II.A.4 Pressurized Steam Reforming of Bio-Derived Liquids for Distributed Hydrogen Production

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Project End Date: Project continuation and
direction determined annually by DOE

Objectives

Evaluate the pressurized steam reforming of bio-derived fuels 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) Reformer Capital Costs

(E) Greenhouse Gas Emissions

Technical Targets

This project is conducting fundamental studies to define feasible pathways that can meet DOE targets for efficiency using the pressurized reforming of bio-derived liquids such as ethanol and glycerol, through the use of systems analysis and is evaluating advanced reactor concepts that combine reactions with separations. The following are some of the relevant DOE targets:
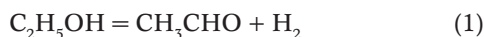
Characteristics	Units	2012 Target	2017 Target
Production Unit Energy Efficiency	% (LHV)	72.0	65-75
Total Hydrogen Cost	$/gge	3.80	<3.00

Accomplishments

- Quantified the improvement in yield resulting from the permeation of hydrogen from a reforming zone operating at elevated pressures.
- Demonstrated the effectiveness of the catalyst on the conversion/suppression of C_2 hydrocarbons.
- Set up and validated a mathematical model of our membrane reactor, which can now be used to predict conditions necessary to meet hydrogen production rates consistent with efficiency targets.

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Introduction

Distributed hydrogen production facilities will need to store and transport hydrogen at pressures in excess of 5,000 psig. Existing production pathways based on natural gas produce the compressed hydrogen in two compression steps: 1) the natural gas feed is compressed to the reforming pressures (~150 psig), and 2) the final product hydrogen from the pressure swing adsorption unit is then compressed to the storage pressure of 5,000 psig. The energy needed for the compression can be equivalent to a significant fraction of the lower heating value (LHV) of the product hydrogen. In this project, we are investigating the option of steam-reforming a bio-derived fuel (e.g., ethanol, etc.) at elevated pressures, since this pathway can greatly reduce the energy cost of compression by feeding a pressurized liquid stream into the reformer.

The challenges in high-pressure reforming of ethanol include (1) high hydrocarbon and low hydrogen yields (at a given temperature and steam-to-carbon ratio) favored by thermodynamic equilibrium; and (2) the potentially higher capital cost associated with pressurized equipment. On the other hand, 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 diverse characteristics to meet an efficiency target (for calendar year 2012) of 72%, to produce hydrogen at a cost of $3.80 per gallon of gasoline equivalent. This project has experimentally established the effect of pressure, temperature, space velocity and steam-to-carbon ratio on the product yields during the steam reforming process. The beneficial effect of hydrogen extraction through a membrane on the yields has been quantified.

Approach

An experimental apparatus has been set up to study the effect of pressure and other operating conditions – temperature (600-750°C), space velocity (<25,000/hr), and steam-to-carbon ratio (3-6), on the achievable product yields and the potential for coke formation. Recognizing that extraction of reforming products (hydrogen, carbon dioxide) can offset the reduction in hydrogen yields that accompanies higher pressure [1], the tests are being conducted in a membrane reactor. Thus far, these tests have been limited to use with hydrogen transport membranes. Systems analysis of the overall process is being conducted to evaluate the prospects of process options that can meet the long term efficiency goal of 72%.

Results

The ethanol-water feed is vaporized and preheated before entering the catalyst bed. Analysis of the product gas entering the catalyst bed shows a mixture of hydrogen, carbon oxides, methane, ethylene, and ethane. The condensable products were analyzed to qualitatively detect the presence of ethanol, acetaldehyde, and acetic acid. The mix suggests the reactions

$$C_2H_5OH = CH_3CHO + H_2 \tag{1}$$

$$C_2H_5OH = C_2H_4 + H_2O \tag{2}$$

$$C_2H_5OH + H_2O = CH_3COOH + 2H_2 \tag{3}$$

$$CH_3CHO = CO + CH_4 \tag{4}$$

$$C_2H_4 + H_2 = C_2H_6 \tag{5}$$

The partially reacted feed stream then passes through the catalyst zone, filled with 0.45 g of catalyst (4 wt% Rh/La-Al$_2$O$_3$), with a resultant product mix where the hydrocarbons are further converted to produce carbon oxides and hydrogen, as shown in Table 1. It is notable that the ethylene and ethane yields are no longer detected, and the CO$_x$ selectivity (defined as the sum of

TABLE 1. Gas Compositions Entering and Exiting the Catalyst Bed During the Steam Reforming of Ethanol (Catalyst Bed Temperature ~700°C)

Conditions: 1,000 psig, S/C=6, SV=14,300/hr		
	After Pre-heater	After Catalyst Bed
H$_2$, mol/mol EtOH	1.52	2.18
CO+CO$_2$, mol/mol EtOH	0.79	0.94
CH$_4$, mol/mol EtOH	0.57	0.59
C$_2$H$_4$, mol/mol EtOH	0.004	not detected
C$_2$H$_6$, mol/mol EtOH	0.07	not detected
COx Selectivity, %	40	47

the carbon oxides as a percentage of the carbon in the feed), increases within the catalyst bed.

Table 2 shows the effect of temperature and pressure on the product yields from the steam reforming of ethanol at a space velocity of 14,300/hr and S/C=6. Hydrogen permeation across the membrane was prevented by valving off the permeate side. Increasing the temperature from 600° to 700°C, results in ~27% higher hydrogen yields at 100 psig. Increasing the pressure shows the opposite effect in that the hydrogen yields are lower – increasing from 100 to 1,000 psig at 700°C results in a 53% reduction in the hydrogen yield. The relatively low CO$_x$ selectivities, especially at the higher pressure, indicate the difficulty in releasing the hydrogen from the hydrocarbons at elevated pressure. For reference, the table also shows the hydrogen and methane yields that should exist at equilibrium conditions. Table 3 shows the hydrogen and methane yields when hydrogen is allowed to permeate across a palladium-membrane located in the reaction zone. With the space velocity through the reaction zone maintained the same (14,300/hr), the amount of permeated hydrogen increases with both temperature and pressure and is the result of a combination of factors. Higher temperature promotes the conversion of hydrocarbons to produce hydrogen. On the other hand, higher

TABLE 2. Product Yields as a Function of Temperature and Pressure During the Steam Reforming of Ethanol (SV=14,300/hr, S/C=6)

Catalyst Bed Temperature, °C	~600		~650		~700	
	Exptl.	Equilibrium	Exptl.	Equilibrium	Exptl.	Equilibrium
Pressure, psig	100 psig					
H$_2$, mol/mol EtOH	3.63	3.97	4.38	4.71	4.60	5.14
CH$_4$, mol/mol EtOH	0.52	0.46	0.24	0.24	0.12	.095
COx Selectivity, %	69	77	80	88	83	96
Pressure, psig	1,000 psig					
H$_2$, mol/mol EtOH	1.46	1.73	1.98	2.30	2.18	2.91
CH$_4$, mol/mol EtOH	0.95	1.05	0.82	0.90	0.59	0.72
COx Selectivity, %	38	47	46	55	47	64

TABLE 3. Effects of Temperature and Pressure on the Product Yields from the Steam Reforming of Ethanol in a (Hydrogen Transport) Membrane Reactor (S/C=6, SV=14,300/hr)

Catalyst Bed Temperature, °C	S/C=6, SV=14,300/hr					
	~600°C		~650°C		~700°C	
Pressure, psig	100	1,000	100	1,000	100	1,000
H_2 in Permeate, mol/mol EtOH	0.03	0.87	0.09	1.11	0.13	1.39
H_2 in Raffinate, mol/mol EtOH	3.61	1.37	4.15	1.78	4.31	1.91
Total H_2, mol/mol EtOH	3.64	2.24	4.24	2.89	4.44	3.30
CH_4, mol/mol EtOH	0.49	0.87	0.22	0.70	0.10	0.47
COx Selectivity, %	69	45	78	58	80	58

pressure (thermodynamically) inhibits the conversion of hydrocarbons but provides a larger driving force for the transport of hydrogen through the membrane, which in turn favors the conversion of hydrocarbons.

Figure 1 shows the effect of the gas hourly space velocity on the product yields from the membrane reactor. At space velocities below 15,000 per hour, the hydrogen yield increases but the effect is amplified in the case with hydrogen permeation. The longer residence time allows more hydrogen to permeate through which favors the conversion of hydrocarbons and leads to higher hydrogen yields. At space velocities less than
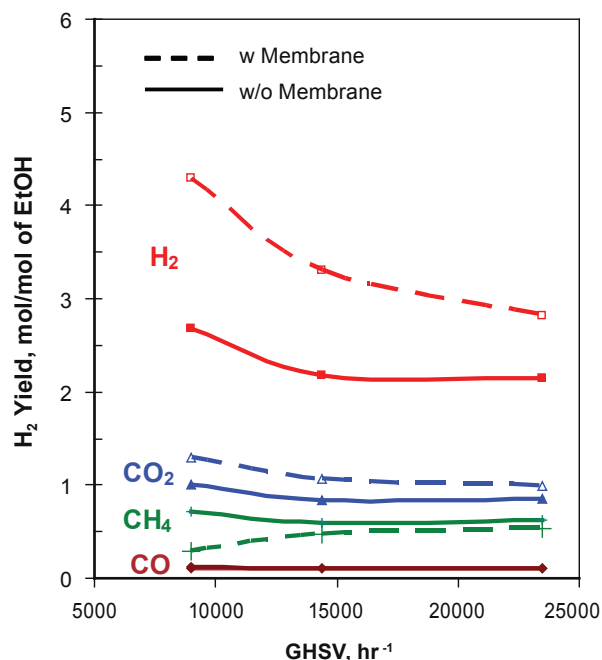
10,000 per hour, the combined (permeate + raffinate) hydrogen yield exceeds 4 moles per mole of ethanol feed. The maximum hydrogen yield possible from the steam reforming of ethanol is 6 moles of hydrogen, per the stoichiometric equation: $C_2H_5OH + 3H_2O = 2CO_2 + 6H_2$.

A mathematical model of the membrane reactor has been set up to predict the reaction conditions that can match the hydrogen yields consistent with the efficiency targets. The model was validated with the experimental results. The model is based on assumptions of fast reaction kinetics, no gas-phase mass transfer limitations, and that the membrane follows Sievert's and Arrhenius' laws [2]. Figure 2 shows the effects of temperature and gas hourly space velocity on the hydrogen yield, as calculated with the model. Lowering the space velocity from 10,000 to 5,000 per hour, at 650°C, improves the hydrogen yield by 1.9 moles. Increasing the temperature from 600° to 700°C, at a space velocity of 5,000 per hour raises the hydrogen yield to ~5 moles per mole of hydrogen. Figure 3 shows the calculated hydrogen yield (permeate only) and is found to match the experimental data quite closely.

The study of pressurized steam reforming of glycerol, a bio-derived liquid resulting from the production of biodiesel, has recently been started. Preliminary results from the reforming tests with this three carbon fuel are shown in Table 4, with gas compositions of samples taken before (after pre-heater) and after the catalyst bed for two temperature settings. Similar to the tests with ethanol, the large yields of hydrogen and CO_x in the gas entering the catalyst bed confirm that some of the glycerol reacts in the pre-heater. Going through the catalyst zone

FIGURE 1. Effect of Gas Hourly Space Velocity on the Product Yields During the Steam Reforming of Ethanol (675°C, 1,000 psig, S/C=6)
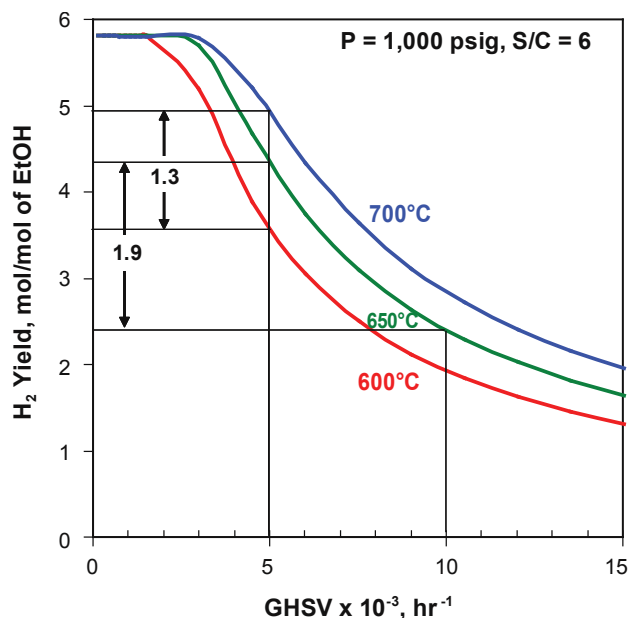

FIGURE 2. Model Calculation Showing the Effects of Temperature and Space Velocity on the Hydrogen Yield (Permeate Only) During the Steam Reforming of Ethanol
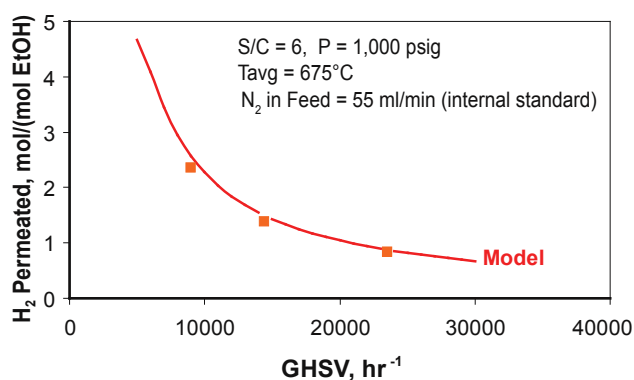
FIGURE 3. Comparison of Modeled (Calculated) and Experimental Hydrogen Yield During the Steam Reforming of Ethanol

TABLE 4. Gas Compositions Entering and Exiting the Catalyst Bed During the Steam Reforming of Glycerol (100 psig, S/C=6, SV=8,000/hr)

	After Pre-heater	After Catalyst Bed	After Pre-heater	After Catalyst Bed
Catalyst Bed Temperature	650-700°C		700-750°C	
H_2, mol/mol Glycerol	2.17	4.56	3.58	5.06
$CO+CO_2$, mol/mol Glycerol	1.64	2.51	2.17	2.56
CH_4, mol/mol Glycerol	0.29	0.26	0.29	0.18
C_2H_4, mol/mol Glycerol	0.057	0.002	0.024	not detected
C_2H_6, mol/mol Glycerol	0.107	0.055	0.067	0.006
COx Selectivity, %	55	84	72	85

increases the hydrogen yield and the CO_x selectivity. With the catalyst zone at above 700°C (100 psig, S/C=6, SV=8,000/hr), the hydrogen yield exceeds 5 moles per mol of glycerol, which accounts for 73% of the theoretical amount of hydrogen possible from the steam reforming reaction ($C_3H_8O_3 + 3H_2O = 3CO_2 + 7H_2$).

Conclusions and Future Directions

We are pursuing an advanced reactor concept that will reduce the energy required to compress the product hydrogen, and are promising for the steam reforming of bio-derived liquids, some of which may incorporate membrane reactors for in situ separation and purification.

• The project has generated experimental data on pressurized reforming of ethanol defining the conditions that favor high hydrogen yields. Preliminary tests have been conducted with glycerol

and are continuing to define the preferred operating conditions.

• The experimental membrane reactor studies are being guided by a reactor model.

• Preliminary results indicate that hydrogen yields that can meet efficiency targets may be possible with a combination of operating conditions. For example, with ethanol reforming in a membrane reactor, a combination of 1,000 psig, S/C=6, 700°C, and a space velocity of less than 5,000/hr can yield 5 moles of highly pure hydrogen per mole of ethanol feed. This represents 83% of the theoretical hydrogen possible from ethanol steam reforming.

• A systems analysis is in progress to define highly efficient process designs and conditions for producing high pressure hydrogen from bio-derived liquids. Current year focus is on defining the process designs and conditions where the reforming is conducted with hydrogen extraction across a membrane and able to meet the efficiency targets.

• The analysis is expected to continue evaluating other process options, especially those that maintain the hydrogen at the elevated operating pressure. These include options such as the transport of CO_2 across a membrane within the reformer to offset the negative aspects of pressurized reforming, and reformate purification using pressure swing adsorption. The most favorable approach will then be pursued further by addressing the key technical challenge that limits the pathway to industry participation and commercial feasibility.

FY 2008 Publications/Presentations

1. High Pressure Steam Reforming of Bio-Derived Liquids, presented at the Bio-Liquids Working Group Meeting, Laurel, MD, 2007.

2. Steam Reforming of Ethanol at Elevated Pressures for Distributed Hydrogen Production, presented at the Fuel Cell Seminar, San Antonio, TX, 2007.

3. Pressurized Steam Reforming of Bio-Derived Liquids for Distributed Hydrogen Production, presented at the 2008 Hydrogen Program Annual Merit Review, Arlington, VA, 2008.

References

1. Lattner, J.R.; Harold, M.P., Comparison of conventional and membrane reactor fuel processors for hydrocarbon-based PEM fuel cell systems. *International Journal of Hydrogen Energy* **2004,** 29, 393-417.

2. Gallucci, F.; Comite, A.; Capannelli, G.; Basile, A., Steam Reforming of Methane in a Membrane Reactor: An Industrial Case Study. *Industrial and Engineering Chemistry Research* **2006,** 45, 2994-3000.