ProEcoPolyNet

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Best practice Sheet
" BIO-HYDROGEN"

RTD Project Identification

RTD Project Name: BIO-HYDROGEN

RTD Contract No.: 17819

Programme: FP6

Objectives and Description of Technology

Development of a Biogas Reformer for Production of Hydrogen for PEM Fuel Cells

Objectives

BIO-HYDROGEN aimed at the development of a stable and cost effective biogas reforming system (6 kW hydrogen) for decentralised application with biogas from agricultural biogas plants, municipal waste water treatment plants and landfills. Costs of 1 EUR/kWh Hydrogen were targeted.

The first main objective was the development of a biogas reformer system which exhibits a better compatibility with biogas and hence shows an improved efficiency.

The second objective was the implementation of a cost effective cleaning unit for biogas. Biofiltration was believed to give good results in terms of cost-efficiency. Biofilters had been investigated for various applications but up to then their usage for siloxane* removal had not been realised. A laboratory prototype was intended to be the basis for the development of a biotrickling filter system capable to treat 1-2 m^3/h biogas. The aim was to integrate this new biotrickling filter for siloxane removal to an already developed biotrickling filter for hydrogen sulphide (H_2S).

The produced "bio-hydrogen" is going to be used in PEM (Polymer Electrolyte Membrane) fuel cells.

Basic principles

Hydrogen (H_2) can be generated by a reforming process (mainly **steam reforming**) of methane, which is contained in natural gas or biogas, giving place to a mixture of hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2) and water (H_2O).

Steam reforming is a widely-used process to produce hydrogen-rich synthesis gas from methane (CH_4) or lightly volatile hydrocarbons.

$C_nH_m + nH_2O \Rightarrow nCO + ((n+m)/2)H_2$ (1)

$CH_4 + H_2O \Leftrightarrow CO + 3H_2$ (2)

$CO + H_2O \Leftrightarrow CO_2 + H_2$ (3)

During the steam reforming process of methane a mixture of H_2, CO, CO_2 and H_2O is generated. (see **(1)**, **(2)**, **(3)**) To encrease the hydrogen yield this gas mixture must be fed to a water gas shift reactor (CO shift) in which CO reacts with steam over a catalyst to produce more hydrogen and carbon dioxide.

Because of the similar composition of biogas and natural gas the technology applied for biogas reforming should be similar to the technology used for natural gas reforming. However, there are a number of decisive differences:

- The use of biogas requires some purification before the reforming and the produced hydrogen needs further clean-up befor its use in low-temperature fuel cells. The catalyst in the reformer unit (usually a nickel or a noble-metal-based catalyst) can be poisoned by sulphur and halogen containing compounds. The final level of these compounds in the produced gas is given by the tolerance of the fuel cell. PEM fuel cells require virtually zero sulphur and the use of a pure hydrogen fuel.

- Besides the contaminants the greatest difference beteween biogas and natural gas is the fact that biogas shows a high content of CO_2 (~ 35%). Within the Bio-Hydrogen project the improvement of the heat and steam management for CO_2 containing gas will be targeted with the aid of simulation and modelling.
- A screening of the catalysts currently used for the reforming reaction will be performed in order to evaluate and compare their stability, performance and durability when used for biogas reforming.

* Volatile Methyl Siloxanes (VMS) are the result of hydrolysis of Polydimethylsiloxane (PDMS), an organosilicon compound which is used in a wide range of consumer applications (e.g. Silly Putty, silicone adhesives, lubricants, food additive (anti-foaming agent,…). Due to its widespread use, PDMS can be found in land fill gas and sewage sludge. The use of these PDMS contaminated substrates in an anaerobic digester leads to VMS-containing biogas, which can have negative effects on the catalyst of the reformer or the fuel cell.

Results of the project – Technical characteristics of the prototypes

Biogas reforming system

Within the project a biogas steam reformer prototype system for a capacity of 6 kW hydrogen was constructed, manufactured and implemented for testing at a pilot biogas plant at a Spanish slaughterhouse (Frieres / Langreo). (see **Fig**. 1)

Laboratory scale testing showed that commercially available catalysts for methane steam reforming are also suitable for biogas reforming. In addition it was demonstrated in the laboratory that a state of the art natural gas steam reformer (consisting of a pre reformer, a reformer, a shift reactor and a heat integration system) is also appropriate to the reforming of clean model biogases.

This steam reformer, which was delivered by the ZBT gGmbh, was the basis for the development of the biogas steam reformer prototype system. In order to create a fully independent reformer system, supply lines for the necessary reformer inputs (deionised water, biogas, air and cooling water) were designed and manufactured. The German Technical Inspection Authority “TÜV Rheinland Group” in cooperation with University Duisburg-Essen prepared a safety analysis of the prototype system.

The performance of the prototype system with respect to the biogas conversion (CH_4 content in product gas), the shift operation (CO concentration in product gas) and the hydrogen efficiency was investigated (see **Fig**. 2).

All tests performed confirmed the functional capability of the prototype system. The peripheral components, which are necessary for the operation of the system (e.g. pumps, valves, measurement devices), and the safety devices operated as desired. The conversion rate of biogas (methane) and the hydrogen content in the product gas fulfilled the expectations. The CH_4-content in the input gas (biogas) was about 66%. The reformer gas obtained contained more than 70% H_2. The methane content in the product gas was kept below 2%.

Biogas upgrading system

Before biogas is used in a steam reformer it needs purification (e.g. H_2S and siloxane removal).

Within the Bio-Hydrogen project a siloxane laboratory filter - a biofilter - was designed and tested. (see **Fig. 3a**) Up to now biofilters have not been used for siloxane removal before. The bacteria population selected to inoculate the biofilter was a mixture of cultures from a silicon manufacturer waste water treatment plant and a municipal waste water treatment plant. The removal efficiency of the different types of siloxanes was identified with > 50% in average. The proof of quantitative biodegradation was done and led to an up-scaling to a system up to 0,5-1 m³/h biogas flow rate. Long term tests of an adapted lab system were carried out at the University of Nitra (see **Fig. 4**).

The developed siloxane biofilter prototype is combined with an H_2S biotrickling filter (developed in a previous project), which reaches a removal efficiency of >95% (see **Fig. 3b**). Both together form the complete biogas upgrading system.

Location and use

The biogas upgrading and reforming system is intended for decentralised application. Biogas produced by agricultural biogas plants, municipal waste water treatment plants and landfills should be utilised.

Capital investment and maintenance costs

Assessment: Reformer cost estimation based on the steam reformer tested led to production costs of cleaned hydrogen of 0,18 - 0,12 EUR/kWh H_2 for a 5 and a 15 kW reformer. This value is lower than the cost target for the production itself, which was estimated to 0,25 EUR/kW. Primarily costs of 1 EUR/kWh H_2 were targeted.

State of Development/Market implementation

The biogas reforming system and the biogas upgrading system are prototypes. Both prototypes were tested and all tests performed confirmed the functional capability of the prototypes.

Benefits and obstacles

Bio-Hydrogen will play an important role in the future energy industry as a clean energy source with a neutral CO_2 balance that is suitable, e.g., for use in fuel cell systems. In particular, the mutual transformability of hydrogen and electricity is viewed as one of the biggest advantages of this energy source. Hydrogen can be used in the transport sector as well as for decentralized power generation.

However, to reach marketability far more research is essential. Furthermore storage systems, cost-effective technolgies and infrastructure for H_2 are required.

Contact and further information

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Fig. 1 *Prototype for a biogas reformer at biogas plant in Frieres constructed by University Duisburg-Essen*

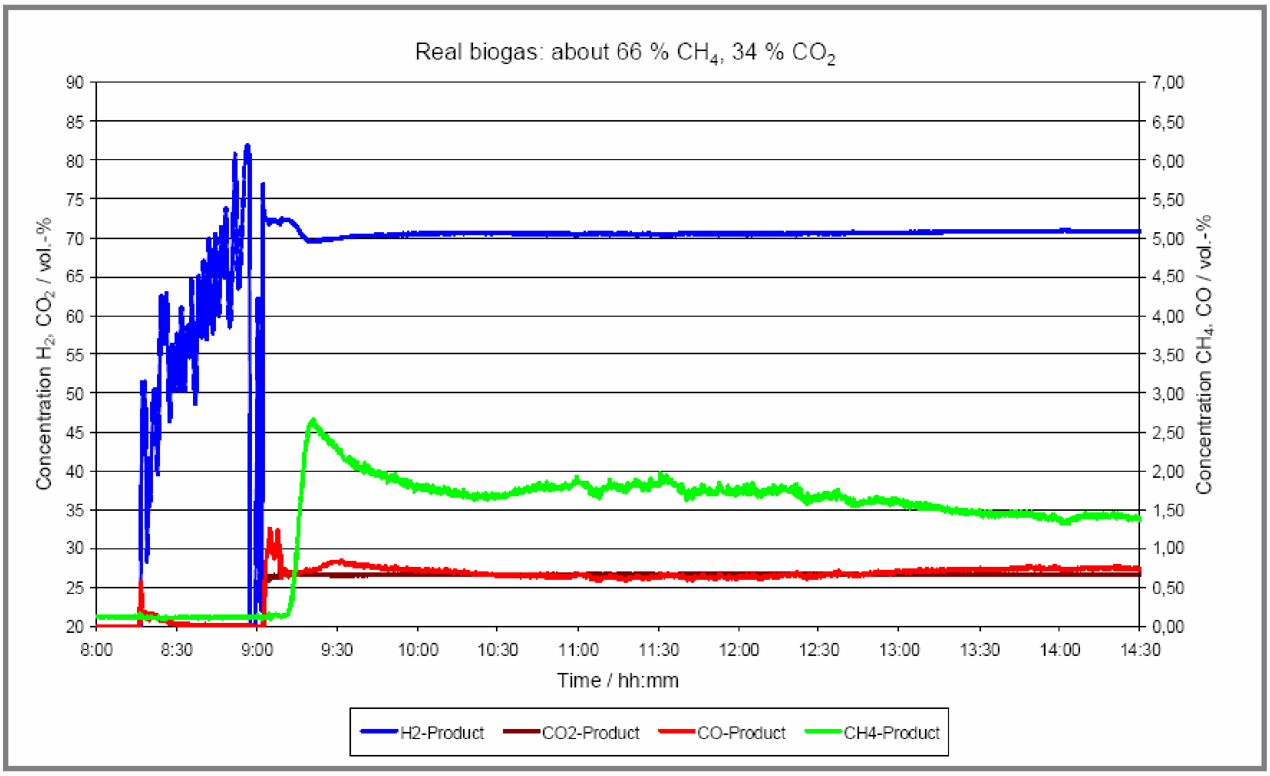

Fig. 2 *Composition of the reformed gas obtained during operation with real biogas in Frieres*

Fig. 3a and 3b *Laboratory trickling filter for biological siloxane cleaning at Profactor GmbH and combined trickling filter for H_2S and siloxane cleaning at biogas plant in Frieres*

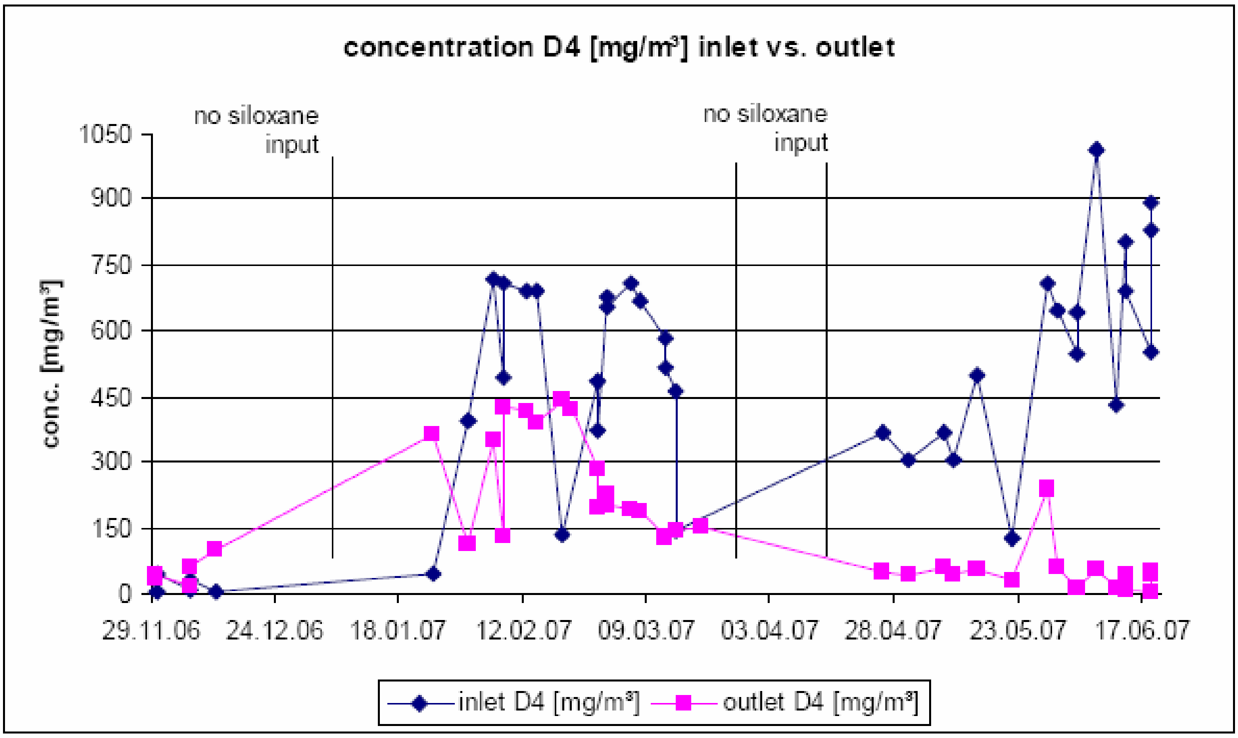

Fig. 4 *Siloxane concentration of D4 at inlet and outlet of the durability test at Nitra*