

BIOGAS UPGRADING AND UTILISATION



IEA Bioenergy

Task 24: Energy from biological
conversion of organic waste

UPGRADING AND UTILISATION OF BIOGAS

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Flotec water scrubbing



Kompogas carbon molecular sieves



Cirmac Membrane Gas upgrading



Selexol scrubbing

Introduction

Anaerobic digestion (AD) has successfully been used for many applications that have conclusively demonstrated its ability to recycle biogenic wastes. AD has been successfully applied in industrial waste water treatment, stabilisation of sewage sludge, landfill management and recycling of biowaste and agricultural wastes as organic fertilisers. Increasingly the AD-process is applied for degrading heavy organic pollutants such as chlorinated organic compounds or materials resistant to aerobic treatment.

Today, farm-based manure facilities are perhaps the most common use of AD-technology. Six to eight million family-sized low-technology digesters are used in the far East (Peoples Republic of China and India) to provide biogas for cooking and lighting. There are now over 800 farm-based digesters operating in Europe and North America. Thousands of digesters help to anaerobically stabilise and thicken sewage sludge before it is either used on agricultural land, dried and incinerated or landfilled. More than 1 000 high-rate anaerobic digesters are operated world-wide to treat organic polluted industrial waste water including processors of beverages, food, meat, pulp and paper, milk among others.

Gas recovery from landfills has become a standard technology in most of the industrialised countries for energy recovery, environmental and safety reasons. Increasingly the gas is used in combined heat and power (CHP) engines or as a supplement to natural gas.

There are more than 120 AD plants operating or under construction using the organic fraction of source separated municipal solid waste to produce a high quality compost or mechanically separated MSW to stabilise the organic fraction before landfilling. The total installed capacity is close to five million tonnes.

The product of anaerobic digestion is a mixed gas primarily composed of methane CH₄ and carbon dioxide which commonly is called biogas. In small scale installations the gas is primarily utilised for heating and cooking. In larger units CHP's are fueled with biogas. In any case, the driving force for the gas utilisation was to economise fossil fuels or wood as in developing countries.

More recently, as discussed at the conferences of Rio and Kyoto, various airborne emissions have caused serious concern about climatic, environmental and health impacts. Discharges of acid and green house gases are actually at levels that require immediate actions to counter severe future problems. This is particularly true for the transport sector. Alternative fuels might help considerably to reduce emissions. This has been recognised by a number of governments which brought forward programs (such as the EU ZEUS project which stands for Zero Emission vehicles in Urban Society) and legislations (e.g. the Californian clean fuel act).

In particular, biogas as a fuel could bring substantial reductions in green house gases, particles and dust or nitrogen oxide emissions. This has been acknowledged among others by the Swedish Ministry of Environment who suggest to fully free biogas from fuel taxes as the only biofuel before methanol and ethanol from bio-based origin or rapemethylester (RME). In Switzerland biogas is exempt of all fuel taxes for a limited pilot period. There are good chances that it will be fully freed in the near future.

When biogas is used as a vehicle fuel it has to be upgraded and compressed. A number of technologies have been developed during the passed ten years. This brochure provides an insight of the 1999 status of biogas upgrading and utilisation.

1 000 high-rate anaerobic digesters are operated world-wide to treat organic waste water and 120 AD plants to digest totally 5 million tons of MSW and other biogenic solid wastes.

From Arthur Wellinger, Switzerland and Anna Lindberg, Sweden.

Biogas Composition

Biogas produced in AD-plants or landfill sites is primarily composed of methane (CH_4) and carbon dioxide (CO_2) with smaller amounts of hydrogen sulphide (H_2S) and ammonia (NH_3). Trace amounts of hydrogen (H_2), nitrogen (N_2), carbon monoxide (CO), saturated or halogenated carbohydrates and oxygen (O_2) are occasionally present in the biogas. Usually, the mixed gas is saturated with water vapour and may contain dust particles and siloxanes.

maximal workplace concentration is 5 ppm). When biogas is burned SO_2/SO_3 is emitted which is even more poisonous than H_2S . At the same time SO_2 lowers the dew point in the stack gas. The sulphurous acid formed (H_2SO_3) is highly corrosive.

- Removal of water because of potential accumulation of condensate in the gas line, the formation of a corrosive acidic solution when hydrogen sulphide is dissolved or to achieve low dew points when biogas is stored under elevated pressures in order to avoid condensation and freezing.

- Removal of CO_2 will be required if the biogas needs to be upgraded to natural gas standards or vehicle fuel use. It dilutes the energy content of the biogas but has no significant environmental impact.

- Landfill gas often contains significant amounts of halogenated compounds which need to be removed prior to use. Occasionally the oxygen content is high when too much air is sucked in during collection of the landfill gas.

Characteristics of different fuel gases

Parameter	Unit	Natural Gas	Town Gas	Biogas (60% CH_4 , 38% CO_2 , 2% Other)
Calorific value (lower)	MJ/m ³	36.14	16.1	21.48
Density	kg/m ³	0.82	0.51	1.21
Wobbe index (lower)	MJ/m ³	39.9	22.5	19.5
Max. ignition velocity	m/s	0.39	0.70	0.25
Theor. air requirement	m ³ air/ m ³ gas	9.53	3.83	5.71
Max. CO_2 -conc. in stack gas	vol%	11.9	13.1	17.8
Dew point	°C	59	60	60-160

The characteristics of biogas are somewhere in-between town gas (deriving from cracking of cokes) and natural gas. The energy content is defined by the concentration of methane. 10 % of CH_4 in the dry gas correspond to approx. one kWh per m³.

For many applications the quality of biogas has to be improved. The main parameter that may require removal in an upgrading systems are H_2S , water, CO_2 and halogenated compounds:

- Desulphurisation to prevent corrosion and avoid toxic H_2S concentrations (the

Gas utilisation

Biogas can be used for all applications designed for natural gas. Not all gas appliances require the same gas standards. There is a considerable difference between the requirements of stationary biogas applications and fuel gas or pipeline quality.

Heating

Boilers do not have a high gas quality requirement. Gas pressure usually has to be around 8 to 25 mbar. It is recommended to reduce the H₂S concentrations to values lower than 1.000 ppm which allows to maintain the dew point around 150°C. The sulphurous acid formed in the condensate leads to heavy corrosion. It is therefore recommended to use stainless steel for the chimneys or condensation burners and high temperature resistant plastic chimneys. Most of the modern boilers have tin-laminated brass heat exchangers which corrode even faster than iron chimneys. Where possible, cast iron heat exchangers should be utilised.

It is also advised to condense the water vapour in the raw gas. Water vapour can cause problems in the gas nozzles. Removal of water will also remove a large proportion of the H₂S, reducing the corrosion and stack gas dew point problems.

CHP-engines

The utilisation of biogas in internal combustion engines is a long established and extremely reliable technology. Thousands of engines are operated on sewage works, landfill sites and biogas installations. The engine sizes range from 45kW (which corresponds to approx. 12 kW_{el}) on small farms up to several MW on large scale landfill sites.

Requirements to remove gaseous components depending on the biogas utilisation

Application	H ₂ S	CO ₂	H ₂ O
Gas heater (boiler)	< 1000 ppm	no	no
Kitchen stove	yes	no	no
Stationary engine (CHP)	< 1'000 ppm	no	no condensation
Vehicle fuel	yes	recommended	yes
Natural gas grid	yes	yes	yes

Gas engines do have comparable requirements for gas quality as boilers except that the H₂S should be lower to guarantee a reasonable operation time of the engine. Otto engines designed to run on petrol are far more susceptible to hydrogen sulphide than the more robust diesel engines. For large scale applications (> 60 kW_{el}) diesel engines are therefore standard. Occasionally, organic silica compounds in the gas can create abrasive problems. If so, they should be removed.

A diesel engine can be rebuilt into a spark ignited gas engine or a dual fuel engine where approx. 8-10 % of diesel are injected for ignition. Both type of engines are often applied. The dual fuel engine has a higher electricity efficiency. The requirements for the gas upgrading are the same; small CHP (< 45 kW_{el})

Boilers and CHP-engines are reliable gas utilisers. They do not have a high gas quality requirement. Usually upgrading is limited to water condensation and eventually H₂S control.





Transportation of the biowaste with biogas operated trucks allows to fully close the natural carbon cycle: No non renewable energy is required

Replacement of diesel or petrol by biogas reduces the emissions and also the engine noise considerably.



achieve practical electric efficiencies of 29 % (spark ignition) and 31 % (dual fuel). Larger engines have efficiencies of up to 38 %.

In biogas engines NO_x emissions are usually low because of the CO_2 in the gas. CO -concentration is often more of a problem. Catalysts to reduce the CO are difficult to use because of the H_2S in the gas. However, from an environmental point of view CO is a far smaller problem than NO_x because it is rapidly oxidised to CO_2 which makes part of the



natural carbon cycle.

Best results are achieved with lean burn engines. At air-fuel ratios (λ) of 1.5, NO_x and CO concentrations of less than 500 ppm can be achieved.

A promising application of electrical generation is the use of gas turbines. Modern engines are equally efficient as internal combustion engines and very robust. They allow recovery of the heat in form of valuable steam. Unfortunately, the efficient turbines are available only at scales greater than 800 kW_{el} . Their gas requirements are comparable to those of CHP engines.

Vehicle fuel

The utilisation of biogas as vehicle fuel uses the same engine and vehicle configuration as natural gas. In total there are more than 1 million natural gas vehicles all over the world, this demonstrates that the vehicle configuration is not a problem for use of biogas as vehicle fuel. However, the gas quality demands are strict. With respect to these demands the raw biogas from a digester or a landfill has to be upgraded. Through upgrading we obtain a gas which:

- has a higher calorific value in order to reach longer driving distances,
- has a regular/constant gas quality to obtain safe driving,
- does not enhance corrosion due to high levels of hydrogen sulphide, ammonia and water,
- does not contain mechanically damaging particles,
- does not give ice-clogging due to a high water content,
- has a declared and assured quality.

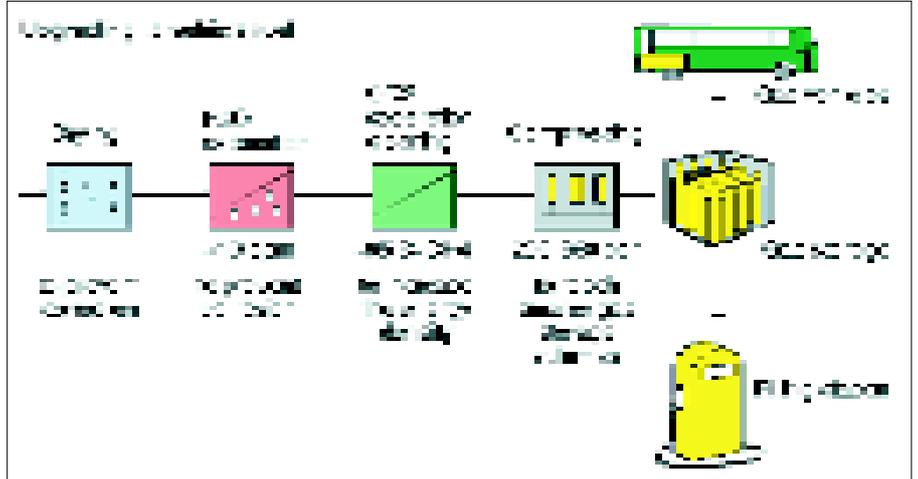
In practice this means that carbon dioxide, hydrogen sulphide, ammonia, partic-

les and water (and sometimes other trace components) have to be removed so that the product gas for vehicle fuel use has a methane content above 95 vol%. In different countries different quality specifications for vehicle fuel use of biogas and natural gas are applied.

Upgraded biogas is actually the cleanest vehicle fuel possible with respect to environment, climate and human health. A 1995 Swedish report on alternative fuels classified biogas on top long before bio-based methanol and ethanol (resp. their tertiary butylesters) as well as rapemethylester (RME). In 1998 two Swiss studies confirmed the Swedish findings. Different methods of environmental rating gave natural gas a 75 % over all advantage over diesel and a 50 % advantage over petrol. Human toxicity gave a 70 % lower value, the ozone potential was reduced by 60 to 80 %, acid formation by more than 50 %. Parallel monitoring of comparable car engines fueled with either petrol, diesel or natural gas in a town cycle (EU standard) demonstrated a reduced NO_x emission for gas of 57 % resp. 88 % when compared to petrol resp. diesel, a 96 % reduction of the ozone potential and virtually no emission of cancerogenic compounds. Non-methanogenic hydrocarbon emission was reduced by 73 %. Only the methane emission was increased with the gas fueled engines which reduced the advantage of green house gas emission to 25 %.

Fuel cells

Fuel cells (FC) are power generating systems that produce DC electricity by combining fuel and oxygen (from the air)



The four steps of biogas upgrading to vehicle fuel.

in an electrochemical reaction. There is no intermediate process which first converts fuel into mechanical energy and heat. Therefore fuel cells have extremely low emissions. The reaction is similar to a battery however, fuel cells do not store the energy with chemicals internally.

In a first step the fuel is transformed into hydrogen either by a catalytic steam reforming conversion or by a (platinum) catalyst. The H₂ is converted to direct electrical current. The by-products of the reaction are water and CO₂.

Conversion efficiency to electricity is expected to exceed 50 %. FC's demonstrate relatively constant efficiencies over a wide range of loads. There are five types of fuel cells, classified by the type of electrolyte: Alkaline (AFC), Phosphoric Acid (PAFC), Molten Carbonate (MCFC), Solid Oxide (SOFC) and Proton Exchange Membrane (PEM) fuel cells.

Alkaline fuel cell technology is used extensively in NASA's space shuttle program but is more difficult to use for terrestrial applications because of its intolerance to carbon oxides.

Different methods of environmental rating gave natural gas a 75% over all advantage over diesel and a 50% advantage over petrol.

Quality demands in different countries for utilisation of biogas as vehicle fuel

	Unit	France ¹⁾	Switzerland ¹⁾	Sweden
Wobbe index _{lower}	MJ/nm ³			45,5
Wobbe index _{upper}	MJ/nm ³			48,2
Water dewpoint	°C		5° lower than the lowest ambient temperature	
Energy content upper	kWh/nm ³	10.7		
Water content, maximum	mg/nm ³	100	5	32
Methane minimum	vol%		96	97
Carbon dioxide, maximum	vol%			3
Oxygen, maximum	vol%	3.5	0.5	1
Carbon dioxide, + oxygen + nitrogen, maximum	vol%	3	3	3
Hydrogen, maximum	vol%			0,5
Hydrogen sulphide, maximum	mg/nm ³	7	5	23
Total sulphure	mg/nm ³		14.3	
Particles or other solid contaminants, max. diameter	mm			5
Halogenated hydrocarbons	mg/m ³	1	0	

¹⁾ Basically there are no specific requirements for fuel gas. The requirements are valuable for biogas introduction into the grid from where it is also used for fuel gas. In Switzerland the gas quality corresponds to natural gas quality type H.

All the other technologies could be applied with upgraded biogas.

Currently, **phosphoric acid fuel cells** are the only commercialised technology. Utility-scale PACF have been in operation since 1983. A number of power plants in the 200 kW to 2 MW range are operated in Japan and the USA. A 200 kW plant is also running in Switzerland. The largest unit of 11 MW is operated by the Tokyo Electric Power Company. The practical electric efficiency is 41 %.

A number of PAFCs have been installed on water treatment plants, such as Portland, USA. A feasibility study has shown

that a PACF can be operated on biogas without CO₂ removal however, with careful cleaning of halogens and hydrogen sulphide.

Molten-Carbonate Fuel Cells are a type of direct fuel cell that eliminate external fuel processors. Methane (from natural gas) and steam are converted into hydrogen-rich gas in the reforming anode which is part of the fuel cell stack. MCFC pilot plants have demonstrated up to 50 % electric efficiency. They can operate from 25 up to 125 % of the nominal plant design. They are far more compact than PAFC's.

At the end of 1999 a first demonstration project of an MCFC using digester gas as a fuel will be completed near Seattle at the King County's waste water treatment plant.

Solid Oxide Electrolyte Fuel Cells

usually are utilising doped zirconia or yttrium as the electrolyte. It operates at atmospheric pressure or slight overpressure at temperatures above 900°C.

There are several features of SOFC that make the technology attractive: One is the high tolerance to fuel contaminant and two, the high temperature does not require expensive catalyst and permits direct fuel processing.

Sulzer Hexis has developed a ZrO₂-Ceramic fuel cell. One of two test stacks of 1 kW electrical power has over 10.000 hours of operation with H₂. 10 pilot plants of 2 kW are in operation at potential clients. With an expected electric efficiency of 40 % and low emissions, they are thought to have a role as heat and power plants in living areas.

Proton Exchange Membrane Fuel Cells are the most compact technology and

Types of fuel cells

Fuel Cell and Characteristics	PAFC	MFC	SOFC	PEM
Electrolyte	Phosphoric Acid H ₃ PO ₄	Molten Carbonate LiKCO ₃	Solid Oxide Y ₂ O ₃ and ZrO ₂	Membranes
Operating Temperature	200°C	650°C	1000°C	50-120°C
System Efficiency (%)	40-45%	50-57%	45-50%	
Module Size	200 kW-2 MW	2 MW	3-100 kW	
Fuel type	Natural, coal or landfill gas, etc.			Gases MeOH
Commercial Availability	now	1999	2001	2004

the only ones which operate at temperatures below boiling point of water.

They are therefore particularly interesting for vehicles. All the major car industries are heavily investing in the development of the PEMFC technology. Two major improvements made the success possible:

One, the amount of the platinum catalyst could be reduced by a factor of 30 and two, new membranes are boosting PEM performance at lower cost.

Gazelle, a 200 kW natural gas operated phosphoric acid fuel cell has been in operation since 1995 with an electric efficiency of 41 %.



Gas upgrading technologies



Water scrubbing of carbon dioxide and hydrogen sulphide is often applied in Sweden, France and the U.S.A. The process is especially simple and usefull in sewage and industrial waste water treatment plants where the water does not have to be regenerated and recycled. The picture shows the Renton plant (Seattle, U.S.A.) with a capacity of 4.000 nm³ per day.

A number of gas upgrading technologies have been developed for the treatment of natural gas, town gas, sewage gas, landfill gas etc. However, not all of them are recommended for the application with biogas because of price and/or environmental concerns.

Carbon dioxide removal

For an effective use of biogas as vehicle fuel it has to be enriched in methane. This is primarily achieved by carbon dioxide removal which then enhances the energy value of the gas to give longer

driving distances with a fixed gas storage volume. Removal of carbon dioxide also provides a consistent gas quality with respect to energy value. The latter is regarded to be of great importance from the vehicle manufacturers in order to reach low emissions of nitrogen oxide. At present four different methods are used commercially for removal of carbon dioxide from biogas either to reach vehicle fuel standard or to reach natural gas quality for injection to the natural gas grid.

These methods are:

- water absorption,
- Polyethylene glycol absorption,
- carbon molecular sieves,
- membrane separation.

Below the methods are described in more detail.

Water scrubbing

Water scrubbing is used to remove carbon dioxide but also hydrogen sulphide from biogas since these gases are more soluble in water than methane. The absorption process is purely physical. Usually the biogas is pressurised and fed to the bottom of a packed column where water is fed on the top and so the absorption process is operated counter-currently.

Water scrubbing can also be used for selective removal of hydrogen sulphide since hydrogen sulphide is more soluble than carbon dioxide in water. The water which exits the column with absorbed carbon dioxide and/or hydrogen sulphide can be regenerated and recirculated back to the absorption column. The regeneration is made by de-pressurising or by stripping with air in a similar column. Stripping with air is not recommended when high levels of hydrogen sulphide are handled since the water will soon be contaminated with elementary sulphur which causes operational

problems. The most cost efficient method is not to recirculate the water if cheap water can be used, for example, outlet water from a sewage treatment plant.

Polyethylene glycol scrubbing

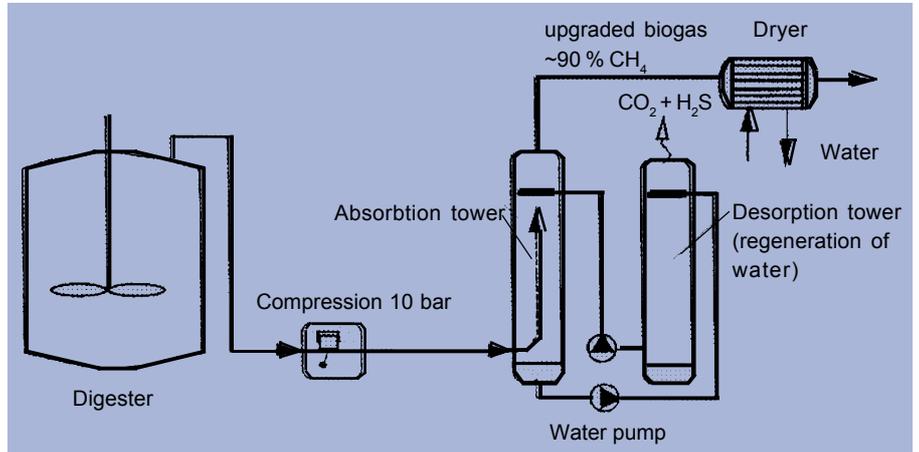
Polyethylene glycol scrubbing is like water scrubbing a physical absorption process. Selexol is one of the trade names used for a solvent. In this solvent, like in water, both carbon dioxide and hydrogen sulphide are more soluble than methane. The big difference between water and Selexol is that carbon dioxide and hydrogen sulphide are more soluble in Selexol which results in a lower solvent demand and reduced pumping. In addition, water and halogenated hydrocarbons (contaminants in biogas from landfills) are removed when scrubbing biogas with Selexol.

Selexol scrubbing is always designed with recirculation. Due to formation of elementary sulphur stripping the Selexol solvent with air is not recommended but with steam or inert gas (upgraded biogas or natural gas). Removing hydrogen sulphide on beforehand is an alternative.

Carbon molecular sieves

Molecular sieves are excellent products to separate specifically a number of different gaseous compounds in biogas. Thereby the molecules are usually loosely adsorbed in the cavities of the carbon sieve but not irreversibly bound. The selectivity of adsorption is achieved by different mesh sizes and/or application of different gas pressures.

When the pressure is released the compounds extracted from the biogas are desorbed. The process is therefore often called “pressure swing adsorption” (PSA). To enrich methane from biogas the molecular sieve is applied which is



Schematic flow sheet for water absorption with recirculation for removal of carbon dioxide and/or hydrogen sulphide from biogas.

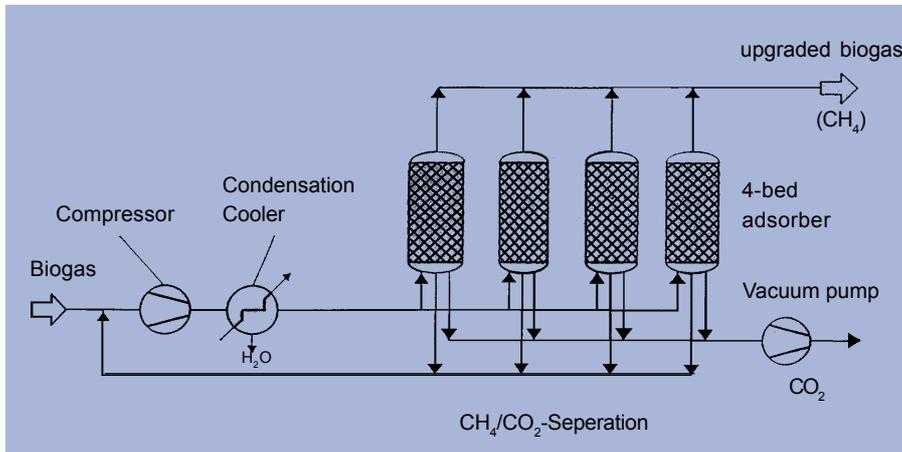
produced from coke rich in pores in the micrometer range. The pores are then further reduced by cracking of the hydrocarbons.

In order to reduce the energy consumption for gas compression, a series of vessels are linked together. The gas pressure released from one vessel is subsequently used by the others. Usually four vessels in a row are used filled with molecular sieve which removes at the same time CO₂ and water vapour.

After removal of hydrogen sulphide, i.e. using activated carbon and water condensation in a cooler at 4°C, the biogas flows at a pressure of 6 bars into the adsorption unit. The first column cleans the raw gas at 6 bar to an upgraded biogas with a vapour pressure of less than

Pressure swing adsorption of biogas on activated carbon with removal of H₂S (right), halogenated hydrocarbons (middle) and 4-bed CO₂ adsorption (left).





Schematic flow sheet for upgrading of biogas to vehicle fuel standards with carbon molecular sieves.

10 ppm H₂O and a methane content of 96 % or more.

In the second column the pressure of 6 bar is first released to approx. 3 bar by pressure communication with column 4, which was previously degassed by a slight vacuum. In a second step the pressure is then reduced to atmospheric pressure. The released gas flows back to the digester in order to recover the methane. The third column is evacuated from 1 bar to 0.1 bar. The desorbed gas consists predominantly of carbon dioxide but also some methane and is therefore normally released to the environment. In order to reduce methane losses the system can be designed with recirculation of the desorbed gases.

The product gas of column 1 is monitored continuously for CH₄ by an infrared analyser. If the required Wobbe index is not maintained the gas flows back to PSA. If the methane content is high enough, the gas is either introduced into the natural gas net or compressed in a 3 stage compressor up to 250 bar. Continuous monitoring of a small-scale installation (26 m³/hr) demonstrated excellent results of gas cleaning, energy efficiency and cost.

First experiences have shown that the high pressure gas separation membranes can last up to 3 years which is comparable to the lifetime of membranes for natural gas purification.

Membranes

There are two basic systems of gas purification with membranes: a high pressure gas separation with gas phases on both sides of the membrane, and a low-pressure gas liquid absorption separation where a liquid absorbs the molecules diffusing through the membrane.

High pressure gas separation

Pressurised gas (36 bar) is first cleaned over for example an activated carbon bed to remove (halogenated) hydrocarbons and hydrogen sulphide from the raw gas as well as oil vapour from the compressors. The carbon bed is followed by a particle filter and a heater. The membranes made of acetate-cellulose separate small polar molecules such as carbon dioxide, moisture and the remaining hydrogen sulphide. These membranes are not effective in separating nitrogen from methane. The raw gas is upgraded in 3 stages to a clean gas with 96 % methane or more. The waste gas from the first two stages is recycled and the methane can be recovered. The waste gas from stage 3 (and in part of stage 2) is flared or used in a steam boiler as it still contains 10 to 20 % methane.

First experiences have shown that the membranes can last up to 3 years which is comparable to the lifetime of membranes for natural gas purification - a primary market for membrane technology - which last typically two to five years. After 1½ years permeability has decreased by 30 % due to compaction. The clean gas is further compressed up to 3.600 psi (250 bar) and stored in steel cylinders in capacities of 276 m³ divided in high, medium and low pressure banks.

The membranes are very specific for given molecules, i.e. H₂S and CO₂ are se-

parated in different modules. The utilisation of hollow-fibre membranes allows the construction of very compact modules working in cross flow.

Gas-liquid absorption membranes

Gas-liquid absorption using membranes is a separation technique which was developed for biogas upgrading only recently. The essential element is a microporous hydrophobic membrane separating the gaseous from the liquid phase. The molecules from the gas stream, flowing in one direction, which are able to diffuse through the membrane will be absorbed on the other side by the liquid flowing in counter current. The absorption membranes work at approx. atmospheric pressure (1 bar) which allows low-cost construction.

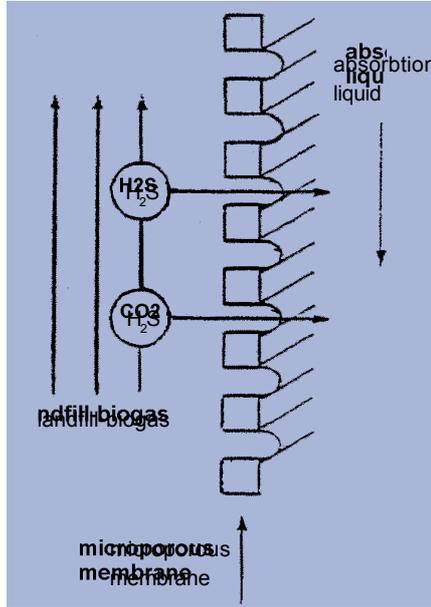
The removal of gaseous components is very efficient. At a temperature of 25 to 35°C the H₂S concentration in the raw gas of 2 % is reduced to less than 250 ppm. The absorbent is either Coral or NaOH.

H₂S saturated NaOH can be used in water treatment to remove heavy metals. The H₂S in Coral can be removed by heating. The concentrated H₂S is fed into a Claus reaction or oxidised to elementary sulphur. The Coral solution can then be recycled.

CO₂ is removed by an amine solution. The biogas is upgraded very efficiently from 55% CH₄ (43 % CO₂) to more than 96% CH₄. The amine solution is regenerated by heating. The CO₂ released is pure and can be sold for industrial applications.

Hydrogen sulphide removal

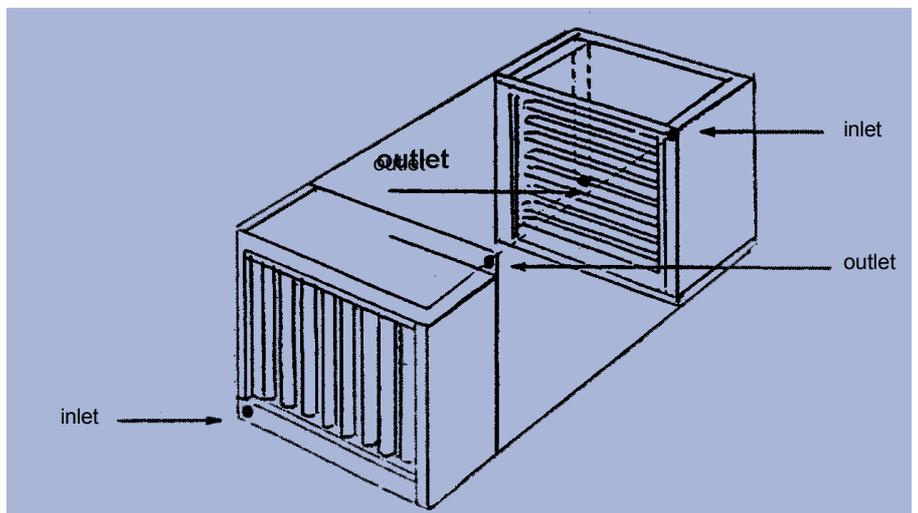
Hydrogen sulphide is always present in biogas, although concentrations vary with the feedstock. It has to be removed



Gas-liquid absorption using hydrophobic membranes is a recent development working at atmospheric pressures which allows a low-cost construction.

in order to avoid corrosion in compressors, gas storage tanks and engines. Hydrogen sulphide is extremely reactive with most metals and the reactivity is enhanced by concentration and pressure, the presence of water and elevated temperatures. Due to the potential problems hydrogen sulphide can cause, it is recommended to remove it early in the process of biogas upgrading. Experience has also shown that two of the

The cross-flow gas absorption membrane is particularly well adapted for the removal of H₂S with NaOH or coral as an absorbant. The latter can be regenerated.



The simplest method of desulphurisation is the addition of air into a storage tank serving at the same time as gas holder. Microorganisms reduce the H_2S concentration by 95 % to less than 50 ppm.

most commonly used methods for hydrogen sulphide removal are internal to the digestion process: 1) air/oxygen dosing to digester biogas and 2) iron chloride dosing to digester slurry. The most common commercial methods for hydrogen sulphide removal are described below:

- air/oxygen dosing to digester biogas,
- iron chloride dosing to digester slurry,
- iron sponge,
- iron oxide pellets,
- activated carbon,
- water scrubbing,
- NaOH scrubbing,
- biological removal on a filter bed,
- air stripping and recovery.

Biological desulphurisation

Desulphurisation of biogas can be performed by micro-organisms. Most of the sulphide oxidising micro-organisms belong to the family of Thiobacillus. Most

Addition of 2 to 6 % of air to the biogas allows the indigenous Thiobacilli to oxidise the H_2S to natural sulfure adhering to the digester surface or the digestate.



of them are autotrophic i. e. they are using carbon dioxide from the biogas to cover their carbon need. The products formed are predominantly elementary sulphur but also sulphate. The latter forms in solutions sulphuric acid which may cause corrosion.

For the microbiological oxidation of sulphide it is essential to add stoichiometric amounts of oxygen to the biogas. Depending on the concentration of hydrogen sulphide this corresponds to 2 to 6 % air in biogas.

Air/oxygen dosing to digester biogas.

The simplest method of desulphurisation is the addition of oxygen or air directly into the digester or in a storage tank serving at the same time as gas holder. Thiobacilli are ubiquitous and thus systems do not require inoculation. They grow on the surface of the digestate, which offers the necessary micro-aerophilic surface and at the same time the necessary nutrients. They form yellow clusters of sulphure. Depending on the temperature, the reaction time, the amount and place of the air added the hydrogen sulphide concentration can be reduced by 95 % to less than 50 ppm. Measures of safety have to be taken to avoid overdosing of air in case of pump failures. Biogas in air is explosive in the range of 6 to 12 %, depending on the methane content). In steel digesters without rust protection there is a small risk of corrosion at the gas/liquid interface.

Biological filters

In large digesters there is often a combined procedure of water scrubbing (absorption) and biological desulphurisation applied. Either raw waste water or press-separated liquor from digestate is dispensed over a filter bed. In the bed, liquor and biogas meet in counterflow manner. In the biogas 4 to 6 % air is added before entering the filter bed. The filter bed offers the required surface for scrubbing as well as for the attachment of the desulphurisation micro-organisms.

The system is applied in several installations for industrial waste water treatment and in many of the Danish agricultural and co-digestion plants.

Iron chloride dosing to digester slurry

Iron chloride can be fed directly to the digester slurry or to the feed substrate in a pre-storage tank. Iron chloride then reacts with produced hydrogen sulphide and form iron sulphide salt (particles). This method is extremely effective in reducing high hydrogen sulphide levels but less effective in attaining a low and stable level of hydrogen sulphide in the range of vehicle fuel demands. In this respect the method with iron chloride dosing to digester slurry can only be regarded as a partial removal process in order to avoid corrosion in the rest of the upgrading process equipment. The method need to be complemented with a final removal down to about 10 ppm.

The investment cost for such a removal process is limited since the only investment needed are a storage tank for iron chloride solution and a dosing pump. On the other hand the operational cost will be high due to the prime cost for iron chloride.

Iron oxide

Hydrogen sulphide reacts easily with iron hydroxides or oxides to iron sulphide. The reaction is slightly endothermic, a temperature minimum of approximately 12°C is therefore required to provide the necessary energy. The reaction is optimal between 25 and 50°C. Since the reaction with iron oxide needs water the biogas should not be too dry. However, condensation should be avoided because the iron oxide material (pellets, grains etc.) will stick together with water which reduces the reactive surface.

The iron sulphides formed can be oxidised with air, i. e. the iron oxide is recovered. The product is again iron oxide or hydroxide and elementary sulphur. The process is highly exothermic, i.e. a lot of heat is released during regeneration.

Therefore, there is always a chance that the mass is self-ignited. The elementary sulphur formed remains on the surface and covers the active iron oxide surface. After a number of cycles depending on the hydrogen sulphide concentration the iron oxide or hydroxide bed has to be exchanged.

Usually an installation has two reaction beds. While the first is desulphurising the biogas, the second is regenerated with air.

The desulphurisation process works with plain oil free steel wool covered with rust. However, the binding capacity for sulphide is relatively low due to the low surface area.

Iron oxide wood chips

Wood chips covered with iron oxide have a somewhat larger surface to volume ratio than plain steel. Their surface to weight ratio is excellent thanks to the low density of wood. Roughly 20 grams of hydrogen sulphide can be bound per 100 grams of iron oxide chips.

The application of wood chips is very popular particularly in the USA. It is a low cost product, however, particular care has to be taken that the temperature does not rise too high while regenerating the iron filter.

Iron oxide pellets

The highest surface to volume ratios are achieved with pellets made of red mud, a waste product from aluminium production. However, their density is much higher than that of the wood chips. At hydrogen sulphide concentrations between 1.000 ppm and 4.000 ppm totally 50 grams can be loaded on 100 grams of pellets. Most of the German and Swiss sewage treatment plants without dosing of iron chloride are equipped with an iron oxide pellet installation.

Iron chloride dosing to digester slurry is an extremely efficient method to reduce hydrogen sulphide levels, but does not allow to achieve vehicle fuel demands.

Hydrogen sulphide reacts with iron oxide (rust) to iron sulphide. The latter can be reoxidised with air. The product is again iron oxide and elementary sulphure.

Hydrogen sulphide reacts easily with iron oxide or hydroxide which is usually bound on wood chips or red mud pellets to increase the reaction surface. In a two-column plant one column binds H_2S where as the other is regenerated.



Impregnated activated carbon

With PSA systems H_2S usually is removed by activated carbon doted with potassium iodide (KI). Like in biological filters in presence of air which is added to the biogas, the hydrogen sulfide is catalytically converted to elementary sulphur and water. The sulphur is adsorbed by the activated carbon. The reaction works best at a pressure of 7 to 8 bar and a temperature of 50 to 70°C. The gas temperature is easy to achieve through the heat formed during compression. Usually, the carbon filling is adjusted to an operation time of 4.000 to 8.000 hours. If a continuous process is required the system consists of two vessels. At H_2S concentrations above 3.000 ppm the process is designed as a regenerative system.

Water scrubbing

Water scrubbing is a purely physical absorption process, described above, which can be used for selective removal of hydrogen sulphide. The cost for selective removal has not yet been shown to be competitive with other hydrogen sulphide removal methods. Thus water scrubbing probably only will

be considered for the simultaneous removal of carbon dioxide in order to meet vehicle fuel demands on biogas quality.

Selexol scrubbing

Selexol scrubbing is like water absorption on a purely physical absorption process described above. Selexol is one of the trade names for a solvent mainly constituting of a dimethylether of polyethylene glycol (DMPEG). The cost for selective hydrogen sulphide removal has not yet shown to be competitive and so Selexol scrubbing will probably only be considered for simultaneous removal of carbon dioxide and hydrogen sulphide in order to meet vehicle fuel demands on biogas quality.

Sodium hydroxide scrubbing

Absorption in a water solution of sodium hydroxide (NaOH) enhances the absorption capacity of the water and the absorption process is no longer purely physical but chemical. Sodium hydroxide reacts with hydrogen sulphide to form sodium sulphide or sodium hydrogen sulphide. Both these salts are insoluble and the method is not regenerative. Since the absorption capacity of water is enhanced lower volumes are needed and pumping demands are reduced. The main disadvantage is the disposal of the large volumes of water contaminated with sodium sulphide.

Halogenated hydrocarbon removal

Higher hydrocarbons as well as halogenated (FHC) hydrocarbons, particularly chloro- and fluoro-compounds are predominantly found in landfill gas. They cause corrosion in CHP engines, in the combustion chamber, at spark plugs, valves, cylinder heads, etc. For this reason CHP engine manufacturers claim maximum limits of halogenated hydrocarbons in biogas.

They can be removed by pressurised tube exchangers filled with specific activated carbon. Small molecules like CH_4 , CO_2 , N_2 and O_2 pass through while larger molecules are adsorbed. The size of the exchangers are designed to purify the gas during a period of more than 10 hours. Usually there are two parallel vessels. One is treating the gas while the other is desorbed. Regeneration is carried out by heating the activated carbon to 200°C , a temperature at which all the adsorbed compounds are evaporated and removed by a flow of inert gas.

Siloxane removal

Organic silicon compounds are occasionally present in biogas which can cause severe damage to CHP engines. During incineration they are oxidised to silicon oxide which deposits at spark plugs, valves and cylinder heads abrading the surfaces and eventually causing serious damage. Particularly in Otto engines this might lead to major repairs. Dual fuel engines are less susceptible because the temperature of the entire motor body is much higher than with Otto engines.

Because of the increased wearing of combustion chambers caused by silica deposits nowadays manufacturers of

CHP engines claim maximum limits of siloxanes in biogas.

It is known that the organic silicon compounds in biogas is in the form of linear and cyclic methyl siloxanes.

These compounds are widely used in cosmetics and pharmaceutical products, and as anti-foaming agents in detergents.

Siloxanes can be removed by absorption in a liquid medium, a mixture of hydrocarbons with a special ability to absorb the silicon compounds. The absorbent is regenerated by heating and desorption. A full scale removal plant for biogas from a landfill is in operation in Dortmund-Huckarde since 1993.

Removal of oxygen and Nitrogen

Oxygen and in part also nitrogen in the biogas is a sign that air has been sucked in. This occurs quite often in landfills where the gas is collected through permeable tubes by applying a slight underpressure. Low concentrations of oxygen is not a problem. Higher concentration however bear a risk of explosion. Biogas with a methane content of 60 %, the rest being predominantly carbon dioxide, is explosive in concentrations between 6 and 12 % in air.

Oxygen and nitrogen can be removed by membranes or low temperature PSA however, removal is expensive. Preventing the introduction of air by carefully monitoring the oxygen concentration is far cheaper and more reliable than gas treatment.

Halogenated hydrocarbons predominantly found in landfill gas cause corrosion in CHP engines. They have to be removed by specific activated carbon.

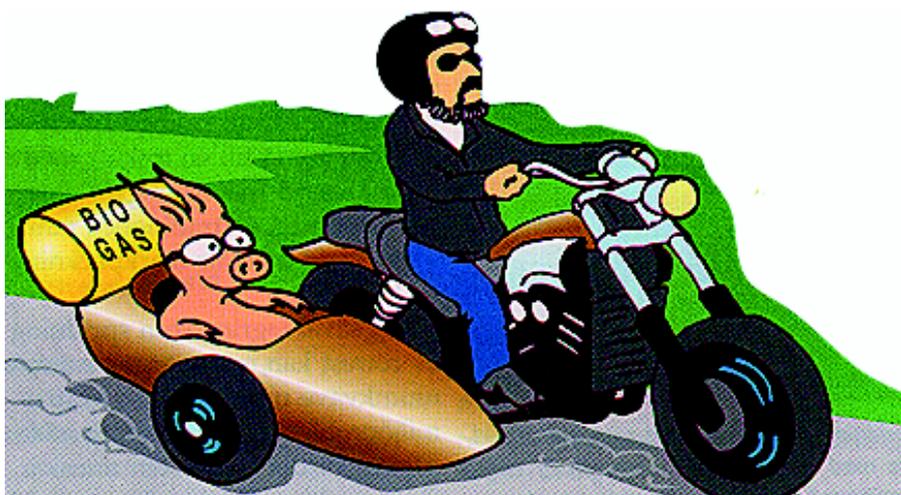
Organic silicon compounds are occasionally present in biogas. They are used in cosmetics, pharmaceutical products and detergents. They can be removed by liquid hydrocarbons.

List of selected reference plants with full gas

Country	City	Product gas utilisation gas grid or vehicle fuel	Biogas Production (landfill/ sewage sludge/waste/ manure)	CH ₄ Requirement %	CO ₂ - removal (technique)	H ₂ S- removal (technique)	Raw gas flow	In operation since
Czech Rep.	Bystrany/ Teplice	Vehicle fuel	Sewage sludge	95	Water scrub.	Water scrub.	368	1985
	Bystrica	Vehicle fuel	Sewage sludge	95	Water scrub.	Water scrub.	186	1990
	Chanov/Most	Vehicle fuel	Sewage sludge	95	Water scrub.	Water scrub.	186	1990
	Liberec	Vehicle fuel	Sewage sludge	95	Water scrub.	Water scrub.	368	1988
	Zlin/Tecovice	Vehicle fuel	Sewage sludge	95	Water scrub.	Water scrub.	186	1990
France	Chambéry	Vehicle fuel	Sewage sludge	96,7	Water scrub.	Biol. filter/ water scrub.	30	
	Lille	Vehicle fuel	Sewage sludge		Water scrub.	Water scrub.	100	1995
	Tours	Vehicle fuel	Landfill		Water scrub.	Water scrub.	200	1994
The Netherlands	Collendorn	Natural gas	Landfill	88	Membranes	Activated carbon	375	1991
	Gorredijk	Natural gas	Landfill	88	Membranes	Activated carbon	400	1994
	Nuenen	Natural gas	Landfill	88	Carbon molecular sieves	Activated carbon	1 500	1990
	Tilburg	Natural gas	Sewage sludge Landfill	88	Water scrub.	Iron oxide pellets	2 100	1987
	Wijster	Natural gas	Green waste Landfill	88	Carbon molecular sieves	Activated carbon	1 150	1989
New Zealand	Christchurch	Vehicle fuel			Water scrub.			
Sweden	Eslöv	Vehicle fuel	Sewage sludge	97	Water scrub.	Water scrub.	40	1998
	Göteborg	Vehicle fuel	Vegetable waste Sewage sludge	97	Carbon molecular sieves	Activated carbon	6	1992
	Helsingborg	Vehicle fuel	Slaughterhouse waste	97	Carbon molecular sieves	Activated carbon	16	1996
	Kalmar	Vehicle fuel	Sewage sludge + manure + slaughterhouse waste	97	Water scrub.	Water scrub.	30	1998
	Linköping	Vehicle fuel	Sewage sludge + manure + slaughterhouse waste	97	Water scrub.	Iron chloride dosing + water scrub	700	1997
		Vehicle fuel			Carbon molecular sieves		200	1991
	Stockholm Trollhättan	Vehicle fuel	Sewage sludge	97	Water scrub.	Water scrub.	45	1997
Vehicle fuel	Sewage sludge + fish waste	97	Water scrub.	Water scrub.	200	1996		

upgrading to natural gas/vehicle fuel standards

Country	City	Product gas utilisation gas grid or vehicle fuel	Biogas Production (landfill/ sew. sludge/waste/ manure)	CH ₄ Requirement %	CO ₂ - removal (technique)	H ₂ S- removal (technique)	Raw gas flow	In operation since
Sweden	Uppsala	Vehicle fuel	Sewage sludge + manure	97	Water scrub.	Water scrub.	200	1997
Switzerland	Bachenbülach	Vehicle fuel	Biowaste	96	Carbon molecular sieves	Activated carbon		
	Otelfingen	Vehicle fuel	Biowaste	96	Carbon molecular sieves	Activated carbon		
	Rümlang	Vehicle fuel	Biowaste	96	Carbon molecular sieves	Activated carbon		
	Samstagern	Natural gas	Biowaste	96	Carbon molecular sieves	Activated carbon		
USA	Croton landfill, Westchester Co. (NY)	Vehicle fuel	Landfill	90	Selexol scrubbing	Selexol scrubbing	120	1993 (reused from Tork Landfill Wisc. 1996)
	Fresh Kills, Staten Island (NY)	Natural gas	Landfill		Selexol scrubbing	Selexol scrubbing	13 000	1981
	Puente Hill Landfill, Los Angeles (CA)	Vehicle fuel	Landfill	96	Membranes	Activated carbon	2 600	1993
	Renton (WA) Mc Carty Road (NY)	Natural gas Natural gas	Sewage sludge Landfill	98	Water scrub. Selexol scrubbing	Water scrub. Selexol scrubbing	4 000 9 400	1984 + 1998 1986



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Task 24: Energy from biological conversion of organic waste

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