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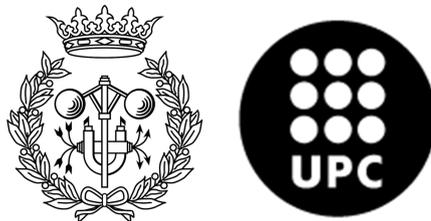
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Sewage Biogas Energy Valorization via Solid Oxide Fuel Cells

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“All wealth becomes waste, but that waste has a golden value”

(Victor Hugo)

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Abstract

A more sustainable and secure energy supply is required for the forthcoming generations; where the actual dependence on the fossil fuel reserves should be replaced by self-sufficiency and use of renewable energy resources. The research presented in this dissertation relies on linking an alternative source of energy with a promising and high-efficient technology; presenting a sustainable solution for energy generation both in economic and environmental terms. The opportunities for sewage biogas energy valorization via Solid Oxide Fuel Cells in order to improve the energy self-sufficiency of Waste Water Treatment Plants are assessed in this PhD thesis.

Biogas treatment technologies adapted to the stringent quality requirements of fuel cells are experimentally validated: biotrickling filters for biogas main desulphurization and adsorption processes for H₂S and siloxanes deep polishing. Furthermore, the occurrence and fate of organic silicon compounds in sewage treatment is evaluated; and several sampling methodologies for their accurate and reliable analysis are assessed. Finally, a technical and economic comparison of Solid Oxide and Molten Carbonate Fuel Cells with conventional technologies for Combined Heat and Power, such as Internal Combustion Engines and Micro-Turbines, is conducted in order to define the potential for fuel cell technology deployment in the sewage sector. The research activities were conducted in Mataró Waste Water Treatment Plant (Barcelona, Spain), where a biogas-powered 2.8 kW_e fuel cell pilot plant was designed, constructed and operated in continuous over the long-term.

Keywords

Biogas clean-up; Solid Oxide Fuel Cell; energy valorization; desulphurization, siloxanes removal; Waste Water Treatment Plant; biogas quality monitoring; Combined Heat and Power

Preface

Conventional sewage treatment is an energy consuming process, or more specifically, an electricity consuming process. Notwithstanding, energy on Waste Water Treatment Plants is not only considered in terms of consumption reduction, but also in terms of production of renewable energy in form of biogas. Today, achieving energy self-sufficiency is limited by the low electrical efficiencies of conventional biogas-powered Combined Heat and Power systems; but fuel cell technology is appearing on the scene in the recent years offering both a higher electrical efficiency and a further reduced environmental impact. Biogas energy valorization in fuel cells combines a high-efficient technology for electrical generation, i.e.: fuel cell, with the use of a renewable fuel, i.e.: biogas.

Raw biogas contains a wide range of contaminants, mainly sulfur and organic silicon compounds (siloxanes), which pose a risk to Solid Oxide Fuel Cell operation; hence biogas requires a thorough conditioning and cleaning process upstream the fuel cell unit. Moreover, monitoring of siloxanes levels remained somewhat controversial with discrepancies on optimal sampling procedure as well as quantification technique; hindering the design and operation of siloxanes removal technologies.

This work is devoted to studying and validating the whole biogas energy valorization line, including the biogas treatment system and the fuel cell operation. The integration of low-cost biological desulphurization and deep polishing physico-chemical adsorption processes with a Solid Oxide Fuel Cell has been studied in an industrial 2.8 kW_e pilot plant installed in a Waste Water Treatment Plant in Spain, showing that the stringent gas quality requirements of 0.5 ppm_v S and 1 mg Si/Nm³ can be satisfied with over the long-term. The technical and economic comparison of Solid Oxide and Molten Carbonate Fuel Cell performance with conventional Internal Combustion Engines and Micro-Turbines has been also conducted, confirming the relevant role that fuel cells can play on carbon neutral sewage treatment; particularly in small- and medium-size plants.

Today the final justification for biogas valorization in fuel cell systems needs to be found in environmental issues as some improvements both in the performance and costs are still required. Nonetheless, this thesis demonstrates that the economics for this next-generation technology are expected for the short-term. Further collaborative research between biogas producers, suppliers of biogas treatment systems and manufacturers of fuel cells is required in the near future for Solid Oxide Fuel Cell technology deployment in the sewage sector.

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List of Acronyms

A2/O: Anaerobic, Anoxic, Oxidic

A2/O reversed: Anoxic, Anaerobic, Oxidic

AC: Activated Carbon

AC: Alternating Current

AD: Anaerobic Digestion

AFC: Alkaline Fuel Cell

ASE: Accelerated Solvent liquid Extraction

ATD-GC-MS: Automated Thermal Desorption Gas Chromatography coupled to Mass Spectrometry

ATR: Auto-Thermal Reforming

BET: Brunauer-Emmett-Teller

BOD: Biological Oxygen Demand

BTEX: Benzene, Toluene, Ethyl-benzene, Xylene

BTF: Biotrickling Filter

CAPEX: Capital Expenditures

CES: Centre Européen des Silicones

CHP: Combined Heat and Power

CMAR: Carcinogenic, Mutagenic, Asthmogenic or Reproductive toxic

COD: Chemical Oxygen Demand

COPROX: CO PReferential OXidation

c-VMS: Cyclic volatile methyl siloxane

DNA: Deoxyribo Nucleic Acid

DC: Direct Current

DOE: Department Of Energy

DMDS: Di-Methyl Di-Sulfide

DMS: Di-Methyl Sulfide

DMR: Dry Methane Reforming

DOC: Dissolved Organic Carbon

DSC: Differential Scanning Calorimetry

EBRT: Empty Bed Residence Time

EC: Elimination Capacity

ECS: Energy Conversion System

EPE: Energy Police for Europe

EPS: Extracellular Polymeric Substance

EU: European Union

FFD: Flame Failure Device
FIT: Feed-In Tariff
FTIR: Fourier Transformed Infrared Spectroscopy
GC: Gas Chromatography
GC-AES: Gas Chromatography coupled to Atomic Emission Spectroscopy
GC-APCI-MS/MS: Gas Chromatography coupled to Atmospheric Pressure Chemical Ionization and Mass Spectrometry
GC-FID: Gas Chromatography coupled to Flame Ionization Detector
GC-MS: Gas Chromatography coupled to Mass Spectrometry
GC-PID: Gas Chromatography coupled to Photolionization Detector
GHG: Green House Gas
HEN: Heat Exchange Network
HTFC: High Temperature Fuel Cells
HS-GC-MS: Head Space Gas Chromatography coupled to Mass Spectroscopy
HS-SPME: Headspace Solid Phase Micro-Extraction
IRR: Internal Rate of Return
LCE: Levelized Cost of Energy
LFG: Landfill Gas
LOD: Limit Of Detection
LOQ: Limit Of Quantification
LR: Loading Rate
LSM: Lithium-Strontium-Manganite
LTFC: Low Temperature Fuel Cells
LVI-GC-MS: Large Volume Injection Gas Chromatography coupled to Mass Spectroscopy
ICE: Internal Combustion Engine
ICP-AES: Inductively Coupled Plasma coupled to Atomic Emission Spectroscopy
l-VMS: linear volatile methyl siloxane
MCFC: Molten Carbonate Fuel Cell
MSW: Municipal Solid Waste
MT: Micro-Turbine
NE: North East
NSFE: Normalized Savings in Fossil Energy
OPEX: OPERational EXpenditures
OUT: Operational Taxonomy Unit
O/C: Oxygen-to-carbon ratio
PAFC: Phosphoric Acid Fuel Cell
PBT: Persistent, Bioaccumulative and Toxic

PCR: Polymerase Chain Reaction
PDMS: Poly-Di-Methyl-Siloxanes
PE: Population Equivalent
PEMFC: Proton Exchange Membrane Fuel Cell
PER: Primary Energy Ratio
PID: Proportional, Integrative, Derivative
POC: Particulate Organic Carbon
POX: Partial OXidation
PP: Poly-Propylene
PP: Payback period
PTFE: Poly-Tetra-Fluoro-Ethylene
P&ID: Piping and Instrumentation Diagram
RE: Removal Efficiency
REACH: Registry, Evaluation and Authorization of Chemical Substances
RSD: Relative Standard Deviation
SE-GC-MS: Solvent Extraction Gas Chromatography coupled to Mass Spectroscopy
SEM-EDS: Scanning Election Microscopy coupled to Energy Dispersive X-Ray
SET: Strategic Energy Technology plan
SIM: Selective Ion Monitoring
SLE: Solid-Liquid Extraction
SMR: Steam Methane Reforming
SOB: Sulfur Oxidizing Bacteria
SOFC: Solid Oxide Fuel Cell
SRB: Sulfur Reducing Bacteria
SS: Suspended Solids
TGA: Thermo-Gravimetric Analysis
TMS: Try-Methyl-Silanol
TOE: Tone Oil Equivalent
TSA: Temperature Swing Adsorption
UK: United Kingdom
USA: United States of America
USA-DLLME: UltraSound-Assisted Dispersive Liquid-Liquid Micro-Extraction
VOC: Volatile Organic Compound
VOSiC: Volatile Organic Silicon Compounds
vPvB: very Persistent and very Bioaccumulative
VSD: Variable Speed Driver
WERF: Water and Environment Research Foundation

WGS: Water Gas Shift

WWTP: Waste Water Treatment Plant

XRD: X-Ray Diffraction

YSZ: Yttrium-Stabilized Zirconia

Chapter 1

Introduction

1. Introduction

1.1. Renewable energy and biogas

In 2014, fossil fuels (oil, natural gas and coal) accounted for 86.3% of the worldwide primary energy consumption, while nuclear, the other non-renewable primary energy source, reached 4.4% (BP Statistical Review of World Energy, June 2015). The increasing energy demand resulting from the economic and industrial development in several countries accelerates the depletion of these resources and thus increases the cost of energy. In addition, the contribution of fossil fuels to the climate change is well known. As a result of this, it is necessary to look for alternative energy sources with low environmental footprint and to develop new technologies for energy production.

The European Union (EU) puts much emphasis on developing means of dealing with both climate change control and energy market and is committed to transforming Europe into a high energy-efficient and new low-carbon technologies economy. The EU has set itself a long-term goal of reducing greenhouse gas emissions by 80 – 95% when compared to 1990 levels by 2050. The Energy Roadmap 2050 explores the transition of the energy system in ways that would be compatible with this greenhouse gas reductions target while also increasing competitiveness and security of supply.

Today, biomass currently accounts for 2/3 of renewable energy in Europe and bioenergy will play a key role in achieving the ambitious targets approved. The European primary biogas production accounted for 156 TWh_{in} in 2013 (i.e.: 13.4 Mtoe, million tones oil equivalent); 21% from landfill, 9.4% from sewage and 52% from other biogas sources, such as agriculture (Euroobserver Biogas Barometer, 2014). This energy resource is expected to increase around 50% by 2020. In terms of number of biogas plants, in 2013 there were more than 14,000 methanisation plants in Europe; with Germany having a leading role with almost 4,000; most of them on farms for cogeneration. Despite the gaining interest of biomethane in the recent years, with around 258 facilities in Europe in 2014; electricity production is still the main biogas energy recovery form regardless if it is produced stand-alone or in Combined Heat and Power (CHP) units (Euroobserver Biogas Barometer, 2014). However, when the biogas is used as an energy carrier for stationary application, the cogeneration power yields are low. Therefore, the EU only produced 52.3 TWh_e from biogas in 2013 (33% of the primary production) converted mainly in internal combustion engines. Self-consumed heat (i.e.: consumed on the site of the biogas plant) stood for 23.4 TWh_t (15%) and heat sold to district heating networks for 5 TWh_t (3%). These numbers suggest that there is a huge potential to optimize biogas energy recovery in order to use its total technical potential.

1.2. Energy consumption and production in conventional wastewater treatment

Conventional sewage treatment, as overviewed in Figure 1.1, is an energy consuming process, or more specifically, an electricity consuming process as large quantities of electricity are required to run the pumps which move the wastewater and the sludge along the Waste Water Treatment Plant (WWTP) and the compressors/blowers to supply the air to

the aeration basin. In fact, sewage treatment can account for about 3 – 5% of the total electricity consumption in most developed and developing countries (McCarty *et al*, 2011). As a consequence, around 30 – 50% of the total operating costs in a WWTP are associated to energy consumption (Guo *et al*, 2010; Shen *et al*, 2015; Caporgno *et al* 2015); hence savings in energy consumption can significantly cut-off the overall sewage treatment costs. The average electricity consumption for conventional wastewater treatment is around 0.6 – 1 kWh_e/kg COD_{IN} (Plappally and Lienhard, 2012; Elías-Maxil *et al*, 2014). This figure varies significantly from plant to plant depending on the population served, its age, the organic load and effluent quality achieved, and the installed processes. Energy efficiency measures are focused on reducing consumption; e.g.: new diffusers with improved oxygen transfer into the liquid phase (Rosso *et al*, 2008); advanced control systems for aeration optimization based on nutrient sensors (NH₄⁺, NO₃⁻) (Martín de la Vega *et al*, 2013) and other control strategies (Ostace *et al*, 2013); new low-energy processes such as Anammox for nitrogen treatment in the supernatant or the main line (van Loosdrecht *et al*, 2004; Morales *et al*, 2015), etc.

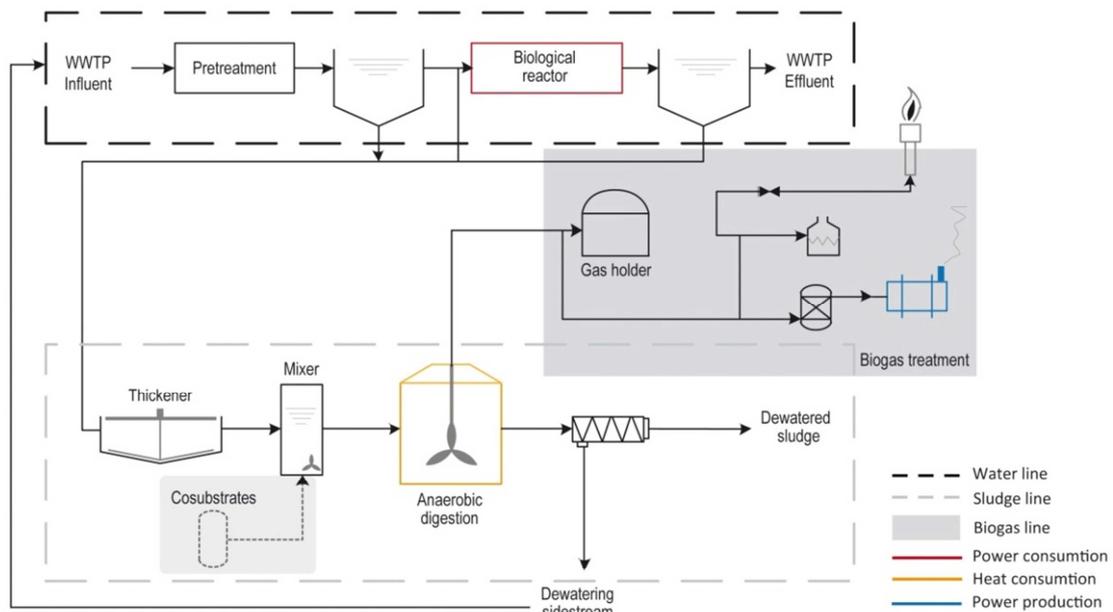


Figure 1.1. Process flow schematic of a conventional WWTP (sewage, sludge and gas lines)

On the other hand, energy on WWTP is not only considered in terms of demand but also in terms of production of renewable energy. In this context, anaerobic digestion (AD) is widely used to treat sewage sludge (Cao and Pawlowski, 2012) because it provides volume and mass reduction of the input material and also produces biogas suitable for energy production. The average energy production in a WWTP with conventional AD is around 0.8 – 1.1 kWh_{biogas}/kg COD_{IN} (Metcalf and Eddie, 2003; McCarty *et al*, 2011; Hao *et al*, 2015). Larger values can be obtained if sludge is subjected to different physical, chemical, thermal, mechanical or biological pretreatment steps to break down organic matter (Phothilangka, 2008; Cho *et al*, 2014; Tian *et al*, 2015) and/or if co-digestion with external organic substrates is implemented (Edelmann *et al*, 2000; Gupta *et al*, 2012; Nghiem *et al*, 2014). Alternative processes to produce energy from sludge are pyrolysis, gasification, incineration, supercritical water oxidation, etc. (Tyagi and Lo, 2013).

Biogas is used on-site to produce electricity and/or heat in Energy Conversion Systems (ECS) or flared. In CHP units, electricity is generated with gas engines, micro-gas turbines or dual fuel diesel engines, while the exhaust heat is recovered in a heat exchanger and utilized. As for the electrical balance, as it is depicted on Figure 1.2, achieving energy self-sufficiency on a conventional WWTP is hindered by the low electrical efficiencies of CHP units, i.e.: 30 – 36% (Deublein and Steinhauser; 2008; Yingjian *et al*, 2014). Consistently, Silvestre *et al* (2015) estimated that the energy self-sufficiency of 5 conventional WWTPs ranged between 39 – 76%; while Hao *et al* (2015) obtained a 53% carbon-neutrality for an inlet concentration of 400 mg/L Chemical Oxygen Demand (COD). While energy consumption mainly depends on the efficient design and operation of the wastewater treatment processes, energy production strongly depends on the organic matter concentrations in the initial wastewater and on the efficiency of the cogeneration unit.

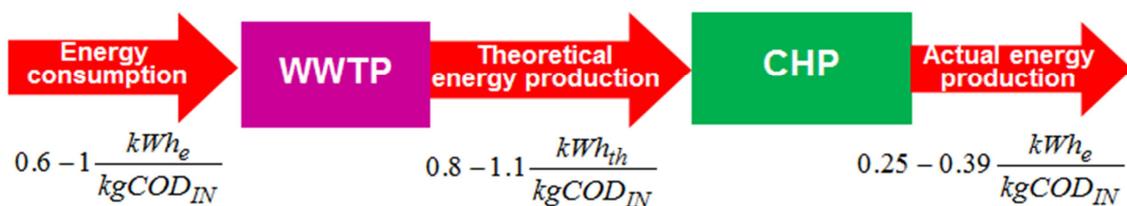


Figure 1.2. General figures of the electrical balance for a conventional WWTP equipped with anaerobic digestion and conventional CHP

As for the thermal balance, heat production is usually in excess of the needs in a WWTP; and, because of the location of these facilities, the transport of this heat to other sites can be economically compromised. The result is a huge loss of heat which causes poor yields of total energy; which consequently hinders the economic viability of CHP projects in WWTP. For example, in United States, there are just 270 plants out of the 1,241 WWTP equipped with AD which produce electricity on-site; while most the remaining plants just use biogas for digester and/or office building heating (Shen *et al*, 2015). On the other hand, in Japan, only 30 WWTPs out of 1,900 are equipped to valorise all the biogas they produce (Bin Basrawi *et al*, 2012). Although there are technical, economic, social and regulatory barriers that can explain the low impact of electricity production from biogas in WWTPs, it is clear that technological improvements and optimization should focus not only on biogas production but also on biogas energy valorization.

Within this context, fuel cells are new promising technologies which have been developed in the recent years offering both a higher electrical efficiency, i.e.: 45 – 50% (Edwards *et al*, 2008; Papadias *et al*, 2012; McPhail *et al*, 2012; Papurello *et al*, 2015), and a further reduced environmental impact. Biogas energy valorization in fuel cells combines a high-efficient technology for electrical generation, i.e.: fuel cell, with the use of a renewable fuel, i.e.: biogas. Generally speaking, biogas-powered fuel cells are a significant cornerstone on waste-to-energy infrastructure as they simultaneously deal with minimization of waste and maximization of efficiency. As Figure 1.3 collects, due to their larger electrical efficiencies, fuel cells can significantly improve the energy balance of conventional WWTP without significant retrofitting or changes on the currently operated processes. Moreover, they seem to be particularly interesting for sewage biogas energy recovery as electricity requirements in WWTP represent the most significant energy consumption.

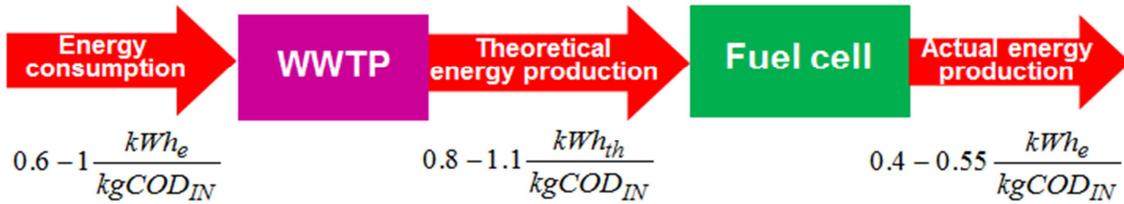


Figure 1.3. General figures of the electrical balance for a conventional WWTP equipped with anaerobic digestion and fuel cell

1.3. Fuel cells: operating principle and types

Energy transformation in conventional CHP systems requires of several stages. First, chemical energy in the fuel is transformed into thermal energy (combustion). Afterwards, thermal energy is transformed into mechanical energy (piston in reciprocating engines; blades in turbines). Finally, mechanical energy is transformed into electrical energy (alternator). Overall, the electric efficiency is low; in the range of 25 – 40% as a result of the irreversibilities (losses) on the different stages. This process is optimized in fuel cells as the energy transformation pathway is much shorter: chemical energy is directly converted into electrical energy through electrochemical reactions, hence leading to an improvement on the electrical efficiency up to 40 – 50%.

There are many types of fuel cells, but they all consist of an anode (negative electrode), a cathode (positive electrode) and an electrolyte that allows charges to move between the two sides of the fuel cell. Electrons are drawn from the anode to the cathode through an external circuit, producing direct current (DC) electricity. A power inverter (DC/AC) may be required to use the electricity in alternating current (AC) electrical equipment. In addition, a transformer may be also required depending on the voltage. Fuel cells can be classified according to their operating temperature; hence the terms high-temperature fuel cell (HTFC) and low-temperature fuel cell (LTFC) are generally used. The most important fuel cells types are collected in Table 1.1 (PEMFC = Proton Exchange Membrane Fuel Cell; PAFC = Phosphoric Acid Fuel Cell; MCFC = Molten Carbonate Fuel Cell; SOFC = Solid Oxide Fuel Cell):

Table 1.1. Fuel cell stack types and their main characteristics

	PEMFC	PAFC	MCFC	SOFC
Operating temperature (°C)	60 – 90 (LTFC)	190 – 250 (LTFC)	600 – 700 (HTFC)	800 – 1000 (HTFC)
Anode / Electrolyte / Cathode	Pt / H ⁺ conducting membrane (Nafion) / Pt-graphite	Pt / Solid matrix (PTFE) impregnated with H ₃ PO ₄ / Pt-graphite	Ni / Ceramic matrix (LiAlO ₂) impregnated with a molten salt (Na ₂ CO ₃ /K ₂ CO ₃) / NiO	Cermet (Ni-YSZ) / Ceramic (YSZ: Yttrium Stabilized Zirconia) / Semiconductor (LSM: Lanthanum Strontium Manganite)
Electrical efficiency (%)	50 – 60	40 – 45	50 – 55	50 – 60
Oxidant	O ₂ , air	O ₂ , air	O ₂ , air	O ₂ , air
Accepted fuels	H ₂	H ₂	H ₂ , CO (mixture) CH ₄ (to a lesser extent)	H ₂ , CO (mixture) CH ₄ (to a lesser extent)

1.4. Fuel cleaning requirements for fuel cells

In general, fuel inlet requirements for fuel cells are very stringent. Several compounds are poisonous and harmful both for low- and high- temperature fuel cells, affecting fuel cell catalytic processes and stack lifetime, and must be removed from the biogas. Despite several studies are available (Xu *et al*, 2010; Sasaki *et al*, 2011; Madi *et al*, 2015), the precise damaging effect of each biogas contaminant on the fuel cell is not very well understood; and manufacturers usually tend to protect themselves by setting very stringent limits. It was beyond the scope of this work to determine the level of biogas contamination which should be accepted by fuel cells. The critical aspects for the most important biogas physical and chemical parameters are explained as follows:

Sulfur: The major constituent of sulfur species in sewage biogas is H_2S , although organic sulfur compounds (i.e.: mercaptanes and organic sulfides) are also sometimes present. As Figure 1.4 shows, $H_2S(g)$ is produced in anaerobic conditions by Sulfate Reducing Bacteria (SRB) which reduce sulfates present in sewage sludge to sulfide; which is further stripped to the gas phase. Sulfur contamination causes corrosion to the equipment and poison the fuel cell anode and reforming catalyst (producing nickel sulfide and also causing the loss of electrolyte for some particular types of fuel cell), hence fuel cell manufacturers suggest a limit of 0.5 – 1 ppm_v S. In order to meet the stringent S tolerance limits, a deep desulfurization cleaning has to be carried out.

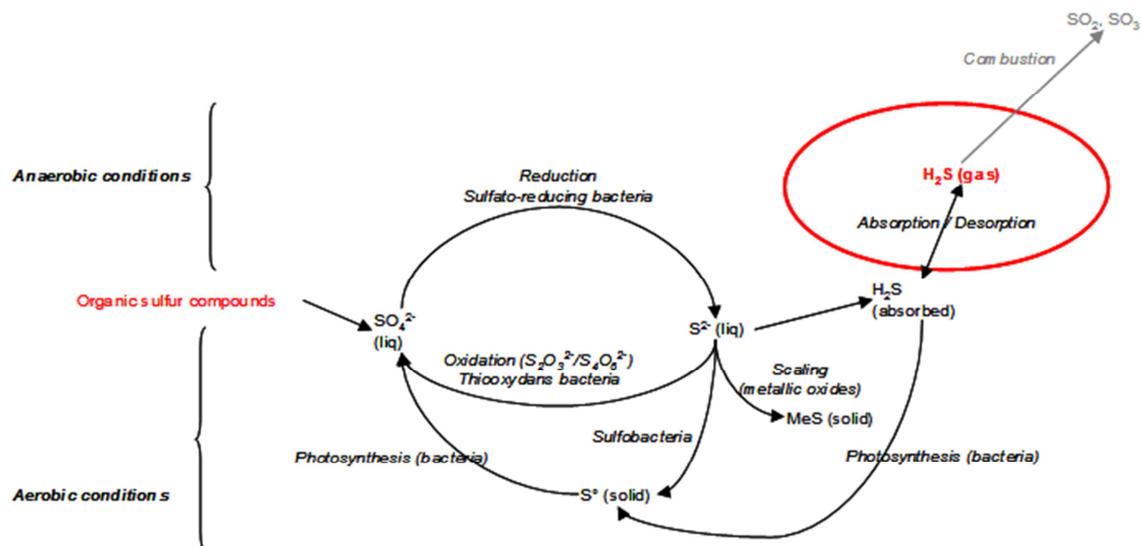


Figure 1.4. Sulfur cycle and relevant processes in anaerobic and aerobic conditions

Siloxanes: Siloxanes are organic silicon compounds (VOSiC) which are produced by the degradation and/or volatilization of organosilicon materials present in the sludge. Although their occurrence and fate in wastewater treatment process is not well understood (Mueller *et al*, 1995; Dewil *et al*, 2006), they are finally transferred to the biogas phase. Despite very little reliable information exists on the adverse effect of siloxanes in the fuel cells stacks, it is expected that siloxanes would be transformed into silica within the stack, which would block catalyst adsorption sites progressively reducing the efficiency of the fuel cell; hence siloxanes removal is required upstream the fuel cell. In fact, fuel cell developers suggest a very stringent value of less than 0.5 mg Si/Nm³ in the biogas.

Halogens: Halogens (represented as X), mainly chloride- and fluoride- derived compounds, can also be present in the biogas due to volatilization and may cause also negative effect due to corrosion that lead to a rapid damage of the cells stack. This is usually not an important issue for sewage biogas since the halogen volatile compounds that have been detected in sewage biogas samples are relatively rare and low (i.e.: below detection limits, 0.1 mg X/Nm³). Nevertheless, halogen removal technologies are sometimes required, mainly when biogas is produced via co-digestion with feedstock having halogens derived compounds or for landfill biogases. As they were not detected in sewage biogas, they have not been within the scope of this work.

Other specifications

Although they are not as critical as the previous biogas contaminants, attention should be paid at the following parameters:

- *Oxygen:* Oxygen is often present in raw sewage biogas but at levels below 0.5%. It would damage portions of the fuel cell system, thus a de-oxygenation catalyst is required for fuels containing oxygen. In fact, biogas reforming catalysts allow this reaction, but as methane is consumed in this reaction and its lower heating value lost, the electrical efficiency is reduced.
- *Moisture:* Raw sewage biogas is often saturated with water from the digestion process and, depending on the biogas temperature, it can represent between 2 – 4%. Note that depending on the gas pipe length and material, outlet temperatures and the eventual presence of condensate traps, moisture content is below saturation conditions. Condensates can block the fuel flow and disrupt system instrumentation, thus they should be prevented. In order to ensure that no liquid water is condensed from sewage biogas, temperature should be maintained around 10°C above the dew point.
- *Methane/Carbon Dioxide:* Full power output can be obtained for CH₄ concentrations greater than 60%, as it is the normal case for sewage biogas. For the range 50 – 60%, fuel cell performance is expected to be lower especially in terms of electrical efficiency. Little experience is available for fuels more diluted than 50%, but the power output will start to be negatively affected in a non-linear rate. On the other hand, variability of the heating value of the fuel by more than ±1% may have an impact on the performance of the fuel cell. Fuel supply variability and low methane content can be dealt by incorporating a fuel blending system with natural gas, which makes the fuel more stable, reliable and concentrated.

Table 1.2 compiles the threshold quality specifications for different biogas components on each type of fuel cell (Kordesch and Simader, 1996; Fuel cell handbook, 2000; Dayton *et al*, 2001; Papadias *et al* 2012). Not only intrinsic biogas contaminants as described above but also components produced during biogas reforming processes (i.e.: H₂ and CO; see section 1.6) have been included. As shown, the most relevant difference between quality requirements in high- and low-temperature fuel cells is CO; which is a fuel for the former and a poison for the latter. Regardless the operational temperature, it must be emphasized that, for technical and operational reasons, the required degree of biogas purity differs largely between conventional cogeneration technologies and fuel cells (e.g.: sulfur requirements in micro-turbines and internal combustion engines can be as high as 10,000 and 1,000 ppm, respectively; Deublein and Steinhauser; 2008). Notwithstanding, gas clean-up is necessary on principle, as contaminants which are not removed upstream the Energy

Conversion System will be downstream emitted as uncontrolled emissions to the atmosphere. Therefore, biogas deep purification is not strictly restricted to the type of ECS used; but also to the air quality requirements. As the removal of contaminants in exhaust gases is usually less cost-effective (e.g.: larger volumes have to be treated at more diluted concentrations), the installation of in-depth biogas clean-up systems upstream the fuel cell guarantees clean emissions to the atmosphere while optimizing its performance over the long-term.

Table 1.2. Fuel cell specifications (adapted from several sources)

	PEMFC	PAFC	MCFC	SOFC
CH₄	Inert Fuel with reformer	Inert Fuel with reformer	Fuel Reformed internally or externally	Fuel Reformed internally or externally
CO₂	Diluent	Diluent	Re-circulated	Diluent
H₂	Fuel	Fuel	Fuel	Fuel
CO	Poison 10 ppm _v	Poison 1%(v/v) at anode	Fuel With water –shifted to make H ₂	Fuel With water – shifted to make H ₂
C₂-C₆		Poison <0.5%(v/v) olefins	Fuel (with reformer) Saturated Hydrocarbons (CH ₄ included) – 12%(v/v) Olefins – 0.2%(v/v) Aromatics – 0.5%(v/v) Cyclics – 0.5%(v/v)	Fuel – similar to MCFC in regards to high molecular weight hydrocarbons
Oxygen	-	-	Poison 2 – 3%(v/v)	Poison 2 – 3%(v/v)
Particles	-	-	Poison 10 ppm _v ; <0.1g/l of particles size >3µm	-
Sulfur	Poison 0.1 ppm _v	Poison < 20 ppm _v H ₂ S < 50 ppm _v H ₂ S + COS	Poison < 10 ppm _v H ₂ S in fuel < 1 ppm _v SO ₂ in oxidant <0.5 ppm _v H ₂ S <0.1 ppm _v H ₂ S	Poison <1 ppm _v H ₂ S
NH₃	-	Poison < 0.2%(v/v) Ammonium phosphate in electrolyte	Inert < 1%(v/v)	Fuel < 5,000 ppm _v
Halogens (X)	-	Poison 4 ppm _v	Poison < 1 ppm _v <0.1 ppm _v	Poison <1 ppm _v
Alkali metals	-	-	Poison 1 – 10 ppm _v	-
Siloxanes	Poison 0,2 mgSi/Nm ³	Poison 0,5 – 1 mgSi/Nm ³	Poison 0,5 – 1 mgSi/Nm ³	Poison 0,5 – 1 mgSi/Nm ³

1.5. Biogas treatment technologies

Biogas desulfurization: There are numerous techniques available for H₂S removal from gas streams which can be classified as biological, physical and chemical processes (Abatzoglou and Boivin, 2009). Biological treatments are cost effective and environmentally friendly

processes (Shareenfdeen *et al*, 2003; Ng *et al* 2004), commonly used to reduce the emissions of malodorous gases and other pollutants into the atmosphere (Ramírez-Sáenz *et al*, 2009) which have been implemented in the recent years for biogas treatment (Fortuny *et al*, 2008; Mannucci *et al*, 2012; Fernández *et al*, 2014). Physicochemical processes can be classified as precipitation (by dosing of ferric salts); physical absorption (high pressure water washing); reactive absorption (soda, iron or amine washing); adsorption (iron adsorbents, activated carbon) techniques; and concentration with membranes; and are mostly appropriated for low H₂S concentrations. Table 1.3 summarizes a qualitative comparative assessment of the most relevant biogas desulfurization technologies. Comparison is made at 5 levels; where positive figures mean good technical and economic performance; while negative figures mean bad performance. On the one hand, the assessed technical indicators include the sulfur chemistry/corresponding removal mechanism (transfer from gas to liquid, oxidation, precipitation); applicability for different WWTP sizes (namely Small, Medium and Large); and H₂S removal efficiency. On the other hand, the assessed economic indicators include the investment cost (CAPEX); and the operating cost (OPEX), which is split by the most relevant categories (energy, chemicals, and maintenance and manpower)

Siloxanes removal: Several siloxane removal technologies from biogas have been reported in the literature based on adsorption, absorption, refrigeration/condensation, membrane separation and biological degradation (Popat and Deshusses, 2008; Accettola *et al*, 2008; Boulinguiez *et al*, 2009; Abatzoglou and Boivin, 2009; Matsui *et al*, 2010; Nam *et al*, 2013; Yu *et al*, 2013); and some of them have been commercialized at the industrial level. As the chemical backbone of siloxanes is very stable, chemical reaction of siloxane bonds (Si–O–Si) is not expected unless strong chemical agents are used (high or low acids); which pose operational concerns associated with corrosion and safety. Moreover, biological degradation is limited due to siloxanes high partition coefficient, low water solubility and low biodegradability. Therefore, siloxane removal at industrial facilities has been mainly addressed through physical methods; which transfer siloxanes from the biogas phase to other phases (liquid or solid). Concretely, the most common concept implemented is non-regenerative adsorption on fixed beds of activated carbon or other inorganic materials (e.g.: silica gel, metal oxides). Nonetheless, adsorption on a fluidized bed has been also implemented for siloxane removal. In this system, and differently from temperature swing adsorption systems (TSA) where regeneration is conducted periodically, part of the adsorbent material is continuously directed to a desorption unit, where previously adsorbed siloxanes (and other compounds) are stripped from the exhausted media by a hot gas, which is later flared. The regenerated adsorbent directed back to the fluidized bed after cooling. Similarly to desulfurization technologies, Table 1.4 collects a qualitative comparative assessment of the most relevant siloxanes removal technologies.

Table 1.3. Technical and economic comparison of different biogas desulfurization technologies

	Precipitation	Membranes	High pressure water absorption	Adsorption			Reactive absorption			Biological desulfurization	
				Activated carbon adsorption	Metal oxides adsorption	Soda	Iron Solution	Amine solution	Free culture and regeneration	Fixed culture	
S behavior	FeS (Sludge)	H ₂ S concentrated gas	H ₂ S absorbed (liq)	H ₂ S/S ⁰ (s) adsorbed (on media)	FeS, S ⁰ (s) adsorbed (on media)	S ⁰ (washing solution)	FeS(s), S ⁰ (s)	SO ₄ ²⁻ , S ⁰ (s) or complex with amine	S ⁰ (s)	S ⁰ (s)/SO ₄ ²⁻	
Size of WWTP*	All	S, M	M, L	All	All	S, M	M, L	L	M, L	All	
Removal efficiency**	+/-	+	+	++	++	+	+	++	+	+	
CAPEX	++	--	-	+	+	+/-	+/-	--	-	+/-	
OPEX Energy	++	--	-	+	+	+	+	--	++	++	
OPEX Chemical	--	++	+	--	--	+/-	-	-	+/-	++	
OPEX Maintenance & Manpower	++	-	-	+	+	+/-	+/-	-	+/-	+/-	
Total OPEX	--	-	-	+/-	+/-	+/-	-	--	+	++	

*WWTP size: Small (<100,000PE); Medium (100,000 – 500,000PE); Large (>500,000PE)

** Removal efficiency: ++ (>95%); + (70 – 95%); +/- (50 – 70%); - (30 – 50%); -- (<30%)

Table 1.4. Technical and economic comparison of different siloxanes removal technologies

	Temperature			Adsorption			Absorption			Biological
	Membranes	Refrigeration (0 – 5°C)	Deep chilling (-70 – 0°C)	Activated carbon adsorption	Silica gel/zeolites adsorption	Fluidized bed adsorption	Selextol™ (glycol mixture)	Strong acids	Fixed culture	
Si behavior	Siloxanes concentrated gas	Solubilized in the water stream	Condensed	Siloxanes adsorbed – Polymerized	Siloxanes adsorbed – Polymerized	Siloxanes adsorbed and later burned.	Siloxanes (washing solution)	Destroyed by chemical agent (mechanism not clear)	Degraded by micro-organisms (mechanism not clear)	
Size of WWTP*	S, M	All	L	All	All	L	M, L	M, L	All	
Removal efficiency**	+/-	+/-	+	++	++	++	++	+/-	-	
CAPEX	--	+	--	+	+	-	--	--	+/-	
OPEX Energy	--	+	--	+	+	-	--	--	++	
OPEX Chemical	++	++	++	--	--	+	--	--	++	
OPEX Maintenance & Manpower	-	+/-	-	+	+	+	-	--	+/-	
Total OPEX	-	+	--	+/-	+/-	+	--	--	++	

*WWTP size: Small (<100,000PE); Medium (100,000 – 500,000PE); Large (>500,000PE)

** Removal efficiency: ++ (>95%); + (70 – 95%); +/- (50 – 70%); - (30 – 50%); -- (<30%)

1.6. Fuel reforming processes

Fuel cells cannot be directly powered with clean sewage biogas; hence a fuel reforming stage is necessary upstream the cell to convert biogas into hydrogen. Therefore, the design and operation of the hydrogen production unit and the corresponding reforming chemistry has a key significance in the development of biogas-powered fuel cell systems. Since the main component present in cleaned biogas is CH_4 , biogas reforming processes are adapted from technologies for hydrogen production from hydrocarbons. Depending on the reforming agent used and the cleaned biogas composition, different chemical reactions will occur within the fuel processor which will impact reformed gas composition: steam methane reforming (SMR, steam), dry methane reforming (DMR, carbon dioxide), partial oxidation (POX, air), and autothermal reforming (ATR, combination of air and steam). All these reactions are carried out at high temperatures (i.e.: 500 – 700°C), thus even if a LTFC is used, a part of the system will operate at high temperature.

Despite producing a reformed gas with lower H_2/CO ratio, DMR seems to be the most promising alternative for the conversion of biogas since both carbon dioxide and methane are present on the raw gas. However, as the CO_2 quantity available is not sufficient to reform all CH_4 into H_2 , steam should be also supplied in any case. As both steam and dry reforming are endothermic reactions, the fuel processor requires an external heat source, which reduces the overall efficiency of the system. This problem can be overcome by introducing air to the reforming reactor to promote the exothermic POX (Xuan *et al*, 2009). However, this results in lower hydrogen yields and a lower hydrogen partial pressure in the reformed gas as a consequence of the presence of nitrogen from air; which will reduce the electrical efficiency of the system (van Herle *et al*, 2004a). Overall, the combination of SMR, DMR and POX (which is called autothermal reforming) allows reducing the reforming reactor size, softening the operating conditions and obtaining a higher H_2/CO ratio. Finally, the prevention of soot formation should be also taken into account when selecting the biogas reforming conditions. Carbon deposition can be produced within the reactor as a result of methane cracking, Boudouard disproportionation and reversed gasification reactions. Although the pros and cons on the different reforming process have been widely studied (van Herle, 2004b; Piroonlerkgul *et al*, 2008; Farhad *et al*, 2010), the selection of the most suitable reforming agent and operating conditions to integrate the biogas reformer with a SOFC stack should be further evaluated and optimized.

For LTFC, CO purification process (by Water Gas Shift and CO Preferential Oxidation) should be also installed downstream the biogas reforming unit as carbon monoxide represents a poison; while it is a fuel for HTFC. Altogether, as depicted in Figure 1.5, the entire gas processing chain for LTFC is more extensive and consists of more stages than for HTFC. The reduced gas processing requirements in HTFC is a direct consequence of their adaptation to be fuelled by hydrocarbons; hence they are more suitable for biogas applications. Moreover, this explains, as it will be collected in section 1.7, why they are the most installed technology today. As a result, this PhD thesis is focused on HTFC.

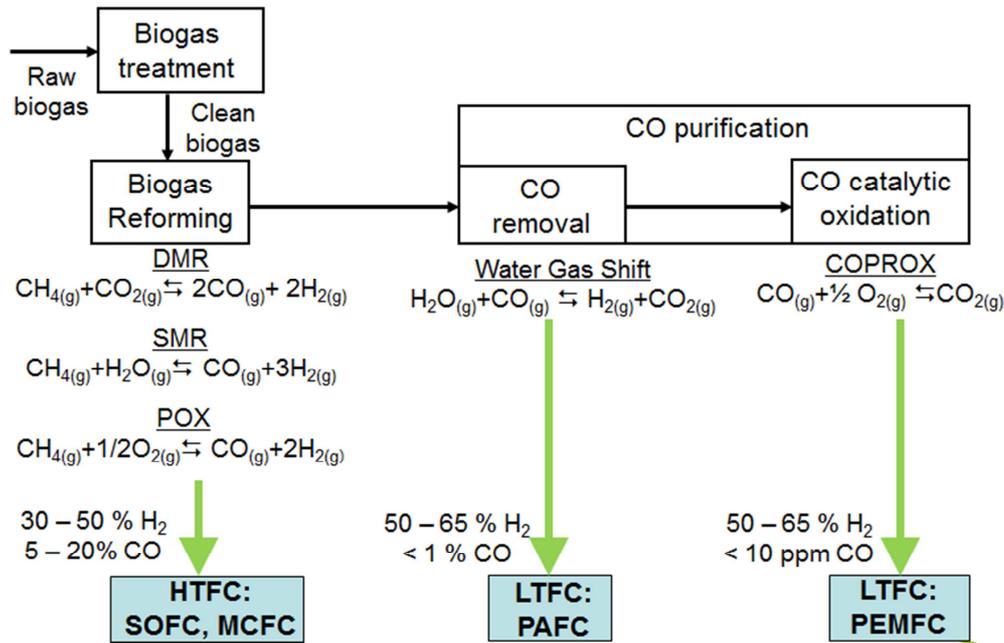


Figure 1.5. Biogas fuel processing chemistry and reactions for different types of fuel cells (SOFC: Solid Oxide Fuel Cell; MCFC: Molten Carbonate Fuel Cell; PAFC: Phosphoric Acid Fuel Cell; PEMFC: Proton Exchange Membrane Fuel Cell)

1.7. Current full-scale experiences with biogas fuel cells

Several demonstration projects have been conducted in the recent years to demonstrate the technical feasibility of fuel cells powered with biogas. Indeed, the first prototype references of MCFC were collected by Baaske and Trogisch as early as 2004. The first full-scale European biogas-powered MCFC was installed in Aalen WWTP (Germany) in 2005 and had a nominal power of 250 kW_e (Krumbeck *et al*, 2006). On the other hand, further relevant full-scale MCFC references from Fuel Cell Energy (Danbury, Connecticut, USA) were started in WWTP in California in the late 2000s: Tulare WWTP (900 kW_e, 2007), Dublin San Ramon WWTP (600 kW_e, 2007), San Francisco Southeast WWTP (600 kW_e, 2008), Rialto WWTP (900 kW_e, 2008), Eastern Municipal Water District WWTP (750 kW_e, 2008), and Turlock WWTP (1.2 MW_e, 2008). The growth of biogas-powered MCFC technology, both in number of references and installed power, has been maintained since 2010 onwards: South Bay WWTP (1.4 MW_e, 2011), San Jose-Santa Clara WWTP (1.4 MW_e, 2012), Ontario WWTP (2.8 MW_e, 2012), etc. MCFC technology clearly masters the biogas-powered fuel cell market with at least 27 on-going references in 2014; accounting for around 23 MW_e installed power as it can be seen in Figure 1.6. PAFC technology also contributes with an important role with 11 references; although most of them were installed before 2010 and the market seems not pushing for this technology in biogas applications. Significantly behind, the contribution of biogas-powered PEMFC and SOFC systems is almost negligible; being limited to pilot-scale references. A general overview of the situation of fuel cells operated with biogas in the world since the 1990s until 2014 (including the currently decommissioned and planned projects) can be consulted in Appendix A.

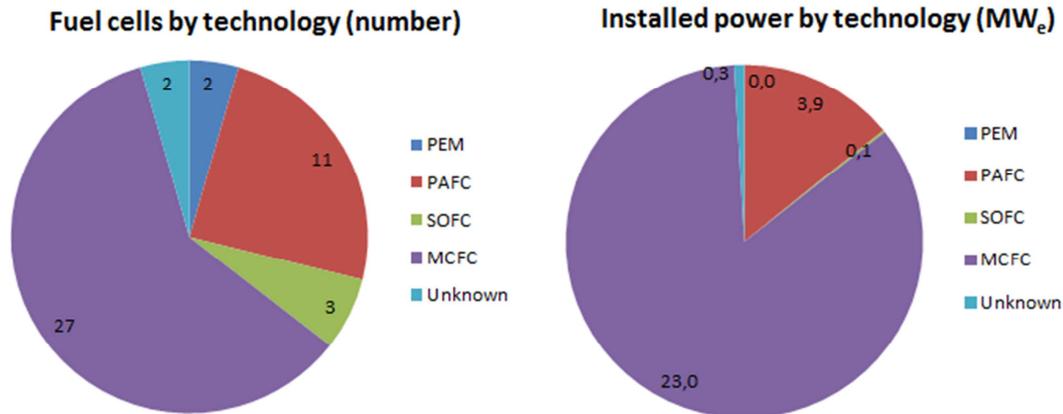


Figure 1.6. On-going biogas-powered fuel cell references (left) and corresponding installed power (MW_e, right) by fuel cell type as for 2014

As Figure 1.7 shows, the vast majority of references are installed in the USA (especially California), Japan and Europe (especially Europe). In addition, the most common origin of the biogas used is sewage biogas, accounting for more than 50% of the number of references in biogas powered fuel cells. Other relevant sources of biogas which are valorized in fuel cells are landfill gas and biogas from anaerobic digestion of food waste. It should be noted that the term “directed biogas” means that the fuel cell works with natural gas from the grid, but the company purchases the rights about an equivalent amount of purified biogas introduced into the gas network elsewhere. In that way, the net balance is the same as if the company had used biogas in its fuel cell.

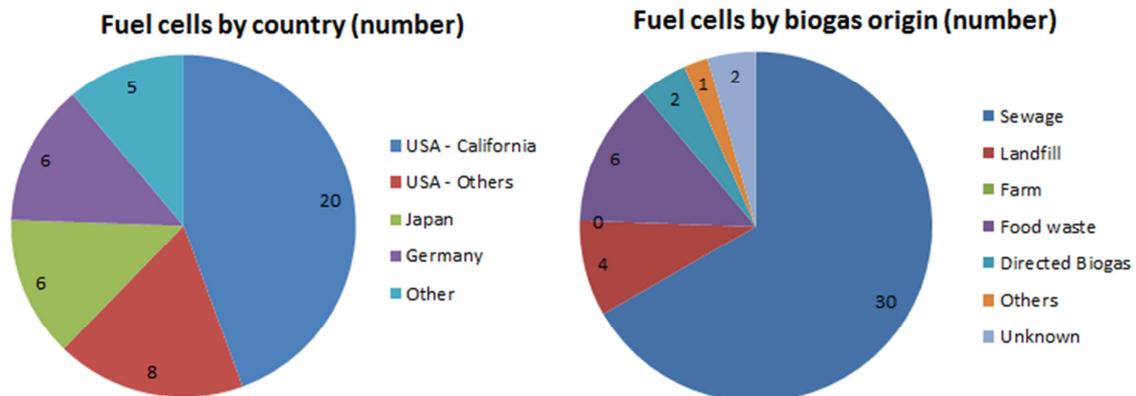


Figure 1.7. On-going biogas-powered fuel cell references by country (left) and biogas origin (right) as for 2014

Although SOFC technology appears to be well developed today, as it has been illustrated, its commercial market is still very limited. Compared to the well-established MCFC technology, SOFC is a suitable alternative for the application of biogas as a result of the significant potential for reducing the investment cost through the development of new ceramic materials (van Herle *et al*, 2004a; Siefert and Litster, 2014). Moreover, its higher operating temperature (800°C vs 650°C) allows for a higher degree of fuel internal reforming, and promotes rapid kinetics to produce high quality heat for energy conversion. However, as a result of its reduced Technology Readiness Level (TRL) compared to MCFC, most of the efforts have been devoted either to modeling (Lanzini *et al*, 2011; Ni, 2013; Trendewicz and Braun, 2013) or to lab-scale experiments with synthetic biogas mixtures: Papadam *et al*, 2012 (the performance of a mW-scale stack was investigated with CH₄:CO₂ 66:33, 50:50 and

33:66 at 675 and 875°C without pre-reforming); Guerra *et al*, 2013 (a tubular stack was operated with different CO₂-rich biogas mixtures for dry reforming achieving electrical efficiencies of 43%); Jahn *et al*, 2013 (a 0.8 kW_e planar stack from Fraunhofer-IKTS was fueled with biogas at CH₄:CO₂ 50:50 reformed at oxidative dry conditions showing 51% electrical efficiency); and Papurello *et al*, 2014 (a 3-cell stack was tested with biogas CH₄:CO₂ 60:40 processed by steam reforming reaching similar performance than when operated with H₂).

As it has been said, very scarce examples with real biogas samples powering a SOFC system at a relevant scale are reported in the literature. For example, Sulzer Hexis (Winterthur, Switzerland) performed in 2001 a trial with a 1 kW_e unit in Lully (Switzerland) with biogas from food waste anaerobic digestion. In 2008, Accumetrics (Westwood, Massachusetts, USA) installed two 5 kW_e SOFCs on the scope of the BIOSOFC project (LIFE06 ENV/E/000054); one in a landfill site in Barcelona (Spain) and the other at the environmental information center GlashusEtt in Stockholm (Sweden). However, not only a thorough cleaning of the biogas to remove contaminants was required; but also an upgrading up to more than 80% methane. Haldor Topsoe (Lyngby, Denmark) tested a 20 kW_e SOFC unit with real landfill gas in Vaasa (Finland) in 2010; but the unit was finally decommissioned and the company is today more focused on electrolyzer technology rather than fuel cells. More recently, Papurello *et al* (2015) operated a 0.5 kW_e pilot scale SOFC unit with real biogas produced from the digestion of the Organic Fraction of Municipal Solid Waste (OFMSW).

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Chapter 2

Objective and Methodology

2. Objective and Methodology

2.1. Aim and general objective

The general aim of this PhD thesis is to evaluate the technological and economic feasibility as well as the opportunities for sewage biogas energy valorization via Solid Oxide Fuel Cells (SOFC) at a pilot scale and to compare its performance versus other Combined Heat and Power (CHP) technologies. As previously commented in chapter 1, High Temperature Fuel Cells (HTFC) are the most adapted fuel cell technology for biogas applications; and while Molten Carbonate Fuel Cell (MCFC) is fully developed and deployed with a significant number of full-scale references, relevant pilot references with SOFC technology powered with real biogas are very scarce and limited. Therefore, this work is focused on studying the prospects and limitations of biogas energy recovery with SOFC systems. Due to their stringent quality specifications, the whole valorization line, as depicted in Figure 2.1, including the biogas treatment system and the fuel cell, will be assessed. The effectiveness and efficiency of treatment technologies to achieve fuel cell stringent quality requirements as well as fuel cell electrical and thermal performance will be particularly targeted.

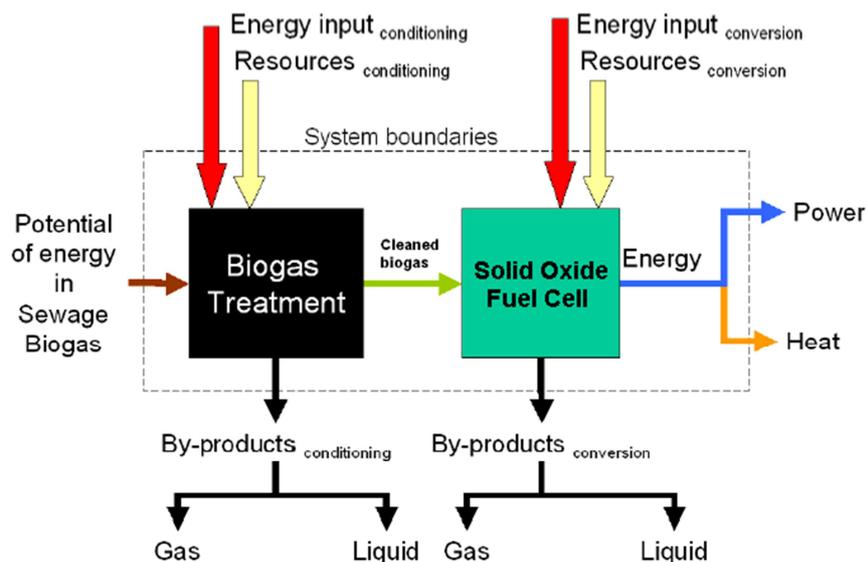


Figure 2.1. Aim of this PhD thesis, addressing both biogas treatment and Solid Oxide Fuel Cell

2.2. Specific objectives

This thesis has been built as an integration of different processes and systems related to biogas energy recovery; namely desulfurization, siloxanes analysis and removal, fuel cell performance, and comparison with conventional CHP systems. While some of them have been addressed through experimental activities; others have focused on summarizing and analyzing the data generated to achieve the main goal of this work. Therefore, the specific objectives of this PhD thesis are listed below:

- Assess the performance of biological desulfurization systems operated at extremely acidic conditions under different H_2S loading rates. Assess biological oxidation selectivity to partial and full oxidation (chapter 3)

- Understand the occurrence and fate of siloxanes within wastewater treatment processes, its further presence in sewage biogas and their impact in Energy Conversion Systems (chapter 4)
- Select the most adequate and reliable biogas sampling methodology to measure siloxanes and trimethylsilanol concentration in sewage biogas (chapter 5)
- Assess the performance of adsorption materials for sulfur and siloxanes deep removal. Understand the basics of the adsorption mechanisms involved (chapter 6)
- Select the reforming conditions (steam addition and temperature) to reduce the risks of carbon formation upstream the fuel cell stack. Assess the electrical and thermal performance of a Solid Oxide Fuel Cell powered with clean sewage biogas (chapter 7)
- Conduct a detailed technical and economic assessment of the different alternatives for on-site cogeneration with sewage biogas; including Internal Combustion Engines, Micro-Turbines, Molten Carbonate Fuel Cells and Solid Oxide Fuel Cells (chapter 8)

2.3. Methodology

A combination of activities was conducted in order to accomplish with the main objective and the specific objectives of this thesis:

- Design, construction and operation of a biogas-powered Solid Oxide Fuel Cell (SOFC) pilot plant at Mataró WWTP (Barcelona, Spain)
- Assess several biogas sampling methodologies adapted to siloxanes analysis
- Audit 6 full-scale biogas energy valorization plants installed in WWTP, and conduct a technical and economic comparison of fuel cells performance with conventional CHP technologies

2.2.1. SOFC pilot plant description

The Mataró WWTP depicted in Figure 2.2 collects wastewater from different towns and villages in the Maresme region (North-East of Barcelona, Spain) and its wastewater treatment capacity is around 30,000 m³/day. Sewage treatment line consists of pre-treatment (screens, grit and fats), primary sedimentation in rectangular settling tanks, biological treatment in plug-flow reactors (anoxic and oxic chambers) and secondary sedimentation in circular settling tanks. Treated wastewater is discharged into the sea. On the other hand, the sludge treatment line consists of sludge thickening (primary sludge by gravity; and secondary sludge in thickening tables with the addition of cationic polyelectrolyte), anaerobic digestion at mesophilic conditions and sludge dewatering in centrifuges (also with the addition of cationic polyelectrolyte). Dewatered sludge is used in agriculture. Biogas production accounts for 190 Nm³/h and the gas line consists of a gas holder, a dual fuel boiler (oil and biogas) and a flare. Until 2012, digester heating was the only biogas energy valorization conducted on site; while energy excess was flared. Today, the vast majority of biogas production is used for district heating and cooling in public buildings (hospitals, schools, etc.).



Figure 2.2. Aerial view of Mataró WWTP, location of the pilot plant

The pilot plant showed in Figure 2.3 treated $10 \text{ Nm}^3/\text{h}$, representing around 5% of the full-scale biogas production, and consisted of a biotrickling filter (BTF) followed by a polishing stage (adsorption on iron containing adsorbent, drying and activated carbon) and the SOFC unit for on-site electricity and thermal energy production. The selection of the treatment processes was conducted according to the criteria defined on Tables 1.3 and 1.4. The different stages of the pilot plant are described as follows.



Figure 2.3. Sewage biogas powered Solid oxide Fuel Cell pilot plant

Biotrickling filter (BTF)

A biotrickling filter (DMT Environmental Technology, Joure, the Netherlands) showed in Figure 2.4 was installed as the main desulfurization technology. The detailed P&ID of the biotrickling filter can be consulted in Appendix B. The process was operated at extremely acidic conditions to reduce the operating cost. Although most of the previous references on

biological desulfurization were run at neutral/alkaline conditions to favor H_2S dissolution into the liquid phase (Fortuny *et al*, 2011; Fernandez *et al*, 2013; Montebello *et al*, 2013), operation at acidic pH was selected in order to reduce caustic consumption and to obtain a reduced microbial consortium (avoiding competition with other cultures which may grow in wastewater).

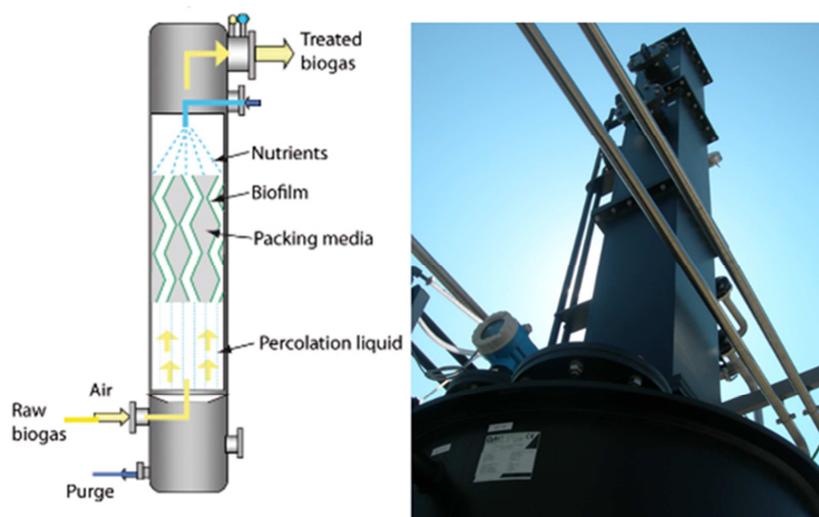


Figure 2.4. Biotrickling filter installed for biogas main desulfurization in the biogas-powered SOFC pilot plant

The BTF unit was always operated up-flow, counter-current mode and the scrubbing column had a square-section of 0.093 m^2 and a packed bed height of 1.8 m tightly filled with HD Q-PAC® (Lantec Products Inc., Agoura Hills, CA, USA) (specific surface area of $433 \text{ m}^2/\text{m}^3$ and an initial porosity of 88%). A liquid tank of 1.1 m^3 , equipped with a centrifugal pump (Arbo, Smilde, the Netherlands), re-circulated the liquid phase over the packing material at a flow rate of 800 – 1000 L/h (9 – 11 m/h). The tank was also equipped with an electrical heater and a thermostat (Eriks, Halesowen, UK) to adjust the operating temperature. The operation pH range was maintained between 1.5 – 2 by automated addition of treated sewage effluent; which was previously filtered for suspended solids removal. Aerobic conditions in the system were guaranteed by continuous perpendicular air injection to the gas phase with a SLL-20 diaphragm air blower (Bibus Ltd, Wooburn Green, UK). Air supply was PID-controlled with a Visiform Dissolved Oxygen sensor (Hamilton, Bonaduz, Switzerland) to ensure an O_2 content in the treated gas. Air was injected into the gas-phase because liquid-phase injection can cause significant dilution of the outlet biogas due to the low oxygen transfer efficiencies of diffusers and ejectors.

Polishing stage

The polishing system illustrated in Figure 2.5 and based on adsorption technologies was installed downstream the BTF unit as adsorption processes allow the achievement of the stringent fuel cell requirements regarding sulfur and siloxanes quality (Bagreev *et al*, 2005; Cabrera-Codony *et al*, 2014). The configuration consisted of (i) iron-containing adsorbent, (ii) biogas drying with refrigeration and (iii) activated carbon. The detailed P&ID of the polishing system can be consulted in Appendix C. A lateral channel blower (FPZ, Concorezzo, Italy) and a back-pressure regulator were respectively installed upstream and downstream in order to cope with pressure losses through the line and adjusting the pressure to the requirements of the fuel cell, i.e.: 100 mbar(g).

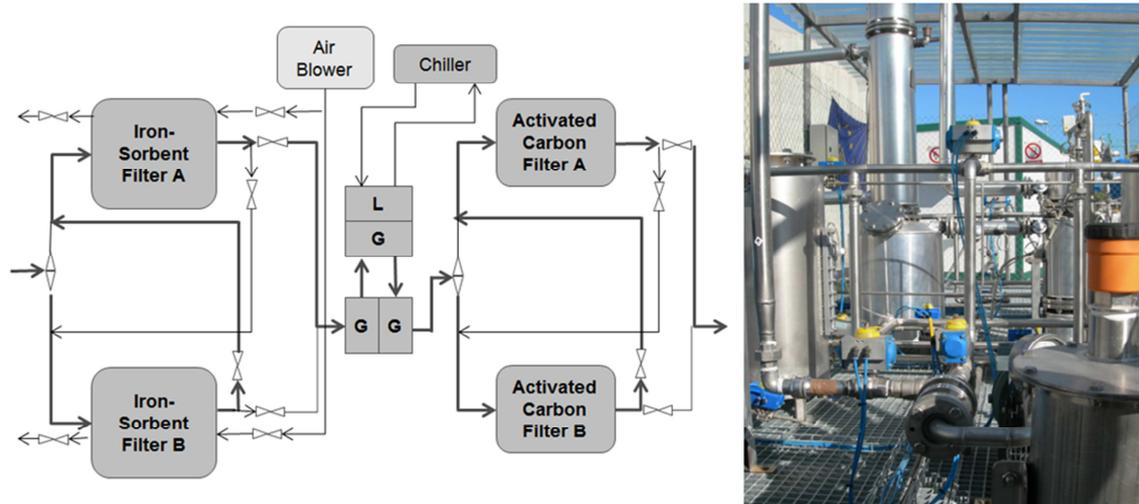


Figure 2.5. Biogas deep polishing system for removal of sulfur and siloxanes traces in the biogas-powered SOFC pilot plant

Iron-containing adsorbent filters: Bi-On-Fe (Bioconservación, Gavà, Spain), a regenerable pelleted adsorbent (diameter 2 – 4 mm and bed density 840 kg/m³), was used for sulfur polishing through chemio-sorption, transforming H₂S into FeS(s) and elemental sulfur in a molar relation of 2:1 (Cherosky and Li, 2013). Biogas was not dried before as moist conditions were recommended to facilitate the reaction. The material can be regenerated with atmospheric air at ambient temperatures, oxidizing FeS(s) to elemental sulfur, and rendering again iron for a subsequent adsorption. Each vessel had a volume of 83 L; with a diameter (D) of 0.4 m and a height (H) of 0.66 m; leading to linear velocities of 1.3 – 2 cm/s.

Biogas drying: A heat exchanger system (with a refrigerator) was installed in order to reduce biogas relative humidity. The biogas drying unit consisted of two heat exchangers: biogas first flowed through a gas-gas heat exchanger (thermal exchange surface 0.8 m²), increasing energy recovery, and afterwards through a gas-liquid heat exchanger (thermal exchange surface 2 m²) with water-ethylene glycol; which was cooled on atmosphere-condensing chiller (Cupla Técnica Frigorífica, Castellar del Vallès, Spain).

Activated carbon filters: Bi-On-AC (Bioconservación, Gavà, Spain), an extruded activated carbon (diameter 1.5 – 4 mm, BET surface 1,020 m²/g and bed density 450 kg/m³), was used to remove siloxanes and the other biogas contaminants (linear and aromatic hydrocarbons) through physical adsorption due to its meso-porous structure in the range of 2 – 8 nm (Ortega and Subrenat, 2008). The vessel had a volume of 89 L; with a diameter (D) of 0.45 m and a height (H) of 0.56 m; leading to linear velocities of 0.9 – 1.5 cm/s.

Solid Oxide Fuel Cell

After the thorough biogas treatment, around 1 Nm³/h directly fuelled the fully integrated SOFC unit (EBZ Entwicklungs- und Vertriebsgesellschaft Brennstoffzelle mbH, Dresden, Germany) showed in Figure 2.6 for simultaneous on-site production of electrical and thermal energy (nominal electrical power 2.8 kW_e; thermal power 1 – 2 kW_t, and operating temperature 850°C). The rest of the treated biogas, i.e.: 9 Nm³/h, could not be used for on-site energy production and was therefore re-injected in the main biogas pipe. The fuel cell unit mainly consisted of two sub-systems: the electrochemical stack (2 x 1.4 kW_e) and the

thermal integration unit (including the hot water production system). The detailed P&ID of the Solid Oxide Fuel Cell unit can be consulted in Appendix D.

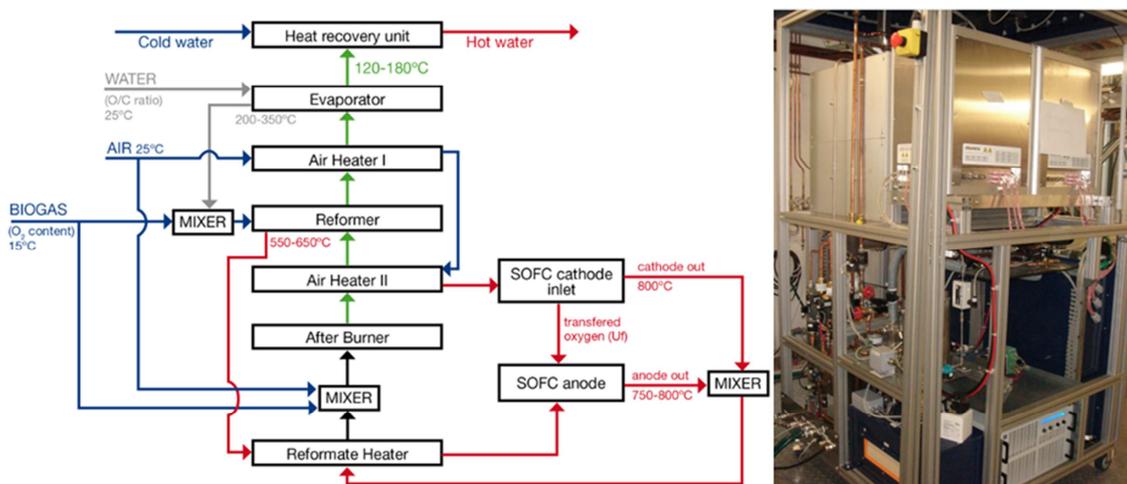


Figure 2.6. Solid Oxide Fuel Cell for electrical and thermal power generation in the biogas-powered SOFC pilot plant

On the one hand, the stack (Staxera, Dresden, Germany) converted the chemical energy within the fuel into electrical energy and consisted of 2 stacks in parallel each of 60 electrolyte-supported cells (total surface area 255.6 cm²). Cells were made of a porous nickel-based anode, a p-semi-conductor cathode (LSM: Lithium-Strontium-Manganite) and a ceramic solid electrolyte (YSZ: Yttrium-Stabilized Zirconia). The generated electricity (DC at 60A/42V) was dissipated through an electronic charge, as there was no scientific interest on actually using it (a transformer and DC/AC inverter was used). On the other hand, the heat integration unit allowed for heating gases to the operating temperature, producing steam for the internal reforming process and burning stack off-gases to supply the required heat. It also used the remaining waste heat on the exhaust gases to produce sanitary hot water at 50°C. It basically consisted of heat exchangers, an evaporator, a reformer and a porous after-burner. Pieces of equipment were made of Necrofer 2.4633, a high-chromium content alloy well adapted to high temperature applications, and Microtherm® wool (Microtherm Group, Hadzor, UK) was used as insulation material.

Biogas on-line monitoring system

The most significant physical parameters (pressure, temperature and flow) were on-line monitored at different points. Moreover, chemical analysis of biogas major compounds (i.e.: CH₄, CO₂, O₂ and H₂S) was also on-line revealed at several points of the pilot plant using the AwifLEX® analyzer (Awite Bioenergie GmbH, Langenbach, Germany) equipped with different sensors (infrared for CH₄ and CO₂, paramagnetic for O₂ and electrochemical for H₂S). Biogas was first dried through condensation at 5°C with a chiller, cleaned of particles with a filter and pressure adjusted with pressure regulators. Humidity measurements were also conducted using a portable Humicap® HM70 probe (Vaisala, Vantaa, Finland).

2.2.2. Assessment of several biogas sampling methodologies adapted to siloxanes analysis

At the beginning of this PhD thesis, the analytical reporting of siloxanes remained somewhat controversial with discrepancies on optimal sampling procedure as well as

necessary sample preparation and quantification technique. Although gas chromatography coupled to mass spectrometry (GC–MS) was most frequently used for these analyses, the most practical and reliable sampling technique was not clearly identified. Several authors had used canisters (Niessner and Schweigkofler, 1999), Tedlar® bags (Ajhar *et al*, 2010), sorbent tubes (Dewil *et al*, 2007; Rasi *et al*, 2010) or even on-line measurement techniques combining GC and Fourier transform infrared spectroscopy (FTIR) (Arnold and Kajolinna, 2010) to analyze siloxanes, but no studies comparing the different sampling techniques were published.

Three different sampling techniques for the analytical reporting of eight siloxanes and trimethylsilanol (TMS) were studied: (a) activated coconut charcoal (24–40 mesh) adsorbent tubes divided into two beds (A 400 mg and B 200 mg) (Sigma Aldrich, San Luis, USA); (b) 1 L Tedlar® bags with a single polypropylene (PP) septum fitting (SKC, Eighty Four, USA); and (c) impingers filled in with a non-polar solvent (n-hexane) submerged into an ice-water bath (two impingers with 20 mL n-hexane; fritted; and connected in series) (SKC, Eighty Four, USA). The further analysis of siloxanes and TMS was carried out by GC–MS according to a methodology developed out of the scope of this thesis.

2.2.3. Audits on full-scale biogas energy valorization plants

As collected in Table 2.1, 6 audits on full-scale WWTP with different CHP technologies were conducted in the USA (2 plants), Germany (1 plant), Italy (1 plant) and Spain (2 plants). Audits allowed collecting the most relevant technical and economic operational indicators both from the biogas treatment technologies and the Energy Conversion Systems (ECS) implemented on-site; in order to assess sewage biogas-powered fuel cells application field. Data was collected from historical databases from the operators and its quality was minimum one-year averages.

Table 2.1. Description of the gas trains and Energy Conversion Systems at the audited WWTP

Audit	Biogas treatment	ECS
USA 1	Scrubber + iron sponge + drying + activated carbon	MCFC
USA 2	Drying + activated carbon	MT
Germany	Drying + activated carbon	MCFC
Italy	Scrubber + drying + adsorbent materials	ICE
Spain 1	Bio-scrubber + drying + activated carbon	ICE
Spain 2	Drying	ICE
SOFC pilot	Iron sponge + drying + activated carbon	SOFC

2.4. PhD thesis organization

The following chapters of this thesis cover the specific topics and results obtained in the biogas-to-energy valorization chain as depicted in Figure 2.7. Specifically; the chapters correspond to the following articles published in Journals:

- Chapter 3: *Biogas biological desulfurization under extremely acidic conditions for energetic valorization in Solid Oxide Fuel Cells*. Chemical Engineering Journal 255 (2014): 677–685

- Chapter 4: *Understanding the effects of the origin, occurrence, monitoring, control, fate and removal of siloxanes on the energetic valorization of sewage biogas – A review*. Renewable and Sustainable Energy Reviews 52 (2015): 366–381
- Chapter 5: *Analytical methodology for sampling and analyzing eight siloxanes and trimethylsilanol in biogas from different wastewater treatment plants in Europe*. Analytica Chimica Acta 812 (2014): 83– 91
- Chapter 6: *Biogas deep clean-up based on adsorption technologies for Solid Oxide Fuel Cell applications*. Chemical Engineering Journal 255 (2014): 593–603
- Chapter 7: *Evaluation of a pilot-scale sewage biogas powered 2.8 kWe Solid Oxide Fuel Cell: Assessment of heat-to-power ratio and influence of oxygen content*. Journal of Power Sources 300 (2015): 325–335
- Chapter 8: *On-site cogeneration with sewage biogas via high-temperature fuel cells: Benchmarking against other options based on industrial-scale data*. Fuel Processing Technology <http://dx.doi.org/10.1016/j.fuproc.2015.07.006>

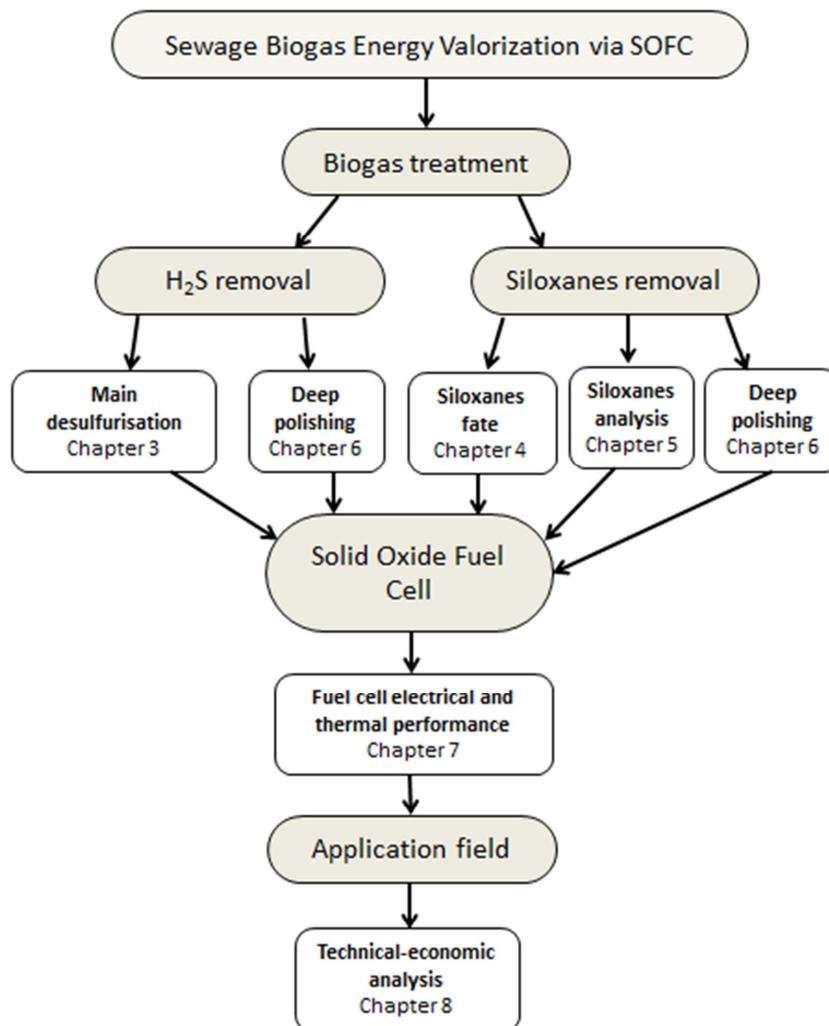


Figure 2.7. Organization of this PhD thesis

2.5. References

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ATTENTION !

Pages 56 to 120 of the thesis are available at the web of the editor:

- Chapter 3: *Biogas biological desulphurisation under extremely acidic conditions for energetic valorisation in Solid Oxide Fuel Cells* Chemical Engineering Journal 255 (2014): 677 – 685
<http://www.sciencedirect.com/science/article/pii/S1385894714008043>
- Chapter 4: Understanding the effects of the origin, occurrence, monitoring, control, fate and removal of siloxanes on the energetic valorization of sewage biogas—A review Renewable and Sustainable Energy Reviews 52 (2015): 366 – 381
<http://www.sciencedirect.com/science/article/pii/S1364032115007534>
- Chapter 5: Analytical methodology for sampling and analysing eight siloxanes and trimethylsilanol in biogas from different wastewater treatment plants in Europe Analytica Chimica Acta 812 (2014): 83 – 91
<http://www.sciencedirect.com/science/article/pii/S0003267013015766>
- Chapter 6: Biogas deep clean-up based on adsorption technologies for Solid Oxide Fuel Cell applications Chemical Engineering Journal 255 (2014): 593 – 603
<http://www.sciencedirect.com/science/article/pii/S1385894714008031>
- Chapter 7: Evaluation of a pilot-scale sewage biogas powered 2.8 kWe. solid oxide fuel cell : assessment of heat-to-power ratio and influence of oxygen content. Journal of Power Sources 300 (2015): 325 – 335
<http://www.sciencedirect.com/science/article/pii/S0378775315303463>
- Chapter 8 : On-site cogeneration with sewage biogas via high-temperature fuel cells: Benchmarking against other options based on industrial-scale data Fuel Processing Technology 138, (2015) 654-662
<http://www.sciencedirect.com/science/article/pii/S0378382015300837>

Chapter 9

Conclusions

9. Conclusions

The world is slowly but conscientiously converging into the acceptance that a more sustainable and secure energy supply is required for the forthcoming generations, where the actual dependence on the fossil fuel reserves should be replaced by self-sufficiency and use of renewable energy resources. Accordingly, policymakers and governments are progressively implementing measures aimed at reducing primary energy consumption and increasing resource efficiency. Making this real requires a compromise between technological, economic and social challenges, which show the necessity for transversal solutions that should be available. In this PhD thesis, the potential of using sewage biogas produced in Waste Water Treatment Plants (WWTP) to produce sustainable energy in high efficient Solid Oxide Fuel Cells (SOFC) has been studied. Although improvements both in the performance and cost have been highlighted on the different chapters, this work shows that this next-generation technology is already starting to be available. Over the following pages the most relevant findings raised in the previous articles, first on biogas treatment and afterwards on fuel cells, are summarized. Moreover, recommendations and challenges are also overviewed. As the road ahead is still difficult and arduous, prospects for future work are finally detailed.

9.1. Key findings on biogas treatment technologies

9.1.1. H_2S removal

Main desulfurization

As depicted in chapter 3, biotrickling filters (BTF) operated on the long-term (920 hours) under extremely acidic conditions (pH 1.5 – 2) achieved removal efficiencies of 72 – 94% at 30°C and loading rates of 170 – 210 g $H_2S/m^3_{bed}/h$; confirming that this process is suitable for biogas main desulfurization. This loading rate was higher than other BTF experiences for biogas desulfurization from the literature. The absence of sulfide species on the liquid phase indicated that under these loading rate conditions, the system was mass-transfer limited; rather than kinetically.

The extreme conditions (high H_2S , low oxygen and low pH) resulted in a strong monoculture development inside the BTF; with more than 99% of the bacterial consortium being *AcidithiobacillusThiooxidans*, a Sulfur Oxidizing Bacteria (SOB). This illustrates the selective pressure of the acidic environment on microbial diversity. SOB activity showed ability to recover when the BTF was subjected to temperature reduction (recovery in 24 hours) and oxygen-limiting conditions (recovery in 36 hours); showing process reversibility to these two disturbances.

The key issue at this high loading rate was that desulfurization was oriented to elemental sulfur formation as a result of a high selectivity (i.e.: 70%) towards partial oxidation. This caused a progressive increase on the pressure drop in the scrubbing column; which eventually led to BTF stop and NaOH cleaning; reducing the availability of the system and increasing the operational costs. Sulfate and total sulfur analyses on the liquid phase showed a clear correlation for S content; indicating that SO_4^{2-} was the only S-containing

specie on the bleed. As no elemental sulfur was flushed from the system, it accumulated within the packing material, explaining the progressive increase in the pressure drop observed in the column.

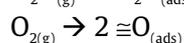
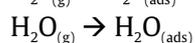
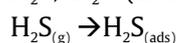
Altogether, it is concluded that the applied loading rate, despite showing high removal efficiency, overloaded the system, favoring partial oxidation and eventually process underperformance. Moreover, as a consequence of progressive filter clogging, the available surface area for the desulfurization reaction was reduced and consequently process kinetics was also reduced. Therefore, operation at lower loading rates is recommended; which would not only promote selectivity towards full oxidation but also improve removal efficiency

H₂S polishing

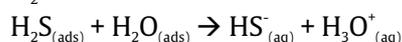
As described in chapter 6, the iron-containing adsorbent in lead-lag configuration reached the stringent sulfur requirements of fuel cell systems, showing an overall adsorption capacity of around 20%(w/w). H₂S peaks larger than 0.5 ppm_v were observed after the first bed even before breakthrough; hence two beds in series were required in the long-term performance. Regenerations with air were conducted at the end of each breakthrough cycle but its efficiency was limited to 50 – 60%. Therefore, adsorption capacities showed a progressively decreasing trend: 12% in cycle 1; 6% in cycle 2; and 3% in cycle 3.

The H₂S adsorption mechanism was postulated by conducting Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD) and a pH leachate test on virgin and saturated samples. As a result of the presence of oxygen in the biogas (2 – 3%) and moisture (relative humidity 80 – 90%) in the biogas, H₂S adsorption mechanism was more oriented to its oxidation to elemental sulfur and gypsum rather than to crystalline FeS(s) formation. This can explain the low regeneration efficiencies observed in the iron-containing adsorbent. Acidification took place during adsorption as the pH was reduced from 9.5 (virgin) to 6.8 (saturated). The mechanism postulated for H₂S removal is described below:

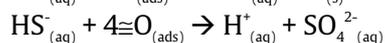
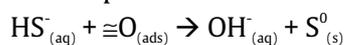
- H₂S, H₂O (humidity) and O₂ adsorption on activated carbon surface:



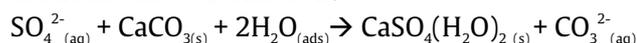
- H₂S dissolution in the water film:



- Sulfide partial and full oxidation by adsorbed oxygen:



- Calcium sulfate formation:



9.1.2. Siloxanes removal

Siloxanes occurrence and fate

As described in chapter 4, siloxanes are used in several industrial and domestic applications, including as antifoaming agents, in automotive care products as coatings, in construction as sealants, and in cosmetics and personal care products. The vast majority of siloxanes from

fluid applications are lost either into the atmosphere as a result of their volatility or into the wastewater system from rinse-off products. It is estimated that 10% of Volatile Methyl Siloxanes (VMS) enter domestic sewage systems; therefore, WWTP are one of the most important routes for siloxane introduction into the environment. Total siloxanes concentrations (linear and cyclic) in the inlet of WWTP are usually below 100 µg/L.

Siloxanes main removal mechanisms in the sewage and sludge processes of a WWTP mainly include adsorption on the sludge, volatilization/stripping into the atmosphere (especially in aerated reactors), volatilization into the biogas (in the anaerobic digester) and to a minor extent biodegradation. However, mass balances do not accurately match; and it is difficult to conclude on the relevance of each of them. Downstream the sewage and sludge lines, siloxanes adverse effects in Energy Conversion Systems (ECS) on the short- and long-term are not yet well-understood. Despite quantitative silica deposition on piston heads, oxygen sensors, spark plugs and lubrication oils was observed, current studies are not conclusive to establish scientifically-sound inlet concentration limits.

Siloxanes sampling and analysis

As depicted in chapter 5, Tedlar® bags, which is the preferred sampling method by WWTP operators as it is easy-to-use and is accepted in most commercial laboratories, proved to give reliable siloxanes concentrations compared both to impingers (with n-hexane) and adsorbent tubes (activated coconut charcoal; solvent desorption); regardless showing higher standard deviation in triplicate analysis. On the other hand, adsorbent tubes allowed the lowest limit of detection (0.01 mg/m³); hence they are recommended when quantification at very low concentration levels is required; e.g.: downstream biogas treatment system. The three sampling methodologies showed that D4 and especially D5 are the most commonly observed silicon compounds in sewage biogas; with overall siloxanes concentrations ranging 14 – 18 mg/m³ in mesophilic anaerobic digestion. Presence of linear siloxanes, other cyclic siloxanes (D3 and D6) and trimethylsilanol was discarded.

Siloxanes polishing

The most widely implemented and efficient siloxanes treatment technology is a preliminary refrigeration/condensation stage followed by physio-sorption. Adsorbent materials with high BET surface areas and high and balanced micro- and meso-pore volumes should be selected. Small micro-pores do not play a role on siloxanes removal. As described in chapter 6, biogas drying increased activated carbon lifetime around 10% as a result of siloxanes removal through condensation and solubilization in the condensed water stream. Removal efficiencies of 98 – 100% were observed for siloxanes and linear hydrocarbons; confirming that activated carbon can achieve the stringent silicon requirements of fuel cells. Nevertheless, removal efficiency for aromatic hydrocarbons (specifically toluene and p-/m-xylene) was of 88%.

The siloxanes adsorption capacity of virgin activated carbon was found to be of 2%(w/w); 10-fold smaller than the adsorption capacity observed for H₂S in the iron-containing adsorbent. Despite its lower concentration in raw biogas, cyclic siloxane D4 was the first compound to breakthrough; probably as a result of a roll-up phenomenon due to the mesoporous nature of the adsorbent.

9.2. Key findings on fuel cell technologies

9.2.1. Solid Oxide Fuel Cell performance

As it is shown in chapter 7, Solid Oxide Fuel Cell operation with cleaned sewage biogas is technically possible over a large period of time, i.e.: 700 hours. A wide range of power-to-heat ratios, i.e.: 0.5 – 3, was tested, showing that SOFC systems have high flexibility in terms of heat and power production; which represents an important advantage compared to conventional CHP technologies. Although the electrical and thermal efficiencies varied significantly for each power-to-heat level, cogeneration efficiency remained constant at around 59 – 62% for all the ratios tested.

The thermal demand for sludge heating at mesophilic conditions would be covered at a heat-to-power ratio of 0.8; and under these conditions the system's electrical and thermal efficiencies accounted for 34% and 28% respectively. Although these figures do not significantly exceed the performance of conventional Combined Heat and Power (CHP) units, it should be pointed out that stack electrical efficiencies of 45 – 53% were obtained; which do exceed those of Internal Combustion Engines and Micro-Turbines. These efficiencies were observed at fuel utilizations of 65 – 75%, which are low enough to satisfy the thermal demand for fuel reforming and pre-heating with the remaining energy. On the other hand, the operating conditions for biogas reforming were established at an O/C ratio of 1.3 (through steam addition) and 550°C to avoid carbon formation. Notwithstanding, the reformer was later operated at an O/C ratio of 2.1 to provide an operational safety margin; which had a negative impact both on the electrical (lower H₂ partial pressures in the anode) and thermal efficiency (larger demand for steam production) of the integrated SOFC unit. Therefore, a more efficient thermal design to avoid heat losses and operation closer to the critical O/C ratio can lead to significant performance improvement.

Finally, it should be emphasized that high O₂/CH₄ ratios in the treated biogas reduced the electrical efficiency up to 2.5 percentage points of the SOFC unit due to partial biogas consumption in the reformer through the POX reaction before the stack. The biotrickling filter caused biogas dilution, increasing the oxygen and nitrogen contents in the treated gas. As a result, bio-scrubbers (or other scrubbing technologies not injecting oxygen in the biogas) followed by adsorption would be recommended for fuel cell applications.

9.2.2. Technical-economic performance of fuel cell systems

Molten Carbonate Fuel Cell (MCFC) systems are the most efficient cogeneration technology as concluded in chapter 8, allowing the achievement of an electrical self-sufficiency of 71 – 75% for the 100,000 PE plant (60% larger compared to conventional cogeneration; which was limited to 40 – 46%). A more moderate improvement of 30% was observed for the 500,000 PE plant; indicating that small and medium-scale WWTP are the most relevant application field for fuel cells. The electrical self-sufficiency values obtained in this study confirm the important role that fuel cells can play on carbon neutral sewage treatment on the one hand; but on the other that additional measures and technologies should be fostered and promoted together with efficient biogas energy recovery.

Regardless the plant size, payback periods of MCFC projects were 3 – 4 times larger than Internal Combustion Engines (ICE); which is still today the most profitable technology for

sewage biogas energy recovery. The high investment cost and reduced lifetime of fuel cells are the two most relevant limitations which should be improved before fuel cells can become a deployable technology in WWTP in the short-term. While SOFC systems have a comparable technical performance with ICE, the economic profitability is still far away from industrial deployment (further than MCFC); hence the impact of this technology in sewage treatment is expected for the medium-term.

Moreover, the study showed that while the biogas pollution level affects the profitability of cogeneration projects; it did not have a large impact on the energy performance of the biogas valorization line. On the other hand, plant size affected both the profitability of cogeneration projects and the energy performance of the biogas valorization line.

Finally, the comparative assessment allowed concluding that today a final justification for biogas valorization in fuel cell systems will have to be found in environmental issues; which are difficult to quantify in economic parameters. Once significant breakthrough on the economy of installing a fuel cell unit and on the performance depreciation profile occur, both MCFC and SOFC technologies will have a certain potential to promote biogas energy recovery in WWTP (and other biogas sources) as the economic profitability of the cogeneration project will be less dependent on the possibilities to sale heat at a reasonable price. Regarding conventional cogeneration, economic factors (investment and maintenance costs) and regulations (electricity costs) will be the determining factors for installation.

9.3. Recommendations on biogas treatment configuration coupled to fuel cells

The results presented in this PhD thesis on biogas treatment confirm that the integration of biogas treatment and fuel cell technologies is technically possible and the very stringent fuel cell specifications for a wide range of pollutants can be met. As depicted in Figure 9.1, the following elements should be considered when designing the biogas treatment:

- *Cascade configuration:* a low cost main desulfurization technology for rough H₂S abatement followed by a deep polishing system based on adsorption processes divides the overall cost (investment and operational over five years) by two compared to stand-alone adsorption process (480 k€ vs 910 k€ for a 190 Nm³/h plant); hence improving the economic profitability of biogas fuel cell projects.
- *Main desulfurization:* advanced and conventional caustic scrubbers, differently from biotrickling filters, do require oxygen injection for H₂S removal, which eventually lead to larger electrical efficiencies of the system; maximizing the advantages of fuel cells. Therefore, they are recommended for the main desulfurization stage. Due to the larger investment costs and reduced operational costs of advanced scrubbers, this technology is recommended for large biogas flows (i.e.: above 65 Nm³/h) in order to improve the economic profitability. Conventional scrubbers are therefore suitable for small biogas flows.
- *Polishing:* adsorption processes are the only system which can reduce the concentration of H₂S and siloxanes to the very low requirements of fuel cells. Due to

the different properties and concentration levels in sewage biogas of these two contaminants, the use of two different adsorbent materials is recommended. H₂S polishing is implemented upstream. Nonetheless, the siloxanes polishing stage also acts as a final redundant protection for H₂S, as it will adsorb remaining traces of sulfur species which may be present periodically after H₂S polishing due to inefficient operation.

- *Adsorbent beds in lead-lag configuration:* when coupled to fuel cells, detection of the breakthrough point of adsorption systems needs to balance compliance with fuel cell quality requirements and increased adsorbent material's lifetime. In this context, adsorption beds in series with reversing capability (lead-lag configuration) allows detecting the breakthrough point based on the entire history of the adsorption process rather than on a threshold value; which maximizes contaminant loading on the adsorbent material while guarantees fuel cell limits as any breakthrough in the upstream bed will be adsorbed in the downstream bed.
- *Refrigeration/condensation:* biogas drying through a Heat Exchange Network (HEN) should be accomplished upstream or downstream the adsorbent filters depending on the moisture requirements of the adsorbent materials. Both for the iron-containing adsorbents (desulfurization) and for virgin activated carbon (siloxane removal), upstream location is recommended.
- *Biogas compression:* pressurizing is necessary to meet pressure requirements of fuel cell systems. It is carried out after main desulfurization in order to prevent corrosion; hence lifetime of the gas compression equipment is enhanced. Compressor should not be installed at the end of the system to have positive pressures through the entire treatment line. Rotatory positive displacement machines (roots and screw compressors) are generally used. The installation of Variable Speed Drivers (VSD) controlled by end-of-pipe pressure sensors is recommended to guarantee adequate biogas pressure at the fuel cell despite pressure losses through the treatment line.

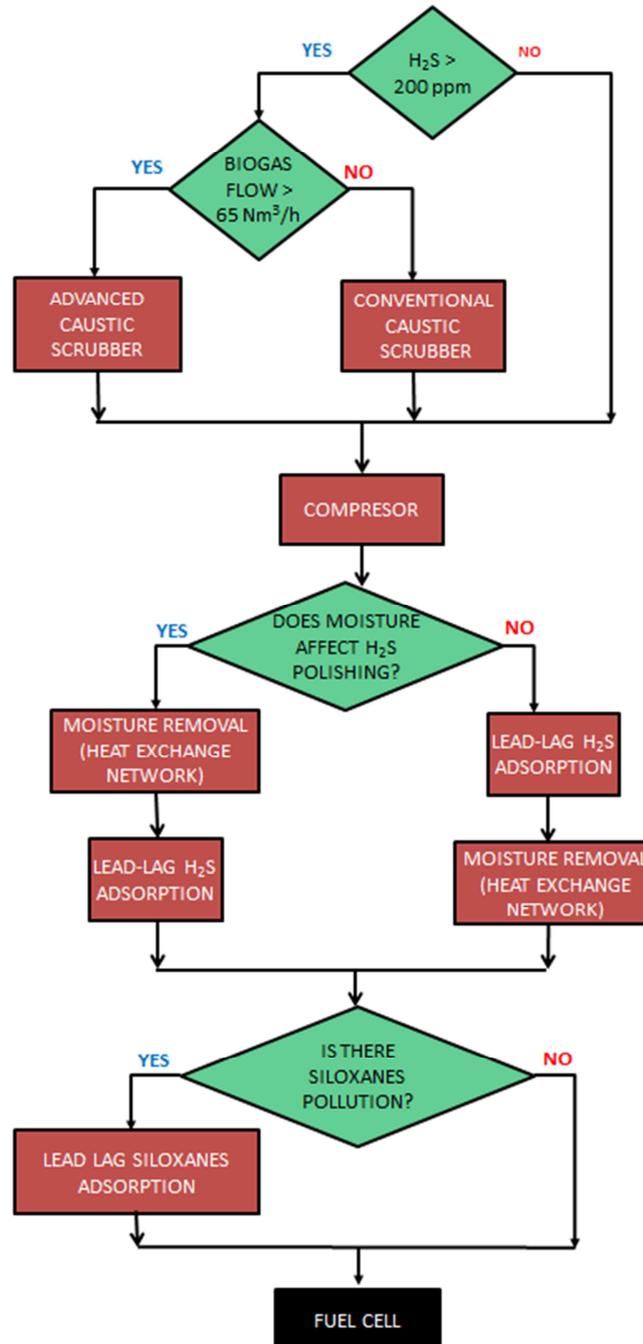


Figure 9.1. Decision tree for the design of the biogas treatment line adapted to fuel cells

9.4. Challenges for fuel cell implementation in WWTP

The results presented in this PhD thesis on fuel cells allowed identifying the most relevant challenges required for their future full-scale implementation in WWTP. They have been classified according to 4 major areas: technical/technological performance, economic performance, EU regulations and practicality (Table 9.1). Biogas producers, biogas treatment suppliers and fuel cell manufacturers should address together all these issues through collaborative research, development and innovation.

Table 9.1. Identified challenges for biogas-powered fuel cell implementation in WWTP

Area	Challenge	Description
Technical/ technological performance	Fuel cell performance	The Department of Energy (DoE) in the USA set specific performance targets for natural gas powered fuel cells: electrical energy efficiency 42.5%; CHP energy efficiency 87.5%; availability 98%; and operating lifetime 40,000 hours. Although these values can be also a practical reference for biogas, it will be necessary to establish specific targets for this fuel. While SOFC systems still do not meet any of those indicators, MCFC systems are starting to comply with some of them.
	Development of conventional CHP technologies	Fuel cell systems will always compete with conventional CHP technologies. Technology development that marginally improves the performance of conventional CHP technologies and extends their useful lives steadily raises the hurdle for alternative technologies. For example, Jenbacher's engine J920 of 9.5 MW, claims to have an electrical efficiency of 48.7%. Although this power range is too big for WWTP, it shows the ambition of ICE manufacturers to improve the performance of their systems.
	Gas quality factors	Knowledge on the degradation of fuel cell systems due to the presence of biogas contaminants is currently limited, thus manufacturers set very stringent and conservative (and often unpractical) quality requirements. Although long-term compliance with gas quality requirements is already state-of-the-art, research on the precise effect of biogas pollutants on fuel cells' performance and degradation, development of materials with robustness to impurities and development of innovative treatment technologies and processes is required in order to reduce the treatment cost and operating risks.
Economic performance	CAPEX reduction	The investment cost of the fuel cell system (4.5 k€/kW, for MCFC units in 2014) needs to be improved in order to compete with ICE (0.8 – 1.2 k€/kW). Continuous development on mass production systems and manufacturing automation is required. The Department of Energy (DoE) in the USA set a stack cost target of 700 \$/kW for 2015; which has not been achieved.
	OPEX reduction – stack lifetime improvement:	Stack lifetime (aprox. 5 years for MCFC units in 2014) needs significant improvement to match the values of ICE (15 – 20 years). The stack, which accounts for around 40% of the total investment costs, needs to be replaced as a result of progressive degradation (loss of voltage at a constant current value), constituting an OPEX. Continuous development on long-standing materials is required. Gas quality is also an important factor to guarantee reduced degradation. The Department of Energy (DoE) in the USA set a stack operating lifetime of 40,000 hours; which has been achieved.
	Existence of subsidies for Biogas Utilization in CHP systems	As a consequence of different European regulations (Directive on the promotion of cogeneration (2004-8-EC) and Directive on the promotion of the use of energy from renewable sources (2009-28-EC)), several subsidizing and financing schemes are in place in the different member countries to assist green electricity production. The level and typology of subsidy is very different from country to country in Europe. As grid parity has not been achieved yet (Levelized Cost of Energy are over 10 c€/kWh, in fuel cells), it is necessary to maintain subsidy schemes to deploy these technologies in WWTP.
EU Regulations	Relative subsidies CHP – biomethane	The relative level of financial support for biogas-to-electricity generation in CHP (both fuel cells and conventional technologies) and for upgrading to biomethane quality and injecting it into the natural gas grids (granted by Directive 2003/55/EC on natural gas market), will play an important role on selecting the biogas energy recovery route to implement in each WWTP. This decision should be studied through a case-by-case approach as different specific parameters should be taken into account. Some European countries like Germany set ambitious targets to replace natural gas by biomethane (6% of the total domestic natural gas consumption in 2020; and 10% in 2030) but the market and possibilities are still very different at each member state.

Table 9.1. Identified challenges for biogas-powered fuel cell implementation in WWTP (cont.)

Area	Challenge	Description
	<p>Thermal efficiency conditions that apply to CHP generation</p>	<p>The compliance of specific indicators for electrical and thermal efficiencies can be either compulsory or allows receiving additional revenues. For example, in Germany and the Netherlands it is necessary a minimum utilization of waste heat of > 50% to receive the Feed-In-Tariffs (FIT). On the other hand, in Spain, biogas CHP plants had to comply with a <i>Rendimiento Eléctrico Equivalente</i> of 50% (RD661/2007; now suppressed) to become eligible to receive a bonus, which multiplied the "standard" FIT per >10%. At this stage, it is important to highlight that, according to some regulations, heat for digester heating may not be considered computed as "useful heat". The possibility of operating fuel cell systems at different heat-to-power ratio allows fuel cells to adapt its performance to comply with thermal efficiency conditions; which turns into an advantage compared to conventional CHP.</p>
EU Regulations	<p>Requirement for zero-emission technologies of local pollutants</p>	<p>Some regional/national pieces of legislation exist today on emission limits for small-scale CHP plants (i.e.: < 50 MW_{th}, which is the case for WWTP); e.g.: <i>Technische Anleitung zur Reinhaltung der Luft</i> in 2002 in Germany or the <i>Decret 319/1998 de la Generalitat de Catalunya</i> in Spain. Conventional CHP technologies are prepared to meet the current limits for CO, NO_x and SO₂ (which range from 1,000 – 2,000; 500 – 3,000 and 300 mg/Nm³ (at 5%O₂) respectively), usually with some additional equipment (e.g.: Jenbacher's control system LEANOX™ or three-way catalysts) which does not represent a significant CAPEX/OPEX. Therefore, the superior performance on local pollutants emissions of fuel cells compared to conventional technologies is not taken into account. However, this is different in California, where regulations requiring very stringent emissions standards (e.g.: South Coast Air Quality Management District Rule 1110-2) have been placed. For sewage biogas, these limits are 40 and 900 mg/Nm³ (at 5%O₂) for NO_x and CO respectively; which cannot be met with conventional CHP technologies unless a high CAPEX/OPEX post-treatment such as a DENOX process is installed.</p>
	<p>Fuel cell offer (manufacturers, guarantees, fuel flexibility and power range)</p>	<p>Both the number of manufacturers offering turn-key commercial fuel cell products and the power range of their units is still very limited in comparison to conventional CHP technologies. In addition, operational guarantees given by the fuel cell industry are very limited. Moreover, not all fuel cell manufacturers consider biogas within their target market, as they are more focused on other more conventional fuels (e.g.: natural gas or hydrogen), further delaying deployment in WWTP. All these factors should be progressively solved as the other challenges are solved.</p>
Practicality	<p>Long-term returns of experience from WWTP operators</p>	<p>WWTP operators are reluctant on changing from conventional CHP technologies to fuel cells, not only because of the reduced level of worldwide deployment but also as there is not enough communication of industrial-scale references. Therefore, in the following years, not only more biogas-powered fuel cell experiences are necessary but also a proactive dissemination on their operating performance, advantages and problems. Both the scientific community and the final users should actively contribute to a better understanding of the fuel cell potentials.</p>

9.5. Prospects for future work

Biogas is a highly attractive fuel for SOFC technology and biogas clean-up technologies have proved to fulfill with the quality specifications set for fuel cell systems. Nevertheless, additional research is required for market deployment. Collaborative research between biogas producers, suppliers of biogas treatment systems and manufacturers of fuel cell units should take place to address the most relevant prospects for future work, as detailed below:

Biotrickling filters

- The optimum H_2S loading rate should be determined in order to reduce the required reactor volume while satisfying high removal efficiency and reduced elemental sulfur formation. Sulfur mass balances (elemental sulfur, sulfate, thio-sulfate, sulfide) at different H_2S loading rates should be established to contribute to this optimization.
- More efficient air supply systems (e.g.: venturi jets) to improve the oxygen mass transfer into the liquid-phase (more oxygen) should be developed to guarantee full oxidation to sulfates while reducing residual O_2 content in the treated gas.
- Effective systems/operating conditions for solids flushing from the column should be established to contribute in mitigating the elemental sulfur accumulation within the scrubbing column.

H_2S deep polishing

- Regenerative adsorbent materials should be developed to reduce the operational costs of deep desulfurization in the presence and absence of oxygen. The adsorption and desorption chemistry of H_2S removal with iron-containing materials in the presence of oxygen should be further understood.
- Additional analytical techniques should be used to precisely determine the H_2S adsorption mechanisms. For example, Fourier Transformed Infrared (FTIR) Spectroscopy could confirm water adsorption and formation resulting from H_2S oxidation (OH bond vibrations). Thermo-Gravimetric Analysis (TGA) combined with Differential Scanning Calorimetry (DSC) (or with Temperature Programmed Desorption) could confirm water peaks (around $100^\circ C$), elemental sulfur peaks (which should be spread around boiling point, $445^\circ C$) and sulfates/sulfides (over $800^\circ C$).

Siloxanes occurrence and fate

- Accurate siloxanes mass balances at conventional wastewater treatment processes in the sewage and sludge lines should be conducted to better understand the involved mechanisms and determine the specific contribution of each mechanism in the WWTP. This would also allow smarter operation of the treatment processes at specific conditions to avoid siloxanes-related problems.
- Better understanding of the short- and long-term effects of siloxanes on Energy Conversion Systems (both on conventional cogeneration systems and on fuel cells) is required to establish scientifically-sound quality limits.
- Efforts should be devoted to express siloxanes concentrations in $mg\ Si/Nm^3$ (or $mg\ siloxanes/Nm^3$).

Siloxanes removal

- Materials with higher percentage of micro-pores or mixtures of several materials with different pore sizes should be studied to prevent and/or delay the early breakthrough of D4 or other light siloxane components.
- More selective and regenerative siloxanes removal systems should be developed in order to reduce the associated operating costs; and even allow silicon recovery and valorization.
- Advanced on-line siloxane monitoring equipment (e.g.: through FTIR) should be promoted to improve the control and reliability of biogas treatment trains, guaranteeing a more stable and safer operation of the energy conversion unit.

Solid Oxide Fuel Cell

- The biogas reforming conditions (O/C, temperature) should be optimized to reduce the operational risks due to soot formation and improve the electrical and thermal efficiency of the SOFC unit.
- A more efficient thermal integration of the SOFC unit is required to operate the stack at large fuel utilizations (i.e.: high electrical efficiency) without compromising thermal management.
- The exhaust gas emissions in the SOFC unit should be measured at the different heat-to-power ratios and compared to conventional CHP.

9.6. References

1998/319 Decret de la Generalitat de Catalunya sobre límits d'emissió per a instal·lacions industrials de combustió de potència tèrmica inferior a 50 MWt i instal·lacions de cogeneració http://www.girbauconsulting.com/Legislacio_agroindustrial/Decret_319-1998_emissio_instalacions_industrials.pdf (Accessed on-line June 2015).

2002 Technische Anleitung zur Reinhaltung der Luft Germany <http://www.bmub.bund.de/fileadmin/bmu-import/files/pdfs/allgemein/application/pdf/taluft.pdf> (Accessed on-line June 2015).

2003/55/EC Directive of the European Parliament and of the Council of 26 June 2003 concerning common rules for the internal market in natural gas.

2004/8/EC Directive of the European Parliament and of the Council of 11 February 2004 on the promotion of cogeneration based on a useful heat demand in the internal energy market.

2007/661 Real Decreto de 25 de mayo, por el que se regula la actividad de producción de energía eléctrica en régimen especial.

2009/28/EC Directive of the European Parliament and of the Council of 23 April 2009 on the promotion of the use of energy from renewable sources.

2012 Rule 1110-2 South Coast Air Quality Management District <http://www.aqmd.gov/docs/default-source/rule-book/reg-xi/rule-1110-2.pdf?sfvrsn=4> (Accessed on-line June 2015).

Appendices

A: Worldwide biogas-powered fuel cells

B: P&ID Biotrickling

C: P&ID Polishing

D: P&ID SOFC

Appendix A. Worldwide biogas-powered fuel cell references 2014

Appendix A collects a general overview of the situation of fuel cells operated with biogas in the world, from their beginning in the 1990s till the time of this PhD thesis. The compiled data was obtained from the following sources:

- Fuel Cells 2000 State Fuel Cell and Hydrogen Database: Compilation of all the installed fuel cells in the USA.
- Fuel Cells 2000 Worldwide Fuel Cell Installation Database: Compilation of all the installed fuel cells all over the world (excluding USA).
- Fuel Cells 2000 case studies (2012): Some relevant major projects are detailed, emphasizing the facts that make fuel cells investment worthwhile.
- Fuel Cells 2000 case studies (2013).
- CIEMAT (Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas): “Utilización de biogás en pilas de combustible” (Biogas use in fuel cells) document (2008).
- USA Department of Energy (DoE): Fuel Cells technologies market report, Table 7. (referred as DoE T7) (2010).
- Fuel Cell Today: A reference website on fuel cell technologies.
- Manufacturers and costumers websites.

Tables A.1 and A.2 collect the most relevant information on different biogas-powered fuel cell projects (both on-going and decommissioned). Some fuel cell projects may not be reflected, since their information may not be available in the consulted databases and websites.

Table A.1. References of existing fuel cells operated with biogas (2014)

Manufacturer	Customer	Location	Fuel cell and power	From-To	Reference	Biogas type
FuelCell Energy	Inland Empire Utilities Agency	Ontario, California - USA	2.8 MW MCFC	2012 - Ongoing	Fuel Cell Today	WWTP
FuelCell Energy	San Jose/Santa Clara Water Pollution Control Plant	San Jose, California - USA	1.4 MW MCFC	2012 - Ongoing	DoE T7	Sewage
FuelCell Energy	Inland Empire Utilities Agency	Chino, California - USA	2.8 MW MCFC	2012 - Ongoing	FC2000 Database	Sewage
FuelCell Energy	UC San Diego	San Diego, California - USA	2.8 MW MCFC	2011 - Ongoing	DoE T7	Sewage (directed biogas)
FuelCell Energy	South Bay Water Reclamation Plant (pumping)	San Diego, California - USA	1.4 MW MCFC	2011 - Ongoing	DoE T7	Sewage (directed biogas)
FuelCell Energy	Point Loma WWTP	San Diego, California - USA	300 kW MCFC	2011 - Ongoing	DoE T7	Sewage
FuelCell Energy	EMWD	Riverside, California - USA	2x300 kW MCFC	2011 - Ongoing	DoE T7	Sewage
UTC Power	Orange County Sanitation District	Orange County, California - USA	250 kW PAFC	2011 - Ongoing	FC2000 Database	Sewage

Not known	Joint Base Lewis McChord Hydrogen - Fueling Station	Tacoma, Washington - USA	19 x Not known	2011 - Ongoing	FC2000 Database	WWTP
FuelCell Energy	Perris Valley Regional Water Reclamation Plant	Perris Valley, California - USA	2x300 kW MCFC	2011 - Ongoing	FC2000 Database	WWTP
UTC Power	Rancho Santa Margarita	Orange County, California - USA	2x400 kW PAFC	2011 - Ongoing	FC2000 Business cases 2012	NG + Biogas
FuelCell Energy	Rialto WWTP	Rialto, California - USA	3x300 kW MCFC	2010 - Ongoing	FC2000 Database	Sewage
FuelCell Energy	Gills Onions	Oxnard, California - USA	2x300 kW MCFC	2009 - Ongoing	FC2000 Database	Food waste
FuelCell Energy	Dublin San Ramon Services District Regional Wastewater Treatment Plant	Pleasanton, California - USA	2x300 kW MCFC	2008 - Ongoing	FC2000 Database	Sewage
FuelCell Energy	EMWD	Moreno Valley, California - USA	3x250 kW MCFC	2008 - Ongoing	FC2000 Database	Sewage
FuelCell Energy	Riverside Wastewater Treatment Plant	Riverside, California - USA	1MW MCFC	2008 - Ongoing	FC2000 Database	Sewage (Industrial waste co- digestion)
FuelCell Energy	Tulare WWTP	Tulare, California - USA	4x300 kW MCFC	2008 - Ongoing	FC2000 Database	Sewage
FuelCell Energy	Turlock WWTP	Turlock, California - USA	1200 kW MCFC	2008 - Ongoing	FC2000 Database	Sewage
FuelCell Energy	Alliance Power, Sierra Nevada Brewing	Chico, California - USA	4x250 kW MCFC	2005 - Ongoing	FC2000 Database	Sewage (brewery)
Fuji Electric	Kajima, NEDO	Yamagata City, Japan	2x100 kW PAFC	05/02 - Ongoing	FC2000 Database	Sewage
Not known	T-Mobile datacenter	Munich, Germany	1x250 kW Not known	Ongoing	Thermax	Not known
MTU CFC	Erdinger Weißbräu	Erding, Germany	300 kW MCFC	2009 - Not known	FC2000 Database	Sewage (brewery)
Tropical S.A.	Centre of Environment	Ptolemaida, Greece	1 kW PEM	2008 - Not known	FC2000 Database	Landfill
MTU CFC	Kläranlagen GmbH	Moosburg, Germany	250 kW MCFC	2008 - Not known	FC2000 Database	Sewage

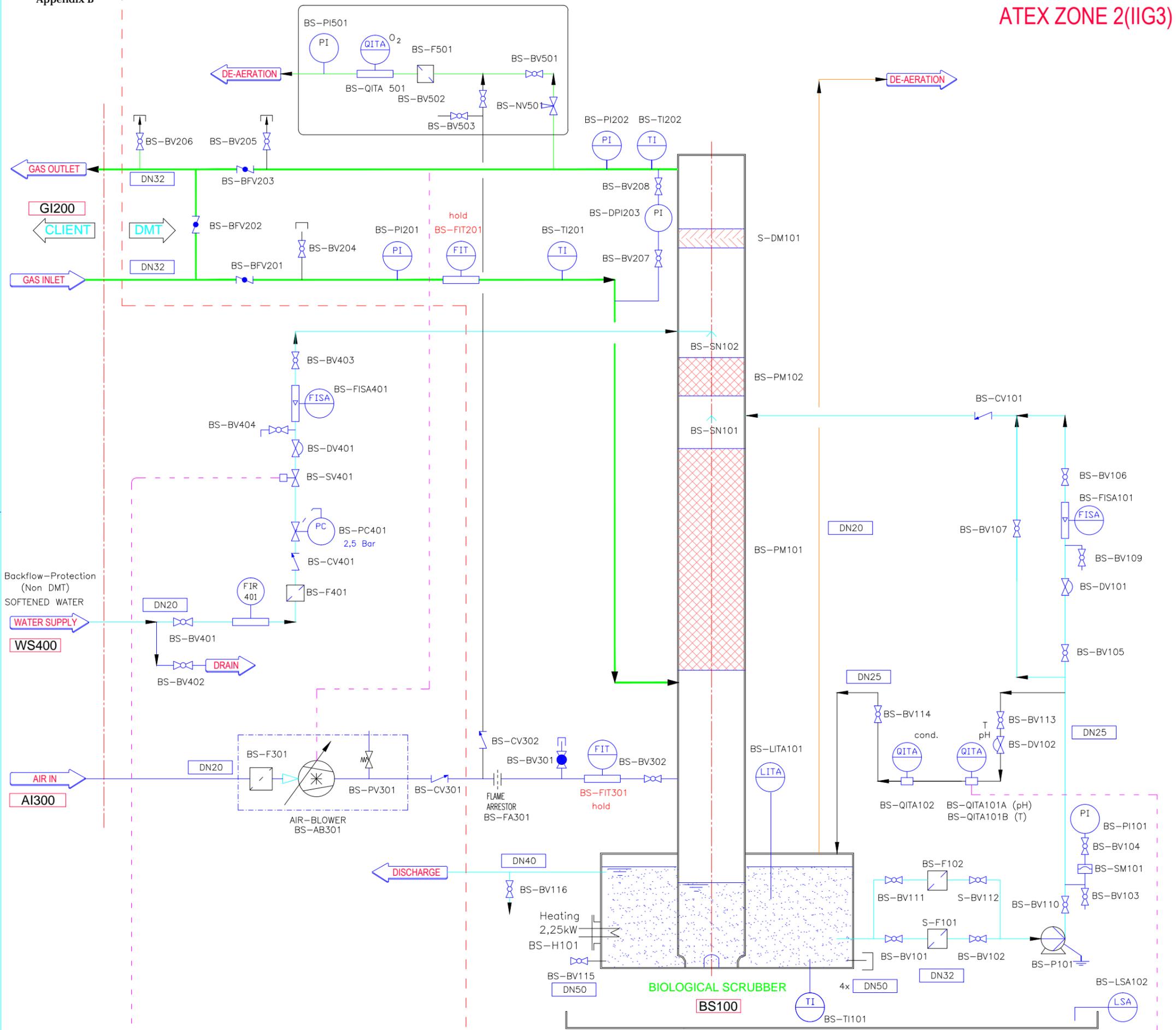
Acumentrics corporation	GlashusEtt environmental information center	Stockholm, Sweden	1x5 kW SOFC	2007 – Not known	FC2000 Database	WWTP
MTU CFC	T-Systems	München, Germany	250 kW MCFC	2007 – Not known	CIEMAT	Food waste (Energy crops)
MTU CFC	Waste Management Corporation of the District of Böblingen	Leonberg, Germany	250 kW MCFC	2006 – Not known	CIEMAT	Landfill
FuelCell Energy	RWE, MTU-CFC	Ahlen, Germany	250 kW MCFC	2005 – Not known	FC2000 Database	Sewage
FuelCell Energy	Marebuni, Bioenergy	Tokyo, Japan	250 kW MCFC	2005 – Not known	FC2000 Database	Food waste
FuelCell Energy	Mitsubishi, Bioenergy	Tokyo, Japan	250 kW MCFC	2004 – Not known	FC2000 Database	Food waste
FuelCell Energy	LA County Sanitation Districts, Quinn Power Caterpillar	Palmdale, California - USA	250 kW MCFC	2004 – Not known	CIEMAT	Sewage
MTU CFC	Erdinger Weißbräu	Erding, Germany	300 kW MCFC	2009 – Not known	FC2000 Database	Sewage (brewery)
Tropical S.A.	Centre of Environment	Ptolemaida, Greece	1 kW PEM	2008 – Not known	FC2000 Database	Landfill
MTU CFC	Kläranlagen GmBH	Moosburg, Germany	250 kW MCFC	2008 – Not known	FC2000 Database	Sewage
Acumentrics corporation	GlashusEtt environmental information center	Stockholm, Sweden	1x5 kW SOFC	2007 – Not known	FC2000 Database	WWTP
MTU CFC	T-Systems	München, Germany	250 kW MCFC	2007 – Not known	CIEMAT	Food waste (Energy crops)
MTU CFC	Waste Management Corporation of the District of Böblingen	Leonberg, Germany	250 kW MCFC	2006 – Not known	CIEMAT	Landfill
UTC Power	NY Power	Queens, New York - USA	2x200 kW PAFC	2002 – Not known	CIEMAT	Sewage
Fuel Cell Technologies	Hamarby Sjostad	Stockholm, Sweden	10x5 kW SOFC CHP	2002 – Not known	FC2000 Database	Not specified
H Power Corp	Naps Systems, Birka Energy	Stockholm, Sweden	4 kW PEM	06/02 – Not known	FC2000 Database	Landfill

Sulzer Hexis	Herr Chabloz	Lully, Switzerland	1 kW SOFC	2001 – Not known	FC2000 Database	Food waste (Agricultural)
UTC Power	NY Power	Staten Island, New York - USA	200 kW PAFC	1997 – Not known	CIEMAT	Sewage
UTC Power	NY Power	Yonkers, New York - USA	200 kW PAFC	1997 – Not known	FC2000 Database	Sewage
UTC Power	Town of Groton, US EPA, International Fuel Cells	Groton, Connecticut - USA	200 kW PAFC	1996 – Not known	FC2000 Database	Landfill
Toshiba	Hokubu Sludge Treatment Center	Yokohama, Japan	1x200 kW PAFC	Not known	FC2000 Database	WWTP
Topsoe Fuel Cell	Vaasa Landfill	Vaasa, Finland	1x20 kW SOFC	2010 – Decommissioned	FC2000 Database	Landfill
FuelCell Energy	King County, US EPA	Renton, Washington	4x250 kW MCFC	2004 – 2006	FC2000 Database	Sewage
FuelCell Energy	Marubeni	Fukuoka, Japan	250 kW MCFC	2003 – 2005	FC2000 Database	Sewage
IHI	Chubu Electric	Shin-Nagoya, Japan	300 kW MCFC	2002 – 2004	CIEMAT	Landfill
MTU CFC	University of Nitra	Nitra, Slovak Republic	300 kW MCFC	2002 – 2004	FC2000 Database (LIFE EFFECTIVE Project)	Food waste (Agricultural)
MTU CFC	Seaborne GmbH	Owschlag, Germany	300 kW MCFC (Mobile Unit)	05/2002 – 11/2002	FC Chart (LIFE EFFECTIVE Project)	Sewage (Industrial Waste)
MTU CFC	Linz AG	Linz, Austria	Not known	03/2003 – 05/2003		Landfill
MTU CFC	Urbaser, CIEMAT	Pinto, Spain	Not known	02/2004 – Summer 2004		Landfill
Ballard	N/A	Tomakomai, Japan	250 kW PEM	07/01 – 11/02	FC2000 Database	Sewage
UTC Power	Gas, Elektrizitats und Wasserwerk	Cologne, Germany	200 kW PAFC	2000 – 2010	FC2000 Database	Sewage
UTC Power	Köln-Rodenkirchen WWTP	Germany	200 kW PAFC	2000 – 2001	CIEMAT	Sewage
UTC power	Hog farm	Guangzhou, China	1x200 kW PAFC	2000 – Decommissioned	FC2000 Database	Farm methane + LPG
UTC Power	Braintree Electric Light Department	Massachusetts, Boston - USA	200 kW PAFC	1999 – 2004	CIEMAT	Landfill

UTC Power	City of Portland	Portland, Oregon - USA	200 kW PAFC	1999 – Decomissioned	FC2000 Database	Sewage
UTC Power	Sapporo Brewery	Sapporo, Japan	200 kW PAFC	1998 – Decomissioned	CIEMAT	Sewage (brewery)
UTC Power	Deer Island Sewage Treatment Plant	Massachusetts, Boston - USA	200 kW PAFC	1997 – 2002	FC2000 Database	Sewage
UTC Power	US EPA	Penrose Sun Valley, California - USA	200 kW PAFC	1994 – 1996	CIEMAT	Landfill
UTC Power	Las Virgenes WWTP	Calabasas, California - USA	2x200 kW PAFC	1990s – Decomissioned	FC2000 Database	Sewage

Table A.2. References of planned fuel cells operated with biogas (2014)

Manufacturer	Customer	Location	Fuel cell and power	From-To	Reference	Biogas type
Not known	Sonoma County	Sonoma County, California - USA	1x1,400 kW Not known	Planned for 2015	FC2000 Database	Kitchen waste
Ballard Power Systems	Humboldt County	Humboldt County, California - USA	1x175 kW PEM	Planned	FC2000 Database	Syngas from biomass
FuelCell Energy	Dairy farm	Sacramento, California - USA	1x? kW SOFC	Planned	FC2000 Database	Farm biogas
UTC Power	Microsoft Data Center	Cheyenne, Wyoming - USA	1x300 kW PAFC	Planned	FC2000 Database	WWTP

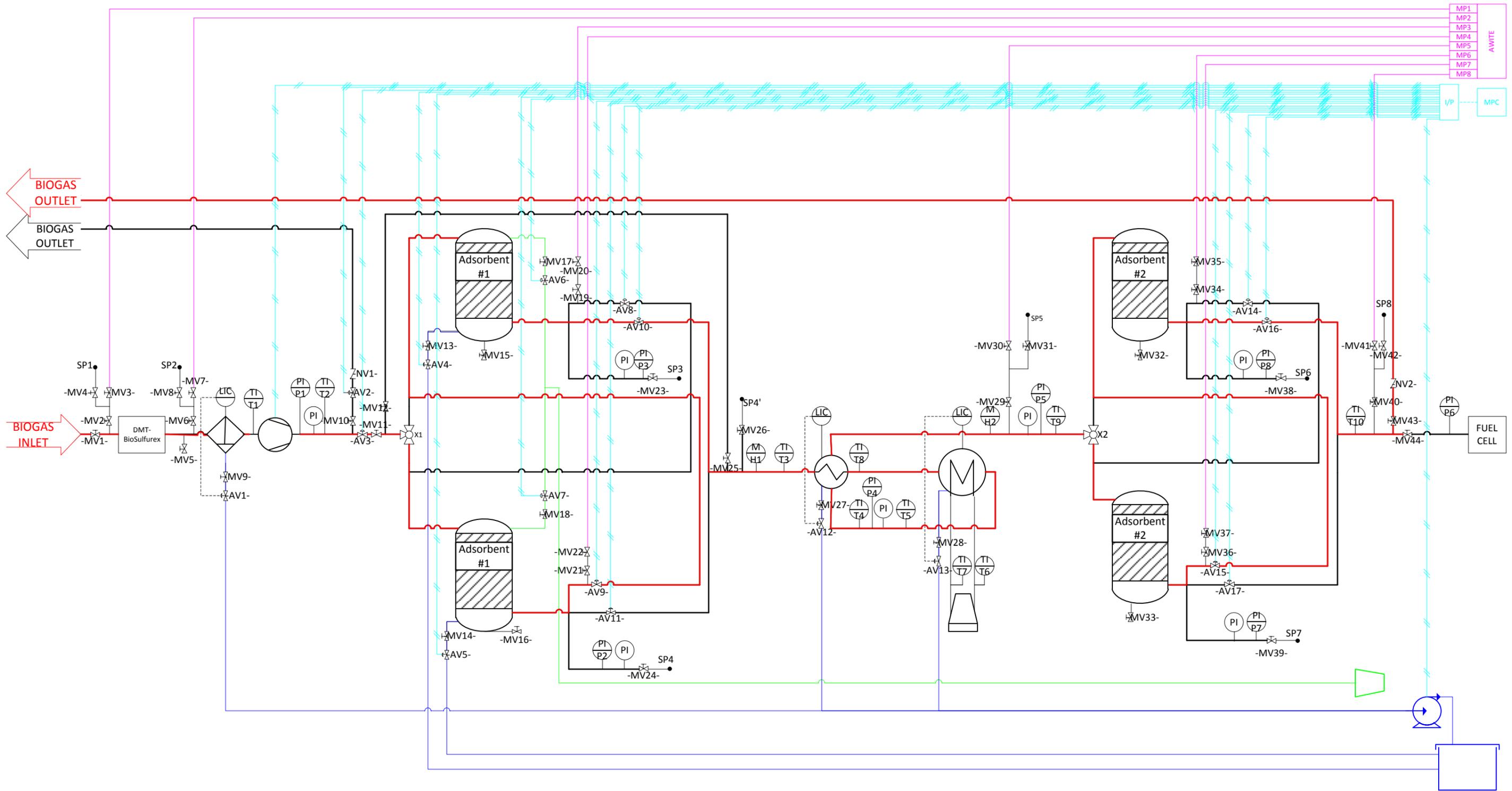


FOR INFORMATION ONLY

BIOGAS



F					
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CHANGE	DATE	DESCRIPTION	CHANGE	CHECKED	APPROVED
CET AQUA BIOSULFUREX BIOGAS DESULPHURIZATION PLANT -> P&ID <-					
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- X: Throttle valve
- MV: Manual valves
- AV: Automated valves
- NV: Non-return valves
- : Sampling points
- : Main biogas pipes
- : Secondary biogas pipes
- : Biogas
- : Air
- : Water
- : On-line analysis
- : Control system
- Water trap
- Blower
- Adsorbent filter
- Gas/gas heat exchanger
- Liquid/gas heat exchanger
- Refrigerator
- Air compressor
- Condensates pump
- Water container
- P: Pressure sensor
- T: Temperature sensor
- M: Relative humidity sensor
- L: Level sensor

BIOGAS TREATMENT PILOT PLANT	
MCFC catalyst and stack component degradation and lifetime: Fuel Gas CONT aminant effects and EX traction strategies	
	Author: CETaqua, Water Technology Centre Date: 16/05/2014

