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Compact Single-Stage Fuel Processor for PEM Fuel Cells

Final Report

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ABSTRACT

Various strategies have been investigated to develop an efficient and reliable method for converting hydrocarbon fuels to hydrogen. Steam reforming of hydrocarbon fuels, described by equations 1-3, is an efficient method for producing hydrogen. The major products observed in steam reforming are CO, CO₂, CH₄ and H₂.

Our objective for this Phase I CARAT effort was to develop a steam reformer that produces high purity hydrogen from hydrocarbon fuels for use as a fuel in PEM fuel cells. Membrane reactors are known to work well with equilibrium controlled reactions. In steam reforming, removal of hydrogen increases the residence time for a given volume of reactor and drives the equilibrium-limited reactions towards completion, thus improving yields and efficiency. The proposed prototype reactor combines a steam reformer with hydrogen permeable membranes so that the hydrogen produced can be extracted through the membranes. The net results are smaller reactors and lower reaction temperatures. Economically, there are considerable advantages to reducing the size and lowering the reaction temperature. For example, the reformer can be constructed from low cost materials. A membrane reactor provides the additional advantage of delivering pure hydrogen for use in a fuel cell and eliminates any need for shift and PROX reactors to remove the CO.

During the Phase I effort, we designed a laboratory prototype steam reformer without hydrogen separation membranes and demonstrated its use with methane, ethanol, and octane. We also tried commercially available gasoline, but this fuel contained ~200 ppm sulfur that poisoned the reforming catalyst. Using our steam reforming catalyst, we obtained 100% yields of gaseous products based on the carbon balance. We did not observe any performance degradation after long term tests; 140 hours for ethanol, 40 hours for octane, and 140 hours for methane using a steam/carbon ratio of 5. Based on these long term tests, we estimated that the reformer could operate for about 1000 hours without regeneration, and could meet the DOE target of a 5000 hour lifetime by regenerating the catalyst every 1000 hours.

In collaboration with REB Research and Consulting, we also fabricated a laboratory scale reactor with hydrogen separation membranes. At 550°C and 400 psig we extracted 78% of the hydrogen produced in reforming ethanol, and with some improvements in catalyst packing, we were able to extract 88% of the hydrogen produced in reforming methane at 550°C and 300 psig. We expected ethanol and methane to be completely reformed at 550°C in the membrane reactor, but they were not. Therefore, improvements in reformer design are needed which will be investigated in future efforts.

We were successful in reforming all the sulfur-free fuels tested in the laboratory prototype reactor. In addition, the hydrogen extracted through the membrane did not contain any detectable amounts of CO or other impurities. A preliminary cost analysis indicated that the cost of the membranes must be substantially reduced to meet the DOE cost target of \$10/kW.

1. Phase I Objectives

Our objective for this effort was to produce high purity hydrogen for use as a fuel in PEM fuel cells by steam reforming hydrocarbon fuels. The proposed prototype reactor is illustrated in Figure 1 and was to be fabricated with hydrogen permeable membranes so that the hydrogen produced during steam reforming can be extracted. The membrane reactor achieves high efficiencies by combining a steam reformer that generates hydrogen with a semipermeable membrane that extracts it. Removal of hydrogen increases the residence time for a given volume of reactor and drives equilibrium-limited reactions towards completion. The net result is smaller reactors, lower capital cost, and often fewer side-reactions. Economically, there are considerable advantages to reducing the size and lowering the reaction temperature. For example, the reformer can be constructed from low cost materials. A membrane reactor provides the additional advantage of delivering pure hydrogen for use in a fuel cell and eliminates any need for shift and PROX reactors to remove the CO.

Figure 1. Schematic of the proposed single-stage fuel processor.

For Phase I, our objectives were to:

- Design and develop a pressurized single-stage catalytic steam reformer running at 550°C and 300 psig while maximizing production of hydrogen and carbon dioxide.
Select catalyst, design reactor, fabricate, and test
- Demonstrate performance for gasoline, ethanol, and natural gas (methane).
- Determine pertinent characteristics, such as startup time and load response.
- Estimate expected lifetime of reformer.
- Perform cost analysis and commercial potential.

To accomplish these objectives, the project was divided into the following tasks.

- Task 1. Design and Fabricate Proof-of-Concept Prototype
- Task 2. Laboratory Testing and Proof of Concept.
- Task 3. Cost Analysis.
- Task 4. Management and Reporting.

During this Phase I CARAT project, we focused our effort on designing a laboratory prototype reactor and on testing the prototype reactor for steam reforming ethanol, gasoline and methane.

We met our Phase I objectives by:

- Holding a kickoff meeting at DOE in Washington, DC where it was recommended that we focus on the steam reforming of ethanol, methane, and gasoline.
- Developing a gas chromatographic method to analyze gaseous reforming products to determine the efficiency of reforming catalysts for forming hydrogen.
- Designing a laboratory proof-of-concept prototype reformer without hydrogen separation membranes.
- Purchasing parts and fabricating a prototype laboratory reactor.
- Preparing reforming catalyst supported on alumina.
- Beginning testing steam reforming of ethanol to test the reactor design.
- Calculating equilibrium concentrations of CO, CO₂, H₂ and CH₄ for steam reforming ethanol at a steam/carbon ratio of 5.
- Using the calculated concentrations to guide experiments and determine effectiveness of reforming catalyst.
- Conducting experiments to eliminate carbon formation in the prototype reactor.
- Eliminated coking by optimizing the steam and reactor temperatures.
- Obtaining 100% yield of gaseous products based on our model.
- +Observing no degradation in performance after steam reforming ethanol for 140 hours.
- Discussing design of prototype membrane reactor Dr. Robert Buxbaum of REB Research and Consulting (<http://www.rebresearch.com>).
- Fabricating the prototype reactor with hydrogen separation membranes so that we can take it apart to test hydrogen extraction performance with several different steam reforming catalysts before scaling up.
- Steam reforming ethanol in a reactor with hydrogen permeable membranes and observing almost complete conversion of ethanol to H₂ and CO₂.
- Extracting 78% of the hydrogen produced through the membrane at 550°C and 400 psig.
- The observed membrane permeance suggests that we can increase the fuel flow rate 3 to 4 times in the 7 membrane reactor and still extract ~80% of the hydrogen produced.
- Conducting experiments to steam reform Exxon 87 octane gasoline.
- Observing evidence that the sulfur in gasoline may deactivate reforming catalysts.
- Conducting experiments on steam reforming octane.
- Observing a pressure increase after 40 hours of steam reforming octane.
- Identifying coke resistant catalysts that should improve reforming of octane and gasoline.
- Conducting steam reforming of methane.
- Calculating equilibrium concentrations for reforming methane.

- Running steam reforming of methane in prototype reactor for over 140 hours with no decrease in performance
- Running steam reforming of methane in prototype reactor with hydrogen separation membranes.
- Extracting 88% of the hydrogen produced at 550°C and 300psig.

The results that we obtained for the steam reforming of ethanol, gasoline, and methane are summarized in this report.

2. Background

Various methods have been investigated to develop an efficient and reliable method for converting gasoline and other hydrocarbon fuels to hydrogen. Hydrocarbons can be viewed as hydrogen storage materials, and, if the hydrogen can be efficiently extracted, the hydrogen can be used as a fuel for fuel cell power systems. In this effort, we investigated steam reforming to produce hydrogen from ethanol, methane and gasoline.

There are many commercially available catalysts used to promote reactions including steam reforming. The production of methane is favored at low temperatures and the reaction forms the basis of several gas-making processes. At low pressures and high temperatures, hydrogen is favored.

One major problem is that coking of the catalysts can occur as a result of the reactions

These coking reactions (4 and 5) can be minimized by operating with an excess of steam so that the thermodynamics preclude formation of carbon after establishment of equilibrium. In addition, steam, hydrogen, and carbon dioxide may gasify any carbon that is produced. Nevertheless, catalyst poisoning by coke formation does occur. The net accumulation of coke depends on the deposition and removal rates.

The steam reforming reactor designed for this effort was fabricated with hydrogen selective membranes to separate the hydrogen and shift the equilibrium of the steam reforming reaction to favor the production of hydrogen. By removing the hydrogen as it is produced, the equilibrium for reaction 2 is shifted to the right and for reaction 3 is shifted to the left resulting in reduced methane production. The result of removing hydrogen as it is formed is that the reaction temperature can be lowered to reduce the coke deposition rate and extend the useful life of the catalyst.

3. Results

3.1 Analysis

We developed a gas chromatographic method to determine the efficiency of the catalytic reformer. We fitted a Hewlett Packard 5890 GC with a 30 meter Supelco SPB-1 nonpolar methysilicone 0.32 mm ID fused silica capillary column which can separate the hydrocarbons in gasoline according to their boiling points (maximum temperature of column = 320°C). A Varian 3300 GC fitted with a HeySep Q packed column was used to determine the composition of volatile gases produced. The HeySep column effectively separates the CO, CO₂, and C₁-C₆ hydrocarbons. The combination of these two GCs allowed us to analyze the composition of both gas and liquid phases while the steam reformer is operating. Therefore, we monitored the efficiency of the reformer versus operation time, pressure, and temperature very effectively.

3.2 Design of Prototype Reformer

As our first priority, we designed a prototype reformer without hydrogen separation membranes which is illustrated by the schematic diagram shown in Figure 2. We purchased two high pressure pumps to control the fuel flow rate. We tested the steam generator, and we converted 7 mL water/min to 500°C steam using a 450 watt heater. The steam generator has a volume of 13 cm³ (6 inch hot zone) with our first prototype. During our tests, we obtained a constant flow rate and were able to control the pressure at any desired level with the back pressure regulator. The second steam generator we tried had a volume of 27.5 cm³ (12 inch hot zone) and we successfully tested it at a flow rate of 9 mL/min.

Figure 2. Prototype reactor.

3.3 Catalyst Preparation

An alumina supported catalyst was prepared using the incipient wetness method. The alumina support was 1/8th inch spheres that were impregnated with a solution of the metal nitrate(s). After impregnation, the catalyst was dried and heated to 400°C. The catalyst was loaded (18g) into the steam reforming reactor and activated under flowing H₂ at 500-600°C for 2 hours.

3.4 Reforming of Ethanol

3.4.1 Equilibrium Concentrations for Ethanol

To calculate the equilibrium concentrations for reforming ethanol, we assume that the following reaction represents the conversion of ethanol to hydrogen.

Under reforming conditions, the following reactions will take place:

The equilibrium equation can be written as follow:

$$K_1 = [\text{P}_{\text{CO}}][\text{P}_{\text{H}_2}]^3 / [\text{P}_{\text{CH}_4}][\text{P}_{\text{H}_2\text{O}}] \quad (9)$$

$$K_2 = [\text{P}_{\text{CO}_2}][\text{P}_{\text{H}_2}] / [\text{P}_{\text{CO}}][\text{P}_{\text{H}_2\text{O}}] \quad (10)$$

In our initial tests, the steam/carbon ratio was 5, and that at pressure p, the equilibrium concentration of CH₄ is x. The equilibrium concentrations can be calculated as follows:

$$\begin{aligned} \text{CH}_4 &= x & \text{CO}_2 &= 2-y & \text{CO} &= y-x \\ \text{H}_2 &= 6-3x-y & \text{H}_2\text{O} &= 7+x+y \\ \text{Total moles} &= 15-2x \end{aligned}$$

$$(y-x)(6-3x-y)^3 p^2 / x(7+x+y)(15-2x)^2 = K_1 \quad (11)$$

$$(2-y)(6-3x-y) / (y-x)(7+x+y) = K_2 \quad (12)$$

The equilibrium concentrations of dry gases calculated at different pressures at 500°C is shown in Figure 3. The equilibrium concentrations of hydrogen at different temperatures and pressures are illustrated in Figure 4.

The main gaseous products produced in the steam reforming of ethanol are CH₄, CO₂, CO, and H₂. The concentration of CO₂, CO, and CH₄ were determined directly from the gas chromatogram. In our experiments, a 1 mL sample of the gas was analyzed by gas chromatography after the water had been condensed from the effluent gas stream. The

TC detector is not very sensitive to hydrogen, so its concentration was determined by subtraction. Since the volume of each gas is directly proportional to the moles, we calculated the mole fraction (y) of each gaseous product.

Figure 3. Calculated equilibrium concentration of gases *versus* pressure at 500°C.

Figure 4. The equilibrium concentrations of H₂ *versus* pressure for H₂O/C = 5.

The coefficients for the following reaction were calculated from the data:

In our calculations, we have assumed that all of the ethanol is converted to the products listed in the above reaction and there is no ethanol slip at the conditions used. The concentration of ethanol reacted (y_{EtOH}) was calculated from the amount of hydrogen (y_{H_2}) produced. We assumed that 100% of the hydrogen in the ethanol was converted to H₂ or CH₄ and no hydrogen containing products remained in the reactor.

$$y_{\text{EtOH}} = \frac{(4*y_{\text{CH}_4} + 2*y_{\text{H}_2} - 2*y_{\text{H}_2\text{O}})}{6} \quad (13)$$

$$y_{\text{H}_2\text{O}} = 2*y_{\text{CO}_2} + y_{\text{CO}} - y_{\text{EtOH}} \quad (14)$$

Substitution of y_{EtOH} into equation 14 gives $y_{\text{H}_2\text{O}}$ (amount reacted) as a function of CO₂, CH₄, CO and H₂:

$$y_{\text{H}_2\text{O}} = 3*y_{\text{CO}_2} + 1.5 y_{\text{CO}} - y_{\text{CH}_4} - 0.5 y_{\text{H}_2} \quad (15)$$

$$C_{in} = 2 * y_{EtOH} \quad (16)$$

$$C_{out} = y_{CH_4} + y_{CO_2} + y_{CO} \quad (\text{Dry Gases}) \quad (17)$$

$$\% \text{Yield (Gaseous Products)} = (C_{out}/C_{in}) * 100 \quad (18)$$

The above equation for %Yield determines the conversion of ethanol to gaseous products. The amount of residual carbon ($y_{C \text{ residual}}$ = carbon not accounted for as gaseous products) is equal to 100-%Yield.

$$C_{total} = y_{CH_4} + y_{CO_2} + y_{CO} + y_{C \text{ residual}} \quad (19)$$

As an example, one experimental result obtained at 400 psig and 600°C produced 0.40 mL CH₄; 0.24 mL CO₂; 0.003 mL CO; and 0.35 mL H₂. The coefficients for the reaction were calculated by the above equations to give:

In this example, the %Yield was 98% and the amount of residual carbon was 2%. The calculated C_{residual} could be due to the formation of coke in the reactor and other hydrocarbons that we have not accounted for at this point.

3.4.2. Results of Ethanol Steam Reforming Without Hydrogen Separation

In our initial experiments, we steam-reformed ethanol in a reactor without membranes using the following conditions: steam/carbon = 5; flow rate = 3mL/min; catalyst and steam temperature = 400, 500 and 600°C; and system pressure = 100psig, 300psig and 400psig. Figure 5 shows the initial data that we obtained for the steam reforming of ethanol using our reforming catalyst. The products produced are close to the equilibrium values indicating that our catalyst is active for the reforming of ethanol. Figure 6 summarizes the relationship between temperature, pressure and the concentration of hydrogen produced.

Figure 5. Concentrations of H₂, CO, CO₂ and CH₄ obtained at 300 psig as a function of temperature. The equilibrium concentrations (eq) are also plotted.

As shown in Figure 6, the best yields of hydrogen were obtained at 600° C and 100 psig which agrees with expectations based on the concentrations predicted from the thermodynamic calculations. The highest yields of hydrogen are expected at low pressures. As the pressure increases, the amount of methane increases and the amount of hydrogen decreases. We will show that in the membrane reactor, the equilibrium is shifted to favor the production of hydrogen although the reaction is carried out at high pressure.

Figure 6. Plot showing the relationship between pressure, temperature and hydrogen concentration (% of Dry Gases).

In the experiments that we ran using our first prototype reactor shown in Figure 2, the measured catalyst temperature was higher than the expected inlet steam temperature. To correct this problem, the first change that we made in the design of the prototype reactor was to control the steam temperature at the exit of the steam generator instead of at the middle of the steam generator. After this correction was made in the prototype's design, we could control the steam temperature so that it was similar to the catalyst temperature.

The experimental results listed in Table 1 show that we improved our control of reactor conditions after changing the point where the temperature is controlled. In addition, the results indicated that the yield of gaseous products improved at lower catalyst temperatures as shown by the data listed in Table 1 under the C_{out}/C_{in} column after the change in the point where the temperature was controlled.

Table 1. Comparison of controlling the wall temperature or the steam temperature for the steam reforming of ethanol using the first prototype. EtOH + 10H₂O at 6ml/min.

Time	Cat Temp	Pressure (psig)	CO%	CH ₄ %	CO ₂ %	H ₂ %	C_{out}/C_{in}
Controlled steam generator's wall temperature					Control Temp. = 500°C		
1:25	500	0	1.05	25.57	21.77	51.61	83.20
1:40	555	300	1.01	17.40	23.94	57.66	97.21
1:55	553	200	1.91	9.68	22.04	66.37	84.66
2:05	553	200	1.81	9.37	22.32	66.49	86.42
2:20	555	200	1.95	8.80	21.80	67.44	82.44
Changed to control the steam temperature					Control Temp. = 500°C		
2:50	500	300	0.67	23.61	22.64	53.08	86.33
3:00	500	300	0.54	32.12	23.84	43.49	94.96
3:15	500	300	0.50	30.66	23.79	45.06	94.26
3:20	500	400	0.59	38.14	23.79	37.47	95.35
3:30	502	400	0.60	36.47	23.44	39.49	93.17
3:40	500	400	0.52	37.12	23.92	38.43	95.73

We also ran the reactor using a steam/C ratio of 3 and the results are listed in Table 2. The yield of gaseous products remained about the same, and the pressure drop between P1 and P2 (Figure 2) increased with time indicating that coke was still forming in the reactor.

Table 2. Reforming of ethanol at a steam/C ratio of 3 and a fuel + water flow rate of 3 mL/min.

Time	Temp of catalyst	Pressure (psig)	CO%	CH ₄ %	CO ₂ %	H ₂ %	C_{out}/C_{in}
2:40	507	50	0.76	39.76	28.04	31.43	126.70
2:50	493	50	0.80	28.83	24.02	42.21	97.29
3:00	499	50	0.79	33.13	24.83	41.25	102.92
3:25	490	50	0.97	26.56	25.99	47.47	105.79
3:43	485	50	1.12	24.57	22.89	51.42	90.53
3:55	485	50	1.07	24.08	22.88	51.96	90.16
4:00	485	50	1.31	24.21	23.12	51.37	93.09
4:15	485	50	1.22	24.87	23.53	50.38	95.71

A more important problem was that we observed a pressure drop between the P1 and P2 of 550 psig after 3 hours of operation at 500°C even with a steam/C ratio of 5. This

phenomenon led us to believe that the reactor was forming carbon that resulted in clogging the reactor.

After disassembling the reactor, we found carbon deposits had collected at the inlet to the reforming reactor. We considered three possibilities: 1) the aluminum silicate fiber used to hold the catalyst in place was catalyzing decomposition of the ethanol, 2) the ethanol was thermally decomposed in the steam generator forming carbon that was being deposited at the inlet to the reforming reactor, or 3) the ethanol was reacting immediately with the catalyst near the inlet and forming coke.

To test these three hypotheses, we first removed the aluminum silicate fiber from the reactor and repeated the steam reforming experiment. We observed the same phenomena and concluded that carbon was forming in the steam generator due to thermal decomposition of ethanol. To confirm our assumption concerning the source for the carbon formation, we introduced ethanol after the steam generator as shown in Figure 7 and found a significant improvement. We observed only a 20 psig pressure drop after 3 hours of operation at 500°C. The results are listed in Table 3 and showed an improvement in the calculated yield (C_{out}/C_{in}) of gaseous products which agrees with the reduction in carbon deposits.

Figure 7. Redesigned prototype reactor.

We conducted another test to determine if coke is forming on the catalyst nearest the inlet to the reactor. We still found coke at the inlet to the catalyst bed when we used a steam

temperature of 500°C. Introducing the ethanol at the inlet to the catalyst bed only reduced the coking rate, but coke still formed resulting in an increasing pressure drop.

Table 3. Results for the steam reforming of ethanol using the 2nd prototype reactor.
EtOH flow rate = 0.73ml/min and H₂O flow rate = 2.7ml/min

Time	Temp of Cat	Pressure psig	CO%	CH ₄ %	CO ₂ %	H ₂ %	Cout/Cin
1:00	531	300	0.61	44.18	23.95	31.26	96.67
1:10	520	300	0.64	37.03	23.57	38.77	94.13
1:23	519	300	0.48	39.17	23.36	36.99	92.47
1:50	513	300	0.40	39.08	23.36	37.15	92.18
2:05	514	300	0.41	34.60	23.78	41.20	94.19
2:15	519	300	0.48	41.05	23.76	34.71	94.90
2:30	519	300	0.37	35.42	23.73	40.49	93.71
2:45	517	300	0.38	36.32	24.12	39.18	96.22
3:00	518	300	0.46	36.26	23.86	39.42	95.03
3:30	516	300	0.41	36.07	24.29	39.24	97.38
3:45	516	300	0.36	35.12	24.24	40.28	96.84
4:00	517	300	0.39	36.95	24.02	38.64	95.69

To fully reach the potential of the membrane reactor, we needed to understand and solve the coking problem. We considered several ways to minimize coking: one was to run the reactor at lower temperatures, and the reactor shown in Figure 8 was used to investigate the effect of temperature on the formation of carbon.

Figure 8. Reactor used to test coke formation.

We filled the bottom part of the reactor with the alumina support and the top part with 6 inches of our catalyst supported on alumina. There was a hollow sheath in the middle of the reactor, which allowed the thermocouple to be moved up and down. This reactor design allowed us to determine the temperature profile of the catalyst and steam generator. The catalyst was supported on alumina and the volume of catalyst was 2.65 cubic inches. The catalyst was reduced at 550°C under flowing H₂. In the reforming experiments conducted, the ethanol/water ratio was 1:10 giving a carbon/steam ratio of 1/5. The fuel/water flow rate was 3 mL/min.

We ran the reactor at 0, 300, and 400 psig (Tables 1 and 2 in Appendix) and measured the concentration of CO, CO₂, CH₄ and H₂. The ratios of P_{CO_2}/P_{CO}^2 were calculated to determine if we were operating within coke free operating conditions. The results indicated that temperatures between 500 and 630°C at 300 psig should be acceptable as shown in Figure 9.

Figure 9. Observed P_{CO_2}/P_{CO}^2 ratios and calculated equilibrium constants versus temperature.

The wall and catalyst bed temperature profile was measured at regular intervals by passing the movable thermocouple through a sheath in the catalyst bed and measuring the temperature at different points through the bed. The temperature profile measured using a reactor wall temperature of 400°C at the inlet to the catalyst bed is shown in Figure 10. At these conditions, the catalyst bed reached a temperature of 530°C at the exit when reforming ethanol. The catalyst temperature at the exit when only water was present, was about 600°C. At all positions, the catalyst temperature was lower when ethanol was introduced than when only water was used. These results show that the reforming reaction is endothermic. The temperature profile can be used to measure the activity of catalyst and the active volume at a steam inlet temperatures of ~200°C. The differences between the wall and catalyst temperature are also plotted and listed as 'Difference' and 'Diff EtOH' for water only and water with ethanol respectively.

After lowering the temperatures, we tested the reactor for reforming ethanol using these conditions and we found the system was very stable for over 6 hours and there was no pressure drop through the catalyst bed.

Figure 10. Temperature profile of catalyst bed at 400°C inlet wall temperature.

Steam reforming of ethanol for 140 hours.

Since we observed stable operation for 6 hours, we used these same parameters to run continuously for about 140 hours and measured the temperature of the catalyst bed at 1 inch intervals. The results are summarized in Figure 11. The difference between the wall temperature and the catalyst temperature (Wall-Cat) is also plotted in Figure 11. The catalyst temperatures measured at the various positions in the catalyst bed are shown in Figure 12. There was no pressure drop through the catalyst bed for the 140 hour run.

Figure 11. Temperature profile for the reactor wall and catalyst *versus* position in the catalyst bed. Steam inlet temperature was 200°C and the reactor wall temperature was controlled at 550°C at 4" from the inlet.

The data suggests that the catalyst activity has changed a little during the 140 hour run. The inlet temperature remained relatively constant over the 140 hour test while the temperature at the middle and exit increased a small amount. The temperature at the 2 inch mark decreased indicating that the reforming reaction is more endothermic at that point than it was at the beginning of the experiment. Since the steam reforming reaction is endothermic the observed decrease in temperature is expected if the most active region in the reactor shifts toward the exit as the catalyst ages. However, it appears that our

temperature data is not accurate enough to draw any conclusions concerning catalyst life at this time.

Figure 12. Temperature of catalyst at the middle and exit of the catalyst bed versus time.

We analyzed the products by GC, and the results are illustrated in Figure 13 and listed in the Table 3 in the Appendix. The gaseous products produced are CH_4 , CO , CO_2 , and H_2 . The concentration of CO_2 , CO , and CH_4 were determined directly from the GC, and the hydrogen concentration was determined by calculating the difference assuming that CO_2 , CO , CH_4 , and H_2 are the only products generated.

Figure 13. Concentration of CH_4 , CO_2 , and H_2 versus time in the product gases at 300 psig.

The measured concentrations of CO and CO_2 are very close to those expected from equilibrium calculations. The H_2 concentration is a little higher and the methane concentration is a little lower than expected from the equilibrium values. The %yield of gaseous products, which is $(C_{\text{out}}/C_{\text{in}}) \cdot 100$ from our model, were approximately 100%.

3.4.3 Steam Reforming of Ethanol in Membrane Reactor:

To test the effectiveness of hydrogen separation on the steam reforming process, we used a tubular type membrane reactor that we had obtained from REB Research and Consulting. The reactor was $\frac{3}{4}$ th inch in diameter and was fabricated with seven

hydrogen separating membranes. The metal membranes were palladium coated metal (Ta)¹ tubes that were 9 inches long by 3/32nd inches in diameter and had a total effective surface area for hydrogen separation of 119.6 cm². These metal membranes are only permeable to hydrogen. A schematic of the membrane reactor is shown in Figure 14.

Figure 14. Schematic of the membrane reactor.

The mechanism for hydrogen permeation through these membranes is a multistep process illustrated in Figure 15 and involves the following steps.

1. adsorption of molecular hydrogen on the Pd surface of the membrane,
2. reversible dissociation of hydrogen on the Pd surface of the metal membrane,
3. diffusion of atomic hydrogen through the metal membrane,
4. association of the hydrogen on the Pd surface of the membrane, and
5. de-adsorption of the hydrogen molecules to form the permeate.

Figure 15. Transport mechanism of hydrogen through a metal membrane.

Hydrogen diffusion through the membrane is usually the rate determining step. Hence the rate of hydrogen permeation, J , can be expressed as

$$J = \frac{QA}{t} (P_H^{0.5} - P_L^{0.5})$$

where Q is the permeation coefficient, A is the surface area, t is the thickness of the membrane, and P_H and P_L are the partial pressures of hydrogen on the high pressure side and the low pressure side of the membrane. An example of the data obtained using the membrane reactor with 7 membrane tubes is listed in Table 4. The inlet steam temperature was 300°C.

Figure 16 illustrates the total hydrogen (permeate + effluent), methane, CO and CO₂ concentrations *versus* reaction pressure that were obtained for reforming ethanol in the tubular reactors with and without membranes. The obvious conclusion is that more of the methane produced was reformed in the reactor with hydrogen separation at 550°C and resulted in a corresponding increase in the amount of hydrogen produced.

Table 4. Results for reforming ethanol in tubular reactor with H₂ separation membranes. Steam temperature was ~300°C and steam/carbon ratio was 5.0

°C exit	Psig	%CH ₄ effluent	%CO ₂ effluent	%CO effluent	%H ₂ effluent	%H ₂ permeate	Permeance mol/m ² min Pa ^{1/2}	H ₂ Flow mL/min Calc.	H ₂ Flow mL/min obs
550	0	5.5	21.4	3.8	69.3	0	0	0	
550	150	13.3	23.9	1.3	35.7	25.7	0.011	374	369
550	200	12.8	24.3	1.1	28.4	33.2	0.009	501	524
550	250	11.6	24.4	0.9	21.6	41.6	0.008	631	638
550	300	10.7	24.8	0.8	20.1	43.7	0.007	709	714
550	380	9.0	23.4	0.7	14.2	52.7	0.006	792	807
550	400	9.5	24.5	0.6	13.8	51.6	0.006	840	829

Figure 16. Calculated equilibrium and observed concentrations of H₂, CO, CO₂, and CH₄ *versus* reaction pressure at 500°C for reforming ethanol at a steam/carbon ratio of 5 in the reactor with hydrogen separation membranes.

The catalyst used in this study was active enough to produce close to equilibrium concentrations of reforming products under the test conditions. Therefore, the decreased level of methane and increased amounts of hydrogen produced in the membrane reactor is related to a shift in the equilibrium due to the removal of hydrogen through the membrane. The data shows that as the pressure increases, the equilibrium shifts to favor the complete reforming of ethanol to H_2 and CO_2 .

To calculate the amount of hydrogen that passes through the membranes, we assumed that the yields are similar (100%) in both the reactor with and without hydrogen separation membranes. We also assumed that the concentration of gases in the effluent represents the concentration of gases in the reactor at the point permeation through the membrane reached its maximum rate at the reaction conditions being studied.

Figures 17 and 18 show the partial pressures of H_2 inside the reactor (partial pressure of hydrogen inside the reactor = $P_{H_2 \text{ in}}$ which was calculated assuming no hydrogen removal from the reactor) and observed in the retentate ($P_{H_2 \text{ out}}$) *versus* the reaction pressure. The bottom curve in Figure 17 illustrates the effect of reaction pressure on the partial pressure of hydrogen measured in the retentate (effluent) gases ($P_{H_2 \text{ out}}$). The partial pressure of hydrogen in the retentate approached 2 atmospheres upon an increase in the reaction pressure. The partial pressure of hydrogen on the permeate side is 1 atmosphere under all conditions. The difference between the two curves represents the driving force for extracting hydrogen through the membrane, and supports the observation that more hydrogen was extracted from the reactor at higher reaction pressures.

Figure 17. Partial pressure of hydrogen on the reaction side (◆) and observed in retentate (■) as a function of pressure (for the steam reforming of ethanol in the reactor with hydrogen separation membranes at 550°C).

The results in Figure 18 illustrate the H_2 partial pressures inside the reactor ($P_{H_2 \text{ in}}$) and in the effluent ($P_{H_2 \text{ out}}$) divided by the reactor pressure. The data shows that the hydrogen partial pressure in the reactor is still increasing as the pressure increases indicating that the reaction has not reached completion under these reaction conditions

(550°C). The partial pressure of H_2 in the effluent continues to decrease as the pressure increases, indicating that more hydrogen is removed through the membrane as the pressure is increased. However, hydrogen permeation through the membrane is probably the rate-limiting step.

Figure 18. Partial pressure of hydrogen in the reactor (◆) and observed in the effluent (■) as a function of pressure (for steam reforming of ethanol in the reactor with hydrogen separation membranes at 550°C).

Figure 19 shows the flow rate of H_2 through the membrane based on experimental results where 0.025g/min ethanol was injected into the membrane reactor operating at 550°C. For the amount of fuel used in this Phase I effort, the maximum amount of H_2 produced was ~840 mL/min. No CO was detected in the hydrogen permeate.

Figure 19. The H_2 permeate flow rate as a function of the reaction pressure at 550°C.

Figure 20 illustrates the percentage of hydrogen removed from the reactor as a function of pressure. At 400 psig we observed that >78% of the hydrogen was removed from the reactor. The remainder of the hydrogen is discarded with the effluent, but can be combusted to provide the heat needed for the endothermic reactions.

Figure 20. Percentage of hydrogen removed from the reactor through the hydrogen permeable membranes as a function of reaction pressure.

The Membrane Permeance Calculated from Observed Data: We ran the steam reforming membrane reactor at 550°C at 400 psi (27.7 atm) at a steam/carbon ratio of 5 and obtained the following results:

We used 0.73 mL ethanol per min. This volume of ethanol is equal to 0.58 g/min or 0.0126 mol/min ethanol. We observed that the ethanol is ~100% converted to gaseous products, and we produced 3.8 mole H₂ per mole of ethanol or 0.0479 mole of H₂ per min. Complete conversion to H₂ would have produced 6 mole of H₂ per mole of ethanol.

The total amount of hydrogen produced was = 0.0479 mole/min and our analysis indicated that we recovered 78% of the hydrogen or 0.0373 mole/min (840 mL H₂/min).

At 400 psi, the partial pressure of H₂ in the reactor was $0.345 \times 27.7 = 9.55$ atm (967,653 Pa) and the partial pressure of H₂ in the permeate was 1 atm (101,325 Pa) assuming that 1 atm = 101,325 Pa.

$$N (\text{flux}) = \frac{0.0373 \text{ mole/min}}{\text{area}} = (P_{\text{in}}^{1/2} - P_{\text{out}}^{1/2}) * (\text{permeance})$$

Where P_{in} is the partial pressure of H₂ inside the reactor and P_{out} is the partial pressure of H₂ at the permeate side of the membrane.

$$[(967,653 \text{ Pa})^{1/2} - (101,325 \text{ Pa})^{1/2}] * (\text{permeance}) = (984 - 318)\text{Pa}^{1/2} * (\text{permeance}) = 0.0373 \text{ mole/reactor area}^2 \text{ min}$$

$$\text{permeance} = 0.000056 \text{ mole/area}^2 \text{ min Pa}^{1/2}$$

The area available for hydrogen permeation equals:

$$7 \text{ tubes that are } 3/32 \text{ inch in diameter by 9 inch long} = 17.09 \text{ cm}^2 \times 7 = 119.6 \text{ cm}^2 = 0.01196 \text{ m}^2$$

permeance = $0.000056/0.01196 = 0.00468 \text{ mole/m}^2 \text{ min Pa}^{1/2}$ or $7.8 \times 10^{-5} \text{ mole H}_2/\text{m}^2 \text{ s Pa}^{1/2}$ at 550°C .

Buxbaum¹ reported that the expected permeance should be $1.47 \times 10^{-3} \text{ mole H}_2/\text{m}^2 \text{ s Pa}^{1/2}$. Our value is 19 times lower. Also, our permeance values are dependent on the pressure, and they should be independent of pressure. For example, at 150 psig the permeance calculated was 1.8×10^{-4} and is only 8 times lower than Buxbaum's.

Currently, we do not know why our permeance is lower than Buxbaum's, but the most likely explanation for these results is that we are not producing enough hydrogen in the reactor to observe the maximum permeance that can be obtained. Buxbaum's values indicate that we can increase the fuel flow 3 to 4 times to produce more H_2 and still extract >80% of the hydrogen produced.

3.5 Steam Reforming of Gasoline

After successfully testing ethanol steam reforming, we started to investigate the steam reforming of gasoline. The gasoline we are using is 87 octane purchased from Exxon. We had the gasoline analyzed for C, H, and S, with the following results: C = 85.68%; H = 13.5%; and S = 207 ppm.

We used a 5.5 inch steam generator, and 6 inch long reactor loaded with 18.3g of our catalyst. The flow rate of gasoline was 0.5 mL/min, and the water flow rate was 2.2 mL/min to give approximately a $\text{H}_2\text{O/C}$ ratio of 5. The fuel and water were pumped into the steam generator which was set for 300°C . The reactor temperature was set as 500°C at the exit of the reactor. The results are listed in Table 4 in the Appendix.

We observed that there was gasoline slip after a 30 hour run indicating that the catalyst was deactivated at that point. When we opened the reactor, we didn't see any carbon deposits. Most likely the catalyst was poisoned by the sulfur components in the gasoline since sulfur is a known poison for reforming catalysts. Based on the concentrations of gaseous products shown in Figure 21, the catalyst's activity began to change after 20 hours as indicated by the change in the H_2 and CH_4 concentrations.

Figure 21. Concentration of H_2 , CH_4 , CO_2 , and CO obtained for reforming gasoline at 300 psig and 500°C as a function reaction time.

Since the above results were disappointing, we re-tested the steam reforming of gasoline in our reactor. A gasoline flow rate of 0.5mL/min, and a water flow rate of 2.2mL/min gave a steam-to-carbon ratio of 5. Fuel and water were pumped into the steam generator, which was set at 300°C (wall temperature, center of tube). The reactor temperature, measured at the steam reformer exit, was set at 550°C. We verified our previous test results for reforming gasoline. The results obtained in a reactor without membranes versus temperature are illustrated in the Figure 22.

Figure 22. Steam reforming of gasoline at 300 psig and a steam/carbon ratio of 5.

After 30 hours of steam-reforming gasoline over this catalyst, we ceased to observe flammable products, indicating the complete deactivation of the catalyst at that point. We observed no coke in the reactor or on the catalyst when we opened the reactor. This result was the same as our previous test using gasoline. Since coking is therefore not responsible for the catalyst deactivation, we conclude that the organo sulfur compounds in the gasoline poisoned the catalyst.

The gasoline contained 207 ppm sulfur which very high — certainly high enough to poison the catalyst under the conditions used in our experiments. Sulfur is invariably present as inorganic and /or organic sulfides in naturally occurring feedstocks, and is a powerful poison for reforming catalysts such as that used in the steam reformer. Organic and inorganic sulfides poison the primary reforming catalyst, decreasing its activity. As a result, the reformer begins to run hotter and the methane concentration in the gas leaving the reformer rises. With a naptha-containing feedstock such as gasoline, the aromatic slip also increases. If this situation is allowed to continue, it will lead to carbon deposition (coking), a large pressure drop, and irreversible damage to the catalyst.

The sensitivity of the reforming catalysts to poisoning increases at lower operating temperatures. This observation is demonstrated in Figure 23. While poisoning of the catalyst occurs with about 5 ppm sulfur at 800°C, concentrations on the order of 0.01 ppm will poison the catalyst at 500°C, because the poisoning process may be represented as a simple exothermic absorption process.

Figure 23. Minimum sulfur concentration to poison catalysts at different temperatures.⁴

It is well known that poisoning by sulfur is the main factor in the deterioration of steam reforming catalysts. It is not so well known that that deposition of carbon onto the catalyst can be reduced or even eliminated if the sulfur content in the feed gas is reduced to 5 ppb or less. Means of attaining such high-grade desulfurization has been disclosed in U.S. Patents 5,685,890 and 5,130,115.

3.6 Steam Reforming of Octane

Since the main components of gasoline are $C_6 - C_{10}$ hydrocarbons, we also tested octane because this hydrocarbon can be purchased essentially sulfur free. We will use the results from steam reforming octane to guide our testing of gasoline. The results of octane steam reforming are listed in Table 5 in the Appendix and illustrated in Figure 24.

After over 40 hours of continuous octane steam reforming, we observed a small change in catalyst activity as indicated by a slow increase in the methane concentration and a corresponding decrease in the hydrogen concentration. We also observed a small pressure increase after 40 hours indicating coke was forming in the reactor. The concentration of hydrogen produced from octane is ~5-10% lower than from gasoline.

During the experiment, we also measured the temperature profile of the catalyst bed. At 300 psig, the inlet temperature (steam temperature) of the reactor fluctuated between 440°C and 460°C. Compared with the temperature profile we observed for ethanol steam reforming, the temperature distribution for octane steam reforming was more uniform.

Figure 24. Concentration of H₂, CH₄, CO₂, and CO obtained for reforming octane at 300 psig and 500°C as a function of reaction time.

Evidently, the catalyst was rapidly deactivated during the steam reforming of gasoline which we currently believe is due to sulfur present in gasoline. Even when we steam reformed octane, we observed evidence of coking under the experimental conditions used for the present experiments, and there is a small change in catalyst activity from our GC results for a 40 hour run.

3.7 Steam Reforming of Methane

Steam reforming of methane is described by equations 22 and 23.

The kinetics of catalytic steam reforming of methane have been studied by many investigators, and the conversion described by reaction 23 occurs very fast so that the gas consumption may be assumed to be in equilibrium at every point in the reactor. Methane reforming can be described as a first order reaction, irrespective of operating pressure. At low temperature the molecular diffusion rate is much higher than the reaction velocity so that, theoretically, the catalyst activity can be fully utilized. If the temperature is high, the conversion rate is determined by pore diffusion, and the catalyst's efficiency is reduced. Therefore, large surface catalysts offer an advantage and increase catalytic activity.

The conversion of methane to hydrogen is limited by chemical equilibrium. It is enhanced by high temperatures and low pressures and a high steam content. In industrial plants the temperatures around 800-850°C are used which requires expensive alloys for the reactors.

The products that are observed in methane steam reforming are CO, CO₂, and CH₄ along with the hydrogen produced. It is not generally appreciated that CO₂ is the favored product at low temperatures and the concentration of CO increases as the reaction

temperature increases. Therefore, temperatures below 700°C are preferred to maximize the concentration of hydrogen produced and minimize the amount of CO produced.

Economically, there are considerable advantages to lowering the reaction temperature. Therefore, the reaction should be run at low pressure or in a membrane reactor. In steam reforming of natural gas, carbon deposition usually does not occur for steam inlet temperatures less than 650°C. The temperature required for complete consumption of methane is approximately 650-700°C at 0 psig. We expect to achieve these conversion efficiencies at 500-600°C in our membrane reactor. If a palladium membrane reactor is used, it provides the additional advantage of delivering pure hydrogen for use in a fuel cell.

3.7.1 Results of Methane Steam Reforming Without Hydrogen Separation.

We steam reformed methane at various pressures and temperatures using our reforming catalyst and a steam/carbon ratio of 5. The results for reforming methane at 0, 100, and 300 psig are summarized in Figure 25 and listed in Tables 6-11 in the Appendix. The concentrations of CO, CO₂, CH₄, and H₂ were determined and were very close to those expected from equilibrium values. These results indicate that our catalyst is active for the steam reforming of methane at these temperatures. The results also show that almost 100% of the methane can be reformed into H₂, CO and CO₂ at 700°C at 0 psig.

Figure 25. Concentrations of H₂ observed for steam reforming of methane.

Long term test for reforming methane

Since short term test went well, we steam reformed methane for 140 hours at 300 psig and 550°C wall temperature, and we analyzed the products by GC. The results are illustrated in Figures 25. The dry gaseous products produced are CH₄, CO, CO₂, and H₂. The concentration of CO₂, CO, and CH₄ were determined directly from the GC, and the hydrogen concentration was determined by calculating the difference. The concentration of CO is shown in Figure 26 and the concentrations of CO₂, CH₄, and H₂ are shown in Figure 27.

Figure 26. Observed concentrations of CO during steam reforming of methane.

Figure 27. Observed concentration of CO, CO₂, CH₄, and H₂ for methane steam reforming.

The measured concentrations of CO and CO₂ are very close to those expected from equilibrium calculations. The H₂ concentration is a little lower and the methane concentration is a little higher than expected from the equilibrium values. The %yield of gaseous products, which is $(C_{out}/C_{in}) \cdot 100$ from our model, were approximately 100%.

The partial pressures for CO, CO₂, CH₄ and H₂ were calculated and used to calculate P_{CO_2}/P^2_{CO} and $P^2_{H_2}/P_{CH_4}$ ratios which are plotted in Figures 28 and 29. According to the

ratio of H_2 and CH_4 we are not producing carbon from the decomposition of methane. The concentrations of CO and CO_2 remained in the coke free region for the duration of the run.

Figure 28. Observed P_{CO_2}/P^2_{CO} ratios and calculated equilibrium constants for the Boudouard reaction at 300 psig.

Figure 29. Observed $P^2_{H_2}/P_{CH_4}$ ratios and calculated equilibrium constants for the decomposition of methane at 300 psig.

Catalyst Lifetime

The simulation of catalyst aging is one of the most difficult tasks in determining catalyst performance. What we need is a method that is equivalent to some months or years in the full scale reactor. There are two broad objectives in this work: to find out how far the catalyst performance has deteriorated and why.

There were three questions that we needed to answer about the prototype catalytic reactor.

- 1. What size of reactor will be needed to produce the required amount of hydrogen for a given fuel cell by steam reforming?

- 2. Given a particular reactor, how will it behave under a given set of operating conditions?
- 3. Given the size of the reactor and its behavior under a given set of operating conditions, what is the activity of the catalyst?

The catalyst performance is defined as the catalyst activity multiplied by the active volume. If all of the catalyst is gradually being deactivated by poisoning or sintering, the performance changes with time. Using the kinetics associated with the catalyst, its activity or die off behavior can be calculated from the installed volume of catalyst. The catalyst volume is a function of a large number of variables: temperature, pressure, gas composition and reaction conversion, catalyst formulation, catalyst particle size and catalyst activity.

The estimated catalyst life based on the limited data that we have obtained is illustrated in Figure 30. Over the 140 hour test, the methane concentration gradually increase and the hydrogen concentration decreased. These results suggest that the catalyst activity is decreasing with time. A linear decay in activity predicts that the catalyst will need to be regenerated about every 1000 hours of use to maintain a hydrogen generation of 40% at a reaction temperature of 500°C at the exit of the catalyst bed. The catalyst would be regenerated 4 times to achieve the 5000 h lifetime required. Achieving this lifetime is reasonable since Ni/CaO/Al₂O₃ last for 2-4 years in industrial plants. These catalysts are deactivated by sintering and carbon formation and can be regenerated 4-5 time before they need to be replaced. We expect to observe similar deactivation behavior and obtain similar lifetimes for catalysts in our reactor.

Figure 30. Estimate of catalyst lifetime for steam reforming methane.

3.7.2 Steam Reforming of Methane in Membrane Reactor

Success in developing hydrogen separation membranes has led to applications in steam reforming hydrocarbons.² To test the effectiveness of hydrogen separation on the steam reforming process, we purchased two tubular type membrane reactor from REB Research and Consulting. The reactors were 3/4th inch in diameter and were fabricated with seven 9 3/8th inch long by 3/32nd diameter tubes with an effective surface area for hydrogen separation of 123.6 cm².

Thirty five grams of catalyst was loaded into a membrane reactor and heated to 550°C. Hydrogen flow was started to generate the catalyst at 0 psig. We noticed that gas began flowing from the permeate side of the reactor. We tested the reactor with nitrogen and found that a least one of the membranes was leaking gas.

To avoid activating the catalyst in the membrane reactor, the second time we activated the catalyst in a tube furnace. Thirty five grams (35g) of the catalyst was reduced in a tube furnace under the following conditions: the temperature was increase at 5° C/min from RT to 550° C, held at 550° C for 15h, and then cooled at 5° C/min to RT. The H₂ flow rate was 100 mL/min. The catalyst was removed from the furnace and transferred to a nitrogen atmosphere glove box. It then was loaded into the membrane reactor under a N₂ atmosphere. After loading the reactor with the catalyst, we tested the reactor with N₂, and it didn't leak at RT and 200psig. We then measured the H₂ flux using pure hydrogen in the reactor. The results are plotted in Figure 31, and for comparison, Buxbaum's values are illustrated in Figure 32.

Figure 31. Hydrogen flux as a function of the upstream temperature and pressure.

Figure 32. Hydrogen flux as a function of upstream pressure (R. Buxbaum Results).

Our values were about 33% lower than Buxbaum's, except for one point where we observed 48 mL H₂ /cm² at 400°C and 100 psig which was the only data point that agreed with the values reported by Buxbaum. However, Buxbaum has indicated that he has observed an increase in permeance with time and more tests are needed to measure the hydrogen permeation of the membranes, especially over longer periods of time.

The catalyst was partially oxidized, because the catalyst was exposed to air during transfer to a nitrogen atmosphere. For this reactor, we used methane and water to reactivate the catalyst. The system was run under the following conditions: the surface temperature of the reactor was set at 500°C, the system pressure was 0 psi, the CH₄ flow rate was 620 mL/min and the H₂O flow rate was 2.5 mL/min which corresponds to H₂O/C = 5. The methane flow rate was decreased until the equilibrium values for the reforming products were obtained. The system was run for 20 hours before we started to increase the pressure. The results are listed in Table 5.

Table 5. Concentrations of CO, CH₄, CO₂ and H₂ as a function of the methane feed rate.

CH ₄ (mL/min)	H ₂ O (mL/min)	Cat. Temp	CO%	CH ₄ %	CO ₂ %	H ₂ %
620	2.5	500	0.42	24.42	14.25	60.92
420	2.5	500	0.46	16.62	15.89	67.04
310	1.25	500	0.84	12.23	16.33	70.60
Equilibrium		500	1.86	12.12	16.09	69.93

In the membrane reactor, assuming that the removal of hydrogen shifts the equilibrium toward the right, we should be able to produce mostly hydrogen and carbon dioxide. Since we introduced 310mL/min CH₄, we should be able to get a maximum of 1240 mL/min hydrogen. We collected around 690 mL/min of hydrogen at a 550°C wall temperature and 300 psig.

We also measured the concentration of gas products from the effluent of the membrane reactor, and observed that the hydrogen flux increased as the temperature and pressure increased. We first tried methane steam reforming at 400° C at 0-300 psig. No hydrogen was extracted under these conditions. The GC analysis showed that the products consisted of large amounts of methane and only a small amount of CO₂ indicating that our catalyst was not active at 400°C. When the temperature was increased to 500°C, the hydrogen flow rate in the permeate was around 84 mL/min at 300 psig and around 122 mL/min at 350 psig. These values correspond to a hydrogen flux at 500° C and 300 psig of 0.6764 mL/min•cm² and at 500° C and 350 psig of 0.992 mL/min•cm². The concentrations of CO, CO₂, and CH₄ indicated that not enough hydrogen was extracted at 500°C (~20%) to shift the equilibrium.

We increased the reactor wall temperature to 550°C. The data obtained using the membrane reactor with 7 membrane tubes is listed in Table 6. The inlet steam temperature was 300°C. Figure 33 illustrates the total hydrogen concentrations (permeate + retentate) *versus* reaction temperature that were obtained for reforming methane in the tubular reactors with and without membranes at a wall temperature of 550°C. Figure 34 shows the corresponding levels of methane concentrations as a function of reaction temperature in both the regular and membrane tubular reactors. The obvious conclusion is that more methane was reformed in the reactor with hydrogen separation at 550°C and resulted in a corresponding increase in the amount of hydrogen produced. Unfortunately, the maximum temperature for the membrane reactor is 550°C, and we could not increase the temperature further. In fact, the membrane reactor started to leak after 20 hours of use. A more thermally stable and robust membrane reactor is needed for methane reforming.

Figures 35 and 36 summarize the results obtained for reforming methane in the reactor with hydrogen separation membranes. As the pressure was increased more hydrogen was extracted through the membranes and the amount of hydrogen observed in the permeate increased. At 300 psig we extracted 88% of the hydrogen to obtain

Table 6. Reforming of methane at 550°C and a methane flow rate of 310 mL/min.

Pressure psig	CO%	CH ₄ %	CO ₂ %	H ₂ % effluent	H ₂ % permeate	H ₂ Flow
0	0.84	12.23	16.33	70.60	0	
0	0.92	16.11	15.53	67.43	0	
50	0.20	29.44	14.19	31.20	24.96	199
50	0.18	29.54	14.01	33.09	23.16	179
100	0	26.07	14.77	17.64	41.46	326
100	0.19	25.29	14.58	26.06	33.88	347
150	0.05	25.27	14.85	14.59	45.23	448
150	0.05	21.09	15.77	18.02	45.05	433
200	0.04	19.27	16.09	11.75	52.89	539
200	0.04	18.62	16.30	11.61	53.42	536
300	0.04	16.56	16.64	7.85	58.89	678
300	0.04	15.67	16.97	7.92	59.39	696

Figure 33. Concentration of hydrogen observed at 300 psig in reactor with and without hydrogen separation membranes.

Figure 34. Concentration of methane observed at 300 psig in reactor with and without hydrogen separation membranes.

At these reaction conditions we did not observe any CO but only 50% of the methane was reformed. To obtain the same results in a reactor without membranes at 300 psig, the reactor temperature would be 700°C or 150°C higher than used with the membrane reactor.

Figure 35. Concentrations of H₂, CO, CO₂ and H₂ observed in membrane reactor.

Figure 36. Concentration of hydrogen extracted in permeate at 550°C.

To calculate the amount hydrogen that passes through the membranes, we assumed that the yields are 100% in both the tubular and the membrane reactor. We also assumed that the concentration of gases in the effluent represents the concentration of gases in the reactor. The amount of hydrogen extracted through the membrane was measured, and the total hydrogen produced is the sum of the hydrogen observed in the effluent and in the permeate.

Figures 37 and 38 show the partial pressures of H₂ in the reactor ($P_{H_2 \text{ in}}$ was calculated assuming no hydrogen removal and is the total amount of hydrogen produced) and observed in the effluent *versus* the reaction pressure. Figure 37 illustrates the effect of reaction pressure on the partial pressure of hydrogen measured in the effluent gases

($P_{H_2 \text{ out}}$). The partial pressure of hydrogen in the effluent approached 1 atmosphere upon an increase in the reaction pressure, indicating that more hydrogen was efficiently removed from the reactor through the membrane at higher reaction pressures. The partial pressure of hydrogen on the permeate side is 1 atmosphere under all conditions. Figure 37 also shows the calculated partial pressure of hydrogen in the reactor ($P_{H_2 \text{ in}}$) assuming no hydrogen was removed through the membranes.

Figure 37. Partial pressure of hydrogen on the reaction side (◆) and observed in effluent (■) as a function of pressure (for the steam reforming of octane in the reactor with hydrogen separation membranes at 550°C).

The results in Figure 38 illustrate the H_2 partial pressures inside the reactor ($P_{H_2 \text{ in}}$) and in the effluent ($P_{H_2 \text{ out}}$) normalized with respect to the reaction pressure. The data shows that the hydrogen partial pressure in the reactor does not increase significantly at pressures greater than 300 psig indicating that the reaction has reached completion under these reaction conditions (550°C). However, the partial pressure of H_2 in the effluent continues to decrease as the pressure increases, indicating that more hydrogen is removed through the membrane as the pressure is increased up to 300 psi. At 300 psi the partial pressure of H_2 in the effluent is ~ 1 atmosphere.

Figure 38. Normalized partial pressure of hydrogen in the reactor (◆) and observed in the effluent (■) as a function of pressure (for steam reforming of octane in the reactor with hydrogen separation membranes at 550°C).

Figure 39 shows the flow rate of H_2 through the membrane based on experimental results where 0.025g/min octane was injected into the membrane reactor operating at 550°C. For the amount of fuel used in this Phase I effort, the maximum amount of H_2 produced was ~700 mL/min. No CO was detected in the hydrogen permeate by gas chromatography. Our detection limit is around 2 ppm.

Figure 39. The H_2 permeate flow rate as a function of the reaction pressure at 550°C.

Figure 40 illustrates the percentage of hydrogen removed from the reactor as a function of pressure. At 300 psig we observed that 88% of the hydrogen was removed from the reactor. The remainder of the hydrogen is discarded with the effluent, but can be burnt to provide the heat needed for the endothermic reactions.

Figure 40. Percentage of hydrogen removed from the reactor through the hydrogen permeable membranes as a function of reaction pressure.

It has been reported that palladium membranes are deactivated by deposition of carbonaceous matter.³ In this research program, however, we did not observe any decrease in membrane performance *versus* time.

The Membrane Permeance Calculated from Observed Data: We ran the steam reforming membrane reactor at 550°C at 300 psig (21.0 atm) at a steam/carbon ratio of 5.0 and obtained the following results:

We used 310 mL per min methane flow rate. This volume of methane is equal to 0.0138 mol/min methane. We observed that the methane is 50% converted to H₂, and we produced 0.0276 mole H₂ per mole of octane or 0.0276 mole of H₂ per min.

The total amount of hydrogen produced was = 0.0276 mole/min and our analysis indicated that we recovered 88% of the hydrogen or 0.024 mole/min (548 mL H₂/min at stp; 690 mL at 70°C).

At 300 psi, the partial pressure of H₂ in the reactor was 0.38 x 21 = 8.04 atm (814,653 Pa) and the partial pressure of H₂ in the permeate 1 atm (101,325 Pa) assuming that 1 atm = 101,325 Pa.

$$N (\text{flux}) = \frac{0.024 \text{ mole/min}}{\text{area}} = (P_{\text{in}}^{1/2} - P_{\text{out}}^{1/2}) * (\text{permeance})$$

Where P_{in} is the partial pressure of H₂ inside the reactor and P_{out} is the partial pressure of H₂ at the permeate side of the membrane.

$$[(814,653 \text{ Pa})^{1/2} - (101,325 \text{ Pa})^{1/2}] * (\text{permeance}) = (902 - 318)\text{Pa}^{1/2} * (\text{permeance}) = 0.024 \text{ mole/reactor area}^2 \text{ min}$$

$$\text{permeance} = 0.000041 \text{ mole/area}^2 \text{ min Pa}^{1/2}$$

The area available for hydrogen permeation equals:

$$7 \text{ tubes that are } 3/32 \text{ inch in diameter by } 9 \text{ } 3/8^{\text{th}} \text{ inch long} = 17.66 \text{ cm}^2 \times 7 = 123.6 \text{ cm}^2 = 0.01236 \text{ m}^2$$

$$\text{permeance} = 0.000041/0.01236 = 0.0033 \text{ mole/m}^2 \text{ min Pa}^{1/2} \text{ or } 5.5 \times 10^{-5} \text{ mole H}_2/\text{m}^2 \text{ s Pa}^{1/2} \text{ at } 550^\circ\text{C}.$$

Buxbaum¹ reported that the expected permeance should be $1.47 \times 10^{-3} \text{ mole H}_2/\text{m}^2 \text{ s Pa}^{1/2}$. Our value is 27 times lower. Also, our permeance values are dependent on the pressure, and they should be independent of pressure. For example, at 50 psig the permeance calculated was 1.47×10^{-4} and is only 10 times lower than Buxbaum's. Based on our data, there appears to be a resistance to hydrogen permeation as the pressure increases.

The differences in permeance are due to the effects of other gases, such as steam, CO₂, and CO, in the reactor on the palladium membrane. More detailed experiments are needed to determine the effects of these reaction products on the performance of membrane reactors.

4 Preliminary Cost Analysis

In conducting a cost analysis for our reformer concept, we examined the requirements imposed by automotive applications. A reformer feeding a fuel cell with a 50-kW peak electric power output need not be sized to operate at maximum efficiency at this peak output level. The automobile engine rarely runs at peak power. In fact, the cruising power requirement is seldom more than 50% of the engine's peak power output and is often considerably lower. Because peak power is only rarely required, the engine's efficiency at peak power may be sacrificed to achieve overall cost and weight savings; the power train should be designed to operate at maximum efficiency under the usual power demand of 50% of peak. This principle reduces the size requirement for the reformer. For a 50 kW peak power fuel cell, a reformer is optimally sized to operate at 80% efficiency at 25 kW. Such a reformer will operate at approximately 50% efficiency at 50 kW, but because the car seldom operates at peak power the efficiency loss is irrelevant.

This established, we can examine the subsystems of the proposed power train: the fuel cell and the steam reformer. Our steam reformer concept is comprised of three major components: the desulfurizer, the boiler, and the reformer. For this analysis, the cost of the desulfurizer was not included since it is not needed with all the fuels in question.

The boiler and the steam reformer, combined, require a heat input of 1 kW per 1 kW electric power output, assuming a 50% efficient fuel cell. For medium sized (20-100 kW) specialized boilers, a high-end price is about \$60/kW of heat output. This includes the pump, the expansion tank and all the controls. In mass-production quantities and with special attention paid to the integration of the boiler and the reformer, this cost will drop to \$ 7-15/kW.

The steam reformer is basically a tubular pressure vessel with built-in hydrogen separation membranes. Since the system operates below 600°C, we can construct the pressure vessel from off-the-shelf stainless steel tubing. This, therefore, does not contribute significantly to the cost of the unit when mass-produced. The primary cost of the membrane is in the labor required to manufacture it, rather than in the palladium. REB Research, Inc., the present membrane supplier, has estimated the cost of the membrane in mass quantities to be \$200-800/ft² using a 1 μm coating of Pd on each side of the membrane. To operate at 80% reformer efficiency at peak power, we need a membrane area of 1 ft²/kW. However, as explained above, we can safely size the reformer for 50% efficiency at peak power. The resulting reduction in area lowers the membrane cost to less than \$120/kW, which includes the support for the membrane. The cost of the pressure vessel and the controls, based on rule-of-thumb engineering practices and at high quantities, will be in the \$7-10/kW range. We need about 400 g of reformer catalyst per kW of electric power. This catalyst is quite inexpensive at about \$1/kW in quantities.

Thus, our preliminary projection is that a 20 kW peak power reformer will cost about \$2,500 and a 50 kW unit around \$6,390. If the fuel cell efficiency exceeds the projected 50%, this cost will be reduced accordingly.

The exact cost of the system will depend on the final design. At this stage of the development of this concept it is difficult to predict an accurate cost. It is important, however, to note that certain advantages of our system allow it to feature a lower cost than higher-temperature reformers.

1. The low operating temperature of our system allows us to use off-the-shelf stainless steel tubing. Reformers operating at 800-1000 °C require exotic – and expensive – alloys.
2. The low operating temperature of our system permits us to construct the pressure vessels with a thinner wall thickness and less insulation. This reduces not only the cost of our system, but will significantly decrease the weight of the power train, leading to secondary efficiency increases.
3. The high purity hydrogen produced by our system reduces the per-kilowatt cost of the fuel cell by increasing its power density. This benefit alone may completely outweigh the cost of the reformer.

To estimate the cost of the steam reformer we

- Selected the system level performance level
- Selected the materials required to manufacture the system
- Estimated the individual component prices and the component assembly cost.

We have based our cost estimates on the assumption of manufacture at high volume using design-for-manufacture equipment, as would be the case for a supplier to the U.S. auto industry. The projected costs are in 1999 dollars, and include provisions for material, labor, manufacturing overhead, and expenses. For the cost study, the fuel processor was divided into the sub-components listed below.

I. Containment vessel	II. Steam generator	III. Membrane reactor
A. Outer shell	A. Burner	A. Membranes
B. Insulation	B. Stainless Steel Tube	B. Tube
IV. Catalysts	V. Fuel system	
A. Reforming catalyst	A. Fuel and Water Pumps	
	B. Catalyst bed	
	C. Fuel and water tanks	

Cost projections are listed in Tables 7 and 8. The cost contributions of the various components are illustrated in Figures 41 and 42. In this case, the membranes comprise 88% of the total cost, and the total cost is estimated to be 8-9 times more than a partial oxidation (POX) system. The materials used in the steam generator and steam reformer are stainless steel and no high temperature alloys are needed. In a membrane reactor, pure hydrogen is produced which improves the efficiency of the fuel cell and decreases the complexity of the fuel processing system. A POX system, while cheaper, involves a technical complexity that invites a short system lifetime and/or low reliability.

Table 7. Cost projections for a 50 kW peak steam reformer.

Component		\$/unit	\$/kW
Shell			
Outer shell		50	
Insulation		10	
	Sub total	60	1.20
Catalyst			
reforming catalyst		50	
	Sub total	50	1.00
Steam generator			
Burner		230	
Stainless steel tube		30	
Fittings		70	
	Sub total	330	6.60
Reformer			
Reformer tube		30	
Palladium (1 μ m thick)		625	
Tantalum supports (25 ft ² @ \$200/ft ²)		5000	
Fittings		70	
	Sub total	5725	114.50
Fuel System			
Pump and Tanks		100	
Controls		125	
	Sub total	225	4.50
	TOTAL	6,390	127.80

Figure 41. Cost contribution of components for a 50 kW peak fuel processor with 0.5 ft² membrane area per kW and 1 μ m Pd coating on each side of the membrane tube.

If we need to design the power train to have 80% efficiency at its peak power of 50 kW, then we need 1 ft² of membrane per kW and the per-unit cost jumps to \$12,015 (\$240.30/kW). The percentage of the cost due to the membranes would increase to a maximum of 94% of the total cost of such a system.

Figure 42. Cost contribution of components for a 50 kW fuel processor with 1 ft² membrane area per kW.

We believe that the cost of the membrane tubes can be reduced to \$40/ft² by using niobium which reduces the material costs by a factor of 3, by simplifying the membrane design, by automating the reactor fabrication, and by decreasing the thickness of the palladium coating to 0.1 μm. These improvements would lower the cost of the membrane reactor to \$36.56/kW which gets us to the \$10/kW target cost. We have just started a DARPA supported Phase II effort to address some of these issues. Table 9 lists the component costs that are required to meet the DOE costs targets of ~\$10/kW. To meet this target, membrane costs will need to be reduced to \$4/ft².

5. Conclusions

Based on our observations during the steam reforming of ethanol, we conclude that carbon was forming in the steam generator due to the thermal decomposition of ethanol. Since ethanol is being thermally decomposed, we were operating the steam generator at too high of a temperature. The thermal degradation of ethanol was confirmed by using a GC with a flame ionization detector. We observed trace amounts of additional hydrocarbons other than methane in the effluent which we assume may be ethane and ethylene.

We identified the operating conditions that allowed us to steam reform ethanol for an acceptable amount of time. These conditions were a steam temperature of 200°C and a wall temperature of 400°C at the center of the reactor. The calculated ratios of CO₂/CO

indicate that we can lower the potential for carbon deposition from the Boudouard further by reducing the pressure.

Table 8. Projected costs for a mass-produced 50 kW peak steam reformer.

Component		\$/unit	\$/kW
Shell			
	Outer shell	50	
	Insulation	10	
	Sub total	60	1.20
Catalyst			
	reforming catalyst	50	
	Sub total	50	1.00
Steam generator			
	Burner	230	
	Stainless steel tube	30	
	Fittings	70	
	Sub total	330	6.60
Reformer			
	Reformer tube	30	
	Palladium (0.1 μ m thick)	63	
	Niobium supports (25 ft ² @ \$40/ft ²)	1000	
	Fittings	70	
	Sub total	1163	23.26
Fuel System			
	Pump and Tanks	100	
	Controls	125	
	Sub total	225	4.50
	TOTAL	1,828	36.56

We demonstrated the reforming of ethanol in a reactor with hydrogen separation membranes and have extracted 78% of the hydrogen for use as a fuel in PEM fuel cells. The hydrogen is pure and contains no CO or other impurities. The reformer efficiency based on the HHV of ethanol and hydrogen was estimated to be 77%. We successfully demonstrated the feasibility of producing hydrogen by the steam reforming of ethanol.

We identified the operating conditions that allowed us to steam reform methane to obtain ~100% gaseous products and operated the reformer for 140 hours with no catalyst deactivation. These conditions were a steam temperature of 300°C and a wall temperature of 500°C at the center of the reactor. We estimated that the catalyst would need regenerating every 1000 hours to maintain activity and would have a useful life of 5000 hours. We also demonstrated the reforming of methane in a reactor with hydrogen separation membranes and have extracted 88% of the hydrogen for use as a fuel in PEM fuel cells. The hydrogen is pure and contains no CO or other impurities. We successfully demonstrated the feasibility of producing hydrogen by the steam reforming of methane.

6. Future Work

Our results look excellent and are comparable to those in the published literature. However, there are many topics that need investigation in any future efforts. Further work is needed to improve the robustness of membrane reactors so that the reactor can be operated at higher temperatures and pressures. Also the hydrogen permeation appears to be affected by the reaction conditions employed during steam reforming. We observed that the permeance is pressure dependent and decreases as the pressure increases indicating there is resistance to permeation at the reforming conditions.

Table 9. Component cost targets for a 50 kW peak steam reformer.

Component	\$/unit	\$/kW
Shell		
Outer shell	15	
Insulation	10	
Sub total	25	0.50
Catalyst		
reforming catalyst	50	
Sub total	50	1.00
Steam generator		
Burner	50	
Stainless steel tube	20	
Fittings	25	
Sub total	95	1.90
Reformer		
Reformer tube	30	
Palladium (0.1 μm thick)	63	
Membrane supports (25 ft^2 @ \$4/ ft^2)	100	
Sub total	193	3.86
Fuel System		
Pump and Tanks	100	
Controls	50	
Sub total	150	3.00
TOTAL	513	10.26

7 References

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APPENDIX

Table 1. Steam reforming of ethanol at a wall temperature of 450°C. The steam temperature was 200°C and the water/fuel flow rate was 3 mL/min.

Time	Temp Cat Exit °C	Pressure psig	CO%	CH ₄ %	CO ₂ %	H ₂ %	%Cout/Cin
12:25	630	0	4.84	0.00	19.84	75.32	80.16
12:40	620	0	5.29	0.00	19.18	75.53	76.72
12:50	630	0	5.52	0.00	19.11	75.37	77.84
13:00	640	0	5.46	0.00	18.77	75.77	73.92
13:15	620	300	1.54	16.93	22.43	59.09	87.89
13:35	620	300	2.88	11.38	21.65	64.09	88.29
13:45	630	300	3.20	11.36	22.06	63.38	94.40
14:00	630	300	3.14	10.96	21.85	64.05	91.83
14:15	630	300	3.14	11.02	22.05	63.79	93.80
14:30	630	400	2.85	13.87	22.32	60.96	94.75
14:40	630	400	3.00	13.32	21.88	61.79	91.66
14:55	630	400	3.03	13.20	22.08	61.68	93.70
15:30	475	400	0.64	37.38	24.06	37.93	97.10
15:40	465	400	0.51	40.00	24.50	34.99	99.28
15:50	465	400	0.58	40.41	0.24	34.78	97.96
16:00	460	300	0.47	37.33	0.25	37.60	99.71
16:10	460	300	0.46	37.26	0.24	38.02	97.48
16:20	464	300	0.50	37.34	0.25	37.50	100.18

Table 2. Steam reforming of ethanol at a wall temperature of 400°C. The steam temperature was 200°C and the water/fuel flow rate was 3 mL/min.

Time	Temp Cat Exit °C	Pressure psig	CO%	CH ₄ %	CO ₂ %	H ₂ %	%Cout/Ci n
10:30	505	300	0.45	39.06	24.15	36.34	96.88
10:45	515	300	0.72	30.87	24.56	43.84	100.76
11:00	500	300	0.86	32.06	24.31	42.78	99.64
11:15	497	300	0.74	32.96	24.32	41.98	99.15
11:30	499	300	0.64	32.90	24.48	41.98	99.73
11:45	505	300	0.67	31.17	24.31	43.85	98.68
12:00	505	300	0.72	31.54	24.29	43.45	98.77
12:20	505	300	0.65	31.51	24.22	43.62	97.95
12:45	505	300	0.63	31.31	24.16	43.90	97.47
13:00	503	300	0.62	30.79	23.66	44.93	94.03
13:20	525	300	0.78	28.14	24.42	46.66	100.02
13:40	525	300	0.86	27.60	23.60	47.94	94.51
13:55	515	300	1.05	28.53	24.20	46.21	99.96
14:10	508	300	0.86	30.48	23.97	44.69	97.30
14:30	525	300	0.73	29.72	23.70	45.85	94.75
14:50	525	300	0.87	29.69	24.46	44.99	100.80
15:10	520	300	0.80	30.68	24.16	44.36	98.33
15:30	521	300	0.77	29.67	24.07	45.49	97.48
15:50	527	300	0.83	27.81	23.72	47.64	95.23
16:10	527	300	0.78	27.17	23.91	48.14	96.23
16:30	528	300	0.77	28.61	23.93	46.69	96.44

Table 3. Concentrations of CO, CH₄, CO₂ and H₂ observed in the reforming of ethanol for 140 hours.

Reaction Time (h)	CO%	CH ₄ %	CO ₂ %	H ₂ %	Cout/Cin
0.00	1.06	32.00	24.35	42.59	101.0
0.50	1.06	32.07	24.29	42.58	100.6
0.92	1.03	33.54	24.55	40.89	102.2
1.17	1.07	32.62	24.40	41.91	101.4
1.67	1.07	32.31	24.15	42.47	99.7
2.00	1.06	32.69	24.26	41.99	100.4
18.33	1.08	32.32	24.33	42.28	101.0
19.00	1.00	32.23	24.06	42.71	98.7
19.50	1.07	32.71	24.25	41.97	100.4
20.00	1.11	32.18	24.02	42.70	99.0
20.50	1.08	31.85	24.35	42.72	101.1
20.83	1.07	31.55	24.22	43.16	100.2
22.67	1.02	32.15	24.31	42.52	100.5
23.50	1.11	32.16	23.94	42.79	98.4
24.17	1.07	31.87	24.26	42.79	100.4
25.00	1.10	32.30	24.20	42.40	100.2
25.33	1.07	32.01	24.28	42.64	100.6
25.67	1.02	32.07	24.27	42.63	100.3
32.33	1.13	32.76	24.45	41.66	102.1
42.33	1.03	31.67	24.53	42.76	102.2
42.67	1.07	31.48	24.48	42.97	102.0
43.50	1.04	31.36	24.56	43.04	102.5
44.00	1.14	31.63	24.62	42.61	103.5
44.50	1.10	32.13	24.50	42.27	102.3
45.00	1.06	31.04	24.48	43.42	102.0
45.83	1.10	32.16	24.21	42.53	100.2
46.25	1.09	31.70	24.61	42.60	103.1
48.33	1.09	32.91	24.53	41.47	102.4
49.50	1.09	30.89	24.42	43.60	101.7
51.83	1.06	31.20	24.33	43.41	100.9
66.17	1.06	32.38	24.62	41.93	103.0
67.50	1.04	32.24	24.34	42.38	100.8
68.00	1.01	32.97	24.75	41.27	103.6
68.25	0.97	32.87	24.47	41.69	101.4
69.00	1.00	33.05	24.66	41.29	102.9
70.33	1.04	32.79	24.50	41.67	102.0
71.00	1.03	32.77	24.57	41.62	102.4
72.33	1.04	32.81	24.63	41.51	102.9
90.50	1.07	31.90	24.37	42.65	101.2
90.83	1.10	31.72	24.54	42.64	102.6
91.17	1.07	31.89	24.71	42.32	103.7
91.50	1.32	32.76	23.91	42.01	99.3
91.50	1.15	31.40	24.45	43.00	102.3
92.50	1.10	31.41	24.46	43.03	102.0
93.00	1.15	31.57	24.63	42.65	103.6

Table 3 continued					
Reaction Time (h)	CO%	CH ₄ %	CO ₂ %	H ₂ %	C _{out} /C _{in}
93.25	1.11	31.58	24.47	42.84	102.2
94.00	1.16	31.37	24.28	43.19	101.1
95.00	1.16	31.16	24.15	43.53	100.1
95.67	1.14	31.37	24.19	43.30	100.3
96.25	1.19	30.82	24.21	43.78	100.7
112.25	1.12	31.27	24.42	43.19	101.9
113.00	1.13	32.00	24.58	42.29	103.0
113.50	1.07	32.00	24.66	42.27	103.3
114.00	1.11	31.65	24.35	42.89	101.3
114.50	1.12	32.06	24.53	42.30	102.6
115.00	1.14	30.61	23.99	44.25	98.9
116.50	1.12	31.96	24.23	42.69	100.5
117.00	1.05	31.43	24.17	43.36	99.7
117.50	1.11	31.84	24.22	42.83	100.4
119.17	1.14	31.84	24.37	42.65	101.6
136.25	1.17	32.03	24.68	42.11	104.1
137.00	1.14	31.85	24.63	42.38	103.5
137.50	1.14	31.59	24.65	42.62	103.6
138.00	1.09	31.68	24.65	42.58	103.3
138.50	1.15	31.59	24.49	42.77	102.5
139.00	1.08	31.79	24.69	42.44	103.6
139.50	1.11	31.38	24.41	43.10	101.7

Table 4. Steam reforming of Exxon 87 octane gasoline.

Time h	Temp/Cat °C	Pressure psig	CO%	CH ₄ %	CO ₂ %	H ₂ %	C _{out} /C _{in}
0	500	0	2.73	25.69	23.21	48.36	104.1
0.5	500	0	1.08	6.28	23.95	68.69	99.0
0.75	500	0	1.66	15.66	23.51	59.17	99.6
1	500	0	2.61	32.10	23.06	42.24	102.1
1.25	500	0	3.14	24.03	22.87	49.96	103.9
2	500	300	0.95	40.55	24.04	34.47	100.5
2.3	500	300	0.61	42.61	24.45	32.33	101.5
2.75	500	300	0.63	43.19	24.89	31.29	104.2
19.5	500	250	0.75	44.19	24.66	30.40	103.3
20	500	300	0.78	44.95	24.56	29.71	102.8
20.5	500	300	0.71	44.70	24.68	29.91	103.2
20.67	500	300	0.72	44.91	24.94	29.44	104.8
21	500	300	0.71	44.30	24.81	30.19	104.0
24.5	500	300	0.73	38.09	23.08	38.10	93.7
25	500	300	0.76	38.07	22.98	38.19	93.3
26	500	300	0.72	37.08	22.72	39.48	91.5
3:30	500	300	0.93	38.12	22.82	38.13	93.1
26.5	500	300	1.68	33.40	21.32	43.61	87.0
27.5	500	300	0.89	34.35	22.04	42.73	87.9

Table 5. Reforming of pure octane.

Time h	Temp/Cat °C	Pressure psig	CO	CH ₄	CO ₂	H ₂	C _{out} /C _{in}
0	500	0	2.20	24.38	19.91	53.51	86.8
20	500	0	2.35	24.52	19.67	53.46	86.1
40	500	0	3.42	39.43	17.16	39.99	83.2
55	500	0	3.05	34.03	17.90	45.02	83.3
1	500	300	0.77	51.89	21.51	25.83	97.2
1.5	500	300	1.01	50.60	20.51	27.88	93.2
1.75	500	300	0.77	52.06	21.11	26.07	95.4
18.75	500	300	0.74	52.97	21.79	24.49	98.7
19.5	500	300	0.80	54.41	21.56	23.24	98.0
24	500	300	0.72	50.84	19.96	28.49	89.9
24.5	500	300	0.69	51.86	21.78	25.67	98.2
25.08	500	300	0.73	53.13	21.23	24.91	96.0
25.67	500	300	0.72	53.49	21.67	24.11	98.1
42.58	500	300	0.73	55.25	21.67	22.34	98.4
46.5	500	300	0.76	54.87	22.00	22.37	99.9
46.75	500	300	0.74	54.24	22.03	23.00	99.9

**Table 6. Steam reforming of methane at 400°C at a steam/carbon ratio of 5.
(620 mL/min CH₄ + 2.5mL/min H₂O)**

Time	Temp/Cat °C	Pressure psig	CO	CH ₄	CO ₂	H ₂	C _{out} /C _{in}
13:30	400	0	0	39.99	14.55	45.46	113.2
14:15	400	0	0	41.56	15.02	43.41	117.4
14:30	400	0	0	40.66	12.66	46.67	103.8
15:00	400	100	0	66.91	6.48	26.60	99.5
15:10	400	100	0	58.59	7.44	33.97	96.9
15:20	400	100	0	59.28	6.37	34.34	93.7
15:35	400	300	0	65.64	5.06	29.29	94.0
15:50	400	300	0	64.60	5.32	30.075	94.1
16:00	400	300	0	65.19	5.07	29.75	93.7
16:15	400	300	0	67.61	4.44	27.96	93

**Table 7. Steam reforming of methane at 500°C at a steam/carbon ratio of 5.
(620 mL/min CH₄ + 2.5mL/min H₂O)**

Time	Temp/Cat	Pressure	CO%	CH ₄ %	CO ₂ %	H ₂ %	Cout/Cin
11:30	500	0	1.09	20.46	15.74	62.72	1.05
11:45	500	0	1.06	19.26	15.29	64.39	1.00
13:00	500	0	1.06	19.75	15.77	63.42	1.04
13:30	500	100	0.50	41.28	11.77	46.46	1.02
13:45	500	100	0.56	41.16	11.76	46.52	1.02
14:00	500	100	0.58	40.82	11.77	46.83	1.02
14:30	500	300	0.34	51.92	9.56	38.18	1.01
14:45	500	300	0.34	55.73	9.07	34.86	1.02
15:00	500	300	0.34	50.98	9.97	38.72	1.02
15:30	500	300	0.33	50.88	9.93	38.85	1.02
16:00	500	300	0.34	51.57	9.80	38.29	1.02

**Table 8. Steam reforming of methane at 550°C at a steam/carbon ratio of 5.
(620 mL/min CH₄ + 2.5mL/min H₂O)**

Time	Temp/Cat	Pressure	CO%	CH ₄ %	CO ₂ %	H ₂ %	Cout/Cin
13:20	550	0	2.13	10.79	16.80	70.28	1.06
13:45	550	0	2.22	11.96	16.63	69.18	1.07
14:00	550	0	2.11	11.55	16.77	69.57	1.07
14:15	550	100	1.06	24.04	15.13	59.77	1.05
14:30	550	100	1.27	27.25	14.21	57.26	1.04
14:45	550	100	1.24	26.86	14.35	57.55	1.04
15:05	550	300	0.80	37.60	12.48	49.12	1.03
15:15	550	300	0.83	39.63	12.08	47.45	1.03
15:30	550	300	0.71	38.03	12.51	48.75	1.03
15:45	550	300	0.84	36.91	12.52	49.72	1.03

**Table 9. Steam reforming of methane at 600°C at a steam/carbon ratio of 5.
(620 mL/min CH₄ + 2.5mL/min H₂O)**

Time	Temp/Cat	Pressure	CO%	CH ₄ %	CO ₂ %	H ₂ %	Cout/Cin
12:30	600	0	3.84	6.16	16.53	73.47	1.085
12:45	600	0	3.94	6.06	15.84	74.16	1.020
13:00	600	0	3.88	5.85	15.90	74.37	1.017
13:15	600	0	3.75	5.67	16.31	74.27	1.046
13:40	600	100	2.30	16.50	14.82	66.39	0.997
13:55	600	100	2.53	17.21	14.14	66.12	0.972
14:10	600	100	2.34	15.03	14.99	67.64	0.990
14:20	600	100	2.58	17.67	13.84	65.91	0.960
14:40	600	300	1.65	24.75	13.11	60.49	0.962
14:55	600	300	1.58	25.42	13.14	59.86	0.969
15:10	600	300	1.51	24.31	13.40	60.79	0.967
15:30	600	300	1.54	24.87	13.47	60.13	0.979
16:05	600	300	1.52	25.32	13.28	59.89	0.973

**Table 10. Steam reforming of methane at 650°C at a steam/carbon ratio of 5.
(620 mL/min CH₄ + 2.5mL/min H₂O)**

Time	Temp/Cat	Pressure	CO%	CH ₄ %	CO ₂ %	H ₂ %	C _{out} /C _{in}
13:00	650	0	5.84	2.79	15.73	75.64	1.11
13:15	650	0	6.44	3.17	14.80	75.59	1.06
13:30	650	0	5.51	2.51	15.46	76.52	1.04
13:45	650	100	4.39	14.81	13.84	66.96	1.02
14:00	650	100	4.06	12.29	14.64	69.01	1.03
14:15	650	100	4.08	12.37	14.59	68.95	1.03
14:35	650	300	2.79	18.68	14.16	64.38	1.01
14:50	650	300	2.83	19.58	13.68	63.91	0.99
15:05	650	300	2.79	19.32	13.97	63.91	1.01
16:00	650	300	2.82	18.57	14.12	64.50	1.01

**Table 11. Steam reforming of methane at 700°C at a steam/carbon ratio of 5.
(620 mL/min CH₄ + 2.5mL/min H₂O)**

Time	Temp/Cat °C	Pressure psig	CO	CH ₄	CO ₂	H ₂	C _{out} /C _{in}
11:15	700	0	6.43	1.36	15.76	76.45	114.3
11:35	700	0	7.10	1.33	14.81	76.75	108.9
11:50	700	0	7.52	1.44	14.48	76.56	109.1
12:40	700	0	7.12	1.33	15.44	76.11	117.2
12:55	700	0	7.72	1.34	14.64	76.30	112.9
13:10	700	100	6.71	8.97	13.54	70.79	106.3
13:25	700	100	7.99	11.14	12.00	68.87	105.2
13:40	700	100	7.90	10.68	12.29	69.13	106.4
14:45	700	100	8.00	12.93	11.79	67.28	106.4
15:00	700	100	8.10	12.80	12.02	67.08	108.8
15:30	700	300	4.72	18.41	14.10	62.76	111.7
15:45	700	300	5.06	17.47	13.13	64.34	104.9
16:00	700	300	5.13	19.45	12.34	63.07	102.4
	700	300	4.82	17.10	13.12	64.96	102.9

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