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NON-CONVENTIONAL WASTE-DERIVED FUELS
FOR MOLTEN CARBONATE FUEL CELLS

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**Non-Conventional Waste-Derived Fuels for
Molten Carbonate Fuel Cells:
Experimental Investigations and
Technical-Economical Evaluations**

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A chi c'è stato...

A chi c'è...

A chi ci sarà...

A me che ci ho tanto creduto, con volontà, entusiasmo, ed energia!

SYNOPSIS

Global energy consumption is expected to increase dramatically in the next decades, driven by the rising of the standards of living and by the growth of population worldwide. The increased need of energy will require enormous growth in energy generation capacity, more secure and diversified energy sources, and a successful strategy to control and to reduce greenhouse gases emissions. There is a huge challenge to provide an everyday product, energy – that is taken absolutely for granted – in a radically different, difficult, but fundamentally improved way, at accustomed and competitive cost.

Also on the demand side severe corrections have to be undertaken: product and associated waste flows have to be interpreted differently, efficiency and sustainability becoming key issues.

One of the most immediate, and effective, ways to tackle this challenge is to minimize losses and waste by maximizing the exploitation efficiency of the resources that are utilised. One valid way to reduce fossil fuels dependence and demand, for example, is the use of alternative or non-conventional fuels, derived from waste or biomass. These fuels, by nature of their transient origins, are generally poor in energy content, which imposes localized deployment and maximum efficiency in their utilization in order to obtain a useful amount of work and/or heat.

In the effort to maximize the energetic yield from alternative energy sources like waste or biomass, and wanting to minimize environmental impact in terms of polluting or CO₂ emissions, the coupling of Molten Carbonate Fuel Cells (MCFCs) to the fuel gas produced from these sources is an attractive option. Combining these resources with fuel cell applications would provide a significant contribution to environmentally friendly, efficient energy use.

Currently, biofuels from waste and biomass are mainly used in engines and turbines with fairly low efficiencies and generate significant amounts of regulated pollutants (NO_x, SO_x and particulates).

Replacement of these conventional heat engines with MCFCs would allow a more efficient use of biofuels but, more significantly, would reduce NO_x, SO_x and particulates to insignificant levels and increase CO₂ benefits.

This work is part of an ambitious Research Project under the Agreement between ENEA (Italian National Agency for New Technologies, Energy and Sustainable Economic Development) and MSE (Italian Ministry of Economic Development) on the MCFCs Research and Development. One of the main topics of this project is the use of MCFC with biofuels (biogas from anaerobic digestion and syngas from biomass gasification).

The current Ph.D. work is finalized towards the coupling of a molten carbonate fuel cell (MCFC) to an anaerobic digestion process of organic residues or sludge from a wastewater treatment plant, and it has been carried out under the supervision of the Hydrogen & Fuel Cell Project, Energy Technologies, Renewable Energy Sources and Energy Saving Department, ENEA, Rome, Italy.

The biogas produced through anaerobic digestion is ideally suited for electrochemical conversion in an MCFC thanks to the large content of readily reformable methane and the necessary diluent CO₂.

The crucial link between these two technologies (anaerobic digestion and the MCFC), however, is formed by the gas clean-up step. This is because the raw produced biogas contains trace elements that originate from the organic nature of the feedstock, and that have detrimental effects on fuel cell performance and durability. The most common contaminant contained in the biogas is hydrogen sulphide (H₂S), relevant for harmful effects, both on the fuel cell electrodes as on the reforming catalysts.

A large part of the current study was dedicated to the particular effects of H₂S on the MCFC anode.

In the last years several studies on the effects of H₂S on the MCFC anode are reported in the literature, but the knowledge is still incomplete and requires more in depth study. Based on this knowledge a full experimental study was performed looking at the accurate knowledge of the conditions which are deleterious to MCFC, in order to facilitate safe and reliable operation of the fuel cell.

A systematic experimental campaign was carried out, the results of which will be presented and discussed, showing the effects and implications of cell poisoning with H₂S observed at several different levels of diagnosis (chemical, electrochemical, electrical, material).

The objective is to ultimately identify the true, effective tolerance limits of current MCFC materials, especially as regards different concentrations of H₂S that can occur due to composition variations of the produced biogas.

In order to achieve this objective, many hours of long-term experimentation has been required and different single cells have been operated in MCFC Laboratory, at Center for Fuel Cell Research, Energy & Environment Research Division, KIST – Korea Institute of Science and Technology, Seoul, South Korea.

The results of this experimental study allow to identify the main effect on the MCFC anode side by H₂S and also to evaluate the important role played by the Electrochemical Impedance Spectroscopy (EIS) as added value for the interpretation of this results. The impedance measurements are carried out to identify the processes which take place in the anode and to better understand the reversibility of sulphur poisoning under the regeneration processes.

After the technical approach, it's relevant to consider also the economic feasibility to understand how and when the MCFC systems fed with biogas can be competitive with other technologies currently present on the market, as Internal Combustion Engine and Gas Turbine.

A Cost-Benefit model will be performed and, based on it, a technical-economical analysis will be illustrated and discussed, considering the use of biogas in a 1.4 MW MCFC plant, in order to identify the most important economic parameters that affect the use of biogas in MCFC.

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LISTS OF SYMBOLS

AD	Anaerobic Digestion
ADG	Anaerobic Digester Gas
AFC	Alkaline Fuel Cell
CHP	Combined Heat and Power
CSTR	Continuous Stirred Tank Reactor
EI	Equivalent Inhabitants
EIS	Electrochemical Impedance Spectroscopy
GC	Gaschromatograph
GHG	Greenhouse Gas
HHV	Higher Heating Value (MJ/Nm ³)
IDLH	Immediate Dangerous to Life of Health (ppm)
Ir	Internal Resistance (mΩ)
LFG	Landfill Gas
LHV	Lower Heating Value (MJ/Nm ³)
MCFC	Molten Carbonate Fuel Cell
NPV	Net Present Value (€)
OCV	Open Circuit Voltage
OHPA	Obligatory Hydrogen-Producing Acetogenic bacteria
PAFC	Phosphoric Acid Fuel Cell
PBT	Payback time (t)
PEFC	Polymer Electrolyte Fuel Cell
RDF	Refuse Derived Fuels
SNG	Syngas from biomass gasification
SOFC	Solid Oxide Fuel Cell
STEL	Short Term Exposure Limit (ppm)
TWA	Time Weighted Average (ppm)
VFA	Volatile Fatty Acids (ppm)
VOC	Volatile Organic Compounds (ppm)

I – Waste-to-Energy Chain

1.1 Introduction

The pressing environmental and political necessities of modern international society call for a suitable array of contingency solutions to the energy question.

Increasing energy density of the consumption pattern, strongly oscillating barrel prices, persistent disputes about the viability of nuclear power, continuing dependency on overseas fuel imports and being at the mercy of volatile governments and organisations, growing environmental concern and very practical directives and deadlines to be met, are all elements that are putting the way we think about and organize our energy supply under pressure. Also on the demand side severe corrections have to be undertaken: product and associated waste flows have to be interpreted differently, efficiency and sustainability becoming key issues. In addition, there is a huge challenge to provide an everyday product, energy – that is taken absolutely for granted – in a radically different, difficult, but fundamentally improved way, at accustomed and competitive cost.

One of the most immediate, and effective, ways to tackle this challenge is to minimize losses and waste by maximizing the exploitation efficiency of the resources that are utilised. One valid alternative to way to reduce fossil fuels dependence and demand, for example, is the use of alternative or non-conventional fuels, derived from waste or biomass.

Fuels from waste or biomass, by nature of their transient origins, are generally poor in energy content, which imposes localized deployment and maximum efficiency in their utilization in order to obtain a useful amount of work and/or heat. The use of these sources however, is crucial to decrease dependence on fossil fuels and to increase the security and sustainability of energy supply as well as local productivity.

Examples of these resources are sewage sludge, organic fraction from municipal solid waste, agricultural or forestry activities, dedicated energy crops, landfill, waste material like Refuse Derived Fuels (RDF), industrial waste (e.g. from the paper or food industries) or secondary process flows from refineries and the chemical

industry. Utilization of these alternative energy sources is crucial to decrease dependence on fossil fuels and to increase the security and sustainability of our energy supply as well as to stimulate local productivity.

In the effort to maximize the energetic yield from alternative energy sources like biomass, sewage sludge, manure, waste flows from the food and agriculture industries, and wanting to minimize environmental impact in terms of polluting or CO₂ emissions, the coupling of molten carbonate fuel cells (MCFCs) to the fuel gas produced from these sources is an attractive option. Combining these resources with fuel cell applications would provide a significant contribution to environmentally friendly, efficient energy use.

Wherever localized collection and exploitation of such resources is feasible and heat and power off-take are readily available, the conditions are set for a truly virtuous chain of activities where interaction between parties is maximized and wastage is reduced to the absolute minimum; where refuse is converted to resource, closing an effectively organic cycle. Following these principles, the natural tendency of the energy infrastructure will be to shift towards a decentralised system, based on small-to-medium scale, high-efficiency generation and distribution.

1.2 System Principle

There is a growing scientific consensus that increasing levels of greenhouse gas (GHG) emissions (e.g., CO₂, CH₄) are responsible for global warming. With increasing energy demand and energy consumption worldwide it is therefore important to replace fossil fuels with sustainable and renewable energy sources.

Fuel cells are regarded as clean, reliable, quiet and efficient power sources running on hydrogen to produce electricity and water. However, sufficiently pure hydrogen is not readily available. The hydrogen needed for the fuel cell is at present often generated via the reforming of fossil fuels, such as methane.

Steam reforming is commonly used as it is a mature technology already used in industry for the large-scale production of hydrogen. Steam is added to the carbonaceous fuel and, under the effect of a catalyst and at elevated temperatures, hydrocarbons are converted to hydrogen and carbon monoxide. However, such

processes produce net CO₂ emissions. Therefore for a fuel cell to be a true renewable energy source with no net CO₂ emissions the fuel should come from a renewable source.

The high-temperature fuel cells, as MCFC in particular, can be a current potential for implementation of clean, high-efficiency, electrochemical conversion of fuel, thanks to their capability to operate relatively easily on hydrocarbon-based fuels, rather than relying on pure hydrogen as is the case for low-temperature fuel cells. The modular build-up of MCFCs makes them adamantly eminently suitable to a decentralised energy infrastructure, which relieves dependencies on primary energy carrier imports and encourages local productivity.

Thus, for stationary heat and power generation utilising fuels from alternative sources, the MCFC is the most suited for short-term market penetration, thanks also to their field experience and extensive improvements obtained in the past decade.

MCFCs could thus operate on such different fuels as:

- ④ biogas from anaerobic digestion of:
 - sewage sludge (originating from the process of treatment of waste water or manure)
 - organic waste (from the biodegradable fraction of municipal solid waste (MSW))
 - biomass (from agricultural, agro-industrial residues or dedicated energy crops)
- ④ landfill gas from decomposition under anaerobic conditions of the organic fraction of waste accumulated on dumping sites
- ④ syngas from a thermal gasification or pyrolysis process using:
 - waste material like Refuse Derived Fuel (RDF) from municipal solid waste, sewage sludge exiting from waste water treatment plants, or industry-specific wastes such as pulp and paper residues
 - biomass containing lingo-cellulosic materials (from forest residues, dedicated energy crops or residues from the food industry)
- ④ secondary process flows from refineries and the chemical industry
- ④ bio-(m)ethanol and bio-diesel.

There are several possible technologies for conversion of such non-conventional energy sources as mentioned above, each more or less suited to a given type of feedstock. At varying levels of development and technological complexity, landfill, anaerobic digestion, gasification, pyrolysis, esterification, etc. are examples of processes that transform the main substances in the alternative source to lighter hydrocarbons, readily utilisable as a fuel.

However, the contaminant levels in these fuels are often unacceptable for durable performance of a MCFC. This sets demanding requirements on the gas clean-up stage and it is thus desirable to establish precisely – and improve – the tolerance to residual contaminants of the fuel cell.

The drives for using biofuels in fuel cells are mainly environmental and financial. The use of waste and biomass for energy generation is an attractive alternative which can bring important environmental benefits by mitigating greenhouse gas emissions, and also by acting as a carbon sink (i.e. it consumes CO₂).

Currently, biofuels from waste and biomass are mainly used in engines and turbines with fairly low efficiencies and generate significant amounts of regulated pollutants (NO_x, SO_x and particulates).

Replacement of these conventional heat engines with fuel cells would allow a more efficient use of biofuels but, more significantly, would reduce NO_x to insignificant levels and increase CO₂ benefits.

Furthermore, the use of biofuels can, in theory, reduce the overall cost of fuel cell operation. Some types of biofuels are cheaper than conventional fuels such as hydrogen or natural gas. In fact, biofuels can even be inexpensive when generated on-site as a bi-product of a process, e.g. biogas produced from an on-site wastewater treatment plant.

Such systems would be practical on islands and in remote and rural areas where connection to the grid can be expensive and where biofuels can be produced on site at no significant extra cost. Compared to other energy generation devices, fuel cells would bring the added advantages of low maintenance, low noise and low emissions combined with high efficiency. Another possible and important market could be in developing countries which, with rapidly growing energy needs, would benefit from the combination of the available biomass with clean and efficient fuel cells leading to sustainable energy development.

Schematically, the chain considered is shown in Figure 1.1.

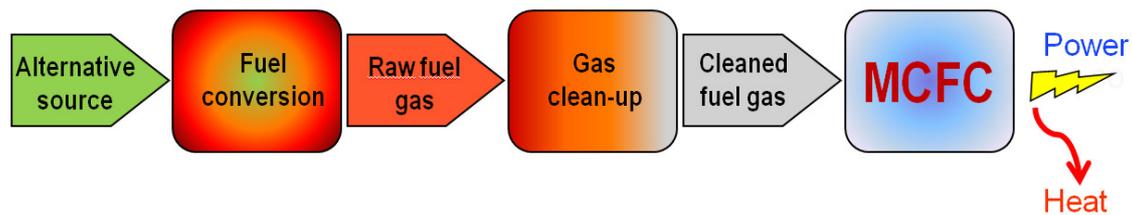


Figure 1.1: Principle of conversion of a generic alternative source to electricity and heat using a molten carbonate fuel cell

The main components of the Waste-to-Energy chain under analysis are grouped into the following three subsystems:

- ④ Fuel production from waste and biomass
- ④ Gas clean-up and conditioning
- ④ High-efficiency biofuel conversion to electricity and heat by a MCFC

The research carried out in this work encompasses the entire chain presented above, and is finalized towards the coupling of a molten carbonate fuel cell (MCFC) to an anaerobic digestion process of organic residues or sludge from a wastewater treatment plant.

Apart from the considerable benefit of neutralizing biological activity, the microbial decomposition of these cumbersome waste flows yields a highly calorific, combustible gas and leaves a residue (or *digestate*) that is a highly efficient fertilizer. The digestate reintegrates the nutrients in the soil that gave rise to the original feedstock and the *biogas* transfers the solar energy that was encapsulated in the growing process, in a concentrated and convenient form, to the end utilisation. As it happens, the gross composition of the biogas produced is ideally suited for electrochemical conversion in an MCFC thanks to the large content of readily reformable methane and the necessary diluent CO_2 .

The crucial link between these two technologies (anaerobic digestion and the MCFC), however, is formed by the gas clean-up step. This is because the raw producer gas contains trace elements that originate from the “visceral”, organic nature of the feedstock, and that have detrimental effects on fuel cell performance and durability.

In developing the argumentation in favour of the particular Waste-to-Energy system described above, a brief overview will be given of the main interesting processes for biofuels production: anaerobic digestion, landfill and gasification. Comparison of these processes will lead to focusing particularly on anaerobic digestion.

The characteristics of the main contaminants contained in biogas will be touched upon, laying more emphasis on H₂S due to its importance in terms of quantity and harmful effect, both on the fuel cell electrodes as on the reforming catalysts. Considering the crucial link between biofuel production and application in a MCFC, also the most common H₂S removal processes will be reviewed.

Three general approaches to solve the sulphur problem in the MCFC are possible. The first is to prevent the formation of hydrogen sulphide at the source: favouring conditions that inhibit its production during fermentation. Secondly, removal of the generated sulphur species to very low levels before the gas enters the fuel cell. The third approach is to identify the sulphur tolerance levels of the fuel cell components currently in use and develop sulphur-tolerant components that show long-term electrochemical performance and corrosion stability.

A large part of the current study was dedicated to the particular effects of H₂S on the MCFC. Investigations of the endurance to this insidious and lethal contaminant are few, since experimentation of the effects is necessarily destructive to the MCFC and can be of long duration, but an accurate knowledge of the conditions which are deleterious to MCFC operation are fundamental and would facilitate safe and reliable operation of the fuel cell.

A systematic experimental campaign was carried out, the results of which will be presented and discussed, showing the effects and implications of cell poisoning with H₂S observed at several different levels of diagnosis (chemical, electrochemical, electrical, material). The objective is to ultimately identify the true, effective tolerance limits of current MCFC materials, especially as regards different concentrations of H₂S that can occur due to composition variations of the produced biogas.

Finally a technical-economical analysis will be illustrated, considering the use of biogas in a 1.4 MW MCFC plant.

II – Decentralised Non-Conventional Fuel Production

2.1 Introduction

Biofuels are gaseous, liquid, or solid fuels that are produced from raw biological material, biomass or waste (plants, sewage, dry waste, cane sugar, wood pulp, etc) through combustion or fermentation.

Concerning waste, the problem of management is a major issue nowadays, where the primary concern must be to prevent waste generation. After this, in order of priority, waste handling should be aimed at the minimization, reutilization and recycling of excess material. If this is no longer possible, energy recovery, as in the “Waste-to-Energy” chain, can provide a significant contribution to our environmental and energy necessities, and only in the last instance should waste disposal be considered.

Currently biomass accounts for 15% of global energy use. In less developed countries, biomass remains an important energy resource, averaging around 38% of energy use and rising to 90% in some countries. Over two thirds (32 EJ) of biomass is used for cooking and heating in developing countries. The remaining 15 EJ of the energy use of biomass takes place in industrialised countries (3 EJ in Europe only) where biomass is utilised both in industrial applications within the heat, power and road transportation sectors and in the heating purposes of the private sector. The global biomass power generation capacity is approximately 44 GW (2007).

The use of biomass for energy production can be increased considerably from the current level over the next decades, when fossil fuels will become scarce and more expensive. In the light of the Kyoto Protocol, the use of biomass for energy production will be increased especially in the industrialised countries which are aiming to decrease the emission of greenhouse gases.

Waste or biomass-based energy technology has to be locally supported and utilised and will therefore not have the scales of economy enjoyed by fossil fuel-based

energy technology. This is mainly because of the low energy content of waste and biomass compared to fossil fuels, and the correlated inefficiency of their transportation over long distances. Especially in the case of biomass, the distances from the regions where the biomass grows to the regions with unsaturated biofuel markets can be considerable, and concentration of the energy content has to take place first through local treatment (dehumidification, pelletization, pyrolysis or similar; or even direct conversion to electricity).

Depending on the biomass availability, location of the processing plant and the end user (in order of desirability: next to the biomass production site, near sea ports or railway stations), optimum size of the processing plant may lie between 0.1 and 100 MWe, which is in the small-to-medium range.

As mentioned, biomass and waste, by their very nature, are variable in composition, energy content and availability, which renders optimization and standardization of the processing plants difficult and operation of the latter something to monitor continuously.

Biofuels that have been identified as potential fuel for fuel cells are anaerobic digester gas (ADG), landfill gas (LFG), syngas from biomass gasification (SNG), bioethanol. Biodiesel, levulinic acid and pyrolysis oil could also be of interest, but there are not enough data on their application in fuel cells.

ADG, LFG and SNG are gaseous biofuels. Their composition varies according to the feedstock and conversion techniques used, as summarised in Table 2.1. In addition to gaseous species, these biofuels can also contain a variety of contaminants and impurities such as sulphur compounds (H₂S, COS, etc), halides, tars, dust, ammonia, siloxanes, etc.

BIOFUEL	Average Composition
ADG	60-65% CH ₄ , 30-40% CO ₂ , 1-10% N ₂ , 0-1% H ₂ Traces: O ₂ , sulphur compounds (up to 5000 ppm), halogens, organics
LFG	60% CH ₄ , 40% CO ₂ , 0.5% N ₂ , 0.2% H ₂ , 0.2% O ₂ Traces: alkanes, aromatics, chlorocarbons, sulphur compounds, higher hydrocarbons, siloxanes
SNG	40-50% N ₂ , 22-27% CO, 10-15% H ₂ , 10-15% CO ₂ , 2-3% CH ₄ Traces: heavy hydrocarbons, particulates

Table 2.1: Average biofuel gas composition for Anaerobic Digestion Gas (ADG), Landfill Gas (LFG) and syngas from biomass gasification (SNG)

There are several ways to convert the raw energy-containing material into a suitable fuel for fuel cell applications. Essentially these are divided in “hot” and “cold” technologies, where the former adopt thermal disassembling of the organic compounds in the raw fuel to create a synthetic gas consisting essentially of hydrogen, carbon monoxide and dioxide, whereas the latter type of conversion is a process in which micro-organisms break down biodegradable material in the absence of oxygen, with the production of biogas – a mixture of methane and carbon dioxide.

Regarding the “hot” technologies of non-conventional fuel production, compared to those of fossil fuel production and utilisation, these are far from optimized at the moment and face considerable technical and economic challenges. This is related to the non-uniform and diluted nature of the resources utilized, their relatively low heating value and high ash and moisture content. Thus, it is still necessary to build confidence in these technologies, particularly with respect to tar reduction, ash behaviour, gas cleaning, stability of the process with the diverging nature of the prime material.

Regarding the “cold” technologies of non-conventional fuel production, biological conversion happens spontaneously in landfill sites and anaerobic digestion facilities. The latter has been utilised for many years for the stabilisation of wastewater and animal manure, and is gaining interest as a renewable method of producing combustible biogas. Thus, it is a process that is well known in rural societies.

ADG results from the anaerobic (i.e. in the absence of oxygen) digestion of biomass waste using bacteria (agricultural waste, wastewater treatment plant, etc). The digester gases produced are also called biogas and are generally made of methane and carbon dioxide with some hydrogen and nitrogen and traces of oxygen, sulphur compounds, halogens and organics. The H₂S content can be as high as 3000 ppm. The process of anaerobic digestion leads to some significant variability in the ADG composition depending on the feedstock, temperature, etc. To a certain extent, LFG and ADG composition are similar, i.e. mainly CH₄ and CO₂.



Figure 2.1: Anaerobic Digester

LFG arises from the degradation of municipal solid waste by anaerobic micro-organisms to produce mainly CH₄ and CO₂, with traces of alkanes, aromatics, chlorocarbons, sulphur compounds, higher hydrocarbons, siloxanes, etc. This composition varies depending on the age of the landfill site. CH₄ is twenty-one times more potent than CO₂ for GHG, therefore if LFG are recovered and not vented to the atmosphere, net benefits towards GHG emissions can be accomplished.

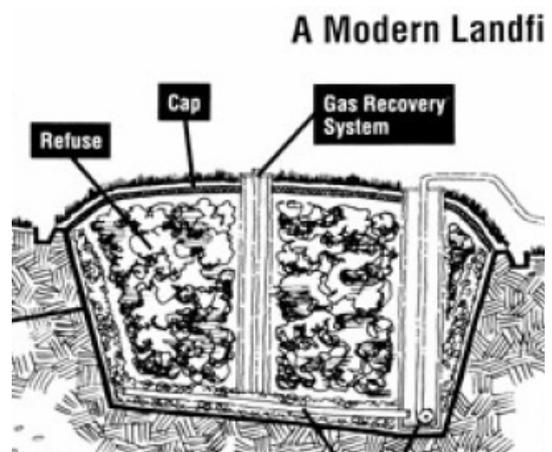


Figure 2.2: Landfill

Gasification of waste or biomass is a process by which solid fuel is converted into combustible gases by a combination of oxidation, pyrolysis and reduction processes. Various types of gasifiers exist (downdraft, updraft, fluidized bed, etc), relying on different processes and hence resulting in different gas compositions. In addition, the feedstock and operating conditions of the gasifier will strongly impact on the gas composition.



Figure 2.3: Gasifier

Finally, bioethanol ($\text{CH}_3\text{CH}_2\text{OH}$) is obtained by the fermentation of the sugar components of biomass, for example, from sugar cane. Yeast is added to the extracted sugar to run the fermentation process. But bioethanol can also be produced from cellulosic biomass such as cropwastes (sawdust, etc.), municipal solid waste and recycled newsprint. Cellulosic materials first need to be processed to form sugar that can then be fermented. Bioethanol is a liquid fuel and an alcohol. Compared with ADG, LFG, and SNG, bioethanol is a relatively clean fuel and does not require complex clean-up processes.

Input feedstock conditioning before and product fuel upgrading after this first conversion step are crucial in achieving efficient conversion to a suitable fuel for the high-temperature fuel cell, as MCFC. Important considerations here are drying, excess air utilisation, elimination of particles and desulphurization.

The recyclability of the ultimate refuse flow that is expelled from the conversion process is an important factor in terms of disposal cost saving. This should partially offset the increased costs of fuel treatment. Subsequently, the transmission of the product fuel to the fuel cell should be tailored to reduce energy loss and parasitic energy consumption to a minimum. In this process, thermodynamic, chemical and logistical optimization should be carefully considered.

2.2 Anaerobic Digestion

Anaerobic digestion is an established technology for environmental protection through bacterial treatment of organic substrates. Wastewater treatment facilities all over the world use anaerobic digestion to neutralise the organic compounds of sewage sludge. Fermentation in the absence of oxygen is also being considered to treat animal wastes, organic fraction of municipal solid waste and agro-industrial wastes.

Currently, anaerobic digestion is receiving new attention as it can potentially reduce global warming via the (CO₂ neutral) utilization of the produced biogas as an energy source.

In anaerobic digestion, a process which takes place in the absence of oxygen, a mixed population of bacteria catalyses the breakdown of the polymers found in biomass to give biogas. This primarily consists of methane and carbon dioxide but may also contain ammonia, hydrogen sulphide and mercaptans, which are corrosive, poisonous and malodorous.

The other products of this process are: a solid residue, which can be used as compost after composting treatment, and a liquor that can be used as a fertilizer.

2.2.1 The Process

During the digestion process, organic substrates are converted in a digestate rich in nutrients and a mixture of gas, called biogas. The biogas has a Lower Heating Value (LHV) of about 23,000 MJ/Nm³ and its composition depends on the organic matter utilized and the value of operating parameters adopted.

The anaerobic process is carried out by the concerted action of at least five groups of microorganisms including primary fermenting bacteria, secondary fermenting bacteria and two types of methanogens. The function of the fifth group, homoacetogenic bacteria, is less well understood.

The overall process can be divided into four distinct phases, schematically visualised in Figure 2.4:

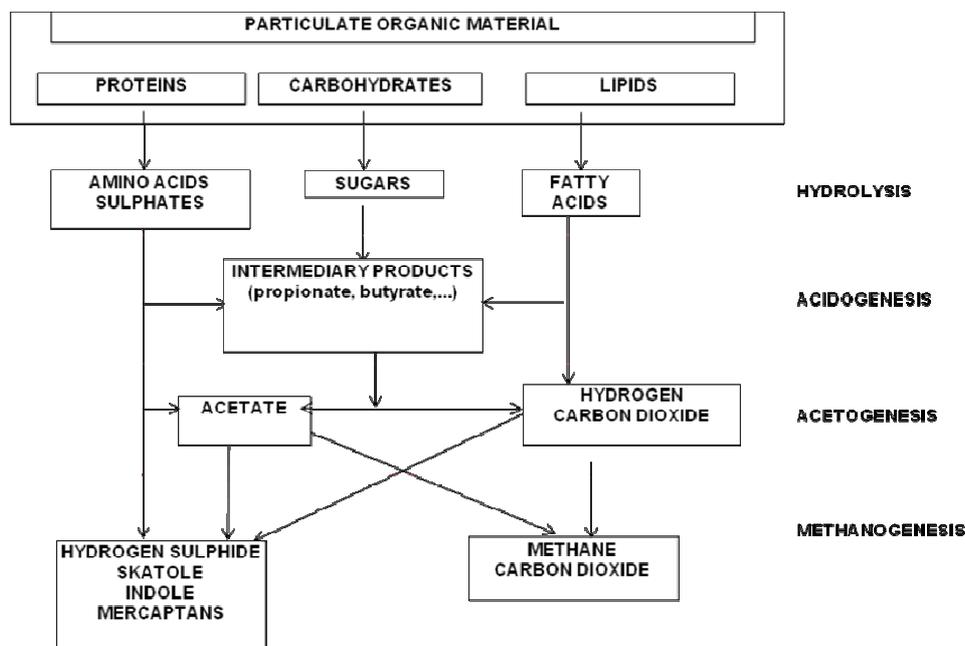


Figure 2.4: Conversion processes in anaerobic digestion

- hydrolysis:** hydrolytic enzyme excreted by acidogenic or primary fermentative bacteria (strict anaerobes like Bactericides and Clostridia or facultative anaerobic bacteria as Sterptococci) hydrolyze the complex organic matter, composed of carbohydrates, proteins and lipids, leading to C1 compounds (e.g. carbon dioxide, formate etc.), hydrogen and acetate which are the substrate for methanogens (see below). Soluble compounds like monomers, amminoacids, alcohols, organic acids are also formed at

this stage becoming substrate for the secondary fermenting bacteria which are representative of the next phase Ceramic foam in silicon carbide (SiC);

- ④ acidogenesis: acidogenic bacteria convert the products of previous stage in short chain organic acids (so called Volatile Fatty Acids (VFA) as propionic, butyric, valeric and acetic), releasing carbon dioxide and hydrogen;
- ④ acetogenesis: VFA are metabolised predominantly in acetic acid by two families of acetogenic microorganisms, both being identified as secondary fermenting bacteria: the first is called OHPA (obligatory hydrogen-producing acetogenic bacteria), which oxidise VFA to acetic acid and further to hydrogen and carbon dioxide as end-products. The second family stops the degradation to acetate (the main form of acetic acid in the neutral pH condition of digester). The homoacetogenic bacteria, on the contrary, utilise hydrogen and carbon dioxide for acetate biosynthesis. In certain environments, they may even successfully compete with hydrogenotrophic methanogens (see below) and take over their function to various extents;
- ④ methanogenesis: acetoclastic methanogenic bacteria (Methanosarcina spp., Methanotherix spp.) reduce acetic acid to methane and carbon dioxide (which accounts for 70% of methane produced). Hydrogenotrophic methanogenic bacteria (Methanobacterium, Methanococcus) utilise hydrogen and carbon dioxide formed by OHPA producing methane.

The well balanced management of mutual dependence among these bacterial types is the key to optimization of the anaerobic process. Due to the small energy available in methanogenic conversion, the bacteria community is forced to be act in highly efficient cooperation.

The mutual dependence of partner microorganisms, with respect to energy, can go so far that neither partner can operate without the other and that together they

exhibit a metabolic activity that neither could accomplish on its own. Such cooperation is called a syntrophic relationship.

There are some syntrophic relationships between the five groups described, that determine overall equilibrium and contrast feedback inhibition phenomena (i.e. the hindering of a reaction or conversion process through the inactivating action of the products of the same reaction or process).

The development of different bacterial communities, on the other hand, is strictly bound to the chemical equilibriums present within the substrate and to the operating conditions adopted, like temperature, pH, mixing mode, sludge retention time, hydraulic retention time and type of inoculum used. However, the energetic kinetics and the dynamics of nutritional groups are still not clear in literature, even though anaerobic processes have been applied for a long time. Due to the complexity and the high degree of variability of the biological pathways involved during digestion, integration of engineering, biological and chemical knowledge is necessary to establish the parameters that regulate the process and their monitoring together with the efficiency rate.

2.2.2 Environmental Factors Affecting Anaerobic Digestion Process

There are a number of factors which influence the digestion process, including, temperature, bacterial consortium, nutrient composition, moisture content, pH, and residence time.

Ⓢ Temperature

Temperature is an important factor for microbial activity. There are mainly three temperature intervals, which are considered as optimal for AD. These interval are called psychrophilic, mesophilic and thermophilic (Table 2.2).

Mesophilic methanogenesis occurs at its best around 35°C. Thermophilic digestion has been reported to have several advantages over those at mesophilic temperature, such higher reaction rates and pathogen-killing effect.

	Temperature range (°C)	Temperature optimum (°C)
Psychrophilic	0-20	15
Mesophilic	15-45	35
Thermophilic	45-75	55

Table 2.2: Temperature ranges and optimum for various intervals

Nutrients

For optimal AD a number of substances are necessary. Carbon, nitrogen and phosphorus are fundamental for growth and multiplication. The nitrogen content of a substrate is important since digestion of nitrogenous compounds will contribute to the neutral pH stability by releasing ammonium. Different advice for C:N ratios of the substrate can be found in literature. An optimum C:N ratio for AD is suggested to be 20:1 to 30:1. Micronutrients are required in AD as in any other microbial process. The most important needed to stimulate growth are sulphur, vitamins and traces of minerals.

Toxicants

Biological process are sensitive to a number of toxic compounds. These inhibitory substances can occur in feedstock, but they can also be produced as a results of microbial activity, converting non-inhibitory substances to inhibitory substances.

Toxic substances can be inorganic, such as heavy metal, hydrogen sulphide, salts and ammonia, and also organic, as for example in the case of waste originating from different agricultural products that contains diverse assortments of natural polyphenolic compounds, which can be inhibitory to methanogenesis.

Toxicity of the anaerobic process is a complex phenomenon; it can also be dependent on the concentration of other substances which can have synergistic or antagonistic effects.

④ pH and alkalinity

To maintain a stable methanogenic activity, a pH between 7 and 8 is desired. The methanogenic process is alkalizing in itself, that is, it consumes hydrogen ions.

Unstable conditions caused by overloading or the presence of toxic compounds lead to the accumulation of volatile fatty acid, which causes a drop in pH. Recycling of digester effluent for dilution of incoming substrate can be a way of enhancing the buffer capacity, this contributing to pH stability.

④ Water content

The water content of the substrate is important from several aspects. It is essential for biological activity, since nutrients must be dissolved in water before they can be assimilated. In addition, water enhances the mobility of microorganisms facilitating their contact with the substrate. Water is also known to influence mass transport limitations. The low moisture content with difficult mass transport as well as poor penetration, diffusion and distribution of microorganisms throughout the substance can complicate the digestion of solid wastes when using dry AD.

2.2.3 Substrates for Anaerobic Digestion Process

In general, all wastes that contains organic matter can be utilized for biogas production, easily degradable homogenous concentrated streams are the most favourable. Table 2.3 summarizes sources of wastes that are presently used for biogas production, the waste streams are divided into solid wastes, waste slurries and wastewater.

Solid Waste	Domestic	Separately collected vegetable, fruit and yard waste. The organic fraction of source-sorted household waste. Organic residual fraction after mechanical separation of integral collected household waste
	Agricultural	Crops residues Undiluted manures
Waste slurries	Domestic	Primary and secondary sewage sludge
	Agricultural	Liquid manure
	Industrial	Slaughterhouses and meat-processing Fish processing
Wastewater	Domestic	Sewage, Black Water Sewage
	Industrial	Diary, sugar, starch, coffee processing, breweries and beverage, distilleries and fermentation, chemical, pulp and paper, fruit and vegetable processing

Table 2.3: Origins of organic waste streams that can be utilized for the production of biogas

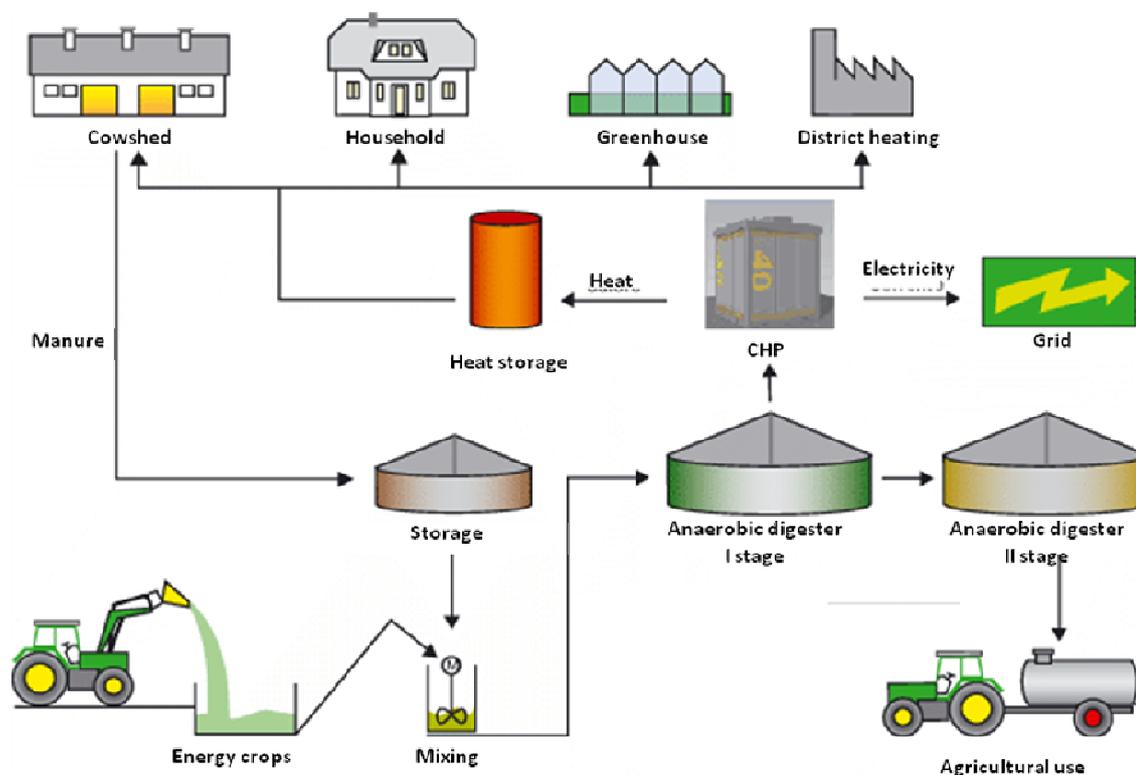


Figure 2.5: Example of Co-digestion process

To minimize transport costs, wastes are often digested on site. However, in Europe there are some cases where centralized co-digestions are widely used. Co-digestion is usually the digestion of manure mixed with other organic waste streams, for example vegetables, fruit and green waste or energy crops.

Industrial wastewaters, which contain high concentrations of organic matter are attractive waste streams for AD. Effluents from the food and beverage industries contain the highest concentration of organic compounds; anaerobic wastewater treatment is widely applied in the industry as well as in the pulp and paper industry.

2.2.4 Anaerobic Digestion Technologies

The AD technologies can be divided mainly into two categories: dry fermentation systems and wet fermentations systems.

ⓐ Wet fermentation

These techniques are used for the treatment of slurries and organic solid waste and require a low solid content, so in some cases the solid waste streams have to be diluted with recycled process water. The continuous stirred tank reactor (CSTR) is the most used reactor type to digest low solid waste streams. It is used for the anaerobic stabilization of sewage slurries produced in wastewater treatment plants and for the treatment of the piggery waste.

ⓑ Dry fermentation

These techniques are used when the fermenting mass has a solid content of more than 20%. Therefore, dry AD digesters are smaller in size, require less process water and require less heating compared to wet fermentation systems. However, due to the high viscosity of the waste streams transport and handling requires special equipment. In addition, the dry fermentation systems are plug-flow reactors, contrary to wet systems where complete mix reactors are usually used. Different reactor configurations were specifically developed for the digestion of the organic fraction of municipal solid waste, where some pre- and post-treatment steps are necessary.

2.2.5 Products of Anaerobic Digestion

④ Biogas

Biogas consists mainly of methane (CH₄) and carbon dioxide (CO₂), with smaller amounts of water vapor and trace amounts of hydrogen sulfide (H₂S), and other impurities.

Biogas can be used to produce power in equipment designed for natural gas fueling but provisions must be made to account for the unique characteristics of biogas.

These include:

- Lower calorific value – The calorific value of biogas is generally 6,5 kWh/Nm³. By comparison, natural gas calorific value is typically near 10 kWh/Nm³. Many power generation equipment manufacturers offer optional systems that can be fueled with biogas.
- Saturated with water – Biogas production is a wet process; raw biogas is saturated with water vapor. The presence of liquid water in the fuel gas, carried over or condensed, can result in unsteady fuel supply, can damage compression and power generation equipment, and can promote corrosion of fuel handling equipment.
- Contamination by reduced sulphur compounds – The primary reduced sulphur compound of concern is hydrogen sulphide (H₂S) which may be present in biogas at concentrations up to several thousand parts per million by volume. When in contact with condensed water, H₂S can be corrosive to gas handling equipment materials. Additionally, combustion of H₂S leads to sulfur dioxide emissions, which have harmful environmental effects. Removing H₂S as soon as possible is recommended to protect downstream equipment, increase safety, and enable possible utilization of more efficient technologies such as micro-turbines and fuel cells.

Digestate

Anaerobic digestion draws carbon, hydrogen and oxygen from the substrate. Essential plants nutrients (N, P and K) remain largely in the residue (digestate). The digestate from a wet fermentation system can be dewatered into a solid and a liquid fraction. Most of the phosphorous will then end up in the solid fraction and most of the ammonia-nitrogen will end up in the liquid phase. In addition, the digestate contains bulky organic matter, more than compost derived from aerobic degradation. Therefore, digestate is suitable as fertilizer as a soil conditioner, after a composting process. The quality of the digestate depends on the quality of the feedstock . Impurities like heavy metals and persistent organic contaminants will remain in the digestate.

2.2.6 Why Anaerobic Digestion?

Anaerobic digestion can be regarded as an energy-efficient technology for the mineralization of organic compounds in waste streams, as it result in the production of energy-rich compounds (biogas). There is a tendency towards centralization of plants in very large scale facilities to reduce costs and increase earnings. With the recent opening of the energy market, there is an incentive to develop alternative, low cost and on site electricity production technologies in an environmental friendly way. Thus, anaerobic conversion of organic wastes gets a facelift from “waste processing” into “energy production”. This allows upgraded anaerobic digestion plants to be integrated in the energy cycle and thus contribute to sustainable development both in rural and industrialised areas.

During the year 2007 the primary energy production of biogas in European Union was 5,9 Mtoe, representing a 20,5% increase with respect to 2006.

Of these, 887 ktoe were obtained from treatment of sewage sludge wastewater and 2108 ktoe were produced in decentralized agricultural plants, organic fraction of municipal solid waste plants, and centralized codigestion

In Europe, Germany is the most prolific producer of biogas. At the end of 2007, approximately 3750 biogas units were in service, 250 more than in 2006, principally connected to small farm units providing Combined Heat and Power

(CHP). However, the rate of growth of its production units has decreased markedly in relation to 2006, a year in which around 800 units were installed.

Considering together landfill gas and biogas, the gross electricity production is growing very strongly in European Union: 18% with respect to 2006, for a total of 19,9 TWh in 2006, divided in 8,3 TWh from electricity plants and 11,64 TWh from cogeneration plants.

In Italy, with respect to 2007, the gross electricity production from biogas is 1,400 GWhe: 1,204 GWhe from landfill, 9 GWhe from sewage sludge, 53,3 GWhe from manure and 137,7 GWhe from agricultural residues.

During the year 2009, the Italian biomass database has been updated, taking into account 2007 as reference year. This project, called “*Atlante delle Biomasse*”, has been part of an ambitious Research Project under the Agreement between ENEA (Italian National Agency for New Technologies, Energy and Sustainable Economic Development) and MSE (Italian Ministry of Economic Development), concerning the evaluation of the biomass potential for Italy.

Within this project the potential of biogas production from manure (bovine and swine), sewage sludge from wastewater treatment plants and organic fraction of municipal solid waste has been estimated.

The “Maximum Potential” (MP), defined taking into account technical and economical evaluations for each biomass category, is about 2,700 MNm³/a.

The “Real Potential” (RP), defined taking into account technical and economical evaluations for each biomass category, is about 910 MNm³/a.

Considering this two cases, some calculations has been implemented.

It's relevant to underline that this two values include also the biomass that is currently treated and from which the biogas is produced and used in CHP plants.

The calculation presented below consider the overall potential for both cases.

According to RP value, the gross electricity production potentially producible with three different CHP systems could be in the range between 1,900 and 2,900 GWhe, with 1 - 1.5 Mton of avoided CO₂ (Table 2.4).

This values can be improved considering the MP value: in this case the gross electricity production potentially producible with three different CHP systems could be in the range between 5,700 and 8,700 GWhe, with 3 - 4.6 Mton of avoided CO₂ (Table 2.5).

“Real Potential” case	Internal Combustion Engine η_e 38% η_{th} 40%	Gas Turbine η_e 33 % η_{th} 51%	Molten Carbonate Fuel Cell η_e 50% η_{th} 40%
Electricity produced (GWh _e /a)	2,212	1,917	2,920
Heat produced (GWh _{th} /a)	2,360	2,979	2,360
% of Italian Electricity Demand (318,952 GWhe)	0.6%	0.69%	0.92%
Avoided ktoe	414	359	546
Avoided CO ₂ (ton)	1,175	1,018	1,551

Table 2.4: Energetic evaluation considering the “Real Potential” for the biogas production, Italy 2007

“Real Potential” case	Internal Combustion Engine η_e 38% η_{th} 40%	Gas Turbine η_e 33 % η_{th} 51%	Molten Carbonate Fuel Cell η_e 50% η_{th} 40%
Electricity produced (GWh _e /a)	6,599	5,719	8,711
Heat produced (GWh _{th} /a)	7,039	8,887	7,039
% of Italian Electricity Demand (318,952 GWhe)	2%	1.8%	2.7%
Avoided ktoe	1,234	1,069	1,629
Avoided CO ₂ (ton)	3,504	3,037	4,625

Table 2.5: Energetic evaluation considering the “Maximum Potential” for the biogas production, Italy 2007

2.3 Landfill

A landfill is a site for the disposal of waste materials by burial and is the oldest form of waste treatment. Historically, landfills have been the most common methods of organised waste disposal and remain so in many places around the world.

Municipal solid waste contains significant portions of organic materials that produce a variety of gaseous products when dumped, compacted, and covered in landfills. Psychrophilic anaerobic bacteria thrive in the oxygen-free environment of a sealed landfill, resulting in the decomposition of the organic materials and the production of (primarily) carbon dioxide and methane. Carbon dioxide may leach out of the landfill because it is soluble in water. Methane, on the other hand, which is less soluble in water and lighter than air, will migrate out of the landfill.

Landfill gas is produced from decomposition under anaerobic conditions of the organic fraction of waste accumulated on dumping sites. Extraction of this gas from landfill sites takes place through the drilling of vertical wells which are capped by a collection system.

Anaerobic bacteria thrive in the oxygen-free environment of the dumping site, resulting in the decomposition of the organic materials and the production of primarily carbon dioxide and methane.

Carbon dioxide is likely to leach out of the landfill because it is soluble in water. Methane, on the other hand, which is less soluble in water and lighter than air, is likely to migrate out of the landfill. Collecting landfill gas is a necessary step to avoid it escaping to the atmosphere: due to the high methane content, this gas has a global warming effect 20 times stronger than CO₂. Usually, landfill gas energy facilities capture the methane and combust it for energy, thereby also preventing its emission to the atmosphere.

During the year 2007 the primary energy production of landfill gas in the European Union was 2,905 Mtoe.

2.3.1 Landfill Gas

Landfill gas consists of 40-45% of CH₄, 35-50% CO₂, smaller amounts of hydrogen sulphide and ammonia. The trace compounds as chlorine content can vary significantly. Landfill gas is usually rich in siloxanes.

The landfill gas production is generally estimated by applying literature models or monitoring a real dumping site.

The landfill gas yield depends on degradation conditions inside the dumping site and on time expired, see Figure 2.6. It is thus not possible to give standard values.

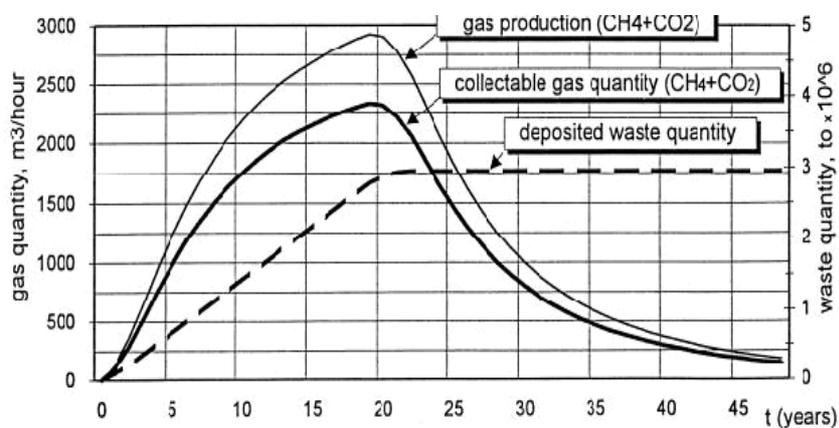


Figure 2.6: Typical trend of landfill gas production

The principal characteristics are:

- Lower calorific value – The calorific value of biogas is generally 6,5 kWh/Nm³. By comparison, natural gas calorific value is typically near 10 kWh/Nm³.
- Contains siloxanes – Siloxanes (volatile silicon compounds) are generally present in landfill gas and wastewater treatment plant sludge digester gas in concentrations of 10 ppmv or less. Siloxanes are converted to solid silica in flames. The solid silica may accumulate on surfaces inside power generation equipment, may erode parts exposed to high velocity gas streams, and may be a culprit in premature deactivation of exhaust catalysts used to control NO_x, CO, and unburned hydrocarbons. Siloxanes and silica may also be a culprit in premature deactivation of catalytic surfaces in fuel cells.

- Contains halogenated volatile organic compounds (VOC)– Landfill gas may contain halogenated hydrocarbons, generally from discarded refrigerants, in concentrations up to 10 parts per million by volume. Halogenated VOCs are converted to hydrogen chloride and hydrogen fluoride in flames. These compounds cause electrolyte loss in molten carbonate fuel cells and are suspected in premature deactivation of catalytic surfaces in fuel cells. They are generally not present in sufficient concentrations to cause adverse effects on combustion engines.

Concerning both biogas (ADG) and landfill gas (LFG), various types of engines are used to produce power. The most widely used are internal combustion engines. Micro-turbines are a more recent option that has gained popularity primarily due to their small footprint, modular form, and ability to run economically in small applications. Larger combustion turbines, such as those that power natural gas-fueled gas-turbine power plants, are available for biogas-fueling, but their deployment is rare due to their large size in comparison with the biogas resource at a single site. Emerging technologies include Stirling engines, and fuel cells.

2.4 Gasification

Gasification is the thermal decomposition of ground or pelletized solid fuel to a combustible gas, rich in carbon monoxide and hydrogen. By using a limited, sub-stoichiometric amount of oxygen in the thermal reaction, oxidation will be partial, thereby generating the heat required for the decomposition but maintaining abundant calorific value in the product gas.

Moisture content of freshly cut biomass is usually 30-60%. Fed biomass for fuel conversion is maintained at 10-20%, which means a drying step is usually necessary before feeding it into the reactor.

The gasification is partial combustion of solid fuel (biomass or waste) and takes place at temperatures of about 1000°C. The reactor is called gasifier.

The combustion products from complete combustion of biomass generally contain nitrogen, water vapor, carbon dioxide and surplus of oxygen. However in gasification where there is a surplus of solid fuel (incomplete combustion) the products of combustion are combustible gases like carbon monoxide (CO), Hydrogen (H₂) and traces of methane and non-useful products like tar and dust. The production of these gases is by reaction of water vapor and carbon dioxide through a glowing layer of charcoal. Thus the key to gasifier design is to create conditions such that a) biomass is reduced to charcoal and, b) charcoal is converted at suitable temperature to produce CO and H₂.

2.4.1 Types of Gasifiers

Since there is an interaction of air or oxygen and biomass or waste in the gasifier, they are classified according to the way air or oxygen is introduced in it. There are three types of gasifiers (Figure 2.7); Downdraft, Updraft and Crossdraft.

And as the classification implies updraft gasifier has air passing through the biomass from bottom and the combustible gases come out from the top of the gasifier. Similarly in the downdraft gasifier the air is passed from the tuyers in the downdraft direction.

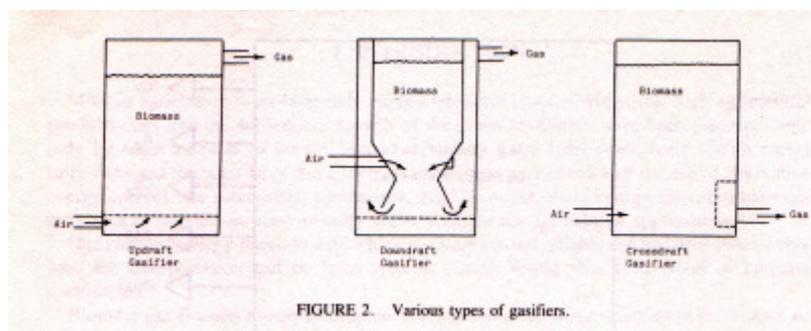


Figure 2.7: Types of gasifiers

With slight variation almost all the gasifiers fall in the above categories.

The choice of one type of gasifier over other is dictated by the fuel, its final available form, its size, moisture content and ash content. Table 2.3 lists therefore, the advantages and disadvantages generally found for various classes of gasifiers.

Gasifier Type	Advantages	Disadvantages
Updraft	<ul style="list-style-type: none"> • Small pressure drop • Good thermal efficiency • Little tendency towards slag formation 	<ul style="list-style-type: none"> • Great sensitivity to tar and moisture content of fuel • Relatively long time required for start up of IC engine • Poor reaction capability with heavy gas load
Downdraft	<ul style="list-style-type: none"> • Flexible adaption of gas production to load • Low sensitivity to charcoal dust and tar content of fuel 	<ul style="list-style-type: none"> • Design tends to be tall • Not feasible for very small particle size of fuel
Crossdraft	<ul style="list-style-type: none"> • Short design height • Very fast response time to load • Flexible gas production 	<ul style="list-style-type: none"> • Very high sensitivity to slag formation • High pressure drop

Table 2.6: Advantages and disadvantages of various gasifiers [15]

The gasifier concept determines the exact moisture constraints, but also system optimization has a considerable influence on what the ideal moisture content of the raw fuel should be.

A second important factor in gasifier operation is the fluidizing medium, which can be air, oxygen or steam. Air-blown gasifiers have the obvious advantage of using a medium which is available in abundance, but the large component of inert nitrogen can be cumbersome to the reactions. Using pure or diluted oxygen avoids this problem, but since a minimum amount of gas flow is required to fluidize the reactor bed, exaggerated oxidation or even combustion could occur, nullifying the gasifying process. Finally, using steam creates the extra difficulty of having to generate it, and the heat necessary for the gasification process is not supplied directly by the partial oxidation of the feedstock as it happens when air or oxygen is used. Therefore, an external heat supply is required, which can be provided by the combustion of recirculated syngas or of the char, residue of the gasification process, in a separate combustion chamber. Auxiliary fuel can be used if necessary. Steam gasification produces cleaner syngas with higher heating value, and richer in hydrogen than the other methods, without the diluting effects of nitrogen in air or the need of an expensive oxygen generation plant. For these reasons, it is probably the most suitable form of gasification for fuel cell applications.

At the end of the gasification stage some reduction of tars and char (respectively complex hydrocarbon compounds and carbonaceous residues, accounting for up to 10% of the syngas HHV, but not utilisable in fuel cells) can occur, yielding extra production of H₂ and CO. The temperature has to be sufficiently high for this endothermic reaction to take place (T≈1200°C).

After the gasifier, the produced syngas is still rich in contaminants, of which it has to be relieved before it can be transferred to the cogeneration system (as MCFC).

2.4.2 Syngas Characteristics

Syngas is the gas product from the gasification process, rich in carbon monoxide and hydrogen. Characteristics and yield depend on feedstock, type of gasifier and process conditions.

Almost any carbonaceous or biomass can be gasified under experimental or laboratory conditions. However the real test for a good gasifier is not whether a combustible gas can be generated by burning a biomass fuel with 20-40% stoichiometric air but that a reliable gas producer can be made which can also be economically attractive to the customer. Towards this goal the fuel characteristics have to be evaluated and fuel processing done.

Many a gasifier manufacturers claim that a gasifier is available which can gasify any fuel. There is no such thing as a universal gasifier. A gasifier is very fuel specific and it is tailored around a fuel rather than the other way round.

Thus a gasifier fuel (SNG) can be classified as good or bad according to the following parameters:

- ④ Energy content of the fuel
- ④ Bulk density
- ④ Moisture content
- ④ Dust content
- ④ Tar content
- ④ Ash and slagging characteristic

2.4.3 Why Gasification?

Excellent survey of current status of gasification technology has been carried out by several authors. They have reviewed the status in both developed and developing countries. However there is confusion regarding the number of manufacturers of gasification equipment. Quite a number of these manufacturers have just produced few units, which are still in experimental stages.

In Europe there are many manufacturers especially in Sweden, France, West Germany and Netherlands who are engaged in manufacturing gasification systems for stationery applications. Most of market for these European manufacturers has been in developing countries.

Most preferred fuels for gasification have been charcoal and wood. However biomass residues are the most appropriate fuels for on-farm systems and offer the greatest challenge to researchers and gasification system manufacturers, but very limited experience has been gained in gasification of biomass residues.

Most extensively used and researched systems have been based on downdraft gasification. However it appears that for fuels with high ash content fluidized bed combustion may offer a solution.

At present no reliable and economically feasible systems exist.

The biggest challenge in gasification systems lies in developing reliable and economically cheap cooling and cleaning trains.

Future applications like methanol production, using producer gas in fuel cell and small scale irrigation systems for developing countries offer the greatest potentialities.

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III – Biogas Clean up

3.1 Introduction

The role of gas clean-up is to abate harmful contaminants (like particulate, ammonia, hydrogen-sulphide, halogenated hydrocarbons, siloxanes) in the fuel gas and thus to assure a higher degree of operational effectiveness and longevity of the downstream fuel-converting equipment, regardless of the technology utilised.

As already mentioned, biogas composition depends heavily on the feedstock, but mainly consists of methane and carbon dioxide, with smaller amounts (ppm) of hydrogen sulphide and ammonia. Trace amounts of organic sulphur compounds, halogenated hydrocarbons, hydrogen, nitrogen, carbon monoxide, and oxygen are also occasionally present. Usually, the mixed gas is saturated with water vapor and may contain dust particles and siloxanes.

In Table 3.1 are shown some biogas characteristics, compared to natural gas.

Component	Natural Gas	Wastewater Sludge	Landfill Gas	Animal Waste	Industrial
Methane	93% min	55-70%	45-60%	50-70%	50-75%
Carbon Dioxide (%vol)	1-1.5%	30-45%	35-40%	30-50%	a.s.
Nitrogen (%vol)	1-1.5%	n.d.a.	0-3%	0-3%	a.s.
H ₂ S and other sulphur compounds (ppmv)	<20	150-3,000	10-200	up to 5,000	up to 3,000
Siloxanes (ppmv)	none	2-15	0.1-3.5	n.e.	a.s.
Halogenated organics (%vol)		6.5	5-70	n.d.a.	a.s.
Non-methane organics (% dry weight)	15 % max	n.d.a.	0-25%	n.d.a.	a.s.
Volatiles organics (% dry weight)		n.d.a.	0-0.1%	n.d.a.	a.s.
Other organics (% vol)	2% max	Gasoline traces	no data available	n.d.a.	n.d.a.
Hydrogen (%vol)		n.d.a.	Trace to >1%		a.s.

Oxygen (%vol)	0.2 % max	None	0-2%	n.d.a.	a.s.
Carbon Monoxide (%vol)		None	0-0.2%	n.d.a.	a.s.
Humidity		100%	100%	100%	a.s.

a.s.: application-specific

n.d.a.: no data available

n.e.: none expected

Table 3.1: Typical biogas characteristics – compared to commercial natural gas [1]

Principal gas phase impurities that may be present are listed in Table 3.2 below. Other constituents that may be problematic include water or other condensates, and particulate matter. Hydrocarbons, such as methane, are the desired product gases.

Principal Gas Phase Impurities
Hydrogen sulphide
Carbon dioxide
Water vapor
Sulphur dioxide
Nitrogen oxides
Volatile organic compounds (VOC)
Volatile chlorine compounds (HCl, Cl ₂)
Volatile fluorine compounds (HF, SiF ₄)
Basic nitrogen compounds
Carbon monoxide
Carbonyl sulphide
Carbon disulphide
Organic sulphur compounds
Hydrogen cyanide

Table 3.2: Principal gas phase impurities [1]

The MCFC can operate on a variety of different, non-conventional fuels, but the poisoning effect of some substances contained in these needs to be tackled and resolved. Essentially, these species have a poisoning effect on the catalytic properties of the cell electrodes leading to detrimental performance and durability, although damage can be brought to all peripheral equipment, such as sealants, reformer catalysts, metallic components, as well. The crucial link between the two technologies (non-conventional fuel production and MCFC), therefore, is formed by the gas clean-up step.

The characteristics of the H₂S will be illustrated below, laying more emphasis on due to its importance in terms of quantity and harmful effect, both on the fuel cell electrodes as on the reforming catalysts. Considering the crucial link between biofuel production and application in a MCFC, also the most common H₂S removal processes will be reviewed.

Moreover, a brief overview will be given of the siloxanes characteristics, considered other contaminants with a detrimental effect on the MCFC, but not yet well defined.

3.2 H₂S

Sulphur in the waste streams from which the biogas is produced is generally converted to hydrogen sulphide (H₂S) with minor amounts of organic sulphur compounds. High concentrations of H₂S are toxic. In lower concentrations, H₂S is a strong odorant as are the organic sulphur compounds. Indeed, capture and destruction of these compounds is often the primary reason for installing animal manure digesters. Hydrogen sulphide is poisonous, odorous, and highly corrosive. Some characteristics of H₂S are described in Table 3.3. Because of these characteristics, hydrogen sulphide removal is usually performed directly at the gas-production site.

Physical, Chemical and Safety Characteristics of H₂S	
Molecular weight	34.08
Specific gravity (relative to air)	1.192
Auto ignition temperature	250°C
Explosive range air	4.5-5.5%
Odor threshold	0.47 ppb
8-hour time weighted average (TWA) (OSHA)	10 ppm
15-minute short term exposure limit (STEL) (OSHA)	15 ppm
Immediate dangerous to life of health (IDLH) (OSHA)	300 ppm

Table 3.3: Physical, chemical and safety characteristics of H₂S [1]

3.3 Siloxanes

Siloxanes are a family of man-made silicon-containing compounds derived from break-down of silicone found in personal care and industrial products. They are commonly encountered in biogas from wastewater treatment plants and landfills. They are hydrophobic (having little solubility in water) but are miscible in most oils. Siloxanes have the unique property of being fairly volatile despite their high molecular weight, yet stable against degradation except when burned. They are converted to solid silica in flames which deposits on surfaces exposed to combustion products. Over time these deposits can build up and cause damage to turbine blades and internal engine parts. Silica particles may also erode components in nozzles and other high speed gas paths in turbines.

Over the past 20 years there has periodically been a desire to employ exhaust gas catalysts to reduce NO_x, CO, and unburned hydrocarbons to levels comparable to natural gas-fuelled power generators. The general experience has been, however, that these various catalysts have failed after a few days of operation and in some cases only hours of operation. The silica resulting from combustion of the siloxanes has been supposed to be a primary cause of the failures.

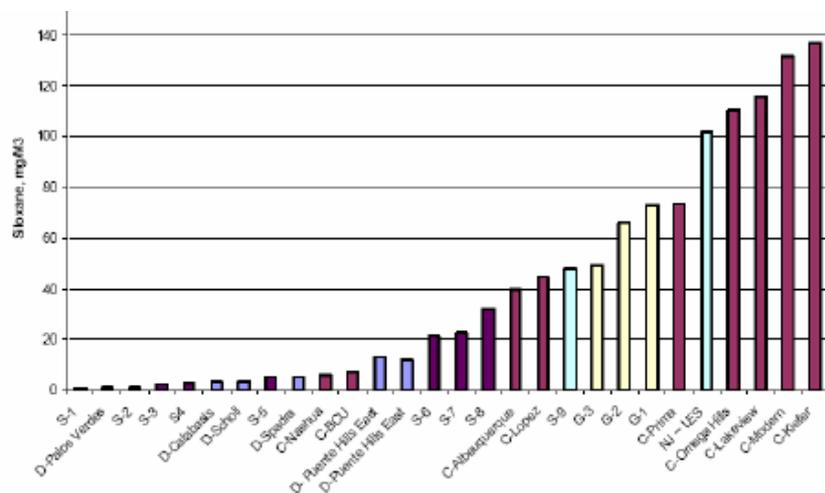
Common levels of total siloxanes can vary considerably, depending on feed to the wastewater treatment plant or landfill, but are generally found in the range of 2 to 5 ppmv. Siloxanes are not usually found in animal or industrial waste.

Figure 3-1 provides siloxane data from twenty-eight landfills.

The landfills represented cover open and closed landfills, landfills in arid climates and wet climates, and landfills containing relatively old and new waste.

The data has been normalized to 50% methane.

Figure 3.1: Siloxanes in landfill gas



Common volatile siloxanes are listed in Table 3-4.

Name	Formula	MW	V.P. mmHg 77°F	Abb.	B.P. °F	W.S. (mg/l) 25°C
Hexamethylcyclotrisiloxane	$C_{12}H_{18}O_3Si_3$	222	10	D ₃	275	1.56
Octamethylcyclotetrasiloxane	$C_8H_{24}O_4Si_4$	297	1.3	D ₄	348	0.056
Decamethylcyclopentasiloxane	$C_{10}H_{30}O_5Si_5$	371	0.4	D ₅	412	0.017
Dodecamethylcyclohexasiloxane	$C_{12}H_{36}O_6Si_6$	445	0.02	D ₆	473	0.005
Hexamethyldisiloxane	$C_6H_{16}O_2Si_2$	162	31	L ₂ , MM	224	0.93
Octamethyltrisiloxane	$C_8H_{24}O_3Si_3$	236	3.9	L ₃ , MDM		0.035
Decamethyltetrasiloxane	$C_{10}H_{30}O_4Si_4$	310	0.55	L ₄ , MD ₂ M		
Dodecamethylpentasiloxane	$C_{12}H_{36}O_5Si_5$	384	0.07	L ₅ , MD ₃ M		

V.P.: vapor pressure

Abb.: abbreviations

B.P.: boiling point

W.S.: water solubility

Table 3.4: Selected cyclic and linear organosiloxane properties [1]

Due to the length of the names of the various siloxanes, abbreviations are commonly used to identify the compounds. Siloxanes that are cyclic in structure have a single abbreviation of D. Siloxanes that have a linear structure have two abbreviations using either an L or M nomenclature. Table 3-4 also identifies the molecular weight, vapour pressure, boiling point, chemical formula, and water solubility of these compounds.

A few generalizations can be made about the data:

- Landfills with older average waste ages generally have lower siloxane levels. It may be that this is due to the gradual exhaustion of siloxane over time or it may be because there was less siloxane in the waste to begin with since the use of siloxane has increased in recent years. Active landfills generally have higher siloxane levels than closed landfills. This finding may simply be due to their younger age.

- D3, D4, D5, L2 and L3 are the only siloxanes generally observed above detection limits at landfills. On an average basis, D4 is the largest contributor to total siloxane (about 60% of total), followed by L2, D5 and L3 in that order.
- In general, landfill gas contains L2 and L3 and digester gas does not. One theory explaining this difference between the two biogases is the relative solubility. L2 is much more water-soluble than D4 and D5. L3 is more water-soluble than D5 and is comparable to D4.

3.4 Quality Requirements for Biogas Utilization

Biogas can be used for all applications designed for natural gas, assuming sufficient purification. On-site, stationary biogas applications generally have fewer gas processing requirements. A summary of potential biogas utilization technologies and their gas processing requirements are given in Table 3.5.

	Heating Boilers	Internal Combustion Engines	Microturbines	Stirling Engines	PEM	PA FC	MC FC	SO FC	NG Upgrade
H ₂ S (ppmv)	<1000	<100	up to 70,000	<1000	remove	<20	<10	<1	<4
Siloxanes (ppmv)		remove	remove	0.42 as D ₄		<1	<1	<1	remove
Halides (ppmv as Cl)		60-491	200	232 as HCl		<4	<1	<1	
CO					<10	<10			
CH ₄									<95%
CO ₂									<2%

Table 3.5: Gas requirements [1]

Technologies such as boilers and Stirling engines have the least stringent gas processing requirements because of their external combustion configurations. Internal combustion engines and micro-turbines are the next most tolerant to contaminants. Fuel cells are generally less tolerant to contaminants due to the potential for catalytic poisoning. Upgrading to natural-gas quality usually requires

expensive and complex processing and must be done when injection into a natural-gas pipeline or production of vehicle fuel is desired.

For technical and operational reasons, the estimated required degree of fuel gas purity in terms of H₂S differs largely between internal combustion engines (<1000 ppm), turbines (<10 000 ppm) and high-temperature fuel cells like the MCFC (<1 ppm). In considering these purity requirements however, it must be remembered that emission to the atmosphere is the governing limitation, for environmental reasons. Therefore, extensive clean-up (depending on local emissions regulations) will always have to be carried out before the final exhausted gases are expelled to the atmosphere. In the case of combustion-based technologies this means that the flue gas has to undergo thorough cleaning of SO_x, the oxidised products of sulphur compounds in the fuel. For a fuel cell, clean-up has to be carried out before oxidation of the fuel because of the low tolerance of the electrocatalysts to the contaminants: this has the advantage that lower mass flows are involved in the clean-up process because the oxidant stream is not superimposed. On the other hand the sulphurous compounds are more heterogeneous at this stage.

Regarding in particular the MCFC, it should be mentioned that apart from the intolerance of the anode to the impurities mentioned in Table 3.6, in the event of anode off-gas recirculation to provide CO₂ to the oxidant stream, also the cathode has to be made resistant in the same degree to more or less the same harmful species. Generally, the recirculated gas goes through catalytic combustion prior to being fed to the cathode, so that mainly SO₂ and NO_x are found at the cathode inlet. Studies show that NO_x has no negative effects on cathode performance in concentrations up to 50 ppm. SO₂ is acceptable in the oxidant only up to 1 ppm.

Contaminant	Tolerance	Effects	Cleaning method
Sulphides: H ₂ S, COS, CS ₂	0.5-1 ppm	Electrode deactivation Reaction w electrolyte to form SO ₂ .	Methanol washing (T < -50°C) Carbon beds (T < 0°C) Scrubber (T < 100°C) ZnO/CuO adsorption (T < 300°C) High-T CeO ads. (T > 700°C)
Halides: HCl, HF	0.1-1 ppm	Corrosion Reaction w electrolyte	Alumina or bicarbonate Activated carbon
Siloxanes: HDMS, D5	10-100 ppm	Silicate deposits	Ice absorption (T = - 30°C) Graphite sieves
NH ₃	1-3%	NB: Fuel at low conc. Reaction w electrolyte to form NO _x .	Catalytic cracking Bag filter as NH ₄ Cl
Particulates	10-100 ppm	Deposition, plugging	Cyclone + bag/ceramic filter Electrostatic precipitator
Tars	2000 ppm	C deposition	Catalytic cracking T > 1000°C
Heavy metals: As, Pb, Zn, Cd, Hg	1-20 ppm	Deposition Reaction w electrolyte	Bag/ceramic filter Electrostatic precipitator

Table 3.6: Contaminants and their tolerance limits for MCFCs [11, 12, 13, 14]

The tolerance levels mentioned in Table 3.6 are indicative and the extent of their harmful effect may depend on the partial pressure of other species in the gas (e.g. hydrogen), the current density at which the fuel cell is operated and the fuel utilization factor. Elaborate investigations into the endurance to contaminants are few, since experimentation of these effects is necessarily destructive and of long duration, but an accurate knowledge of the conditions which are deleterious would facilitate safe operation of the fuel cell.

Nevertheless, the tolerance levels should be increased, especially of sulphides. This is both because of the drastic effect of sulphur-containing compounds, which is irreversible upon enduring exposure to concentrations of more than about 10

ppm, and because of the significant content of sulphur in many organic substances, especially sewage sludge, for example.

3.5 H₂S Removal Methods

There are several methods to remove harmful impurities, which can be classified into two groups: physical-chemical (catalytic purification, adsorption, scrubbing, membrane separation, condensation) and biotechnological methods (biofilters, bioscrubbers, biotrickling filters).

Most of these biotechnological methods are cheaper than the physical-chemical ones having the same or even higher efficiency (99%) than these (though they cannot handle inorganic contaminants like siloxanes or particulates).

Moreover, no chemicals need to be added, energy requirements are lower and there is no formation of secondary contaminant streams that need to be specifically treated. The main problem of these systems is their slow reaction under load fluctuations, which poses the risk of contaminant breakthrough.

Regarding the H₂S removal, its fraction has to be dramatically reduced from 300-4000 ppm (average concentration in biogas) to the lower tolerance limit (0.5÷1 ppm), to avoid deactivation of catalysts and loss of electrolyte in MCFC.

H₂S is typically the most problematic contaminant in biogas because it is toxic and corrosive to most equipment and, when burned, results in sulphur dioxide emissions which contribute to acid rain. Removing H₂S as soon as possible is recommended to protect downstream equipment and increase safety. Hydrogen sulphide removal is not unique to biogas systems; it is a common contaminant in natural gas and other gas streams. Thus, there is a large market for hydrogen sulphide removal equipment for sweetening coke oven gas and natural gas and many technologies have been developed.

As long as the chemical/petrochemical process industries have existed, different desulphurisation processes have been backstage their progress. In some cases biological processes (together with the digestion phase) are provided. Catalytic or oxidative processes can be used. Adsorption processes, exploiting various type of adsorbents, are also widespread. New desulphurization processes and new economical, regenerable, with high selectivity materials are under investigation.

The clean up technologies can be broadly classified by the ultimate fate of the sulphur as follows:

- ④ Precipitation (from solution) as iron sulphide.
- ④ Dry chemical capture from the gas phase as iron sulphide or zinc sulphide.
- ④ Biological sulphur oxidation to solid sulphur or sulphate.
- ④ Adsorption-desorption with oxidation to solid sulphur.

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IV – MCFC for Decentralized Power Generation

4.1 Introduction

The implementation of biogas biotechnology for the treatment of organic wastes is one of the strategic objectives of important European Union (EU) legislation, namely the EU Landfill of Waste Directive (Council Directive 1999/31/EC of 26 April 1999) (European Union, 1999), in which the pressure for using alternative means of disposal, neither landfills nor incineration, is high.

For this reason, the use of biogas from anaerobic decomposition to produce energy is being developed, and its use in fuel cells is being tested in some applications, as they provide higher generating efficiencies than traditional combustions engines.

The use of biogas produced from local waste as an alternative to landfill disposal is being investigated as a key energy solution for islands and remote rural communities. In this case, the methane produced is reformed to provide hydrogen to power an alkaline fuel cell installation, which operates in Combined Heat and Power (CHP) mode.

Research is being carried out into the use of biogas, produced by anaerobic digestion, as a fuel in Molten Carbonate Fuel Cells.

There has also been some research dealing with the pre-treatment requirements necessary to use biogas in fuel cells; the cleanup system, removal requirements and efficiency are all dependent of the biomass source and the fuel cell type.

The biogas plant and fuel cell system is viewed as an alternative to landfill disposal of local organic waste, but it is recognised that the problem of high cost remains an issue. Hence work to find a cost competitive process continues in order to take best advantage of fuel cells operated on biogas.

4.2 Traditional Technologies using Biogas

The equipment commonly used to convert biogas into power consists of combustion engines (prime movers), which burn the fuel to create shaft work, generators, which convert shaft work to electricity and ancillary equipment to distribute electricity either locally within a facility or to an external power grid.

Figure 4-1 shows a simplified block diagram for a typical waste/biogas-to-electricity system. The biogas can come from a municipal, agricultural, or industrial waste digester, or from a covered landfill.

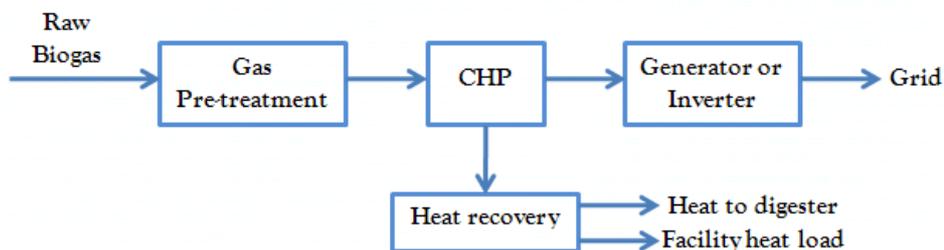


Figure 4.1: Biogas-to-Energy system

For systems that produce biogas using digesters there is usually a need to recover engine heat for digester temperature control. Other applications for recovered heat include facility hot water, or facility space heating using exhaust gases. In most landfill gas applications there is no use for the heat and heat recovery equipment is not commonly employed.

The electricity produced can be routed internally to power the local facility or exported to the local power grid. Facilities vary in their needs for the power produced. A typical waste water treatment plant producing power from a sludge digester may be able to serve up to half of its power needs from digester biogas. Most dairy farms that have installed manure digesters produce enough power to supply the entire farm, with some excess available to export to the power grid. Landfills, on the other hand, have little on-site need for the power, and would export most of that which is produced.

The prime mover is the most basic component of the system. Various types of engines are used to produce power from biogas. The most widely used are internal-combustion, reciprocating engines. Micro-turbines are a more recent option that

has gained popularity primarily due to their small footprint, modular form, and ability to run economically in small applications. Larger combustion turbines, such as those that power natural gas-fuelled gas-turbine power plants, are available for biogas-fuelling, but their deployment in this application is rare due to their large size in comparison with the biogas resource at a single site.

Emerging technologies (with little track record) include Stirling engines, and fuel cells.

4.3 Fuel Cell - General Overview

A fuel cell is a device for directly converting the chemical energy of a fuel into electrical energy in a constant temperature process. In many ways the fuel cell is analogous to a battery, but a battery which is constantly being recharged with fresh reactants.

Because the intermediate steps of producing heat and mechanical work typical of most conventional power generation methods are avoided, fuel cells are not limited by thermodynamic limitations of heat engines such as the Carnot efficiency. In addition, because combustion is avoided, fuel cells produce power with minimal pollutant.

Fuel cells could potentially be used to replace conventional power equipment in many cases. The main applications are likely to be in stationary power generation, transportation, and battery replacement.

Unit cells form the core of a fuel cell. These devices convert the chemical energy contained in a fuel electrochemically into electrical energy. The basic physical structure, or building block, of a fuel cell consists of an electrolyte layer in contact with an anode and a cathode on either side.

A schematic representation of a unit cell with the reactant/product gases and the ion conduction flow directions through the cell is shown in Figure 4.2.

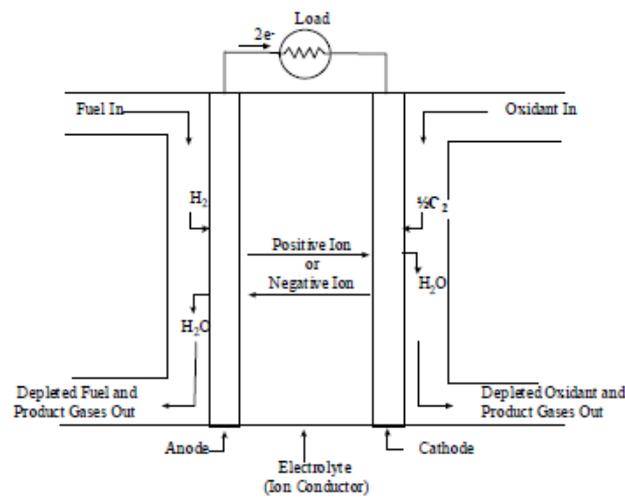


Figure 4.2: Scheme of a fuel cell [1]

In a typical fuel cell, fuel is fed continuously to the anode (negative electrode) and an oxidant (often oxygen from air) is fed continuously to the cathode (positive electrode).

The electrochemical reactions take place at the electrodes to produce an electric current through the electrolyte, while driving a complementary electric current that performs work on the load. Although a fuel cell is similar to a typical battery in many ways, it differs in several respects.

The battery is an energy storage device in which all the energy available is stored within the battery itself (at least the reductant). The battery will cease to produce electrical energy when the chemical reactants are consumed (i.e., discharged). A fuel cell, on the other hand, is an energy conversion device to which fuel and oxidant are supplied continuously. In principle, the fuel cell produces power for as long as fuel is supplied.

Under load a single cell produces about 0.7 Volts, so in order to achieve a useful output power individual cells are connected together in a “stack”. This is achieved using an interconnect or bipolar plate, which joins the anode of one cell to the cathode of the next cell. The interconnect also separates and often distributes the fuel and oxidant.

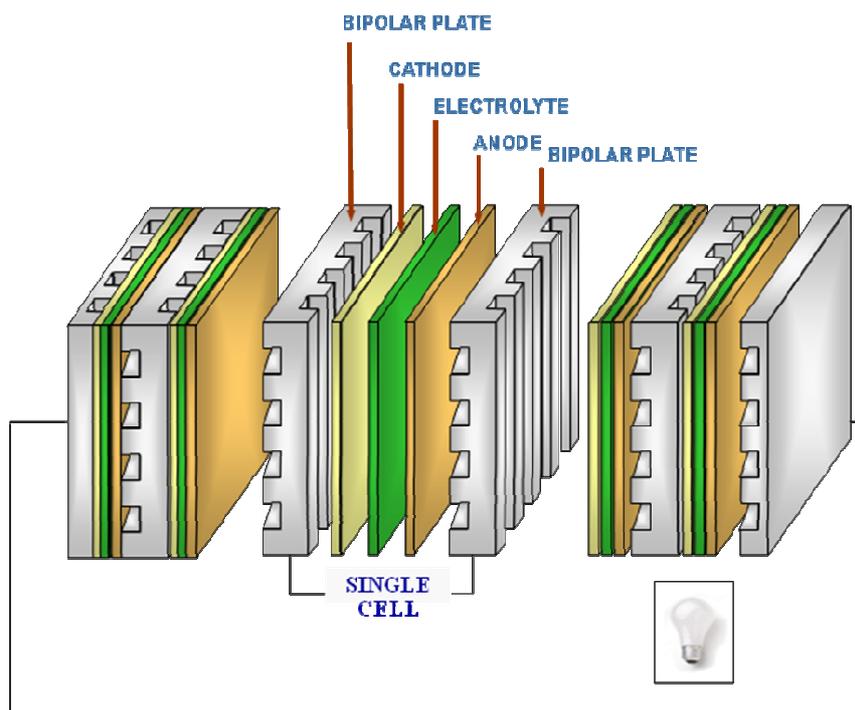


Figure 4.3: Fuel cell stack

The fuel cell differs from conventional heat engine technology (such as the internal combustion engine or the gas turbine), in that it does not rely on raising the temperature of a working fluid such as air in a combustion process.

Fuel cells are classified according to the choice of electrolyte and fuel, which in turn determine the electrode reactions and the type of ions that carry the current across the electrolyte. Though the direct use of conventional fuels in fuel cells would be desirable, most fuel cells under development today use gaseous hydrogen, or a synthesis gas rich in hydrogen, as a fuel. Hydrogen has a high reactivity for anode reactions, and can be produced chemically from a wide range of fossil and renewable fuels, as well as via electrolysis. For similar practical reasons, the most common oxidant is gaseous oxygen, which is readily available from air.

There are five main classes of fuel cells, each with differing characteristics, and differing advantages and disadvantages.

The most common classification of fuel cells is by the type of electrolyte used in the cells and includes 1) polymer electrolyte fuel cell (PEFC), 2) alkaline fuel cell (AFC), 3) phosphoric acid fuel cell (PAFC), 4) molten carbonate fuel cell (MCFC),

and 5) solid oxide fuel cell (SOFC). Broadly, the choice of electrolyte dictates the operating temperature range of the fuel cell. The operating temperature and useful life of a fuel cell dictate the physicochemical and thermo-mechanical properties of materials used in the cell components (i.e., electrodes, electrolyte, interconnect, current collector, etc.). Aqueous electrolytes are limited to temperatures of about 200 °C or lower because of their high vapor pressure and rapid degradation at higher temperatures. The operating temperature also plays an important role in dictating the degree of fuel processing required. In low-temperature fuel cells, all the fuel must be converted to hydrogen prior to entering the fuel cell. In addition, the anode catalyst in low temperature fuel cells (mainly platinum) is strongly poisoned by CO. In high-temperature fuel cells, CO and even CH₄ can be internally converted to hydrogen or even directly oxidized electrochemically. Table 4.1 provides an overview of the key characteristics of the main fuel cell types.

	PEFC	AFC	PAFC	MCFC	SOFC
Electrolyte	Hydrated Polymeric Ion Exchange Membranes	Mobilized or Immobilized Potassium Hydroxide in asbestos matrix	Immobilized Liquid Phosphoric Acid in SiC	Immobilized Liquid Molten Carbonate in LiAlO ₂	Perovskites (Ceramics)
Electrodes	Carbon	Transition metals	Carbon	Nickel and Nickel Oxide	Perovskite and perovskite/metal cement
Catalyst	Platinum	Platinum	Platinum	Electrode material	Electrode material
Interconnet	Carbon or metal	Metal	Graphite	Stainless steel or Nickel	Nickel, ceramic or stell
Operating Temperature	40-80°C	65-220°C	205°C	650°C	600-1000°C
Charge carrier	H ⁺	OH ⁻	H ⁺	CO ³⁻	O ⁻
External Reformer for hydrocarbon fuels	Yes	Yes	Yes	No, for some fuels	No, for some fuels and cell design
External shift	Yes, plus	Yes, plus	Yes	No	No

conversion of CO to hydrogen	purification to remove trace CO	purification to remove CO and CO ₂			
Prime Cell Components	Carbon-based	Carbon-based	Graphite-based	Stainless-based	Ceramic
Product Water Management	Evaporative	Evaporative	Evaporative	Gaseous Product	Gaseous Product
Product Heat Management	Process Gas+Liquid Cooling Medium	Process Gas+Electrolyte Circulation	Process Gas+Liquid Cooling Medium or Steam Generation	Internal Reforming+Process Gass	Internal Reforming +Process Gass

Table 4.1: Summary of major differences of the fuel cell types [1]

The low temperature fuel cells can be distinguished by the following common characteristics:

- ④ They generally incorporate precious metal electrocatalysts to improve performance;
- ④ They exhibit fast dynamic response and short start-up times;
- ④ They are available commercially;
- ④ They require a relatively pure supply of hydrogen as a fuel. This usually means that a fuel processor is required to convert primary fuels such as natural gas.

In contrast, the high temperature fuel cells can be classed as having the following general features:

- ④ Fuel flexibility: they can be operated on a range of hydrocarbon fuels;
- ④ Their increased operating temperature reduces the need for expensive electrocatalysts;
- ④ They can generate useful “waste” heat and are therefore well suited to co-generation applications;
- ④ They exhibit long start-up times and are sensitive to thermal transients;
- ④ They can require expensive and exotic construction materials to withstand the operating temperature, particularly in the balance of plant (piping, heat exchangers, etc.);

- Ⓢ Reliability and durability is a concern, again due to the operating temperature;
- Ⓢ They can be integrated with a gas turbine, offering high efficiency combined cycles;
- Ⓢ They are at the demonstration stage with some cases available commercially.

4.3.1 Non-Conventional Fuels for Fuel Cells

Any type of fuel cell could, in theory, but technological implications of low temperature fuel cells and high temperature fuel cells are different. As low temperature fuel cells, such as polymer electrolyte fuel cell (PEFC), alkaline fuel cell (AFC), phosphoric acid fuel cell (PAFC), require relatively pure hydrogen, the biofuel from waste and biomass needs first to be treated to eliminate impurities and contaminants, and also reformed into usable hydrogen. This involves the use of two additional processes: gas clean-up and fuel reforming. Reformers generally operate at high temperatures (700-950°C) and therefore result in poor thermal integration with low temperature fuel cells. In addition, CO is produced during reforming and PEFCs and PAFCs do not tolerate high levels of CO. Therefore, a separate water-gas shift reactor is needed for PEFCs and PAFCs followed by a CO selective oxidation catalyst in order to reduce the CO content to less than 100ppm.

However, for high temperature fuel cells, namely Molten Carbonate Fuel Cells (MCFCs) and Solid Oxide Fuel Cells (SOFCs), the reforming stage can be avoided as reforming can take place within the fuel cell due to their high operating temperatures. In addition, high temperature fuel cells are believed to be more tolerant to contaminants than low temperature fuel cells.

Regarding the balance of plant, thermal integration of biomass gasification is likely to be better achieved with high temperature fuel cells (MCFC and SOFC) as the temperature of the gasification process (600-800°C) is closer to that of the fuel cell operation. On the other hand, with LFG and ADG the biofuel temperature is low and a gas pre-heater would be required independently of the choice of fuel cell to either enter the fuel reformer (700-950°C) or the high temperature fuel cell (600-1000°C). The possible ways of integrating biofuels into fuel cells are illustrated (in

a simplistic view) in Figure 4.4, highlighting the need for a reformer in low temperature fuel cells. Therefore, as low temperature fuel cells require more technical steps than high temperature fuel cells when run on biofuels, they result in higher investment and operation costs.

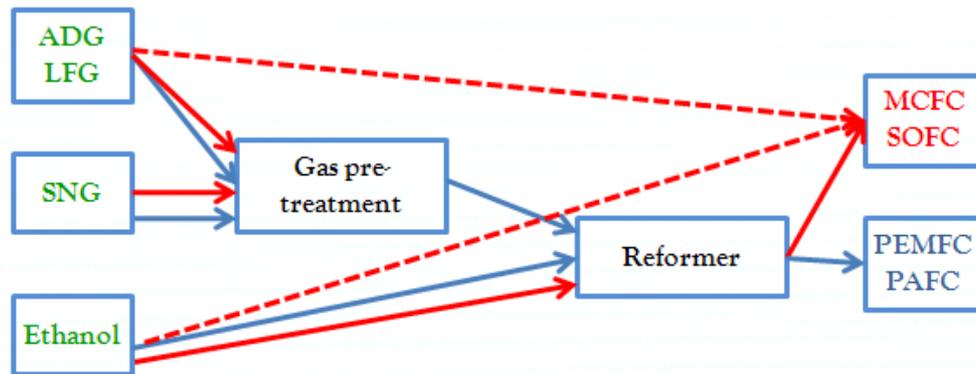


Figure 4.4: Diagram of possible routes from Anaerobic Digestion Gas (ADG), Landfill Gas (LFG), Syngas from gasification (SNG) and Ethanol to **low temperature fuel cells (PEMFCs and PAFCs)** or **high temperature fuel cells (MCFCs and SOFCs)**. Dotted arrows denote path that might be possible but not yet proven [2]

Finally, Table 4.2 summarises the compatibility of PEMFCs, PAFCs, MCFCs and SOFCs with various types of biofuels.

Fuel Source	PEMFC	PAFC	MCFC	SOFC
ADG	~	+	++	++
LFG	~	+	++	++
SNG	~	+	++	++
Ethanol	+	+	++	++

~ Not very compatible
 + Some compatibility
 ++ Strong long-term potential

Table 4.2: Compatibility of four types of biofuels (ADG, LFG, SNG, Ethanol) with four type of fuel cells [2]

4.4 Molten Carbonate Fuel Cell

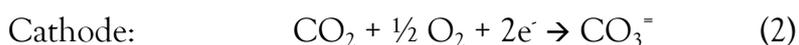
The coupling of Molten Carbonate Fuel Cells to Non-Conventional Fuels has potentially enormous benefits, in terms of highly efficient energy use and low environmental impact, in line with a sustainable concept of energy supply. Combining the useful exploitation of waste flows with clean and high quality power generation is a major promise for the stability of Europe's energy infrastructure.

In this study we are focusing on the utilisation of biogas from anaerobic digestion. Although the composition of biogas may vary considerably – depending on the feedstock composition, process conditions, type of digester, etc. – the produced gas, due to its organic origins, will always contain a high quantity of carbon compounds (CH₄ and CO₂). Low-temperature fuel cells like the PEMFC (Polymer Electrolyte Membrane Fuel Cell) cannot handle these compounds as they require pure hydrogen for operation. High temperature fuel cells like the MCFC can make use of the high-quality excess heat produced to convert methane to hydrogen and CO – both perfectly convertible inside the fuel cell. CO₂ acts as a charge carrier and therefore is also compatible (even necessary) with the MCFC.

Molten Carbonate Fuel Cells are composed of a porous nickel-based anode, a porous nickel-oxide-based cathode and Molten Carbonate salts as electrolyte within a porous lithium aluminate matrix.

At the cathode inlet oxygen reacts electrochemically with carbon dioxide to form Carbonate ions. The ions travel through the electrolyte towards the anode. At the anode inlet hydrogen reacts with the Carbonate ions to form water and carbon dioxide.

The half cell electrochemical reactions are:



The overall cell reaction, with cell standard potential equal to 1.027 V, is thus:



Connecting the cells in series makes it possible to construct a power system of any size, without loss of efficiency in the electrochemical conversion.

Thus, an MCFC system can attain 48-50% electrical efficiency (>90% thermal) at small-to-medium scales (0.1-10 MW) where conventional power trains cannot usually surpass 30% net efficiency. Thus, for equal power production, the MCFC can significantly reduce the necessity of energy sources. In addition, a high efficiency is translated into reduced carbon dioxide emissions.

The typical structure of a single MCFC is schematically illustrated in Figure 4.5.

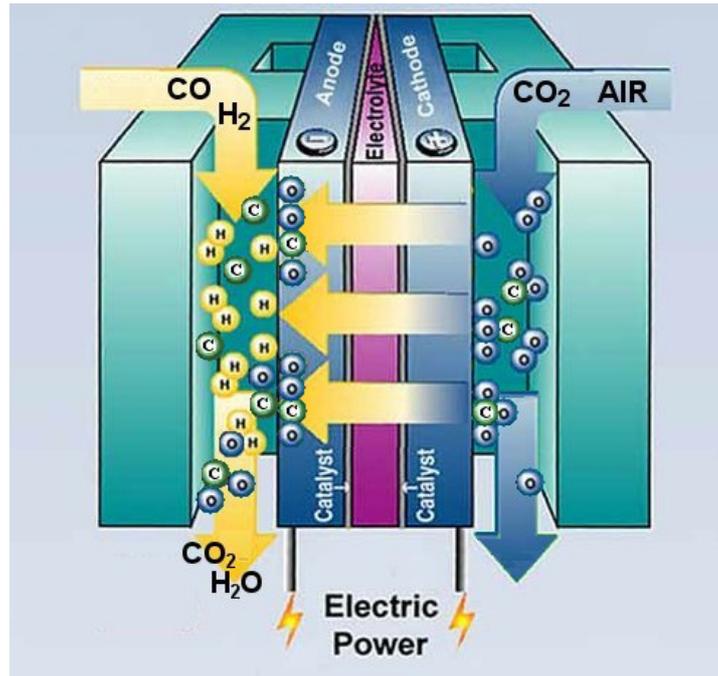
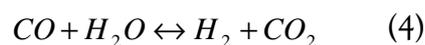


Figure 4.5: Schematic representation of a functioning MCFC

The MCFC operates at about 650°C, thus, differently from low temperature fuel cells, no precious metal is required as the fuel catalyst. Together with production cost saving, the main consequence of this is that carbon monoxide is not a poisoning element, but, on the contrary, can be used as a fuel. This happens chiefly through the shift reaction which can take place either directly inside the anode compartment of the fuel cell itself or in an integrated reformer element, utilising the heat produced by the operating MCFC:



This means that it is possible to feed MCFC with alternative energy sources, like biogas, because they are able to use both carbon monoxide and methane after

reforming as fuel gas, which can take place directly inside the cell (with a suitable catalyst), or utilising an integrated reformer element.

The operation of MCFC is not restricted to hydrogen availability alone, and allows the utilization of a variety of hydrocarbon fuels, such as natural gas, syngas derived from biomass or coal, landfill gas, gas derived from industrial or agricultural by-products. At present, for economical and ecological reasons, there is a strong interest towards the use of secondary fuels, by-products from various industrial and agricultural processes.

As a consequence of reactions (1) and (2), water is formed in the anode side and CO₂ is needed on the cathode side. Since the CO₂ required for the cathode reaction is the same formed as consequence of the anode reaction, spent anodic gas is generally recycled back to the cathode. This feature can be potentially be exploited to use the MCFC also as a CO₂ separator/concentrator, providing the possibility for sequestration, which could be of large interest regarding the achievement of the requirements of the Kyoto protocol.

Among the high-temperature fuel cell types, the MCFC benefits from advanced field experience and a more consolidated scientific background. Several developers have usefully demonstrated the MCFC's performance and flexibility in decentralized and niche applications, and an increasing number of small-to-medium-scale plants (250kW-2MW) are being installed over the world, particularly where stringent environmental constraints are in place (e.g. California) or strong government backing and vision provide impetus to their implementation (e.g. South Korea).

Importantly, due to the high quantity of methane in many non-conventional, renewable fuels, the established grid of natural gas could function as a widely available stepping stone for the large-scale implementation and acceptance of high-temperature fuel cells, and facilitate their insertion in non-conventional applications. The chief technical obstacle to definitive market penetration of the MCFC at the moment, is durability beyond 30,000 operating hours, in particular when coupling with non-conventional fuels is considered. Despite the high-potential of this synergetic solution, the contaminant levels in the biogas are often unacceptable for enduring performance of an MCFC stack. This sets demanding requirements on the contaminant detection and gas clean-up stage, which increase

system liability and total cost per kW installed. To be able to profit from the characteristic advantages of fuel cell power supply (high, load-independent efficiency, premium quality power and heat, combustion-free conversion and associated low-level emissions, silent operation), combined with waste utilization and sustainability, it is thus essential to establish precisely – and enhance – the tolerance to residual contaminants of the MCFC.

4.5 Impact of H₂S on MCFC

Hydrogen sulphide, which can be present in biogas within a wide range from 80-4000 ppm, is the most important poison and low levels of it in the reducing gas at the anode already deeply affect cell performance.

Hydrogen sulphide is formed in the biogas plants by the transformation of sulphur-containing proteins, but also inorganic sulphur, particularly sulphates, can be biochemically reduced to H₂S in the fermentation chamber.

Hydrogen sulphide interacts with all cell components involved in the oxidation reaction. At the electrolyte, hydrogen sulphide can react chemically with Carbonates to form either sulphide or sulphate ions. This mechanism usurps electrochemically active charge carriers which would otherwise be available for the hydrogen oxidation mechanism, reducing cell performance. However, hydrogen sulphide can also react electrochemically with Carbonates, releasing electrons, but yielding harmful, ionised sulphate compounds.

Similarly, hydrogen sulphide reacting with the nickel of the anode can block and deactivate the sites meant for hydrogen oxidation. Thus, also catalytic activity of the anode for the water gas shift reaction (4) is inhibited, disturbing the equilibrium conditions of the cell. The affected sites give rise to morphological changes in the anode structure, and can thereby cause further deterioration of cell performance through secondary effects like impeded gas diffusion, volume change or reduced wetting by the electrolyte.

A simplified schematic of the attack by H₂S is given in Figure 4.6.

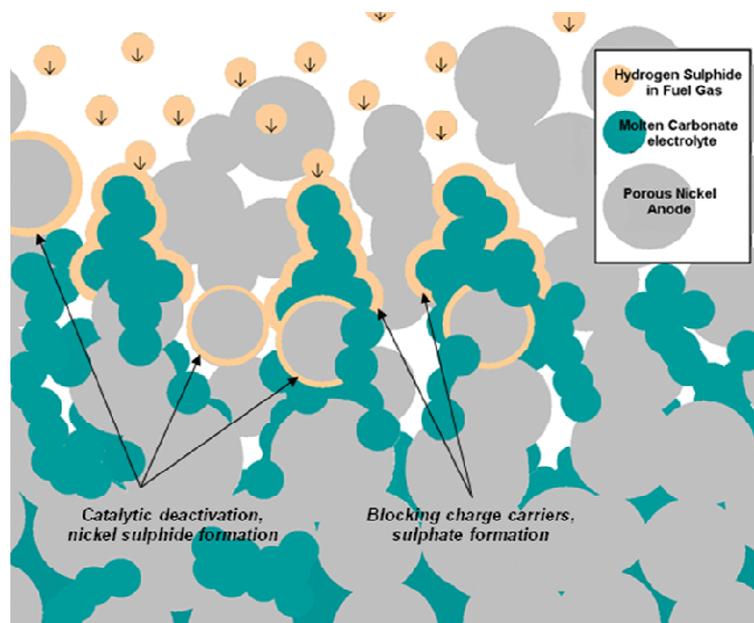


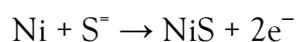
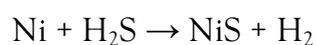
Figure 4.6: Schematic representation of H₂S poisoning

The complex interaction of chemical, electrochemical, static and dynamic mechanisms governing the fate of H₂S in MCFC operating conditions make it exceedingly difficult to separate and quantify the several poisoning effects of hydrogen sulphide.

Though at low concentrations the effects are generally reversible by passing over H₂S-free hydrogen or water vapour, at enduring contaminated conditions surface structure changes take place and cause permanent damage and deactivation of the anode, and thus cell performance degradation.

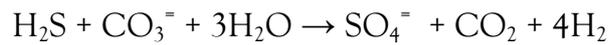
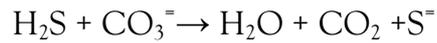
There are two main interactions of H₂S with cell components, with the anode and with the electrolyte.

With the anode, H₂S either can be chemisorbed on nickel surfaces or can react chemically with nickel to form nickel sulphide. Nickel sulphides can be formed also electrochemically by oxidation of sulphide ions in the electrolyte.



Hydrogen sulphide reacting with nickel can block electrochemically active sites for the hydrogen oxidation, can poison catalytic sites for the water gas shift reaction, and can change the wettability of the anode toward Carbonates.

With the electrolyte, H₂S can chemically (and also electrochemically) react with Carbonates forming either sulphide S⁼ or sulphate SO₄⁼ ions.



The conditions and limits for the above reaction to be reversible are under investigation and could provide a crucial, added operating parameter to guarantee long term reliability of the MCFC stack.

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V - Experimental Analysis on MCFC Single Cell

5.1 Introduction

A large part of the current study was dedicated to the particular effects of hydrogen sulphides (H_2S) on the MCFC, with particular attention to the operating conditions of the MCFC-Standard Single Cell.

The experimental campaign has been carried out with the objective to establish the boundary conditions for durable MCFC operation in the presence of a key contaminant like H_2S . To achieve this, many hours of long-term experimentation has been required and different single cells have been operated in MCFC Laboratory, at Fuel Cell Research Division, KIST - Korea Institute of Science and Technology, Seoul, South Korea.

5.2 MCFC Single Cell

MCFC-Single Cell tests have been performed in order to investigate the impact of H_2S on the anode side. Different MCFC-Single Cells have been operated, with different gas flow rates and compositions.

A picture of the 10W Single Cell is shown in Figure 5.1, and the experimental setup for testing MCFC-Single Cell with simulated gas poisoned by H_2S is showed in Figure 5.2.

Figure 5.1: 10W MCFC-Single Cell testing facility



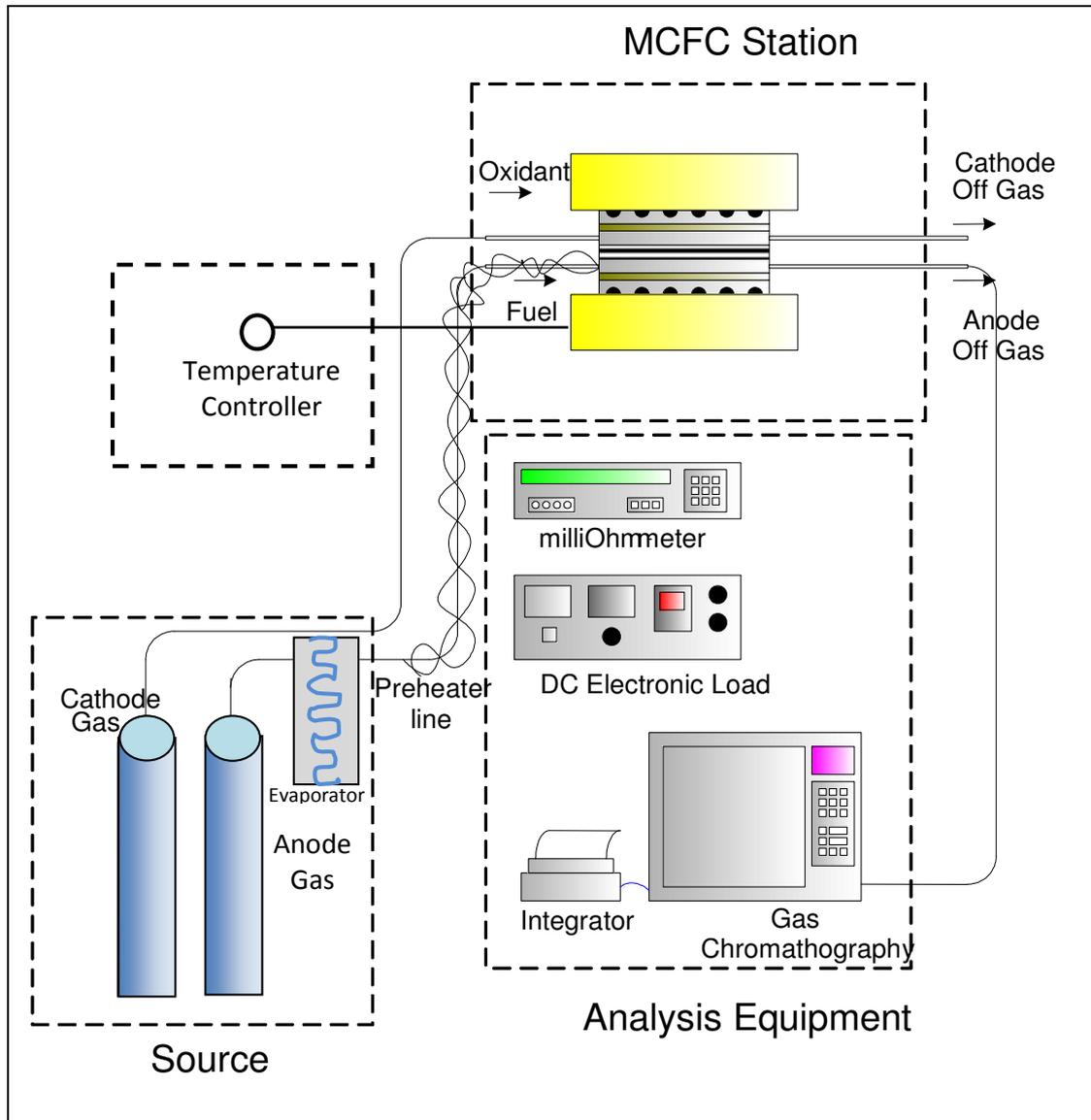


Figure 5.2: Setup of the MCFC-Single Cell testing facility

The experimental conditions and characteristics of the cell operation are summarized in Table 5.1:

<u>Unit cell components</u>	<u>Characteristics</u>
Cell frame of anode and cathode	
Size (cm x cm)	13 x 13
Material	Aluminized SUS-316 L
Anode electrode and current collector	
Size (cm x cm)	11 x 11
Thickness (mm)	ca. 0.69
Porosity	ca. 55-60%
Material (electrode; current collector)	Ni + 5%wt Al; Ni
Mole ratio of fuel gas (H ₂ :CO ₂ :H ₂ O)	72:18:10
Total flow rate	792.3 ml/min
Cathode electrode and current collector	
Size (cm x cm)	10 x 10
Thickness (mm)	ca. 0.70
Porosity	ca. 60-65%
Material (electrode; current collector)	Lithiated NiO; SUS-316 L
Mole ratio of fuel gas (Air:CO ₂)	70:30
Total flow rate	951 ml/min
Electrolyte	
Li ₂ CO ₃ /K ₂ CO ₃ mole ratio	62:38
Matrix	γ-LiAlO ₂

Table 5.1: Experimental conditions and characteristics of the MCFC-Single Cell

The cell has been operated at atmospheric pressure with the different reference gas compositions and flow rates. Periodic characterisation are carried out including voltage – current (V-I) characteristics at constant gas flow rates, utilisation curves at constant gas compositions, gas chromatographic (GC) analyses on the process gases and electrochemical impedance analysis at OCV (Open Circuit Voltage).

The V-I characteristic are recorded by means of an electronic load that fixed currents steps and by a voltmeter that measured the cell voltages. Each V-I

characteristic point is maintained for not less than 10 min thus allowing a complete thermal stabilisation.

The gas composition and flow rates are controlled by a set of mass flow controllers. GC measurements of the inlet gas mixture compositions allows us to verify that the mass flow controllers properly operated during long lasting cell runs. GC analyses, however, are mainly devoted to monitor the gas cross-over trend by carefully measuring the amount of hydrogen at the cathode outlet with the cell at open circuit.

After pre-treatment, the temperature of the gas in the MCFC was maintained at 650 °C. The anode gas consisted of H₂, CO₂, and H₂O in a 72:18:10 mole ratio; the cathode gas consisted of air and CO₂ in a 70:30 mole ratio.

After 1300 hours of hot time at 650 °C, the anodic gas was polluted with increasing concentrations of H₂S, from 1, 3, 5, 8 ppm. Each concentration was maintained at least 170 hours, under the constant load of 100 mA/cm², after which the system was returned back to normal gas conditions until the voltage values at different currents were constant.

Poisoning tests have been conducted replacing part of the pure hydrogen at the anode with hydrogen containing a certified amount of H₂S.

To evaluate the effects upon introduction of H₂S, the I-V curve, the open circuit voltage (OCV), the performance, the N₂ cross-over, the internal resistance and the electrochemical impedance spectra were all measured during cell operation

5.3 Results and Discussions

From preliminary tests, it can be seen how - at different currents and concentrations of H₂S - the cell voltage drops and recuperates upon introduction and discontinuation of the contaminant (Figure 5.3). At higher degrees of poisoning and current load, it can be seen that regeneration is not complete anymore and performance degradation is permanent. To find the governing parameters and conditions that establish the degrees of this reversibility is of exceeding importance to be able to insert the MCFC in a real-world context, where the composition of produced biogas continuously fluctuates.

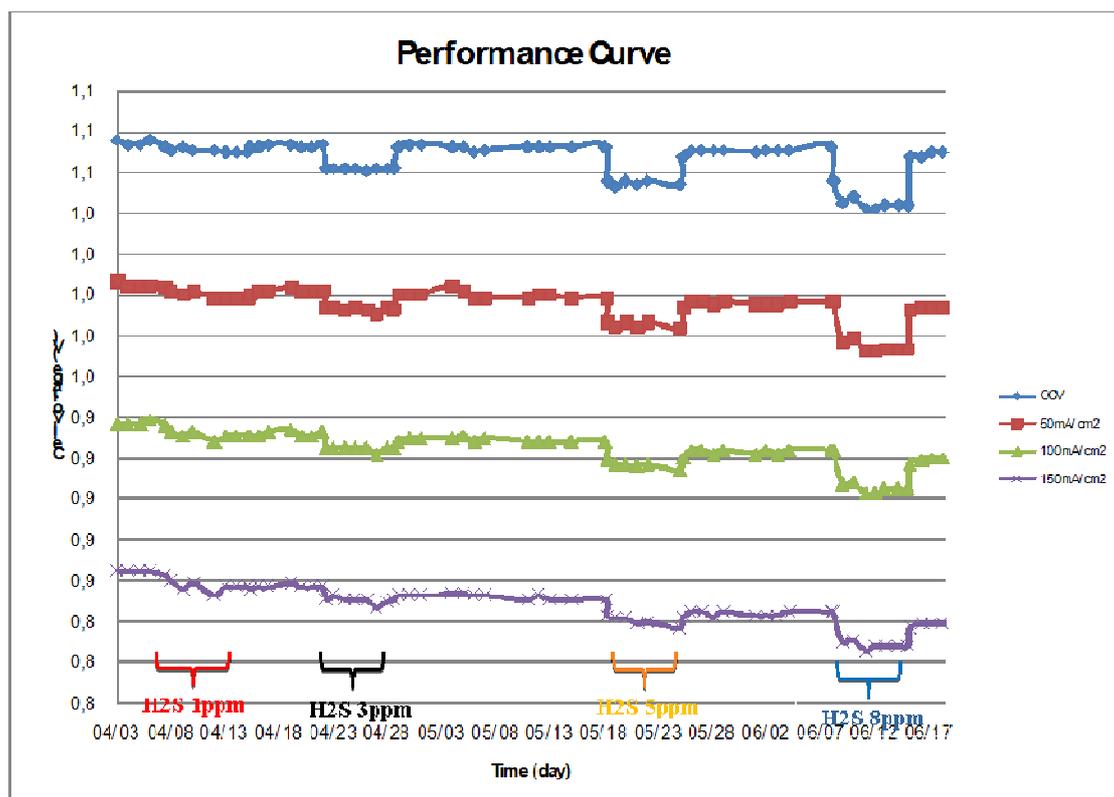


Figure 5.3: Cell voltage values at different current densities (0, 50, 100, 150 mA/cm²) as a function of time before, during and after adding increasing amounts of H₂S

In Figure 5.4, polarization curves at different H₂S concentrations are shown. The slopes of the I-V curves increase upon increasing H₂S content and even at 1 ppm the effect of H₂S is evident. These performance losses can be attributed to several causes: interaction of H₂S with the anode surface either by formation of NiS_x compounds or by H₂S adsorption, H₂S reaction with the electrolyte and consequent replacement of CO₃²⁻ ions by SO₄²⁻, decreasing of the water gas shift reaction rate, changing of electrolyte distribution due to improved wetting of the Ni.

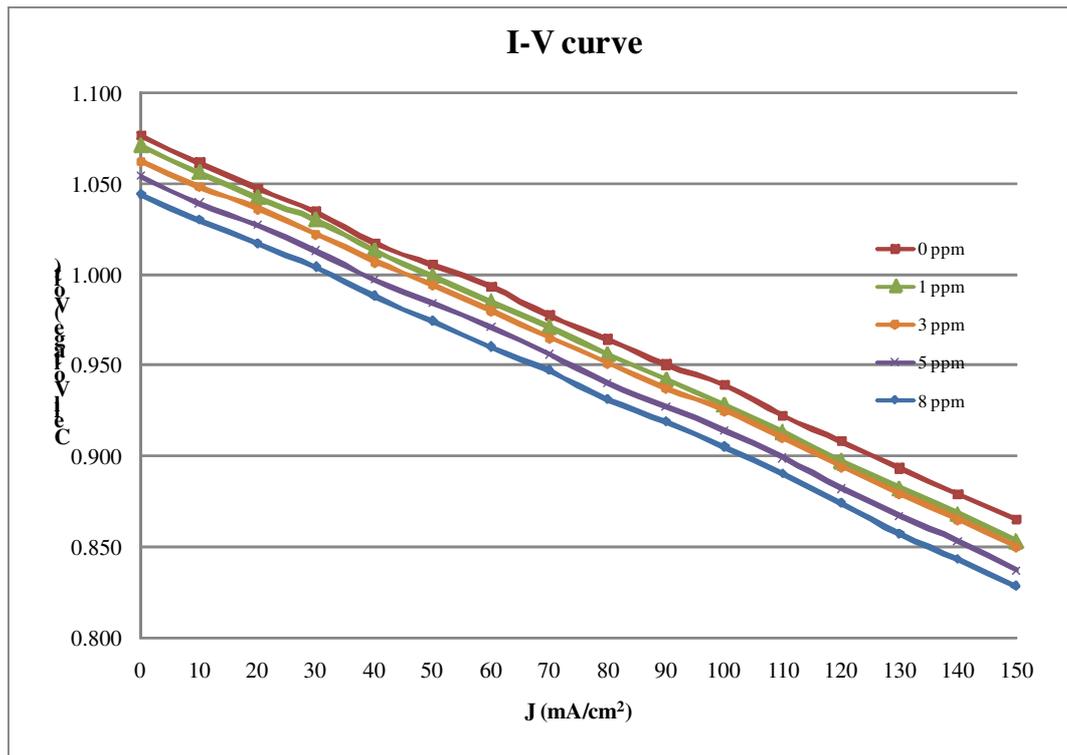


Figure 5.4: Polarization curves at different H₂S concentration (1, 3, 5, 8 ppm)

In order to better understand the effect of H₂S on anode side, the Electrochemical Impedance Spectroscopy (EIS) has been measured. Impedance of the MCFC-Single Cell was measured before, during and after each H₂S cycle, all under current load. The development of the impedance was similar for all of the used H₂S concentrations. The case of 1 ppm and 3 ppm H₂S addition is shown in Figure 5.5, and the case of 5 ppm and 8 ppm H₂S addition is shown in Figure 5.6, as examples; in order to compare the performance after each portion of H₂S, the impedance spectra measured before each new addition of H₂S are shown in these Figures.

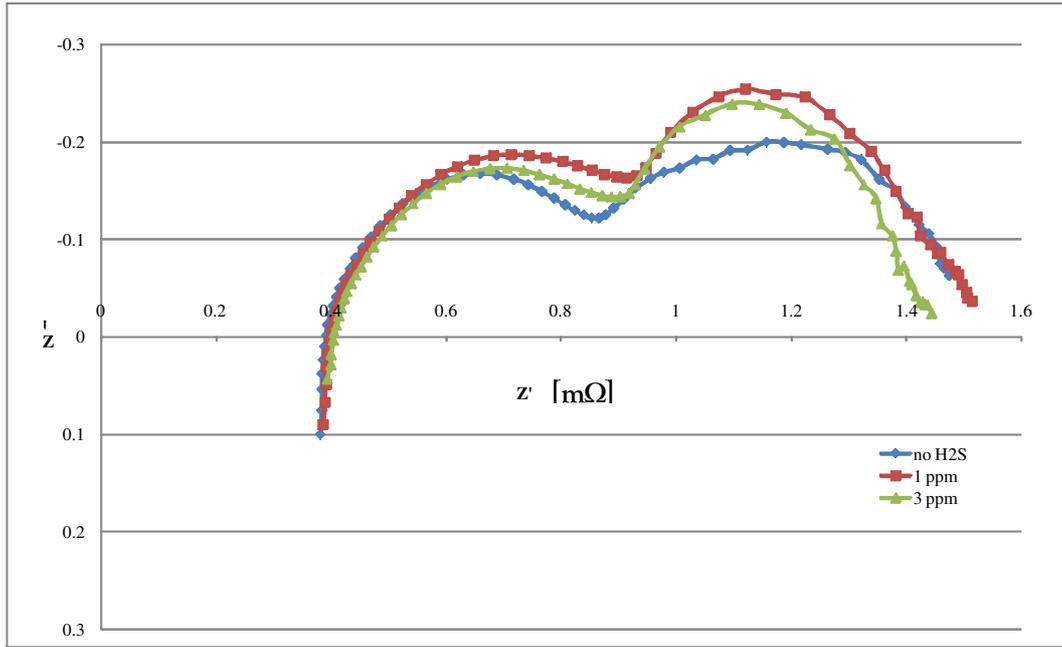


Figure 5.5: Nyquist diagram - Electrochemical Impedance Spectroscopy at different H₂S concentrations - 1 ppm, 3 ppm

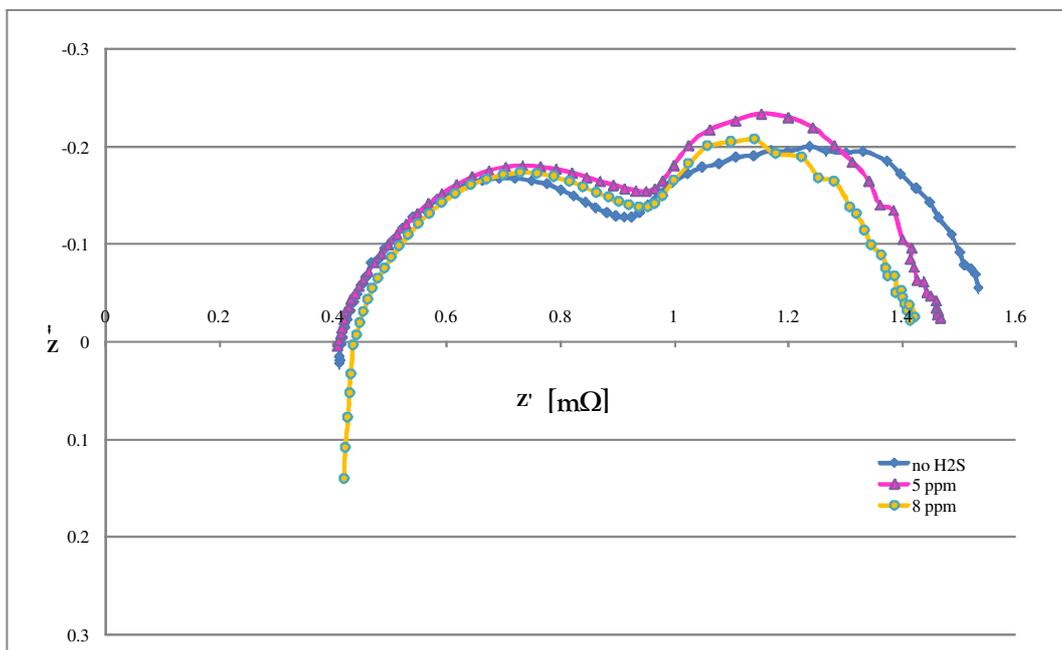


Figure 5.6: Nyquist diagram - Electrochemical Impedance Spectroscopy at different H₂S concentrations - 5 ppm, 8 ppm

As shown in the Figures 5.5 and 5.6 the addition of H₂S did not affect the first semicircle at higher frequencies, but at lower frequencies, changes the second semicircle's shape.

It is found that the impedance curve shifts to the right with the H₂S addition. In these two cases the internal resistance (I_r) is not affected by adding H₂S, being about 4.2 mΩ.

The impedance measurement gave a very important contribution to the evaluation of the regeneration phase. Considering the poisoning with 5 ppm, the curve in Figure 5.7 reveals that the overall dynamic response of the cell is not yet returned to its original value after 20 hours of regeneration, also if the I-V curve shows that this phase is completed.

A longer period of regeneration, about 200 hours, brings the curve to the original position (Figure 5.8).

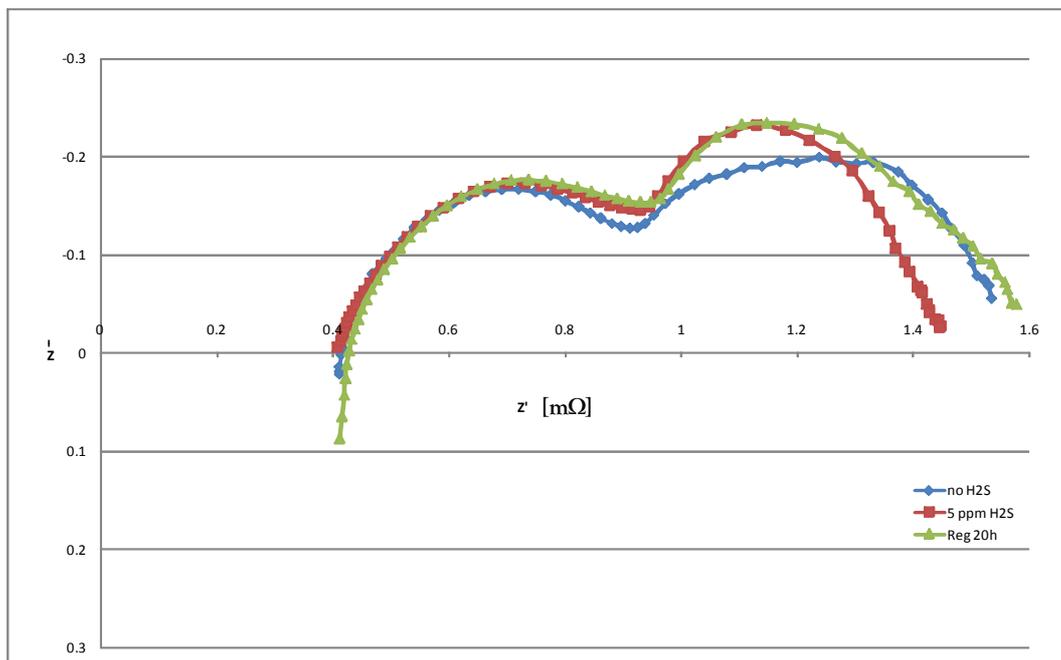


Figure 5.7: Nyquist diagram - Electrochemical Impedance Spectroscopy at 5 ppm, after 20 hr of regeneration

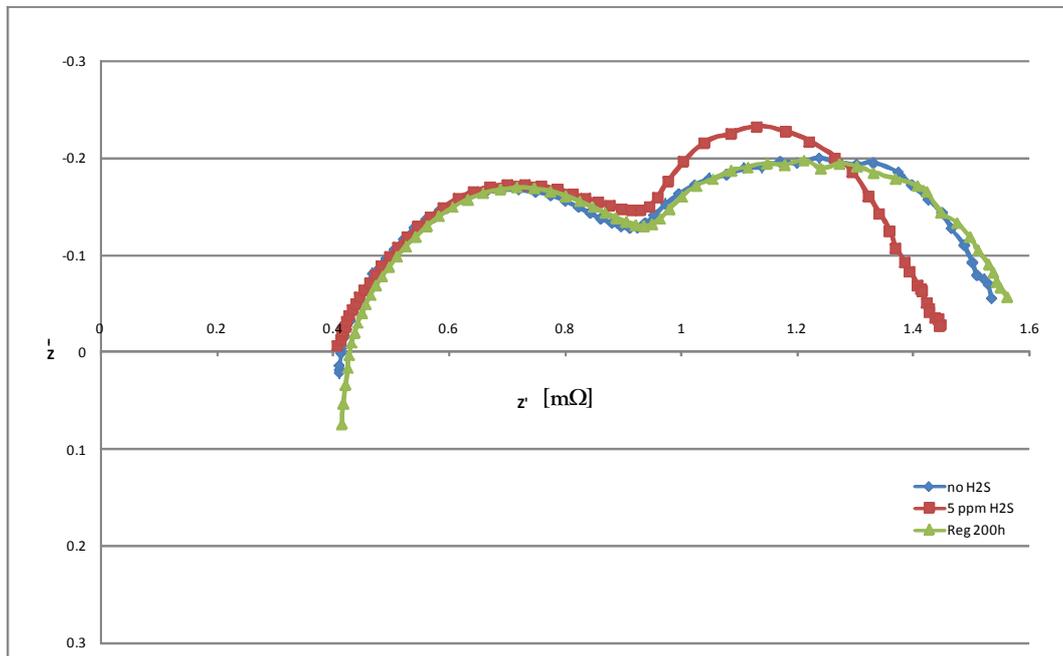


Figure 5.8: Nyquist diagram - Electrochemical Impedance Spectroscopy at 5 ppm, after 200 hr of regeneration

The Figures 5.9 shows the effect of the H_2S poisoning on the outlet gas composition. It was found that CO_2 increases and that CO and CH_4 decrease. The main cause of this effect is the reaction of H_2S with the formation of surface nickel sulphides that can poison catalytic sites for the water gas shift reaction.

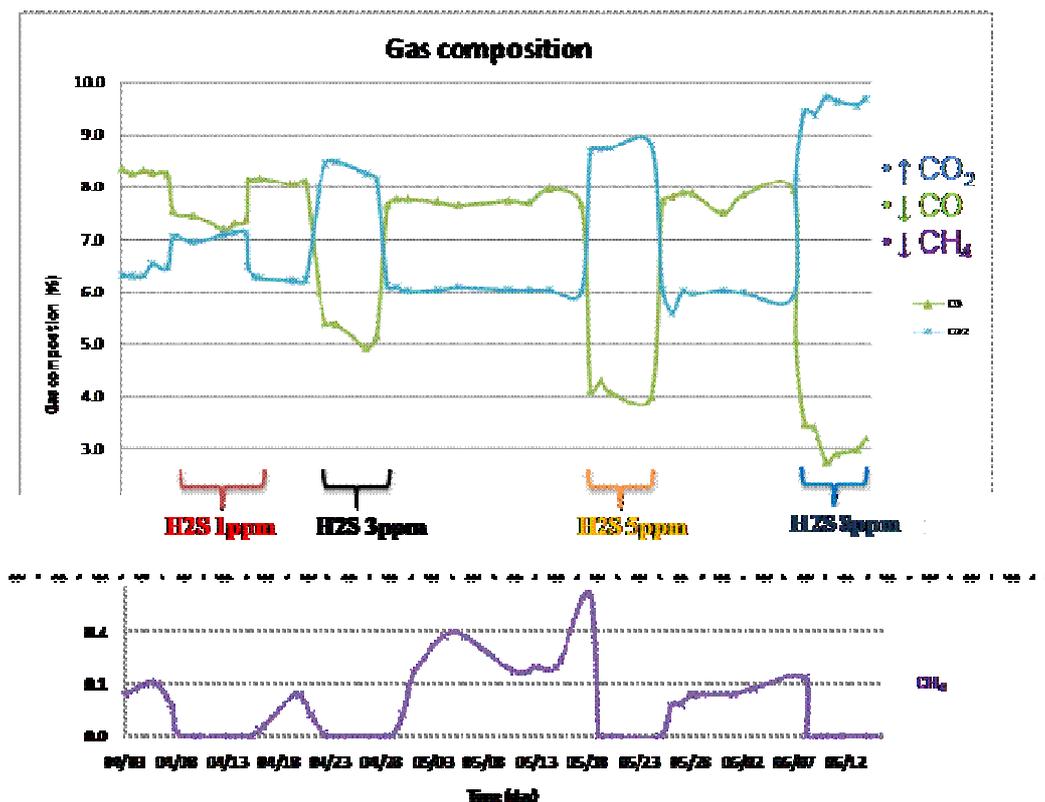


Figure 5.9: Trend of CO₂, CO and CH₄ compositions in the outlet gas at different H₂S concentrations

It was found that H₂S has an immediate effect on cell performance, also at 1 ppm. The effect of sulphur poisoning was observed at the initial H₂S addition, even though the concentration was very low. The poisoning effect is due principally to the formation of nickel sulphides rather than the decreasing of active carbonates. Since this is the initial study related to sulphur poisoning effect on Ni-Al, additional experiments, such as long term testing, coating with different materials, modifying the anode base material should be conducted to enhance the anode properties to achieve high-performance MCFCs suitable for long-term operation. Biogas and MCFC system depend on each other in order to be implemented in a joint way, and their synergy seems to be enormous with view of a sustainable energy supply. In order to develop an efficient system it's necessary to investigate into the effects of long duration poisoning, in order to facilitate safe, durable and cost-effective operation of the fuel cell.

The future work should be focused on:

- ④ Study of different concentrations of H₂S, higher than 10 ppm, as 20 ppm, 50 ppm and 100 ppm, in order to analyse the impact of H₂S poisoning on the anode side;
- ④ Determination and quantification of the effect of operating conditions (fuel humidity, current load, gas compositions) on the degree and reversibility of anode poisoning by H₂S, in order to provide an accurate framework of MCFC tolerance to hydrogen sulphide and other contaminants;
- ④ Study of the “Regeneration process”, comparing the effect of a short and periodic regeneration with a long and durable regeneration on the MCFC-Single Cell, through the analysis of the Impedance spectra curves;
- ④ Development of composite anodes coated with a H₂S “tolerant” material for the selective trapping of hydrogen sulphide (e.g. cerium oxide).

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VI – Technical-Economical Analysis

6.1 Introduction

The research carried out in this work is finalized towards the coupling of a molten carbonate fuel cell (MCFC) to an anaerobic digestion process of organic residues or sludge from a wastewater treatment plant.

As already mentioned, the analysed “Waste-to-Energy” chain concerns three sub-systems:

1. **Anaerobic Digestion:** using local waste sources such as manure from cows and swine, wastewater sludge, organic fraction of municipal solid waste and agro-industrial organic waste; the fuel produced through this treatment, called biogas, primarily consists of methane (CH_4) and carbon dioxide (CO_2) but may also contain undesirable species which are corrosive, poisonous and malodorous; the composition of the biogas may vary considerably depending on the feedstock composition, the process conditions (temperature, pH), and the type of digester used, a generally applicable composition can be given as: CH_4 : 55-65%, CO_2 : 30-45%, N_2 : 1-5%, H_2 : 1-5%, H_2S : 80-4000 ppm.
2. **Biogas clean-up:** the biogas produced by anaerobic digestion needs to be cleaned from harmful contaminants like particulate, hydrogen-sulphide, mercaptans, halogenated hydrocarbons and siloxanes, in order to guarantee safe and reliable operation of the downstream heat and power generator;
3. **MCFC:** clean biogas is reformed and oxidised, generating electricity and releasing heat.

The economic feasibility always plays an important role in whether or not to apply fuel cell technology.

The overall goal of this analysis is to identify the most important parameters that affect the use of biogas in MCFC.

A Cost-Benefit model will be performed and, based on it, a technical- economical analysis will be illustrated. Finally, an assessment of the optimal conditions for introduction of the MCFC system fed with biogas into the market is given.

The analysis takes into consideration the clean up system and the MCFC application, without considering the fuel production through anaerobic digestion process.

Four steps are considered:

1. Input data collection from the different MCFC technologies and clean up systems to fix one set of reference values,
2. Input economical data referred to the Italian energy system;
3. Sensitivity analysis in respect to a series of parameters, to better understand the level of sensitivity of the «economics» of the plants;
4. Comparison between MCFC fed with biogas with H₂S content more than 1500 ppm and MCFC fed with biogas with H₂S content more than 300 ppm.

It has been individuated two different case studies, named Case Study 1 (CS1) and Case Study 2 (CS2) taking into consideration the H₂S content in the biogas.

The composition of the biogas considered (68% CH₄, 32% CO₂) and the flow rate per year produced, could be referred to an anaerobic digestion process inside a wastewater treatment plant of 600.000 Equivalent Inhabitants (EI), to an anaerobic digestion process of the manure from 12.000 bovine, or to a co-digestion of manure and organic fraction of municipal solid waste.

6.2 Cost-Benefit Analysis

The case study analyses the biogas clean up system required for use of gas in MCFC, taking into consideration the quality of standards required for this technologies.

The brief analysis was performed by considering two cases:

- ① Case Study 1: H₂S > 1500 ppm
- ② Case Study 2: H₂S > 300 ppm

The H₂S contained in biogas would be minimised using a combined process in the CS1 (wet + dry) and a dry process in the CS2, in order to achieve 5 ppm of H₂S in the biogas, before fuelling the MCFC.

These are the main input data for the technical-economical analysis:

Fuel Cell type: MCFC
Electric Power: 1.4 MW
Fuel: ADG (LHV 6.78 kWh/Nm³)
Fuel Consumption: 3,500,000 Nm³/a
Electric efficiency: 47%
Thermal efficiency: 42%
Operating hours per year: 7,884
Availability : 90 %
MCFC stack lifetime: 40,000 hours
Considered plant lifetime: 15 years

Electricity produced: 11,038 MWh_e/a
Heat (η heat exchange 90%): 8,877 MWh_{th}/a
Overall efficiency: 89%
Avoided CO₂: 6,000 ton/a

MCFC System

Investment cost:

- I1: 6,000 €/kW (current cost)
- I2: 4,000 €/kW (medium-time target cost)
- I3: 2,000 €/kW (long-time target cost)

O&M cost:

- Worker
- Stack replacement
- Variable costs

Clean up system:

- CS1
 - o Investment cost: 600.000 €
 - o O&M cost: 600.000 €/a
- CS2
 - o Investment cost: 420.000 €
 - o O&M cost: 300.000 €/a

Income: Electricity price 0.22 €/kWh (Italian Green Certificate)

Inflation rate : 3%/a

Interest rate : 6%/a

The yearly profit and costs from the biogas plant using a MCFC are used to calculate the Net Present Value (NPV) of a fuel cell. If the NPV of a fuel cell is positive, then the owners can earn a profit from their investment. Otherwise, the owners will lose money from the fuel cell.

Figure 6.1 shows the results for CS1, where the Payback Time (PBT) is 10 years for I3, and more than 15 years for I1 and I2.

Figure 6.2 shows the results for CS2, where the Payback Time (PBT) is 5 years for I3, 13 years for I2 and more than 15 years for I1.

In order to increase the economic feasibility of the fuel cell, its efficiency has to be improved, and the overall running cost and investment costs of fuel cell need to be reduced.

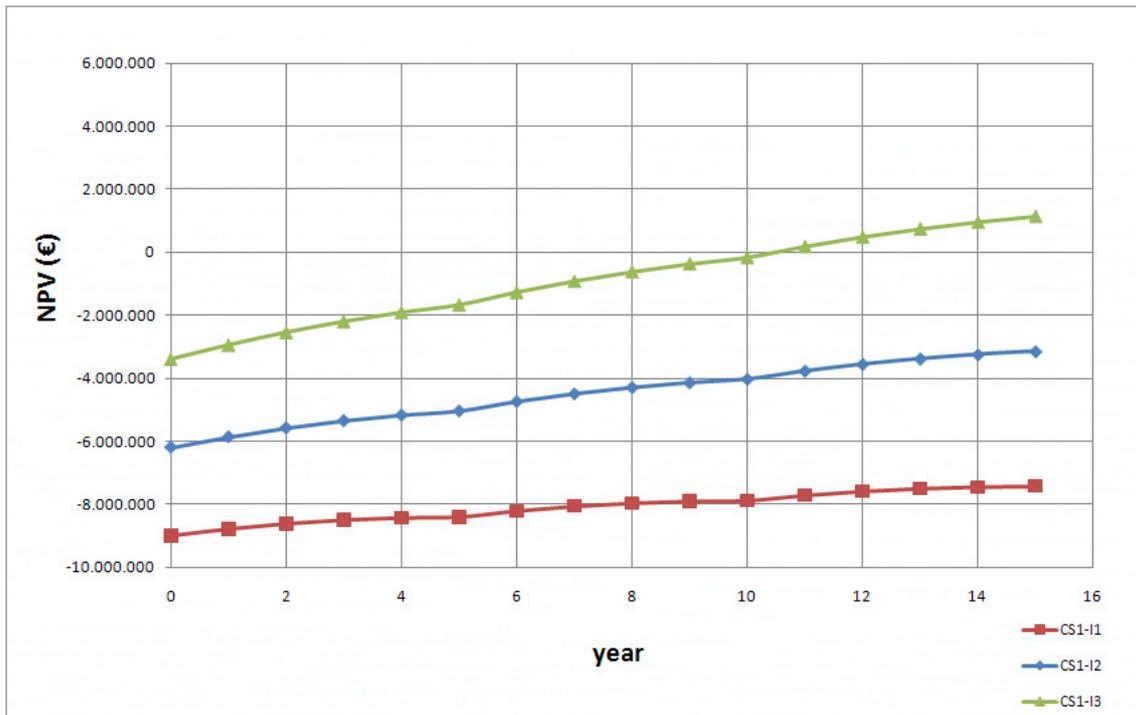


Figure 6.1: Net Present Value trend for CS1

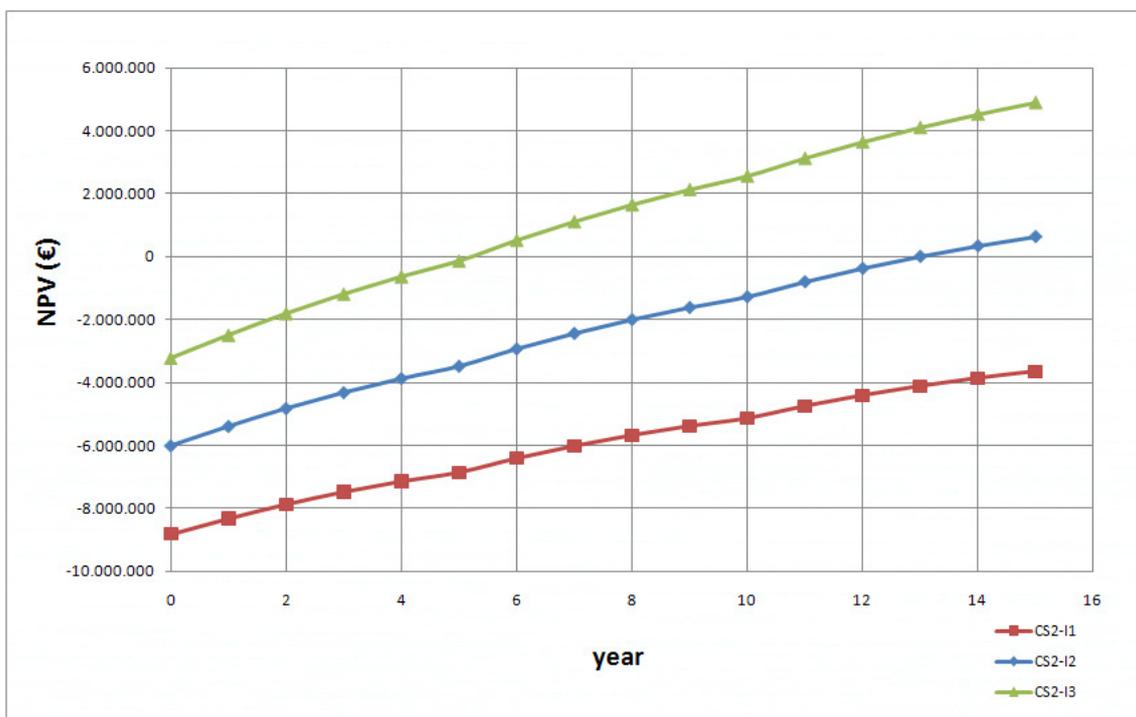


Figure 6.2: Net Present Value trend for CS2

In this two evaluations, ADG price has been considered equal to zero. In this case the fuel is available to the energy plant without any added cost.

It's also interesting to evaluate how the Payback Time (PBT) can vary, in relation with the ADG price. In this case the fuel has a value, from 0 to 0,6 €/Nm³.

Figure 6.3 shows the results for CS1, where the maximum possible ADG price is 0.12 €/Nm³ for I1, 0.22 €/Nm³ for I2 and 0.32 €/Nm³ for I3.

ADG prices more that these values lead to Payback Time (PBT) more than 15 years.

Figure 6.4 shows the results for CS2, where the maximum possible ADG price is 0.21 €/Nm³ for I1, 0.31 €/Nm³ for I2 and 0.41 €/Nm³ for I3.

Also in this case ADG prices more that this value lead to Payback Time (PBT) more than 15 years.

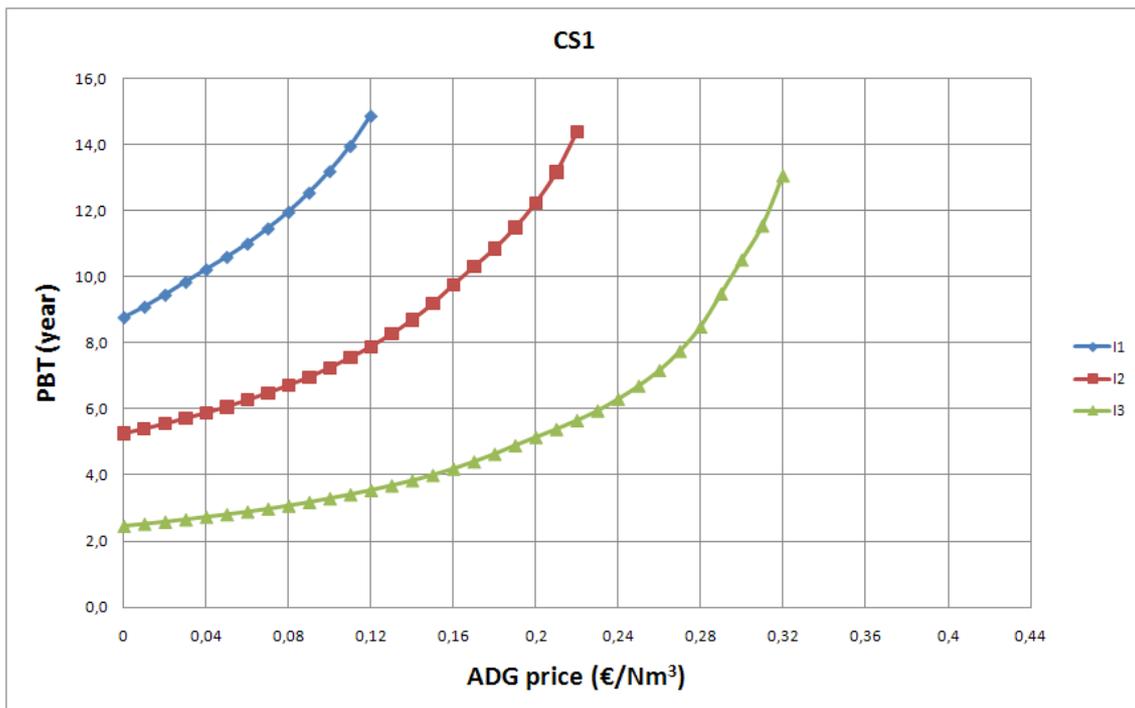


Figure 6.3: Net Present Value trend varying ADG price, CS1

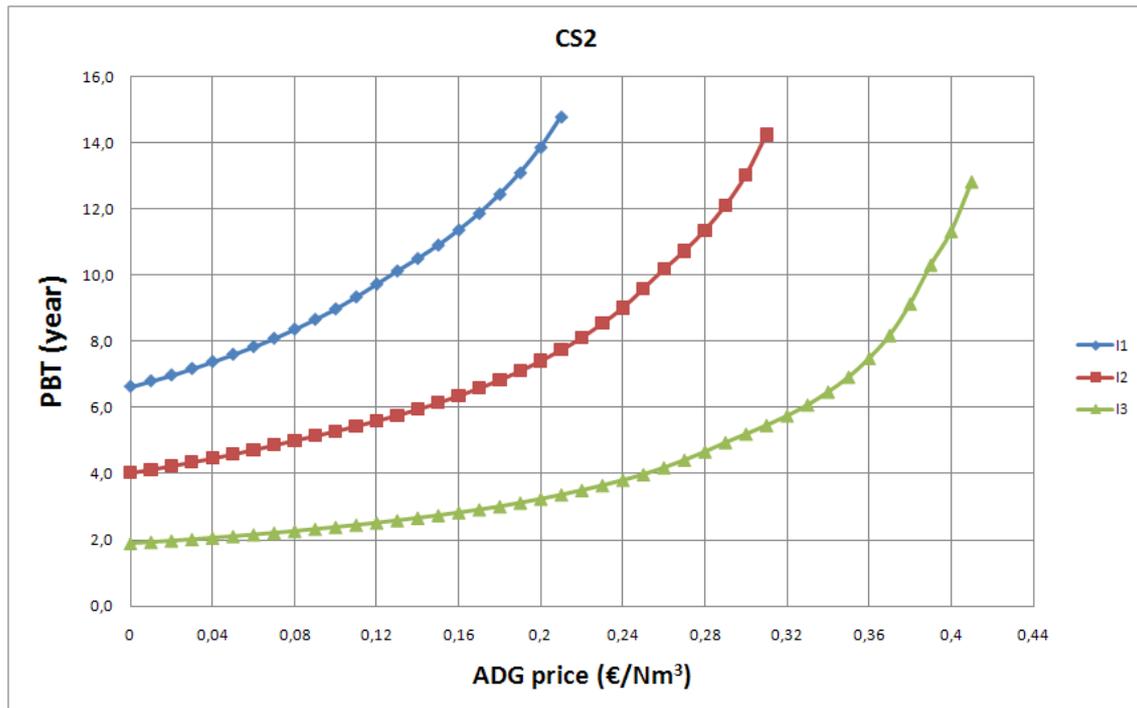


Figure 6.4: Net Present Value trend varying ADG price, CS2

6.3 Conclusions

These case studies are based on use of biogas as a renewable energy source to MCFC. The conclusions from the study are as follows:

- ④ The production of energy from MCFC is more efficient than from CHP engine used nowadays;
- ④ MCFC are not economically viable in the present context unless cost could be reduced further. This could only be achieved with the support from incentives (Green Certificates);
- ④ The H₂S removal is a crucial point

The sensitivity analyses performed in this study clearly demonstrated to what extent the results depended on the specific MCFC Investment cost (€/kW) and ADG price (€/Nm³). The specific ADG cost can differ greatly from country to country, and even within the same country. Moreover in many countries in Europe there exist very «structured» energy and fuel tariffs.

One of the most important parameters for good economics of fuel cell plants is the O&M cost. This is also true for the clean up technologies considered in this study. In conclusion, the introduction of MCFC plant fed by biogas is possible, but not yet currently economically feasible in Italy.

The MCFCs are still far from the “market price” and it should be necessary to have a strong and effective dedicated incentive program, as already exist in Germany, USA, Korea and Japan.

Fuel cell plants still require a reduction in the system cost and an increase of the reliability of the BoP components. Furthermore, the economics of fuel cell plants depends heavily on «local» factors, such as, the fuel price, regulations, environmental requirements, inflation, and interest rates.

Thus, in the huge energy market that exist in the world today, there is clearly a need to introduce the MCFC technology into an area at a relatively high investment cost, and the “Waste-to-Energy” area is practically a solution of “Niche Market Application”.

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VII – MCFC fed with Non-Conventional Fuels

7.1 State of the art in the world

Fuel cell systems based on MCFC technology are under development in Italy, Japan, Korea, USA and Germany. Since the 1990s, MCFC systems have been tested in field trials in the range between 40 kWel and 1.8 MWel.

Figures 7.1 [1] and 7.2 [1] show the relevant quantity of installed MCFC power, compared to other fuel cell technologies, for systems with a nominal power higher than 10 kW. The high number of MCFC installations is mainly due to the strong role played by the American Company, Fuel Cell Energy (FCE) and the German MTU Onsite Energy in putting their products in operation. MTU Onsite Energy developed its 250 kW system, called Hot Module, based on FCE’s fuel cell stacks.

Figures 1a and 1b also show that during the period 1970-2003, Phosphoric Acid Fuel Cells (PAFC) covered a dominant role for this power range, while in the last two years many more MCFC units have been installed.

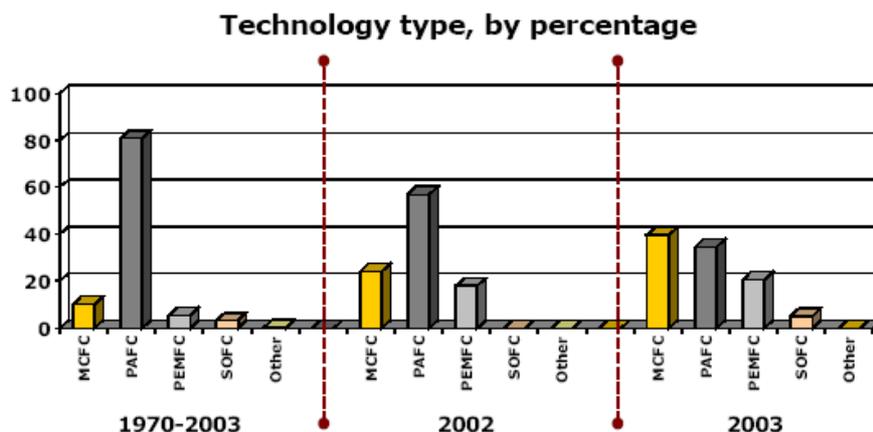


Figure 7.1: Percentage of installed power by technology type from 1970 to 2003 [1]

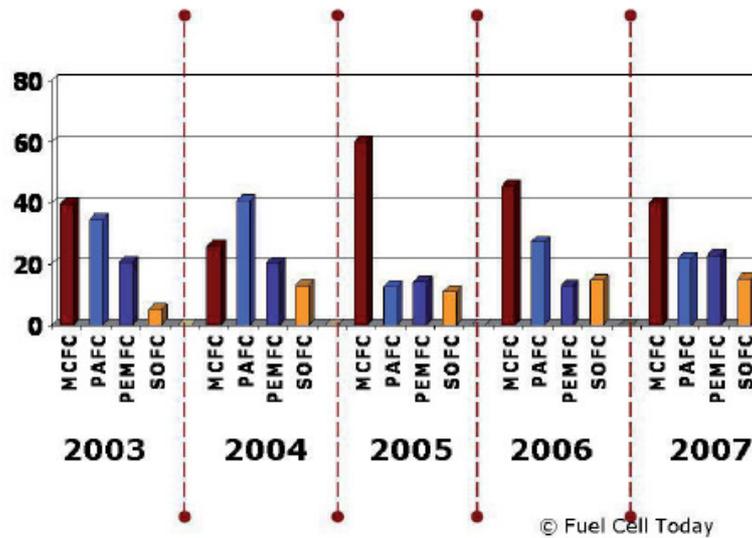


Figure 7.2: Percentage of installed power by technology type from 2003 to 2007 [1]

Six developers are considered as the major in the world:

1. FuelCell Energy (FCE, USA)
2. GENCELL Corporation (USA)
3. MTU Onsite Energy (Germany)
4. Ansaldo Fuel Cells (AFCo, Italy)
5. Ishikawajima-Harima Heavy Industries (IHI, Japan)
6. POSCO (South Korea)

FCE (USA) and MTU Onsite Energy (Germany)

Significant worldwide operational experience has been accumulated with 250 kW power plants running on different fuels and for various applications.

Their systems were originally developed for being operated on natural gas, but other fuels like biogas, landfill gas, coal gas, mine gas, residual gas, were considered as optional feedstock.

In particular, the fuel cell plants using biogas from anaerobic digestion constitute more than 20% of the total installations.

Location	Application	System Model	Nominal Power
Palmdale, CA (USA)	Waste Water Biogas	DFC300	250 kW
Sierra Nevada, CA (USA)	Biogas (waste by-product of the brewing process)	4x DFC 300	1 MW
Terminal Island, San Pedro, CA (USA)	Sewage Digester Gas	DFC 300	250 kW
Santa Barbara, CA (USA)	Waste Water Biogas	2x DFC 300	500 kW
King County, CA (USA)	Waste Water Biogas	DFC 1500	1 MW
Fukuoka (Japan)	Waste Water Biogas	DFC 300	250 kW
Tancheon, Seoul (Korea)	Sewage Digester Gas	DFC 300	250 kW
Kirin (Japan)	Digester Gas from Brewery Process.	DFC 300	250 kW
Tokyo "Super Eco Town" (Japan)	Anaerobic Digester Gas from Food Recycling Facility	DFC 300	250 kW
Chevron Energy Solutions, CA (USA)	Operated on biogas from waste water and kitchen grease	3x DFC 300	900 kW
Southern California Gas Company, Riverside CA	Operated on biogas from waste water treatment	DFC 1500	1 MW

Table 7.1: FCE Installations [1]

Location	Application	System Model	Nominal Power
Ahlen (Germany)	Waste Water Biogas	DFC300	250 kW
Leonberg (Germany)	Anaerobic Digester Gas from "green bin" waste treatment	DFC300	250 kW

Table 7.2: MTU Onsite Energy installations [1]

Figure 7.3 depicts a picture of the 1 MW King County Power Plant (Renton, WA), operated on biogas from a wastewater digester.



Figure 7.3: King County Power Plant (Courtesy of Fuel Cell Energy)

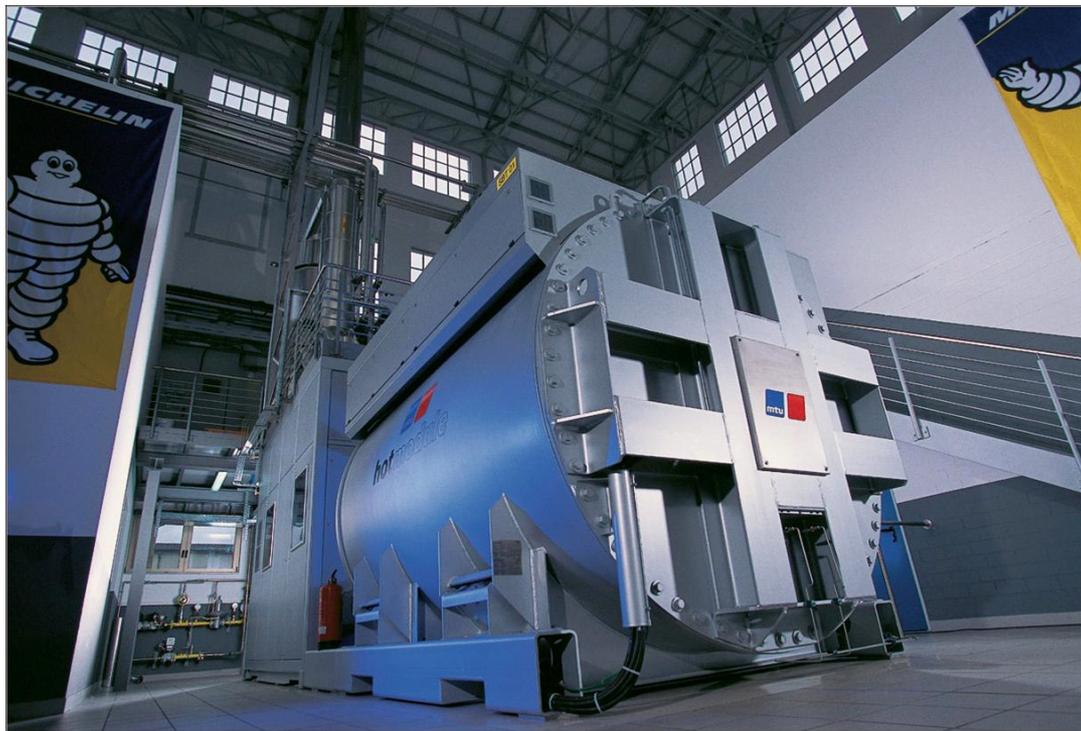


Figure 7.4: MTU Onsite Energy Michelin Plant in Karlsruhe, Germany (Courtesy of MTU Onsite Energy)

ANSALDO FUEL CELLS (AFCo) (Italy)

Size (Class)	Fuel	Site	Objectives	Support
Series 1ST	Biomass gasification	Trisaia, Italy	Demonstration biomass gasification/fuel cell integrated process	EC/Italian Ministry of University & Research
MW class	Waste water ADG, Landfill	Terni, Italy	Scaling-up with ADG and landfill	EC
MW class	Waste water ADG, Landfill	Spain	Scaling-up with ADG and landfill	EC

Table 7.3: Demonstration program at Ansaldo Fuel Cells [1]

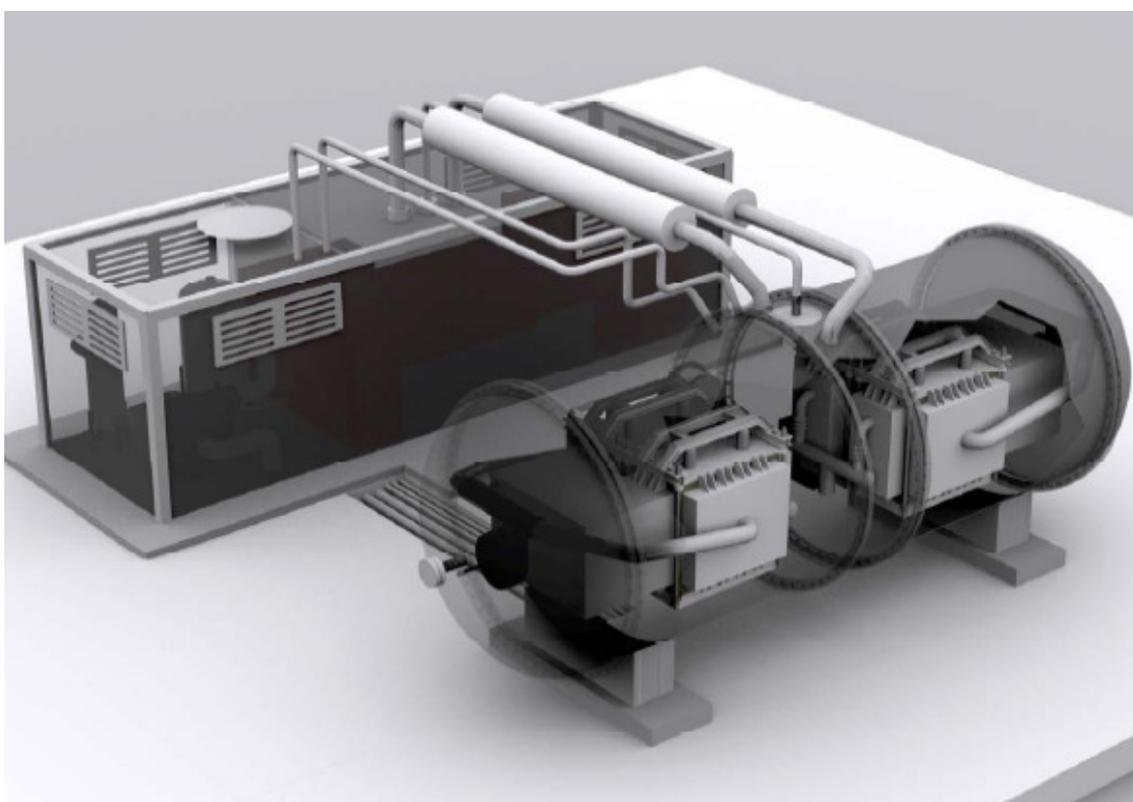


Figure 7.5: MTU AFCo Series 500 Power Plant (courtesy of AFCo)

The demonstration program represents a key part of the present phase of development of AFCo. The final goal of the program is to demonstrate the technology viability for different fuels and applications, with a total power of over 4 MW.

A comprehensive review of these developers has been published by the European Commission [1] gives an overview of the current status of their production strategies and achievements. At this time, Molten Carbonate fuel cells have been demonstrated at several sites, and in different sizes. Focus is mostly on the 200 kW-1 MW range, while scale-up to multi-MW power plants are underway. High investment cost and reduced durability compared to conventional technologies are still two important issues to overcome, in order to ensure proper market penetration. Therefore, R&D activities are still needed before the technology can be considered mature enough to compete with traditional energy systems.

Nevertheless, there are interesting applications where MCFCs already make economical sense. These include applications where gas is available as a by-product of an industrial or agricultural process, where stringent environmental requirements are in place, and/or where Combined Heat and Power (CHP) off-take is guaranteed. Importantly, due to the high quantity of methane in many alternative, renewable fuels, the established grid of natural gas could function as a widely available stepping stone for the large-scale implementation and acceptance of high-temperature fuel cells, and facilitate their insertion in non-conventional applications.

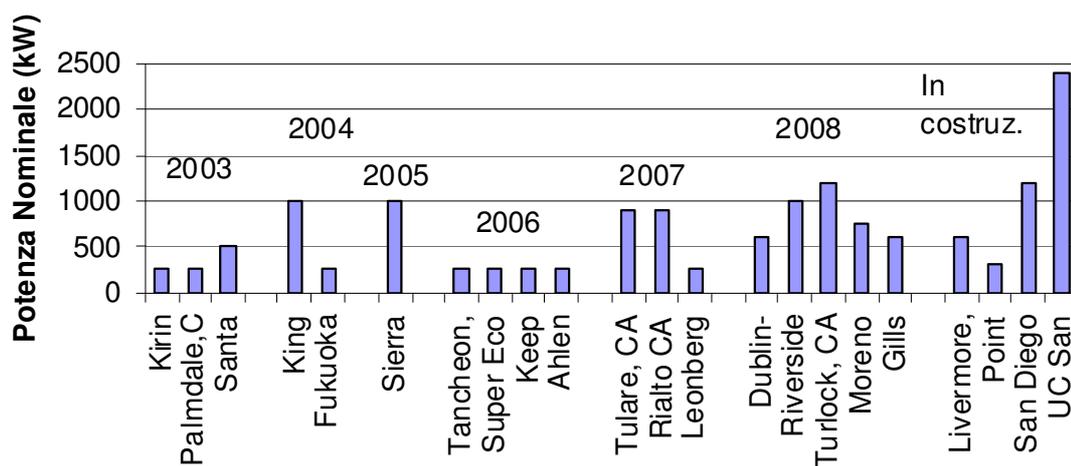


Figure 7.6: Molten Carbonate Fuel Cell Plants fed with Biogas from anaerobic digestion of wastewater and organic waste

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Conclusions

In the light of our dependence on primary energy carrier imports and the current environmental and political necessities, using biomass and waste to produce alternative or non-conventional fuels is a high quality contribution to the energy problem, especially when integrated with high efficiency fuel cell systems.

Since these non-conventional fuel sources are generally poor in energy content, their successful exploitation resides in their decentralised and very efficient application, an attribute which characterise fuel cell systems eminently.

For distributed CHP generation, furthermore, it has been shown that high-temperature fuel cells, like MCFCs, are the most promising due to their suitability for carbon conversion, inherent sturdiness and increasing reliability, and the quality of heat and power produced.

Biogas and MCFC system depend on each other in order to be implemented in a joint way, and their synergy seems to be enormous in view of a sustainable energy supply.

In this Ph.D. work both technical and economical issues have been approached.

Considering the former issues, the problem of contaminants in these fuels – particularly sulphurous compounds – has been tackled and an experimental methodology has been implemented in order to study the effects and implications of cell poisoning with H_2S . It was found that H_2S has an immediate effect on cell performance, also at low concentrations.

In order to develop an efficient system it's still necessary to investigate into the effects of long duration poisoning, in order to facilitate safe, durable and cost-effective operation of the fuel cell.

Moreover, in order to improve both the resistance to corrosion induced by hydrogen sulphide and the regenerative capacity of the cell, composite anodes coated with a H_2S “tolerant” (e.g. ceria oxides) have to be studied, tested, and developed.

Considering the cost benefit analysis, it has been found that the “Waste-to-Energy” chain with MCFC as CHP system is technically possible but not yet currently economically feasible in Italy.

The MCFCs are still rather far from the “market price” and it will be necessary to have a strong and effective dedicated incentive program, as already exist in Germany, USA, Korea and Japan.

Considering the biogas produced from manure, sewage sludge and organic fraction of municipal solid waste, with respect to 2007, the gross electricity production potentially producible with MCFC could be in the range between 3,000 and 8,000 GWhe/a, with 1.5 - 4.6 Mton of avoided CO₂.

In the huge energy market that exist in the world today, the “Waste-to-Energy” area represents a “Niche Market Application” where it is clearly possible to introduce the MCFC despite the relatively high investment cost.

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