



Light alcohols/methane fuelled molten carbonate fuel cells: a comparative study

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Abstract

The configuration of internal reforming has been successfully applied in molten carbonate fuel cells (MCFCs), allowing a flexibility in fuel use unfeasible for other kind of fuel cells, which operate at lower temperatures. On this basis, a theoretical study able to provide useful information on the use of ethanol, methanol or methane as fuel in MCFCs has been carried out. The paper reports the most significant results obtained from this comparative analysis, which allows clear evaluations about the energetic suitability of each examined fuel. This study, developed by the support of a mathematical model, gave as main results the chemical, electrical and thermal power densities obtainable by each raw fuel and evidenced the limits or gains arising from the variation of the MCFCs operative parameters. Leaving out the economical point of view, ethanol present some advantages (natural availability, storage and handling safety, heat distribution on the catalyst, etc.) compared with the other fuels. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

For several years, a lot of researchers pointed their efforts towards the investigation of the problems causing the worsening of the performance and the limitation of the useful lifetime of the molten carbonate fuel cells (MCFCs). At the present state of art, the mechanisms through which these problems affect the MCFCs behaviour are extensively studied [1]. In parallel to these researches, attention has been paid on the problems correlated to the typology of the raw fuel used to supply the anodic compartment of the cell. In fact, MCFCs can be fed with different fuels including carbon monoxide, a very active poison for the Pt based catalysts used in low temperature fuel cells, that is easily converted to hydrogen and carbon dioxide. This policy is in agreement with a more wide need of energy sources diversification, traditionally based on the massive use of fossil hydrocarbons, with alternative fuels like alcohols that can be directly produced by biomass fermentation or by synthesis processes [2].

The MCFCs can use as fuel the hydrogen produced by an external (ER) or internal reformer. In the case of internal, reforming two possible configurations are pur-

suable: direct internal reforming (DIR) or indirect internal reforming (IIR).

The use of alcohols as fuels for MCFCs [3] presents a large theoretical feasibility and does not require any external reformer reactor, since it is enough to apply a proper cell geometry like that of DIR or IIR. With such types of configurations, the reformer section is located inside the cell hardware, thus, the advantage of the direct utilization of the electrochemical heat rejected by the cell to supply the endothermic reforming reaction is evident. Furthermore, the high operational temperature of MCFCs (~ 923 K) allows a thermodynamic equilibrium that guarantees acceptable yields in terms of conversion for fuel as methane, methanol or ethanol.

In particular, the IIR configuration—which differs from DIR because the reforming catalyst is physically separated from the anode compartment—is, at present, the easier and more convenient to be realized. A reduced poisoning of the reforming catalyst, due to the diffusion of electrolyte vapours, is a peculiar advantage of this configuration.

The reactions of methane, methanol and ethanol reforming are known in literature [4–8] both in terms of thermodynamic and kinetic, even if the efforts devoted to the development of catalysts to be used for these processes is very active. On the basis of these assumptions and consid-

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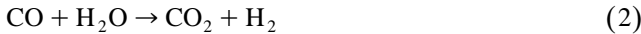
ering the impressive efforts addressed towards the development of MCFCs, a wide investigation has been carried out to evaluate the energetic convenience to supply these systems with methane, methanol or ethanol.

2. Modeling development

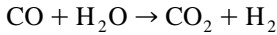
The first step of the modeling approach concerned the selection of the partial reactions than can well represent the methane, methanol and ethanol reforming processes.

García and Laborde [9] have been the first to analyze, from a thermodynamic point of view, the ethanol steam reforming. Recently, Vasudeva et al. [10] improved the model proposed by García, considering also the formation of coke. Finally, Freni et al. [11] and Freni and Maggio [12] applied such models to study the steam reforming reaction in an MCFC based on IIR. These previous studies and literature evidences lead to the following step reactions.

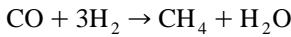
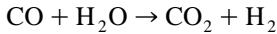
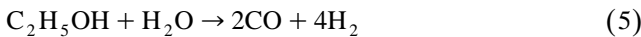
For methane reforming:



for methanol reforming:



for ethanol reforming:



All the processes involve the water gas shift reaction (Eq. (2)), while the methanol and ethanol reforming are characterized by the inverse methane steam reforming reaction (Eq. (4)).

The equilibrium constants associated to the reactions (1)–(5) can be expressed as:

$$K_1 = \frac{x_{\text{CO}} x_{\text{H}_2}^3}{x_{\text{CH}_4} x_{\text{H}_2\text{O}}} \quad (6)$$

$$K_2 = \frac{x_{\text{CO}_2} x_{\text{H}_2}}{x_{\text{CO}} x_{\text{H}_2\text{O}}} \quad (7)$$

$$K_3 = \frac{x_{\text{CO}} x_{\text{H}_2}^2}{x_{\text{CH}_3\text{OH}}} P^2 \quad (8)$$

$$K_4 = 1/K_1 \quad (9)$$

$$K_5 = \frac{x_{\text{CO}}^2 x_{\text{H}_2}^4}{x_{\text{C}_2\text{H}_5\text{OH}} x_{\text{H}_2\text{O}}} P^4 \quad (10)$$

where x_i is the molar fraction of the various gaseous components and P is the total pressure (atm).

Equilibrium compositions have been calculated by solving the systems of non-linear equations formed by the equilibrium constant relationships and the mass balances corresponding to every steam reforming process, according to previously reported models [12].

Because of the complexity of the analytical solution, a mathematical model based on an iterative approach has been used to solve these systems. Starting from an initial approximation for the reaction conversions and from the values of equilibrium constants of the single reactions, determined as a function of the temperature, a multi-dimensional globally convergent method [13] for non-linear system of equations has been used to calculate the anodic outlet gas composition.

The equilibrium constants were determined from thermodynamic data reported in literature [14] (see Appendix A).

When the cell is operating with production of electricity, the corresponding potential is affected by losses due to the electrode overpotentials and to the cell resistance. In this case, the cell potential, V , has been determined by the following expression:

$$V = V_o - (\mu_a + \mu_c) - J r_i \quad (11)$$

where V_o is the equilibrium potential (V) given by the Nernst equation:

$$V_o = E_o + \frac{RT}{2F} \ln \frac{P_{\text{H}_2} P_{\text{O}_2}^{1/2} P_{\text{CO}_2,c}}{P_{\text{H}_2\text{O}} P_{\text{CO}_2,a}} \quad (12)$$

μ_c and μ_a are the cathodic and anodic overpotentials (V), respectively, J the current density (A/cm^2), r_i the cell internal resistance ($\Omega \text{ cm}^2$), E_o the standard potential (V), R the universal gas constant ($8.314 \text{ J}/\text{K mol}$), T the cell temperature (K), F the Faraday constant ($96487 \text{ C}/\text{g-eq.}$) and P_i is the partial pressure of the gases.

The total power density is given as the sum of the electrical, thermal and chemical contributions:

$$W_{\text{tot}} = W_{\text{el}} + W_{\text{th}} + W_{\text{ch}} \quad (13)$$

In particular, the electrical and thermal power densities have been calculated, respectively, as:

$$W_{\text{el}} = J V \quad (14)$$

$$W_{\text{th}} = W_{\text{cell}} + W_{\text{lat}} + \frac{1}{S} C_1 \sum_i n_i (-\Delta H_i) \quad (15)$$

where W_{cell} is the power density due to the electrochemical heat released by the cell and to the ohmic resistance (W/cm^2), W_{lat} that due to the latent heats of steam, methanol and ethanol (W/cm^2), S is the cell surface (cm^2), the ΔH_i is the enthalpy (cal/mol) associated with the process reactions (i.e., (1)–(2) for methane; (2)–(4) for methanol; (2), (4)–(5) for ethanol reforming), n_i is the

corresponding outlet (inlet-converted) gas flows (mol/h) and $C_1 = 1.163 \cdot 10^{-3}$ is the conversion factor from cal/h to W . Besides, the chemical power density has been determined as the contribution due to the unreacted gases (methane, hydrogen, carbon monoxide and eventually methanol or ethanol), when totally burned by an oxygen excess:

$$W_{\text{ch}} = \{ -n_x \Delta H_x^{\text{comb}} - n_{\text{CH}_4} \Delta H_{\text{CH}_4}^{\text{comb}} - n_{\text{CO}} \Delta H_{\text{CO}}^{\text{comb}} - n_{\text{H}_2} \Delta H_{\text{H}_2}^{\text{comb}} \} (S)^{-1} \quad (16)$$

where n_x is equal to zero in the case of methane reforming, while it is equal to the outlet moles of methanol ($n_{\text{CH}_3\text{OH}}$) or ethanol ($n_{\text{C}_2\text{H}_5\text{OH}}$) when the reforming of one of these fuels is considered.

3. Catalysts

The most studied route for hydrogen production appears to be the steam reforming on Ni/MeO_x catalysts. The steam reforming of naphtha, for instance, can be carried out by a co-precipitated Ni/Al₂O₃ catalyst, defined ‘hydrotalcite’ [4], having a formula Ni₆Al₂(OH)₁₆ · CO₃ · H₂O and subsequently modified by the addition of La³⁺ to stabilize the structure. The methane steam reforming, in fact, requires temperatures higher than 773 K, due to the strong endothermicity of the reaction and Mg and/or Ca are usually introduced in the catalyst formulation to have an effective carbon removal from the surface. To lower the reaction start temperature, noble metal addition can be proposed [15], but it is too expensive for practical purposes.

Methanol can be reformed at much lower temperatures than methane on CuO-supported catalysts. Researchers have studied this process by using conventional CuO/ZnO and CuO–ZnO/Al₂O₃ catalysts [16], or modified catalysts by addition of Mn or Cr to operate at $T < 550$ K [5,6].

As provided by thermodynamics [9,10], the hydrogen production by the steam reforming of ethanol requires higher temperature than that of methanol and furthermore the formation of some methane can be expected. Recently, Haga et al. [7], screened several supported metal catalysts prepared by impregnation of aqueous solutions on alumina. Reversely to the methanol, the selectivity to the total oxidation (CO + CO₂) decreases in the order Co > Ni > Rh > (Pt, Ru, Cu) and only few methane is formed on the Cu, Ru, Co/Al₂O₃ catalysts.

The use of metallic membranes between the catalyst and the MCFC anode is recommended to reduce the poisoning of the catalyst due to the interaction with the electrolyte vapours [1]. The investigation on the employment of membranes, further demonstrates their capability to catalyze a wide range of reactions, when supported with appropriate catalysts and to move the equilibria towards

the reaction products. Garnier et al. [17], for instance, recently studied the hydrogen and higher hydrocarbons formation by methane dehydrogenation on Pd–Ag modified membranes and they obtained a C₂₊ yield of 16% at $T = 573$ K. The R&D of catalytic membranes are addressed to improve the endurance of the system easily deactivated by the carbon dissolution into the Pd lattice and the strong chemisorption of dehydrogenated species on the surface.

Any further detail on catalysts used for steam reforming can be found in Ref. [15].

4. Results and discussion

The nature of the methane, considered as the traditional fuel for MCFC, appears to be quite different from that of the ethanol and methanol. These differences are substantial because of the varied physical states at the atmospheric pressure and different molecular complexity. They influence both handling and hazard properties. The most significant differences between these fuels have been summarized in Table 1.

The energy density of a raw fuel is the first parameter to be examined when its use for power plant feeding is considered. Thus, the power density of an MCFC as a function of the nature and flow of the raw fuel has been determined and shown in Fig. 1. As expected, the ethanol presents the highest power density. This depends on the highest number of atoms of hydrogen produced by the reforming of a molecule of ethanol if compared to those of methane and methanol. In fact, by the reforming process, six volumes of hydrogen can be released from one volume of ethanol, four from the methane and three from the methanol.

The use of the ethanol results more advantageous if some other features, like its easier storage respect to the hydrogen and the lower toxicity respect to the methanol, are considered. In fact, at room temperature and pressure, 1 mole of ethanol has a volume of about 50 cm³, while 1 mole of methane corresponds to more than 20 cm³. The methanol presents a specific volume comparable to that of the ethanol, but it is more volatile and toxic than ethanol.

In Fig. 2, the polarization curves related to the three raw fuels, calculated assuming for them the same inlet flow (209.7 l/h), are reported. It is evident that the values of the open circuit voltage (OCV) do not change by changing the raw fuel; this indicates that the ratio between the partial pressures of the reaction products and of the reactants remains constant as well as the other parameters of the Nernst equation (Eq. (12)). On the contrary, the degree of utilization of the raw fuels appears to be different, in fact, at standard conditions (150 mA/cm²), it results to be equal to 25% for the ethanol, 37% for the methane and

Table 1

Physical properties and hazard (*) analysis of methane, methanol and ethanol at ambient conditions

	CH ₄	CH ₃ OH	C ₂ H ₅ OH
Density, g/cm ³	0.72 · 10 ⁻³	0.787	0.789
Combustion heat, KJ/g	55.68	22.67	29.81
Viscosity, g/cm s	1.09 · 10 ⁻⁴ _(g)	5.41 · 10 ⁻³ _(l) 9.68 · 10 ⁻⁵ _(v)	1.2 · 10 ⁻³ _(l)
Specific heat, J/g K	2.22 _(g)	2.53 _(l)	2.41 _(l)
Flammability (in air), % v/v	5.0 _{low} 15.0 _{up}	6.3 _{low} 39.2 _{up}	3.5 _{low} 15.0 _{up}
Autoignition T, K	811	843	698
Flash point, K	288.6 _{open} 285.2 _{closed}	85	286 _{closed}
Toxic acute (ingestion, inhal, skin abs.)	0, 1, 0	3, 2, 2	1, 0, 0
Toxic chronic (ingestion, inhal, skin abs.)	0, 1, 0	2, 2, 2	1, 1, 1
Fire (flame, spontaneous, explosive)	3, 0, 2	3, 0, 2	3, 0, 2
Storage and handling	gaseous fuel	liquid fuel—toxic	liquid fuel

(*) 0 = None; 1 = slight; 2 = moderate; 3 = high.

50% for the methanol. This difference directly influences the overpotential losses due to the gas diffusion and increases with the cell current density, modifying the slope of the specific polarization curve. Thus, a higher slope is noticeable for the curve corresponding to the fuel that present the highest utilization coefficient. For this reason, the polarization curve related to the methanol is lower with respect to the methane and the ethanol. This last one appears to be the most convenient (544 mV of potential at 200 mA/cm²).

The overall energy released by the cell is the resultant of different contributions: electricity, electrochemical, sensible heat, etc. Fig. 3 shows the cell power densities related to these contributions as a function of the type of raw fuel and for two different working conditions: (a) at constant overall power density ($W_{\text{tot}} = 331.79$ mW/cm²); (b) at constant inlet fuel flow (209.7 l/h).

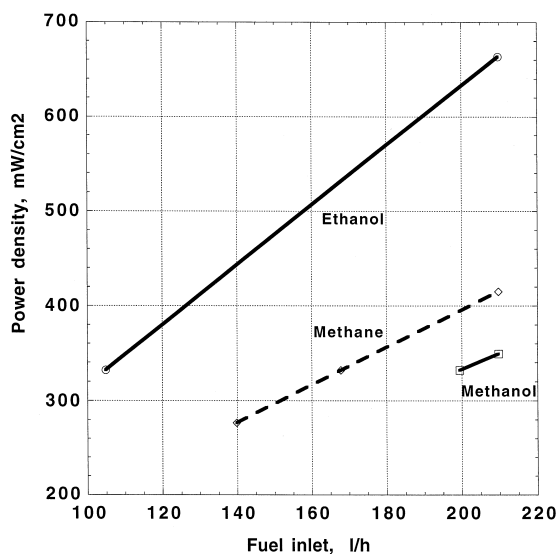


Fig. 1. Total power density vs. fuel inlet flow, calculated at base-line conditions*. Comparative plots for an IIR-MCFC cell fuelled with methane, methanol or ethanol. *Base-line conditions: $T = 923$ K, $P = 1$ bar, $S = 5016$ cm², $r_i = 0.75$ Ω cm².

All these evaluations have been carried out at a current density of 150 mA/cm², therefore, there are no meaningful differences in the electrical power densities corresponding to the use of each fuel, as dictated from Eq. (14). For instance, referring to the case of a constant inlet fuel flow, the ethanol shows the highest electrical power density ($W_{\text{el}} = 104$ mW/cm²) compared with methane and methanol (100.3 and 93.7 mW/cm², respectively), in agreement with cell voltage behaviours (see Fig. 2).

At the same overall power (Fig. 3a), the different power contributions are not significantly influenced by the raw fuel used. In particular, the energy available from the exhaust gas combustion is larger for the methane ($W_{\text{ch}} = 210.8$ mW/cm²) and smaller for ethanol ($W_{\text{ch}} = 202$ mW/cm²) and methanol ($W_{\text{ch}} = 174.4$ mW/cm²). Furthermore, the fuel that allows conditions close to the thermal equilibrium is the methane ($W_{\text{th}} = 24.5$ mW/cm²),

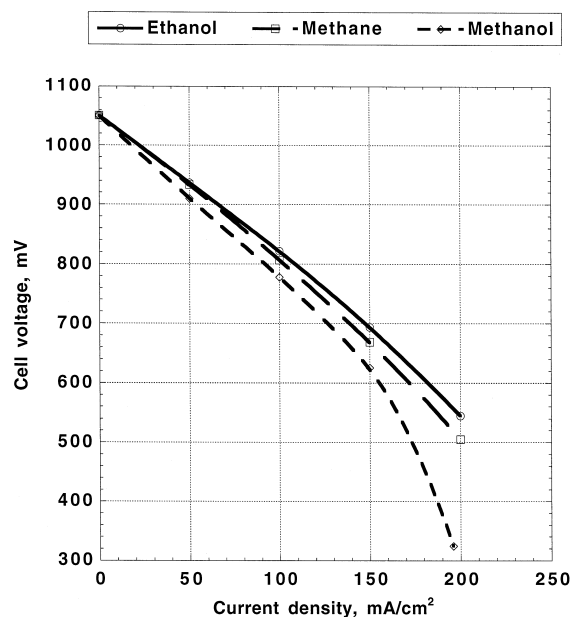


Fig. 2. Cell voltage vs. current density, calculated at base-line conditions and constant inlet fuel flow rate ($F_{\text{tot}} = 210$ l/h).

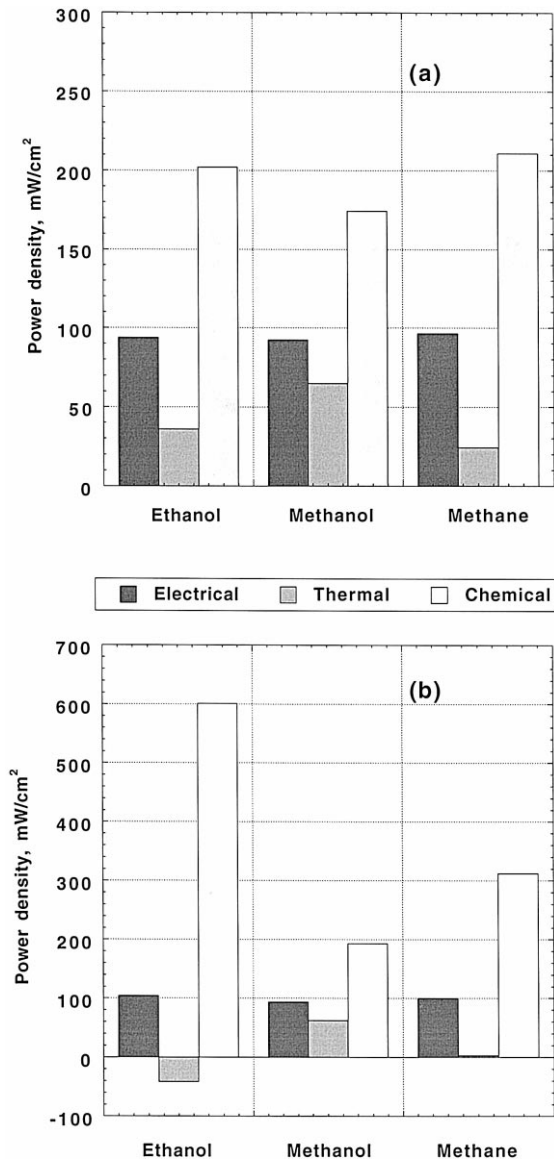


Fig. 3. Outlet power density distribution (electrical/thermal/chemical) for an IIR-MCFC fuelled with methane, methanol or ethanol, calculated at base-line conditions, $J = 150 \text{ mA/cm}^2$ and: (a) constant power density ($W_{\text{tot}} = 332 \text{ mW/cm}^2$); (b) constant inlet fuel flow rate ($F_{\text{tot}} = 210 \text{ l/h}$).

while the methanol established the conditions farthest from this equilibrium ($W_{\text{th}} = 65.1 \text{ mW/cm}^2$).

At the same fuel inlet flow, the MCFC supplied with ethanol produces a larger amount of by-products ($\text{CH}_4 + \text{CO} + \text{H}_2$) with respect to the methane and methanol case. In these conditions (Fig. 3b), the cells are in a thermal equilibrium if supplied with methane ($W_{\text{th}} = 2.7 \text{ mW/cm}^2$), and exothermal ($W_{\text{th}} = 62.3 \text{ mW/cm}^2$) or endothermal ($W_{\text{th}} = -41.7 \text{ mW/cm}^2$) if methanol or ethanol are used. In the case of endothermicity of the cell, i.e., for ethanol, it is necessary to supply heat from some outside sources that can be easily obtained by the combustion and by recycling part of the exhaust anodic gas. This opportunity should allow to improve the heat distribution along

the cell bipolar plates, with a reduction of the problems due to the thermal stresses.

The outlet gas compositions have been determined for a cell with indirect internal reforming (IIR-MCFC), supplied with the same stoichiometric $\text{H}_2\text{O}/\text{fuel}$ inlet ratio (1.0, 2.0 and 3.0 mol $\text{H}_2\text{O}/\text{mol}$ for methanol, methane and ethanol, respectively) and working at $T = 923 \text{ K}$, $P = 1 \text{ bar}$, $W_{\text{tot}} = 332 \text{ mW/cm}^2$ and $r_i = 0.75 \Omega \text{ cm}^2$. These results are shown in the histograms of Fig. 4a,b, where the compositions have been calculated at OCV (Fig. 4a) and at current density of 150 mA/cm^2 (Fig. 4b). In the histograms of Fig. 4, the nitrogen contained in the outlet cathodic flow has not been represented, even if this gas exits with the

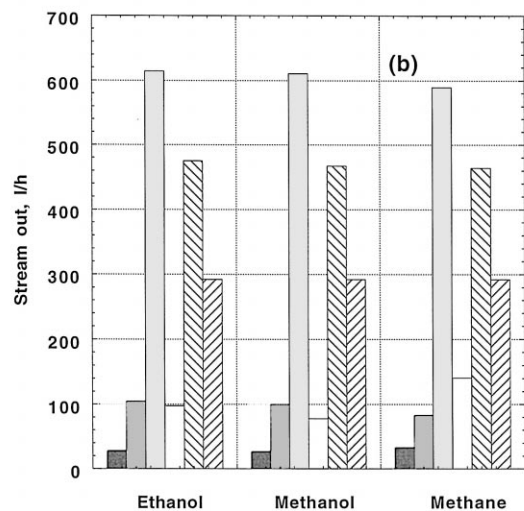
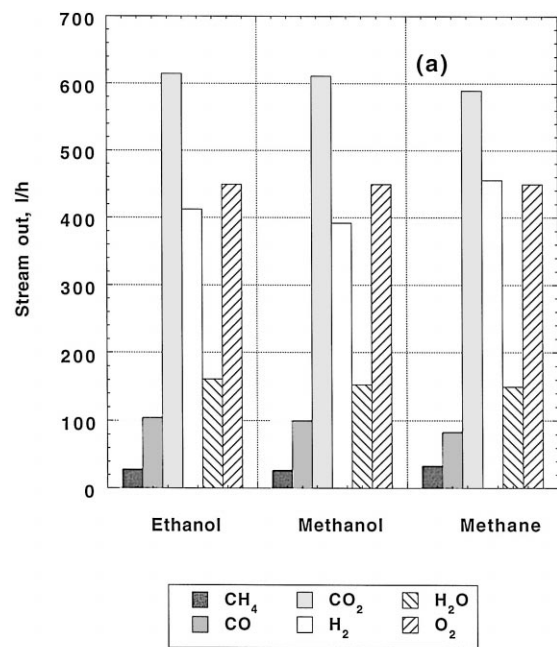


Fig. 4. Outlet anodic flow composition for an IIR-MCFC fuelled with methane, methanol or ethanol, calculated at base-line conditions, $W_{\text{tot}} = 332 \text{ mW/cm}^2$ and: (a) OCV; (b) $J = 150 \text{ mA/cm}^2$.

same volumetric flow (1700 l/h) which has in the cathode inlet chamber, without any active role in the cell reactions.

From the analysis of Fig. 4, it is noticeable that no content of ethanol or methanol has been expected in the outlet gas composition. This indicates that, unlike methane reforming, a total conversion of these fuels has been obtained in the cells and they have been converted in CH₄, CO and H₂. The presence of CO₂ appears to be very consistent in the outlet gas composition and this gas needs to be recycled in the cathodic inlet flow. Furthermore, CO₂ and H₂O can be separated from the other outlet gases and used again for the reforming of the raw fuel or, after an adjustment of their concentration, these gases can be used as reactants for different kinds of industrial reactions (hydrogenations, hydroformylations, Fischer–Tropsch synthesis, etc.).

From the comparison of the steam reforming compositions of the examined raw fuels, it is clear that, independently from the current density, the methane produces the highest H₂/CO ratio (5.48 at OCV and 1.7 at 150 mA/cm²), while the ethanol gives the highest concentration of CO (3% at OCV and 3.2% at 150 mA/cm²). The value of the H₂/CO ratio results to be of interest for the purpose of an industrial reuse of this mixture as syngas. In this sense, today there are several potential applications in the industrial field, like large scale methanol plants, dual product plants (pure CO and pure H₂ or oxogas at H₂/CO = 1 and pure H₂), flexible operation hydrogen plants and low investment ammonia plants [18].

For the cell supplied by methane, working at operative conditions typical of an MCFC, the presence of a residual concentration of methane (~ 1%) in the outlet gas composition has been found. The presence of methane in the anodic outlet gas composition is expected also when using ethanol or methanol. In fact, if the raw fuel is ethanol, at standard working conditions ($T = 923$ K, $P = 1$ bar and $J = 150$ mA/cm²), the outlet gas will contain a percentage of 0.85% of methane that lowers to 0.81% for the methanol reforming. For both cases, it is evident that the equilibrium of the reaction Eq. (4) slightly moves towards the production of methane.

With regard to the outlet cathodic gas, it is noticeable that the oxygen is not completely used (at standard conditions, oxidant utilization is equal to 35%). Thus, the amount of unconverted oxygen will be available to be used for the combustion of the residual CH₄, CO and H₂, with the production of heat for a cogeneration cycle and CO₂ to be supplied to the anodic compartment of the cell.

5. Conclusions

The different nature of the raw fuels produces substantial differences in their application in an indirect internal reforming molten carbonate fuel cell (IIR-MCFC) system.

Thus, the use of the ethanol results more advantageous in terms of energy density, cell voltages and electrical power density. On the contrary, the power contributions are not influenced by the used raw fuel.

Furthermore, the use of ethanol appears promising to control the carbon dioxide production. In fact, the plant biomass, raw material for the ethanol production, adsorbs the CO₂ present in the atmosphere. Thus, the oxidation of the ethanol releases the same CO₂, closing a cycle of few years of length that does not produce any global increase of carbon dioxide.

The problems concerning the catalysts for these processes appear more open. Thus, the need to formulate a catalyst active at very low temperature is not of strategic importance for application in IIR-MCFCs, because of the high operative temperature typical of this kind of fuel cell.

More interesting for this application appears to be the efforts addressed to produce cheaper ethanol. In this sense, the studies carried out on the production of ethanol/water mixture directly by the fermentation of plant biomasses seem very promising. Besides, a subject of further research investigations will be the problem of the thermal and chemical stability of the different catalytic systems when operating under the effect of carbonate electrolyte vapours (Li₂CO₃ and K₂CO₃).

Appendix A

The following relationship has been adopted to express the equilibrium constants K_i , $i = 1, 2, \dots, 5$ as a function of the temperature T (K):

$$K_i = \exp \left[a_i + \frac{b_i}{T} + c_i \ln(T) + d_i T + e_i T^2 + f_i T^3 \right] \quad (\text{A1})$$

The coefficients appearing in Eq. (A1) depend on reaction considered. They have been derived for the reactions (1)–(3) and (5) through manipulation of thermodynamic data [14], and are listed in Table 2. The equilibrium constant for reaction (4) is given by Eq. (9).

At $T = 923$ K, the values of equilibrium constants resulting from application of Eq. (A1) with coefficients of Table 2 are $K_1 = 2.65$, $K_2 = 1.89$, $K_3 = 1.592 \times 10^7$, $K_4 = 0.377$, $K_5 = 8.6 \times 10^9$.

Table 2
Coefficients for equilibrium constants of Eq. (A1) associated to i th reaction

i	a_i	$b_i \times 10^{-4}$	c_i	$d_i \times 10^2$	$e_i \times 10^6$	$f_i \times 10^{10}$
1	-23.142	-2.283	+7.6155	-0.338	-0.1173	+0.979
2	+0.467	+0.487	-1.086	+0.3263	-0.94	+1.24
3	-24.232	-0.896	+8.0926	-0.563	+0.512	+0.408
5	-36.2607	-2.745	+14.4992	-1.297	+2.40	-2.44

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