

Fuel Options for Solid Oxide Fuel Cells: a Thermodynamic Analysis

S. L. Douvartzides, F. A. Coutelieris, A. K. Demin, and P. E. Tsiakaras
University of Thessalia, Dept. of Mechanical and Industrial Engineering,
Pedion Areos, 383 34, Volos, Greece

The eligibility of natural gas (methane), methanol, ethanol, and gasoline as fuels for the generation of electrical power in solid oxide fuel cells (SOFCs) is discussed in terms of efficiency. Each raw fuel was assumed to be processed in a steam reformer to provide a hydrogen-rich gas mixture to the SOFC feedstream. An SOFC system, consisting of an electrochemical section and a reformer, was analyzed thermodynamically assuming initial steam/fuel feed ratios at conditions where carbon deposition is thermodynamically impossible, at atmospheric total pressure, and in the temperature range of 800–1,200 K. Results were obtained in terms of both electromotive force (emf) output and efficiency. Methane seems to be the most appropriate fuel option, with an SOFC system efficiency close to 96%. Furthermore, ethanol and methanol were very promising alternative options (94% and 91%, respectively), while gasoline (83%) utilization requires special reforming conditions.

Introduction

Solid oxide fuel cells (SOFCs) seem to be very promising for the direct conversion of chemical energy into electricity, attaining significantly higher efficiencies with respect to other conventional systems such as gas turbines and internal combustion engines. Various fuel options are considered feasible for SOFC operation, especially after an appropriate external process in order to obtain a gas mixture rich in hydrogen, such as steam reforming. The electrochemically combustible species are H_2 and CO , but it is common system-analysis practice to assume that only H_2 contributes to power generation while CH_4 is consumed through *in situ* steam reforming, providing additional amounts of H_2 and CO and, in turn, CO is consumed through *in situ* gas shift reaction, providing additional amounts of H_2 (Hirschenhofer et al., 1997; Benjamin et al., 1990).

Methane, methanol, ethanol, and gasoline are currently regarded as the most probable SOFC fuels, due to a number of considerations dealing with their accessibility and their physical properties (Thomas and Zalowitz, 1999; Pimentel et al., 1994). Methane was the first fuel that was investigated at high-temperature operating cells both experimentally (Clarke

et al., 1997; Ridler and Twigg, 1996) and theoretically (Demin et al., 1992; Chan and Wang, 2000). Gasoline has also been thermodynamically examined (Docter and Lamm, 1999; Thomas et al., 2000) for fuel-cell vehicle applications. It is a depletable energy source of variable composition, but in calculations can be well represented by *n*-octane.

It is well known that both methane and gasoline are *mineral* fuels, and that their deposits are limited enough to be considered to be an appropriate long-term global solution for the energy problem. Furthermore, these fuels have a significant influence on the surcharge of environmental pollution, mainly due to their high impact on the greenhouse effect. These drawbacks have led researchers to pay significant interest on the utilization of alternative, renewable and environmental-friendly liquid fuels such as methanol and ethanol. Methanol is manufactured exclusively by a mixture of carbon monoxide and hydrogen, most commonly derived by methane steam reforming (Bridger and Spencer, 1996). Thermodynamic analysis of methanol steam reforming has been recently discussed (Lwin et al., 2000), while a lot of experimental investigations have been presented during the last 30 years (Kobayashi et al., 1976; Amphlett et al., 1988). Ethanol can be considered as a very promising and reliable fuel option for fuel cells because it can be alternatively produced biochemically from biomass (Margiloff et al., 1981; McMillan, 1997;

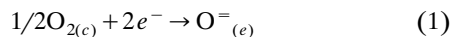
Correspondence concerning this article should be addressed to P. E. Tsiakaras.
Current address of A. K. Demin: Institute of High Temperature Electrochemistry,
S. Kovalevskoy Str 20, 620219, Ekaterinembourg, Russia.

Prince, 1986; Wyman, 1994). Due to the natural availability of bioethanol, it is considered an alternative fuel with a positive impact on the economy (Evans, 1997) and environment. Although ethanol steam reforming has been variously investigated for hydrogen production (Garcia and Laborde, 1991; Vasudeva, 1996; Fishtik et al., 2000), the analysis of ethanol utilization in SOFCs was undertaken recently by Tsiakaras et al. (1999).

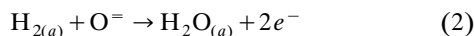
In the present work, a comparison of the eligibility of methane, methanol, ethanol, and gasoline as fuels for generation of electrical power in SOFCs is presented in terms of both electromotive force (emf) output and system efficiency. A mathematical model has been developed in order to adequately estimate, according to the method of the direct minimization of Gibbs free energy, the spatial variance of the molar fractions of the components that are involved to the chemical reactions taking place within the SOFC system.

Model Development

Independently of the fuel used in an SOFC with an oxygen-ion-conducting electrolyte, its operation principle relies on the continuous supply of fuel, H_2 , CO, and CH_4 , at the anode compartment while the cathode is exposed at atmospheric air. According to this operation regime, the following reaction takes place at the cathode



where the subscripts (c) and (e) represent the states at the cathode and in the electrolyte, respectively. At the anode, the electrochemical reaction of hydrogen oxidation occurs



where the subscript (a) represents the state at the anode (Minh and Takahashi, 1995). The reversible electromotive force is given by the Nernst equation

$$E = \frac{RT}{4F} \ln \frac{P_{O_2(c)}}{P_{O_2(a)}} \quad (3)$$

where R is the gas constant, T is the temperature, F is the Faraday's constant, and P_{O_2} is the partial pressure of oxygen on the electrode. Oxygen partial pressure at the anode is calculated taking into account that oxygen is in equilibrium with hydrogen and steam according to the reaction



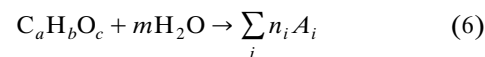
and, therefore, is equal to

$$P_{O_2} = \left(\frac{P_{H_2O,(a)}}{K_4 P_{H_2,(a)}} \right) \quad (5)$$

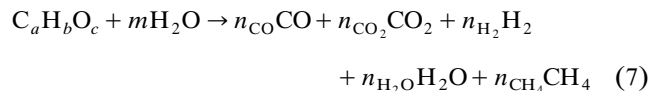
where K_4 is the equilibrium constant of Eq. 4.

In the frame of this consideration it is assumed that oxygen utilization from air fed to the cathode compartment is negligible, so that oxygen partial pressure at the cathode is constant as $P_{O_2,(c)} = 0.209$. Therefore, the value of E depends on the partial pressure of the oxygen in the anode, that is, on the fuel type and composition fed to the anode. Thus, SOFC power output depends both on the fuel choice and on the preliminary fuel-processing method.

The overall reaction of the steam reforming of a fuel represented as $C_aH_bO_c$, can be expressed generally as



or, equivalently, as



where m is the reforming factor (the steam/fuel mole ratio). On the righthand side of Eq. 7, only the species that are allowed to exist in equilibrium with noticeable concentrations have been considered, as follows from previous works (Ridler and Twigg, 1996; Docter and Lamm, 1999; Lwin et al., 2000; Vasudeva et al., 1996). Therefore, the composition of the

Table 1. Free Energies of Formation (ΔG_f^0)_T of Chemical Compounds at Various Temperatures (in J/mol) and Lower Heating Values – ΔH^0 of Four Fuels (in J/mol)

T, K	$\Delta G_{ethanol}^f$	$\Delta G_{methanol}^f$	$\Delta G_{methane}^f$	$\Delta G_{H_2O}^f$	$\Delta G_{CO_2}^f$	ΔG_{CO}^f	$\Delta G_{gasoline}^f$
800	-45,713.9	-35,821	-2,038.07	-203,466	-395,567	-182,450	417,590.8
850	-32,931.9	-22,349.1	3,262.936	-200,767	-395,666	-186,920	458,437.5
900	-20,118.1	-8,841.39	8,605.288	-198,047	-395,761	-191,379	499,258.4
950	-7,280.99	4,695.452	13,982.68	-195,305	-395,852	-195,826	540,031.8
1,000	5,572.138	18,255.79	19,389.65	-192,545	-395,940	-200,261	580,740.5
1,050	18,435.41	31,834.85	24,821.52	-189,769	-396,023	-204,684	621,371.3
1,100	31,304.04	45,428.66	30,274.21	-186,977	-396,102	-209,094	661,914
1,150	44,174.19	59,033.89	35,744.24	-184,171	-396,177	-213,492	702,361.4
1,200	57,042.88	72,647.8	41,228.58	-181,353	-396,248	-217,878	742,708.7
			$-\Delta H_{methane}^0$		820,600		
			$-\Delta H_{methanol}^0$		638,200		
			$-\Delta H_{ethanol}^0$		1,235,000		
			$-\Delta H_{gasoline}^0$		5,074,200		

equilibrium mixture derived by Eq. 7 for each fuel can be calculated according to thermodynamical methods.

In the present analysis, equilibrium compositions were calculated according to the method of the direct minimization of Gibbs free energy (Smith et al., 1996). Therefore, for each initial system of (Fuel + $m\text{H}_2\text{O}$), the following system of 10 nonlinear algebraic equations can be considered

$$(\Delta G_{\text{fuel}}^f/RT)_T + \ln y_{\text{fuel}} + a\lambda_C + b\lambda_H + c\lambda_O = 0 \quad (8)$$

$$(\Delta G_{\text{H}_2\text{O}}^f/RT)_T + \ln y_{\text{H}_2\text{O}} + 2\lambda_H + \lambda_O = 0 \quad (9)$$

$$(\Delta G_{\text{CO}}^f/RT)_T + \ln y_{\text{CO}} + \lambda_C + \lambda_O = 0 \quad (10)$$

$$(\Delta G_{\text{CO}_2}^f/RT)_T + \ln y_{\text{CO}_2} + \lambda_C + 2\lambda_O = 0 \quad (11)$$

$$(\Delta G_{\text{CH}_4}^f/RT)_T + \ln y_{\text{CH}_4} + \lambda_C + 4\lambda_H = 0 \quad (12)$$

$$\ln y_{\text{H}_2} + 2\lambda_H = 0 \quad (13)$$

$$a y_{\text{fuel}} + y_{\text{CO}} + y_{\text{CO}_2} + y_{\text{CH}_4} = b_C/n \quad (14)$$

$$b y_{\text{fuel}} + 2y_{\text{H}_2\text{O}} + 4y_{\text{CH}_4} + 2y_{\text{H}_2} = b_H/n \quad (15)$$

$$c y_{\text{fuel}} + y_{\text{H}_2\text{O}} + y_{\text{CO}} + 2y_{\text{CO}_2} = b_O/n \quad (16)$$

$$y_{\text{fuel}} + y_{\text{H}_2\text{O}} + y_{\text{CO}} + y_{\text{CO}_2} + y_{\text{CH}_4} + y_{\text{H}_2} = 1 \quad (17)$$

In the preceding system, R represents the universal gas constant, $y_i = n_i / \sum_i n_i$ is the molar fraction of the i th chemical species present in thermodynamic equilibrium, b_j are the numbers of the j atoms in the initial (Fuel + $m\text{H}_2\text{O}$) system, and λ_j are Lagrange's multipliers used as scalar parameters. Free energies of formation $(\Delta G_i^f)_T$ of all chemical compounds are listed in Table 1 for each temperature examined.

According to simple analytical manipulations, the preceding system can be written as a 3×3 system of nonlinear algebraic equations and three separate equations solved independently. The system is

$$\left[a - c \left(\frac{b_C}{b_O} \right) \right] K y_{\text{H}_2\text{O}}^c y_{\text{CH}_4}^a y_{\text{H}_2}^{4-c+b-2a} - \left(\frac{b_C}{b_O} \right) y_{\text{H}_2\text{O}} y_{\text{H}_2}^4 + \left[1 - \left(\frac{b_C}{b_O} \right) \right] L y_{\text{H}_2\text{O}} y_{\text{CH}_4} y_{\text{H}_2} + \left[1 - 2 \left(\frac{b_C}{b_O} \right) \right] M y_{\text{H}_2\text{O}}^2 y_{\text{CH}_4} + y_{\text{CH}_4} y_{\text{H}_2}^4 = 0 \quad (18)$$

$$\left[b - c \left(\frac{b_H}{b_O} \right) \right] K y_{\text{H}_2\text{O}}^c y_{\text{CH}_4}^a y_{\text{H}_2}^{4-c+b-2a} + \left[2 - \left(\frac{b_H}{b_O} \right) \right] y_{\text{H}_2\text{O}} y_{\text{H}_2}^4 - \left(\frac{b_H}{b_O} \right) L y_{\text{H}_2\text{O}} y_{\text{CH}_4} y_{\text{H}_2} - 2 \left(\frac{b_H}{b_O} \right) M y_{\text{H}_2\text{O}}^2 y_{\text{CH}_4} + 4y_{\text{CH}_4} y_{\text{H}_2}^4 + 5y_{\text{H}_2}^5 = 0 \quad (19)$$

$$K y_{\text{H}_2\text{O}}^c y_{\text{CH}_4}^a y_{\text{H}_2}^{4-c+b-2a} + y_{\text{H}_2\text{O}} y_{\text{H}_2}^4 + L y_{\text{H}_2\text{O}} y_{\text{CH}_4} y_{\text{H}_2} + M y_{\text{H}_2\text{O}}^2 y_{\text{CH}_4} + y_{\text{CH}_4} y_{\text{H}_2}^4 + y_{\text{H}_2}^5 - y_{\text{H}_2}^4 = 0 \quad (20)$$

where

$$K = e^{(-\Delta G_{\text{fuel}}^f + \Delta G_{\text{H}_2\text{O}}^f + 2\Delta G_{\text{CH}_4}^f)/RT} \quad (21)$$

$$L = e^{(\Delta G_{\text{H}_2\text{O}}^f - \Delta G_{\text{CO}}^f + \Delta G_{\text{CH}_4}^f)/RT} \quad (22)$$

$$M = e^{(2\Delta G_{\text{H}_2\text{O}}^f - \Delta G_{\text{CO}_2}^f + \Delta G_{\text{CH}_4}^f)/RT} \quad (23)$$

Furthermore, the independent equations are

$$\frac{y_{\text{fuel}} y_{\text{H}_2}^{(c-b+2a)}}{y_{\text{H}_2\text{O}}^c y_{\text{CH}_4}^a} = K \quad (24)$$

$$\frac{y_{\text{CO}} y_{\text{H}_2}^3}{y_{\text{H}_2\text{O}} y_{\text{CH}_4}} = L \quad (25)$$

$$\frac{y_{\text{CO}_2} y_{\text{H}_2}^4}{y_{\text{H}_2\text{O}}^2 y_{\text{CH}_4}} = M \quad (26)$$

The nonlinear system (Eqs. 18–20) was solved for $y_{\text{H}_2\text{O}}$, y_{CH_4} , and y_{H_2} by using a complicated Newton's iterative method (Burden and Faires, 1989), while a lot of effort has been expended on assuring the independence of the solution on the arbitrary initial values. Furthermore, y_{fuel} , y_{CO} , and y_{CO_2} are obtained just by substituting $y_{\text{H}_2\text{O}}$, y_{CH_4} , and y_{H_2} from Eqs. 18–20 into Eqs. 24–26.

Considering that carbon formation on the SOFC anode deteriorates the lifetime and performance of its operation (Clarke et al., 1997), the possibility of carbon deposition in the gaseous equilibrium system was examined assuming the Boudouard reaction



For this purpose, the limiting reforming factors above which carbon deposition is thermodynamically impossible were calculated using the carbon-formation criterion

$$\alpha_C = K_{27} \frac{P_{\text{CO}}^2}{P_{\text{CO}_2}} \geq 1 \quad (28)$$

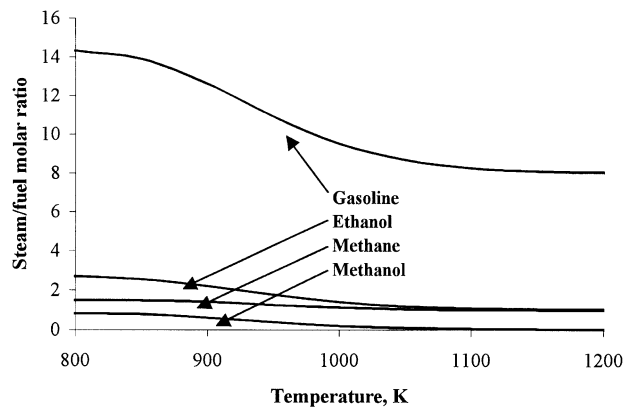
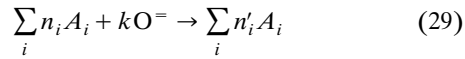


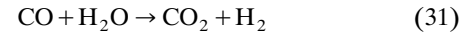
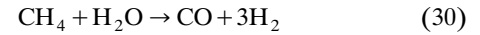
Figure 1. Boundaries of carbonization for methane, methanol, ethanol, and gasoline.

where K_{27} is the equilibrium constant of Eq. 27. From now on, the locus of points corresponding to these minimum reforming factors will be described as “boundary of carbonization” (BC). Moreover, all conditions of the SOFC operation have been selected to correspond above this boundary, where carbon deposition on the anode electrocatalyst are thermodynamically impossible.

The equilibrium gas mixture exiting the reformer reacts in the anode compartment of the SOFC with oxygen ions coming from the cathode, according to the general reaction



where k is equal to 4, 3, 6, and 25 for methane, methanol, ethanol, and gasoline, respectively, and n'_i is the number of moles of the i th component in the SOFC anode outlet mixture. This equation is the sum of the following simultaneous reactions



and Eq. 2.

It is known that the SOFC stack has higher efficiency than a single cell, and, therefore, the present analysis assumes that

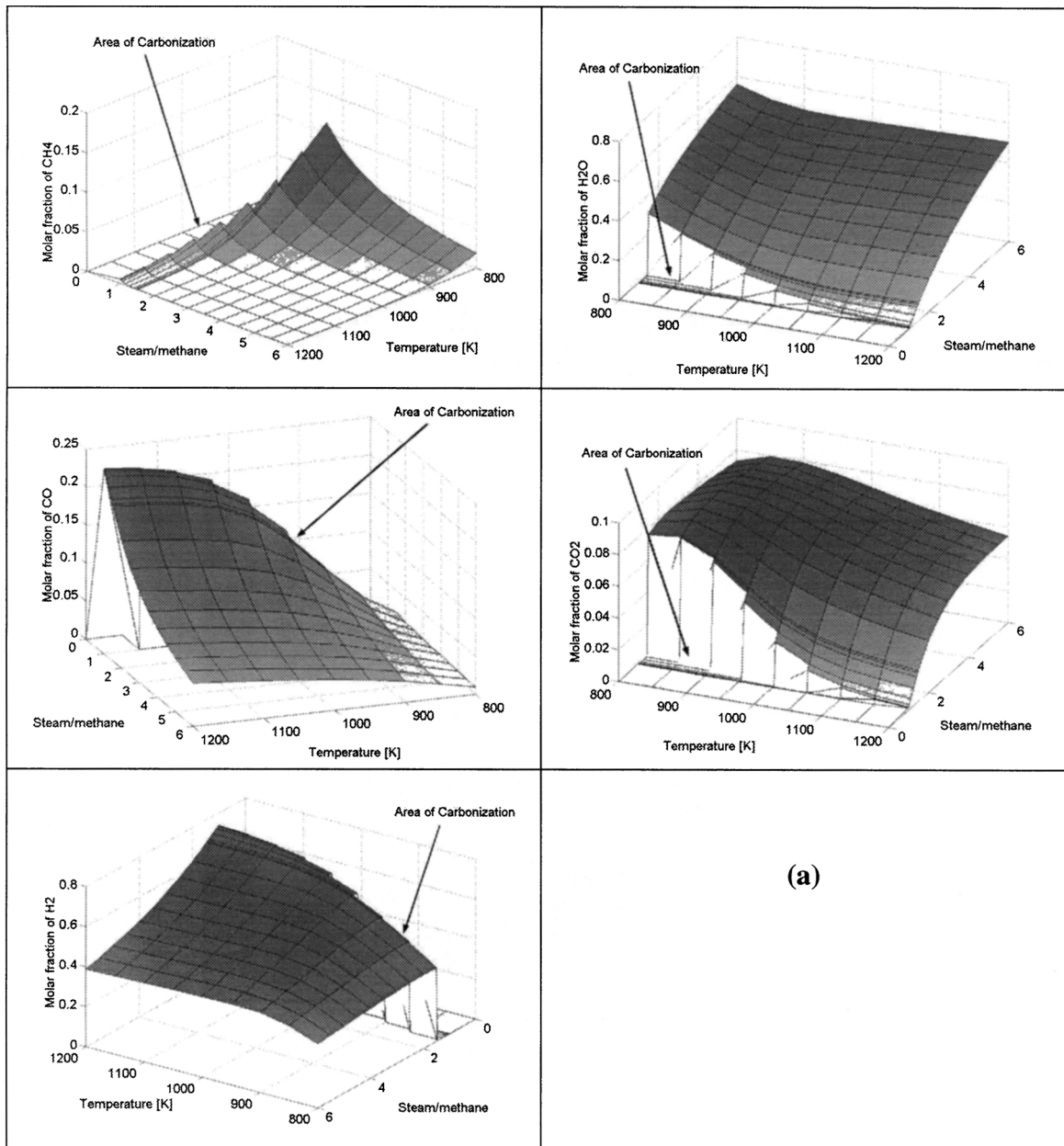


Figure 2A. Equilibrium composition of the steam reforming of (a) methane, (continued).

the electrochemical section represents a stack. Further, the oxygen flux through the solid electrolyte is assumed uniform, and the composition of the anode mixture in any point x of the channel can be calculated by using Eq. 29 and substituting the following value instead of k

$$k(x) = (1 - \alpha)k \quad (32)$$

where $\alpha = x/L$ and L is the length of the anode channel.

After calculation of the anode gas mixture distribution along the channel by using Eqs. 29 and 32, the oxygen partial-pressure distribution is found by using Eq. 5, and, finally, the electromotive force distribution is calculated by using Eq. 3. Then, the average electromotive force, \bar{E} , can be calcu-

lated by means of the numerical integration of E distribution along the cell channel. Thus,

$$\bar{E} = \int_0^1 E(\alpha) d\alpha \quad (33)$$

where $\alpha = x/L$ represents a dimensionless relative channel length. Finally, the maximum SOFC efficiency was calculated as

$$\eta = \frac{q\bar{E}}{\Delta H^\circ} \quad (34)$$

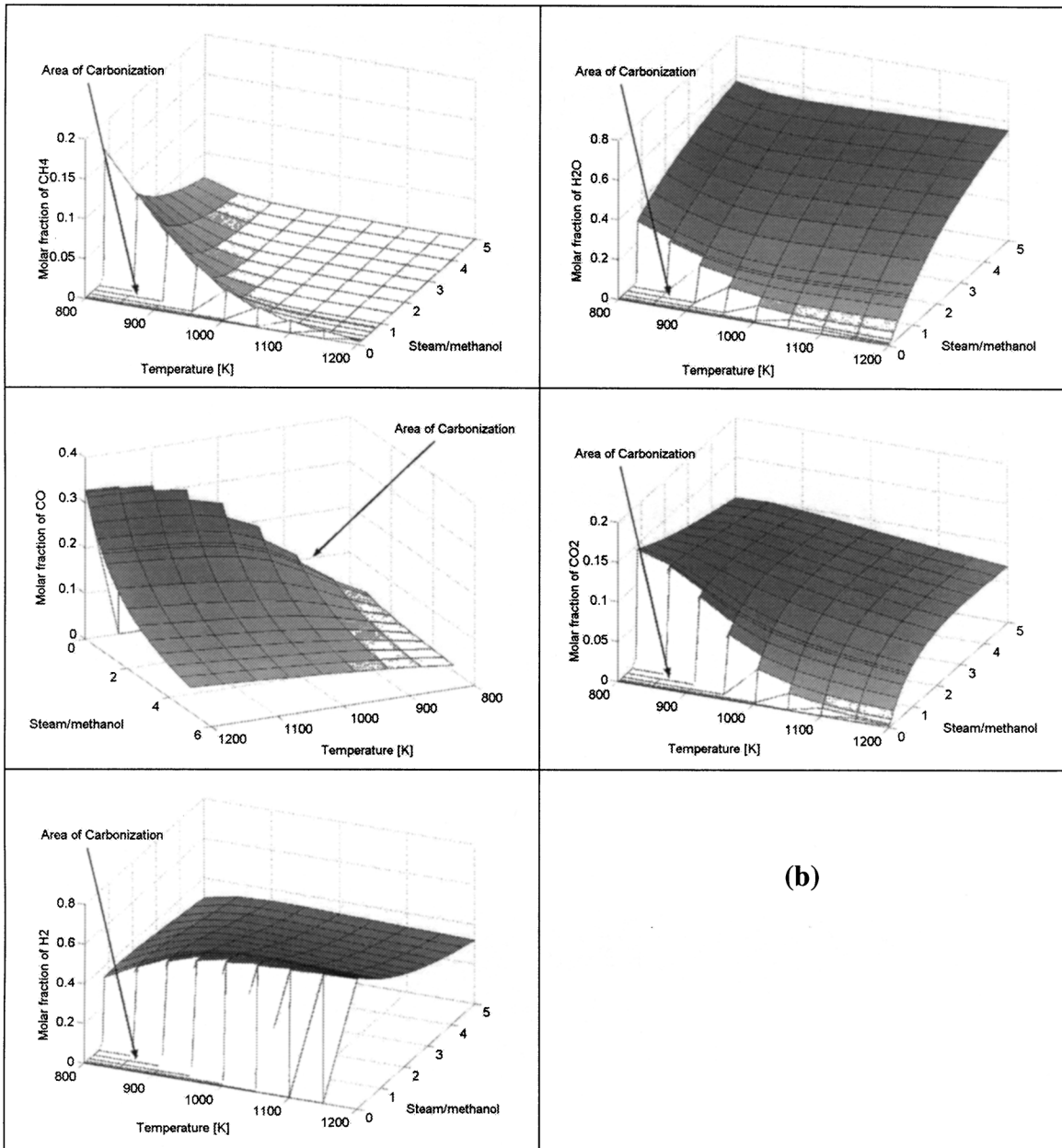


Figure 2B. Equilibrium composition of the steam reforming of (b) methanol, (continued).

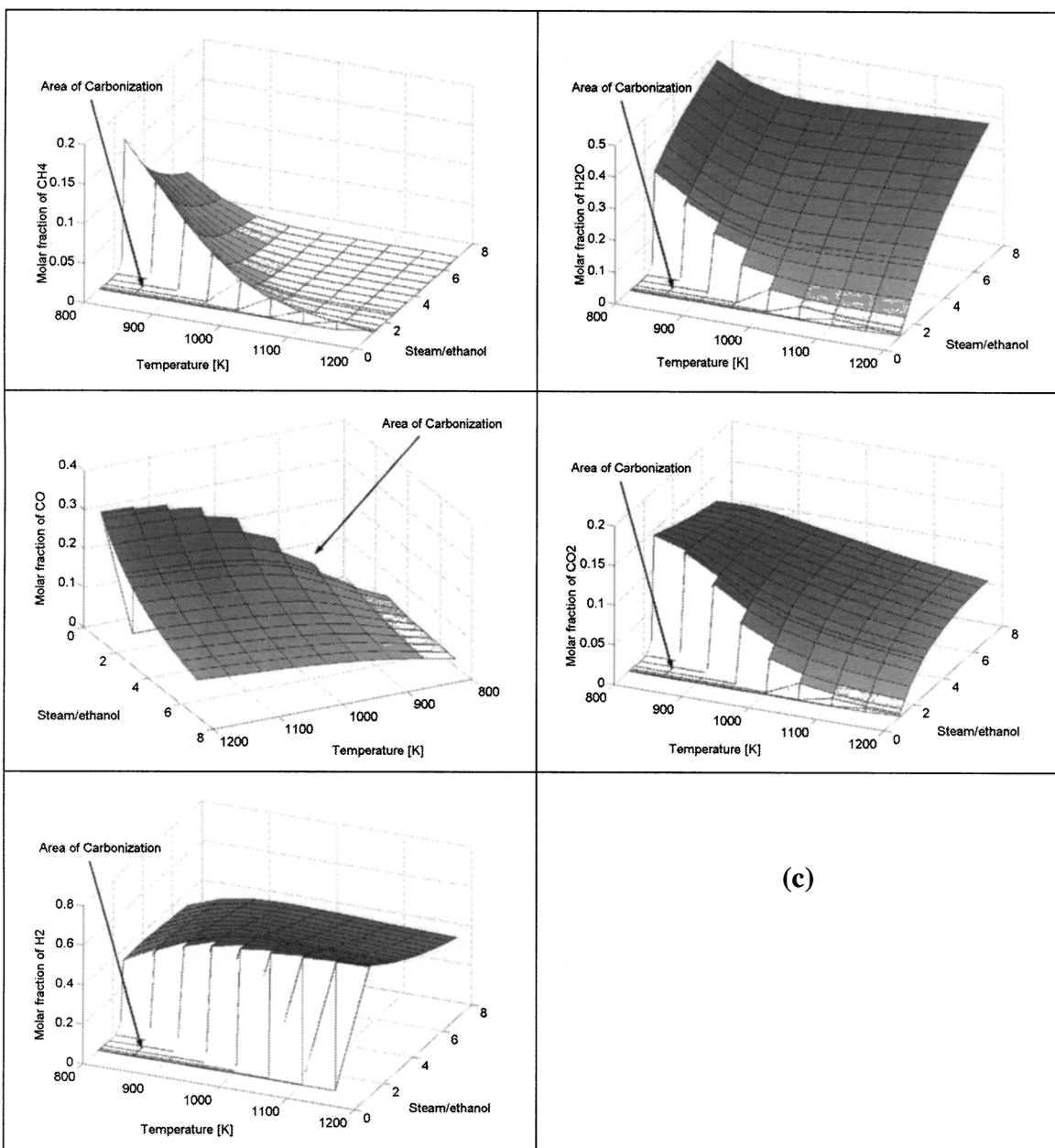


Figure 2C. Equilibrium composition of the steam reforming of (c) ethanol, (continued).

where $-\Delta H^\circ$ is the lower heating value (LHV) of the fuel at the standard conditions (Table 1) and q is the electrical charge passing through the electrolyte, which has been set equal to $q = 8F, 6F, 12F,$ and $50F$ for methane, methanol, ethanol, and gasoline, respectively. Maximum efficiency, η , represents the upper limit for the efficiency of a SOFC running under reversible (that is, zero-load) conditions. The real SOFC runs under nonequilibrium conditions, and the average cell voltage is $\bar{U} < \bar{E}$. In this case, the useful characteristic of the SOFC is a relative power, p_r , equal to the ratio of the current power, P_{actual} , to the maximum (reversible) one, P . It is possible to show that the relative power is determined

by the average electromotive force as

$$p_r = \frac{P_{\text{actual}}}{P} = \frac{4\bar{U}(\bar{E} - \bar{U})}{\bar{E}^2} \quad (35)$$

when all operative parameters (temperature, utilization, and partial pressures of the reagents) remain constant. Furthermore, the actual efficiency of the SOFC system, η_{actual} , can be calculated by substituting \bar{E} by \bar{U} in Eq. 34, and the dependence of the efficiency on the relative power can be obtained through appropriate algebraic rearrangements from the

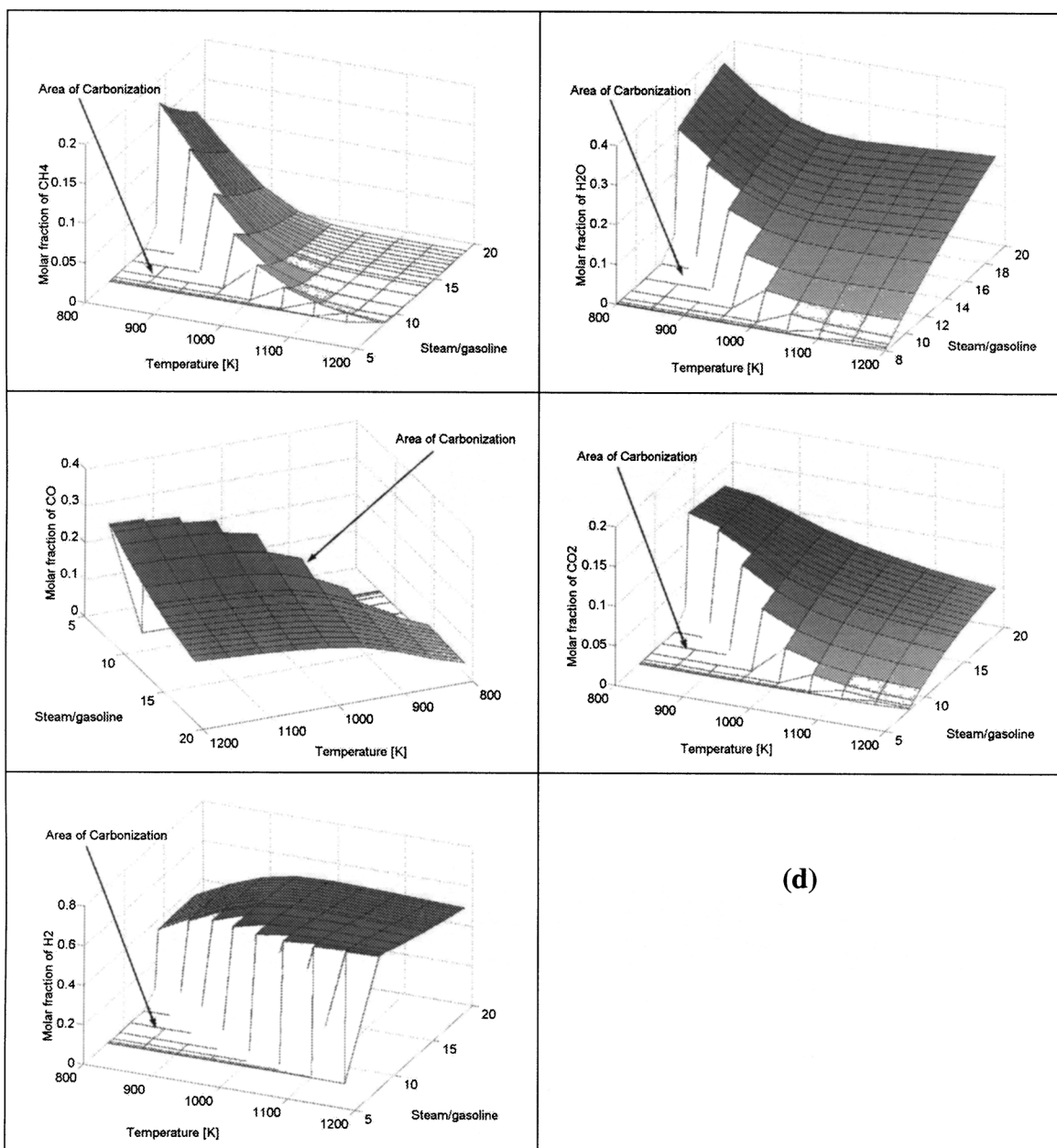


Figure 2D. Equilibrium composition of the steam reforming of (d) gasoline.

expression (Demin and Tsiakaras, 2001)

$$\eta_{\text{actual}} = 0.5\eta(1 + \sqrt{1 - p_r}) \quad (36)$$

Equation 36 clearly shows the importance of the maximum efficiency, η , since this value and the relative power determine the actual efficiency of the SOFC.

Results and Discussion

The conditions that are conducive for carbon formation in the equilibrium mixture of steam reforming for the cases of methane, methanol, ethanol, and gasoline were determined

calculating the carbonization boundaries (BC) of Figure 1. These boundaries represent the limiting steam/fuel ratios above which carbon deposition is thermodynamically impossible. As shown, the higher the carbon content in the mole of a fuel, the higher the reforming factor (at a given temperature) should be in order to avoid carbon deposition. The BC of gasoline lie much higher than the others, while methane requires lower reforming factors than ethanol at low temperatures ($< 1,100$ K) and almost the same at higher temperatures. Finally, methanol has a smaller area of carbonization than all other cases because it contributes the minimum number of carbon atoms per mole and requires the smallest stoichiometric factor for complete reforming. For any fuel, the limiting values at the BC decrease as the temperature

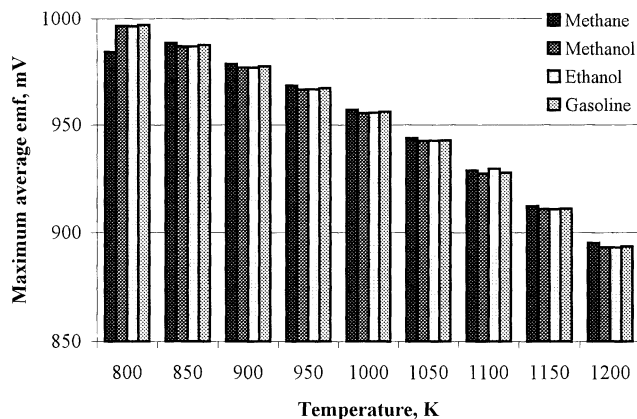


Figure 3. Maximum average emf for any fuel selected in its most suitable conditions.

increases. Furthermore, for the cases of methane and ethanol, a critical value of temperature exists ($\sim 1,100$ K), where both fuels present identical values for the steam/fuel molar ratio. It is obvious that the overall behavior of these fuels is expected to be similar for $T \geq 1,100$ K due to the thermody-

namics, and this is confirmed by the imminent analysis (see Figure 3 and the respective discussion).

The equilibrium compositions of all external reforming processes were calculated by solving the mixed system (Eqs. 18–20 and 24–26) and are presented in Figure 2. The selected reforming factors were taken near the boundary of carbon formation for each fuel, since higher values of m would result in undesirably high percentages of steam in the SOFC feedstream (reforming equilibrium composition). As shown in Figure 2, an increment of the reforming factor results mainly in increases of the molar fractions of steam and carbon dioxide and in decreases in the molar fractions of hydrogen, carbon monoxide, and methane. These last three are the only species that contribute to the generation of electricity in the SOFC. The equilibrium percentages of hydrogen and carbon monoxide increase as the temperature increases, while the concentration of methane is practically diminished at high temperatures and reforming factors. In particular, this is a useful coincidence because all the difficulties that arise for the electrochemical oxidation of methane can be avoided at the preceding conditions.

The analysis employed for the estimation of the distribution of emf along the cell channel revealed that the optimum conditions for the operation of the SOFC system correspond

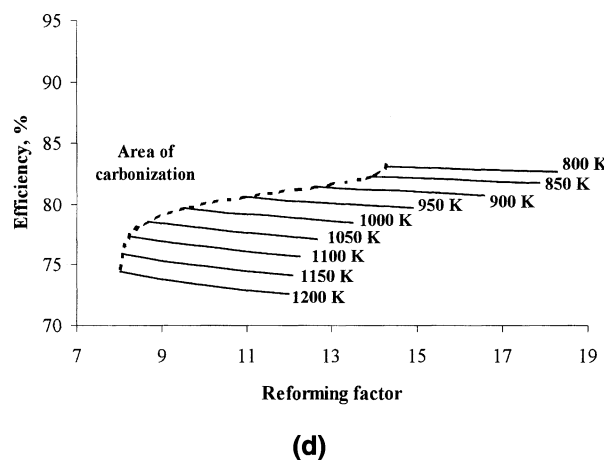
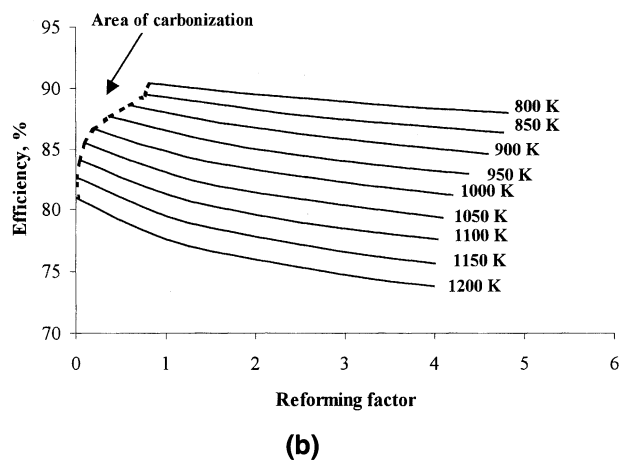
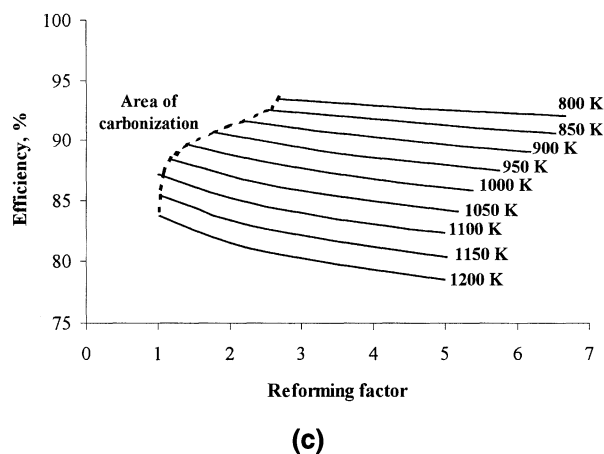
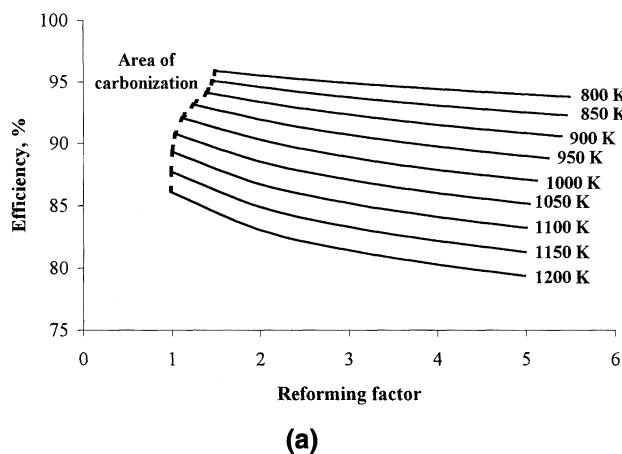


Figure 4. Overall efficiency distribution for (a) methane, (b) methanol, (c) ethanol, and (d) gasoline fed SOFC systems.

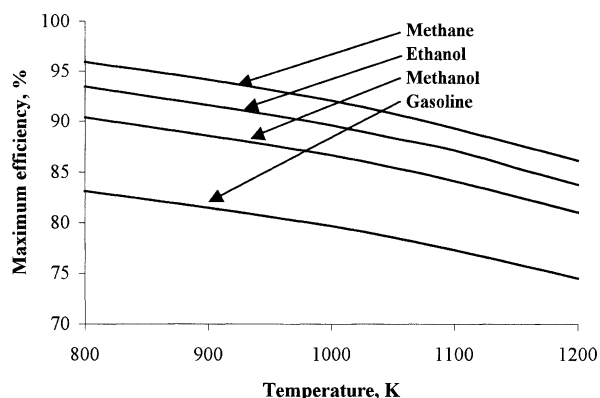


Figure 5. Maximum overall efficiency.

at conditions (T , m) at the boundary of carbon formation of each fuel option. This observation is reasonably explained, as these optimum conditions of steam reforming provide the maximum possible ratio of combustibles/oxidants in the SOFC feedstream. Therefore, Figure 3 presents the maximum average electromotive force, \bar{E} , obtained by Eq. 33, at the optimum conditions at the BC of each fuel option. Methanol, ethanol, and gasoline present similar optimum emf outputs, which decrease linearly to the temperature increment.

Figure 4 presents the overall efficiency, obtained by Eq. 34, for any fuel, which has been set at optimal conditions. Temperature is an unfavorable parameter for the efficiency, as it decreases with each temperature increment. This behavior is expected due to the linear dependence of efficiency on the average emf (see Figure 3). Furthermore, as was expected, maximum efficiency is presented, while reforming factors are very close to the boundary of carbon formation of each fuel due to the aforementioned effect of m on the total percentage of the combustible species in the SOFC feedstream.

The dependency of maximum efficiency (at the optimal conditions) on the temperature variation for each fuel is clarified in Figure 5, where the comparison of maximum efficiency for each fuel choice is presented. An almost linear decrement of maximum efficiency as temperature values become higher has been observed. Moreover, it is worth noticing that the worst absolute value for any fuel and temperature is high enough ($> 80\%$) for almost any practical use.

Figure 6 illustrates the dependence of the actual SOFC efficiency on the relative power for all fuel options in optimal conditions. It is also supposed that $T = 1,100$ K. It follows from Eq. 36 that fuel-cell efficiency is half of the maximum efficiency when the fuel cell runs at full power and the same classification of the four fuel options at conditions far from reversibility is used.

Selection of the most appropriate SOFC fuel is a multicriteria task involving both quantitative and qualitative parameters. The analysis made before shows that all fuels have a similar potential for the generation of electricity relative to the expected electromotive force output and the efficiency of the SOFC system. Methane was found to be the optimum fuel that provides the higher feasible electromotive force distribution and system efficiency, while methanol and ethanol

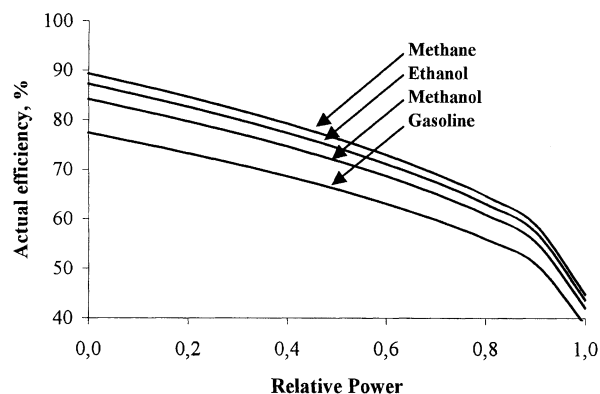


Figure 6. Dependence of the efficiency of SOFC on the relative SOFC power for any fuel option ($T = 1,100$ K).

were found to be promising alternative options. Gasoline utilization also was found to be promising when selecting appropriate conditions (high reforming factors) so as to avoid carbon formation. Thus, quantitative evaluation seems to be weak in order to ensure a definitively valid decision of an optimal fuel choice.

Conclusion

Thermodynamic analysis of the eligibility of methane, methanol, ethanol, and gasoline as fuels for the generation of electrical power in SOFCs is presented here. A mathematical model has been developed in order to adequately represent, according to the method of the direct minimization of Gibbs free energy, the spatial variance of the molar fractions of the components that are involved to the chemical reactions taking place within the SOFC system. The model described earlier also has minimized the influence of the arbitrary initial values needed for the iterative solution of the nonlinear system. All the fuels presented almost equal maximum average electromotive force (emf) output for optimal conditions. Furthermore, the overall system efficiency obtained by the model presented the following sequence for each fuel option: $\eta_{\text{methane}} > \eta_{\text{ethanol}} > \eta_{\text{methanol}} > \eta_{\text{gasoline}}$. Thus, methane seems to be the most appropriate fuel option to feed an SOFC system, while ethanol, methanol, and gasoline were found to be promising alternative options. The preceding fuel classification in terms of the SOFC efficiency remains unchanged, even when the fuel cell runs at actual (nonequilibrium) conditions.

Notation

- a = number of carbon atoms in the molecule of a fuel
- b = number of hydrogen atoms in the molecule of a fuel
- b_j = number of atoms of a chemical element j in the reformer feedstream
- c = number of oxygen atoms in the molecule of a fuel
- E = electromotive force at the relative position x of the SOFC stack, mV
- \bar{E} = average electromotive force of the SOFC stack at reversible operation, mV
- F = Faraday's constant, = 96,484 J/mol·V
- k = number of oxygen ions (O^{2-}) required for the electrochemical oxidation of a mole of a fuel

$k(x)$ = number of oxygen ions ($O^{=}$) traversing the electrolyte at position x according to the uniform oxygen flux assumption
 K_n = equilibrium constant of a respective reaction
 L = length of the anode channel of the SOFC stack
 m = reforming factor (steam/fuel mole ratio in the reformer feedstream)
 n_i = number of moles of the gaseous species i entering the SOFC stack
 n'_i = number of moles of the gaseous species i exiting the SOFC stack
 p_r = dimensionless relative power of the SOFC at nonequilibrium operation
 P = maximum SOFC power at reversible operation
 P_{actual} = SOFC power at nonreversible (actual) operation
 P_i = partial pressure (bar) of the gaseous species i
 q = electrical charge passing through the electrolyte per mol of a fuel
 R = universal gas constant ($= 8.314 \text{ J/mol}\cdot\text{K}$)
 T = absolute temperature, K
 \bar{U} = average electromotive force of the SOFC stack at nonreversible (actual) operation, mV
 x = position in the anode channel of the SOFC stack at distance x from its inlet
 y_i = molar fraction of the gaseous species i

Greek letters and property changes

α = dimensionless relative anode channel length ($= x/L$)
 α_c = carbon activity
 $(\Delta G_f^0)_T$ = Gibbs free energy of formation of a chemical compound i at temperature T , J/mol
 $-\Delta H^0$ = lower heating value (enthalpy of combustion) of a fuel at standard conditions
 η = maximum SOFC efficiency (%) at reversible operation
 η_{actual} = actual SOFC efficiency (%) at nonreversible (actual) operation
 λ_j = Lagrange multipliers

Literature Cited

- Amphlett, J. C., R. F. Mann, and R. D. Weir, "Hydrogen Production by the Catalytic Steam Reforming of Methanol: 3. Kinetics of Methanol Decomposition Using $C_{18}HC$ Catalyst," *Can. J. Chem. Eng.*, **66**, 950 (1988).
 Benjamin, T. G., E. H. Camara, and L. G. Marianowski, *Handbook of Fuel Cell Performance*, Institute of Gas Technology, Chicago (1980).
 Bridger, G. W., and M. S. Spencer, "Methanol Synthesis," *Catalyst Handbook*, Chap. 9, M. V. Twigg, ed., Manson, London p. 441 (1996).
 Burden, R. L., and D. J. Faires, *Numerical Analysis*, PWS-Kent, Boston, MA, p. 536 (1989).
 Chan, S. H., and H. M. Wang, "Thermodynamic Analysis of Natural-Gas Fuel Processing for Fuel Cell Applications," *Int. J. Hydrogen Energy*, **25**, 441 (2000).
 Clarke, S. H., A. L. Dicks, K. Pointon, T. A. Smith, and A. Swann, "Catalytic Aspects of the Steam Reforming of Hydrocarbons in Internal Reforming Fuel Cells," *Catal. Today*, **38**, 411 (1997).
 Demin, A. K., V. Alderucci, I. Ielo, G. I. Fadeev, G. Maggio, N. Giordano, and V. Antonucci, "Thermodynamic Analysis of

- Methane Fueled Solid Oxide Fuel Cell System," *Int. J. Hydrogen Energy*, **17**, 451 (1992).
 Demin, A., and P. Tsiakaras, "Thermodynamic Analysis of a Hydrogen Fed SOFC Based on Proton Conductor," *Int. J. of Hydrogen Energy*, **26**, 1103 (2001).
 Docter, A., and A. Lamm, "Gasoline Fuel Cell Systems," *J. Power Sources*, **84**, 194 (1999).
 Evans, M. K., *The Economic Impact of the Demand for Ethanol*, Midwestern Governors' Conference, Lombard, IL (1997).
 Fishtik, I., A. Alexander, R. Datta, and D. Geana, "A Thermodynamic Analysis of Hydrogen Production by Steam Reforming of Ethanol via Response Reactions," *Int. J. Hydrogen Energy*, **25**, 31 (2000).
 Garcia, E. Y., and M. A. Laborde, "Hydrogen Production by the Steam Reforming of Ethanol: Thermodynamic Analysis," *Int. J. Hydrogen Energy*, **16**, 307 (1991).
 Hirschenhofer, J. H., D. B. Stauffer, R. R. Engleman, and M. G. Klett, *Fuel Cell Handbook*, 4th ed., Business/Technology Books, Orinda, CA (1997).
 Kobayashi, H., N. Takezawa, and C. Minochi, "Methanol Reforming Reaction Over Copper Containing Mixed Oxides," *Chem. Lett.*, **12**, 1347 (1976).
 Lwin, Y., W. R. W. Daud, A. B. Mohamad, and Z. Yaakob, "Hydrogen Production from Steam-Methanol Reforming," *Int. J. Hydrogen Energy*, **25**, 47 (2000).
 Margiloff, I. B., A. J. Reid, and T. J. O'Sullivan, "Ethanol: Manufacture and Applications," *Monohydric Alcohols*, ACS Symp. Ser., Vol. 159, American Chemical Society Washington, DC, p. 47 (1981).
 McMillan, J. D., "Bioethanol Production: Status and Prospects," *Renewable Energy*, **10**(2/3), 295 (1997).
 Minh, N. Q., and T. Takahashi, *Science and Technology of Ceramic Fuel Cells*, Elsevier, Amsterdam, The Netherlands (1995).
 Pimentel, D., G. Rodrigues, T. Wane, R. Abrams, K. Goldberg, H. Staecker, E. M. L. Brueckner, T. C. Chow, U. Govindarajulu, and S. Boerke, "Renewable Energy: Economic and Environmental Issues," *BioScience*, **44**, 536 (1994).
 Prince, R. G. H., "The Outlook for Liquid Fuels from Biomass," *Proc. World Congress on Chemical Engineering*, Tokyo, 489 (1986).
 Ridler, D. E., and M. V. Twigg, "Steam Reforming," *Catalyst Handbook*, Chap. 5, M. V. Twigg, ed., Manson, London, 225 (1996).
 Smith, J. M., H. C. Van Ness, and M. M. Abbott, *Introduction to Chemical Engineering Thermodynamics*, McGraw-Hill, New York (1996).
 Thomas, S., and M. Zalbowitz, *Fuel Cells: Green Power*, Los Alamos National Laboratory, Los Alamos, NM (1999).
 Thomas, C. E., B. D. James, F. D. Lomax, and I. F. Kuhn, Jr., "Fuel Options for the Fuel Cell Vehicle: Hydrogen, Methanol or Gasoline?" *Int. J. Hydrogen Energy*, **25**, 551 (2000).
 Tsiakaras, P., A. Demin, S. Douvartzides, and N. Georgakakis, "Ethanol Utilization in Solid Oxide Fuel Cells: A Thermodynamic Approach," *J. Ionics*, **5**, 206 (1999).
 Vasudeva, K., N. Mitra, P. Umasankar, and S. C. Dhingra, "Steam Reforming of Ethanol for Hydrogen Production," *Int. J. Hydrogen Energy*, **21**, 13 (1996).
 Wyman, C. E., *Applications of Cellulose Conversion Technology to Ethanol Production from Corn*, Alternative Fuel Division, National Renewable Energy Laboratory, CO (1994).

Manuscript received June 20, 2001, and revision received May 29, 2002.