PROCESS INTENSIFICATION IN HYDROGEN PRODUCTION FROM SYNGAS

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Summary

A "one-box" process has been proposed in order to economically produce pure hydrogen from biomass and coal. The heart of the process is a catalytic membrane reactor making use of carbon molecular sieve membranes. The membrane reactor also incorporates a sulfur-resistant Co/Mo/Al_2O_3 catalyst. Experimental studies were carried out to determine the catalytic reaction kinetics and the rate parameters. The system performance has been investigated for a range of pressures and sweep gas ratios, and compared with simulation results from a mathematical model. The model was also used to study the effect of various parameters on system performance.

Keywords

Hydrogen Production, Process Intensification, Membrane Reactor, Clean Coal Processing Technologies

Introduction

With increasing demand for energy, there is an important need to develop new and long-term technologies based on alternative fuels which can substitute for the declining crude oil production. There are also significant environmental concerns associated with petroleum usage. Hydrogen as a fuel is an important example of a non-carbon energy carrier, which can be produced from various renewable and non-renewable sources [1]. H_2 burns clean and, if widely adopted, could potentially diminish the prospect of global warming.

The abundant availability of coal and biomass in the USA make them attractive and comparatively inexpensive energy sources for H_2 production [2]. The current industrial process involves first reacting coal and/or biomass with steam and/or oxygen in a gasifier to produce syngas. The syngas must then be cooled down to remove its contaminants, especially H_2S and NH_3, and further reacted with steam in water-gas-shift (WGS) reactors to maximize its H_2 content. The WGS reaction is exothermic and its equilibrium constant decreases with temperature. Therefore, typically two reactors, one operating at high temperature and another at lower temperature are being used to overcome both kinetic and equilibrium limitations, and to increase CO conversion. Finally, the gas stream exiting the WGS reactors must be treated further in additional separation units to produce pure hydrogen to be used in both stationary and mobile power applications.

In order to avoid the use of the dual WGS reactor system, membrane reactors (MR) have been proposed for this application. By removing H_2 from the reaction mixture through the membrane, the equilibrium is shifted towards the products, ultimately resulting in higher conversions in a single-stage reactor. Palladium (Pd) [3-5], silica [6-8] and carbon molecular sieve (CMS) [9-10] membranes have been used in the MR applications for hydrogen production.

The total process of H_2 production from coal- and/or biomass-derived syngas, as it is now envisioned, is very energy-intensive. "Process intensification," in which gas clean-up, the WGS reaction, and hydrogen separation are all integrated into one system, offers great potential advantages in scaling-up, and provides for better efficiency and lower costs. What was investigated in our study is a novel reactor/separator system, termed the "one-box" process. The heart of this process is a membrane reactor that combines the WGS reaction with hydrogen separation into a single unit, thus eliminating the need for the two separate WGS reactors and a distinct purification section.

The novelty of the WGS-MR under study is that, it uses impurity-resistant CMS membranes and Co/Mo/Al_2O_3 catalysts, both of which show particularly high tolerance for H_2S and NH_3, which are the main impurities in the syngas produced from coal and biomass (in fact, these catalysts require sulfur to be present to remain active). This eliminates the need for gas clean-up upstream of the WGS reactor, which saves energy but, more importantly, significantly simplifies the process design. The project focus has been on experimental investigations in order to prove the feasibility of using the 'one-box' system for H_2 production from coal and/or

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biomass, and to validate the mathematical model developed.

Results

In our study, the kinetics of the WGS reaction over the $Co/Mo/Al_2O_3$ catalyst were investigated and a data-validated rate expression and its kinetic parameters were obtained. Nanoporous CMS membranes were used for *in-situ* hydrogen separation, and their properties were experimentally investigated. An MR model was developed to simulate the experimental results. No adjustable parameters were used in the simulations. Instead, the rate expression obtained by fitting the experimental data and the measured membrane properties were utilized.

Figure 1 shows CO conversion for the 'one-box' system which is higher than that of the conventional packed-bed reactor (because of the limitations of the lab-scale system that holds only one membrane, the conversions are rather moderate). The figure also shows the predictions of the proposed model for both systems. The agreement between the experimental data and the model predictions is satisfactory, which makes it possible to use the model to study the effect of various parameters on WGS-MR performance and to scale-up the lab-scale system for field testing. Figure 2, for example, shows the predicted effect of reactor pressure on CO conversion (further detailed experimental data and analysis will be provided at the meeting).

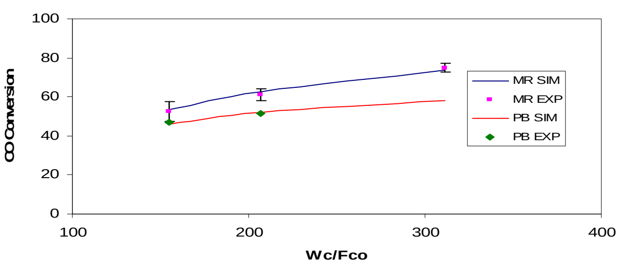

Figure 1. CO Conversion vs. W_c/F_{co}

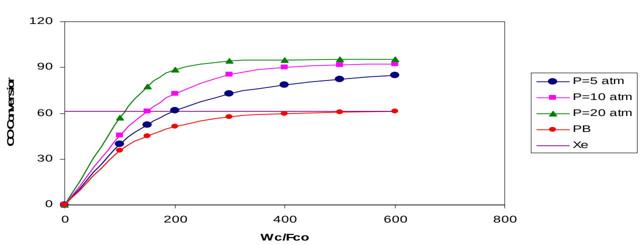

Figure 2. Effect of Pressure on CO Conversion

Conclusions

The experimental studies indicate good agreement with the model predictions without any adjustable parameters. The reactor characteristics were investigated for a range of pressures and sweep ratios. They showed higher conversions than the traditional packed-bed reactor. The effect of membrane properties and experimental conditions on the performance of the system was also investigated. One of the key advantages of the "one-box" system over the traditional system (in addition to improvements in CO conversion and in H_2 yield) is its ability to deliver a product with a significantly lower CO and CO_2 content through the use of the membrane, which preferentially allows the permeation of H_2 while excluding other reactants and products. Using impurity-resistant catalyst adds another advantage by allowing one to perform the reaction in the presence of H_2S and NH_3, which results in considerable energy savings. The CMS membrane also showed great stability in the presence of H_2S and NH_3 for over a month of continuous experimentation. The proposed "one-box" system, therefore, shows good potential for pure hydrogen production and power generation from coal and biomass.

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