

## II.A.11 High Pressure Distributed Ethanol Reforming

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direction determined annually by DOE

### Objectives

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 Production section (3.1.4.2) 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 (O&M)

### Technical Targets

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.

### Accomplishments

- Studied the effect of pressure and gas hourly space velocity on the steam reforming of ethanol over a nickel catalyst.
- Studied the effect of pressure on a rhodium-based catalyst for the steam reforming of ethanol. The rhodium catalyst yielded more hydrogen and was operated coke-free for the duration of the experiments.

### Introduction

Distributed hydrogen production facilities will need to store and transport hydrogen at pressures in excess of 5,000 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 were conducted in an integral micro-reactor loaded with powder and supported (ceramic foam) catalysts, at pressures up to 1,050 psig and temperatures up to 650°C.

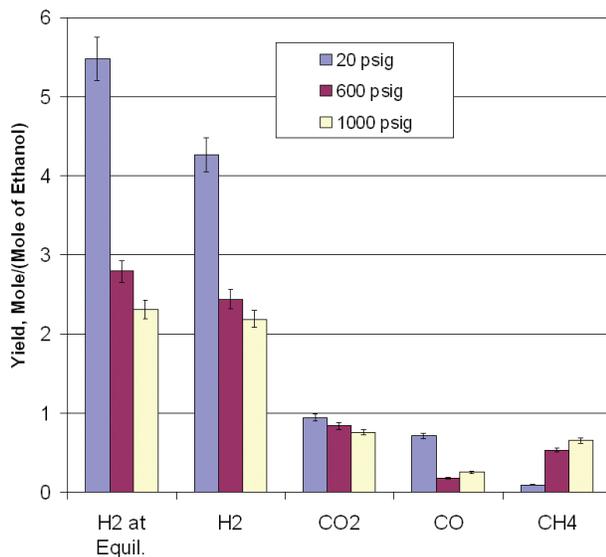
### Results

Experiments have been conducted with a nickel catalyst (0.50 g of 200-300  $\mu\text{m}$ ) from Sud Chemie Inc., packed in a 6.35-mm (0.25-in.) internal diameter reactor tube. The catalyst temperature was controlled by placing the reactor within a tube furnace. The vaporized ethanol-water mixture [steam-to-carbon ratio (S/C): 6-20] was passed over the catalyst at gas hourly space velocities (GHSV) in the range 14,900-83,000 per hour.

Figure 1 shows the effect of pressure on the product composition (dry basis) at a GHSV of 14,900 per hour and S/C=6. Consistent with equilibrium calculations as shown by the first set of columns, “H2 at Equil.,” the hydrogen yield decreased with increasing pressure [1]. Comparing the first two sets of columns, it is seen that the experimental hydrogen yield achievable with the nickel catalyst at these conditions was considerably lower than that predicted by equilibrium, and the discrepancy is larger at the lower pressures. The figure also shows that the higher pressure led to a significant increase in the methane yield.

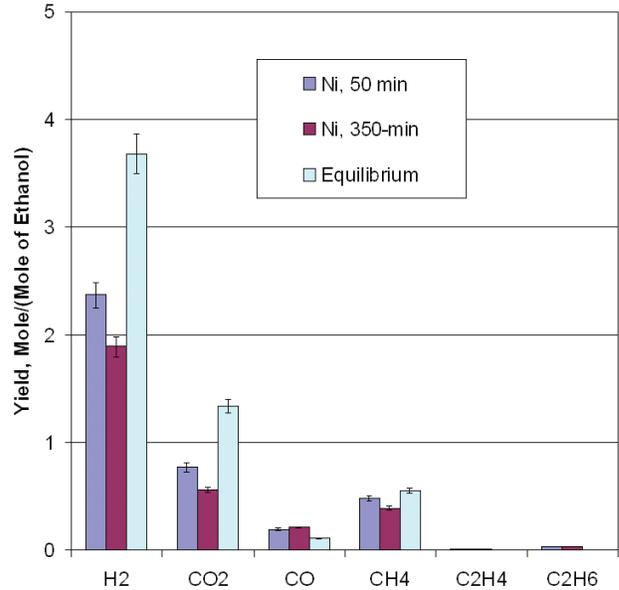
The experiment with the nickel catalyst was continued at the elevated pressure of 1,000 psig (S/C=12, GHSV=83,000 per hour, 650°C) for over 350 minutes. Figure 2 shows that the hydrogen yield dropped quite sharply between 50 minutes and 350 minutes. At the end of the day’s experiment, pure steam was passed through the heated catalyst bed for ~30 minutes. Analysis of the effluent stream showed the presence of small amounts of hydrogen and carbon oxides, indicating the formation of carbonaceous deposits during the experiment. Disassembly of the reactor also revealed deposits of carbonaceous products at downstream locations where the temperatures were not high enough to gasify the deposited coke during steam-cleaning.

The nickel catalyst was replaced with a 4% rhodium with a lanthanum aluminate support and the steam reforming reactions were repeated. Figure 3 compares the performance of the nickel and rhodium catalysts at 20 psig, 650°C, GHSV=83,000 per hour, and S/C=12. As shown in the plot, the hydrogen yield from the rhodium catalyst was much higher than from nickel,

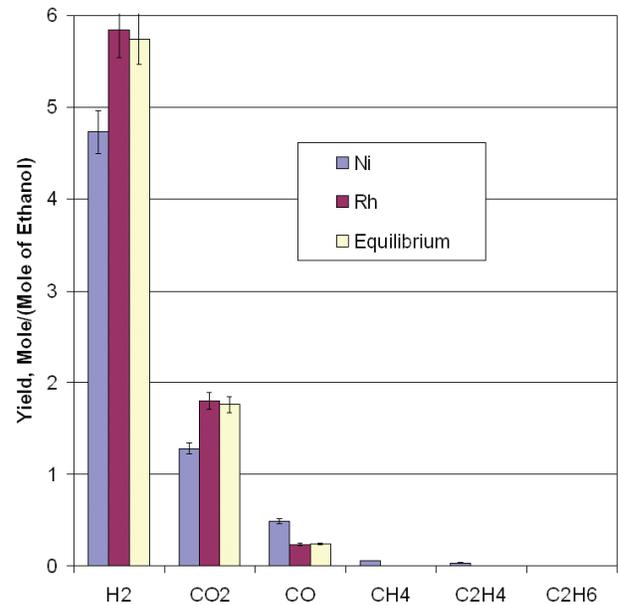


**FIGURE 1.** Effect of Pressure on Product Yields with Nickel Catalyst (S/C=6, GHSV=14,900 per hour, 20, 600, and 1000 psig, 650°C)

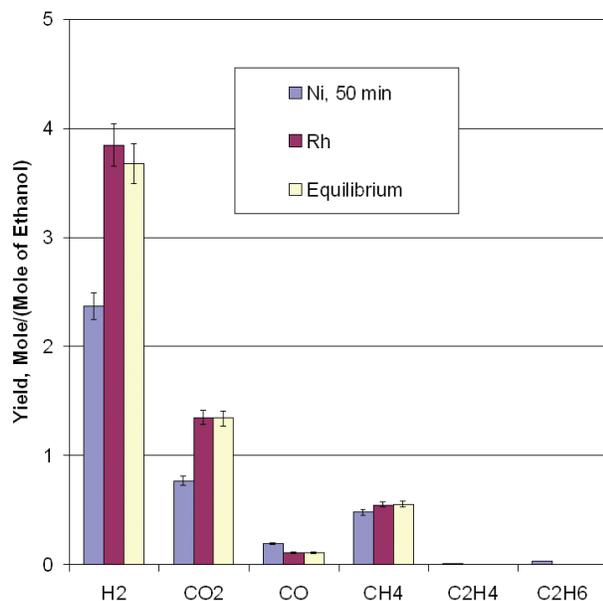
and closely matched the yields predicted by equilibrium calculations. Figure 4 shows a similar comparison at the higher pressure of 1,000 psig. Similar to the trends at low pressure (Figure 3), the rhodium catalyst produces more hydrogen than nickel, and its yields closely approximate the yields anticipated at equilibrium. Figure 5 shows the effect of pressure on the yield performance of the rhodium catalyst. As expected, the hydrogen



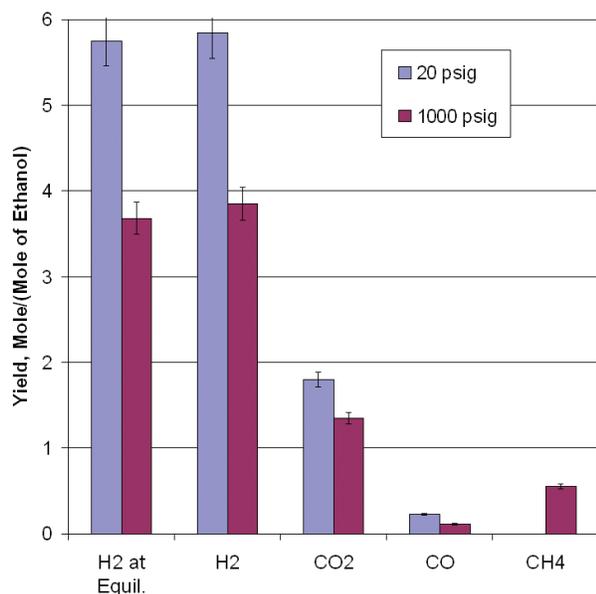
**FIGURE 2.** The Yield from the Nickel Catalyst is found to Deteriorate Over Time; Product Yields Compared to Equilibrium Predicted Yields. (S/C=12, GHSV=83,000 per hour, 1000 psig, 650°C)



**FIGURE 3.** Product Yields with Nickel and Rhodium Catalysts, Compared to Equilibrium Predicted Yields (S/C=12, GHSV=83,000 per hour, 20 psig, 650°C)

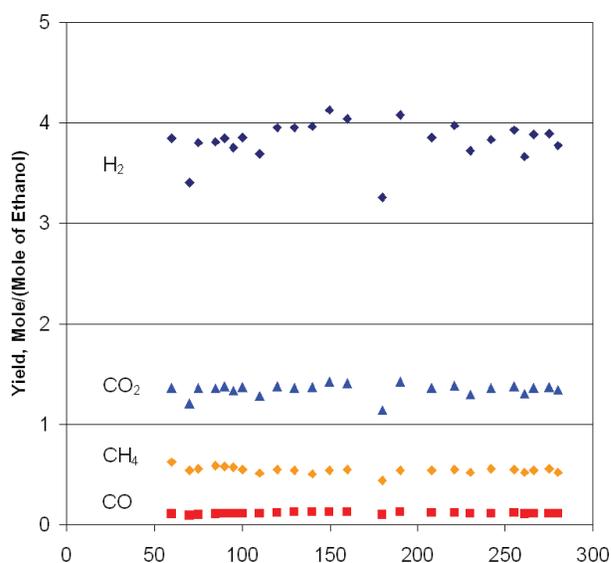


**FIGURE 4.** Product Yields with Nickel and Rhodium Catalysts, Compared to Equilibrium Predicted Yields (S/C=12, GHSV=83,000 per hour, 1,000 psig, 650°C)



**FIGURE 5.** Effect of Pressure on Product Yields with Rhodium Catalyst (S/C=12, GHSV=83,000 per hour, 20 and 1,000 psig, 650°C)

yield decreases while the methane yield increases with pressure. Unlike the nickel catalyst, however, the rhodium catalyst was found to be stable, maintaining its product yield through the day's experiment, as shown in Figure 6. The steam cleaning step at the end of the day's run produced very little carbon oxide, and the reactor assembly was free of any visible carbonaceous deposits.



**FIGURE 6.** Stability of Rhodium Catalyst as Reflected by the Product Yield (S/C=12, GHSV=83,000 per hour, 1,000 psig, 650°C)

## Conclusions and Future Directions

Reforming at elevated pressure leads toward a product mix that favors methane with the commensurate lower hydrogen yield. The nickel catalyst was not very effective even at low pressures; at higher pressures it demonstrated a tendency to form carbonaceous species that deactivated the catalyst quite sharply. The rhodium catalyst performed much better than the nickel catalyst. At the elevated pressures, the hydrogen yield with this catalyst approached the equilibrium predicted values. Unlike the nickel catalyst, the rhodium catalyst did not demonstrate a coking tendency and was able to maintain its product yields during a full day's operation.

## FY 2006 Publications/Presentations

1. S.H.D. Lee, S. Ahmed, R. Ahluwalia, and J. Miller, "Steam Reforming of Ethanol at Elevated Pressure for Distributed Hydrogen Production", Presented at NHA Annual Hydrogen Conference 2006, March 12-16, 2006, Long Beach, CA.
2. S.H.D. Lee, S. Ahmed, and R. Ahluwalia, "Steam Reforming of Ethanol at Elevated Pressure for Hydrogen Production", Accepted for poster presentation at 2006 Fuel Cell Seminar, November 13-17, 2006, Honolulu, HI.

## References

1. S. Ahmed, S. Lee, R. Ahluwalia, "High-Pressure Distributed Ethanol Reforming," DOE Hydrogen Program, Annual Progress Report, pp. 136-140, 2005.