

# Ethanol reforming for supplying molten carbonate fuel cells

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## Abstract

An interesting application of agricultural renewable sources is the use of ethanol for supplying molten carbonate fuel cells (MCFCs). However, ethanol has to be converted into hydrogen by a steam-reforming process. MCFCs are suitable for these applications due to their tolerability to the impurities of the reaction products and their high working temperatures (600–650°C) which allow to integrate the reforming stage to the stack. Ethanol-reforming tests were performed by using pure ethanol or bioethanol obtained by sugar beet syrup fermentation. Tests were performed by a specific reactor designed for its installation into the anodic compartment of small-size MCFCs.

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## 1 INTRODUCTION

Annually  $500 \times 10^9 \text{ Nm}^3$  of hydrogen are produced in the world [1]: 60% by reforming of light hydrocarbons, 30% by cracking of heavy hydrocarbons, 7% by coal gasification and 3% by electrolysis. The mentioned processes demand energy. Thus, the hydrogen produced cannot be considered an energy source, but an energy carrier. The most important benefit obtained by the use of hydrogen in the energetic field is the reduction or even the elimination of the emissions of polluting substances and greenhouse gases. Water is the main product (and often the only product) in the processes that use hydrogen as an energy carrier; typical examples are the use of hydrogen in internal combustion engines or for the electric power generation in fuel cells. However, such environmental benefits are reduced if hydrogen is produced with methods based on its generation from hydrocarbons, which involves a  $\text{CO}_2$  release (of fossil origin). The same remarks may be done for electrolysis; it produces only hydrogen and oxygen, but it is important that the electric power needed for the process is not derived from fossil sources. It is different if the produced hydrogen is obtained from renewable sources (wind, photovoltaic, hydroelectric, geothermal, biomasses); in this case, a globally clean cycle is implemented. Ethanol is a renewable source when obtained from vegetal biomasses. Its production cycle is neutral on the  $\text{CO}_2$  point of view, because the amount of carbon dioxide produced is the same as that consumed in the biomass growth phase. Ethanol represents an optimal 'hydrogen carrier': ethanol steam reforming is a simple, economic

and clean method to produce hydrogen. Thermodynamic studies have shown the feasibility of the ethanol steam-reforming process to produce hydrogen for fuel cell supply [2–3]. The benefits due to this kind of application increase if bioethanol is used. Such product is here intended as ethanol not subjected to a distillation process; thus, its production costs and the employed energy are less than those of the pure ethanol. This paper reports the results of an experimental investigation on steam reforming of pure ethanol and bioethanol: it was made by a reactor which may be integrated to a small-size molten carbonate fuel cell (MCFC).

## 2 BIOETHANOL AND PURE ETHANOL

Experimental reforming tests were made on pure ethanol and bioethanol. Bioethanol is the intermediate product of the bio-energetic chain of ethanol from biomasses (see Figure 1). Both bioethanol and pure ethanol are obtained from alcoholic fermentation of carbohydrate- and sugar-rich agricultural crops, such as cereals (corn, sorghum, wheat, barley), sugar crops (Swiss chard, sugar cane), fruit, potatoes and grape pomaces. Alcoholic fermentation occurs after pre-treatment processes. It is a microaerophilic process which transforms carbohydrates contained in the vegetal crops into bioethanol. A distillation process transforms bioethanol into pure ethanol. Among the biofuels which are recently experimented, bioethanol and pure ethanol are the best compromise among price, availability and performances.

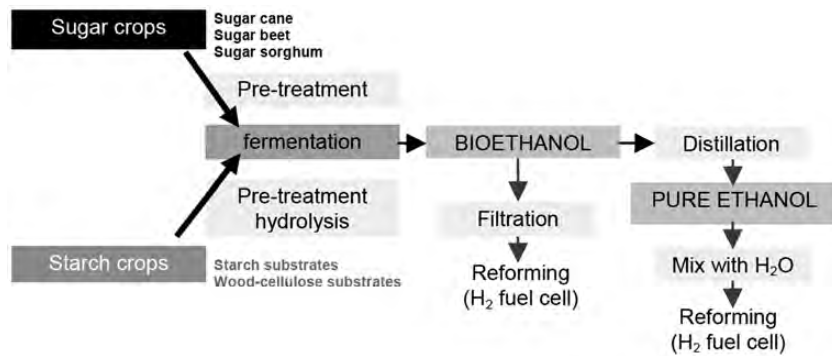


Figure 1. Chain of ethanol from biomasses.

Table 1. Ethanol production data.

Crop	Ethanol production (t/ha)	Production costs (€/t)
Sugar cane	7	140 (Brazil)
Corn	3	450 (USA)
Sugar beet	4	500 (EU)

## 2.1 Pure ethanol

Ethanol is a short-chain alcohol, represented as  $C_2H_6O$ ,  $C_2H_5OH$  or  $CH_3CH_2OH$  etc.

Table 1 shows the typical data of ethanol production from different crops by standard technologies. The energetic balance of the pure ethanol production process is positive; its heating value is higher than the energy which is needed for its production:

- Heating value of pure ethanol = 33.80 MJ/l;
- Energy needed for obtaining 1 l of pure ethanol = 4.9 MJ/l for cultivation process (i.e. corn) + 14.0 MJ/l for distillation process = 18.9 MJ/l [4].

## 2.2 Bioethanol

Bioethanol is constituted by ethanol, water and solid residues. The energetic balance of the bioethanol production process is positive; its heating value is higher than the energy which is needed for its production:

- Heating value of bioethanol = 27.56 MJ/l;
- Energy needed for obtaining 1 l of bioethanol = 4.9 MJ/l for cultivation process (i.e. corn) [4].

Thus, the bioethanol energetic balance is better than the pure ethanol because the distillation process does not occur during bioethanol production. Bioethanol used for reforming tests comprises

- 9% vol. of ethanol ( $CH_3CH_2OH$ );
- 77.5% vol. of water;
- 13.5% vol. of dry substance.



Figure 2. A sample of the bioethanol used for the experimental tests.

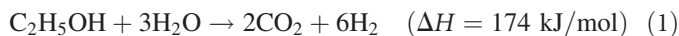
Figure 2 shows a sample of the used bioethanol.

Before the reforming tests, bioethanol was filtered by paper disks in order to eliminate the dry substance. Furthermore, the ethanol–water ratio slightly changed after the filtering process: in fact, the paper disks filter not only the dry substance, but also small, different amounts of ethanol and water. The following mixture was obtained during the filtering process:

- 10% vol. of ethanol ( $CH_3CH_2OH$ );
- 90% vol. of water.

### 3 ETHANOL REFORMING

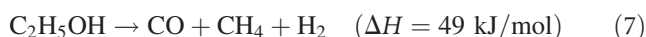
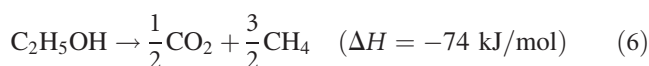
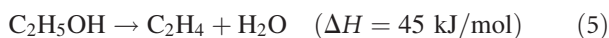
The following is the reforming reaction for pure ethanol and bioethanol:



Thus, a theoretical yield of 6 mol of hydrogen per 1 mol of ethanol can be obtained. It seems a simple reaction, but it effectively corresponds to a complex system whose kinetic parameters must be estimated [5]. In fact, many products can be obtained by the reforming process: ethylene, acetaldehyde, carbon monoxide, carbon dioxide, methane and hydrogen. In particular, many secondary reactions may affect the hydrogen selectivity. However, the ethanol decomposition is very fast and the reaction can be influenced by heat transfer and boundary layer mass diffusion [5]. Previous investigations carried out using catalyzers, similar to the ones used in the proposed tests, demonstrated that unwanted products may occur due to the following reactions [6–7]:



In particular, it was found that the reaction given by Eq. (2) may be characterized by a power law kinetic expression with a 0.75 order for ethanol that may be independent of water concentration [8]. Furthermore, ethanol hydrogenolysis given by Eq. (3) may occur, especially if helped by a high hydrogen content into the reformer [9]. Further secondary reactions may produce unwanted substances. In particular, ethanol dehydrogenation to acetaldehyde, dehydration to ethylene, carbon dioxide and methane and decomposition into carbon monoxide, methane and hydrogen are given by the following reactions:



However, previous studies showed that acetaldehyde and ethylene usually appeared in the effluent at very short space times and at the experiment start-up, when the catalyst worked under transient conditions [5]. Furthermore, ethanol cracking given by Eq. (6) may occur, especially at low temperatures ( $T < 200^\circ\text{C}$ ) [9]. Ethanol cracking given by Eq. (7) may also occur at very low temperatures ( $< 100^\circ\text{C}$ ), but it improves its efficiency when the temperature increases: this process may be followed by a methane steam-reforming process [10].

### 4 THE EXPERIMENTAL FACILITY

#### 4.1 The catalyst

The catalyst for the reforming process was obtained by an adsorption/precipitation technique applied to an alumina ultra-fine powder. The treatment is characterized by the adsorption deposition of a thin nickel layer on the alumina powder surface by using acetyl-acetonate. Successively, the powder is subjected to a thermal treatment in a furnace with nitrogen inert atmosphere: the furnace temperature grows up to  $650^\circ\text{C}$  and is kept for 2 h. The final powder is ultra-fine, with the same granulometry of the initial alumina powder. The final powder was subjected to IR analysis (FTIR) for evaluating its catalytic efficiency through the molecule CO probe, with satisfactory results. The choice of the catalyzer was made by taking into account technical and economic aspects. In particular, the catalyzer is characterized by:

- (a) Easiness of preparation;
- (b) Adaptability of the preparation method to pellet system;
- (c) Repeatability of the technique in an industrial scale;
- (d) Reduction or elimination of environmental impact problems.

Figure 3 shows a scanning electron microscopic picture of the catalyzer.

#### 4.2 The reformer device

The reformer device is constituted by a cylindrical steel reactor; its geometrical dimensions are suitable for inserting it into the anodic compartment of a small-size MCFC which was built at the Terni Laboratory of the University of Perugia [11]. The reactor is made of steel plates and rings with a 170-mm external diameter in which 95-mm diameter metallic nets are interposed for the catalyzer deposition. Figure 4 shows the catalyzer deposited onto a steel netting. The assembled reformer was brought to a  $650^\circ\text{C}$  working temperature by using a ceramic band resistor. K-type thermocouples were installed for the

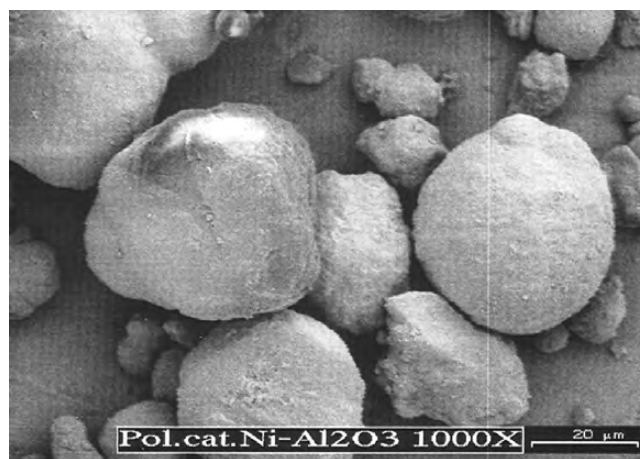


Figure 3. Scanning electron microscopic picture of the catalyzer ( $\times 1000$  magnification).

temperature control. The reactor working temperature was the same of the MCFC in order to integrate the reforming systems with the fuel cell in a future investigation. Recent studies [12–13] demonstrated that when the water–ethanol molar ratio is determined at atmospheric pressure, the hydrogen production is maxima for such temperature when carbon monoxide and methane generation is minimized (avoiding carbon deposits on the catalyst). Reforming tests were carried out both for pure ethanol (the liquid was mixed with bi-distilled water) and for bioethanol. Ethanol–water mixture and bioethanol were supplied by an electromagnetic pump with a dry membrane; it was characterized by a 0.75 l/h maximum flow rate and a 10.3 bar maximum pressure. A heat exchanger was installed upstream for the mixing/vaporization of the supplied mixture. The heating system of the vaporizer/mixer is constituted by a ceramic band resistor similar to the one used for the reformer heating.

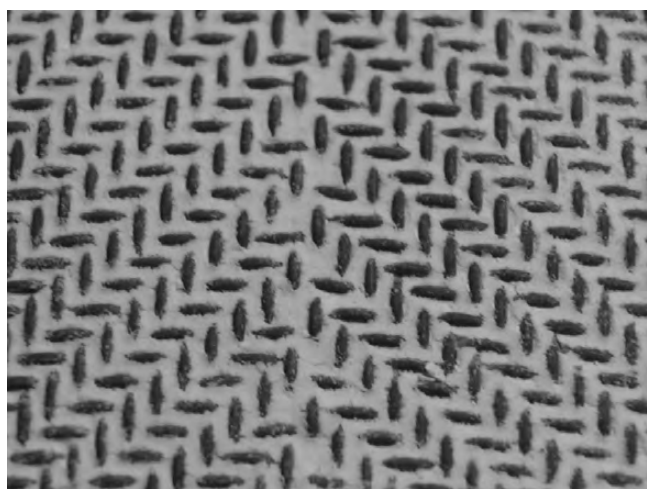


Figure 4. The catalyst deposited onto a steel netting.

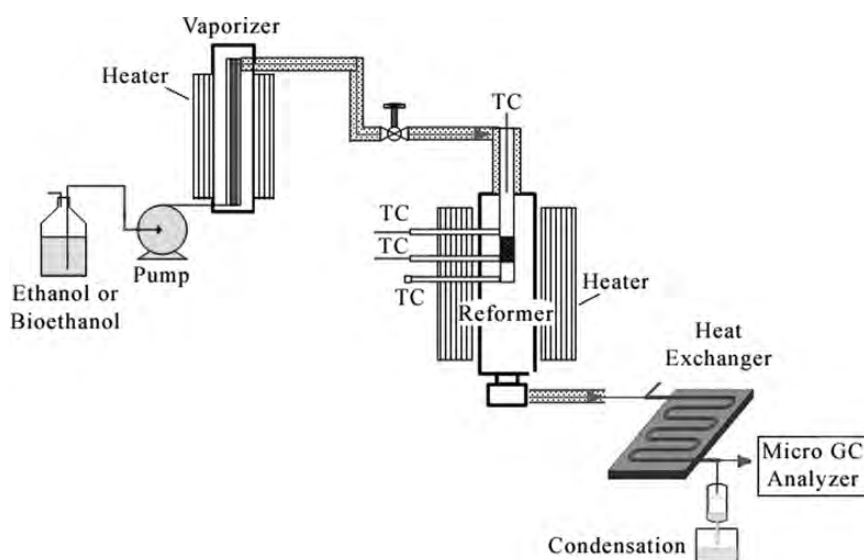


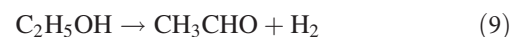
Figure 5. Layout of the reforming facility.

The gases at the reformer outlet were cooled through a water–gas double pipe heat exchanger that allows condensing and eliminating the gas vapors. The gases at the cooling exchanger outlet were picked up and analyzed by a gas chromatograph unit in order to determine their composition and to verify the reformer performances in terms of the hydrogen produced. Figure 5 shows the layout of the reformer facility.

## 5 EXPERIMENTAL RESULTS

### 5.1 Pure ethanol reforming

A mixture constituted by bi-distilled water and ethanol was employed as reformer fuel. Ethanol volume concentration is 20%. The flow rate of the supplied mixture was 0.1 l/h. The reformer device temperature was set to 650°C and kept constant for all test duration. Outlet gas samples were continuously picked up for 85 h. The gas samples were analyzed by a gas chromatograph unit in order to determine the amount of the produced hydrogen and the other compounds contained in the outlet gases. Figure 6 shows the volume concentration of the produced hydrogen that characterized the reformer outlet gas during the experimental tests. Table 2 reports the average concentration of the main components of the reformer outlet gas. The high carbon monoxide, methane and hydrogen concentration suggests that an ethanol decomposition into carbon monoxide, methane, hydrogen and/or the ethanol adsorption/dehydrogenation to acetaldehyde occurred together with the main reforming reaction:





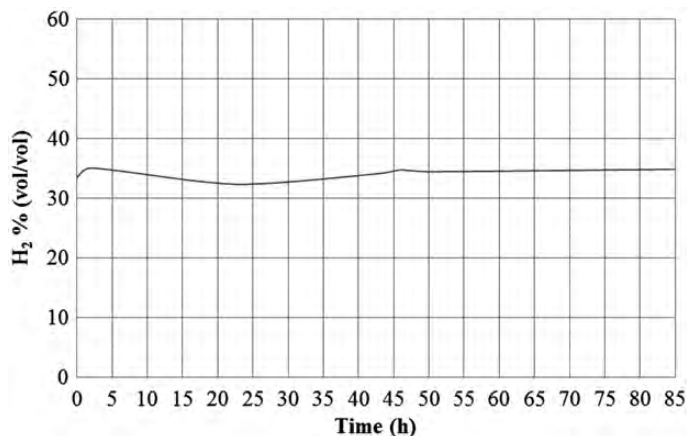


Figure 6. Hydrogen volume concentration in the outlet gases of the reformer (ethanol–water mixture).

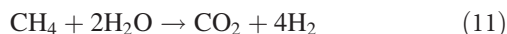
Table 2. Average concentration of the reformer outlet gases (ethanol–water mixture as supplied fuel).

Substance	Volume concentration (%)
H <sub>2</sub>	35.31
O <sub>2</sub>	0.38
N <sub>2</sub>	6.15
CH <sub>4</sub>	20.79
CO	21.80
CO <sub>2</sub>	2.98

## 5.2 Bioethanol reforming

Bioethanol was employed as reformer fuel in the next tests. The flow rate of the supplied mixture was 0.75 l/h (the maximum pump flow rate). The reformer device temperature was set to 650°C and kept constant at all tests. The outlet gas samples were continuously picked up for 85 h. The gas samples were analyzed by a gas chromatograph unit in order to determine the amount of the hydrogen produced and the other compounds contained in the outlet gases. Figure 7 shows the volume concentration of the produced hydrogen that characterized the reformer outlet gas during the experimental tests.

Table 3 reports the average concentration of the main components of the reformer outlet gas. The high carbon monoxide and methane concentration suggests that methane generation and reforming reactions occurred together with the main reforming reaction:



Thus, bioethanol gave the best results in terms of hydrogen production. It seems to be due to the highest water–ethanol ratio supplied to the reformer and the chosen pump flow rate; however, it has to be considered that hydrogen production may

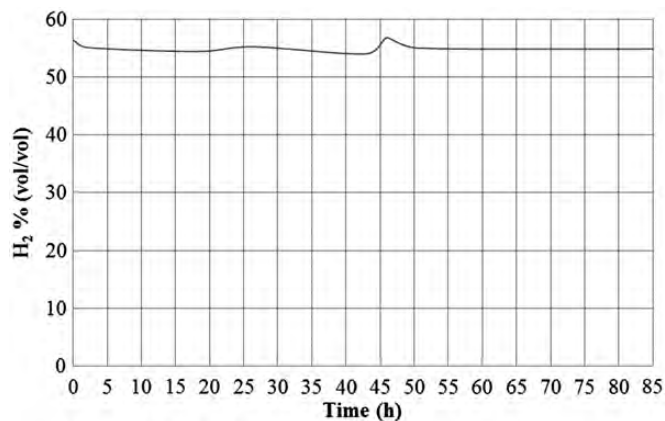


Figure 7. Hydrogen volume concentration in the outlet gases of the reformer (bioethanol).

Table 3. Average concentration of the reformer outlet gases (bioethanol as supplied fuel).

Substance	Volume concentration (%)
H <sub>2</sub>	56.02
O <sub>2</sub>	0.37
N <sub>2</sub>	3.04
CH <sub>4</sub>	8.49
CO	—
CO <sub>2</sub>	19.03

be higher also because carbon monoxide and methane generation is lower (reducing carbon deposits on the catalyst) in the bioethanol tests.

Furthermore, the different values of the final gas volume concentrations with respect to the supplied water–ethanol ratio and the main reforming reaction characteristics may be due to the following reasons:

- the results are referred to a dry output gas (due to the condensation stage);
- apart the reactions described in Eqs (8–9) for pure ethanol or Eqs (10–11) for bioethanol, many other secondary and unwanted reactions may occur, giving undesired results [5];
- the uncertainty of the measurements and the experimental tests.

About the methane content, bioethanol gave the best results (lower volume concentration values). However, high values for the defined purposes (supply of MCFCs) were obtained (8.49%). It may be due to the low temperatures of the ethanol reforming process: the produced methane may be reformed, but the optimal working temperatures of the methane steam reforming are usually 800–1000°C, while the proposed tests were made at 650°C [14]. In fact, the reformer is designed to be integrated to an MCFC anodic compartment; thus, the temperature of the ethanol-reforming process cannot be changed

(it corresponds to the MCFC typical working temperature). However, when a continuous hydrogen consumption is obtained by the MCFC, the methane reforming efficiency may improve.

About the carbon dioxide content, the highest values were obtained by the bioethanol reforming, showing that ethanol conversion is better; in fact, the optimal conditions would be showed with the conversion of all the carbon in carbon dioxide: this component is not a polluting substance for MCFCs, because it is used in the cathodic reaction.

## 6 CONCLUSIONS

This paper deals with the design and the realization of an experimental system for hydrogen production by pure ethanol or bioethanol reforming. The investigation dealt with the catalyst study and successively the design and the implementation of all the components (vaporizer, reactor, condenser) of a reformer facility. The obtained results are fundamental for future investigations regarding the integration of the proposed reformer with small-size MCFCs. About the ethanol reformer tests, good performances were obtained in terms of hydrogen production (the average hydrogen volume concentration in the reformer outlet gas was  $\sim 35\%$ ), but unwanted compounds were produced during the reforming process, such as carbon monoxide (22% volume concentration) and methane (21% volume concentration). The methane content may be reduced when a continuous hydrogen consumption is obtained by the MCFC (methane steam reforming may be helped). Carbon monoxide is not desired, but a shift reaction may also occur and give a carbon dioxide and hydrogen production in a specific further stage integrated to the methane steam-reforming stage. However, methane and carbon monoxide concentration values are very high: thus, the mentioned reactions cannot completely help to obtain optimal working conditions for the MCFC stack. Better results were obtained by bioethanol reforming: the bioethanol reformer process showed an efficiency, in terms of hydrogen conversion, approximately twice the one obtained with the ethanol–water mixture (the average hydrogen volume concentration in the reformer outlet gas was  $\sim 56\%$ ). Better results were obtained also about the presence of unwanted products in the reactor outlet gas. A lower concentration was found for methane ( $\sim 8.5\%$  volume concentration that may be reduced when a continuous hydrogen consumption is obtained by the MCFC) and carbon monoxide (less than the minimum measurable value). A not negligible carbon dioxide concentration was also measured both for ethanol and for bioethanol tests; however, such substance is not a polluting compound for MCFCs (it is also used as reagent for the

cathodic reaction). Thus, bioethanol may allow higher hydrogen production, but also energetic benefits with respect to the pure ethanol–distilled water mixture. In fact, the bioethanol production process does not include the distillation demanded for pure ethanol production; this fact makes the bioethanol energetic balance better than the ethanol one. Future developments of the proposed experimentation will deal with tests on adjustments on the proposed reformer in order to increase its efficiency and the experimental evaluation of the performances of an MCFC integrated with the proposed reformer.

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