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Hydrogen Fuel Purity Impacts for Fuel Cell Vehicles

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Abstract

The purity of hydrogen fuel can have a significant impact on the performance of a fuel cell vehicle and on the production cost of hydrogen fuel. A model has been developed to evaluate the effect of impurities on fuel cell performance and to assess the impacts on hydrogen fuel costs. The model correlates impurity concentrations with the efficiency of hydrogen production and recovery using steam methane reforming (SMR) and pressure-swing-absorption (PSA). Key parameters included are the steam/carbon ratio, pressure, PSA inlet temperature, and sorbent proportions. The results quantify the impacts of fuel quality requirements on hydrogen costs. For CO concentrations in the product hydrogen fuel ranging from 0.1 ppm to 1 ppm, the results of our SMR-PSA modeling studies show that the cost of hydrogen is only secondarily affected by the major operating parameters used in the analyses. On the other hand, the CO content in the fuel H_2 affects significantly the performance of the automotive fuel cell and the resulting fuel economy of the fuel cell vehicle. While the calculated cost of H_2 decreases only slightly, from $3.63/kg to $3.62/kg, as the permissible CO content increases from 0.1 ppm to 1 ppm, the fuel cell efficiency decreases significantly, from 50.7% to 46.4%. This results in an increase in hydrogen consumption from 1,970 kg to 2,065 kg (over 100,000 miles of driving a mid-size sport utility vehicle), and a corresponding increase in fuel costs, from $7,152 to $7,467. The production costs of hydrogen by the SMR-PSA process are primarily influenced by the cost of the feedstock natural gas. For the 2007 average industrial natural gas price of $7.60/million BTU, the resulting hydrogen fuel costs are $3.50 and $3.70 for production efficiencies of 75% and 65%, respectively.

Keywords: hydrogen, hydrogen production, hydrogen cost, fuel cells

1 Introduction

Various stakeholders involved in the development and commercialization of fuel cell automobiles, (such as fuel cell developers, vehicle manufacturers, fuel suppliers, standards development organizations, and regulatory agencies) are discussing the development of fuel quality guidelines and standards for hydrogen dispensed to fuel cell vehicles. The issues being addressed include the effects of different contaminants on fuel cell performance and durability, the production and purification of hydrogen to meet the quality guidelines, and the trade-offs in the associated costs of designing the fuel cell system to operate on the fuel gas of the given quality as well as the costs of providing hydrogen of that quality. While considerable effort is being devoted to examining the effects of fuel impurities on fuel cell systems, relatively little work has been reported on the design of hydrogen production/purification systems to achieve different trace levels of specific contaminants that are known to be deleterious to fuel cell performance or lifetimes.

At present, about 95% of the commercial merchant hydrogen is produced by reforming natural gas, mostly by the steam-methane reforming (SMR) process in large facilities (1). On a dry basis, the product gas mixture contains primarily hydrogen and carbon oxides, much smaller amounts of methane and nitrogen, and trace levels of ammonia, hydrogen sulfide, and other species. Species other than hydrogen are removed from this gas mixture by pressure-swing adsorption (PSA).

2 Hydrogen Production and Purification Process Model

We have developed a model of hydrogen production and purification by the SMR-PSA process, in particular, as it might be used at the relatively small scale of 1500 kg/day of H_2 in distributed forecourt production at neighborhood hydrogen fueling stations. The objective of this work was to evaluate the effects of setting various allowable levels of contaminants in the hydrogen (dispensed to fuel cell vehicles) on the production/purification efficiency, hydrogen recovery, and the cost of the hydrogen. Combining the results of this model with the observed and modeled effects of impurities on fuel cell performance can yield a better understanding of the effects of setting various contaminant level specifications on the costs of the hydrogen, and the performance and costs of the automotive fuel cell systems using that hydrogen.

In the SMR-PSA process, shown schematically in Fig. 1, natural gas is compressed from the supply pressure of 3 atm to the operating pressure of the steam reformer. The reformate is cooled and fed to the water-gas shift (WGS) reactor. The product reformate gas mixture is cooled to condense out the bulk of the water in it, and then it is fed to the PSA unit. The contaminants currently included in the SMR-PSA model are carbon monoxide, carbon dioxide, nitrogen, methane, and hydrogen sulfide. The high purity hydrogen product from the PSA is compressed to 430 atm for off-board storage. The PSA tail-gas containing the unrecovered hydrogen and the impurities (CO, CO2, N2, and CH4) is combusted to provide the heat for the steam reforming reaction. Under conditions of high hydrogen recovery, where the tail-gas alone cannot meet the thermal needs of the reformer, additional natural gas is fed to the burner.

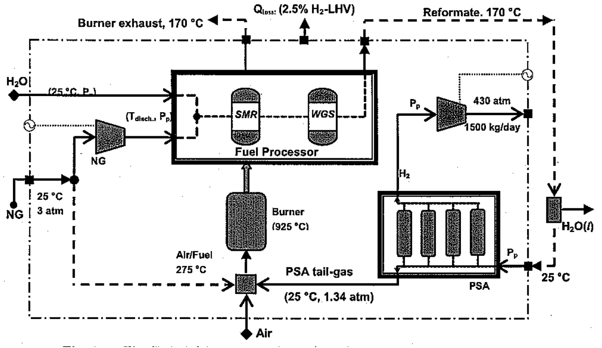

Fig 1. SMR-PSA process schematic

Pressure swing adsorption is widely used in industrial applications, such as air fractionation, gas drying, and hydrogen purification (2,3). The PSA process uses sorbents, typically activated carbons and zeolites, to preferentially adsorb impurities at a high partial pressure and then release them at a lower partial pressure for sorbent regeneration. Because hydrogen is adsorbed much less strongly than other species (except helium), a PSA process yields a purified hydrogen stream at the feed pressure. The PSA is a cyclic process that uses multiple beds operating in a staggered time sequence to provide a nearly constant product and tail-gas flow. Large-scale processes typically employ a large number of beds with several pressure equalizations for high hydrogen recovery and process efficiency. For the relatively small system considered here, we have modeled a PSA process using four beds and eight cyclic steps, with two pressure equalizations (4). The carbon and zeolite PSA beds are usually preceded by a silica or alumina layer to remove water vapor; for the present analyses, however, we assume that the feed to the PSA unit is dry.

3 SMR-PSA Modeling Results and Discussion

Proposed limits for some of the impurities in hydrogen fuel dispensed to fuel cell vehicles are

100 ppm N_2 (as N_2 + Ar), 0.2 ppm CO, 2 ppm CO_2, 0.004 ppm total S (H_2S, COS, etc.), 0.1 ppm NH_3, and similarly small values for some other contaminants, per the Society of Automotive Engineers' Technical Information Report SAE TIR J2719 (5).

In this study, the major operating parameters and their ranges are a steam-to-carbon molar ratio of 3 to 6, SMR and PSA operating pressures of 8 to 22 atm, PSA inlet temperatures of 25ºC or 40ºC, and carbon fractions of 20% to 80% in the carbon/zeolite PSA beds. For the reference base case, the selected parameter values were: steam-to-carbon molar ratio of 4, 8 atm pressure, 750ºC SMR exit temperature (equilibrium), 435ºC WGS exit temperature (equilibrium, but with no change in CH_4 concentration from that at the SMR exit), 25ºC PSA inlet temperature, and 80% carbon fraction in the PSA beds.

Results of the SMR-PSA model are shown in Fig 2. Because the sorption capacity of the PSA beds for N_2 is much lower than that for any of the other impurities considered in this study, N2 shows the highest concentration in the product H_2, followed by CO. Of the impurity species considered, the purified hydrogen product gas is very low in CO_2 (<10–15 ppm) and CH_4 (10–5 to 10–10 ppm), which species essentially do not show any significant breakthrough for the H_2 recovery values investigated.

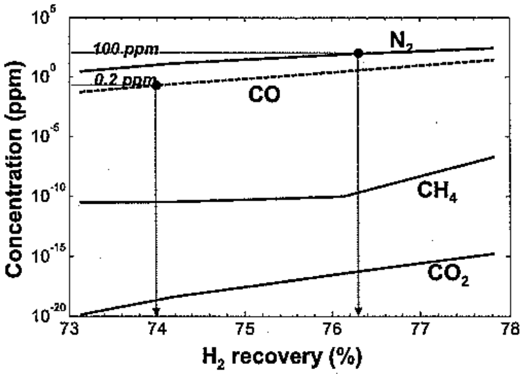

Fig 2. For the base case, CH_4 and CO_2 levels in the product are very low.

The H_2S, despite the relatively high concentration of 100 ppm in the feed to the PSA, is effectively removed without any indication of breakthrough. The main contaminant species of interest are CO and N2.

The overall efficiency of the SMR-PSA production and purification process is shown in Fig 3.

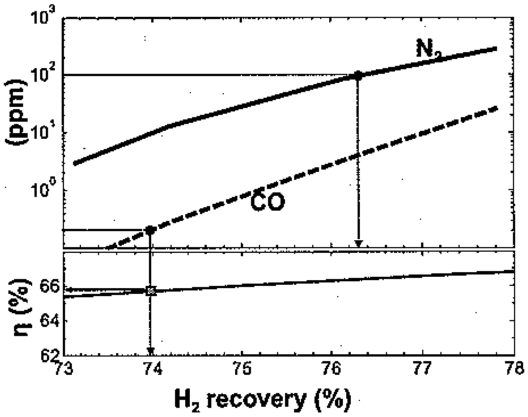

Fig 3. A CO requirement of <0.2 ppm limits H2 recovery to 74% and yields an efficiency of 66%.

Operating the PSA with a hydrogen recovery of ~76% would meet the SAE guideline value of 100 ppm for N_2, but would result in a CO level that exceeds the guideline value of 0.2 ppm. Alternatively, reducing the H_2 recovery to 74% would yield concentrations of 0.2 ppm CO and 10 ppm N_2, meeting the guideline values for all species covered by the model. Thus, for the base case, CO is the limiting species, in that the maximum H_2 recovery is limited by the allowable CO concentration in the product hydrogen. The production efficiency corresponding to 74% H_2 recovery is calculated to be ~66%, defined as the ratio of the lower heating value of the product H_2 to the lower heating value of the natural gas fed to the SMR-PSA system.

4 Costs of Hydrogen Production and Use in Fuel Cell Vehicles

The production costs of H_2 by the SMR-PSA process are greatly influenced by the cost of the feedstock natural gas. For the 2007 average industrial natural gas price of $7.60/million BTU, the corresponding H_2 costs are $3.50 and $3.70 for production efficiencies of 75% and 65%, respectively.

For CO concentrations in the product H_2 ranging from 0.1 ppm to 1 ppm, the results of our SMR-PSA modeling studies show that the cost of H_2 is only secondarily affected by the major operating parameters used in the analyses, i.e., steam-to-carbon molar ratio, PSA inlet temperature and pressure, and the carbon fraction in the PSA beds. On the other hand, the CO content in the fuel H_2 affects significantly the performance of the automotive fuel cell and the resulting fuel economy of the fuel cell vehicle (6,7). While the calculated cost of H_2 decreases only slightly, from $3.63/kg to $3.62/kg, as the permissible CO content increases from 0.1 ppm to 1 ppm, the fuel cell efficiency decreases significantly, from 50.7% to 46.4%. This results in an increase in H_2 consumption from 1,970 kg to 2,065 kg (over 100,000 miles of driving a mid-size sport utility vehicle), and a corresponding increase in fuel costs, from $7,152 to $7,467.

The US Department of Energy's Hydrogen Quality Working Group is using the results of such analyses to help develop hydrogen quality guidelines to minimize the life-cycle costs of hydrogen fuel cell vehicles, including the costs of the hydrogen to fuel such vehicles (8).

Acknowledgments

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