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# Electricity from ethanol fed SOFCs: the expectations for sustainable development and technological benefits

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## Abstract

Based on a thermodynamic and economic analysis presented in the first part of this paper, ethanol is considered as an alternative fuel with suitable characteristics for electricity generation in SOFCs. Ethanol fed steam reformer-SOFC systems attain high theoretical efficiencies in the range of 83.7–93.4% operating at carbon-free conditions between 800 and 1200 K. These efficiencies classify ethanol as the second most valuable fuel option for SOFCs after natural gas, higher than important other fuel candidates such as gasoline and methanol. A discussion is made upon the benefits obtainable from the utilization of ethanol for generation of electricity in SOFCs and a complete “ethanol scenario” is proposed as a competitive energy policy and a step forward to the target of sustainable development. The analysis reveals the cost relations between each fuel scenario and focuses upon the measures required so as the “ethanol scenario” to break through the threshold of economic viability. © 2003 International Association for Hydrogen Energy. Published by Elsevier Ltd. All rights reserved.

*Keywords:* Ethanol energy; SOFC; Energy policy

## 1. Introduction

Solid oxide fuel cells have grown in recognition as a viable high temperature fuel cell technology able to convert chemical energy directly into electricity with high efficiencies unattainable from all conventional thermal engines [1]. The high operating temperature of SOFCs ( $> 650^{\circ}\text{C}$ ), allows internal reforming, promotes rapid kinetics with non-precious materials and offers high flexibility in fuel choice. Various fuel options such as natural gas, methanol, ethanol and gasoline [2,3] are considered feasible for SOFC operation, offering a very significant ecological dimension in the problem of effective energy conversion.

It is well known that both natural gas and gasoline are *mineral* fuels and their deposits are limited enough to be considered as an appropriate global solution for the energy

problem. Furthermore, both these fuels have a significant influence to the increment of the 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. In this direction, it is of great importance that these fuels can be manufactured directly from agricultural cultivations, providing extra benefits through strengthening agricultural activities and lowering environmental pollution.

Ethanol has been proposed as raw material for many applications, such as the production of useful chemicals and/or electrical power. The basic difference of ethanol in comparison with other fuels is the feasibility of its production from biomass with biochemical processes [4,5]. Manufacturing technology of ethanol from biomaterial is practically unchanged for years and relies on the microbial fermentation of the sugars or on the hydrolysis of the starch-containing compounds to the corresponding sugar containing [4–6]. In this respect, ethanol can be considered as an economically

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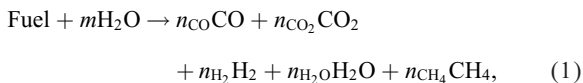
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attractive alternative green power source promising low pollutant emissions and controlled combustion having positive impact both on economy and the environment [7].

An appropriate external process in the fuel is necessary in order to obtain a gas mixture rich in hydrogen. Steam reforming is a commonly used process, where the reformates are considered as the SOFC feedstream. Ethanol steam reforming has been investigated for hydrogen production in various reports [8–10], while Tsiakaras et al. [11] undertook the analysis of ethanol utilization in SOFCs. In this work, ethanol steam reforming was recognized as the most appropriate external process allowing SOFC efficiencies of order of 90%.

## 2. Thermodynamic analysis of various fuel options for SOFCs

Before routed in the SOFC, all carbonaceous fuels must be transformed in a mixture of gases rich in hydrogen reacting with steam in a reformer operating at elevated temperature. The equilibrium gas mixture coming from the reformer contains only five components of noticeable concentration: carbon monoxide, carbon dioxide, hydrogen, steam and methane [8,9,12]. Therefore, the full transformation of the initial fuel-steam system into the equilibrium mixture can be expressed as follows [11]:



where  $m$  represents the steam to fuel mole ratio, which is alternatively denoted as “reforming factor”. The equilibrium composition derived from steam reforming was described by a non-linear system of logarithmic equations [3,11]. After some manipulations, the unknown molar fractions  $y_{\text{fuel}}$ ,  $y_{\text{CO}}$ ,  $y_{\text{CO}_2}$ ,  $y_{\text{H}_2\text{O}}$ ,  $y_{\text{CH}_4}$  and  $y_{\text{H}_2}$  can be derived numerically [3].

The basic operation principle of a SOFC relies on the continuous supply of its anode by a mixture of hydrogen, carbon monoxide and methane while its cathode is exposed to atmospheric air. Carbon monoxide and methane are gradually oxidized by steam providing secondary hydrogen and hydrogen oxidation is considered as the primary electromotive reaction in the cell. Electromotive force (emf) was then calculated according to the Nernst equation

$$E = \frac{RT}{4F} \ln \frac{p_{\text{O}_2(c)} p_{\text{H}_2(a)}^2}{p_{\text{H}_2\text{O}(a)}^2} \quad (2)$$

where  $R$  is the universal gas constant,  $T$  is the absolute temperature of the cell,  $F$  is the Faraday constant and “a” and “c” stand for anode and cathode, respectively. It was supposed that the SOFC cathode space is fed by air and therefore  $p_{\text{O}_2(c)} = 0.209$ . Furthermore, the average emf of a

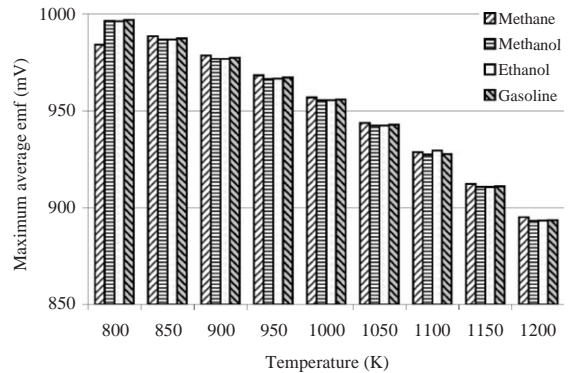


Fig. 1. Comparison of the maximum theoretical average emf established in a SOFC stack fed with various fuels.

multi-cell SOFC stack was defined as

$$\bar{E} = \int_0^1 E(x) dx, \quad (3)$$

where  $x = x^*/L$  represents an independent dimensionless spatial variable and  $L$  is the length of the multi-cell anode channel. Maximum overall (average) emf, obtained by Eq. (1), is presented in Fig. 1 for the most suitable conditions in terms of  $m$ . Finally, the maximum SOFC efficiency was calculated as

$$\eta = \frac{W}{-\Delta H^0} = \frac{q\bar{E}}{-\Delta H^0}, \quad (4)$$

where  $-\Delta H^0$  represents the lower heating value (LHV) of each fuel at the standard conditions and  $q$  is the electrical charge passing through the electrolyte. Although such high utilizations are practically unattainable, fuel utilization in the SOFC anode channel for all the cases examined was set equal to 99.99% because the first law of thermodynamics concerns the maximum theoretically allowable values.

Fig. 2 presents the overall efficiency obtained by Eq. (4). Temperature of the SOFC is an unfavourable parameter for the efficiency as it decreases with temperature increment. This behavior is expected due to the linear dependence of efficiency on overall emf (see Fig. 1). Furthermore, maximum efficiency is presented while reforming factor is very close to the boundary of carbonization and reduces, as its values become higher.

The dependency of maximum efficiency in optimal conditions on the variation of the operational temperature is presented in Fig. 3. Furthermore, a comparison of maximum efficiency produced by ethanol with those produced by natural gas, methanol and gasoline [3] is presented. An almost linear decrement of maximum efficiency as temperature values become higher has been observed. Moreover, the worst absolute efficiency value for any fuel and temperature is high enough for almost any practical use.

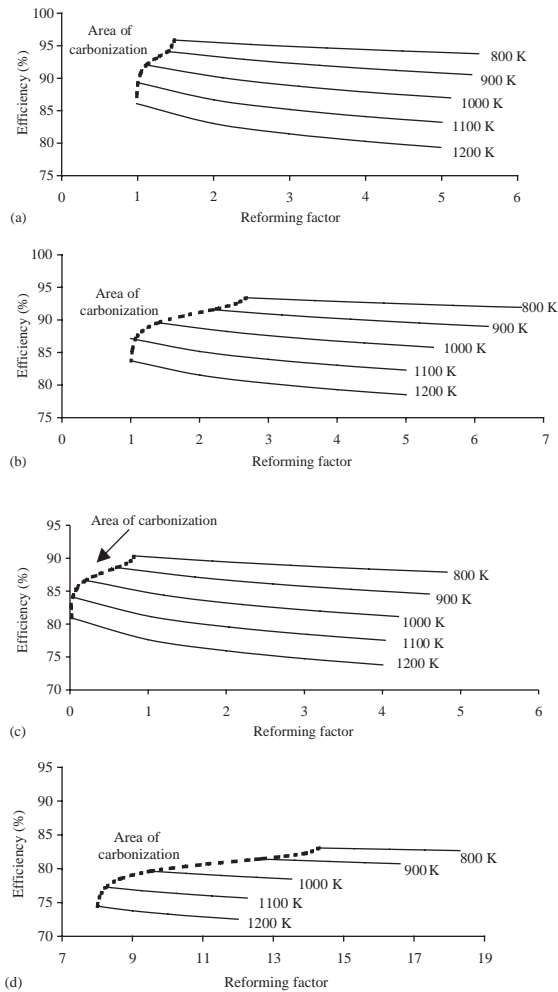


Fig. 2. Effect of temperature and reforming factor on the theoretical efficiencies of a SOFC stack fed by: (a) methane; (b) ethanol; (c) methanol; and (d) gasoline.

Maximum efficiency represents an upper limit for the efficiency of a SOFC run under zero-load conditions. The real SOFC runs under non-equilibrium conditions, i.e. at conditions where the average cell voltage is less than  $\bar{E}$ . The actual SOFC efficiency can be obtained as [12]

$$\eta_{\text{actual}} = 0.5\eta(1 + \sqrt{1 - p_r}). \quad (5)$$

where  $p_r$  is a relative power equal to a ratio of the current power to the maximum one.

### 3. Economic analysis

Selection of the most appropriate SOFC fuel is a multi-criteria task involving both quantitative and qualitative parameters. As was showed above, all commonly used

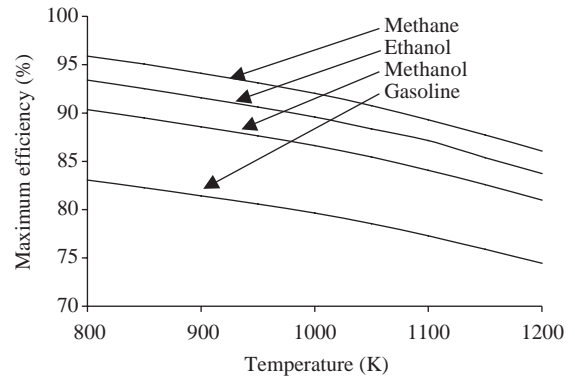


Fig. 3. Comparison of the maximum (optimum conditions) theoretical efficiencies for methane, ethanol, methanol and gasoline.

fuels have similar potential for generation of electricity with respect the expected emf output and the efficiency of the combined system. Thus, quantitative evaluation seems to be weak in order to accurate a definitively valid decision of an optimal fuel choice. Some fundamental qualitative parameters, which are characteristic for each fuel, should be examined; the existed infrastructure, the production costs as well as the environmental impact. Furthermore, some relative parameters like the self-sufficiency in energy resources and the agricultural assistantship in national level should also be considered.

Considering a standard cost for 1 kg of natural gas, one can express as  $\theta$  the ratio of the cost of 1 kg of ethanol, methanol, or gasoline to this cost of natural gas. Then, expressing as  $\xi$  the cost of the joule of electricity produced in a steam reformer-SOFC system fuelled with any of these fuels to the associated cost of electricity produced similarly from natural gas at the same operation temperature, one can write the following relation [13]:

$$\xi = \frac{M_{\text{fuel}} \Delta H_{\text{meth}}^0 \eta_{\text{meth}}}{M_{\text{meth}} \Delta H_{\text{fuel}}^0 \eta_{\text{fuel}}} \theta, \quad (6)$$

where  $M_i$ ,  $\Delta H_i^0$ , and  $\eta_i$  are molecular weight, enthalpy of combustion at standard conditions, and maximum efficiency of SOFC at a given temperature for natural gas and ethanol, methanol or gasoline, respectively. It is obvious that Eq. (6) implies a linear dependence of  $\xi$  on  $\theta$ . Fig. 4, illustrates this dependence for ethanol, methanol and gasoline and shows the limiting  $\theta$  values below which every fuel scenario becomes competitive to the scenario of natural gas. It was found that the cost of ethanol must be less than 53% of the cost of natural gas (per kg) in order the price of electricity of the “ethanol scenario” to be more competitive to that provided by natural gas. Similarly, the limiting values for methanol and gasoline are calculated equal to 42% and 86% of the cost of a kg of natural gas, respectively. This analysis provides a simple index for the evaluation of the relative

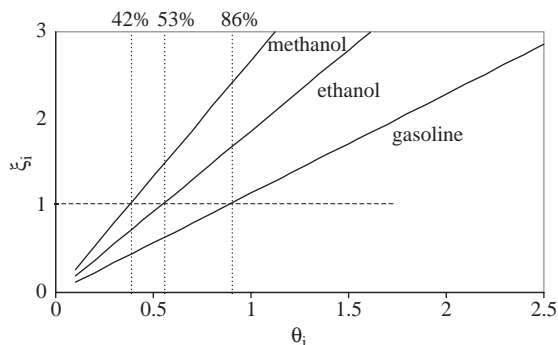


Fig. 4. Cost competitiveness of each fuel scenario with the scenario of natural gas ( $\theta$  is cost relation per kg and  $\xi$  is cost relation per Joule of electricity,  $i$  = fuel index).

cost of the joule of electricity provided by each fuel when their prices are known.

#### 4. The “ethanol scenario”

On the basis of the technological analysis made above, ethanol exhibits quite similar performance with all other fuels when fed in SOFCs. However, in contrast to all other fuel options, ethanol has an intrinsic advantage of great importance during designing an energy policy: it is renewable. The possibility of ethanol manufacture through hydrolysis and/or fermentation of cellulosic biomass is known for years and relative know-how is currently in a level that can ensure low cost production. On the other hand, when made from agricultural products, ethanol can undergo a complete circle of life from cultivation to products through combustion and vice versa through photosynthesis. This circle can assure negligible environmental damaging unfeasible from the utilization of mineral fuels. In this respect, rational utilization of bioethanol in SOFCs can be considered a scenario of high ecological value. Moreover, ethanol is an easily transportable liquid and less toxic than methanol and gasoline.

The complete implementation of the “ethanol scenario” requires an agricultural orientation to crops and plants such as sugar beets, sugar canes, corn or sorghum that can provide high yields of ethanol with low manufacture cost. In this respect, this scenario can break through the threshold of economic viability acquiring a substantial market share only in case it can provide a rise in farm income. In accordance to an economical report made in USA during 1997 [7] the key characteristic for the viability of the “ethanol scenario” is the demand of ethanol which influences positively both farm income and cultivation size. In addition, it is shown that ethanol demand can also have combined multiplying effects in economy increasing employment due to higher farm income, to higher investments in farm equipment and finally due to operation of ethanol plants.

The economic impact of bioethanol production for generation of electricity in SOFCs is of positive character for two more reasons. The first is related with the financial savings due to the domestic manufacture of ethanol. Being a domestic feedstock, bioethanol rises independence on fuel imports, declines national budget deficit, increases state or local tax receipts and improves foreign trade balance. All these benefits have magnitude directly proportional to the extension of ethanol market and, obviously, can lead in a mid- or long-term policy aiming at competitive prices of electricity. The second influence results directly from the technological benefit of energy saving due to electricity generation in a highly efficient energy conversion device as a SOFC. When all conventional electricity generators exhibit efficiencies below 45%, SOFC technology is capable to exploit usefully up to 90% of the heating value of a fuel, as shown earlier. In other words, if SOFCs are to be technologically developed in a level that their real performance be close to theoretical, the useful value of every fuel (also of ethanol) can be almost doubled. Further, ethanol utilization in SOFCs can occur directly after its production without requirements for high purity that involve distillation costs. The dilution of the raw product of ethanol manufacture is typically with a molar ratio of water/ethanol between 8.4 and 12 that can undergo directly the process of the external reforming. The by-products of ethanol processing in a large-scale utilization of this scenario can boost national exports offering additional revenues.

#### 5. Discussion

Just like all new energy policies, the “ethanol scenario” requires initial theses that will kick-start implementation in an environment of low risk for investments. The existed infrastructure of ethanol distribution is limited and needs expansion. Accordingly, an initial period of subsidies is inevitably necessary to boost required processes and break through market barriers. In fact, some of the most important impediments will inevitably be reluctance in investments and lack of awareness of the overall policy or technology.

From economical point of view, fuel cells are currently considered a relatively expensive technology. Endeavors to reduce capital cost as well as to increase performance are underway in research and pilot level worldwide. More precisely, stack lifetime and power density influence stack replacement costs and maintenance requirements, while electrical efficiency and plant availability influence the likely payback time for a given capital cost. Therefore, “ethanol scenario” can be completely exploited as a retributive policy only after optimization of these cost-performance relations. However, the principle of “accumulative experience” might contribute significantly in successful results if efforts were undertaken to fulfil the scenario even immediately. Practice has shown that the unit cost of a technology decreases with time because experience is accumulated regarding

manufacture, maintenance and operation. As the learning rate of the technology increases, it increases also the retributive revenues from its utilization and it reduces the time period of cost depreciation. To appreciate this suggestion, one can refer to policies of technology procurement, which have already been active in some European countries [14,15].

The Fifth Framework Program of the European Union that was adopted at the end of 1998, emphasizes the need for research to respond to important economic, social and environmental challenges enabling greater opportunities for innovation [16]. This approach implies that fuel cell commercialization should be taken as a challenge coherent to the development of energy policies that can contribute in solution of different simultaneous problems. As a result, the “ethanol scenario” may be considered as a complete energy policy proposal on the basis of both innovation and usefulness. Innovation originates directly from the application of a new efficient technology for large-scale power production whilst usefulness is expressed by meeting a multiple target on the contract of all contemporary economical, environmental and social challenges. Finally, the liberalization policy of the electricity markets may be considered another ally of the “ethanol scenario”. Liberalization means opening up of formerly closed monopoly markets to competitive forces [17]. Under this definition, the liberalization of the electricity markets in Europe not only allows private capital to take part in electricity policies but also prompts vertical integrated companies to develop exogenous differentiated activities through independent management. Therefore, innovation and diversification in electricity industries are in reality challenging targets also for the so-called monopolistic electricity producers.

## 6. Conclusions

Based on both technical and economical considerations, the present study provides a complete scenario of energy policy suggesting domestic manufacture of ethanol from appropriate agricultural cultivation and subsequent electricity generation in ethanol fed SOFCs. The viability of this scenario is closely related with the development of an ethanol market with increased demand for ethanol production and utilization. If this scenario achieve to acquire substantial market share, it is expected to provide multiple benefits in economical, social and environmental level.

Ethanol utilization in SOFCs exhibits quite similar potential for power generation with all other mineral fuels. However, being a renewable energy source it is capable of minimizing net CO<sub>2</sub> accumulation in atmosphere as well as to provide substantial economical benefits rising farm income, increasing employment and reducing national dependency on fuel imports. All these benefits have magnitude

proportional to the demand of ethanol and may be considered feasible in short-term following a kick-start policy of appropriate subsidies.

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## References

- [1] Hirschenhofer JH, Stauffer DB, Engleman RR, Klett MG. Fuel cell handbook. Orinda, USA: Business/Technology Books, 1997.
- [2] Thomas S, Zalowitz M. Fuel cells: green power. New Mexico, USA: Los Alamos National Laboratory, 1999.
- [3] Douvartzides SL, Coutelieres FA, Tsiakaras PE. Fuel options for SOFCs: a thermodynamic analysis. *AICHE* 2003;49: 248–57.
- [4] McMillan JD. Bioethanol production: status and prospects. *Renewable Energy* 1997;10(2/3):295–302.
- [5] Wyman CE. Applications of cellulose conversion technology to ethanol production from corn. Colorado, USA: Alternative Fuel Division, National Renewable Energy Laboratory, 1994.
- [6] Margiloff IB, Reid AJ, O’Sullivan TJ. Ethanol: manufacture and applications, in monohydric alcohols. ACS Symposium Series, Washington, DC, USA, 1981.
- [7] Evans MK. The economic impact of the demand for ethanol. In: Proceedings of the Midwestern Governors’ Conference. Lombard, IL, 1997.
- [8] Garcia EY, Laborde MA. Hydrogen production by the steam reforming of ethanol: thermodynamic analysis. *Int J Hydrogen Energy* 1991;16(5):307–12.
- [9] Vasudeva K, Mitra N, Umansankar P, Dhingra SC. Steam reforming of ethanol for hydrogen production: thermodynamic analysis. *Int J Hydrogen Energy* 1996;21(1):13–8.
- [10] Fishtik I, Alexander A, Datta R, Geana D. A thermodynamic analysis of hydrogen production by steam reforming of ethanol via response reactions. *Int J Hydrogen Energy* 2000;25: 31–45.
- [11] Tsiakaras P, Demin AK, Douvartzides S, Georgakakis N. Ethanol utilization in SOFCs: a thermodynamic approach. *Ionics* 1999;5:206–12.
- [12] Demin A, Tsiakaras P. Thermodynamic analysis of a hydrogen fed SOFC based on proton conductor. *Int J Hydrogen Energy* 2001;26:1103–8.
- [13] Douvartzides S, Tsiakaras P. Thermodynamic analysis of SOFC systems with external steam reforming of natural gas and ethanol. *Energy Sources*, in press.
- [14] McDonald A, Schratzenholzer L. Learning rates for energy technologies. *Energy Policy* 2001;29:255–61.
- [15] Olerup B. Technology development in market networks. *Energy Policy* 2001;29:169–78.
- [16] Borthwick WKD. The European Union approach to fuel cell development. *J Power Sources* 2000;86:52–6.
- [17] Baentsch F. Liberalisation—challenges and opportunities for fuel cells. *J Power Sources* 2000;86:84–9.