



## Hydrogen production by reforming of liquid hydrocarbons in a membrane reactor for portable power generation—Experimental studies

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### ABSTRACT

One of the most promising technologies for lightweight, compact, portable power generation is proton exchange membrane (PEM) fuel cells. PEM fuel cells, however, require a source of pure hydrogen. Steam reforming of hydrocarbons in an integrated membrane reactor has potential to provide pure hydrogen in a compact system. Continuous separation of product hydrogen from the reforming gas mixture is expected to increase the yield of hydrogen significantly as predicted by model simulations. In the laboratory-scale experimental studies reported here steam reforming of liquid hydrocarbon fuels, butane, methanol and Clearlite<sup>®</sup> was conducted to produce pure hydrogen in a single step membrane reformer using commercially available Pd–Ag foil membranes and reforming/WGS catalysts. All of the experimental results demonstrated increase in hydrocarbon conversion due to hydrogen separation when compared with the hydrocarbon conversion without any hydrogen separation. Increase in hydrogen recovery was also shown to result in corresponding increase in hydrocarbon conversion in these studies demonstrating the basic concept. The experiments also provided insight into the effect of individual variables such as pressure, temperature, gas space velocity, and steam to carbon ratio. Steam reforming of butane was found to be limited by reaction kinetics for the experimental conditions used: catalysts used, average gas space velocity, and the reactor characteristics of surface area to volume ratio. Steam reforming of methanol in the presence of only WGS catalyst on the other hand indicated that the membrane reactor performance was limited by membrane permeation, especially at lower temperatures and lower feed pressures due to slower reconstitution of CO and H<sub>2</sub> into methane thus maintaining high hydrogen partial pressures in the reacting gas mixture. The limited amount of data collected with steam reforming of Clearlite<sup>®</sup> indicated very good match between theoretical predictions and experimental results indicating that the underlying assumption of the simple model of conversion of hydrocarbons to CO and H<sub>2</sub> followed by equilibrium reconstitution to methane appears to be reasonable one.

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### 1. Background

One of the most promising technologies for lightweight portable power generation is proton exchange membrane (PEM) fuel cell. PEM fuel cells have several attractive features for small portable power applications: compact size, high power density, rapid start-up, and high energy conversion efficiency. Alternative technologies such as solid oxide fuel cells require very high temperatures of the order of 800–900 °C (1073–1173 K) for successful operation and also need much longer start-up time. PEM fuel cells have a potential to provide compact high energy density portable power, from a few Watts to a few kilowatts, both in consumer industry as well as in military applications. Consumer applications range from back-up

premium power, battery charger, recreational power, e.g. camping, and emergency power. Military applications include lighter and more compact electrical power sources for soldier and robotic missions; and as the available technologies and instrumentation advance, so does the power requirement for equipment. For example, for the modern “land warrior,” electrical energy is needed to power a variety of advanced devices such as a computerized radio system (transmission/receiver); helmet-mounted display, imager, and laser detector; and a weapon subsystem consisting of a laser range-finder, thermal weapon sight, digital compass and a laser aiming light. The desired amount of stored energy depends on application, with energy content of 1 kWh may be considered typical for emergency and back-up power applications [1].

At present, batteries are used for powering such portable devices in military and consumer applications. Although batteries have many desirable features such as reliability, long storage life, air-independent operation, low thermal and acoustic signatures, etc.,

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**Table 1**  
Hydrogen yield and corresponding specific energy of fuel choices.

Fuel	Hydrogen yield (g g <sup>-1</sup> )	Specific energy (Wh kg <sup>-1</sup> )
Compressed hydrogen <sup>a</sup>	0.01	150
Metal Hydrides for storage <sup>a</sup>	0.013	200
NaBH <sub>4</sub> hydrolysis	0.108	1830
Methanol	0.188	3190
Methanol (including water)	0.120	2040
Butane	0.448	7620
Butane (including water)	0.129	2190
Gasoline	0.444	7500
Gasoline (including water)	0.125	2140
JP-8	0.435	7400
JP-8 (including water)	0.123	2090
Clearlite <sup>®b</sup>	0.430	7350
Clearlite <sup>®</sup> (including water)	0.120	2050
Ammonia	0.176	3000

Note that the hydrogen yield and specific energy values for compressed hydrogen cylinders and metal hydride-based canisters are system-based on actual commercially available systems. Hydrogen yield and energy capacities for sodium borohydride hydrolysis and ammonia cracking are based on stoichiometric reactions and are based on the amount of reagents required. The hydrogen yield and energy capacity for methanol is based on its complete decomposition and subsequent stoichiometric water gas shift (WGS) reaction. Hydrogen yield and energy capacities for the hydrocarbons are based on steam reforming and subsequent WGS reaction with 100% conversion and assume a stoichiometric steam to carbon ratio of two. The hydrocarbons noted are those readily available as liquid commercial fuels; <sup>e</sup> electrical.

<sup>a</sup> System-based values for commercially available small systems.

<sup>b</sup> A sulfur-free kerosene available commercially.

the amount of energy that can be stored in primary or rechargeable batteries is limited. Primary standard batteries such as BA5590 (Li/SO<sub>2</sub>) have a specific energy of only 175 Wh kg<sup>-1</sup>. The specific energy of the rechargeable secondary batteries under consideration by Army is even lower, for example specific energy of a BB2847 battery is about 80 Wh kg<sup>-1</sup> and that of a BB390A battery is only 56 Wh kg<sup>-1</sup>. Consumer batteries have much lower energy densities, e.g. a high capacity lead acid battery provides an energy density of about 23 Wh kg<sup>-1</sup>. While many improvements in battery technology are being made and future advances are anticipated, the projected specific energies are still expected to be substantially lower than the desired specific energies of 1000 Wh kg<sup>-1</sup> or greater.

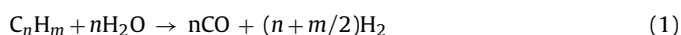
Power densities of large 80–100 kW PEM systems being developed for automotive power application are greater than 0.6 kW kg<sup>-1</sup> and are approaching 1 kW kg<sup>-1</sup>. For smaller, e.g. 20–100-W power systems, a fuel cell power density greater than at least 0.2 kW kg<sup>-1</sup> is expected. PEM fuel cells are therefore very attractive as a power generation unit for the small portable power generation systems. PEM fuel cells, however, require a source of pure hydrogen. Approaches available for supplying hydrogen to a fuel cell include compressed hydrogen cylinders, hydrogen adsorbed on metal hydrides, thermolysis or hydrolysis of metal hydrides, reforming of hydrocarbon fuels, and ammonia decomposition. With a typical 50% energy conversion efficiency of a fuel cell, about 17 kWh of electrical energy can be produced from 1 kg of hydrogen. To provide an energy capacity of 1 kWh, at least 0.06 kg of pure hydrogen must be provided. The commercially available choices for a hydrogen source are compared in Table 1 for their specific energies (electrical) based on the reagent weights alone.

As seen in Table 1, steam reforming of hydrocarbon fuels can provide reagent weight-based specific energies greater than 2000 Wh kg<sup>-1</sup> even after including weight of water. Butane and heavier hydrocarbons such as JP-8 indicate a high specific energy based on hydrocarbon fuel weight alone. However, for portable power applications the weight of water that is required for steam reforming must also be included in determining the overall specific

energies of fuel/water mixture. The net specific energy of a hydrocarbon reforming system may be increased by recovering liquid water from the fuel cell exhaust gas and recycling it to the fuel reformer, however, it will need additional components and add complexity [2,3]. Although ammonia cracking can provide a high specific energy of 3000 Wh kg<sup>-1</sup>, ammonia must be stored under pressure and is also considered toxic for portable use. Hydrocarbon fuels possess desirable characteristics such as ease of fuel storage at low pressures and ambient temperatures, handling and transportation; availability and a lower cost and would be considered as the primary candidates as hydrogen sources for fuel cell-based portable power.

## 2. Steam reforming of hydrocarbon fuels

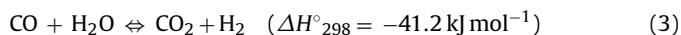
Steam reforming of methane and petroleum feedstocks, e.g. naphtha, is an industry standard process for generating hydrogen commercially and extensive information is available on thermodynamics, kinetics, and catalysis of the reforming reactions [e.g. [4]]. Steam reforming of hydrocarbons in general is a metal-catalyzed reaction described by three stoichiometric reactions. First the hydrocarbon dissociates on the metal surface, and the hydrocarbon fragments react with adsorbed steam to produce CO and H<sub>2</sub>:



(for C<sub>4</sub>H<sub>10</sub>:  $\Delta H^\circ_{298} = +582.4 \text{ kJ mol}^{-1}$ ;

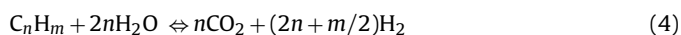
C<sub>8</sub>H<sub>18</sub>:  $\Delta H^\circ_{298} = +1300 \text{ kJ mol}^{-1}$ ).

The CO and H<sub>2</sub> produced by Reaction (1) further undergo methanation and water gas shift (WGS) reactions to establish equilibrium concentrations of CO, H<sub>2</sub>, CH<sub>4</sub>, CO<sub>2</sub>, and H<sub>2</sub>O:



While Reaction (1) is strongly endothermic, the overall heat of reaction may be positive or negative, depending upon process conditions; most typically it is strongly endothermic, and heat must be supplied to the reformer, usually by burning part of the fuel. In a partial oxidation or also termed as autothermal reformer process fuel combustion and subsequent steam reforming of the remaining fuel is conducted in a single reactor. Since air is often used in an autothermal reactor the resulting reformat gas contain much lower concentration of hydrogen than that would be generated by steam reforming of hydrocarbons [5]. This paper addresses the possible utilization of steam reforming of liquid hydrocarbons for providing hydrogen for portable, small, power generation systems. Fuel processors utilizing steam reforming of hydrocarbons are actively being developed for small and micro-scale portable hydrogen generators [3,6,7].

The desired overall hydrocarbon steam reforming reaction, with the stoichiometric steam to carbon ratio of 2 and maximum 100% yield of hydrogen, is represented as



The actual proportion of various species (H<sub>2</sub>, CO, CH<sub>4</sub>, CO<sub>2</sub>, and H<sub>2</sub>O) in the reformat gas at equilibrium depends upon the process temperature and pressure conditions and the steam to carbon ratio used. Conventionally, the fuel reforming process is followed by a separate lower temperature WGS reaction step to increase hydrogen concentration in the product gas. For small portable power systems it would obviously be desirable to generate hydrogen in a single reactor, as considered here, without inter-step cooling.

To overcome the equilibrium limitations of the reforming and WGS reactions, it is customary to use a significant excess of steam in the reforming process to increase the yield of hydrogen. Excess

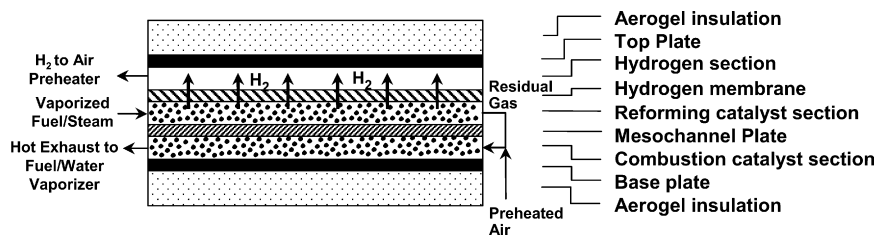


Fig. 1. Schematic of an integrated membrane reactor.

steam is also often considered as a necessity to prevent carbon formation in the reforming process causing deactivation of the catalyst. However, an excess use of steam also causes significant reduction in the reagent weight-based hydrogen yield. For example, stoichiometric steam reforming of butane will produce a maximum of  $0.129 \text{ kg H}_2 \text{ kg}^{-1}$  of reagents (Table 1) representing  $\sim 2200 \text{ Wh kg}^{-1}$  of specific energy (electrical) based on reagent weight alone. With 100% excess steam, however, the maximum hydrogen yield would be reduced to  $0.075 \text{ kg kg}^{-1}$  of reagents representing only  $\sim 1280 \text{ Wh kg}^{-1}$  of specific energy (electrical) based on weight of reagents alone. The specific energy may be increased by condensing and recycling the excess water, however, the recovery is not usually complete and additional energy must be spent in vaporizing the excess water. Greater feed flow rates also increase the size and weight of the reactor and auxiliary systems. For generation of pure hydrogen, even greater excess of steam with steam to carbon ratio of greater than 4 is used in commercial practice. To increase the equilibrium conversion in the hydrocarbon reforming step high temperatures of  $800^\circ\text{C}$  ( $1073 \text{ K}$ ) or more are also commercially used [4].

### 2.1. Membrane reactor concept

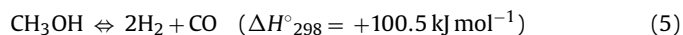
Another way of overcoming the equilibrium limitations as well as of reducing reactor temperatures to milder  $500\text{--}600^\circ\text{C}$  ( $773\text{--}873 \text{ K}$ ) conditions, is to continuously separate the product hydrogen from the reaction mixture forcing the reforming reaction to go forward. For such a concept, a high-flux, high selectivity membrane stable at the reforming conditions is needed. Since the palladium-based hydrogen separation membranes also operate best at the target reforming conditions of  $500\text{--}600^\circ\text{C}$  ( $773\text{--}873 \text{ K}$ ), have high-flux rates, and are completely selective for hydrogen, these membranes are promising candidates for the membrane reactor/reformer concept. In membrane reforming process steam to carbon ratio can also be significantly lower than in a conventional reforming process since the hydrogen separation drives the equilibrium towards continued hydrogen generation. Stoichiometric utilization of steam will reduce the weight of reagents as well as the weight and size of the overall system and will allow realization of the high specific energies noted in Table 1. Utilization of a high selectivity hydrogen separation membrane also provides a purer hydrogen product stream and will reduce any additional purification needed to produce hydrogen product suitable for use in a PEM fuel cell.

In order to realize a high specific energy for the overall reforming process unit, heat must be supplied to the process efficiently while minimizing heat losses. For maximizing thermal energy utilization it is desirable to integrate the generation of heat by fuel combustion with the utilization of heat by the reforming reaction as shown schematically in an integrated “membrane reactor” configuration (Fig. 1). Such configuration may be realized in a planar geometry or in a concentric tubular geometry where the heat transfer surface separates a heat generation (fuel combustion) section from the hydrocarbon reformer section. The heat transfer surfaces

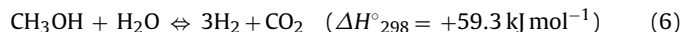
in Fig. 1 are indicated as mesochannel in reference to a possible miniature planar geometry design where the flow channels are etched as grooves on the surface. Several alternative designs are of course possible for example catalyst incorporated in a porous foam structure.

In the combustor section an auxiliary fuel is burned to produce heat. As seen in Fig. 1 schematic, the heat value of the residual gas leaving the membrane reformer section can be used in the combustor section along with any fuel cell anode exhaust gas to minimize or preferably eliminate the auxiliary fuel requirement. To further improve thermal efficiency of the overall system, the heat from the combustor exhaust gases and the hydrogen product may be recovered to preheat the air used for the combustor and to heat/vaporize fuel/water mixture. Furthermore, the heat losses from the system should also be minimized by enclosing the system in an efficient insulation material.

Numerous studies have been conducted for evaluation of the membrane reactor concept for conducting steam methane reforming (SMR) and WGS reactions [8–12]. Palladium alloy foils or tubes have also been incorporated in small hydrocarbon fuel reformers that are being demonstrated [e.g. [13–15]]. Palladium alloy membranes are used either to purify the product hydrogen after a fuel reformer [13,14] or integrated within the fuel reforming process [15] as shown in Fig. 1 schematic. The Part I of this paper [16] presented the results of model simulations conducted for evaluation of the membrane reactor concept for reforming liquid hydrocarbon fuels, butane and methanol. The simulations clearly indicated the enhanced hydrogen conversion and recovery in a membrane reactor configuration. In this companion Part II paper, experimental results obtained for reforming butane, methanol, and Clearlite® (a sulfur free kerosene available commercially) fuels in a palladium-based membrane reactor are compared with model predictions. These fuels were selected because of their commercial availability and also for the different degree of difficulty anticipated in reforming them. Steam reforming of butane and Clearlite® occurs as described by Eqs. (1)–(4) discussed above. Methanol on the other hand decomposes readily at temperatures above  $300^\circ\text{C}$  ( $573 \text{ K}$ ) in an endothermic reaction [9]:



With the subsequent exothermic and equilibrium limited WGS reaction (Reaction (3)) the overall steam reforming of methanol is described as



Enhancement of equilibrium conversion through separation of one of the products by a membrane is not a new concept; and a number of studies have confirmed the merits of the membrane reactor approach [17,18]. Several attempts to use the product permeation concept in reactor technology have emerged through the years. Removing hydrogen product through a palladium membrane tube has also been proposed for the promotion of the dehydrogenation reaction of cyclohexane to benzene beyond thermodynamic

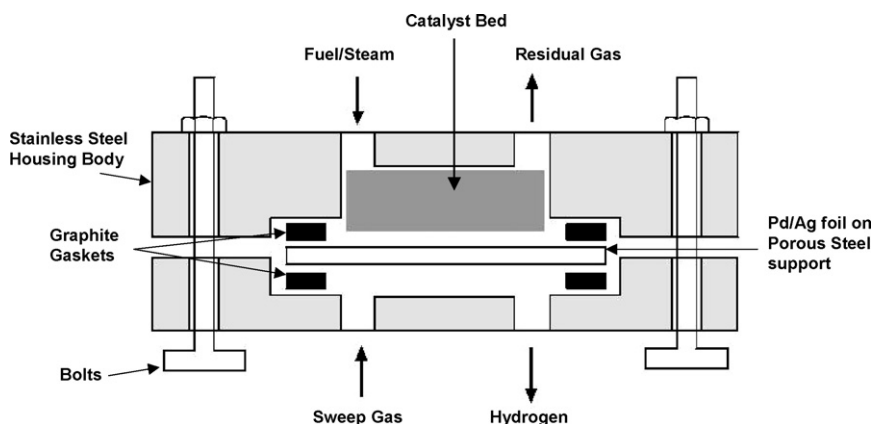


Fig. 2. Schematic of membrane reactor housing–diffusion cell.

equilibrium [19,20]. A reaction conversion of 99.7% was reported compared to 18.7% using an ordinary catalytic reactor. Different types of ceramic membranes have also been investigated as  $H_2$  permeators. A sol-gel alumina membrane was utilized in a ceramic tubular reactor for propane dehydrogenation [21].

In addition to continuous shifting of the reaction equilibrium driving it to completion, the use of a membrane reactor would also allow using lower temperatures ( $600^\circ\text{C}$  {873 K} and lower) for the reforming reaction. Steam methane reforming reaction (Reaction (2)) is favored at a higher temperature ( $>700^\circ\text{C}$  {>973 K}) and a lower pressure to produce increased hydrogen. However, greater conversions are possible at lower temperatures and higher pressures in a membrane reactor since the separation of one of the product species ( $H_2$ ) overcomes the thermodynamic limitations of the reaction. It also permits the use of a smaller reactor and separator, and allows operation at a greater residence time. The benefit is decreased reactor cost (cheaper materials, smaller vessel, and less catalyst), fewer side reactions and improved heat transfer. The WGS shift reaction on the other hand is favored at temperatures below  $400^\circ\text{C}$  (673 K) for increased hydrogen. However, again separation of hydrogen product allows conducting WGS reaction at a much higher temperature of  $600^\circ\text{C}$  (873 K) by shifting the WGS reaction equilibrium. The membrane reactor–steam reformer unit can also conduct both the steam reforming and the subsequent WGS reaction in a single reactor by continuing them simultaneously. Another advantage of the membrane reactor concept is that a large excess of steam to carbon ratio is not necessary for achieving equilibrium. Stoichiometric steam to carbon ratio can be used in the membrane reactor configuration by utilizing appropriate catalysts (e.g. precious metal-based catalysts) resistant to carbon formation.

### 3. Membrane reactor experiments with commercial Pd–Ag foils

For conducting hydrocarbon reforming in a membrane reactor to produce pure hydrogen product, a hydrogen selective membrane capable of operating at the targeted  $500\text{--}600^\circ\text{C}$  (773–873 K) temperature and high-pressure environment is needed. Micro-porous inorganic membranes stable at this temperature, e.g. alumina- and silica-based membranes, exhibit Knudsen diffusion mechanism for gas separation with low separation factors (e.g.,  $H_2$ : $CO_2$  separation factor of 4.7). Moreover, the separation ability of the commercially available 4 nm pore size gamma-alumina membranes as well as silica-based molecular sieve-type membranes depends upon the stability of the membrane pore size, which is adversely affected by the action of steam [22]. The dense ceramic membranes based on inorganic perovskite oxides need considerably high tempera-

tures, greater than  $800^\circ\text{C}$ , to achieve practical hydrogen flux rates. Palladium-based dense membranes are known for their high hydrogen selectivity and permeability over other gases and are suitable for operation in the low temperature ( $400\text{--}650^\circ\text{C}$  (673–923 K)) hydrocarbon fuel reforming and water gas shift reaction environments. In order to be suitable for these target applications, a hydrogen separation membrane must have adequate selectivity and flux rate, must be stable in the reducing gas environment containing steam and hydrogen sulfide, and be economically competitive. Pd-alloy membranes are promising candidates provided their sulfur tolerance is enhanced, e.g. by using Pd–Cu alloys [23–25] or hydrogen sulfide is removed upstream of the membranes. Although palladium alloy tubes have been available for several decades, they are expensive for commercial applications due to the thickness needed for structural stability. The tubular membranes also exhibit low hydrogen flux rates due to their thickness. A number of studies are being conducted to develop low-cost Pd-alloy composite membranes [26–29] although such membranes are not yet commercial. The membrane reactor experiments in these studies were therefore conducted with commercially available Pd–Ag alloy foils (77 wt% Pd), 1 mil (25  $\mu\text{m}$ ) thick supported on porous stainless steel, to demonstrate the membrane reactor approach for steam reforming of butane, methanol and Clearlite® with simultaneous hydrogen separation.

A high temperature membrane housing (diffusion cell) was fabricated to house planar Pd/Ag alloy membrane foils using graphite gaskets. The diffusion cell, shown schematically in Fig. 2, allowed using 2 in.  $\times$  2 in. (5 cm  $\times$  5 cm) membrane foils sealed by 1/4 in.-wide graphite gasket with an effective membrane area of 1.5 in.  $\times$  1.5 in. (3.75 cm  $\times$  3.75 cm) square. The membrane foils were supported by 5 cm  $\times$  5 cm  $\times$  3 mm porous stainless steel squares (Mott Corporation) with an average pore size grade of 2  $\mu\text{m}$  providing a smooth surface for supporting the thin fragile Pd-alloy foils. The 2  $\mu\text{m}$  size grade also assured negligible resistance to the permeate gas flow through the porous material. The diffusion cell allowed hydrocarbon/steam mixture on the feed side of the membrane and a sweep gas on the permeate side with a controllable trans-membrane pressure differential. The feed side of the housing allowed approximately 3.75 cm  $\times$  3.75 cm  $\times$  0.75 cm cavity for catalyst bed and about 10 cm<sup>3</sup> of catalyst bed volume. With an active membrane area of 14.5 cm<sup>2</sup>, the membrane surface area to reactor volume ratio was approximately 1.4 cm<sup>-1</sup>. The diffusion cell/membrane reactor was housed in a short cylindrical furnace with 4 in. (10 cm) diameter  $\times$  6 in. (15 cm) length cavity for controlled heating to a desired operating temperature in  $450\text{--}600^\circ\text{C}$  (723–873 K) range. The commercially available planar membrane samples were first evaluated for their permeation and hydrogen

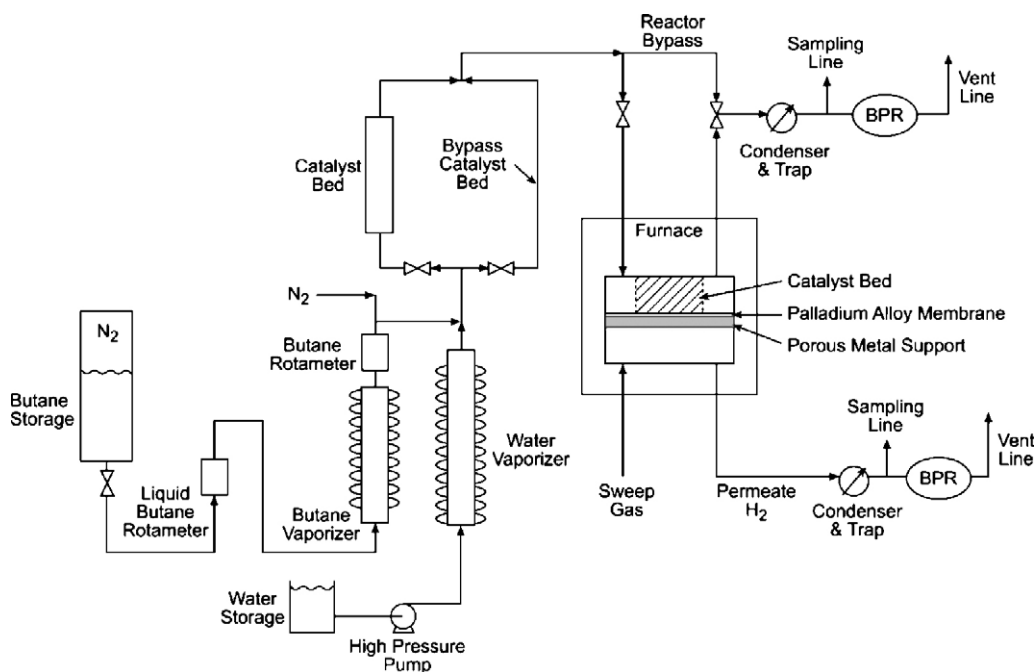


Fig. 3. Schematic of the membrane reactor experimental system.

selectivity characteristics by conducting permeation testing with pure hydrogen and nitrogen components. For a uniform, pinhole-free, thin film membrane, the permeation rate of all other species except hydrogen would be negligible with proper sealing of the membrane.

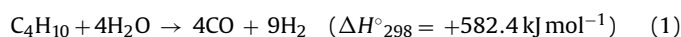
Fig. 3 schematically shows the experimental set-up assembled for conducting steam reforming of both butane and methanol. In the case of butane reforming experiments butane was fed as a liquid under pressure and its flow rate was controlled by a liquid flow rotameter. Water was injected at a desired flow rate by a high-pressure water pump. Both butane and water were vaporized in separate vaporizers before mixing and preheating. In the case of methanol reforming experiments, methanol and water was pre-mixed in 1:1 mole ratio and the mixture was injected into the water vaporizer at a desired rate using the high-pressure liquid pump. Both permeate and the residual outlet gas streams were analyzed by an on-line gas chromatograph during the reforming experiments. All of the butane reforming experiments were conducted at 600 °C (873 K), whereas, bulk of the methanol reforming experiments were conducted at 550 °C (823 K) as described later. The feed side pressure ranged from 60 to 150 psig (0.515–1.136 MPa) with bulk of experiments conducted at 100 psig (0.791 MPa) feed side pressure. No sweep gas flow rate was actually used in any of the butane and methanol reforming experiments due to high enough hydrogen permeation rates to allow on-line gas chromatographic analysis of the permeate. For any given set of experimental conditions of temperature, pressure, feed gas flow rate and steam to carbon ratio, the composition and flow rate of both the residual gas and permeate gas streams were determined by on-line GC analysis and bubble flow meter measurements. The operating conditions were maintained until reproducible composition and flow measurements were observed. These experiments were conducted over a period of several weeks and steaming of the feed side and catalyst bed was periodically conducted to restore membrane hydrogen flux characteristics by gasification of any carbon accumulated in the catalyst bed and on the membrane.

For the intended practical portable hydrocarbon reforming application, the typical membrane operating temperature is

expected to be in the range of 450–650 °C (723–923 K), and the maximum operating pressure is expected to be up to 150 psig (1.136 MPa) due to limitations of a portable compact high-pressure liquid pump. The experimental facility was therefore assembled to allow for testing at these desired operating conditions.

### 3.1. Butane reforming experiments

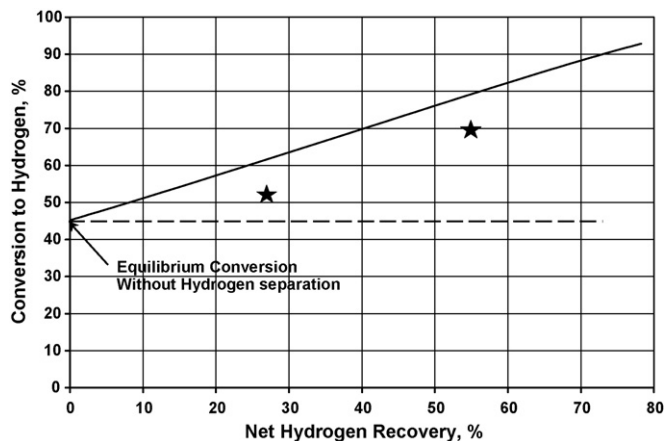
Butane reforming experiments were conducted by feeding butane under pressure as a liquid. These experiments were conducted with commercially available nickel-based catalyst supported on alumina/aluminate at 600 °C (873 K) temperature and 60–150 psig (0.515–1.136 MPa) feed side pressure. The permeate pressure was atmospheric in all experiments. Bulk of the butane reforming experiments were conducted at 100 psig (0.791 MPa) feed side pressure based on the results of model simulations presented in the Part I of this paper [16]. Although these model simulations assumed that the kinetics of all three reactions is fast and Reaction (1) is irreversible so that the reformate gas is always in a dynamic equilibrium; depending upon the operating conditions such as flow rate (space velocity) and catalyst activity the actual species concentrations are expected to be somewhat different than those at equilibrium. The purpose of these experiments was to evaluate the feasibility of the membrane reactor concept for increasing hydrogen yield and hydrocarbon conversion by separation of product hydrogen from the reforming mixture. Another purpose was to evaluate the influence of reaction kinetics on the theoretically expected increase in hydrocarbon conversion and hydrogen yield. The steam reforming of butane is represented as



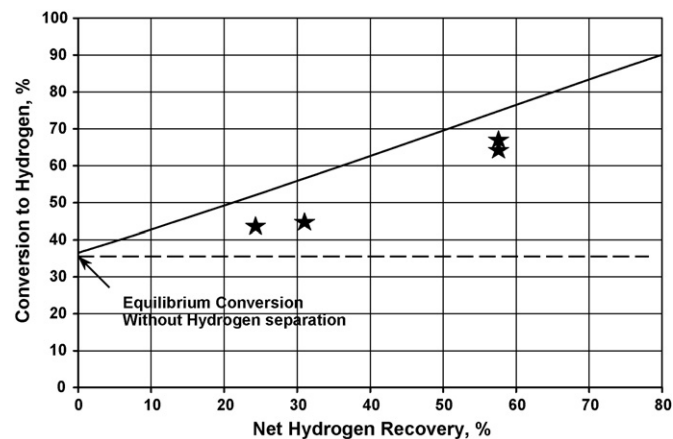
With additional hydrogen production with the WGS reaction the maximum hydrogen production potential in butane reforming is 13 moles of H<sub>2</sub> per mole of butane. Experiments were conducted at different feed flow rates and steam to carbon ratios at 600 °C (873 K) temperature and 100 psig (0.791 MPa) feed side pressure using commercial G-91 EW (Sud-Chemie, Inc.) NiO/CaAl<sub>2</sub>O<sub>4</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst pellets. Experiments were also conducted at 60 and 150 psig

**Table 2**  
Results of steam reforming of butane experiments.

Run condition#	Butane flow rate (cm <sup>3</sup> min <sup>-1</sup> ) (gas)	Steam to carbon ratio	Residual outlet flow rate (cm <sup>3</sup> min <sup>-1</sup> )	Hydrogen permeate flow (cm <sup>3</sup> min <sup>-1</sup> )	Feed side average space velocity (h <sup>-1</sup> )	Residual gas hydrogen partial pressure (MPa)	Conversion to hydrogen (% of max possible)	Hydrogen recovery (% of maximum possible)
1	10.8	4.0	64	77	641	16	70	55
2	18.3	4.0	134	64	1165	20	52	27
3	23.6	3.2	165	73	1198	22	43	24
4	11.0	3.0	60	82	504	16	68	57
5	26.0	2.8	151	105	1169	17	45	31
6	10.6	2.6	54	78	398	16	65	57
7	32.3	2.2	186	91	1225	16	35	22
8	30.6	2.0	167	103	1023	18	37	26



**Fig. 4.** Comparison of butane reforming experimental results with model predictions (600 °C (873 K), 100 psig (0.791 MPa), steam to carbon ratio=4).



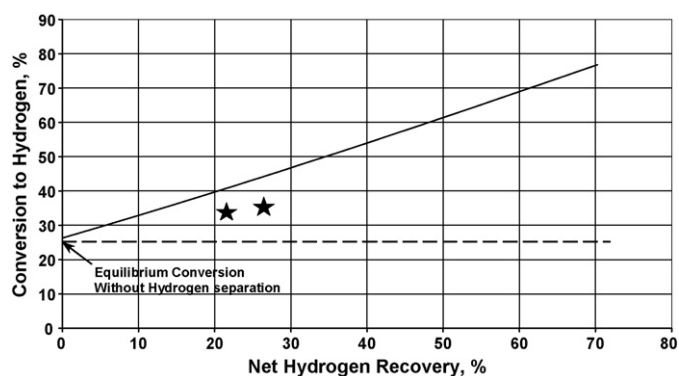
**Fig. 5.** Comparison of butane reforming experimental results with model predictions (600 °C (873 K), 100 psig (0.791 MPa), steam to carbon ratio=3).

(0.515 and 1.136 MPa) pressure to assess the effect of the system pressure on hydrocarbon conversion and product hydrogen yield. The steam to carbon ratio was varied from 4 to the stoichiometric ratio of 2. The butane feed rate was varied to change the gas space velocity through the catalyst bed in the range of 400–2200 h<sup>-1</sup> (0.11–0.61 s<sup>-1</sup>) (determined at the operating conditions). The butane reforming results obtained at 100 psig (0.791 MPa) feed side pressure for different feed flow rates and steam to carbon ratios are summarized in Table 2. The hydrocarbon conversion to hydrogen is expressed as % of the maximum possible hydrogen production based on the hydrocarbon feed rate. The net hydrogen recovery is defined as the amount of hydrogen permeated as a percentage of the maximum possible hydrogen production potential.

The above results are compared in Figs. 4–6 to theoretical predictions provided by a simple one-dimensional model described in the Part I of this paper [16]. A key assumption of this model is that of dynamic equilibrium on the feed side along the length of the membrane as hydrogen is continuously separated from the reacting mixture. The model also assumed the steam reforming of hydrocarbon itself (Reaction (1)) as irreversible, however, allowing reversible methane formation by methanation reaction (Reaction (3)). Essentially the model assumed that the hydrocarbon species is immediately converted to methane as dictated by methanation and WGS reaction equilibria. Model simulation results in Figs. 4–6 were obtained for steam reforming of butane at 100 psig (0.791 MPa) pressure and 600 °C (873 K) temperature and for steam to carbon ratios of 4, 3, and 2, respectively. The model predictions are compared with results for experimental run conditions 1 and 2 in Fig. 4; run conditions 3–6 in Fig. 5, and run conditions 7 and 8 in Fig. 6. All of the experimental results demonstrate increase in hydrocarbon conversion due to hydrogen separation when com-

pared with the hydrocarbon conversion without any hydrogen separation. Increase in hydrogen recovery was also shown to result in corresponding increase in hydrocarbon conversion in these studies.

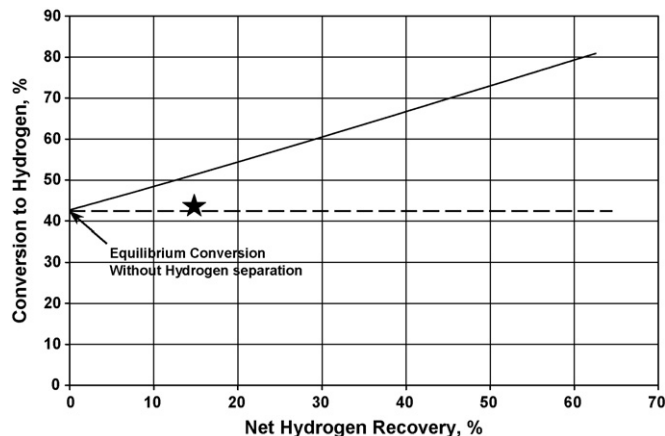
Feed side pressure is expected to affect hydrocarbon conversion in two contrasting ways: (1) increase in feed pressure favors increased methane formation by the methanation reaction (Reaction (3)) reducing the overall hydrocarbon conversion to hydrogen, but (2) on the other hand increase in feed side pressure increases hydrogen flux rate thereby providing a greater shift in equilibrium towards hydrogen production. Effect of feed side pressure was therefore experimentally investigated by conducting butane reforming at 60 and 150 psig (0.515 and 1.136 MPa) feed pressure. These results are summarized in Table 3 where two of the runs from Table 2 are included for comparison of results to those



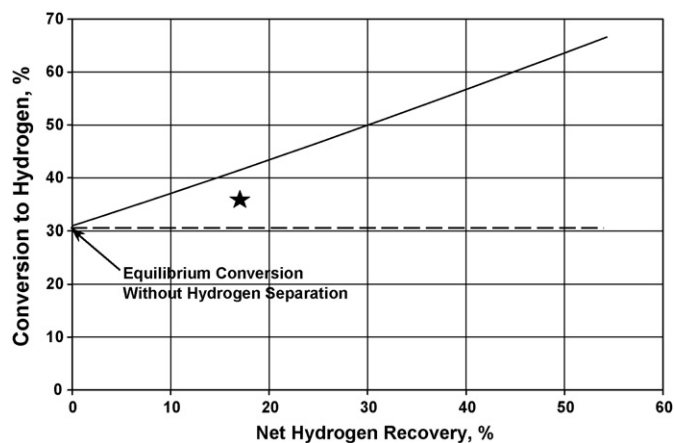
**Fig. 6.** Comparison of butane reforming experimental results with model predictions (600 °C (873 K), 100 psig (0.791 MPa), steam to carbon ratio=2).

**Table 3**  
Results of steam reforming of butane experiments at different feed pressures.

Run condition#	Butane flow rate (cm <sup>3</sup> min <sup>-1</sup> ) (gas)	Feed side pressure (MPa)	Steam to carbon ratio	Residual outlet flow rate (cm <sup>3</sup> min <sup>-1</sup> )	Hydrogen permeate flow (cm <sup>3</sup> min <sup>-1</sup> )	Feed side average space velocity (h <sup>-1</sup> )	Residual gas hydrogen partial pressure (MPa)	Conversion to hydrogen (% of max possible)	Hydrogen recovery (% of maximum possible)
2	18.3	100	4.0	134	64	1165	20	52	27
3	23.6	100	3.2	165	73	1198	22	43	24
9	27.8	60	3.0	204	55	2160	15	42	15
10	37.6	60	2.2	242	84	2220	16	36	17
11	14.3	150	3.7	78	51	877	16	39	27
12	21.3	150	3.3	115	65	906	16	35	24
13	14.2	150	3.0	75	43	712	16	33	24

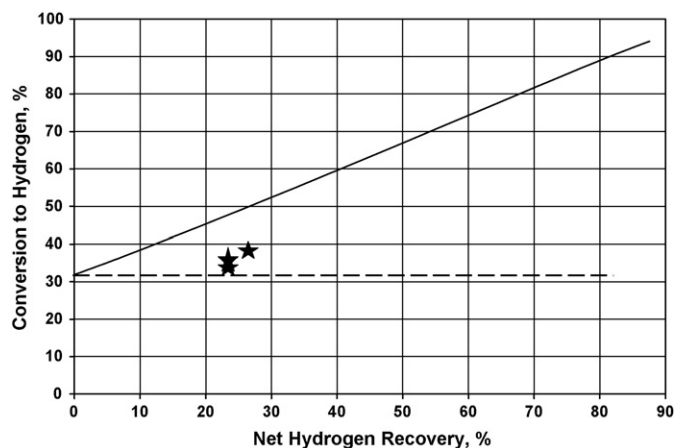


**Fig. 7.** Comparison of butane reforming experimental results with model predictions (600 °C (873 K), 60 psig (0.515 MPa), steam to carbon ratio=3).



**Fig. 8.** Comparison of butane reforming experimental results with model predictions (600 °C (873 K), 60 psig (0.515 MPa), steam to carbon ratio=2).

obtained at 100 psig (0.791 MPa) pressure. The experimental results obtained at 60 psig (0.515 MPa) feed side pressure are compared with model predictions for steam to carbon ratio of 3 and 2, respectively in Figs. 7 and 8. The experimental results obtained at 150 psig (1.136 MPa) feed side pressure are compared with model predictions for steam to carbon ratio of 3 in Fig. 9.



**Fig. 9.** Comparison of butane reforming experimental results with model predictions (600 °C (873 K), 150 psig (1.136 MPa), steam to carbon ratio=3).

**Table 4**  
Results of Steam methanol reforming experiments.

Run condition #	Mixture feed flow rate (cm <sup>3</sup> min <sup>-1</sup> ) (liquid)	Temp. (°C)	Feed pressure (MPa)	Residual outlet flow rate (cm <sup>3</sup> min <sup>-1</sup> )	Hydrogen permeate flow rate (cm <sup>3</sup> min <sup>-1</sup> )	Feed side average space velocity (h <sup>-1</sup> )	Residual gas hydrogen partial pressure (MPa)	Conversion to hydrogen (% of max possible)	Hydrogen recovery (% of maximum possible)
1	0.4	450	60	377	60	1880	32	76	15
2	0.4	550	60	341	118	2106	21	67	26
3	0.4	550	100	336	150	1387	31	64	30
4	0.4	550	150	300	176	888	46	64	36
5	0.2	550	60	141	104	946	17	73	45
6	0.2	550	100	120	108	584	21	72	50
7	0.2	550	150	122	123	411	28	71	53
8	0.2	600	150	115	138	423	22	75	60

Results presented in Table 2 indicate that the butane feed flow rate strongly influenced the observed hydrogen recoveries as well as conversion to hydrogen with the highest recoveries obtained with the lowest butane feed flow rate of about 11 cm<sup>3</sup> min<sup>-1</sup> gas phase (0.035 cm<sup>3</sup> min<sup>-1</sup> liquid phase). The observed hydrogen partial pressures in the reformer exit gas for butane reforming were from 16 to 22 psia (0.11–0.15 MPa) with only a few psi hydrogen partial pressure differential across the membrane for most of the experimental conditions. These data suggest that the kinetics of butane reforming is clearly the dominating factor influencing the membrane reactor performance. The fact that the steam to carbon ratio did not influence the conversion to hydrogen significantly indicates that the reaction mechanism is likely to be based on adsorption of butane (or any intermediate species) on the catalyst and that the hydrocarbon probably did not reform completely to CO and hydrogen (Reaction (1)) before reconstituting to methane as is commonly considered. The exit gases from butane reforming contained significantly high concentration of methane indicating a substantially slow kinetics of butane reforming. The hydrocarbon conversion in all of the butane reforming reaction conditions is somewhat less than that predicted by model simulations for the corresponding reaction conditions. Nonetheless, these experiments prove the membrane reactor concept with greater hydrogen conversion through reaction equilibrium shift as observed by increased hydrocarbon conversion with increased hydrogen separation and recovery.

Attempts to increase the hydrogen recovery by increasing system pressure to 150 psig (1.136 MPa) did not materialize (Table 3—run conditions 3 and 12) due to less conversion of hydrocarbon (methane) to hydrogen as dictated by equilibrium at the higher pressure. The hydrogen recoveries were still similar to those at 100 psig (0.791 MPa) due to greater hydrogen partial pressure differential for hydrogen permeation. Reducing the butane flow rate at high-pressure operation (run conditions 12 and 13) did not increase hydrogen recovery probably because of the increased mass transfer effects at the low gas flow velocity in the feed side section. Reforming at lower pressure of 60 psig (0.515 MPa) resulted in lower hydrogen recoveries due to smaller hydrogen partial pressure differential across the membrane as expected.

### 3.2. Steam methanol reforming experiments

For steam methanol reforming experiments, premixed methanol/water mixture was supplied to the high-pressure water pump and vaporized as a mixture in the steam vaporizer shown in Fig. 3. Only a high-temperature water gas shift catalyst (commercial C-12 Fe–Cr High Temperature WGS Catalyst—Sud-Chemie) was packed in the membrane unit since methanol was found to dissociate rapidly at temperatures above 450 °C (723 K) without any catalyst. Methanol was mixed with water in 1:1 molar proportion for a stoichiometric ratio of steam to methanol in all of the methanol reforming experiments. The maximum hydrogen potential in steam reforming of methanol is 3 moles mole<sup>-1</sup> of methanol. Steam methanol reforming experiments were conducted using membrane reactor temperature, system pressure, and the feed flow rate as system variables. The observed results are summarized in Table 4.

Experimentally observed results at 550 °C (723 K) and 60 psig (0.515 MPa) pressure are compared with theoretical model predictions in Fig. 10. Experimentally observed results at 550 °C (723 K) and 100 psig (0.791 MPa) pressure are compared with theoretical model predictions in Fig. 11 and the results obtained at 550 °C (723 K) and 150 psig (1.136 MPa) feed side pressure are compared with model predictions in Fig. 12. The experimental result obtained at 600 °C (873 K) and 150 psig (1.136 MPa) feed side pressure is



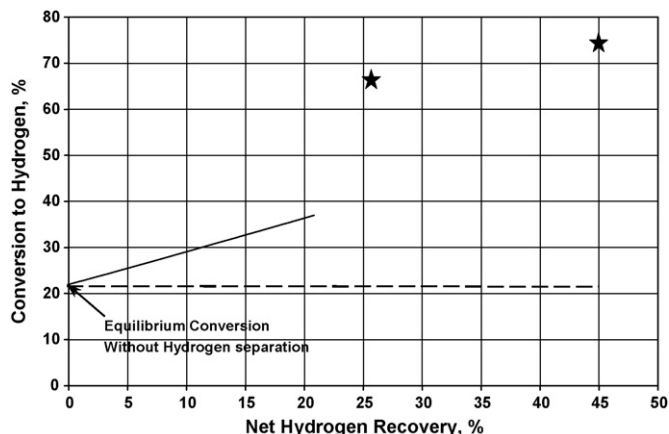


Fig. 10. Comparison of methanol reforming experimental results with model predictions (550 °C (823 K), 60 psig (0.515 MPa), steam to carbon ratio=2).

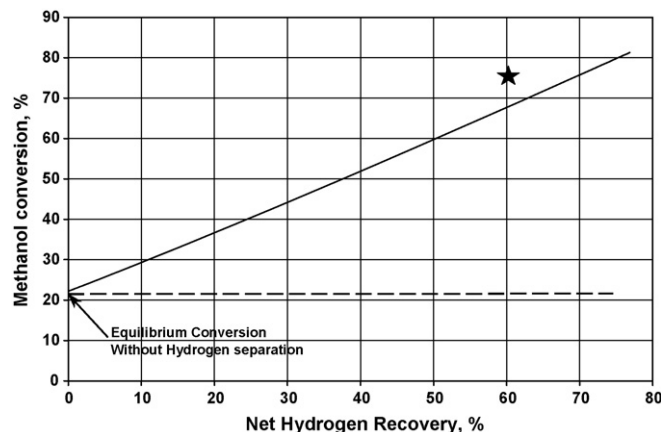


Fig. 13. Comparison of methanol reforming experimental results with model predictions (600 °C (873 K), 150 psig (1.136 MPa), steam to carbon ratio=2).

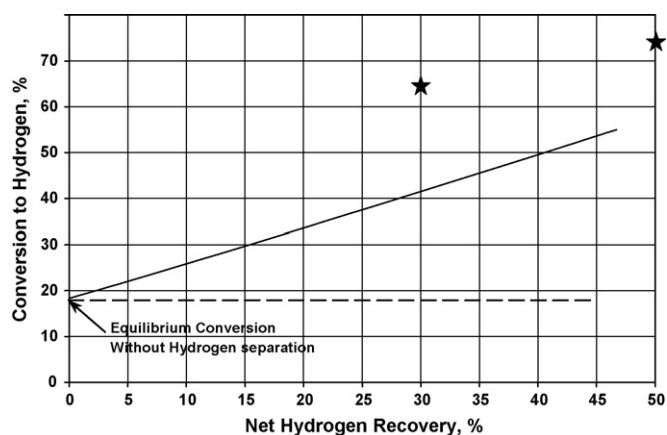


Fig. 11. Comparison of methanol reforming experimental results with model predictions (550 °C (823 K), 100 psig (0.791 MPa), steam to carbon ratio=2).

compared with model predictions in Fig. 13. As seen from the comparison of the experimental results with model predictions in Figs. 10–13 much higher hydrogen recoveries and conversions to hydrogen were observed than those predicted, especially for the low pressure operation at 60 and 100 psig (0.515 and 0.791 MPa). The primary reason for this apparently anomalous behavior is that the model takes into account formation of methane in the

reforming gas mixture to satisfy methanation reaction equilibrium. For membrane reactor conditions of 550 °C (823 K) and 60 psig (0.515 MPa) pressure a maximum hydrogen recovery of only 22% and a maximum conversion to hydrogen of only 37% was predicted by model simulations due to methane formation and corresponding lower hydrogen partial pressures in the reacting mixture. However, no hydrocarbon reforming (methanation) catalyst was used in these experiments since the methanol decomposes readily to CO and H<sub>2</sub> according to Reaction (5). As a result, very little methanation occurred at lower pressure operation. At a higher pressure of 150 psig (1.136 MPa) and at a higher temperature of 600 °C (873 K), the observed results are closer to the model predictions indicating methane formation in spite of the lack of reforming methanation catalyst.

Hydrogen conversion was high at the lower temperature of 450 °C (723 K) and lower pressure of 60 psig (0.515 MPa) (run condition # 1) due to favorable equilibrium conditions for WGS reaction and also due to lower methane formation potential, however, the hydrogen recovery at this condition was poor due to a significantly lower hydrogen flux rate of the Pd-alloy membrane at the lower temperature. In general hydrogen recoveries increased with higher pressure for a given temperature and feed flow rate, with greater temperature for the same pressure and feed flow rate, and with lower feed rate for the same temperature and pressure conditions as expected. At a mixture feed flow rate of 0.2 cm<sup>3</sup> min<sup>-1</sup>, and operating conditions of 600 °C (873 K) and 150 psig (1.136 MPa) observed conversion to hydrogen was 75% with a recovery of 60% of the maximum available hydrogen approaching those theoretically predicted in Fig. 13. The observed methanol conversions to hydrogen were substantially greater than those predicted without any hydrogen separation. In contrast to the steam butane reforming experiments, the observed hydrogen partial pressures at the reactor exit for steam reforming of methanol were greater than 20 psia (0.14 MPa) (except for run # 6 with 60 psig (0.515 MPa) feed side pressure) indicating that the membrane reactor performance (conversion and recovery) were limited by hydrogen permeation rate and the available membrane area especially for the high-pressure operation at 100 or 150 psig (0.791 or 1.136 MPa) and 550 °C (823 K). Membrane reactor operation at 600 °C (873 K) increased hydrogen permeation rate for the same membrane area significantly to approach theoretical model predictions for the hydrogen recovery in Fig. 13. These experiments thus demonstrated the membrane reactor concept by increasing the hydrogen conversion through reaction equilibrium shift caused by hydrogen separation.

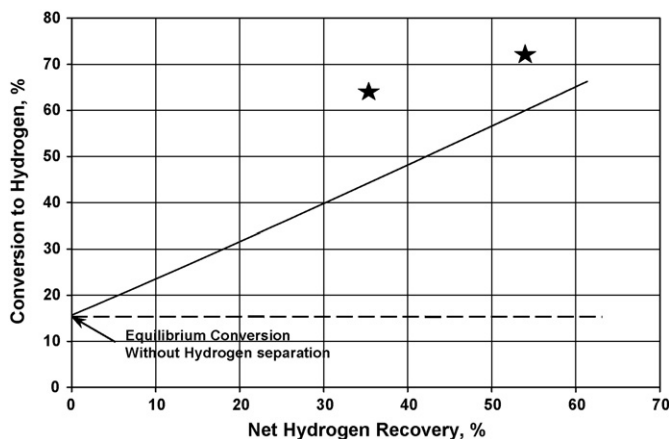


Fig. 12. Comparison of methanol reforming experimental results with model predictions (550 °C (823 K), 150 psig (1.136 MPa), steam to carbon ratio=2).

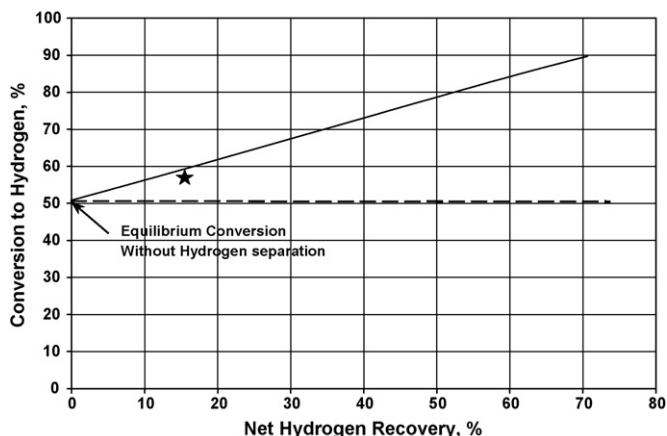


Fig. 14. Comparison of Clerlite<sup>®</sup> reforming experimental results with model predictions (620 °C (893 K), 70 psig (0.584 MPa), steam to carbon ratio=3.5).

### 3.3. Clearlite<sup>®</sup> reforming experiments

Limited range of experiments were conducted with steam reforming of Clearlite<sup>®</sup> (a sulfur-free kerosene available commercially) in a membrane reactor where the primary focus was on demonstration of longer term operation lasting over several hundred hours. A larger membrane reactor and proprietary reforming catalysts were used for steam reforming of Clearlite<sup>®</sup> at 620 °C (893 K), 70 psig (0.584 MPa) feed side pressure, gas space velocity of about 1000 h<sup>-1</sup> (0.28 s<sup>-1</sup>) with a steam to carbon ratio of 3.5. The observed hydrocarbon conversion to hydrogen was about 57% of maximum possible with a net hydrogen recovery of 15% of maximum possible. This data point is compared in Fig. 14 with results of model simulations conducted for the experimental process conditions. Excellent match with theoretical prediction was observed; also the results are similar to that seen in Fig. 7 for steam reforming of butane at 60 psig (0.515 MPa) pressure, 600 °C (873 K) temperature and steam to carbon ratio of 3. Clearlite<sup>®</sup> reforming experiments used proprietary precious metal catalysts that allowed closer approach of experimental results with theoretical model predictions based on fast kinetics and dynamic feed side equilibrium. Low feed side pressure and high steam to carbon ratio contributed to the observed low net hydrogen recovery. The ability of the simple model to predict membrane reactor performance for Clearlite<sup>®</sup> fuel, with a large average carbon number of 12, indicates that the underlying assumption of conversion of hydrocarbons to CO and H<sub>2</sub> followed by equilibrium reconstitution to methane appears to be reasonable one.

## 4. Summary and conclusions

PEM fuel cells provide an attractive option for lightweight, compact, portable power generation. PEM fuel cells, however, require a source of pure hydrogen. Reforming of liquid hydrocarbon fuels is most promising for providing high reagent weight-based hydrogen generation and specific energy; greater than 2 kWh kg<sup>-1</sup> including weight of water. Commonly available liquid hydrocarbon fuels such as butane also possess desirable characteristics such as ease of fuel storage at low pressures and ambient temperatures, handling and transportation, availability, and a low cost. Steam reforming of hydrocarbons produces hydrogen in equilibrium-limited reactions conducted at high pressures and temperatures. Utilization of a membrane reactor with a high temperature hydrogen permeable membrane such as Pd-alloy membrane, has a potential to overcome the equilibrium limitation of the reforming and WGS reactions as

well as for conducting these reactions under milder conditions with enhanced conversion to hydrogen and its recovery.

In the laboratory-scale experimental studies reported here steam methane reforming of liquid hydrocarbon fuels butane, methanol and Clearlite<sup>®</sup> to produce pure hydrogen was conducted in a single step membrane reformer using commercially available Pd–Ag foil membranes and reforming/WGS catalysts. All of the experimental results demonstrated increase in hydrocarbon conversion due to hydrogen separation when compared with the hydrocarbon conversion without any hydrogen separation. Increase in hydrogen recovery was also shown to result in corresponding increase in hydrocarbon conversion in these studies demonstrating the basic concept. The experiments also provided insight into the effect of individual variables such as pressure, temperature, gas space velocity, and steam to carbon ratio.

Steam reforming of butane was found to be limited by reaction kinetics for the experimental conditions used: catalysts used, average gas space velocity, and the reactor characteristics of surface area to volume ratio (~1.4 cm<sup>-1</sup>). To overcome the kinetics limitation and to match hydrogen generation and separation rates a lower surface area to volume ratio should be used along with lower gas space velocity and higher temperature. Steam reforming of methanol in the presence of only WGS catalyst indicated that the membrane reactor performance was limited by membrane permeation, especially at lower temperatures and lower feed pressures due to slower reconstitution of CO and H<sub>2</sub> into methane thus maintaining high hydrogen partial pressures in the reacting gas mixture. The limited amount of data collected with steam reforming of Clearlite<sup>®</sup> indicated very good match between theoretical predictions and experimental results indicating that the underlying assumption of the simple model of conversion of hydrocarbons to CO and H<sub>2</sub> followed by equilibrium reconstitution to methane appears to be reasonable one.

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