaction/regeneration steps. In this work, a novel four-reactor (four-step) HAMR process is investigated, both experimentally and by mathematical simulations. The HAMR incorporates CMS membranes, which were developed by our group (Sedigh et al., 2000) and are currently undergoing field-testing; due to their intrinsic experimental limitations (operating temperature of $< 300\,^{\circ}C$), the low-temperature WGS reaction is selected as the test reaction. A WGS-HAMR system has its own intrinsic value, however, as a potential reformate mixture polishing step, and as a possible important component of the integrated gas combined cycle (IGCC) power generation process, recently attracting attention. The proposed steps for the four-reactor cyclic HAMR process are described below:

1. *Adsorption-reaction-membrane-separation step*: The reactor is initially pre-saturated with H_2 and steam at the desired reaction temperature and pressure. A mixture of steam and CO at the prescribed ratio is then fed into the reactor, and an essentially pure H_2 product is collected at the permeate side. The reaction step is continued up to the time when product stream purity or productivity specs are met. When the H_2 purity and recovery decrease below the predetermined levels, the feed is diverted into a second identical reactor.

2. *Blow-down step*: During this step, the reactor is depressurized to a lower pressure P_L (atmospheric pressure in the lab experiments), countercurrently to the feed flow direction. The effluent stream during the blow-down step contains all components left in the reactor after step 1, and can be recycled as a feed to another reactor or used as a fuel.

3. *Purge-step*: The reactor is countercurrently purged with a weakly adsorbing gas, such as steam and/or H_2, in order to completely desorb the CO_2 (this step is also commonly practiced in the conventional SER in order to assure optimal adsorbent operation). The desorption step operates at atmospheric pressure (P_L). The desorbed gas mixture can again be recycled as a feed to another reactor or can be used as fuel gas.

4. *Pressurization step*: The reactor is countercurrently pressurized to the reaction pressure with a mixture of steam and H_2. At this point, regeneration of the reactor is completed, so that it is ready to undergo a new four-step cycle.

In this four-bed operation, while one bed is undergoing reaction-separation the other three beds are undergoing one of the regeneration steps. It should be noted here, that for an equivalent four-bed