

# DEVELOPMENT OF A ROBUST AND EFFICIENT BIOGAS PROCESSOR FOR HYDROGEN PRODUCTION IN THE FRAMEWORK OF THE EUROPEAN BIOROBUR PROJECT

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## Abstract

The present work deal with the development and testing of a robust and efficient decentralized fuel processor based on the direct autothermal reforming (ATR) of biogas with a nominal production rate of PEM-grade hydrogen of 50 Nm<sup>3</sup>/h. The system energy efficiency of biogas conversion into green hydrogen is 65%, for a reference biogas composition of 60% vol CH<sub>4</sub> and 40% vol CO<sub>2</sub>.

Modelling and simulation (CFD and FEM) were carried out to select the innovative catalyst support with promising results for the BioRobur fuel processor and furthermore, 2D CFD analysis was also used to examine flow uniformity issues due to soot trap integration close coupled to the ATR. X-Ywt.% Ni-Rh/MgAl<sub>2</sub>O<sub>4</sub> - SiSiC structured catalyst was selected as a potential catalyst for the conversion of biogas to hydrogen. Homogenous lattice structure composed of cubic rotated cell showed excellent performances, guaranteeing a high reliability of the process. Moreover, LiFeO<sub>2</sub> catalyst was selected as the most prominent candidate towards to carbon gasification in a reducing atmosphere. The catalyst was in-situ deposited directly over the wall-flow filter. Tests of the coupled system under realistic conditions at the pilot and demonstration scale have showed satisfactory results in terms of, hydrogen yield and pressure drop in the system, reaching the target with a nominal production rate corresponding to 50 Nm<sup>3</sup>/h of hydrogen.

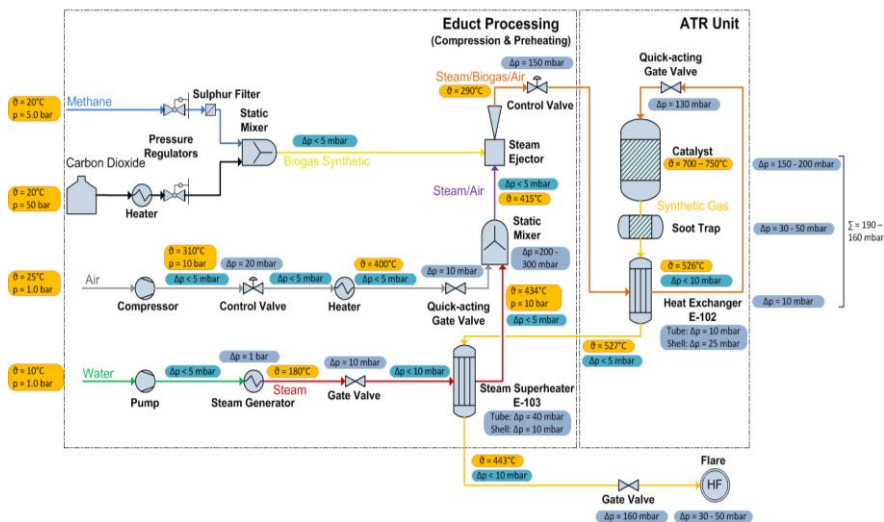
Besides, Aspen simulation and LCA analysis has demonstrated that BioRobur is the most promising process to hydrogen production compared to other types of reforming process. The work is being performed within the SP1-JTI-FCH.2-Collaborative Project 'BIOROBUR'. The partners involved in the Biorobur project bring together a sufficient number of important European actors on the scientific, research and industry level.

## Introduction

Biogas is the result of the anaerobic digestion process of biomass, which comprises principally methane (CH<sub>4</sub>) and carbon dioxide (CO<sub>2</sub>). Hydrogen production from

biogas is a highly promising energy carrier in the sustainable energetic scenario of reduced greenhouse gas emissions [1]. The BioRobur project is focus on green hydrogen production by direct biogas ATR, aimed at covering a wide span of potential applications, from fuel cells feed (both high temperature SOFC or MCFC fuel cells and low temperature PEM ones, requiring a significantly lower inlet CO concentration) up to the production of pure, PEM-grade hydrogen.

Several advantages are obtained using the direct ATR process compared with steam reforming or partial oxidation of biogas [2]. The main characteristic is the fact that heat is directly provided through partial oxidation of the biogas, reducing the need of heat exchangers, and increasing the flexibility of the plant. An overview of the project is illustrated in the Figure 1.



**Figure 1.** Block flow diagram of BioRobur process.

The originality of the project is the use of a structured catalyst to convert the biogas into hydrogen in the ATR unit and the adoption of a catalytic wall-flow filter located close coupled to the ATR to retain the carbon produced.

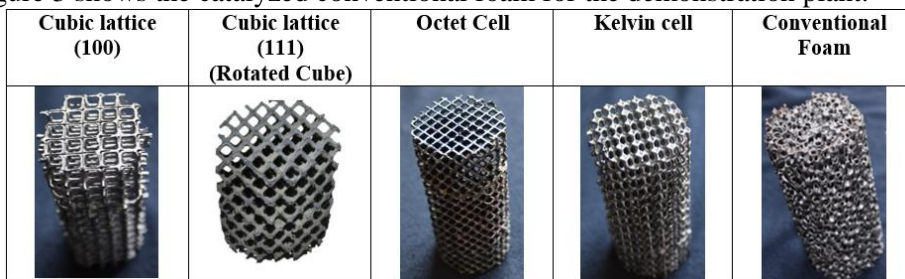
## Experimental

### Structured catalyst supports

Homogenous lattices composed of Cubic, Octet and Kelvin cells and the Conventional random Foam structure were investigated within the BioRobur project (Figure 2) [3] [4]. X-Ywt.% Ni-Rh/MgAl<sub>2</sub>O<sub>4</sub> catalyst was selected as a robust catalyst for ATR of biogas. The catalyst was prepared as described by Luneau [5]. All SiSiC-structures were coated with the same amount of catalyst to ensure identical conditions between the supports in the catalytic activity test in the pilot testing campaign. Based on the achieved results, two structures, conventional

foam and the rotated cube cell supports were selected to be used in the demonstration plant.

Figure 3 shows the catalyzed conventional foam for the demonstration plant.



**Figure 2.** Homogeneous lattices and Foam structure



**Figure 3.** Coated conventional foam a) without canister and b) into the ATR unit

### Catalytic soot trap

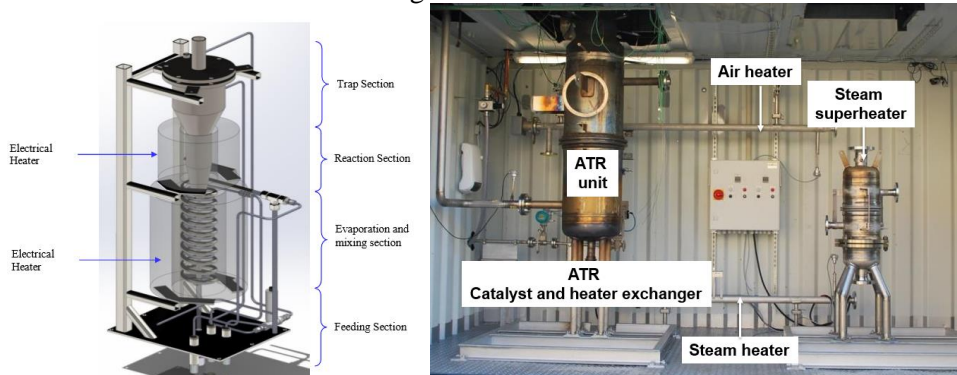
LiFeO<sub>2</sub> catalyst was prepared via a solution combustion synthesis (SCS) method and investigated under realistic conditions as catalysts for the gasification of particulate matter retained in a filter downstream the reformer. The catalyst exhibited high activity toward the catalytic gasification of soot in a synthesis gas mixture [4]. LiFeO<sub>2</sub> catalyst was deposited over the wall-flow filter. For the pilot testing campaign and demonstration plant, the filters were coated with LiFeO<sub>2</sub> up to 20 g/L of loading (Figure 3).



**Figure 3.** a) Monolithic assemblies consisting of 4 smaller monoliths for the pilot scale experiments and b) coated filter for the demonstration plant.

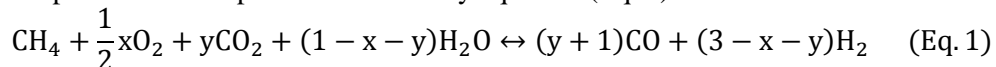
### Catalytic test

First, in order to select a suitable support structure for BioRobur fuel processor, all the catalytic support (Figure 2) were tested in a test-rig under ambient pressure. Different inlet temperature (500, 600, 700 °C), S/C ratio fixed at 2, O/C ratio (1.0, 1.1, 1.2) and GHSV (5000-85000 h<sup>-1</sup> in operation condition (OPC).) were adopted. A "synthetic biogas" was used rather than real biogas to test the fuel processor, because the pilot demonstration is located at a university campus rather than at a biogas site. Later on, two of these structures were selected to be tested coupled with the filter in the pilot and full scale under realistic conditions. The pilot and full scale reactor are illustrated in the Figure 4.

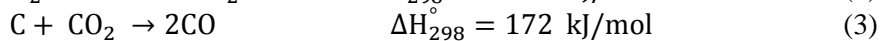
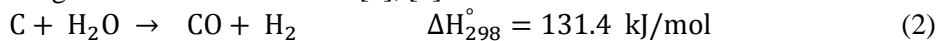


**Figure 4.** 3D view of the pilot-scale reactor (left) and demonstration plant: ATR reactor and steam superheater together with air heater and steam heater heat exchangers (right).

In the ATR process the endothermic (SR) and exothermic (CPOX) reactions are coupled. The ATR process is shown by equation (Eq. 1):



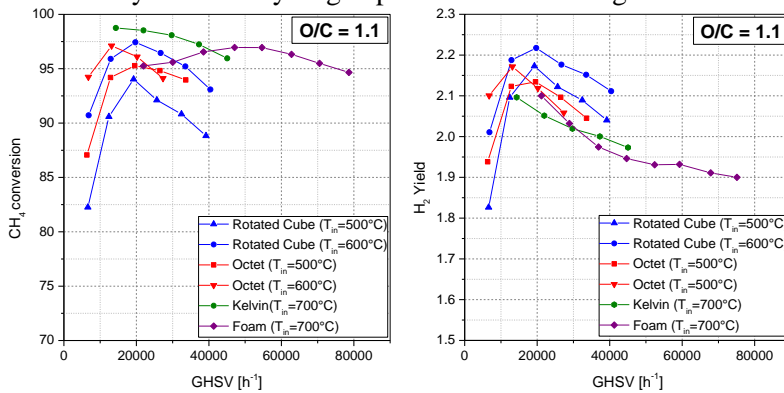
The syngas produced from the reformer is constituted by carbon dioxide (CO<sub>2</sub>), carbon monoxide (CO), hydrogen (H<sub>2</sub>) and steam (H<sub>2</sub>O). The possibility of gassing the soot in this specific environment can be reached according to the following reactions for the carbon [6], [7]:



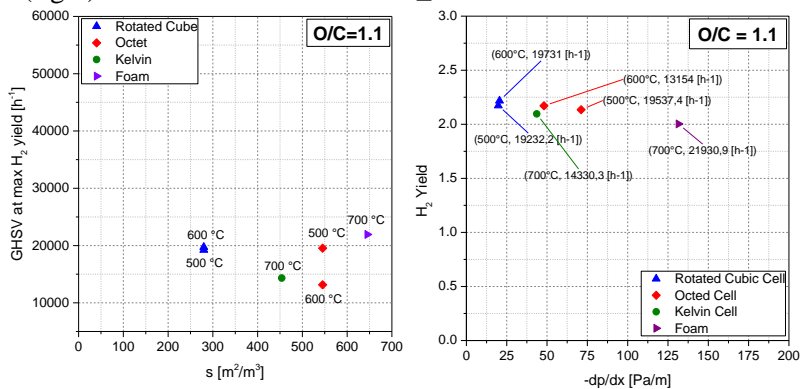
## Results

Figure 5 shows the results of the supports tested in the test-rig. Homogenous lattice composed of cubic rotated cells presented the best performance to convert biogas into hydrogen with a CH<sub>4</sub> conversion of 95% and H<sub>2</sub> yield of 2.2 using an O/C ratio of 1.1, S/C ratio of 2 and GHSV of 20000 h<sup>-1</sup>, moreover, this support presents the lower pressure drop (6-40 Pa/m) with the lower specific surface area comparing with the other structures tested (Figure 7). For the pilot and demonstration coupled

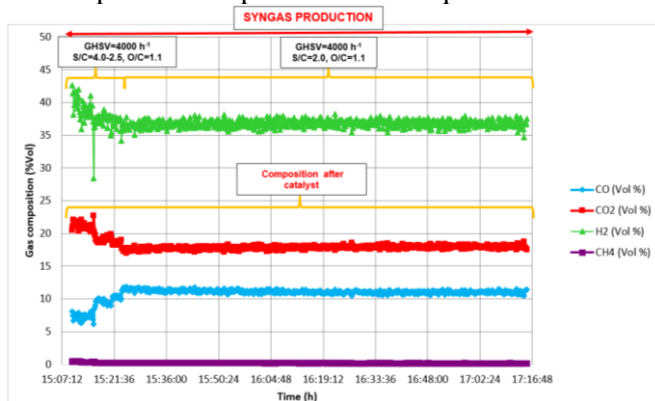
system were selected the conventional foam and rotated cube cell for the test campaign. Figure 7 shows the syngas production during the preliminary tests using the foam as a catalyst for the hydrogen production from biogas.



**Figure 5.** Experimental data for O/C ratio equal to 1.1. CH<sub>4</sub> conversion (left) and H<sub>2</sub> yield (right) as a function of the GHSV<sub>OPC</sub>.



**Figure 6.** Relation of the GHSV at maximum H<sub>2</sub> yield and the Specific surface area (s) (left) and the pressure drop for O/C ratio equal to 1.1.



**Figure 7.** Syngas production during the test using an O/C ratio of 1.1 and S/C ratio of 2 and GHSV= 4000h<sup>-1</sup>.

A long duration test in the pilot plant was performed principally to see the interaction of the reformer part with the filter part, of which, satisfactory results were obtained in terms of hydrogen yield and pressure drop in the system. The system reach predicted concentration creating a negligible pressure drop during the operation time of the processor.

### Conclusion

A robust and efficient decentralized fuel processor based on the direct ATR of biogas with a nominal production rate of hydrogen of 50 Nm<sup>3</sup>/h were developed. Innovative supports were designed and tested. A novel catalytic wall-flow trap located downstream from the ATR unit was performed. The coupled system is being tested at demonstration scale.

### Acknowledgments

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