

ETHANOL REFORMING FOR SUPPLYING MOLTEN CARBONATE FUEL CELLS

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Abstract

An interesting application of agricultural renewable sources is the employment of ethanol for supplying Molten Carbonate Fuel Cells (MCFCs). For that purpose, ethanol has to be converted into hydrogen by a steam reforming process. MCFCs are particularly suitable for this kind of applications due to their high tolerability to the impurities which are contained into the reaction products and also for their high working temperatures (600-650°C) which allow integrating the reforming stage into the stack. This paper reports the results of ethanol reforming tests: pure ethanol and bioethanol obtained by sugar beet syrup fermentation were tested. Tests were carried out by a specific reactor designed for its integration into the anodic compartment of small size MCFCs.

Keywords: reforming, ethanol, MCFC, biomasses

1. Introduction

500·10⁹ Nm³/year of hydrogen are produced in the world [1]: 60% by reforming of light hydrocarbons, 30% by cracking of heavy hydrocarbons, 7% by carbon gasification, 3% by electrolysis. The mentioned processes demand energy. Therefore, the produced hydrogen cannot be considered an energy source, but an energy carrier. Among the benefits obtained by the employment of hydrogen in the energetic field, the most important is the reduction or even the elimination of the emissions of polluting substances. Water is the main product (and often the only product) in the processes that employ hydrogen as energy carrier; typical examples are the use of hydrogen in internal combustion engines or for the electric power generation in the fuel cells. However, such environmental benefits are reduced if hydrogen is produced with methods based on its generation from hydrocarbons, which involves a CO₂ release (of fossil origin). The same remarks may be done for electrolysis; it produces only H₂ and O₂, 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 because it may be obtained from vegetal biomasses. Its production cycle is neutral on the CO₂ point of view, because the produced carbon dioxide amount is equal to the one consumed in the biomass increase 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 for hydrogen production for fuel cell supply [2-3]. The benefits due to this kind of application increase if bioethanol is used. Such product is 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 is integrable into a small size Molten Carbonate Fuel Cell.

2. Bioethanol and pure ethanol

Experimental reforming tests were made on pure ethanol and bioethanol. Bioethanol is the intermediate product of the bioenergetic die of ethanol from biomasses (see Figure 1). Both bioethanol and pure ethanol are obtained from alcoholic fermentation of carbohydrate-rich 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 micro-aerophil process which transforms the carbohydrates contained into the vegetal crops into bioethanol. A distillation process transforms bioethanol into pure ethanol. Considering the biofuels which are recently experimented, bioethanol and pure ethanol are the best compromise among price, availability and performances.

2.1 Pure Ethanol

Ethanol is a short chain alcohol (it is represented as C₂H₆O or C₂H₅OH or CH₃CH₂OH).

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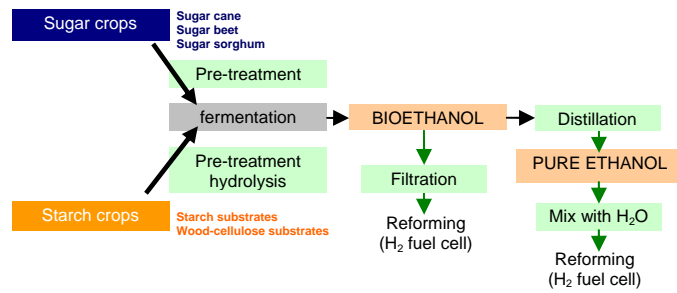


Figure 1. Die of ethanol from biomasses

Table 1 shows typical data of ethanol production from different crops by standard technologies. Energetic balance of 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 1l of pure ethanol = 4,9 MJ/l for cultivation process (i.e. corn) + 14 MJ/l for distillation process = 18,9 MJ/l.

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 (E.U.)

2.2 Bioethanol

Bioethanol is constituted by ethanol (10% vol.), water (80% vol.) and solid residues (10% vol.). Energetic balance of 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 1l of bioethanol = 4,9 MJ/l for cultivation process (i.e. corn).

Bioethanol energetic balance is better than pure ethanol one because the distillation process does not occur for bioethanol production. Bioethanol used for reforming tests is composed by:

- 9% vol. of ethanol ($\text{CH}_3\text{CH}_2\text{OH}$);
- 77,5% vol. of water;
- 13,5% vol. of dry substance.

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 substances. The filtering process allowed obtaining the following mixture:

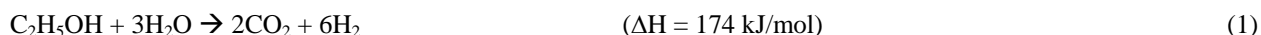
- 10% vol. of ethanol ($\text{CH}_3\text{CH}_2\text{OH}$);
- 90% vol. of water.



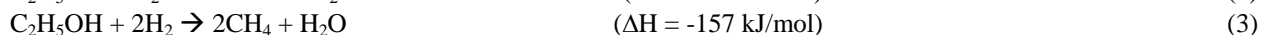
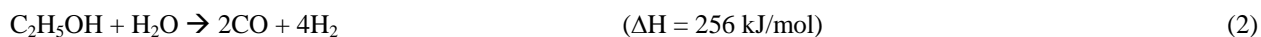
Figure 2. A sample of the bioethanol used for the experimental tests

3. Ethanol reforming

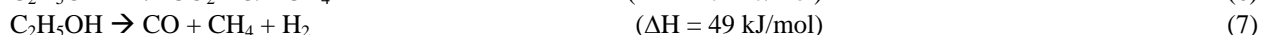
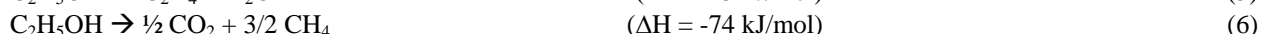
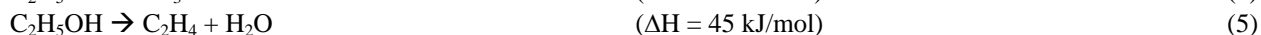
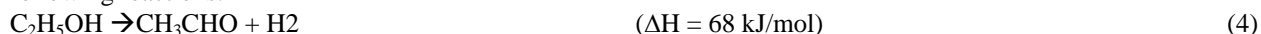
Reforming reaction both for pure ethanol and bioethanol is the following:



Previous investigations carried out by catalysers similar to the ones used in the proposed tests demonstrated that unwanted products may occur due to the following reactions [4-5]:



Other secondary reactions may produce unwanted substances. In particular, ethanol dehydrogenation to acetaldehyde, dehydration to ethylene, CO_2 and CH_4 and decomposition into CO , CH_4 e H_2 are given by the following reactions:



4. The experimental facility

4.1 The catalyst

The catalyst for the reforming process was obtained with 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 using acetyl acetonate. Then, the powder is subjected to a thermal treatment in a furnace with nitrogen inert atmosphere: the furnace temperature grows up to 650 °C and is kept for 2 hours. The final powder is ultra-fine, with the same granulometry of the initial alumina powder. The final powder was subjected to IR analyses (FTIR) for evaluating its catalytic efficiency through the molecule CO probe, with satisfactory results. The choice of the catalyser was made by taking into account technical and economical aspects. In particular, it was characterized by:

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

Figure 3 shows a SEM picture of the catalyser.

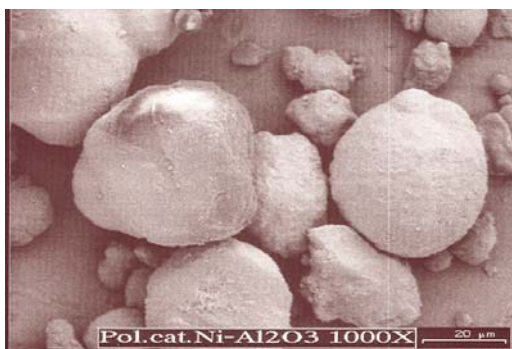


Figure 3. SEM picture of the obtained catalyser (1000x magnification)

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 [6]. The reactor is made of steel plates and rings with a 170 mm external diameter in which 95 mm diameter metallic nettings are interposed for the catalyser deposition. Figure 4 shows the catalyser deposited onto a steel netting. The assembled reformer was carried to a 650°C working temperature using a ceramic band resistor. K-type thermocouples were installed for the temperature control. The reactor working temperature was the same of the MCFC one in order to integrate the reforming systems with the fuel cell in a future investigation. Recent studies [7-8] demonstrated that when the water/ethanol molar ratio is determined at atmospheric pressure, the hydrogen production is maxima for such temperature when CO and CH_4 generation is minimized (avoiding carbon deposits on the catalyst). Reforming tests were carried out both for pure ethanol (the liquid was mixed with distilled water) and 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, 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.

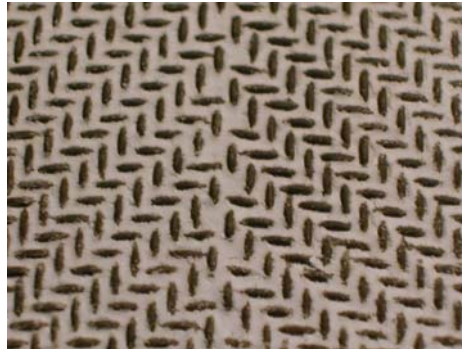


Figure 4. The catalyser deposited onto a steel netting

Gases at the reformer outlet are cooled through a water-gas double pipe heat exchanger that allows condensing and eliminating the gas vapors. Gases at the cooling exchanger outlet are picked up and analyzed with a gaschromatograph in order to determine their composition and to verify the reformer performances in terms of the produced hydrogen. Figure 5 shows the layout of the reformer facility.

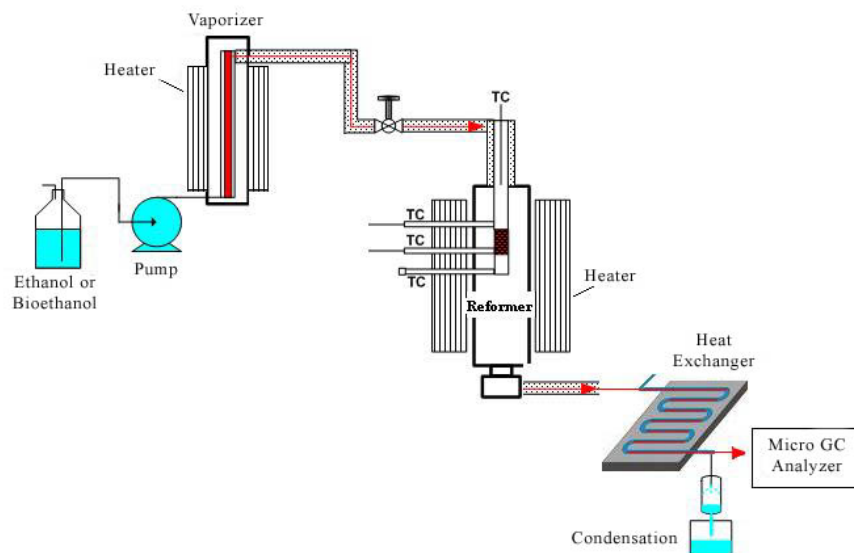


Figure 5. layout of the reforming facility

5. Experimental results

5.1 Pure ethanol reforming

A mixture constituted by bidistilled water and ethanol was employed as reformer fuel. Ethanol volume concentration is 20%. Flow rate of the supplied mixture is 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 hours. The gas samples were analyzed by a gaschromatograph 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 CO, CH₄ and H₂ 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:



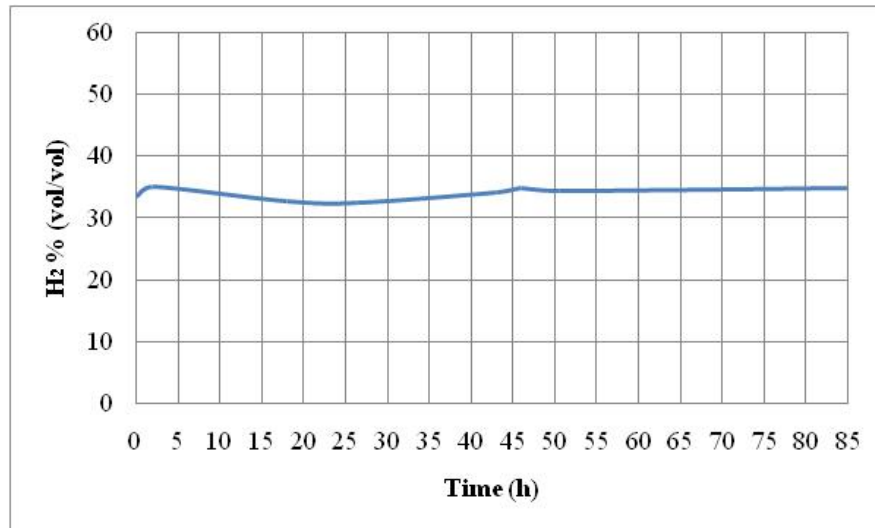


Figure 6. Hydrogen volume concentration in the outlet gases of the reformer (ethanol/water mixture)

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

Substance	Volume concentration (%)
H ₂	35,31
O ₂	0,38
N ₂	6,15
CH ₄	20,79
CO	21,80
CO ₂	2,98

5.2 Bioethanol reforming

Bioethanol was employed as reformer fuel in the next tests. Flow rate of the supplied mixture is 0,75 l/h (maximum pump flow rate). 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 hours. The gas samples were analyzed by a gaschromatograph in order to determine the amount of the produced hydrogen 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.

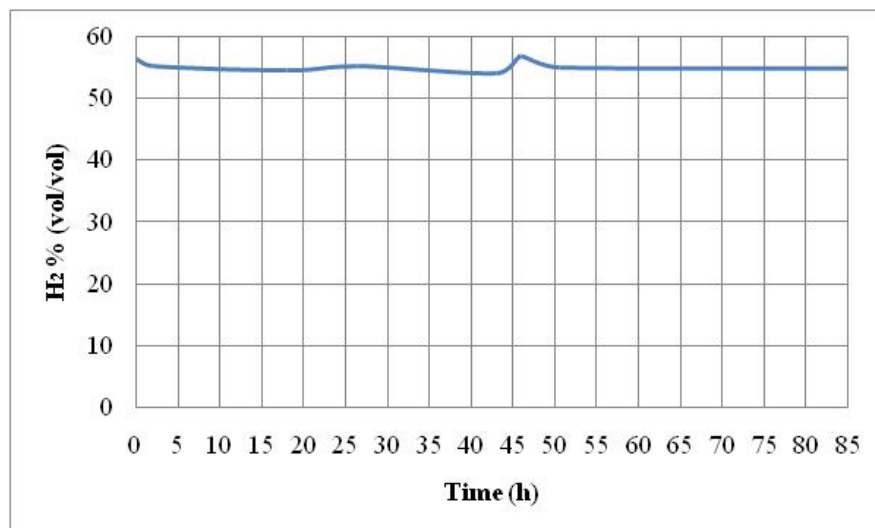


Figure 7. Hydrogen volume concentration in the outlet gases of the reformer (bioethanol)

Table 3 reports the average concentration of the main components of the reformer outlet gas. The high CO and CH₄ concentration suggests that methane generation and reforming reactions occurred together with the main reforming reaction:

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

Substance	Volume concentration (%)
H ₂	56,02
O ₂	0,37
N ₂	3,04
CH ₄	8,49
CO	--
CO ₂	19,03

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 regarded the catalyst study, 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 molten carbonate fuel cells. 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 approximately 35%), but unwanted compounds were produced during the reforming process, such as CO (22% volume concentration) and CH₄ (21% volume concentration). Better results were obtained by bioethanol: bioethanol reformer showed an efficiency, in terms of hydrogen conversion, approximately nearly double than the one obtained with the ethanol/ water mixture (the average hydrogen volume concentration in the reformer outlet gas was approximately 56%). Better results were obtained also about the presence of unwanted products in the reactor outlet gas. A lower concentration was found for CH₄ (approximately 8.5% volume concentration) and carbon monoxide (less than the minimum measurable value). A not negligible CO₂ concentration was also measured both for ethanol and bioethanol tests; however, such substance is not a polluting compound for MCFCs (it is also used as reagent for the cathodic reaction). Thus, bioethanol guarantees a best hydrogen production, but also energetic benefits with respect to the pure ethanol/distilled water mixture. 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 a MCFC integrated with the proposed reformer.

References

- [1] Momirlan M, and Veziroglu T.N, "The properties of hydrogen as fuel tomorrow in sustainable energy system for a cleaner planet" *Int. J. Hydrogen Energy*. 30, 795-802 (2005).
- [2] Garcia E.Y, and Laborde M.A, "Hydrogen production by steam reforming of ethanol: thermodynamic analysis" *Int. J. Hydrogen Energy*. 16, 307 (1991).
- [3] Vasudeva K, Mitra N, Umasankar P, and Dhingra S.C, "Steam reforming of ethanol for hydrogen production: Thermodynamic analysis" *Int. J. Hydrogen Energy*. 21 (1), 13-18 (1996).
- [4] Freni S, Maggio G, and Cavallaro S, "Hydrogen produced from ethanol for internal reforming molten carbonate fuel cell" *J. Power Sources*, 102, 198-204 (2001).
- [5] Ioanides T, "Thermodynamic Analysis of Ethanol Processors for Fuel Cell Applications" *J. Power Sources*, 92, 17-25 (2000).
- [6] Rossi F, and Nicolini A, "A cylindrical small size Molten Carbonate Fuel Cell: experimental investigation on materials and improving performance solutions", *Fuel Cells*, 9 (2), 170-177 (2009).
- [7] Fierro V, Akdim O, and Mirodatos C, "On-board hydrogen production in a hybrid electric vehicle by bioethanol oxidative steam reforming over Ni and noble metal based catalysts" *Green Chem*. 5, 20-24 (2003).
- [8] Klouz V, Fierro V, Denton P, Katz H, Liss J.P, Bouvot-Mauduit S, and Mirodatos C, "Ethanol reforming for hydrogen production in a hybrid electric vehicle: process optimization" *J. Power Sources*. 105, 26-34 (2002).