Available online at www.sciencedirect.com
SCIENCE DIRECT
Journal of Power Sources 145 (2005) 632–638
JOURNAL OF POWER SOURCES
www.elsevier.com/locate/jpowsour

Operation of molten carbonate fuel cells with different biogas sources: A challenging approach for field trials

S. Trogisch [a,*], J. Hoffmann [b], L. Daza Bertrand [c]

[a] *Profactor Produktionsforschungs GmbH, Im Stadtgut A2, A-4407 Steyr/Gleink, Austria*
[b] *MTU CFC Solutions GmbH, Germany*
[c] *CIEMAT, Spain*

Accepted 9 February 2005
Available online 25 April 2005

Abstract

In the past years research in the molten carbonate fuel cells (MCFC) area has been focusing its efforts on the utilisation of natural gas as fuel (S. Geitmann, Wasserstoff- & Brennstoffzellen-Projekte, 2002, ISBN 3-8311-3280-1). In order to increase the advantages of this technology, an international consortium has worked on the utilisation of biogas as fuel in MCFC. During the 4 years lasting RTD project EFFECTIVE two different gas upgrading systems have been developed and constructed together with two mobile MCFC test beds which were operated at different locations for approximately 2.000–5.000 h in each run with biogas from different origins and quality. The large variety of test locations has enabled to gather a large database for assessing the effect of the different biogas qualities on the complete system consisting of the upgrading and the fuel cell systems. The findings are challenging. This article also aims at giving an overview of the advantages of using biogas as fuel for fuel cells.

Keywords: MCFC; Gas upgrading; CO_2 neutral; Large biogas variety

1. Introduction

The combination of biogas and high temperature fuel cells enables an efficient utilisation of a renewable energy source (RES), resulting not only in a reduction of hazardous emissions but of green house gases [3,7,8]. Biogas is produced via anaerobic digestion (AD), which involves the breakdown of organic waste by bacteria in an oxygen-free environment. It is commonly used as a waste treatment process but also produces a methane-rich biogas which usually is used to generate heat and/or electricity with conventional combined heat and power (CHP) units [2]. Its composition and detrimental components vary depending of the source waste. However, the main components are CH_4 (∼60%) and CO_2 (∼40%), with approximately 200–3000 ppm H_2S which has to be removed in order to avoid damage of the fuel cell components [4].

Anaerobic digestion is getting to be a process not only for energy production but also for organic waste treatment. Due to this combination, interesting synergies are arising, enabling to make better use of the available biogas potential [4]. However, within the past years research in the sector of the AD has concentrated on the process itself and not that much on other applications of the biogas than the CHP generation. The main disadvantage of the conventional CHP generation is that the heat mostly can't be used in a satisfactory way due to the lower temperature value (usually 90 °C) and that what is really interesting, the electricity, is not produced with high efficiency due to the limitations of the Carnot process. Therefore, other applications are being searched for. High temperature fuel cell technology can be an interesting alternative due to the fact of the higher achievable electricity efficiency (50–60%), the high temperature (450 °C) which can ideally be used in industrial processes and the limited emissions (out of the CHP exhaust gas) [5].

* Corresponding author. Tel.: +43 7252 885 413; fax: +43 7252 885 101.
E-mail address: steven.trogisch@profactor.at (S. Trogisch).

0378-7753/$ – see front matter
doi:10.1016/j.jpowsour.2005.02.053

Fig. 1. MCFC testbed (left: MCFC unit; right: controlling unit).

In order to use biogas in fuel cell systems the H_2S has to be removed completely. In the EFFECTIVE project this was achieved in two process stages [4]. First, in the gas upgrading process the H_2S is reduced down to less than 10 ppm. For this purpose two different upgrading systems have been constructed in order to compare the different techniques. The remaining amount is removed in the second stage by adsorber materials, such as activated carbon.

The two MCFC testbeds (Fig. 1) are operated each with a 300 W stack (Fig. 2), which is removed after each test cycle for material analysis. Six stacks were available for the planned six test cycles. The test beds have been operated at different locations with different types of biogases (from landfill, waste water, agricultural and co-fermentation facilities) in Spain, Germany, Austria and Slovakia. The first test run was launched during spring 2002 in Owschlag (Schleswig-Holstein/Germany) and the last testcycle was finished in Pinto (Madrid, Spain) in May 2004. After each test cycle, material samples underwent analyses in order to identify undesired interactions between the biogas and the components of the system.

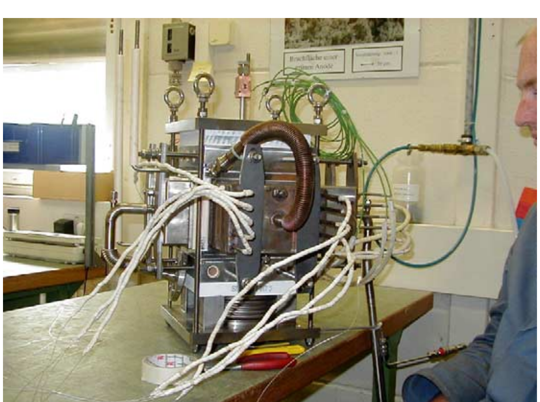

Fig. 2. Assembly of MCFC stack at MTU premises.

2. Synergies by using biogas in fuel cells

By bringing the fields of biomass, (bio) residues, anaerobic digestion and fuel cell technology together, several synergies [4] [12] make such applications attractive:

(i) Utilisation of RES in fuel cell technology leading to a sustainable cycle by using a CO_2 neutral fuel. Such a fuel enhances the environmental advantage of fuel cell technology. Biogas is the renewable energy with very high potential for greenhouse gas reduction.
(ii) Efficient and clean energy conversion of valuable RES: due to the nature of fuel cells, hardly any emissions are produced while converting biogas into electricity. And this is possible with high electrical efficiencies of approximately 50–60%.
(iii) High user potential for utilising the process heat which is released from the MCFC-process: due to the residual heat of (high temperature) fuel cells at approx. 500 °C, it is possible to use this heat for industrial purposes in form of steam as e.g. for steam turbines, sterilization at hospitals. . .
(iv) Decentralisation of the energy production is an approach for a more secure and stable energy supply. Decentralisation is one of the main advantages of RES, as these are in many cases locally available. Biogas plants are to be found usually in the decentralized agricultural sector.
(v) Anaerobic digestion enables a cost reduction of organic residue disposal and new income for the agricultural sector. Alternative organic waste treatment is usually strongly energy demanding, as is the case of composting. Anaerobic digestion has a higher investment cost as e.g. composting facilities but provides the operator with energy which can be sold to the electricity grid. As organic wastes are usually co-digested in agricultural biogas plants, farmers are enabled to produce more electricity, giving them an additional income possibility.

By involving the agricultural sector also for the production of energy crops for the AD process it is possible to close the nutrient cycle, as the digested organic wastes are used as fertilizer on the farming land. By reducing the use of mineral fertilizers farmers contribute to the environment; as such fertilizers are produced with high amounts of energy. The digested substrate in biogas plants can substitute such fertilizers, solving in that way also the question of what to do with these substrates.

3. Approach

In order to use biogas in fuel cell systems the H_2S has to be removed completely. In the EFFECTIVE project this was achieved in two process stages. First, in the gas upgrading process the H_2S is reduced down to less than 10 ppm. For this purpose two different upgrading systems have been constructed in order to compare the different techniques. The remaining amount is removed in the second stage by adsorber materials, such as activated carbon.

The two MCFC testbeds (Fig. 1) are operated each with a 300 W stack (Fig. 2), which is removed after each test cycle for material analysis. Six stacks were available for the planned six test cycles. The test beds have been operated at different locations with different types of biogases (from landfill, waste water, agricultural and co-fermentation facilities) in Spain, Germany, Austria and Slovakia. The first test run was launched during spring 2002 in Owschlag (Schleswig-Holstein/Germany) and the last testcycle was finished in Pinto (Madrid, Spain) in May 2004. After each test cycle, material samples underwent analyses in order to identify undesired interactions between the biogas and the components of the system.

4. Fuel cell requirements on biogas quality

The fuel cell systems are relatively sensitive to trace gases in biogas [9,10]. Low temperature fuel cell systems are especially sensitive to CO, CO_2, CH_4, H_2S, NH_3, whereas in high temperature fuel cell systems the embedded catalytic processes are mainly sensitive to H_2S [1]. The typical components in biogas are the following:

CH_4: 40–70%; CO_2: 30–50%; N_2: 0–20%; O_2: 0–5%; H_2S: 0–4000 ppm; mercaptane: 0–100 ppm; siloxane: 0–100 mg m^{-3}; halogenated hydrocarbones: 0–100 mg m^{-3}. Beside these typical biogas components, other detrimental trace gases are extremely harmful for the fuel cell system as e.g. halides like chlorine and fluorine compounds. These are common in landfill gas as well as in wastewater treatment gas [11,12].

The work within the EFFECTIVE project concentrates mainly on the removal of H_2S since it is considered to be the main harming component in the ordinary biogas (=biogas coming from agricultural co-fermentation plants). It can be said, that gas upgrading is a key issue for coupling biogas and fuel cells.

5. Selection of fuel cell for operation with biogas

There were several good reasons to select the MCFC for this project. As demonstrated in Fig. 3 high temperature fuel cells are better suited for biogas operation since their components are tolerant towards several components of the biogas which are harmful for low temperature fuel cells. Further, high temperature fuel cells enable internal reforming of the fuel, leading to clearly higher system efficiencies (of up to 50% when using MTUs Hot Module). MCFC have additionally the advantage that they can use the CO_2 as reactant in the process, increasing the electrical efficiency by approximately 2% [12]. And last but not least, MCFC are among the high temperature fuel cells in an advanced stage of market penetration (MTUs Hot Module). These are the reasons why the MCFC was selected for the project.

6. Work performed

The work performed on the technical side of the project was the development of both the chemical as well as the biological gas cleaning units with their subsequent analytical tests. This included the setting of common interfaces between the biogas plants, the gas cleaning units and the MCFC unit.

Biological gas cleaning unit (Fig. 4). First results on lab scale showed that the H_2S concentration in the outlet is under the limit of detection of ∼0 ppm (on lab scale!) with an inlet concentration of approximately 800 ppm H_2S. The up-scaled system with a capacity of 200 l biogas h^{-1} has been modified and tested first in the Profactor dependencies and then at the biogas plant in Kolinany (Slovakia), which belongs to the University of Nitra. It was put into operation in January 2002 and is in continuously operation. The obtained results showed that the biological system needs certain time to adapt itself to H_2S peaks in the biogas. If the H_2S concentration in the inlet remains constant, the system can reduce the H_2S concentration from 500 ppm down to less than 5 ppm (Fig. 6). Fig. 6 also shows a typical variation of the H_2S concentration in

Low Temperature FC ← → High temperature FC

FC-Typ Gas comp. / Temp.°C	PEFC 80	AFC 100	PAFC 200	MCFC 650	ITSOFC 800	SOFC 1000
H_2	F	F	F	F	F	F
CH_4, CnHm	IG	poison	IG	IG/F	F	F
CO_2	IG	poison	IG	React.	IG	IG
CO	poison (<50ppm)	poison	poison (<500ppm)	F	F	F
H_2S, COS	nd	poison	poison (<50ppm)	poison (<0.5ppm)	poison	poison (<1.0ppm)
NH_3	poison	F	poison	F	F	F

Analysis on siloxanes, halides, tar, dust, and other contaminants are missing!!!

F.....Fuel, IG.... Inert gas, React. .... Takes part in electrode reaction

Fig. 3. Effect of typical biogas components on the different types of fuel cells.

Fig. 4. Biological H_2S removal unit developed by Profactor, in the fuel cell lab from Uni Nitra (Slovakia).

Fig. 5. Chemical H_2S removal unit developed by Seaborne.

biogas (Biogas plant in Kolinany). The apparent peaks could become a problem for the biological upgrading system. However, PROFACTOR has as result from the experience gained during the experimental runs within this project, changed the design of the filter system to enable a higher flexibility.

The chemical biogas upgrading system (Fig. 5) has been constructed and coupled with the MCFC test bed in May 2002 at SEABORNE R&D Centre. The H_2S removal is steered by the pH of the liquid iron medium. The system has a mass flow capacity of 200 l biogas h^{-1}. It can guarantee a continuous operating of 14 days without regeneration. The regeneration of the liquid iron medium is achieved by airflow through the solution. Under operating conditions the maximum H_2S concentration in the outlet of approximately up to 5 ppm with an inlet concentration of up to 2.400 ppm H_2S. This system was operated at three different locations, cleaning either agricultural biogas in Owschlag/Germany (Seaborne), sewage gas from a wastewater treatment in Linz/Austria (Stadtwerke Linz) or landfill gas in Pinto/Spain (Urbaser facilities in Pinto). The gas cleaning process achieved its aims at all three locations well. One of the lessons learned was that the system had to be continuously in operation in order to avoid long stand still periods, where the iron components tend to precipitate.

MCFC-Single cell tests have been performed in order to investigate the impact of NH_3 on the fuel cells. It has been demonstrated that most of the NH_3 was removed under the operational conditions ($2\,NH_3 \Leftrightarrow N_2 + 3H_2$). In the post-test analyses of the cell components no corrosion could be detected, which was related to the presence of ammonia. These observations have been confirmed in a second single cell experiment. This second cell has also been used to verify the field start-up procedure for the lab stack, which was quite different to the standard lab start-up. After 1 week of operation the single cell was cooled down to room temperature. Then it was reheated again to its operational settings only using the gases, which are available under field conditions. This test was passed successfully without any loss in performance and catalyst activity.

Two test beds have been constructed: Testbed 1 operated at three different locations (together with the chemical gas upgrading system) while testbed 2 was stationed in Slovakia during 2 years (Fig. 6). Each testbed comprises 2 units, one contains the monitoring and control system, the second one the MCFC Stack as well as all other required devices as pre reformer, steam generator, etc. . . (Fig. 1). The Test Beds have been designed according to the TÜV regulations, which are based on the CE labelling. This guarantees a high technical standard and security.

Each stack consists of 10 cells, which provide a maximal power output of 300 W. Each stack is tested under field conditions for an average of between 2.000 and 4.000 h. After concluding these tests, the cells are dismantled and the materials are analysed in order to find out how the contaminants inside the biogas interacted with the stack material. The fuel cell system was made end user friendly with a specially developed software. Fig. 7 shows a screen shot of the upper surface of the control system.

Biological PPU – Biotrickling Filter at Biogas Plant Kolinany / Nitra - period 07/2003 to 06/2004								
Month	H_2S raw gas		H_2S cleaned gas		H_2S loading rate		Elimination capacity	
	[ppm]	[ppm]	[ppm]	[ppm]	[gH_2S/m^3h]		[gS/m^3h]	
	average	max.	average	max.	average	max.	average	max.
July 03	75	168	2	7	1,2	2,6	1,1	2,5
Aug 03	46	186	1	1	0,7	2,8	0,6	2,8
Sept 03	59	315	1	1	0,8	3,7	0,7	3,5
Oct 03	1	24	0	0	0	0	0	0
Nov 03	828	4212	11 [*)]	64 [*)]	3,3	9,7	3,1	0,9
Dec 03	189	621	1	1	2,3	9,8	2,1	9,1
Jan 04	130	409	3	33	1,8	6,0	1,6	5,6
Feb 04	36	694	2	15	0,5	9,0	0,3	2,5
Mar 04	14	150	1	1	0,3	2,2	0,3	2,0
Apr 04	58	222	1	2	1,0	3,2	0,7	3,0
May 04	168	369	4	83 [**)]	0,8	2,9	0,7	2,8
June 04	184	320	0	4	1,0	2,7	0,9	2,5

[*)] In November 2003 the FC test bed was out of operation

[**)] This peak was after the shut down of the 3rd FC stack

Fig. 6. Gas quality at inlet and outlet of the biotrickling filter including the specific H_2S load at the biogas plant in Kolinany (Slovakia).

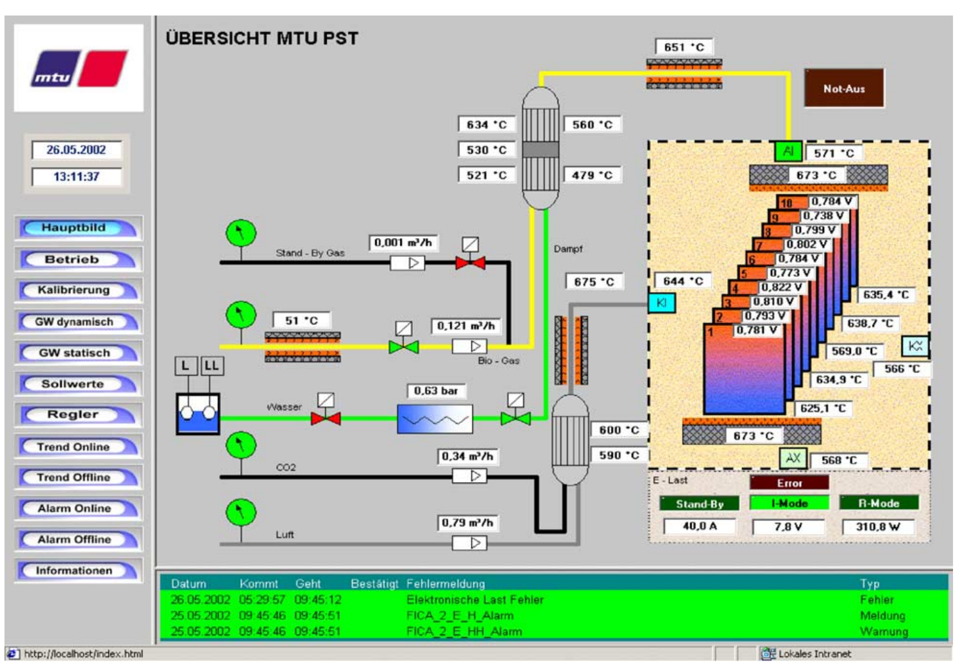

Fig. 7. Screenshot of the control system of the MCFC test bed.

7. MCFC results

The burn-out procedure of the first stack in this project was started in April 2002 in Ottobrunn, Germany, at the facilities of MTU. After a short period of operation ca. 300 h, the stack was cooled down and delivered to R&D-Center of Seaborne (Owschlag, Germany), where it was restarted at the end of May. It has been the first time for MTU that such a lab-stack has been transported outside its testbed. At the end of August the operation of the stack was terminated at an overall operation time of 2500 h with a calculated average efficiency of 40% (based on the LHv of the biogas–maximum efficiency 53%).

Operation example: First cycle in NITRA: the stack was started in October 2002. In December 2002 the stack operation was interrupted after an overall operation time of 1500 h. In March 2003 the stack was re-started again and it operated until late April 2003. In total the stack went through 2300 hot operation hours. Two further testcycles have been done, achieving approximately 6.000 h.

Further test cycles have been made in Linz (Austria) at a wastewater treatment facility, at Pinto (Spain) where landfill gas is used at the waste treatment plant, and in Nitra (a 2nd and 3rd cycle). Total operating tame is approximately 15.000 h.

Material analysis have shown, that biogas has no negative effect on the stack material.

The aim was to determine the nature of contaminants and their behaviour within the process chain: fermentation process–gas upgrading–adsorber–reforming process–fuel cell. This helped to estimate the quality of the gas upgrading system. First of all the adsorber material was analysed for trapped contaminants. Later the reformer catalyst and the material of the stack components were analysed for their contamination. This work was done in collaboration of Ciemat and MTU.

8. Discussion

The results showed to be positive. However, the test beds housing the MCFC showed to be delicate to changes in their environment. Most of the observed problems were subsequently related to this effects (power outages, gas interruptions, etc.). The consortium however, could prove through intensive testing and material analysis that biogas is well suitable for use in high temperature fuel cells, which was the aim of the project. It showed that one of the key issues is the purification of biogas. This is to happen in a sustainable and cost efficient way.

9. Conclusions

The technical conclusions of the project are:

(1) Biogas operation of MCFC without any problems (more than 15.000 h operating experience) provided a suitable biogas purification is available; (2) the key issue is the gas purification: a cost effective and sustainable system is essential; (3) the whole test set up is sensitive towards environmental impacts as it is still a lab system; (4) electrical efficiency of MCFC stack of 50% achieved (Seaborne); (5) post-test analyses indicates no severe interaction between biogas and fuel cell system components; (6) NH_3 reduction by catalytic decomposition in the fuel cell system happens; (7) both gas purification systems fulfilled our expectations; (8) the synergy potential for biogas and fuel cell systems seems to be enormous with view of an sustainable energy supply; (9) using biogas as renewable fuel for fuel cells is a very promising clean application; (10) a specific legal framework should promote this technology; (11) biogas–MCFC technology for CHP is in competition with gas engines. Justification must be found in environmental issues; (12) demonstration sites should be set up in different sectors. Today a proximity to R&D locations as well as transfer points to modern business is preferable.

Now fuel cells have to gain the market with cost competitive prices and high technical standards in order to enable this attractive application for biogas (and fuel cells).

10. Final statement

If fuel cells are chosen as a tool for achieving a sustainable and clean energy future, then it is essential to know where the required prime energy hydrogen will come from. Fuel cells have very important advantages but if the energy they transform into electricity is not sustainable, no advantage will be gained. The used prime energy has to be, up to a certain extent, a renewable energy source and be as far as possible directly suitable for its energy transformation in fuel cells. If the prime energy undergoes several processes in order to adapt it to the fuel cells, the process will lead to high costs. Therefore, biogas upgrading has to be a cost competitive process in order to avoid a neutralisation of the fuel cell and biogas advantages.

Biogas and fuel cell systems depend on each other in order to be implemented in a joint way. Biogas technology is well developed. In Germany, over 2.200 biogas plants are currently in operation, in Austria there are approximately 200. Other countries as Denmark, Sweden and Switzerland are also very experienced with anaerobic digestion involving the agricultural sectors. The potential for their implementation is enormous.

References

[1] BIS Brennstoffzellen Information System, erstellt im Auftrag des Bundesministeriums für wirtschaftliche Angelegenheiten, an der Fakultät für Elektrotechnik und Informationstechnik der Technischen Universität. Wissenschaftliche Betreuung: Dipl.-Ing. Dr. techn. Viktor Hacker (internet link: http://an.e2i.at/bis/).

[2] ATLAS Project, erstellt von der European Network of Energy Agencies (EnR) für Directorate General XVII of the European Commission, (internet link: http://europa.eu.int/comm/energy_transport/atlas/).
[3] Greenhouse Gas Balances of Bioenergy Systems, IEA Bioenergy Task 25, Part G. Jungmeier, 2000.
[4] S. Trogisch, W.E. Baaske, Biogas powered fuel cells: case studies for their implementation, 2004, ISBN 3-85487-626-2.
[5] K. Ledjeff, Brennstoffzellen–Entwicklung, Technologie, Anwendung, C.F. Müller, 1995, ISBN 3-7880-7514-7.
[6] S. Geitmann, Wasserstoff- & Brennstoffzellen-Projekte, 2002, ISBN 3-8311-3280-1.
[7] W. Ahrer, Zukunft Wasserstoff; Forum Brennstoffzelle, 14 und 15 Oktober 2003. Design Center Linz, Herausgeber: Energie AG Oberösterreich, 122–132.
[8] J. Schäfer, Verfahrenstechnische Untersuchungen zur Vergärung von Biomüll und Klärschlamm, Fraunhofer IBR Verlag, 1998, ISBN 3-8167-5231-4.
[9] J.T. Müller, Direktverstromung Flüssiger Energieträger in Brennstoffzellen, Shaker Verlag, 2000, ISBN 3-8265-7003-0.
[10] J. Larminie, A. Dicks, Fuel Cell Systems Explained, Wiley, 2002, ISBN 0-471-49026-1.
[11] S. Trogisch, J. Hoffmann, L. Daza Bertrand, N.O. Vesterager, Efficient energy conversion by using biogas in an MCFC: first experiences, in: Poster presentation, Fuel Cell Seminar, Palm Springs, USA, November 18–21, 2002.
[12] S. Trogisch, Potential applications and synergies of biogas fuel cells as an efficient alternative energy conversion technology, in: (IEA) Conference: hydrogen and fuel cell based energy systems, Vienna, Austria, 31 March and 1 April, 2004.