IV.A.14 High-Pressure Distributed Ethanol Reforming

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Objective

- Evaluate the high-pressure steam reforming of ethanol as an option for the distributed production of hydrogen.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- A. Fuel Processor Capital Costs
- C. Operation and Maintenance

Technical Targets

Distributed hydrogen production facilities will need to store and transport hydrogen at pressures in excess of 5000 psig. This is typically achieved by compressing the product hydrogen, and the compression process consumes 18% to 32% of the lower heating value of the hydrogen produced, a significant parasitic load on the overall process efficiency.

This project will identify process options that can meet the Department of Energy's process efficiency target (2010) of 66%. This is being addressed with system models and experimental development of key technological barriers, namely high-pressure reformability and purification/separation options.

Approach

- Characterize catalytic performance at high pressures as a function of catalyst formulation, temperature, steam-to-carbon ratio, and space velocity.
- Model ideal systems based on reaction stoichiometry, material, and energy balances. Evaluate system models to compare performance (e.g., efficiency, cost, etc.) of alternative process options and identify technical barriers.

Accomplishments

- Material and energy balance calculations indicate that increasing the steam-to-carbon ratio above the stoichiometric value reduces process efficiency.

- Thermodynamic analyses of the reforming reaction indicated that elevated pressures lead to higher hydrocarbon byproducts. Higher temperatures and steam-to-carbon ratios can be used to increase the hydrogen yield.

- A simple GCtool model shows that a staged reformer-hydrogen separation strategy is a promising approach for the high-pressure system.

- Catalytic reactions have been initiated in a pressurized integral micro-reactor built to study the reaction parameters.

Future Directions

- Set up a fuel processing system model to investigate a suitable strategy for high-pressure reforming of ethanol. The efficiency of high-pressure hydrogen production using such a system will be compared with a traditional process in which purified hydrogen is compressed to storage pressures.

- Evaluate the activity, selectivity, and durability of promising catalysts at pressures of 1000 psi and above. The catalyst durability tests will be conducted to define operating conditions (temperature, pressure, steam-to-carbon ratio [S/C]) that permit at least 100 hours of coke-free operation.

Introduction

Distributed hydrogen production facilities will need to store and transport hydrogen at pressures in excess of 5000 psig. This is typically achieved by compressing the product hydrogen, and the compression process consumes 18% to 32% of the lower heating value of the hydrogen produced, a significant parasitic load on the overall process efficiency. This project investigates the option of steam reforming ethanol at elevated pressures, since this pathway almost eliminates the cost of compression by feeding a pressurized liquid stream into the reformer.

The challenges in high-pressure reforming include (1) high hydrocarbon and low hydrogen yields (at a given temperature and steam-to-carbon ratio) favored by thermodynamic equilibrium; (2) the greater tendency to form coke deposits; and (3) the potentially higher capital cost associated with pressurized equipment. The high-pressure process offers the advantages of a more compact system (greater reactivity) and higher driving force for pressure-based separation/purification systems. The system design needs to balance these characteristics to meet an efficiency target (for calendar year 2010) of 66%, to produce hydrogen at a cost of $3.60 per gallon of gasoline equivalent.

Approach

Simple system models have been set up to calculate the efficiencies and product yields

achievable based on reaction stoichiometry (ideal) and thermodynamic equilibrium. The equilibrium calculations were conducted for a single reactor and for simple systems that include reaction, hydrogen extraction, and thermal integration.

An experimental apparatus has been set up to study the ethanol steam reforming reaction as a function of the catalyst formulation, space velocity, steam-to-carbon ratio, temperature, and pressure. The experiments are being conducted in an integral micro-reactor loaded with powder catalysts. The apparatus has been approved for operation at pressures up to 1100 psig and temperatures up to 750°C.

Results

The requisite energy density of hydrogen is usually achieved by storing the hydrogen at elevated pressures. The energy consumed for the compression work is quite significant and represents a major loss in efficiency for the production process. Figure 1 plots the percentage of the lower heating value (LHV) of the hydrogen that is consumed in compressing hydrogen to 6,000 psi (408 atm) as a function of the compressor inlet pressure. Compressing the hydrogen from 10 to 408 atm with a 5-stage compressor, with efficiencies as indicated on the plot, will consume electric energy that is the equivalent of 18.5% of the LHV of hydrogen. This does not include the efficiency loss associated with the conversion of hydrogen to
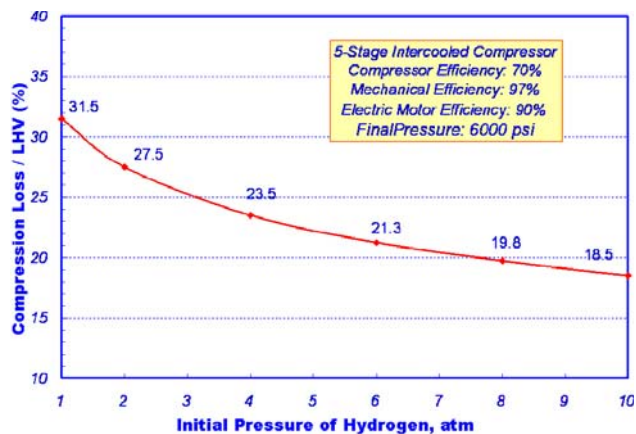
Figure 1. Fraction of the Hydrogen's Lower Heating Value Consumed in Compressing the Hydrogen to 6,000 psi, as a Function of the Inlet Hydrogen Pressure
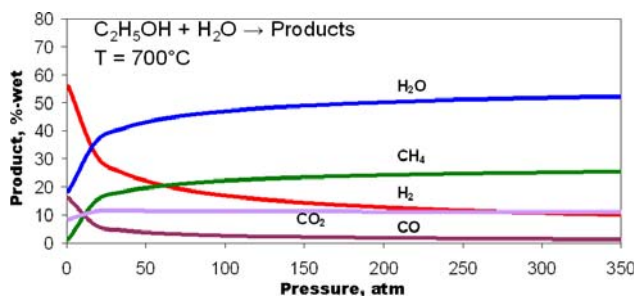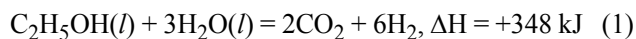

Figure 2. Effect of Pressure on Equilibrium Product Distribution from the Steam Reforming of Ethanol at 700°C

Figure 3. Effect of Temperature and Steam-To-Carbon Ratio on the Equilibrium Product Gas Distribution from the Steam Reforming of Ethanol

electricity. The calculations affirm the advantage of generating the hydrogen at high pressure, especially in the case of steam reforming of a liquid fuel, where the pressurized liquid feeds can be delivered to the fuel processor with negligible energy penalty.

While there is a significant efficiency benefit to pressurizing the fuel processor, there are also some challenges that need novel solutions. The ethanol steam reforming reaction produces more molecules than it reacts. The idealized steam reforming reaction, written as

$$C_2H_5OH(l) + 3H_2O(l) = 2CO_2 + 6H_2, \Delta H = +348\,kJ \quad (1)$$

produces 8 molecules of products from 4 molecules of reactants. In accordance with the Le Chatelier principle, such reactions are thermodynamically not favored at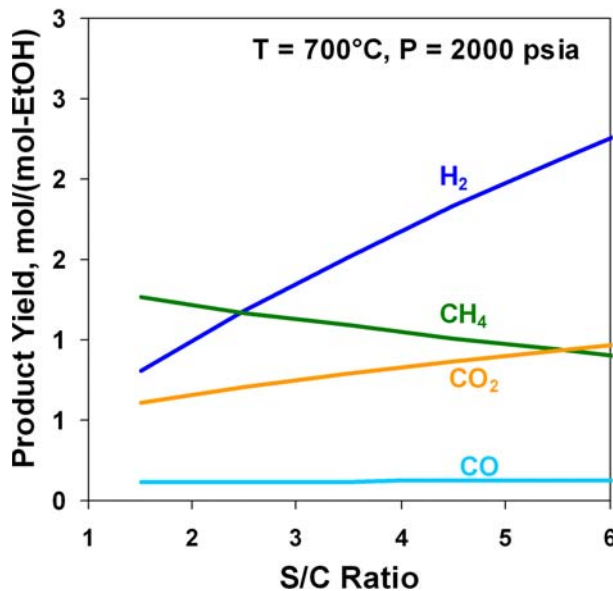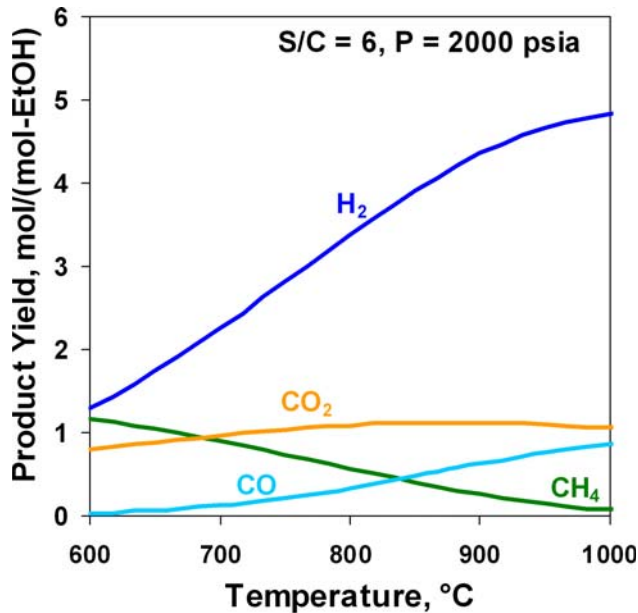 elevated pressures. This is confirmed by equilibrium calculations, as shown in Figure 2, where pressure increases lead to a reduction in hydrogen yields. At 700°C, the carbon and hydrogen are bound in methane, the most stable of the hydrocarbon species.

The negative effect of pressure on hydrogen yield can be offset by operating at higher
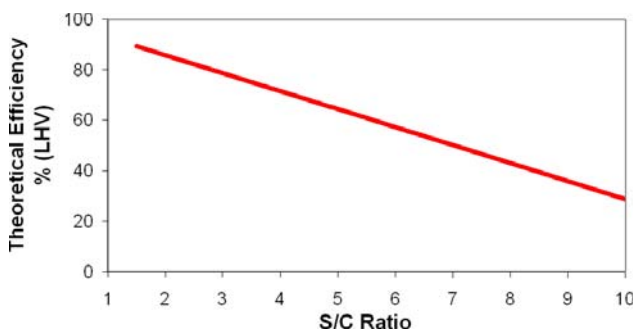
Figure 4. Effect of the Steam-To-Carbon Ratio (S/C) on the Efficiency of an Idealized Reformer

Figure 5. Effect of Reforming Pressure on the Mols of Hydrogen Recovered and the Pressure Across Each of Two Hydrogen Separation Membranes in a 2-Stage Reformer System

temperatures and steam-to-carbon ratios (S/C), as shown in Figures 3(a) and 3(b). Thus, at 2000 psia (136 bar), 900°C, and S/C=6, the reformer will yield 4.4 mols of hydrogen per mol of ethanol under equilibrium conditions, compared with a theoretical maximum of 6 mols achievable per Equation (1). It should be noted that the equilibrium product contains 0.6 mols of CO, most of which can be converted to additional hydrogen via the water gas shift reaction.

A simple, idealized reformer model was set up to calculate the theoretical efficiency, where the reformer reaction was described as in Equation (1). It was assumed that (1) the excess water used in S/C>1.5 ($H_2O/C_2H_5OH>3$) would leave the system in the gas phase and (2) the heat of reaction was obtained by removing and combusting the appropriate amount of hydrogen from the product stream. The efficiency was defined as the LHV of the net hydrogen produced as a percentage of the LHV of ethanol fed to the system:

η, % = [LHV of H_2 produced per Eq.(1) – Heat of reaction of Eq.(1)] × 100/[LHV of Ethanol]   (2)

Figure 4 plots the effect of the steam-to-carbon ratio on the efficiency, showing a maximum of 89% at the stoichiometric S/C (=1.5) and a linear reduction at higher S/C. The energy loss is due to the latent heat of water vaporization that is needed for the gas phase reforming reaction [1]. This energy is typically not recovered from the exhaust.

Increasing the complexity to incorporate thermodynamic equilibria and hydrogen separation through a membrane, the system model approach was used to look at the effect of two stages of reforming. Each reformer was followed by a
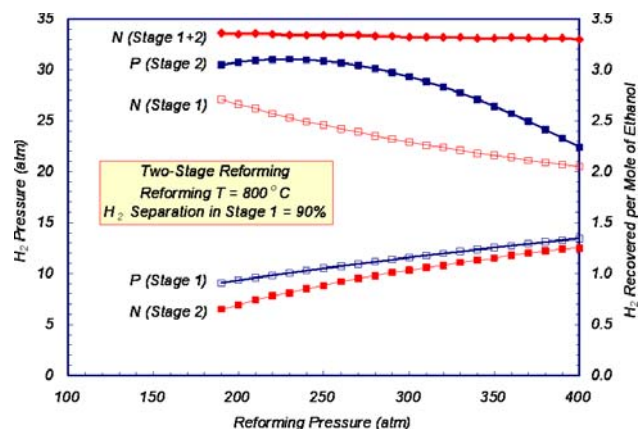
hydrogen separation module. Figure 5 shows the effect of reformer pressure on the mols of hydrogen recovered and the available hydrogen partial pressure across the membrane. Increasing the reforming pressure changes the distribution of hydrogen extracted at each stage; however, the total hydrogen recovered is quite insensitive to the reforming pressure. This is in contrast to a single-stage system (not shown), where the mols of hydrogen were found to decline sharply with increasing pressure. These and other preliminary simulations indicate the need to conduct a more exhaustive analysis of system options to determine the pros and cons of pressurized reforming.

An experimental apparatus has been built for catalytic reaction studies at pressures up to 1100 psi. The ethanol-water mixture is vaporized and then passed over a bed packed with 2.4 g of granular (200-300 μm) nickel catalyst [2] from Sud Chemie, Inc. The 2.4-mm internal diameter reactor tube is placed inside a furnace that is maintained at the desired reaction temperature. The product gas composition is analyzed with a gas chromatograph and a residual gas analyzer.

The experiments have recently been initiated, and preliminary data indicate that at 1020 psig, part of the ethanol reacts within the vaporizer and downstream lines, where the temperatures are limited to 400°C. Table 1 shows the composition of the gas entering the catalyst bed (column 2), containing 58%

Table 1. Product Gas Composition from Steam Reforming of Ethanol (650°C, 1020 psig, Ni catalyst, S/C=20)

	Above Catalyst Bed					Equilibrium
Space Velocity, hr^{-1}		196,000	98,000	46,000	30,000	
H$_2$, %-dry	58.2	60.7	61.3	62.7	63.8	70.6
CH$_4$, %-dry	15.5	13.9	13.5	12.4	11.0	4.0
CO, %-dry	4.8	2.8	2.1	1.3	1.4	1.5
CO$_2$, %-dry	21.3	22.5	23.1.	23.5	23.9	23.9
C$_2$H$_4$, %-dry	0.02					
C$_2$H$_6$, %-dry	0.20	0.13	0.11	0.07	0.04	

hydrogen and 16% methane, indicating considerable breakdown and reaction of the ethanol feed. Contact with the catalyst (decreasing space velocity as shown in Table 1) leads to a reduction in the mole fractions of the hydrocarbons and an increase in hydrogen. The reduction of ethylene is a significant benefit since olefins are known coke precursors. The right column lists the composition that is expected at equilibrium under these conditions, indicating that more of the methane should be reacting to produce hydrogen.

Conclusions

- Pressurized reforming may significantly improve the efficiency of the process for converting ethanol to compressed hydrogen.
- The negative thermodynamics of high-pressure reforming can be offset with additional steam, higher temperature, and hydrogen extraction.

- System modeling shows that multiple staging and alternating with hydrogen separation offers efficiency advantages. Further studies are needed to confirm the benefits and trade-offs of various system options.
- Micro-reactor studies indicate that ethanol decomposes to produce methane within the vaporizer. The nickel catalyst showed an incremental effect of converting the hydrocarbons.

References

1. S. Ahmed and M. Krumpelt, "Hydrogen from Hydrocarbon Fuels for Fuel Cell," Int. J. of Hydrogen Energy, 26 (2001) 291-301.

2. A.N. Fatsikostas and X.E. Verykios, "Reaction Network of Steam Reforming of Ethanol over Ni-based Catalysts," J. Catalysis, 225 (2004) 439-452.