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A Survey of Processes for Producing Hydrogen Fuel from Different Sources for Automotive-Propulsion Fuel Cells

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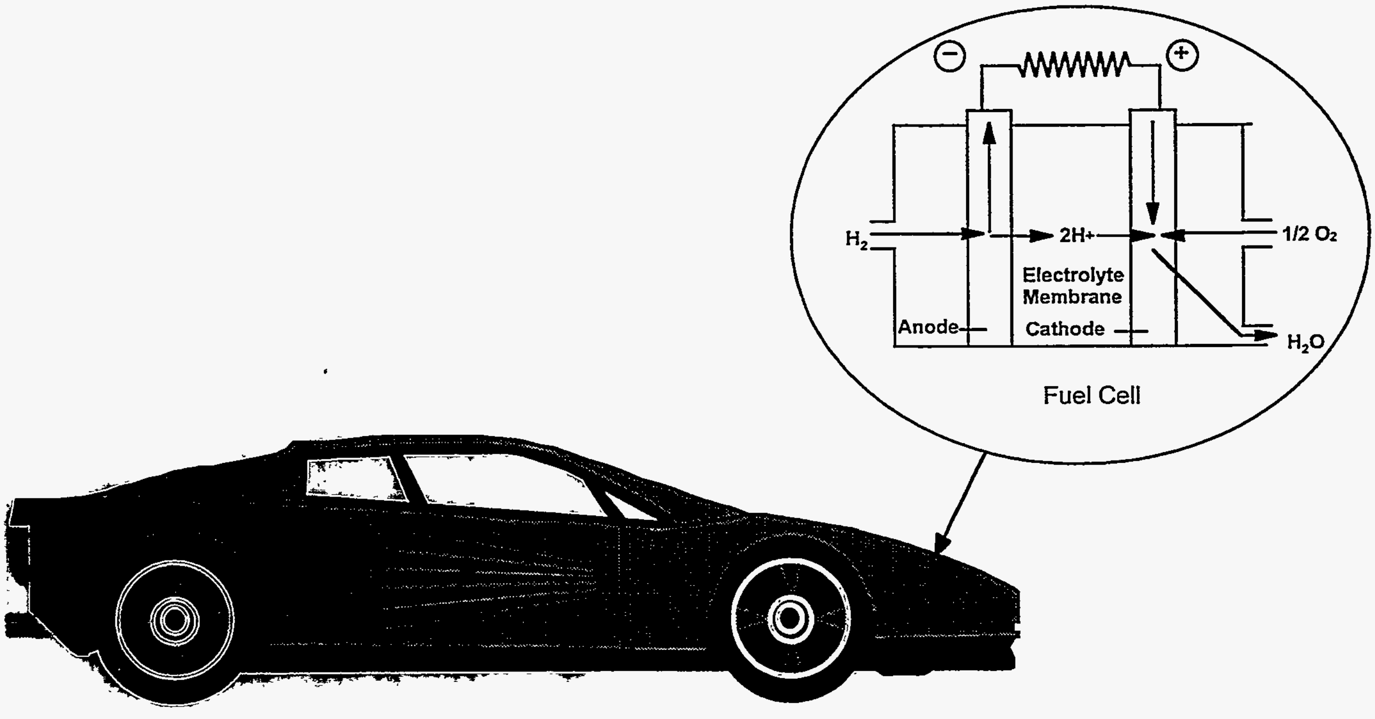
H2
2H+
1/2 O2
Electrolyte
Membrane
Anode
Cathode
H2O
Fuel Cell

MASTER

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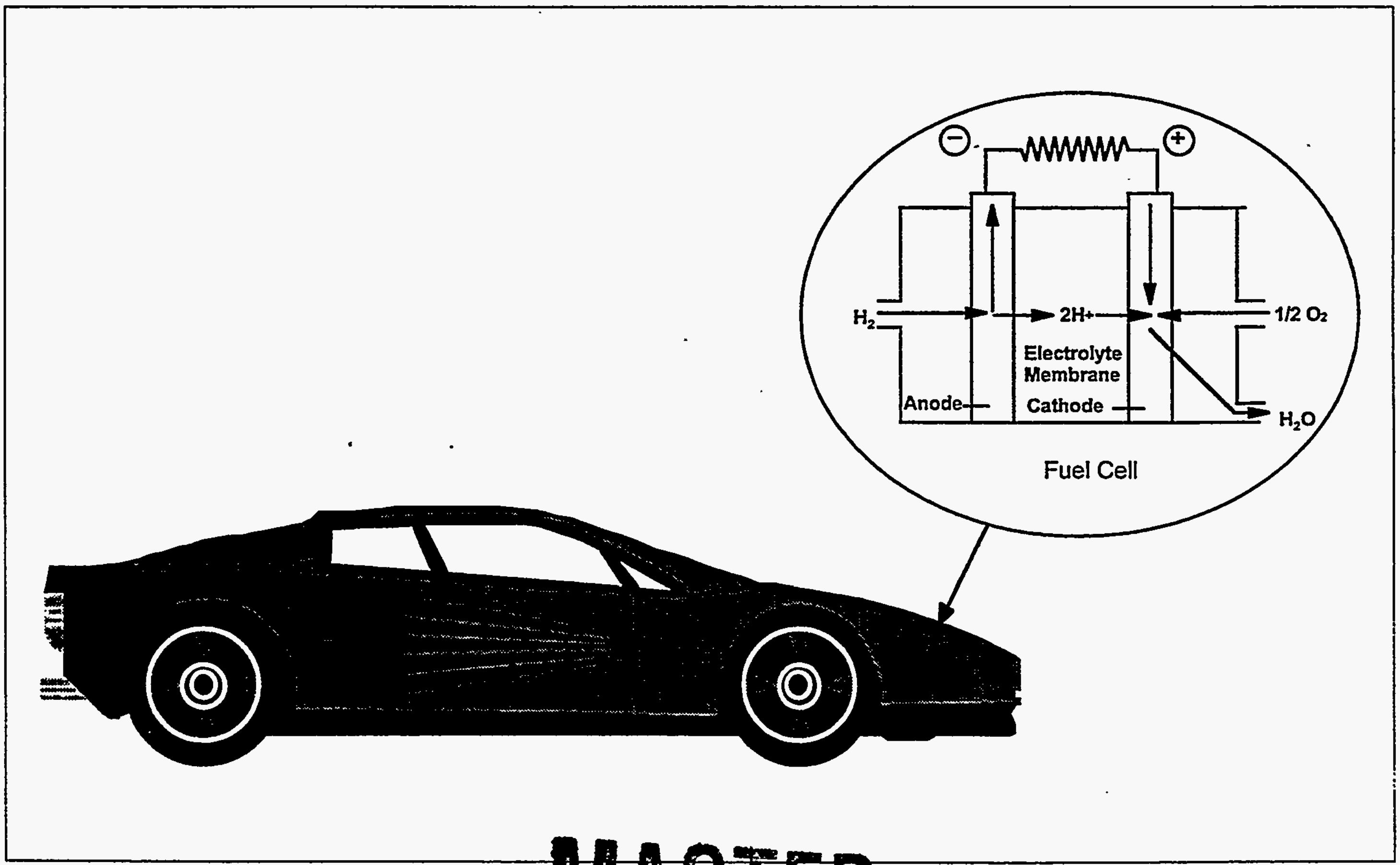
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LA-13112-MS

UC-000
Issued: March 1996

A Survey of Processes for Producing Hydrogen Fuel from Different Sources for Automotive-Propulsion Fuel Cells

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NOMENCLATURE

(Dimensions given below are typical for the parameters. Sometimes different units are used in the text.)

Roman symbols

C_p	Molar heat capacity, J/(mol)(K)
f	Fugacity, atm.
(g)	Indicated substance is in the gas phase.
G	Gibbs energy, J/mol.
H	Enthalpy, J/mol.
K	Equilibrium constant using fugacities of reaction constituents, dimensionless. See Glossary discussion of "Equilibrium Constant."
K_p	Equilibrium constant using partial pressures of reaction constituents. For a reaction of the type $\Sigma \nu_i A_i = 0$, the dimensions of the equilibrium constant K_p are $atm^{\Sigma \nu_i}$. See Glossary discussion of "Equilibrium Constant."
m	Number of hydrogen atoms in a hypothetical hydrocarbon molecule, dimensionless.
n	Number of carbon atoms in a hypothetical hydrocarbon molecule, dimensionless.

p	Partial pressure of subscripted gas, Pa.
P	Total pressure in reacting system, Pa.
R	Gas constant, 8.314 J/(mol)(K).
T	Temperature, K.
x	Ratio of number of hydrogen atoms to carbon atoms in a hydrocarbon fuel, dimensionless.

Greek symbols

Δ	Change in a property upon a change in state or completion of a reaction.
ν	Stoichiometric coefficient of reactant or product in a chemical reaction, dimensionless.

Subscripts

eq	Equilibrium value.
f	Refers to the change of the thermodynamics property upon formation of a particular substance.
r	Refers to the change of the thermodynamics property during the chemical reaction in question.
vap	Occurring during or related to vaporization.

Superscript

0	Indicates that the superscripted quantity is in its standard state, usually 298.15 K temperature and 101.325 kPa pressure for gases. If the superscripted quantity is a change or difference, it means that the change in question occurs between the substances involved in their standard states.

ACRONYMS

ASTM	American Society for Testing and Materials.
DOE	U. S. Department of Energy.
GM	General Motors Corporation.
LANL	Los Alamos National Laboratory.
LHS	Left-hand side (of an equation or expression).
LHV	Lower heating value (see Glossary).
PEM	Proton-exchange membrane (a type of membrane for a fuel cell; also, fuel cells employing this type of membrane).
ppm	Parts per million. If not otherwise specified, this is by volume.
RXNEQ	A thermodynamics equilibrium computer code developed by Haynes (1990).
STANJAN	A thermodynamics equilibrium computer code developed by Reynolds (1987).
STP	Standard temperature and pressure [298.15 K and 101.325 kPa (1 atm)].

GLOSSARY

Equilibrium Constant. For a reaction of the type $\Sigma \nu_i A_i = 0$, the equilibrium constant $K = \Pi(f_i/f_i^0)^{\nu i}$. This equilibrium constant is dimensionless. Another equilibrium constant can be defined in terms of partial pressures as $K_p \equiv \Pi p_i^{\nu i}$. This constant has the dimension $\text{atm}^{\Sigma \nu i}$. The standard-state value for the fugacity is 1 atm. When ideal-gas behavior approximates the true situation, $p_i \approx f_i$. Thus when ideal-gas behavior represents the true situation and the partial pressures are expressed in atmospheres, K_p is numerically equal to K. Thermodynamics texts discuss this in detail (e.g., Smith and Van Ness 1959, Daubert 1985).

Le Chatelier's Principle. A physical chemistry principle stating that application of an outside change (e.g., temperature or pressure) tends to promote a shift in equilibrium that offsets the effects of the outside change. It is also known as the principle of Le Chatelier-Braun.

Lower Heating Value. The heat of combustion of a substance not including the heat evolved during the condensation of any water produced.

Preferential Oxidation. A process within a mixture of carbon monoxide, hydrogen, and oxygen, in which carbon monoxide is oxidized in preference to the hydrogen. Noble-metal catalysts, such as platinum, can promote this process.

Syngas. Synthesis gas, a mixture of hydrogen and carbon monoxide. Depending on the final product to be made from the syngas, the ratio of hydrogen to carbon monoxide in the gas may vary from one to three.

A SURVEY OF PROCESSES FOR PRODUCING HYDROGEN FUEL FROM DIFFERENT SOURCES FOR AUTOMOTIVE-PROPULSION FUEL CELLS

by

Lee F. Brown

ABSTRACT

Seven common fuels are compared for their utility as hydrogen sources for proton-exchange-membrane fuel cells used in automotive propulsion. Methanol, natural gas, gasoline, diesel fuel, aviation jet fuel, ethanol, and hydrogen are the fuels considered. Except for the steam reforming of methanol and using pure hydrogen, all processes for generating hydrogen from these fuels require temperatures over 1000 K at some point. With the same two exceptions, all processes require water-gas shift reactors of significant size. All processes require low-sulfur or zero-sulfur fuels, and this may add cost to some of them. Fuels produced by steam reforming contain ~70-80% hydrogen, those by partial oxidation ~35-45%. The lower percentages may adversely affect cell performance. Theoretical input energies do not differ markedly among the various processes for generating hydrogen from organic-chemical fuels. Pure hydrogen has severe distribution and storage problems. As a result, the steam reforming of methanol is the leading candidate process for on-board generation of hydrogen for automotive propulsion. If methanol unavailability or a high price demands an alternative process, steam reforming appears preferable to partial oxidation for this purpose.

I. EXECUTIVE SUMMARY

The proton-exchange membrane (PEM) fuel cell is currently the favored cell type for fuel-cell-driven automobiles. This report compares some advantages and disadvantages of various primary fuels suggested as hydrogen sources for PEM fuel cells. Seven common fuels are the hydrogen sources evaluated in this report--methanol, natural gas, gasoline, diesel fuel, aviation jet fuel, ethanol, and hydrogen itself. The report surveys the processes used to generate hydrogen from these fuels and calculates theoretical input energies to the processes. To simplify calculations, surrogate substances are used for natural gas, gasoline, diesel fuel, and jet fuel. Methane is a surrogate for natural gas, and hypothetical "compounds" with empirical formulas $C_{7.14}H_{14.28}$, $C_{13.57}H_{27.14}$, and $C_{15}H_{30}$ are used for gasoline, diesel fuel, and jet fuel, respectively.

Table 1 gives some characteristics of the processes for producing fuel-cell hydrogen from the standard fuels considered in this report. It presents temperatures of the processes' initial reactions, the carbon monoxide amounts in the outlet streams from the initial reactions, and the theoretical input energies for the processes. These characteristics are important in judging the utility of these fuels for on-board generation of fuel-cell hydrogen for automotive propulsion.

A PEM fuel cell can tolerate only minuscule quantities (<10-20 ppm) of carbon monoxide in its feed. Steam reforming methanol principally produces carbon dioxide and hydrogen, and only ~1-2% CO. Noble-metal-catalyzed preferential oxidation can remove this small amount. Table 1 shows that all the

Table 1

CHARACTERISTICS OF PROCESSES FOR PRODUCING FUEL-CELL HYDROGEN FROM STANDARD FUELS

Process	CO in Product of Initial Reaction, mol% or vol%	Temperature Range of Initial Reaction, K	Total Theoretical Input Energy to Process, kJ/kg of usable H_2
Steam reforming			
of methane	11.2	1000-1100	0.141
of methanol	0.8	500-560	0.145
of ethanol	14.1	~1000	0.144
of gasoline, diesel fuel, and aviation jet fuel	20.0	1000-1150	0.148
Partial oxidation			
of methane	20.0	1500-1600	0.147
of gasoline, diesel fuel, and aviation jet fuel	25.0	1150-1900	0.169

other processes for creating hydrogen from organic-chemical fuels form large quantities of CO in their products, the quantities ranging from 14% to 25%. These latter processes all require water-gas shift reactors of significant size to lower the product carbon monoxide to a level where preferential oxidation can remove it. This is a significant drawback to these processes.

The steam reforming of methanol takes place in the temperature range 500-600 K. Table 1 shows that all the other processes require steps operating above 1000 K. High-temperature processes tend to be less efficient, require more expensive materials, need finer controls and present more safety concerns than processes operating at lower temperatures. For these reasons, the necessity for high-temperature processing is also a drawback for these processes.

The theoretical input energies do not differ markedly among the different processes considered in this report, as Table 1 shows. The input energies required for the partial oxidations of the heavier hydrocarbon fuels are somewhat higher. This report does not consider many process attributes, such as processing efficiencies, fuel price, etc. Because of such factors, the small differences in theoretical input energies assume a minor role in the possible choice of a process alternative to the steam reforming of methanol.

All the processes studied in this report use catalysts at one or more stages. The catalysts are sensitive to sulfur poisoning. As a result, all the processes must use low-sulfur or zero-sulfur fuels, which may add significant cost to some of the primary fuels. In-situ sulfur removal is not considered a reasonable possibility in automotive propulsion.

Fuels produced by steam reforming contain ~70-80% hydrogen, those by partial oxidation ~35-45%. Lower fractions of hydrogen in the fuel degrade fuel cell performance. This is an additional drawback to fuels produced by partial oxidation.

Hydrogen would be the ideal fuel-cell fuel, but it has severe storage and distribution problems. Until these difficulties are solved, fuel-cell propulsion systems will have to use on-board hydrogen generation employing other fuels. Processes exist for making hydrogen-rich fuel suitable for PEM fuel cells. These processes use common fuels, and have potential for development for on-board use in automotive propulsion systems. The factors considered in this report make the steam reforming of methanol the leading candidate for on-board generation of hydrogen for automotive propulsion. If methanol unavailability or a high price demands an alternative process, steam reforming appears preferable to partial oxidation for this purpose.

II. SCOPE OF REPORT

A. Goal

This report compares some advantages and disadvantages of various primary fuels suggested as hydrogen sources for PEM fuel cells. The report emphasizes the application of PEM fuel-cell systems to automotive propulsion. The LANL/GM/DOE Joint Development Center is now using methanol as its primary fuel. For commercially produced automobiles, alternatives may be necessary should methanol not be available in sufficient quantities or should it prove to be prohibitively expensive. This report surveys some of the possible alternatives. Seven common fuels are the postulated hydrogen sources in this report--methanol, natural gas, gasoline, diesel fuel, aviation jet fuel, ethanol, and hydrogen itself.

Appendix A lists properties of the elements and compounds studied in this report. Appendix B describes the composition and properties of hypothetical compounds used as surrogate hydrogen sources. Appendix C calculates the thermodynamics characteristics of principal reactions for generating hydrogen fuel for fuel cells, and Appendix D describes the equilibrium product compositions that result from steam reforming and partial oxidation of particular hydrocarbons. The references follow the appendixes.

B. The Primary Fuels

1. Methanol. Methanol is a single chemical compound (CH_3OH) commercially produced in large quantities via syngas from steam reforming of natural gas. The price of methanol can vary significantly. Prices during 1993 ranged from $0.40/gal to $0.53/gal (Gavalas et al. 1995); 1994 prices ranged from $0.46/gal to $1.62/gal (Ainsworth 1995). Fiedler et al. (1990) and Gavalas et al. (1995) discuss methanol's properties, grades, prices and manufacture, and cite references for more detail in these areas.

2. Natural gas. As it comes from the ground, natural gas can consist of many individual components. The major constituent is usually methane. Nevertheless, water, other hydrocarbons, hydrogen sulfide, nitrogen, and carbon dioxide can be present in large amounts. Processing usually removes constituents other than light hydrocarbons before transport. As a result, pipeline gas almost invariably consists primarily of methane (~75-85%), some higher light saturated hydrocarbons and small amounts of carbon dioxide (Woodcock and Gottlieb 1994).

For simplicity, this report follows the lead of other works in this area (e.g., A.D. Little 1994, Kumar et al. 1994, Gavalas et al. 1995) and models natural gas as pure methane.

3. **Gasoline.** Unlike methanol or methane, gasoline is not a single compound. It consists of numerous components, and is obtained by processing crude oil in a petroleum refinery. There are many grades of gasoline, each with its own set of properties. In gasoline, no single compound predominates. As a surrogate gasoline, this report uses a hypothetical compound with properties typical of many U.S. gasolines. The assumed molecular formula for the "compound" is $C_{7.14}H_{14.28}$. Creation of this surrogate uses properties and characteristics described by Adler (1986) and Hochhauser (1994). Appendix B-2 describes the bases for the composition and properties of the hypothetical compound, together with the reasoning behind the C_nH_{2n} formula.

4. **Diesel fuel.** Like gasoline, diesel fuel consists of many components and results from processing crude oil in a petroleum refinery. As Appendix B-2 does for gasoline, Appendix B-3 creates a surrogate diesel fuel based on properties and characteristics described by Adler (1986) and Hochhauser (1994). The molecular formula for this "compound" is $C_{13.57}H_{27.14}$.

5. **Aviation jet fuel.** Like gasoline and diesel fuel, aviation jet fuel is a petroleum refinery product consisting of many components. Again, this report uses a hypothetical compound as a substitute for jet fuel, this time based on properties and characteristics described by Dukek (1992). The molecular formula for this "compound" is $C_{15}H_{30}$. Appendix B-4 gives the bases for the composition and properties of the surrogate jet fuel.

6. **Ethanol.** Ethanol is a single chemical compound (C_2H_5OH) with a history dating to pre-recorded times. The currently preferred commercial production route forms ethanol by hydrating ethylene, which is obtained from thermal cracking of petroleum naphthas. The demand for ethanol in oxygenated gasoline has recently stimulated an additional route from corn.

7. **Hydrogen.** Hydrogen is the end product of processing the other fuels considered in this report. While pure hydrogen is the ideal fuel-cell fuel, distribution and storage difficulties pose serious disadvantages to its use for automotive propulsion fuel cells. Section VII.A below discusses these problems.

The principal commercial route to hydrogen presently consists of steam reforming natural gas to produce carbon monoxide and hydrogen. Both high-temperature and low-temperature water gas shifts follow to produce carbon dioxide and more hydrogen. Scrubbing by hot K_2CO_3 solution or other materials removes most of the CO_2, and the remaining carbon oxides are converted to methane using a nickel catalyst. If desired, pressure-swing adsorption brings the hydrogen to a high degree of purity (>99%) (Czuppon et al. 1995).

C. Amount of Hydrogen Needed for Automotive-Propulsion Fuel Cells

A 50 horsepower engine delivers 37 kW, and this is perhaps the minimum for realistic unrestricted automotive propulsion in the United States. This assumes a battery system supplying additional power when needed, making the proposed overall system a hybrid one. Adding subsidiary power requirements such as compressor, fuel pump, interior heating, fan for heat rejection, etc., will bring the minimum power to about 50 kW. This is the needed gross capacity for a fuel-cell system in a hybrid vehicle. While normal driving would not require this amount of hydrogen for long periods, the system must be sized to deliver this quantity upon demand.

At 400 K, hydrogen has a lower heating value (LHV) of 242.847 kJ/mol. Fuel-cell efficiency is the DC power produced divided by the total heating value of the gases fed to the anode. A. D. Little (1994) lists efficiencies of PEM fuel cells in particular scenarios as averaging about 37%. With this efficiency, a 50 kW system would require about 0.55 moles or 1.1 g of usable hydrogen per second. This translates into about 2000 moles or 4 kg of usable hydrogen per hour.

The 37% efficiency may be lower than actually achieved in many fuel cells (e.g., Angrist 1976). Efficiencies somewhat higher than this would decrease slightly the calculated sizes of process vessels. The effect of higher efficiencies is discussed below in Section VII.C.

III. PREVIOUS WORK

Changes in fuel-processing and fuel-cell technologies are rapid, as are changes in the energy situation. Thus only recent efforts are relevant to this work. Three of these treat the efficiency of fuel-cell systems and the fuels they use for producing the needed hydrogen. A report from A. D. Little appeared in May 1994, emphasizing reformers capable of using more than one fuel. That report discusses different processes and the efficiencies associated with various systems. Kumar et al. (1993, 1994) report computer modeling of polymer electrolyte fuel-cell systems. The earlier paper explores different system design configurations, different design operating conditions, and performance at off-design conditions. The second analyzes polymer electrolyte fuel-cell systems using hydrogen, methanol, and natural gas as fuels. The report by Gavalas et al. (1995) deals with systems appropriate for locomotive propulsion, whose requirements differ significantly from those of automotive-propulsion systems. The sections using information in these works cite them where appropriate.

IV. PROCESSES USING PRIMARY FUELS TO MAKE FUEL-CELL HYDROGEN

A. Types of Reactions Used to Make Hydrogen from Primary Fuels

1. Steam reforming and partial oxidation. Two types of reactions dominate the means for creating fuel-cell hydrogen from primary fuels. The first is steam reforming, the second partial oxidation. Steam reforming is always endothermic (cf. Section V), so energy must be supplied for this reaction. Partial oxidation is exothermic, so does not need the supply of energy. Nevertheless, the overall efficiency can suffer because of the production of waste heat. The process of autothermal reforming combines steam reforming and partial oxidation, and the oxidation supplies the energy required by the steam reforming.

Steam reforming has wide industrial application. Methanol synthesis employs the steam reforming of natural gas as its first step (Fiedler et al. 1990). The steam reforming of other hydrocarbons is also widely used for generating hydrogen and syngas (Häussinger et al. 1989). Partial oxidation does not appear to enjoy wide use by itself, but usually appears in autothermal reforming processes. An early stage of ammonia synthesis uses autothermal reforming with air as an oxidant both to supply energy for the reforming and nitrogen for the synthesis reaction (Bakemeier et al. 1989, Czuppon et al. 1992). Commercial autothermal reforming processes reacting heavy hydrocarbons use oxygen rather than air for their oxidant. However, neither pure oxygen nor oxygen separation processes are practical for use in automotive propulsion systems, and this report uses air to supply oxygen to partial oxidation processes.

Steam reforming of natural gas or methane is a nickel-catalyzed process occurring at 1000-1100 K (Renner and Marschner 1989), while steam reforming of other hydrocarbons uses temperatures in the 1000-1150 K range (Czuppon et al. 1995). Partial oxidation uses higher temperatures; partial oxidation of natural gas or methane is carried out around 1500-1600 K (Czuppon et al. op. cit.), while partial oxidation of higher hydrocarbons uses temperatures in the 1150-1900 K range (Bakemeier et al. 1989, Brejc and Supp 1989), with normal processing occurring near the higher temperature.

2. The water-gas shift reaction. Besides steam reforming or partial oxidation, a separate reaction appears in most of the processing schemes. The water-gas shift reaction or its reverse plays a major role in most proposed processes for generating fuel-cell hydrogen. In addition to its potential role in generating fuel-cell hydrogen, the water-gas shift and its reverse have current importance in several industrial processes. Methanol production uses the shift to adjust the syngas' H_2/CO ratio to the value needed by the synthesis. In the commercial manufacture of hydrogen by steam reforming natural gas, the shift reacts CO in the process stream with water to form more hydrogen (Czuppon et al. 1995). Ammonia synthesis processes use the shift to convert CO in the process stream to more easily removable CO_2, producing hydrogen as an added benefit (Czuppon et al. 1992). Manufacturing synthetic fuel from carbonaceous materials requires either the shift or its reverse to adjust the H_2/CO ratio to the proper 3/1 for carrying out methanation (Speight 1994).

Industrial processes using the water-gas shift or its reverse usually carry out the reaction in two stages. The first is at a higher temperature, frequently in the 400°C range. The temperature-equilibrium relationship dictates a lower temperature in the second stage to reduce CO in the product. The low 200's are typical for the low-temperature shift. High-temperature shift catalysts are normally chromium-promoted iron oxide formulations, while copper oxide-zinc oxides are the usual basis for low-temperature shift operations. The high-temperature and low-temperature shift processes each have typical space velocities of 4000 hr^{-1} (Czuppon et al. 1995).

While sulfur-resistant shift catalysts have been developed, current preference appears to favor catalysts sensitive to sulfur poisoning (Häussinger et al. 1989). Thus all processes discussed in this report must use low-sulfur or zero-sulfur fuels. Removal of sulfur is a well-developed technology, but it may add significant cost to some of the fuels evaluated here.

3. Preferential oxidation of CO in the presence of hydrogen. A third reaction can remove small amounts of CO from the process stream before feeding it to a PEM fuel cell. Noble-metal catalyzed preferential oxidation of CO to CO_2, even in the presence of large amounts of hydrogen, accomplishes this (Birdsell et al. 1993, 1994). Present practice feeds twice the stoichiometric amount of oxygen necessary to oxidize the CO to the oxidation system. While this oxidizes a small amount of the hydrogen to water, it results in a stream with only traces of CO.

B. Steam Reforming of Methane

1. The reaction expressions. Steam reforming of methane reacts one molecule of water with one molecule of methane, producing one molecule of carbon monoxide and three molecules of hydrogen. The process requires a nickel catalyst and temperatures above 1000 K:

$$CH_4 + H_2O \xrightarrow[\text{1000-1100 K}]{\text{Ni}} CO + 3H_2 \quad . \qquad \text{(IV-1)}$$

The water-gas shift then combines water with the carbon monoxide to create more hydrogen.

$$H_2O + CO \xrightarrow{\text{forward}} H_2 + CO_2 \qquad\qquad H_2 + CO_2 \xrightarrow{\text{reverse}} H_2O + CO \qquad \text{(IV-2)}$$

Sections V.B and V.E and Appendixes C-2 and C-6 discuss the thermodynamics characteristics of reactions (IV-1) and (IV-2).

2. The process. As mentioned above, the industrial methane-steam reaction uses a nickel catalyst and temperatures in the 1000-1100 K range. Operating pressures as high as 4-10 MPa have been reported (A. D. Little 1994), but normal industrial practice uses pressures in the 2.17-2.86 MPa range (Czuppon et al. 1995). Early commercial versions of the process used atmospheric pressure, but higher pressures improved the efficiency significantly (Renner and Marschner 1989). The reaction is endothermic, with heat supplied by external combustion. The methane-steam reaction produces carbon monoxide and hydrogen. High-temperature and low-temperature water-gas shift reactions convert the carbon monoxide to carbon dioxide and produce additional hydrogen. To prevent soot formation, the feed contains steam in excess of the stoichiometric amount (Hiller and Reimert 1989). Commercial processes use H_2O/C molar ratios of 3-5 (Renner and Marschner 1989).

Expression (IV-1) is the principal reaction in the steam reforming of natural gas. This report approximates natural gas as pure methane. The hypothetical process evaluated in this report has a steam-to-methane feed ratio of 3:1 and operates at 3 atm and 1100 K. The product from this portion of the process is assumed to be at equilibrium. Using the thermodynamics code RXNEQ (Haynes 1990) and including the possible formation of carbon dioxide gives an effluent consisting of 0.2% CH_4, 28.4% H_2O, 11.2% CO, 5.3% CO_2, and 54.9% H_2. After the two shift processes, the effluent emerges at 500 K. Further use of RXNEQ gives a composition of 0.2% CH_4, 0.4% CO, 17.6% H_2O, 16.1% CO_2, and 65.7% H_2 after the shift reactors. Removal of the CO and CH_4 by preferential oxidation requires air injection. Using twice as much air as needed for complete combustion of the CO, calculations assume burning all the CO and CH_4 and a small amount of hydrogen. These give a final product of 64.1% H_2, 16.3% CO_2, 17.8% H_2O, and 1.8% N_2.

At a 50 kW level, Section II.C says the demand flow of hydrogen is approximately 2000 mol usable H_2/hr. The above composition says that the total demand flow rate is about 3200 mol/hr or 72 m^3(STP)/hr. At the previously mentioned shift-reactor space velocity of 4000 hr^{-1}, this would mean a catalyst volume of 0.02 m^3 (0.7 ft^3) for each of the two shift reactors.

C. Steam Reforming of Multi-Carbon Hydrocarbons

1. The reaction expression. The general expression for the reaction of steam with hydrocarbons is

$$C_nH_m + nH_2O \rightarrow nCO + (m/2+n)H_2 \quad . \tag{IV-3}$$

This expression covers a large number of individual reactions. The thermodynamics characteristics of the individual reactions depend on the particular compound represented by the C_nH_m term on the left-hand side (LHS) of Eq. (IV-3).

2. Steam reforming of gasoline, diesel fuel, and aviation jet fuel. Appendix B models these three fuels by the molecular formula C_nH_{2n}. Using this composition in Eq. (IV-3) gives

$$C_nH_{2n} + nH_2O \rightarrow nCO + 2nH_2 \tag{IV-4}$$

as the stoichiometric relationship for the steam reforming of gasoline, diesel fuel, and aviation jet fuel.

As mentioned above, industrial practice uses a H_2O/C ratio of 3-5, and this report's hypothetical reforming processes use three times the stoichiometric amount of steam. This prevents soot formation and provides water for the shift processes. The report also assumes a process operating at 3 atm and 1100 K, and reaction (IV-4) going to completion. (The possible high-temperature formation of carbon dioxide does not affect the composition of the final product after the shift reactions.) For a hydrocarbon whose general molecular formula is C_nH_{2n}, this gives a process stream of 40.0% H_2, 20.0% CO, and 40.0% H_2O. High and low-temperature shifts follow the steam-reforming reaction, and their product emerges at 500 K. The code RXNEQ calculates the composition of the shift product to be 0.4% CO, 20.4% H_2O, 19.6% CO_2, and 59.6% H_2. Preferential oxidation of the CO with twice the stoichiometric amount of air gives a final reformate of 20.6% H_2O, 19.7% CO_2, 58.2% H_2, and 1.5% N_2.

A demand flow of 2000 mol usable H_2/hr and this composition would require a total demand flow rate to be approximately 3400 mol/hr or 76 m^3(STP)/hr. At the previously mentioned space velocity of 4000 hr^{-1}, this would repeat a catalyst volume of about 0.02 m^3 (0.7 ft^3) for each of the two shift reactors.

The above calculations apply to gasoline, diesel fuel, and aviation jet fuel, or to any other hydrocarbon fuel with the approximate molecular formula C_nH_{2n}.

D. Steam Reforming of Methanol

1. The reaction expression. Steam reforming of methanol reacts one molecule of methanol with one water molecule. The reaction uses a copper oxide-zinc oxide catalyst at temperatures in the range 500-600 K and pressures ~0.1-0.3 MPa (Amphlett et al. 1981, 1985). The reaction produces one molecule of carbon dioxide and three molecules of hydrogen.

$$CH_3OH + H_2O \xrightarrow[500\text{-}600\ K]{CuO/ZnO} CO_2 + 3H_2 \ . \qquad \text{(IV-5)}$$

Section V.C and Appendix C-3 discuss the reaction's thermodynamics aspects.

2. The process. The reaction is endothermic, and heat transfer from hot fluids supplies the needed energy. The process analyzed in this report uses a steam-to-methanol ratio of 1.6. Amphlett et al. (1981, 1985) report producing little methane in the product of this reaction, even though equilibrium calculations predict the possibility of significant amounts. This report ignores methane production, assumes equilibrium for this reaction and the simultaneous water-gas shift, and uses reaction conditions of 3 atm and 500 K at the exit. With these conditions, RXNEQ gives a product of 170 ppm CH_3OH, 0.8% CO, 64.4% H_2, 21.0% CO_2, and 13.8% H_2O.

Further processing via preferential oxidation removes the CO and CH_3OH (Birdsell et al. 1993, 1994). Addition of sufficient air to provide twice the oxygen required to oxidize the CO and CH_3OH burns not only the CO and CH_3OH but some H_2. It also dilutes the mixture slightly with nitrogen. The final product consists of 61.8% H_2, 21.1% CO_2, 14.1% H_2O, and 3.0% N_2.

E. Steam Reforming of Ethanol

1. The reaction expression. Reforming ethanol by reacting it with steam requires three water molecules for each molecule of ethanol:

$$C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 6H_2 \ . \qquad \text{(IV-6)}$$

Section V.C and Appendix C-5 treat thermodynamics aspects of this reaction.

2. The process. Steam reforming of ethanol to produce hydrogen is theoretically possible, though information on actual processes is sparse (Garcia and Laborde 1991, A. D. Little 1994). In discussing processes for generating fuel-cell hydrogen, A. D. Little (1994) postulates a process with a steam-to-ethanol feed ratio of 4:1, operating at 1023 K and 3 atm. This report calculates the energy input to A. D. Little's hypothetical process.

In the steam reforming of methanol, experiments have shown very little methane produced in spite of equilibrium predicting a possibly significant CH_4 fraction in the product (Amphlett et al. 1985). This report assumes that ethanol reforming also produces little methane. Assuming equilibrium at 3 atm and 1023 K, the code RXNEQ gives the product of this phase of the process as 52.6% H_2, 14.1% CO, 8.1%

CO_2, and 25.2% H_2O. Using high and low-temperature water-gas shifts to reduce the CO and assuming thermodynamics equilibrium gives a product containing 65.8% H_2, 21.3% CO_2, 12.0% H_2O, and 0.9% CO. Preferential-oxidation processing gives a product with 62.6% H_2, 21.4% CO_2, 12.5% H_2O, and 3.5% N_2.

A demand flow of 2000 mol usable H_2/hr and this composition would require a total demand flow rate of approximately 3100 mol/hr or 70 m^3(STP)/hr. At the previously mentioned space velocity of 4000 hr^{-1}, this would give a catalyst volume of about 0.02 m^3 (0.6 ft^3) for each of the two shift reactors.

F. Partial Oxidation of Methane

1. The reaction expression. The partial oxidation of methane reacts a molecule of methane with an atom of oxygen to produce one molecule of carbon monoxide and two of hydrogen:

$$CH_4 + \tfrac{1}{2}O_2 \rightarrow CO + 2H_2 \ . \qquad \text{(IV-7)}$$

Section V.D and Appendix C-4 discuss thermodynamics quantities for this reaction.

2. The process. Partial oxidation of natural gas reacts a half molecule of oxygen with each atom of carbon in a hydrocarbon. This yields one molecule of carbon monoxide for each atom of carbon and one-half molecule of hydrogen for each atom of hydrogen in the hydrocarbon. The reaction is noncatalytic and exothermic, and processes operate at ~1100-1500°C.

In analyzing this process, this report again approximates the composition of natural gas as pure methane. The equilibrium constants for the reaction to carbon monoxide and hydrogen (Appendix C-4) indicate that the reaction is irreversible for practical purposes. Calculations using RXNEQ indicate that side reactions that form water or carbon dioxide are negligible in the process temperature range. Using air injection to provide the oxygen gives a product of 40.0% H_2, 20.0% CO, and 40.0% N_2. A typical calculation assumes the addition of 20% excess water, completion of the shift reactions, a final temperature of 500 K and attainment of thermodynamics equilibrium. This gives a mixture of 47.2% H_2, 1.2% CO, 14.9% CO_2, 4.4% H_2O, and 32.3% N_2. Removal of the CO by preferential oxidation requires further air injection and gives a final product of 43.8% H_2, 15.4% CO_2, 5.4% H_2O, and 35.4% N_2.

A. D. Little (1994) speaks of the possible formation of ammonia in partial-oxidation systems resulting from the introduction of nitrogen with the air. RXNEQ gives an equilibrium ammonia concentration of only 200 ppm in the product of methane partial oxidation. It is unlikely that even this would be formed, since ammonia formation requires a particular catalyst and very high pressures to form at any reasonable rate. This treatment therefore ignores the formation of ammonia in the partial oxidation reactions.

A demand flow of 2000 mol usable H_2/hr and this composition would require a total demand flow rate to be approximately 5100 mol/hr or 110 m^3(STP)/hr. At the previously mentioned space velocity of 4000 hr^{-1}, this would give a catalyst volume of about 0.03 m^3 (1.0 ft^3) for each of the two shift reactors.

G. Partial Oxidation of Multi-Carbon Hydrocarbons

1. The reaction expression. The general expression for the oxidation reaction in a lean oxygen-hydrocarbon mixture is

$$C_nH_m + \tfrac{1}{2}nO_2 \rightarrow nCO + (m/2)H_2 \quad . \qquad \text{(IV-8)}$$

Like its steam-reforming analog, Eq. (IV-3), this expression covers a large number of individual reactions. The thermodynamics characteristics of the individual reactions depend on the particular compound represented by the C_nH_m term on the LHS of Eq. (IV-8).

2. Partial oxidation of gasoline, diesel fuel, and aviation jet fuel. As developed in Appendix B, this report models gasoline, diesel fuel, and aviation jet fuel as single hypothetical hydrocarbons of formula C_nH_{2n}. Incorporating this formula into Eq. (IV-8) gives

$$C_nH_{2n} + \tfrac{1}{2}nO_2 \rightarrow nCO + nH_2 \quad . \qquad \text{(IV-9)}$$

The ½n moles of oxygen require 2.5n moles of air containing 2n moles of N_2 in addition to the oxygen. It is assumed that only carbon monoxide and hydrogen are formed from this reaction, like the partial oxidation of methane. The resulting product of the reaction is therefore n moles of CO, n moles H_2, and 2n moles of N_2. Addition of 20% excess water, the shift reactions, a final temperature of 500 K, and using RXNEQ to assume equilibrium gives a mixture of 37.4% H_2, 1.1% CO, 18.2% CO_2, 4.9% H_2O, and 38.4% N_2. Removing the CO by preferential oxidation requires further air injection and gives a final product of 32.0% H_2, 19.4% CO_2, 5.8% H_2O, and 42.8% N_2.

A demand flow of 2000 mol usable H_2/hr and this composition would require a total demand flow rate of approximately 5300 mol/hr or 120 m^3(STP)/hr. At the previously mentioned space velocity of 4000 hr^{-1}, this would imply a catalyst volume of about 0.03 m^3 (1.1 ft^3) for each of the two shift reactors.

The above calculations apply to gasoline, diesel fuel, and aviation jet fuel, or to any other hydrocarbon fuel with the approximate molecular formula C_nH_{2n}.

H. Autothermal Reforming

As mentioned above, steam reforming is endothermic and partial oxidation is exothermic. It is possible to react natural gas and other hydrocarbon fuels with a mixture of steam and oxygen and carry out both reactions simultaneously. The exothermic oxidation supplies the energy for the endothermic reforming. Careful control of the oxygen content of the entering mixture is essential in this process for maintaining the proper reaction temperatures. The product of this reaction combination is carbon monoxide and hydrogen. The CO requires high and low-temperature water-gas shifts to oxidize it and provide additional hydrogen.

Except for the autothermal reforming portion of ammonia synthesis, current commercial autothermal reforming processes seem to prefer oxygen to air for supplying the oxidant.

V. THERMODYNAMICS CHARACTERISTICS OF PRINCIPAL REACTIONS FOR GENERATING HYDROGEN FUEL FOR FUEL CELLS

A. Summary of Thermodynamics Property Changes

Appendix C calculates various thermodynamics properties and changes during reactions relevant to this report. Table 2 (next page) summarizes the different thermodynamics changes and equilibrium constants for these reactions. Some of the reactions in Table 2 are used directly for producing hydrogen from individual fuels, others illustrate significant features of other reactions for this purpose. A glance at this table can compare the heats of reaction and equilibrium constants for the different reactions at 300, 600, and 1000 K.

B. Steam Reforming of Hydrocarbons

The steam reforming of hydrocarbons is invariably highly endothermic. In Table 2, the ΔH_r for steam reforming of methane is above +200 kJ/mol of methane at all temperatures. Steam reforming of methane, ethane, and propane all exhibit ΔH_r's around +70 kJ/mole of hydrogen produced (Hiller and Reimert 1989). In commercial steam reforming of hydrocarbons, external combustion normally supplies this high heat of reaction.

The equilibrium constants of the methane-steam reaction at 300, 600, and 1000 K are 2.0×10^{-25}, 4.9×10^{-7}, and 26.1 atm^2, respectively. A glance at these three numbers shows why steam reforming of methane and other hydrocarbons uses temperatures above 1000 K. At the lower temperatures, the steam-methane equilibrium is so far to the left that little methane would react. It requires temperatures above 1000 K to reform essentially all the methane in a single pass.

The reaction equilibria are favored by low pressures, since the reaction produces more molecules than it consumes. The kinetics may be faster at higher pressures, though, so a balance is needed.

C. Steam Reforming of Alcohols

The steam reformings of methanol and ethanol are also endothermic, though less so than the steam reforming of hydrocarbons. The ΔH_r for the steam reforming of methanol is in the vicinity of +20 kJ/mol of hydrogen produced, while that for the steam reforming of ethanol is around +30 kJ/mol of hydrogen produced.

The equilibrium constant of the methanol-steam-reforming reaction is sufficient at 600 K to allow temperatures in the 500-600 K range for the reaction to go to essential completion. For the ethanol-steam reaction, the equilibrium relationships predict a minimum of ~1-2% of ethanol in the product at 600 K and 3 atm, using a feed of 4:1 steam to ethanol. Kinetics may be the primary reason for the higher temperature used in the A.D. Little hypothetical process (cf. Section IV.E.2). The amount of ethanol is high for a PEM fuel-cell fuel, also promoting higher-temperature operation.

Table 2

THERMODYNAMICS PROPERTY CHANGES FOR REACTIONS AT 300, 600, AND 1000 K

Reaction(a)	ΔH_r, kJ/mol	ΔG_r, kJ/mol	K_p
$CH_4 + H_2O \rightarrow CO + 3H_2$			
300 K	+206.24	+141.80	2.04×10^{-25} atm^2
600 K	+217.90	+72.44	4.94×10^{-7} atm^2
1000 K	+225.71	-27.12	26.10 atm^2
$CH_3OH + H_2O \rightarrow CO_2 + 3H_2$			
300 K	+49.56	-3.62	4.28 atm^2
600 K	+61.57	-61.80	2.40×10^{5} atm^2
1000 K	+70.48	-146.92	4.73×10^{7} atm^2
$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2$			
300 K	-35.60	-86.74	1.27×10^{15} $\text{atm}^{1/2}$
600 K	-26.85	-141.64	2.15×10^{12} $\text{atm}^{1/2}$
1000 K	-22.15	-219.83	3.04×10^{11} $\text{atm}^{1/2}$
$C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 6H_2$			
300 K	+173.42	+64.66	5.51×10^{-12} atm^4
600 K	+193.99	-52.71	3.88×10^{4} atm^4
1000 K	+209.25	-222.04	3.97×10^{11} atm^4
$H_2O + CO \rightarrow H_2 + CO_2$			
300 K	-41.15	-28.49	9.12×10^{4}
600 K	-39.04	-16.56	27.8
1000 K	-34.75	-2.84	1.41
$CH_3OH \rightarrow CO + 2H_2$			
300 K	+90.71	+24.86	4.69×10^{-5} atm^2
600 K	+100.44	-45.24	8.68×10^{3} atm^2
1000 K	+105.23	-144.08	3.36×10^{7} atm^2

(a) All reaction constituents are assumed to be in the vapor phase.

Like the steam reforming of hydrocarbons, low pressures favor the alcohol-steam-reforming equilibria. This occurs because more molecules are produced than reacted, the same cause as for the hydrocarbon-steam-reforming reactions.

D. Partial Oxidation of Hydrocarbons

The partial oxidation of methane is highly exothermic, in common with most oxidations. Even though this means that the equilibrium constant will decrease with temperature, the constants are sufficiently high throughout the temperature range of Table 2 that the reaction will essentially go to completion at all temperatures.

The same ideas apply to the operating pressures of these reactions. These reactions create more product moles than there are reactant moles, so in theory lower pressures would promote the reactions. However, the equilibrium constants are sufficiently high that pressure is not a constraining factor in choice of operating conditions. For example, the Texaco and Shell processes for autothermal reforming of heavy hydrocarbons operate at pressures in the 3-9 MPa (30-90 atm) range (Bakemeier et al. 1989). Czuppon et al. (1992) imply that the autothermal reforming stage in ammonia synthesis operates in roughly the same pressure range.

E. The Water-Gas Shift Reaction and Its Reverse

All the reforming and oxidation reactions produce some amount of carbon monoxide, which must be removed before the process stream passes to a PEM fuel cell. The amounts range from the 1-2% produced by the methanol-steam reaction to the 25% from the partial oxidation of multi-carbon hydrocarbons. All processes use the water-gas shift to reduce the CO. The temperature-equilibrium relationship requires that the outlet temperature of the shift system be at most about 500 K. Kinetics considerations require higher temperatures for portions of the process when the amount of CO entering the shift system is large.

Since two molecules of reactant form two molecules of product in this reaction, pressure does not have a significant effect on its equilibrium. Other factors dictate the operating pressure.

F. The Side Reaction of Methanol Decomposition

This reaction occurs in the presence of the methanol-steam reaction, and may be the principal source of CO in the system. Comparison of the changes in equilibrium constants with temperature indicates that high temperatures promote this reaction more than they do the methanol-steam reaction. Low pressures also promote methanol decomposition more than they do the methanol-steam reaction. Thus while high temperatures and low pressures promote the desired reaction, they promote this undesired side reaction even more. Any choice of operating conditions must seek an optimum.

G. Methane Production in Side Reactions

1. Disregarding Methane Production in Report Calculations. This report disregards the production of methane in the different processes. The next paragraphs justify this.

2. Methane Production in Steam Reforming of Hydrocarbons. Sections IV.B.2 and IV.C.2 mention that steam reforming processes typically employ temperatures around 1100 K and H_2O/C ratios of 3-5. Using a pressure of 3 atm, a temperature of 1100 K and a H_2O/C ratio of 3, Appendix D gives the results of thermodynamic equilibrium calculations in which the hydrocarbons are n-decane, 2,2,4 trimethyl pentane (iso-octane), and toluene. These are typical of the hydrocarbons present in gasoline, diesel fuel, and aviation jet fuel. In none of the equilibrium products is there a significant amount of methane. The products of commercial steam reforming processes approach equilibrium compositions (Renner and Marschner 1989), so methane production was not considered in this report's steam reforming calculations.

3. Methane Production in Steam Reforming of Alcohols. As mentioned in Section IV.E.2, very little methane appears to be produced in experiments with the catalytically-promoted steam reforming of methanol (Amphlett et al 1985). This is in spite of significant methane appearing if complete equilibrium is attained (Amphlett et al. 1981). Since experiments show little methane produced, methane production was ignored in this report's methanol-steam-reforming calculations.

Section IV.E.2. states there is little information on the steam reforming of ethanol. Because of this, the assumption was made that methane production in this reaction would mimic that of steam reforming methanol, i.e., the amount produced would be essentially negligible. Thus methane production was also ignored in this report's ethanol-steam reforming calculations.

4. Methane Production in Partial Oxidation of Hydrocarbons. Appendix D presents the equilibrium compositions from partial oxidation of n-decane, 2,2,4 trimethyl pentane (iso-octane), and toluene. As mentioned above, these three are typical of hydrocarbons appearing in gasoline, diesel fuel, and aviation jet fuel, and the compositions reported should be typical of equilibrium attained when subjecting these three fuels to partial oxidation.

The calculations say that at temperatures above 1200 K, essentially only carbon monoxide, hydrogen, and nitrogen are present in an equilibrium product. Other substances appear only in trace quantities. Since partial oxidation processes take place above this temperature, essentially no methane is present in an equilibrium product. Although more methane is present in commercial partial oxidation products than equilibrium predicts (Brejc and Supp 1989), the methane content usually does not exceed 0.6 vol% at pressures around 60 atm (Brejc and Supp op. cit.). Since higher pressures promote methane formation, the amount of methane in partial oxidation products is always low, and this report does not consider methane production in partial oxidation processes.

VI. THEORETICAL ENERGY REQUIREMENTS FOR GENERATING FUEL-CELL FUEL FROM DIFFERENT SOURCES

A. Bases for Calculating Theoretical Energy Requirements

The first basis for all calculations is the generation of 1 mol of usable hydrogen. The fraction of hydrogen utilized depends on the dilution with inert gases; the greater the dilution, the lower the hydrogen utilization (Appleby 1993). To accommodate this, the report assumes that the gas leaving the fuel-cell anode has 8% hydrogen. This makes the hydrogen utilization range from 83% to 97% for the fuels used in the report, and these numbers appear reasonable when compared with those published (Appleby op. cit.). This report treats the 8% as waste. For example, if a fuel consists of 50% hydrogen and 50% carbon dioxide, then the effluent gas from the cell would consist of 92% CO_2 and 8% H_2. One mole of usable hydrogen would require 2.19 moles of this fuel. The effluent would then have 1.095 moles CO_2 and

0.095 mole H_2 for each mole of hydrogen consumed. The processes evaluated in this report use this approach to calculate the amount of primary fuel necessary to produce 1 mole of usable hydrogen.

Treating the 8% H_2 in the exhaust as waste is conservative. Recovery of some of the energy in this hydrogen would not markedly affect the net energy input to the steam reforming processes, but it might improve somewhat the net energy input to the partial oxidation processes.

In addition, this report treats effluents from the fuel cells on a dry basis. This ignores any water in feeds to the cells. For example, if a fuel-cell feed is 40% H_2, 40% CO_2, and 20% H_2O, the cell effluent on a dry basis would be 92% CO_2 and 8% H_2. This is identical with the effluent composition in the previous paragraph.

The report distinguishes two input energies. The theoretical process energy input is the theoretical or minimum energy required by the process itself for carrying out the reaction. A negative process energy input means that the energy must be removed and may be available for other use. The total theoretical energy input is the process energy input plus the heating value of the feed.

This report chooses a temperature of 400 K for the fuel-cell inlet temperature. This is only slightly above typical fuel-cell inlet temperatures, and thermodynamics properties of substances are readily available at this level. The heating value of one mole of hydrogen at 400 K is 242.847 kJ.

B. Hydrogen Fuel from Methanol

As mentioned in the previous paragraph, 400 K is the basis temperature for the calculation. One mole of usable hydrogen is needed from a mixture of 61.8% H_2, 21.1% CO_2, 14.1% H_2O, and 3.0% N_2 (cf. Section IV.D.2). This requires a reforming product of 1.04 moles H_2, 0.35 mole CO_2, 0.24 mole H_2O, and 0.05 mole N_2. An input of 0.35 mole CH_3OH, 0.57 mole H_2O and 0.06 mole air produces this. The heating value of CH_3OH at 400 K is 674.493 kJ/mol, so the heating value of the input material would be (674.493)(0.35) = 236 kJ/mol of usable hydrogen. The heating value of the output material would be (242.847)(1.04) = 253 kJ/mol of usable hydrogen. This means that 253-236 = 17 kJ/mol is the theoretical amount of energy that the system needs during chemical processing to produce 1 mole of usable hydrogen.

To this must be added the energy needed to vaporize 0.35 mole CH_3OH and 0.57 mole H_2O and heat these vapors plus the air from 298 to 400 K. This is equal to

$$\overset{\text{energy input for } CH_3OH}{(0.35)[34.32+(400-298)(0.0479)]} + \overset{\text{energy input for } H_2O}{(0.57)[40.71+(400-298)(0.0339)]} + \overset{\text{energy input for air}}{(0.06)(400-298)(0.0293)}$$
$$= 39 \text{ kJ/mol of usable hydrogen.} \qquad \text{(VI-1)}$$

Thus the energy required for vaporization of the feed is a major portion of the theoretical energy required for the steam reforming of methanol. The theoretical process energy input for steam reforming methanol is 39+17 = 56 kJ/mol of usable hydrogen.

The total theoretical energy input to the process is the sum of the LHV of the input materials plus the enthalpy added while processing the input materials to obtain the 1 mole of usable hydrogen. Thus the theoretical energy input to the methanol steam reforming process is 236 + 56 = 292 kJ/mole of usable hydrogen.

C. Hydrogen Fuel from Methane

1. Hydrogen from steam reforming methane. The temperature of 400 K is again the basis temperature. One mole of usable hydrogen is needed from a mixture of 64.1% H_2, 16.3% CO_2, 17.8% H_2O, and 1.8% N_2. (cf. Section IV.B.2). This requires a reforming product of 1.02 moles H_2, 0.26 mole CO_2, 0.28 mole H_2O, and 0.03 mole N_2. An input of 0.26 mole CH_4, 0.78 mole H_2O and 0.04 mole air produces this. The heating value of methane at 400 K is 801.288 kJ/mol. The heating value of the input material would therefore be (801.288)(0.26) = 208 kJ/mol of usable hydrogen. The heating value of the output material would be (242.847)(1.02) = 248 kJ/mol of usable hydrogen. This means that 248-208 = 40 kJ/mol is the theoretical amount of energy that must be put into the system during chemical processing to produce 1 mole of usable hydrogen.

To this must be added the energy needed to vaporize 0.78 mole of water and heat it from 298 to 400 K, and heating 0.26 mole of methane and 0.04 mole of air from 298 to 400 K. This is equal to

$$(0.26)(400\text{-}298)(0.0567) + 0.78[40.71+(400\text{-}298)(0.0339)] + (0.04)(400\text{-}298)(0.0293)$$
$$= 36 \text{ kJ/mol of usable hydrogen.} \qquad \text{(VI-2)}$$

Again, the energy required for vaporization and heating of the feed is a major portion of the theoretical energy required. Here the theoretical process energy input is 40+36 = 76 kJ/mol of usable hydrogen, about equal to that for the steam reforming of methanol.

The total theoretical energy input to the process again is the sum of the LHV of the input materials and the enthalpy added while processing the input materials to obtain the 1 mole of usable hydrogen. Thus the total theoretical energy input to the methane-steam reforming process is 208 + 76 = 284 kJ/mole of usable hydrogen.

2. Hydrogen from partial oxidation of methane. As above, 400 K is the basis temperature. One mole of usable hydrogen is needed from a mixture of 43.8% H_2, 15.4% CO_2, 5.4% H_2O, and 35.4% N_2. This requires a reforming product of 1.11 moles H_2, 0.39 mole CO_2, 0.11 mole H_2O, and 0.90 mole N_2. An input of 0.39 mole CH_4 and 0.98 mole of air, with later injections of 0.47 mole H_2O and 0.02 mole of air, produces this. The total heating value of the input material would therefore be (801.288)(0.39) = 313 kJ/mol of usable hydrogen. The heating value of the output material would be (242.847)(1.11) = 270 kJ/mol of usable hydrogen. This means that 270-313 = -43 kJ/mol of usable hydrogen is available from the processing.

From this must be subtracted the energy required to vaporize 0.47 mole of water and heat it, 0.39 mole of methane and 1.00 mole of air from 298 to 400 K. This is equal to

$$(0.39)(400\text{-}298)(0.0567) + (0.47)[40.71+(400\text{-}298)(0.0339)] + (1.00)(400\text{-}298)(0.0293)$$
$$= 26 \text{ kJ/mol of usable hydrogen.} \qquad \text{(VI-3)}$$

This means that the theoretical process energy input for the process is 26-43 = -17 kJ/mol of usable hydrogen.

The total theoretical energy input to the process is equal to 313-17 = 296 kJ/mol of usable hydrogen.

D. Hydrogen Fuel from Ethanol

The temperature of 400 K is the basis temperature, as in the previous evaluations. One mole of usable hydrogen is needed from a mixture of 62.6% H_2, 21.4% CO_2, 12.5% H_2O, and 3.5% N_2 (cf. Section V.E.2). This requires a reforming product of 1.04 moles H_2, 0.35 mole CO_2, 0.21 mole H_2O, and 0.06 mole N_2. An input of 0.18 mole C_2H_5OH, 0.71 mole H_2O, and 0.07 mole air produces this. The heating value of C_2H_5OH at 400 K is 1275.880 J/mol, so the heating value of the input material is (1275.880)(0.18) = 230 kJ/mol of usable hydrogen. The heating value of the output material would be (242.87)(1.03) = 250 kJ/mol of usable hydrogen. This means that 250-230 = 20 kJ/mol is the theoretical amount of energy needed by the system during chemical processing to produce 1 mole of usable hydrogen.

To this must be added the energy needed to vaporize 0.18 mole C_2H_5OH and 0.71 mole H_2O and heat the vapors plus the 0.07 mole air from 298 to 400 K. This is equal to

$$(0.18)[38.6+(400-298)(0.0735)] + (0.71)[40.71+(400-298)(0.0339)] + (0.07)(400-298)(0.0293)$$
$$= 40 \text{ kJ/mol of usable hydrogen.} \qquad \text{(VI-4)}$$

The theoretical process energy input for steam reforming of ethanol is 20 + 40 = 60 kJ/mol of usable hydrogen.

The total theoretical energy input to the process is equal to 230 + 60 = 290 kJ/mol of usable hydrogen.

E. Hydrogen Fuel from Multi-Carbon Hydrocarbons

1. Requirements for steam-reforming-product stream containing 1 mole of usable hydrogen. Section IV.C.2 calculates the steam reforming product to consist of 58.2% H_2, 19.7% CO_2, 20.6% H_2O, and 1.5% N_2. To obtain 1 mole of usable hydrogen from this mixture requires a reforming product of 1.03 moles H_2, 0.35 mole CO_2, 0.37 mole H_2O, and 0.03 mole N_2.

2. Steam reforming of gasoline. The temperature 400 K is again the basis temperature. Appendix B-2 estimates the latent heat of vaporization of the gasoline to be 31 kJ/mol and its heat capacity to be 180 J/(mol)(K). For reforming gasoline, the reforming product requires an input of 0.049 mole $C_{7.14}H_{14.28}$ and 1.050 moles H_2O. The heating value of gasoline is 4270 kJ/mol. The heating value of the input material would therefore be (4270)(0.049) = 209 kJ/mol of usable hydrogen. The heating value of the output material would be (242.847)(1.03) = 250 kJ/mol of usable hydrogen. This means that 250-209 = 41 kJ/mol is the theoretical amount of energy that must be put into the system during chemical processing to produce 1 mole of usable hydrogen.

To this must be added the amount of energy required to vaporize 0.049 mole of gasoline and 1.050 moles H_2O and heat them from 298 to 400 K. In addition, this process requires an input of 0.04 mole air, which must be heated from 298 to 400 K. The sum of these energy inputs is

$$(0.049)[31 + (400\text{-}298)(0.180)] + 1.050[40.71+(400\text{-}298)(0.0339)] + (0.04)(400\text{-}298)(0.0293)$$
$$= 49 \text{ kJ/mol of usable hydrogen.} \qquad \text{(VI-5)}$$

Again, the energy required for vaporization and heating of the feed is a significant portion of the theoretical energy required. Here the theoretical process energy input is 41+49 = 90 kJ/mol of usable hydrogen.

The total theoretical energy input to the process again is the sum of the LHV of the input materials and the enthalpy added while processing the input materials to obtain the 1 mole of usable hydrogen. Thus the total theoretical energy input to the gasoline steam reforming process is 209 + 90 = 299 kJ/mole of usable hydrogen.

3. Steam reforming of diesel fuel. The basis temperature is again 400 K. Appendix B-3 estimates the latent heat of vaporization of the diesel fuel to be 47 kJ/mol and its heat capacity to be 340 J/(mol)(K). For reforming diesel fuel, the reforming product requires an input of 0.026 mole $C_{13.57}H_{27.14}$ and 1.050 moles H_2O. (This latter is the same amount of water as for reforming gasoline.) The heating value of diesel fuel is 8080 kJ/mol. The heating value of the input material would therefore be (8080)(0.026) = 210 kJ/mol of usable hydrogen (again, essentially the same as for gasoline). The heating value of the output material would be (242.847)(1.03) = 250 kJ/mol of usable hydrogen. This means that 250-210 = 40 kJ/mol must theoretically be put into the system during chemical processing to produce 1 mole of usable hydrogen.

To this must be added the amount of energy required to vaporize 0.026 mole of diesel fuel and 1.050 moles H_2O and heat them from 298 to 400 K. In addition, this process requires an input of 0.04 mole air, which must be heated from 298 to 400 K. The sum of these energy inputs is

$$(0.026)[47 + (400\text{-}298)(0.340)] + 1.050[40.71+(400\text{-}298)(0.0339)] + (0.04)(400\text{-}298)(0.0293)$$
$$= 49 \text{ kJ/mol of usable hydrogen.} \qquad \text{(VI-6)}$$

Again, the energy required for vaporization and heating of the feed is a significant portion of the theoretical energy required. Here the theoretical process energy input is 40+49 = 89 kJ/mol of usable hydrogen.

The total theoretical energy input to the process again is the sum of the LHV of the input materials and the enthalpy added while processing the input materials to obtain the 1 mole of usable hydrogen. Thus the total theoretical energy input to the diesel-fuel steam reforming process is 210 + 89 = 299 kJ/mole of usable hydrogen. This is the same as the total theoretical energy input for steam reforming gasoline.

4. Steam reforming of aviation jet fuel. The temperature 400 K is again the basis temperature. Appendix B-4 estimates the latent heat of vaporization of the jet fuel to be 50 kJ/mol and its heat capacity to be 370 J/(mol)(K). For reforming gasoline, the reforming product requires an input of 0.023 mole $C_{15}H_{30}$ and 1.050 moles H_2O. (The latter number again is the same amount of water as for reforming gasoline and diesel fuel.) The heating value of jet fuel is 9030 kJ/mol. The heating value of the input material would therefore be (9030)(0.023) = 208 kJ/mol of usable hydrogen (again, essentially the same as for gasoline and diesel fuel). The heating value of the output material would again be (242.847)(1.03) = 250 J/mol of usable hydrogen. This means that 250-208 = 42 kJ/mol is the theoretical amount of energy that the system requires during chemical processing to produce 1 mole of usable hydrogen.

To this must be added the amount of energy required to vaporize 0.023 mole of jet fuel and 1.050 moles H_2O and heat the vapors from 298 to 400 K. In addition, this process requires an input of 0.04 mole air, which must be heated from 298 to 400 K. The sum of these energy inputs is

$$(0.023)[50 + (400-298)(0.370)] + 1.050[40.71+(400-298)(0.0339)] + (0.04)(400-298)(0.0293)$$
$$= 49 \text{ kJ/mol of usable hydrogen.} \tag{VI-7}$$

Again, the energy required for vaporization and heating of the feed is a significant portion of the theoretical energy required. Here the theoretical process energy input is 42+49 = 91 kJ/mol of usable hydrogen.

The total theoretical energy input to the process again is the sum of the LHV of the input materials and the enthalpy added while processing the input materials to obtain the 1 mole of usable hydrogen. Thus the total theoretical energy input to the jet-fuel steam reforming process is 208 + 91 = 299 kJ/mole of usable hydrogen. This is the same total theoretical energy input as for steam reforming both gasoline and diesel fuel.

5. Requirements for partial-oxidation-product stream containing 1 mole of usable hydrogen. Section IV.G.2 calculates the composition of the partial oxidation to be 32.0% H_2, 19.4% CO_2, 5.8% H_2O, and 42.8% N_2. To obtain 1 mole of usable hydrogen from this mixture requires a reforming product of 1.20 moles H_2, 0.73 mole CO_2, 0.22 mole H_2O, and 1.61 moles N_2.

6. Partial oxidation of gasoline. As for the other systems, 400 K is the basis temperature. Appendix B-2 gives the approximate heating value of gasoline as 4270 kJ/mole, the heat of vaporization as 31 kJ/mol, and the heat capacity of the vapor as 0.18 kJ/mol. The reforming product requires the input of 0.102 mole of gasoline ($C_{7.14}H_{14.28}$) and 1.82 moles of air. The postulated process requires a later injection of 0.88 mole of H_2O and an additional 0.21 mole of air. The total heating value of the input material would therefore be (0.102)(4270) = 435 kJ/mol of usable hydrogen. The heating value of the output material would be (242.847)(1.20) = 291.42 kJ/mol of usable H_2. This means that 291-435 = -144 kJ/mol of usable H_2 is available from the processing.

From this must be subtracted the energy required to vaporize 0.102 mole of gasoline and 0.88 mole of H_2O and heat them and 2.03 moles of air from 298 to 400 K. The amount to be subtracted is therefore equal to

$$(0.102)[31 + (400-298)(0.18)] + (2.03)(400-298)(0.0293) + (0.88)[40.71+(400-298)(0.0339)]$$
$$= 50 \text{ kJ/mol of usable } H_2. \tag{VI-8}$$

This means that the theoretical process energy input is 50-144 = -94 kJ/mol of usable H_2.

The total theoretical energy input to the process is equal to 435 - 94 = 341 kJ/mol of usable H_2.

7. Partial oxidation of diesel fuel. As before, the basis temperature is 400 K. Appendix B-3 gives the approximate heating value of diesel fuel as 8080 kJ/mole, the heat of vaporization as 47 kJ/mol, and the heat capacity of the vapor as 0.34 kJ/mol. The reforming product requires the input of 0.054 mole of diesel fuel ($C_{13.57}H_{27.14}$) and 1.82 moles of air. The postulated process requires a later injection of 0.88 mole of H_2O and an additional 0.21 mole of air. The total heating value of the input material would therefore be (0.054)(8080) = 436 kJ/mol of usable hydrogen. The heating value of the output material would be (242.847)(1.20) = 291.42 kJ/mol of usable H_2. This means that 291-436 = -145 kJ/mol of usable H_2 is available from the processing.

From this must be subtracted the energy required to vaporize 0.054 mole of diesel fuel and 0.88 mole of H_2O and heat them and 2.03 moles of air from 298 to 400 K. Appendix B-3 estimates the latent heat of vaporization of the diesel fuel to be 47 kJ/mol. This amount to be subtracted is therefore equal to

$$(0.054)[47 + (400\text{-}298)(0.34)] + (2.03)(400\text{-}298)(0.0293) + (0.88)[40.71+(400\text{-}298)(0.0339)]$$
$$= 49 \text{ kJ/mol of usable } H_2. \qquad \textbf{(VI-9)}$$

This means that the theoretical net energy available from the process is 49-145 = -96 kJ/mol of usable H_2.

The theoretical energy input to the process is equal to 436 - 96 = 340 kJ/mol of usable H_2, essentially the same as the theoretical energy input to the partial oxidation of gasoline.

8. Partial oxidation of aviation jet fuel. As for the other systems, 400 K is used as the basis temperature. Appendix B-4 gives the approximate heating value of jet fuel as 9030 kJ/mole, the heat of vaporization as 50 kJ/mol, and the heat capacity of the vapor as 0.37 kJ/mol. The reforming product requires the input of 0.049 mole of jet fuel ($C_{15}H_{30}$) and 1.82 moles of air. The postulated process requires a later injection of 0.88 mole of H_2O and an additional 0.21 mole of air. The total heating value of the input material would therefore be (0.049)(9030) = 442 kJ/mol of usable hydrogen. The heating value of the output material would be (242.847)(1.20) = 291.42 kJ/mol of usable H_2. This means that 291-442 = -151 kJ/mol of usable H_2 is available from the processing.

From this must be subtracted the energy required to vaporize 0.049 mole of jet fuel and 0.88 mole of H_2O and heat them and 2.03 moles of air from 298 to 400 K. This amount to be subtracted is therefore equal to

$$(0.049)[50 + (400\text{-}298)(0.37)] + (2.03)(400\text{-}298)(0.0293) + (0.88)[40.71+(400\text{-}298)(0.0339)]$$
$$= 49 \text{ kJ/mol of usable } H_2. \qquad \textbf{(VI-10)}$$

This means that the theoretical process energy input is 49-151 = -102 kJ/mol of usable H_2.

The total theoretical energy input to the process is equal to 442 - 102 = 340 kJ/mol of usable H_2, essentially the same as the partial oxidations of gasoline and diesel fuel.

F. Summary

Table 3 summarizes the results of the previous paragraphs' calculations. There are wide variations in the LHVs of the input materials and the process energy inputs, but the total theoretical inputs do not vary by much over all the processes considered. The total input energies required for the partial oxidations of the heavier hydrocarbon fuels are somewhat higher than the others. The lower hydrogen-carbon ratio in the fuels probably contributes to this, as does the use of oxygen instead of water as the first reactant's oxidizing agent.

Table 3

THEORETICAL INPUT ENERGIES TO DIFFERENT PROCESSES FOR PRODUCING HYDROGEN FUEL FOR FUEL CELLS

Process	LHV of Input Materials, kJ/mol of usable H_2	Enthalpy Input to Process, kJ/mol of usable H_2	Total Theoretical Input, kJ/mol of usable H_2	Total Theoretical Input, kJ/kg of usable H_2
Steam reforming				
of methane	208	76	284	0.141
of methanol	236	56	292	0.145
of ethanol	230	60	290	0.144
of gasoline	209	90	299	0.148
of diesel fuel	210	89	299	0.148
of jet fuel	208	91	299	0.148
Partial oxidation				
of methane	313	-17	296	0.147
of gasoline	435	-94	341	0.169
of diesel fuel	436	-96	340	0.169
of jet fuel	442	-102	340	0.169

VII. DISCUSSION

A. The Virtues and Drawbacks of Hydrogen as a Fuel

From the fuel cell's viewpoint, pure hydrogen is the ideal fuel. Nevertheless, distribution and storage difficulties pose serious disadvantages to its use for automotive propulsion fuel cells. Evaluations of using hydrogen for automotive propulsion usually consider three forms of on-board hydrogen storage--compressed gas, liquid hydrogen, and a gas dissolved in metal hydrides. Metal hydride systems are the safest of the three, but they require heat and relatively high temperatures for hydrogen release and they have low mass and volumetric energy densities. The cryogenic storage of liquid hydrogen is complex, expensive, and somewhat hazardous. Loss rates of 1-2% per day occur, and refueling loses 10-25% of the fuel. Storage of practical amounts as a compressed gas requires very large high-pressure vessels. These vessels might pose a safety hazard in any collision.

Distribution presents difficulties as serious as storage. The infrastructure for its widespread distribution does not yet exist, and creation of this infrastructure would be egregiously expensive. Jamal and Wyszynski (1994) discuss these drawbacks to on-board hydrogen systems for automotive propulsion, and cite references for their statements.

As this report has demonstrated, many alternatives exist to using pure hydrogen for fuel-cell automotive propulsion. On-board generation of hydrogen appears possible, though extensive development of a practical process is still necessary.

B. Characteristics of Different Processes

Table 4 presents the operating-temperature ranges for the initial fuel-processing reactions considered in this report. The temperatures listed in the second column show immediately that steam reforming methanol is the only reaction that takes place below 1000 K. Higher-temperature reactions tend to produce more waste energy, require more expensive materials of construction, need finer control than lower temperature reactions, and would present a safety hazard in automobiles. The steam reforming of methanol is the only moderate-temperature process of those evaluated for making hydrogen from organic-chemical fuels.

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Table 4

REACTOR TEMPERATURE RANGES FOR INITIAL PROCESSING OF DIFFERENT FUELS

Reaction	**Temperature Range of Initial Processing, K**
Steam reforming	
of methane	1000-1100
of methanol	500-560
of ethanol	~1000
of multi-carbon hydrocarbons	1000-1150
Partial oxidation	
of methane	1500-1600
of multi-carbon hydrocarbons	1150-1900

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C. The Need for Water-Gas Shift Reactors in Particular Processes

PEM fuel cells can tolerate only a maximum of 10-20 ppm of carbon monoxide in the feed to the cell anode. All the processes considered in this report need an efficient means of removing CO from the process stream. Noble-metal-catalyzed preferential oxidation can remove CO in the presence of hydrogen, but the maximum CO content of the inlet to this process is around 2-3%. Table 5 shows that all the processes considered in this report except for the steam reforming of methanol generate CO contents higher than this. All the processes except steam reforming methanol thus require both high and low temperature water-gas shifts to reduce the CO content to an acceptable level. The sizes of the two shift reactors for a 50 kW system are 0.02-0.03 m^3 (0.6-1.1 ft^3) each, based on a PEM fuel cell efficiency of 37%. Even if the cell efficiency were up into the high 40's, the sizes of the required shift reactors would still be about two-thirds of that listed. The necessity for these reactors is a significant drawback to all systems except the steam reforming of methanol.

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Table 5

CARBON MONOXIDE CONTENTS OF DIFFERENT PROCESS STREAMS AFTER INITIAL REACTION

Reaction	CO in Reaction Product Before Water-Gas Shift, mol% or vol %
Steam reforming	
of methane	11.2
of methanol	0.8
of ethanol	14.1
of multi-carbon hydrocarbons	20.0
Partial oxidation	
of methane	20.0
of multi-carbon hydrocarbons	25.0

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D. Impurities Present in the Primary Fuels

All the processes evaluated in this report use catalysts at some stage, and many catalysts are sensitive to impurities in the process streams. A common process impurity that poisons catalysts is sulfur, and various sulfur compounds are present in several of the primary fuels this report considers. ASTM standards for gasoline specify a maximum content of 1000 weight ppm sulfur (Fabri et al. 1990), for diesel fuel 2000 weight ppm sulfur (Fabri et al. op. cit.), and for aviation jet fuel 3000 weight ppm sulfur (Strauss 1985). These levels of sulfur would be lethal to catalysts used in both the reforming and shift stages of processes creating hydrogen-rich fuels.

Methanol manufacture uses catalysts at different points in its manufacture, so sulfur is removed at an early stage (Fiedler et al. 1990). Commercial methanol therefore possesses essentially no sulfur. The processes of ethanol manufacture preclude the presence of sulfur compounds, and specifications for motor-fuel ethanol do not even include sulfur (Kosaric et al. 1987, Logsdon 1994). The composition of natural gas varies widely; depending on the source and the processing a natural gas may or may not have a significant amount of sulfur (Renner and Marschner 1989). Any sulfur must be removed before use as a feed to the processes considered in this report.

On-board sulfur removal is not viable for automotive propulsion systems. As a result, the processes evaluated here can use only low-sulfur fuels, and this may add significant cost to some of the primary fuels.

Other common catalyst poisons, such as arsenic and lead, do not appear in significant amounts in the primary fuels. Only sulfur is a major concern in this respect.

E. Fuel Compositions from Different Processes

The fuel fed to the fuel-cell anode consists of hydrogen and inerts, with only traces of other components allowable. The fraction of hydrogen in the fuel affects the fuel-cell performance; Kinoshita et al. (1988) talk about the deleterious effects of diluting the hydrogen to a major extent for phosphoric acid fuel cells. The effects of hydrogen dilution on PEM cells should be at least equivalent.

Since the fuel fed to the anode is at 100% relative humidity to prevent dehydration, water is added or removed where necessary. For this reason, compositions of fuels formed from different primary substances should be compared on a dry basis. Table 6 shows the dry-basis compositions of the fuels created by the different processes. The fuels coming from the steam-reforming processes have hydrogen contents ranging from 71-78%. The partial oxidation processes, however, yield fuels with hydrogen percentages in the 30's and 40's. This must be regarded as a significant drawback to using partial

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Table 6

DRY-BASIS COMPOSITIONS OF FUELS ENTERING FUEL-CELL ANODE FROM DIFFERENT PROCESSES

Process	Dry-Basis Composition of Resulting Fuel, mol %		
	H_2	CO_2	N_2
Steam reforming			
of methane	78.0	19.8	2.2
of methanol	71.9	24.6	3.5
of ethanol	71.5	24.5	4.0
of multi-carbon hydrocarbons	73.3	24.8	1.9
Partial oxidation			
of methane	46.3	16.3	37.4
of multi-carbon hydrocarbons	34.0	20.6	45.4

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oxidation to create fuels for automotive-propulsion fuel cells, and gives a clear advantage to steam reforming processes for this purpose.

F. Theoretical Input Energies for the Different Processes

As mentioned above, the theoretical input energies for the different processes listed in Table 3 do not differ appreciably, excepting a somewhat higher input energy required for the partial oxidation of hydrocarbons. This report did not consider processing efficiencies, fuel price, and many other process attributes. These factors would make the small differences in theoretical input energies assume a minor role in any choice of a process alternative to the steam reforming of methanol.

VIII. CONCLUSIONS

Processes exist for making hydrogen-rich fuel suitable for PEM fuel cells. These processes use common fuels, and have potential for development for on-board use in automotive propulsion systems.

The leading candidate process for on-board generation of fuel-cell hydrogen for automotive propulsion is the steam reforming of methanol.

If methanol unavailability or a high price demands an alternative process, steam reforming appears preferable to partial oxidation for on-board processes creating hydrogen-rich fuels for fuel-cell automotive propulsion.

IX. ACKNOWLEDGMENTS

Especially helpful were the suggestions of Nicholas Vanderborgh of the LANL/GM/DOE Joint Development Center. In addition, useful contributions were made by Michael Inbody, Glenn Skala, and William Wangard of the Joint Development Center. David Masten of the Joint Development Center performed some of the thermodynamics calculations, and his assistance is gratefully acknowledged. This work was performed as a portion of the Electrochemical Engine for Automotive Applications Project # DE-AC02-90CH10435, a joint program among the U.S. Department of Energy, General Motors Corporation, and Los Alamos National Laboratory.

Appendix A

PROPERTIES OF ELEMENTS AND COMPOUNDS STUDIED IN THIS REPORT

A-1. Formula Weights, Melting Points and Boiling Points.

	Formula Weight	Melting Point, K	Boiling Point @ atm. press., K
CH_4	16.04	90.7	111.7
CH_3OH	32.04	175-176	337.9
C_2H_5OH	46.07	158.7	280.5
CO	28.01	66	81
CO_2	44.01	$216.6^{5.2\ \mathrm{atm}}$	subl. 194.7
H_2	2.016	14.1	20.5
H_2O	18.016	273.15	373.15
N_2	28.0341	63.14	77.26
O_2	32.00	54.8	90.19
air	28.964		78.8

A-2. Heat Capacities [J/(mol)(K)]. (Unless otherwise noted, taken from Barin et al. 1993)

	@ 300 K	@ 500 K	@ 800 K	@ 1000 K
CH_4	35.707	46.349	62.929	71.782
$CH_3OH(g)$	43.958	59.477	79.794	89.370
C_2H_5OH	65.677	95.182	127.191	140.461
CO	29.144	29.794	31.898	33.183
CO_2	37.217	44.625	51.434	54.308
H_2	28.849	29.260	29.625	30.205
H_2O	33.596	35.230	38.723	41.267
N_2	29.125	29.583	31.430	32.696
O_2	29.385	31.091	33.734	34.870
air(a)	29.17	29.83		

(a) From Liley et al. 1984.

A-3. Constants in Heat Capacity Relationship $C_p = A + BT + CT^2 + DT^3$ (taken from Haynes 1990).

	A, J/(mol)(K)	B x 10^3, J/(mol)(K)^2	C x 10^6, J/(mol)(K)^3	D x 10^9, J/(mol)(K)^4
CH_4	19.24	52.09	11.97	-11.31
$CH_3OH(g)$	21.14	70.88	25.85	-28.50
CO	28.14	1.674	5.368	-2.220
CO_2	22.24	59.77	-34.99	7.464
H_2	29.09	-1.946	4.001	-0.8699
H_2O	32.22	1.922	10.55	-3.593
N_2	28.82	-1.570	8.075	-2.871
O_2	25.46	15.19	-7.151	1.311

A-4. Enthalpy Changes (kJ/mol) (unless otherwise noted, taken from Barin et al. 1993).

	ΔH_{vap} at 1 atm.	ΔH_f (300 K)	ΔH_f (600 K)	ΔH_f (1000 K)
CH_4	8.2(a)	-74.930	-83.331	-89.876
$CH_3OH(g)$	34.32	-201.236	-210.621	-217.252
C_2H_5OH	38.6(a)	-234.904	-247.326	-254.924
CO	6.042(a)	-110.530	-110.185	-112.021
CO_2	15.82(a)	-393.506	-393.805	-394.626
H_2(a)	0.904	0	0	0
$H_2O(g)$	40.71	-241.844	-244.758	-247.858
N_2(a)	5.577	0	0	0
O_2(a)	6.820	0	0	0
air		0	0	0

(a) From Dean 1992.

A-5. Gibbs Energies of Formation (kJ/mol) (taken from Barin et al. 1993).

	ΔG_f (300 K)	ΔG_f (600 K)	ΔG_f (1000 K)
CH_4	-50.607	-22.851	+19.572
$CH_3OH(g)$	-162.208	-119.255	-56.178
C_2H_5OH	-167.786	-95.321	+8.558
CO	-137.345	-164.494	-200.261
CO_2	-394.370	-395.139	-395.810
$H_2O(g)$	-228.538	-214.081	-192.713

Appendix B

COMPOSITION AND PROPERTIES OF HYPOTHETICAL COMPOUNDS USED AS SURROGATE HYDROGEN SOURCES

B-1. Common Considerations

Gasoline, diesel fuel, and aviation jet fuel consist mainly of hydrocarbons. Thus their average molecular formulas share the common form C_nH_{xn}, with x a number in the vicinity of 2. For a fuel composed primarily of straight or branched-chain hydrocarbons, $x > 2$; for fuels composed primarily of cyclic hydrocarbons, $x \approx 2$; for fuels possessing high percentages of olefins or aromatics, $x < 2$. Since current formulations of gasoline, diesel fuel, and jet fuel are combinations of paraffins, olefins, and aromatics, this report assumes $x = 2$. The assumed general molecular formula for the three surrogates is therefore C_nH_{2n}.

Others have used different values for x. Jamal and Wyszynski (1994) use $x = 1.86$ for gasoline, while Kumar et al. (1994) use 2,2,4 trimethyl pentane, whose $x = 2.25$, as a surrogate gasoline. Values of x within this range do not markedly influence this report's calculations, so the value $x = 2$ appears reasonable and convenient.

The lower heating value (LHV) of typical regular gasoline is 42.7 MJ/kg or kJ/g (Adler 1986); that of a typical diesel fuel 42.5 MJ/kg (Adler op. cit.). The LHV of typical aviation jet fuel is 43 MJ/kg (Dukek 1992).

B-2. Composition and Properties of Surrogate Gasoline

The distillation midpoint of a typical gasoline is about 100°C (Adler 1986, Hochhauser 1994). The molecular weight of paraffin petroleum fractions boiling at this temperature is around 100 (Maxwell 1950). Using this molecular weight gives a formula for the surrogate gasoline compound of $C_{7.14}H_{14.28}$. As mentioned above, the LHV of this material is 42.7 MJ/kg, which translates to values of 42.7 kJ/g and 4270 kJ/mol.

From correlations in Maxwell (1950), the latent heat of vaporization of a paraffin hydrocarbon having a normal boiling point of 100°C and a molecular weight of 100 is about 31 kJ/mol. This report uses this ΔH_{vap} for the gasoline's latent heat of vaporization. Maxwell also provides correlations that predict approximate heat capacities of hydrocarbons. These correlations give 180 J/(mol)(K) between room temperature and 400 K for a paraffin hydrocarbon having a normal boiling point of 100°C and a molecular weight of 100. This is the heat capacity of the surrogate gasoline's vapor.

B-3. Composition and Properties of Surrogate Diesel Fuel

The distillation midpoint of typical diesel fuels is not reported in relevant articles (e.g., Adler 1986, Hochhauser 1994), but diesel specifications give a maximum volume fraction of 0.65 vaporized below 250°C. This leads to an assumed mean boiling point of 230°C. The molecular weight of paraffin petroleum fractions boiling at this temperature is about 190 (Maxwell 1950). Using this molecular weight gives a formula for the surrogate diesel fuel compound of $C_{13.57}H_{27.14}$. As mentioned above, the LHV of this material is 42.5 MJ/kg, which translates to values of 42.5 kJ/g and 8080 kJ/mol.

From correlations in Maxwell (1950), the latent heat of vaporization of a paraffin hydrocarbon having a normal boiling point of 230°C and a molecular weight of 190 is about 47 kJ/mol. This report uses this ΔH_{vap} for the diesel fuel's latent heat of vaporization. Maxwell's correlations also predict an approximate heat capacity of about 340 J/(mol)(K) between room temperature and 400 K for a paraffin hydrocarbon having a normal boiling point of 230°C and a molecular weight of 190. This number is the heat capacity of the surrogate diesel fuel's vapor.

B-4. Composition and Properties of Surrogate Aviation Jet Fuel

Like diesel fuel, relevant articles (e.g., Dukek 1992) do not report the distillation midpoint of typical jet fuels. Specifications for two wide-cut jet fuels, Jet B and JP-4, give a volume fraction of 0.50 recovered at a maximum of 190°C. Two other jet fuels, however, Jet A and JP-8, have 10% recovered points of 205°C, meaning a significantly higher distillation midpoint. The jet fuel market is more or less evenly split between the two general categories. The end points of the four grades range from 270 to 300°C. When we choose the Jet A and JP-8 as the typical jet fuels, these numbers lead to an assumed mean boiling point of 245°C. The molecular weight of paraffin petroleum fractions boiling at this temperature is about 210 (Maxwell 1950). Using this molecular weight gives a formula for the surrogate jet-fuel compound of $C_{15}H_{30}$. As mentioned above, the LHV of this material is 43 MJ/kg, which translates to values of 43 kJ/g and 9030 kJ/mol.

From correlations in Maxwell (1950), the latent heat of vaporization of a paraffin hydrocarbon having a normal boiling point of 245°C and a molecular weight of 210 is about 50 kJ/mol. This report uses this ΔH_{vap} for the jet fuel's latent heat of vaporization. Maxwell's correlations also predict an approximate heat capacity of about 370 J/(mol)(K) between room temperature and 400 K for a paraffin hydrocarbon having a normal boiling point of 245°C and a molecular weight of 210. This number is used for the heat capacity of the surrogate jet fuel's vapor.

B-5. Summary of Surrogate Fuels' Compositions and Properties

Table B-1 summarizes the results of the preceding four sections' calculations, listing the composition and relevant properties of the three surrogate fuels used in this report.

Table B-1

COMPOSITION AND PROPERTIES OF SURROGATE FUELS

Fuel	**Molecular Formula of Surrogate**	**Molecular Weight of Surrogate**	**LHV of Surrogate, kJ/mol**	**b.p. of Surrogate, °C**	**ΔH_{vap} of Surrogate, kJ/mol**	**C_p of Surrogate Vapor, J/(mol)(K)**
Gasoline	$C_{7.14}H_{14.28}$	100	4270	100	31	180
Diesel fuel	$C_{13.57}H_{27.14}$	190	8080	230	47	340
Aviation jet fuel	$C_{15}H_{30}$	210	9030	245	50	370

Appendix C

CALCULATION OF THERMODYNAMICS CHARACTERISTICS OF PRINCIPAL REACTIONS FOR GENERATING HYDROGEN FUEL FOR FUEL CELLS

C-1. Applications of the Gibbs Energy Change

The Glossary defines two types of equilibrium constant--a rigorous one based on fugacities, and an approximate one based on partial pressures. At operating conditions considered for the systems of this report, ideal gas behavior approaches the real situation, so this report uses the equilibrium constant based on partial pressures. As described in the Glossary, when ideal-gas behavior exists and the partial pressures are expressed in atmospheres, the equilibrium constant may be calculated from the relationship

$$\Delta G_r = -RT \ln K \overset{\text{numerically}}{=} -RT \ln K_p \quad . \qquad \text{(C-1)}$$

The change in Gibbs energy may give other insights into the reaction. After calculating both the enthalpy and Gibbs energy changes for a reaction, applying the relationship

$$\Delta G = \Delta H - T\Delta S \qquad \text{(C-2)}$$

gives the entropy change of the reaction. Comparison of the reaction's entropy change with that predicted by the change in molecular structure can provide additional understanding of the system.

C-2. Steam Reforming of Methane.

a. The reaction expression. The reaction of steam with natural gas is one of the main industrial sources of hydrogen at this writing. It is usually carried out over a nickel catalyst at around 1000-1100 K. Using methane as the surrogate natural gas,

$$CH_4 + H_2O \overset{Ni}{\rightarrow} CO + 3H_2 \quad . \qquad \text{(IV-1)}$$

The reaction produces four molecules for two reactant molecules, so low pressures should favor the reaction.

b. Enthalpy change of reaction. Using standard heats of formation for the different constituents listed in Appendix A, the enthalpy change of the reaction at 300 K is calculated to be

$$\Delta H_r = -110.530 - (3)(0) + 74.930 + 241.844$$

$$= +206.24 \text{ kJ/mol } CH_3OH \text{ or } CO_2 \qquad \text{(C-3)}$$

The reaction is significantly endothermic. At 600 K,

$$\Delta H_r = -110.185 - (3)(0) + 83.331 + 244.758$$

$$= +217.904 \text{ kJ/mol } CH_3OH \text{ or } CO_2 \qquad \text{(C-4)}$$

and at 1000 K,

$$\Delta H_r = -112.021 - (3)(0) + 89.876 + 247.858$$

$$= +225.713 \text{ kJ/mol } CH_3OH \text{ or } CO_2 \quad . \tag{C-5}$$

c. **Gibbs energy change and equilibrium constant.** At 300 K, the change in Gibbs energy is

$$\Delta G_r = -137.345 - (3)(0) + 50.607 + 228.538$$

$$= +141.80 \text{ kJ/mol } CH_4 \text{ or } CO \quad . \tag{C-6}$$

The equilibrium constant expressed in terms of partial pressures for the steam reforming of methane is

$$K_p = \frac{(p_{CO})(p_{H2})^3}{(p_{CH4})(p_{H2O})} \quad . \tag{C-7}$$

The Gibbs energies of formation used above were evaluated at 300 K, so the equilibrium constant for the methane-steam reaction at this temperature is

$$K_p \overset{\text{numerically}}{=} \exp(-\Delta G_r/RT) = \exp[-(141.80)(1000)/(8.314)(300)]$$

$$= 2.040 \times 10^{-25} \text{ atm}^2 \quad . \tag{C-8}$$

As a check, the code RXNEQ, using a different database, gives a value for K_p at 300 K of 2.05×10^{-25} atm^2.

The relationship

$$\frac{d \ln K_p}{d(1/T)} = \frac{-\Delta H_r}{R} \tag{C-9}$$

gives the change of the equilibrium constant with temperature. Since ΔH_r for this reaction is positive, this equation says that the equilibrium constant for the methanol-steam reaction increases with temperature. Using the Gibbs energies at 600 K from Appendix A,

$$\Delta G_r = -164.494 - (3)(0) + 22.851 + 214.081$$

$$= +72.438 \text{ kJ/mol } CH_4 \text{ or } CO \quad . \tag{C-10}$$

The equilibrium constant at 600 K is

$$K_p \overset{\text{numerically}}{=} \exp(-\Delta G_r/RT) = \exp[-(72.438)(1000)/(8.314)(600)]$$

$$= 4.939 \times 10^{-7} \text{ atm}^2 \tag{C-11}$$

(RXNEQ value: 4.83×10^{-7} atm^2).

The reaction's Gibbs energy change and equilibrium constant at 1000 K are

$$\Delta G_r = -200.261 - (3)(0) - 19.572 + 192.713$$

$$= -27.120 \text{ kJ/mol } CH_4 \text{ or } CO \quad , \qquad \text{(C-12)}$$

and

$$K_p \overset{\text{numerically}}{=} \exp(-\Delta G_r/RT) = \exp[+(27.120)(1000)/(8.314)(1000)]$$

$$= 26.101 \text{ atm}^2 \qquad \text{(C-13)}$$

(RXNEQ value: 24.9 atm^2).

The change in equilibrium constant gives a simple explanation why industrial usage carries out this reaction at temperatures above 1000 K.

d. Pressure effects. Section C.2.a mentions that low pressures should favor this reaction because it produces four molecules for two reacted. In a constant-volume system, the pressure would increase as the reaction proceeds. Le Chatelier's principle, which states that an equilibrium change tends to offset the application of an outside change, requires that an increase in pressure shift the reaction to the left.

The equilibrium change resulting from increasing the operating pressure from 0.3 MPa to 3 MPa (3 atm to 30 atm) shows this. Let there be a 1.5:1 ratio of H_2O:CH_4 in the feed, an operating temperature of 1100 K, and a pressure of 0.3 MPa (3 atm). Under these conditions, the code RXNEQ gives the equilibrium conversion of methane as 94.0%. The equilibrium product contains 1.4% methane. At the same temperature and steam/methane ratio but a pressure of 3 MPa (30 atm), the conversion is down to 51.7% and the equilibrium product contains 13.7% methane.

C-3. Steam Reforming of Methanol

a. The reaction expression. In the overall reaction, one methanol molecule reacts with one water molecule to produce one carbon dioxide molecule and three hydrogen molecules. The stoichiometric reaction expression is

$$CH_3OH + H_2O \rightarrow CO_2 + 3H_2 \quad . \qquad \text{(IV-7)}$$

As in the steam reforming of methane, the reaction produces four molecules for two reactant molecules, so low pressures should also favor this reaction.

b. Enthalpy change of reaction. Again using standard heats of formation for the different constituents listed in Appendix A, the reaction's enthalpy change at 300 K is calculated to be

$$\Delta H_r = -393.506 - (3)(0) + 201.236 + 241.844$$

$$= +49.574 \text{ kJ/mol } CH_3OH \text{ or } CO_2 \quad . \qquad \text{(C-14)}$$

The reaction is endothermic, though methanol-steam's endothermism is not nearly as great as that of the methane-steam reaction [cf. Eqs. (C-3)-(C-5)].

The maximum temperature of operation for on-board generation of hydrogen appears to approach 600 K. Thus 300 and 600 K approximately bracket the usable temperatures. At 600 K,

$$\Delta H_r = -393.805 - (3)(0) + 210.621 + 244.758$$

$$= +61.574 \text{ kJ/mol } CH_3OH \text{ or } CO_2 \quad . \qquad \text{(C-15)}$$

Although 1000 K is higher than the usual operating temperatures for this reaction, the ΔH_r at this temperature is also of interest. It is

$$\Delta H_r = -394.626 - (3)(0) + 217.252 + 247.858$$

$$= +70.484 \text{ kJ/mol } CH_3OH \text{ or } CO_2 \quad . \qquad \text{(C-16)}$$

As the processing temperature rises, the system requires more energy for the reaction to proceed. This means that more heat must be added to the system when the process uses higher temperatures for the main reaction.

c. Gibbs energy change and equilibrium constant. At 300 K, the change in Gibbs energy is

$$\Delta G_r = -394.370 - (3)(0) + 162.208 + 228.538$$

$$= -3.624 \text{ kJ/mol } CH_3OH \text{ or } CO_2 \quad . \qquad \text{(C-17)}$$

The equilibrium constant expressed in terms of partial pressures for the methanol-steam reaction is

$$K_p = \frac{(p_{CO2})(p_{H2})^3}{(p_{CH3OH})(p_{H2O})} \quad . \qquad \text{(C-18)}$$

The Gibbs energies of formation used above were evaluated at 300 K, so the equilibrium constant for the steam-methanol reaction at this temperature is

$$K_p \overset{\text{numerically}}{=} \exp(-\Delta G_r/RT) = \exp[+(3.624)(1000)/(8.314)(300)]$$

$$= 4.22 \text{ atm}^2 \qquad \text{(C-19)}$$

(RXNEQ value: 4.22 atm^2).

Since ΔH_r for this reaction is positive, Eq. (C-9) says that the equilibrium constant for the methanol-steam reaction increases with temperature. This attribute is shared with the methane-steam reaction discussed above. Using the Gibbs energies at 600 and 1000 K from Appendix A,

$$\Delta G_r = -395.139 - (3)(0) + 119.255 + 214.081$$

$$= -61.803 \text{ kJ/mol } CH_3OH \text{ or } CO_2 \text{ (600 K)}, \qquad \text{(C-20)}$$

$$\Delta G_r = -395.810 - (3)(0) + 56.178 + 192.713$$

$$= -146.919 \text{ kJ/mol } CH_3OH \text{ or } CO_2 \text{ (1000 K)}. \qquad \text{(C-21)}$$

The equilibrium constants at these two temperatures are

$$K_p \overset{\text{numerically}}{=} \exp(-\Delta G_r/RT) = \exp[+(61.803)(1000)/(8.314)(600)]$$

$$= 2.40 \times 10^5 \text{ atm}^2 \text{ (600 K)} \tag{C-22}$$

(RXNEQ value: 2.32×10^5 atm^2), and

$$K_p \overset{\text{numerically}}{=} \exp(-\Delta G_r/RT) = \exp[+(146.919)(1000)/(8.314)(1000)]$$

$$= 4.73 \times 10^7 \text{ atm}^2 \text{ (1000 K)} \tag{C-23}$$

(RXNEQ value: 4.44×10^7 atm^2).

As indicated by the reaction enthalpy change, the equilibrium constant increases as the temperature rises. The change in equilibrium constants between 300 and 600 K is almost a factor of 10^5. The two equilibrium constants show that high temperatures favor this reaction.

Applying Eq. (C-2),

$$\Delta G = \Delta H - T\Delta S \quad , \tag{C-2}$$

provides more insight into the reaction. The change in enthalpy at 300 K is moderately positive, but the change in Gibbs energy is slightly negative. A look at the reaction expression shows that the entropy should increase significantly upon reaction; not only are more molecules created than reacted, but those created have greater internal freedom than the reactants. The positive entropy change is what causes the Gibbs energy change to be negative. At higher temperatures, the reaction enthalpy change becomes more positive but the temperature has risen also. Thus the entropy-change term becomes much more negative. The positive value of the entropy change times the temperature dominates the change in Gibbs energy and forces the reaction significantly farther to the right.

d. Pressure effects. Section C.3.a states that low pressures should favor this reaction, because it produces four molecules for two reacted. In a constant-volume system, the pressure would increase as the reaction proceeds. As mentioned in Section C.2.d, Le Chatelier's principle requires that an increase in pressure shift the reaction equilibrium to the left.

The behavior of the methane-steam equilibrium, discussed earlier, shows this. A second example is the equilibrium composition change in the methanol-steam system if the operating pressure is increased from 0.3 MPa to 3 MPa (3 atm to 30 atm). If there is a 1.5:1 ratio of H_2O:CH_3OH in the feed, the operating temperature is 600 K, and the pressure is 0.3 MPa (3 atm), the code RXNEQ gives the equilibrium conversion of methanol as 99.99%. The equilibrium product contains 13 ppm methanol. At the same temperature and steam/methanol ratio (S/M) but a pressure of 3 MPa (30 atm), the conversion is down to 99.0%, and the equilibrium product contains 1300 ppm methanol.

These effects are not as dramatic as the pressure effects in the methane-steam example, but they are important if only a few ppm of methanol are wanted in the product.

C-4. Partial Oxidation of Methane

a. The reaction expression. The partial oxidation of methane reacts one molecule of methane with one atom of oxygen to form one molecule of carbon monoxide and two of hydrogen:

$$CH_4 + \tfrac{1}{2}O_2 \rightarrow CO + 2H_2 \quad . \qquad \text{(IV-9)}$$

b. Enthalpy change of reaction. As before, Appendix A's standard heats of formation provide the reaction's enthalpy change at 300, 600, and 1000 K. At 300 K,

$$\Delta H_r = -110.530 - (2)(0) + 74.930 + (\tfrac{1}{2})(0)$$

$$= -35.600 \text{ kJ/mol } CH_4 \text{ or CO} \quad . \qquad \text{(C-24)}$$

At 600 K,

$$\Delta H_r = -110.185 - (2)(0) + 83.331 + (\tfrac{1}{2})(0)$$

$$= -26.854 \text{ kJ/mol } CH_4 \text{ or CO} \quad . \qquad \text{(C-25)}$$

At 1000 K,

$$\Delta H_r = -112.021 - (2)(0) + 89.876 + (\tfrac{1}{2})(0)$$

$$= -22.145 \text{ kJ/mol } CH_4 \text{ or CO} \quad . \qquad \text{(C-26)}$$

c. Gibbs energy change and equilibrium constant. Again using data from Appendix A, the Gibbs energy changes for the partial oxidation of methane at 300, 600, and 1000 K are

$$\Delta G_r = -137.345 - (2)(0) + 50.607 + (\tfrac{1}{2})(0)$$

$$= -86.738 \text{ kJ/mol } CH_4 \text{ or CO} \quad (300 \text{ K}), \qquad \text{(C-27)}$$

$$\Delta G_r = -164.494 - (2)(0) + 22.851 + (\tfrac{1}{2})(0)$$

$$= -141.643 \text{ kJ/mol } CH_4 \text{ or CO} \ (600 \text{ K}), \qquad \text{(C-28)}$$

$$\Delta G_r = -200.261 - (2)(0) - 19.572 + (\tfrac{1}{2})(0)$$

$$= -219.833 \text{ kJ/mol } CH_4 \text{ or CO} \ (1000 \text{ K}). \qquad \text{(C-29)}$$

The equilibrium constant expressed in terms of partial pressures for the steam reforming of methane is

$$K_p = \frac{(p_{CO})(p_{H2})}{(p_{CH4})(p_{O2})^{1/2}} \quad . \qquad \text{(C-30)}$$

The equilibrium constants at the three temperatures are

$$K_p \overset{\text{numerically}}{=} \exp(-\Delta G_r/RT) = \exp[+(86.738)(1000)/(8.314)(300)]$$

$$= 1.268 \times 10^{15} \text{ atm}^{1/2} \qquad (300 \text{ K}) \qquad \text{(C-31)}$$

(RXNEQ value: 1.27×10^{15} atm^{½}),

$$K_p \overset{\text{numerically}}{=} \exp(-\Delta G_r/RT) = \exp[+(141.643)(1000)/(8.314)(600)]$$
$$= 2.146 \times 10^{12} \text{ atm}^{½} \qquad (600\text{ K}) \qquad \text{(C-32)}$$

(RXNEQ value: 2.12×10^{12} atm^{½}), and

$$K_p \overset{\text{numerically}}{=} \exp(-\Delta G_r/RT) = \exp[+(219.833)(1000)/(8.314)(1000)]$$
$$= 3.043 \times 10^{11} \text{ atm}^{½} \qquad (1000\text{K}) \qquad \text{(C-33)}$$

(RXNEQ value: 2.92×10^{11} atm^{½}).

In spite of the reaction being exothermic, the equilibrium constant declines as the temperature rises. The reaction is only mildly exothermic, and other factors more than compensate for this. In spite of the slight lessening of the equilibrium constant, it remains large enough so the reaction is essentially irreversible throughout the temperature range considered here.

d. Pressure effects. In the partial oxidation of methane, one and one-half molecules react to form three; Le Chatelier's principle dictates that lower pressures favor the reaction. Nevertheless, the essential irreversibility of the reaction at all temperatures makes this a minor consideration. While industrial processes appear to prefer steam reforming of methane to partial oxidation, other partial oxidation processes use pressures in the 4-9 MPa range (Bakemeier et al. 1989).

C-5. Steam Reforming of Ethanol

a. The reaction expression. For the ethanol-steam reaction the stoichiometric expression is

$$C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 6H_2 \ . \qquad \text{(IV-6)}$$

b. Enthalpy change of reaction. Using the same procedure as carried out for previous reactions, the enthalpy changes of the reaction at 300, 600, and 1000 K are

$$\Delta H_r = (2)(-393.506) - (6)(0) + 234.904 + (3)(241.844)$$
$$= +173.424 \text{ kJ/mol } C_2H_5OH \quad (300\text{ K}), \qquad \text{(C-34)}$$

$$\Delta H_r = (2)(-393.805) - (6)(0) + 247.326 + (3)(244.758)$$
$$= +193.990 \text{ kJ/mol } C_2H_5OH \quad (600\text{ K}), \qquad \text{(C-35)}$$

$$\Delta H_r = (2)(-394.626) - (6)(0) + 254.924 + (3)(247.858)$$
$$= +209.246 \text{ kJ/mol } C_2H_5OH \quad (1000\text{ K}). \qquad \text{(C-36)}$$

c. Gibbs energy change and equilibrium constant. At 300, 600, and 1000 K, the changes in Gibbs energies are

$$\Delta G_r = (2)(-394.370) - (6)(0) + 167.786 + (3)(228.538)$$

$$= +64.660 \text{ kJ/mol } C_2H_5OH \qquad (300 \text{ K}), \qquad \text{(C-37)}$$

$$\Delta G_r = (2)(-395.139) - (6)(0) + 95.321 + (3)(214.081)$$

$$= -52.714 \text{ kJ/mol } C_2H_5OH \qquad (600 \text{ K}), \qquad \text{(C-38)}$$

$$\Delta G_r = (2)(-395.810) - (6)(0) - 8.558 + (3)(192.713)$$

$$= -222.039 \text{ kJ/mol } C_2H_5OH \qquad (1000 \text{ K}). \qquad \text{(C-39)}$$

The equilibrium constant expressed in terms of partial pressures for the steam reforming of ethanol is

$$K_p = \frac{(p_{CO2})^2 (p_{H2})^6}{(p_{C2H5OH})(p_{H2O})^3} \; . \qquad \text{(C-40)}$$

The equilibrium constants at the three temperatures are

$$K_p \overset{\text{numerically}}{=} \exp(-\Delta G_r/RT) = \exp[-64.660)(1000)/(8.314)(300)]$$

$$= 5.512 \times 10^{-12} \text{ atm}^4 \qquad (300 \text{ K}), \qquad \text{(C-41)}$$

$$K_p \overset{\text{numerically}}{=} \exp(-\Delta G_r/RT) = \exp[+(52.714)(1000)/(8.314)(600)]$$

$$= 3.884 \times 10^{4} \text{ atm}^4 \qquad (600 \text{ K}), \qquad \text{(C-42)}$$

$$K_p \overset{\text{numerically}}{=} \exp(-\Delta G_r/RT) = \exp[+(222.039)(1000)/(8.314)(1000)]$$

$$= 3.968 \times 10^{11} \text{ atm}^4 \qquad (1000\text{K}). \qquad \text{(C-43)}$$

A glance at the three equilibrium constants shows why the proposed temperature is higher in A. D. Little's postulated process than used for the methanol-steam reaction.

d. Pressure effects. In the reaction expression (IV-8), a total of four reactant molecules form eight product molecules. Thus Le Chatelier's principle says that lower pressures favor the formation of products.

C-6. The Water-Gas Shift Reaction and Its Reverse

a. The reaction and its importance. As mentioned in Section IV, a major player in all the processes for creating hydrogen from primary fuels is either the water-gas shift reaction or its reverse. The forward reaction forms carbon dioxide and hydrogen from carbon monoxide and water, the reverse forms carbon monoxide and water from carbon dioxide and hydrogen:

$$H_2O + CO \xrightarrow{\text{forward}} H_2 + CO_2 \qquad\qquad H_2 + CO_2 \xrightarrow{\text{reverse}} H_2O + CO \qquad \text{(IV-2)}$$

Section IV.A talks about the importance of the water-gas shift and its reverse in industrial processes.

b. Enthalpy change of reaction. For the three temperatures being considered in this appendix, summing the heats of formation of the reaction products and subtracting the heats of the reactants gives

$$\Delta H_r = -0 - 393.506 + 241.844 + 110.530$$

$$= -41.132 \text{ kJ/mol of any of the constituents (300 K)}, \qquad \text{(C-44)}$$

$$\Delta H_r = -0 - 393.805 + 244.758 + 110.185$$

$$= -38.862 \text{ kJ/mol of any of the constituents (600 K)}, \qquad \text{(C-45)}$$

$$\Delta H_r = -0 - 394.626 + 247.858 + 112.021$$

$$= -34.747 \text{ kJ/mol of any of the constituents (1000 K)}. \qquad \text{(C-46)}$$

The reaction is exothermic at all three temperatures. This means the reverse shift reaction is endothermic.

c. Gibbs energy change and equilibrium constant. At 300 K,

$$\Delta G_r = -0 - 394.370 + 228.538 + 137.345$$

$$= -28.487 \text{ kJ/mol of any of the constituents}. \qquad \text{(C-47)}$$

The equilibrium constant for the water-gas shift reaction is expressed as

$$K_p = \frac{(p_{CO2})(p_{H2})}{(p_{CO})(p_{H2O})} \quad . \qquad \text{(C-48)}$$

Using Eq. (C-1), the equilibrium constant for the forward shift at 300 K is

$$K_p \overset{\text{numerically}}{=} \exp(-\Delta G_r/RT) = \exp[+(28.487)(1000)/(8.314)(300)]$$

$$= 9.12 \times 10^4 \qquad \text{(C-49)}$$

(RXNEQ value: 8.90×10^4). The equilibrium constant for the reverse shift at 300 K is

$$K_p = 1/9.12 \times 10^4 = 1.10 \times 10^{-5} \quad . \qquad \text{(C-50)}$$

At 600 and 1000 K for the forward shift:

$$\Delta G_r = +214.081 + 164.494 - 0 - 395.139$$

$$= -16.564 \text{ kJ/mol of any of the constituents (600 K)}, \qquad \text{(C-51)}$$

$$\Delta G_r = +192.713 + 200.261 - 0 - 395.810$$

$$= -2.836 \text{ kJ/mol of any of the constituents (1000 K)}, \qquad \text{(C-52)}$$

and

$$K_p \overset{\text{numerically}}{=} \exp(-\Delta G_r/RT) = \exp[+(16.564)(1000)/(8.314)(600)]$$

$$= 27.8 \text{ (600 K)}, \qquad \text{(C -53)}$$

$$K_p \overset{\text{numerically}}{=} \exp(-\Delta G_r/RT) = \exp[+(2.836)(1000)/(8.314)(600)]$$

$$= 1.407 \text{ (1000 K)} \qquad \text{(C -54)}$$

(RXNEQ values: 26.5 and 1.32, respectively). For the reverse shift at 600 and 1000 K,

$$K_p = 3.61 \times 10^{-2} \text{ (600 K)}, \qquad \text{(C-55)}$$

$$K_p = 0.711 \text{ (1000 K)}. \qquad \text{(C-56)}$$

The water-gas shift may either create or reduce carbon monoxide in a process stream. The above equilibrium values say that at equilibrium there are amounts of CO well above the PEM cell tolerance level at any temperature and pressure approaching reaction conditions. For example, in the methanol-steam system, if the feed has an S/M ratio of 1.5 and essentially all the methanol reacts, there will be about half as many moles of water in the reformate as CO_2 and about three times as much H_2 as CO_2 [cf. Eq. (IV-5)]. Then, using Eq. (C-48), making the substitutions indicated by the previous sentence and assuming the temperature to be 500 K ($K_p = 7.46 \times 10^{-3}$), gives

$$p_{CO} = \frac{(7.46 \times 10^{-3})(p_{CO_2})(3p_{CO_2})}{(0.5p_{CO_2})} = 4.47 \times 10^{-2} p_{CO_2} \quad . \qquad \text{(C-57)}$$

Since CO_2 is roughly one-third the reformate, this means that p_{CO} will be about (0.0447)(0.33P) = 0.015P. There will be in the vicinity of 1.5% CO in the reformate at equilibrium.

d. Pressure effects. A change in pressure has only a slight effect on equilibrium percentages of the components of the water-gas-shift system. In this reaction and its reverse, two molecules react to form two molecules of product. Thus the equilibrium constant is the ratio of partial pressures of two substances over the partial pressures of two other substances. A change in pressure would only increase the individual partial pressures, it would not increase the relative amount of any substance in the system. Changes of the component fugacity coefficients with increasing pressure might alter this conclusion, but the overall effects would be minor.

C-7. The Side Reaction of Methanol Decomposition

a. The reaction expression. As mentioned earlier, PEM fuel cells cannot tolerate any but small traces (10-20 ppm) of carbon monoxide in the feed. This is a drawback, because two side reactions create CO during the methanol-steam reaction. One is the reverse shift reaction, described in the previous section. The other is

$$CH_3OH \rightarrow CO + 2H_2 \quad . \qquad \text{(C-58)}$$

This reaction appears to accompany the methanol-steam reaction invariably. Some mechanisms for the methanol-steam reaction have Eq. (C-41) as the first step in the reaction path, as discussed by Amphlett et al. (1985). This would explain the apparently inevitable appearance of CO when methanol is reacted with steam.

The reaction produces three molecules from one reactant molecule, for a product/reactant ratio of 3. The main methanol-steam reaction has a product/reactant ratio of 2. Thus while low pressures favor the main reaction, they favor the methanol-decomposition side reaction even more.

b. Enthalpy change of reaction. Again using heats of formation for the different constituents, the enthalpy change of this reaction at this appendix's three temperatures are calculated to be

$$\Delta H_r = -110.530 - (2)(0) + 201.236$$

$$= +90.706 \text{ kJ/mol } CH_3OH \text{ or } CO \text{ (300 K)}, \tag{C-59}$$

$$\Delta H_r = -110.185 - (2)(0) + 210.621$$

$$= +100.436 \text{ kJ/mol } CH_3OH \text{ or } CO \text{ (600 K)}, \tag{C-60}$$

$$\Delta H_r = -112.021 - (2)(0) + 217.252$$

$$= +105.231 \text{ kJ/mol } CH_3OH \text{ or } CO \text{ (1000 K)}. \tag{C-61}$$

This reaction too is significantly endothermic, almost twice as endothermic as the methanol-steam reaction. Since this reaction forms only small amounts of CO in the methanol-steam system, however, this endothermism does not affect the system behavior significantly.

c. Gibbs energy change and equilibrium constant. At 300 K, the Gibbs energy change for methanol decomposition is

$$\Delta G_r = -137.345 - (2)(0) + 162.208$$

$$= +24.863 \text{ kJ/mol } CH_3OH \text{ or } CO \quad . \tag{C-62}$$

The partial-pressure equilibrium constant for the methanol decomposition reaction is expressed as

$$K_p = \frac{(p_{CO})(p_{H2})^2}{(p_{CH3OH})} \quad . \tag{C-63}$$

Using Eq. (C-1), the equilibrium constant for this reaction at 300 K is

$$K_p \overset{\text{numerically}}{=} \exp(-\Delta G_r/RT) = \exp[-(24.863)(1000)/(8.314)(300)]$$

$$= 4.69 \times 10^{-5} \text{ atm}^2 \tag{C-64}$$

(RXNEQ value: 4.69×10^{-5} atm^2). Again, Appendix A supplies the Gibbs energy data to obtain the 600 and 1000 K values of methanol decomposition's K_p:

$$\Delta G_r = -164.494 - (2)(0) + 119.255$$

$$= -45.239 \text{ kJ/mol } CH_3OH \text{ or } CO \text{ (600 K)}, \tag{C-65}$$

$$\Delta G_r = -200.261 - (2)(0) + 56.178$$

$$= -144.083 \text{ kJ/mol } CH_3OH \text{ or } CO \text{ (1000 K)}. \tag{C-66}$$

and

$$K_p \overset{\text{numerically}}{=} \exp(-\Delta G_r/RT) = \exp[+(45.239)(1000)/(8.314)(600)]$$

$$= 8.68 \times 10^3 \text{ atm}^2 \text{ (600 K)}, \qquad \text{(C-67)}$$

$$K_p \overset{\text{numerically}}{=} \exp(-\Delta G_r/RT) = \exp[+(144.083)(1000)/(8.314)(600)]$$

$$= 3.36 \times 10^7 \text{ atm}^2 \text{ (1000 K)} \qquad \text{(C-68)}$$

(RXNEQ values: 8.75 x 10^3 and 3.37 x 10^7 atm^2, respectively). A comparison of the two equilibrium constants for methanol decomposition shows that its increase from 300 K to 600 K is even greater than that of the methanol-steam reaction. Methanol decomposition's constant increases by a factor of 10^8 while the increase for the methanol-steam's constant is by 10^5 [cf. Eqs. (C-19) and (C-22)]. Thus, while high temperatures favor the main reaction, they favor this undesired side reaction even more.

d. Pressure effects. Methanol decomposition to CO and $2H_2$ produces three molecules for each molecule reacted. This means that low pressures favor the reaction, and high pressures inhibit it. However, simple equilibrium for this reaction is seldom attained in the methanol-steam reacting system, as either the water-gas shift or its reverse enters the picture.

Appendix D

EQUILIBRIUM PRODUCT COMPOSITIONS RESULTING FROM STEAM REFORMING AND PARTIAL OXIDATION OF PARTICULAR HYDROCARBONS

Table D-1 presents the equilibrium product compositions resulting from the steam reforming of n-decane ($C_{10}H_{22}$), iso-octane or 2,2,4 trimethyl pentane (C_8H_{18}), and toluene (C_7H_8). The process modeled used a H_2O/C ratio of 3 and was carried out at 1100 K and 3 atm. The computer code STANJAN (Reynolds 1987) calculated the product equilibrium compositions. The calculations assumed that the product consisted of methane, carbon monoxide, carbon dioxide, hydrogen, and water.

- -

Table D-1

EQUILIBRIUM COMPOSITIONS OF STEAM REFORMING PRODUCTS AT 3 ATM AND 1100 K

H_2O/C ratio: 3

Hydrocarbon	**Mole Fraction in Product**				
	CH_4	**CO**	**CO_2**	**H_2**	**H_2O**
n-decane ($C_{10}H_{22}$)	0.001	0.12	0.10	0.44	0.34
2,2,4 trimethyl pentane (C_8H_{18})	0.001	0.12	0.10	0.44	0.34
toluene (C_7H_8)	0.001	0.12	0.08	0.49	0.32

- -

The results show almost complete conversion of the hydrocarbon to CO, CO_2, and H_2. Essentially no methane is present in the product.

Table D-2 presents the equilibrium product compositions resulting from the partial oxidation of n-decane ($C_{10}H_{22}$), iso-octane or 2,2,4 trimethyl pentane (C_8H_{18}), and toluene (C_7H_8). The computer code STANJAN (Reynolds 1987) calculated the product equilibrium compositions at pressures of 3 and 10 atm absolute and temperature of 800, 1000, 1100, 1200, 1300, and 1400 K.

The partial oxidation process modeled by the code followed Eq. (IV-8). The hypothetical process used the stoichiometric amount of oxygen required to convert all the carbon in the hydrocarbon to CO. Air supplied the oxygen; this accounts for the nitrogen in the product. The code predicted that the process consumed essentially all the oxygen at all conditions, so no O_2 appears in the product anywhere in the table.

Some trends in the results are immediately apparent. At temperatures above 1200 K, the product consists essentially of carbon monoxide, hydrogen, and nitrogen. Other substances are present only in trace quantities. Since partial oxidation processes are carried out at temperatures well above 1200 K, essentially only CO, H_2, and N_2 are present at equilibrium.

Table D-2

EQUILIBRIUM COMPOSITIONS OF PARTIAL OXIDATION PRODUCTS AT DIFFERENT TEMPERATURES AND PRESSURES

Hydrocarbon	Pressure, atm	Temperature, K	Mole Fraction in Product					
			CH_4	CO	CO_2	H_2	H_2O	N_2
n-decane ($C_{10}H_{22}$)	3	800	0.14	0.07	0.12	0.05	0.02	0.60
		1000	0.04	0.21	0.02	0.20	0.02	0.51
		1100	0.01	0.24	0.007	0.25	0.007	0.49
		1200	0.005	0.25	0.002	0.27	0.003	0.48
		1300	0.002	0.25	0.001	0.27	0.001	0.47
		1400	0.001	0.25	0.0(a)	0.27	0.001	0.47
	10	800	0.16	0.04	0.13	0.03	0.02	0.62
		1000	0.07	0.17	0.05	0.14	0.03	0.54
		1100	0.04	0.21	0.02	0.21	0.02	0.51
		1200	0.02	0.24	0.007	0.24	0.009	0.49
		1300	0.007	0.25	0.002	0.26	0.005	0.48
		1400	0.003	0.25	0.001	0.27	0.002	0.48
2,2,4 trimethyl pentane (C_8H_{18})	3	800	0.14	0.06	0.12	0.06	0.02	0.60
		1000	0.04	0.21	0.02	0.21	0.02	0.51
		1100	0.01	0.24	0.007	0.25	0.008	0.48
		1200	0.005	0.24	0.002	0.27	0.003	0.47
		1300	0.002	0.25	0.001	0.28	0.001	0.47
		1400	0.001	0.25	0.0(a)	0.28	0.001	0.47
	10	800	0.16	0.04	0.13	0.03	0.02	0.62
		1000	0.07	0.17	0.05	0.15	0.03	0.54
		1100	0.04	0.21	0.02	0.21	0.02	0.50
		1200	0.02	0.24	0.007	0.25	0.009	0.48
		1300	0.007	0.24	0.002	0.27	0.005	0.48
		1400	0.003	0.25	0.001	0.27	0.002	0.47

Table D-2 (cont.)

Hydrocarbon	**Pressure, atm**	**Temperature, K**	**Mole Fraction in Product**					
			CH_4	**CO**	**CO_2**	**H_2**	**H_2O**	**N_2**
toluene (C_7H_8)	3	800	0.09	0.17	0.09	0.02	0.002	0.64
		1000	0.03	0.26	0.02	0.12	0.006	0.57
		1100	0.009	0.28	0.006	0.15	0.003	0.55
		1200	0.003	0.29	0.002	0.16	0.001	0.55
		1300	0.001	0.29	0.001	0.16	0.001	0.55
		1400	0.001	0.29	0.0(a)	0.16	0.0(a)	0.55
	10	800	0.10	0.15	0.09	0.005	0.001	0.65
		1000	0.05	0.23	0.04	0.08	0.009	0.60
		1100	0.02	0.27	0.02	0.12	0.007	0.57
		1200	0.009	0.28	0.005	0.15	0.004	0.55
		1300	0.004	0.29	0.002	0.16	0.002	0.55
		1400	0.002	0.29	0.001	0.16	0.001	0.55

(a) Mole fractions lower than 0.0005 are reported as 0.0.

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