

## Application 2035



### **Analysis of CO<sub>2</sub> separation with MCFCs operating on simulated exhaust gases from biogas engines**

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#### Background and motivation

The project is finalized to an experimental validation of simulations related to the application of MCFC to CO<sub>2</sub> recovery from exhaust stream coming from biogas reciprocating engines. This integration lies in the field of innovative CCS systems, because it exploits the possibility to use MCFCs as active carbon capture devices, due to their capability to migrate carbon dioxide from one electrode (cathode) to another (anode). Furthermore, thanks to the fuel cell operation, an additive power output and a better electric efficiency can be obtained. A number of works applying this concept to gas turbine based power plants, either stand-alone [1] or integrated in gas and steam combined cycles [2], or dealing with different plant configurations [3], are available in literature though the application to biogas reciprocating engines has not been experimentally studied yet, with the exception of the modeling activity connected to this proposal.

Reference operating features and plant layout are described in the ref. article [4]. The reference sewage plant is assumed to incorporate a combined heat and power island composed by three reciprocating engines, where all the biogas is burnt in approximately stoichiometric conditions. Heat rejected by the cooling circuit of the engine jackets and a fraction of the available heat in the exhaust gases is recuperated and transferred to the anaerobic digesters by means of an intermediate closed water loop. In the new layout, the use of molten carbonate fuel cells (fed by a mixture of biogas and natural gas) downstream the reciprocating engines is proposed. The exhaust gases from the engines are fed to the cathode of the cell along with a certain amount of air to provide the oxygen required by cell reactions. In this way MCFC plays the role of active carbon sequestration system: carbon dioxide is partly removed from the exhaust gases whilst, at the same time, electricity is produced. The cathode inlet stream and the fuel fed to the anode must be free of sulphur compounds, which would harm the cell. For this reason a set of active carbon beds, already incorporated in the water treatment facility, can be used carrying out adsorption-regeneration cycles. The fuel fed to the anode side can be natural gas or biogas, (respecting a max 10% total use of natural gas in the ICE + MCFC plant due to Spanish regulation limits for the entitlement of renewable plant). The anode of the cell is so fed with fuel and steam to allow for internal reforming within the cell vessel. The exhaust gases from the anode side are composed by carbon dioxide (product from the reforming of natural gas and the oxidation of hydrogen), steam (product from the oxidation of hydrogen) and excess hydrogen (product from the reforming of natural gas). In order to recover the unconverted fuel and bring the CO<sub>2</sub> at the required level of purity (for the correct transport and storage operation) the anode exhaust gas can be burnt with oxygen

produced by an Air Separation Unit (ASU). Then combustor effluents can be cooled down to condensate water and isolate carbon dioxide. The heat released in the combustion process can be recovered for the digesters [4-5].

Given these basic characteristics, three different arrangements have been proposed:

- 1) In the first one all the available biogas is burnt in the engines whereas the fuel cell is run with natural gas, respecting the 10% limit on overall fuel use). Nevertheless, in spite of supplying as much additional fuel as possible, and given the large amount of carbon dioxide existing in the engine exhaust gases, hydrogen (fuel) ends up being the limiting reactant in the cell. The carbon capture capacity of the system as well as the fuel cell output are affected accordingly.
- 2) In the second case, one third of the available biogas is directed to the fuel cell whilst the remaining two thirds are burnt in two engines; the third engine is hence put out of service. Based on this fuel distribution, and performing an elementary analysis of the combustion stoichiometry in the engine and the reforming process in the fuel cell, each kilogram of biogas yields 0.0843 kmol of hydrogen (by reforming in the anode of the cell) and 0.0334 kmol of carbon dioxide (by combustion in the engine). It is so deduced that the limiting reactant in this configuration is carbon dioxide for which a maximum utilisation of 0.555 can be achieved.
- 3) The third scheme is based on opening a recirculation loop from the anode outlet to the cathode inlet, which allows for higher fuel consumption due to the higher low rate of carbon dioxide supplied to the cathode. This nevertheless brings about a higher demand for air in the cell owing to the increased heat release rate in the new operating conditions. Such penalty on auxiliary power consumption can be partially offset though by increasing the rate of cathode exhausts recirculation, which has the effect of augmenting the sensible heat absorbed by the cathode stream and therefore reduces the need to supply air.

#### Proposed experimental activity

Based on these three possibilities, we propose to carry out experiments on MCFC cells to verify their performances using different flue gas compositions at the cathode and anode inlet in order to validate the model in particular as far as voltage / current density prediction and actual CO<sub>2</sub> separation capability or CO<sub>2</sub> utilization factor are concerned, and to better identify the optimal fuel cell operative parameters. The test condition should cover the following compositions:

Case1 - Molar composition: XCO<sub>2</sub>=12.3, XH<sub>2</sub>O=15.5, XO<sub>2</sub>=2.8, XN<sub>2</sub>=69.5.

Case2 - Molar composition: XCO<sub>2</sub>=9.1, XH<sub>2</sub>O=11.5, XO<sub>2</sub>=7.4, XN<sub>2</sub>=71.9.

Case3 - Molar composition: XCO<sub>2</sub>=7.3, XH<sub>2</sub>O=9.9, XO<sub>2</sub>=13.0, XN<sub>2</sub>=69.8.

On the anode side, the fuel compositions for each case are (reformer inlet):

Case1 - Molar composition: XCH<sub>4</sub>=24.0, XCO<sub>2</sub>=0.1, XH<sub>2</sub>O=75.1, XN<sub>2</sub>=0.4, XC<sub>2</sub>H<sub>6</sub>=0.4, XC<sub>3</sub>H<sub>8</sub>=0.1

Case2 - Molar composition: XCH<sub>4</sub>=15.6, XCO<sub>2</sub>=9.1, XH<sub>2</sub>O=74.0, XN<sub>2</sub>=1.3.

Case3 - Molar composition: XCH<sub>4</sub>=17.1, XCO<sub>2</sub>=7.5, XH<sub>2</sub>O=74.2, XN<sub>2</sub>=1.1, XC<sub>2</sub>H<sub>6</sub>=0.1.

On the anode side, the fuel compositions at the cell inlet (reformed fuel) are:

Case1 - Molar composition:  $X_{CO}=7.92$ ,  $X_{CO_2}=8.84$ ,  $X_{H_2}=58.48$ ,  $X_{H_2O}=24.49$ ,  $X_{N_2}=0.27$ .

Case2 - Molar composition:  $X_{CO}=5.51$ ,  $X_{CO_2}=13.32$ ,  $X_{H_2}=42.05$ ,  $X_{H_2O}=38.13$ ,  $X_{N_2}=0.99$ .

Case3 - Molar composition:  $X_{CO}=5.98$ ,  $X_{CO_2}=12.44$ ,  $X_{H_2}=45.36$ ,  $X_{H_2O}=35.4$ ,  $X_{N_2}=0.82$ .

Tests should be carried out at different current density, where possible keeping constant at different values the fuel utilization (50, 60, 70 % and up to the maximum allowed by the cell), and the CO<sub>2</sub> utilization (from 30-40% up to 70% or the maximum value allowed by the cell), finding the corresponding cell voltage.

An experimental validation of MCFC behavior could strongly confirm the validity of the proposed fuel cell model and could represent an excellent improvement of the whole study.

Furthermore, first results obtained by the initial experimentation of simulated flue gases (related to gas compositions of cases 1,2 and 3) could be very useful in the investigation of the ideal plant arrangement, in terms of optimization of re-circulated streams to the cathode side and of fuel composition to the anode side.

#### EXPERIMENTAL PROJECT PATH\*

##### ACTIVITIES DESCRIPTION

- |    |  |                    |
|----|--|--------------------|
| A1 | Test plan and test-bench adjustment  | I Week / II Week   |
| A2 | Reference tests, based on the available data   | II Week / III Week |
| A3 | Tests according to the agreed optimal working conditions                                     | III Week / IV Week |
| A4 | Comparison test with the starting conditions<br>(degradation issues check) and data analysis | IV Week            |

\* time sequence and duration of each activity will be varied on the basis of actual interests and instruments availability