

Chapter 4

Biogas Technology – Controlled Gas Flow for Enhanced Mixing, Heating, and Desulfurization

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Abstract History and current use of biogas utilization demonstrates that with simple approaches useful methane can be produced. From experience with small-scale plants, a new 4-chamber technology named BIO4GAS was developed that allows production of biogas in reactors that do not require mechanical stirring. On the basis of data from a demonstration plant set in operation in 2008, the 4-chamber technology and its advantages are described in detail. In particular, the low operational energy requirement and the high quality of the obtained biogas (in terms of low H₂S levels) are emphasized.

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4.1 Historical Developments

4.1.1 Europe

Plinius, always a good source for first reports on natural phenomena, noted the appearance of flickering lights emerging from below the surface of swamps and Van Helmont recorded the emanation of an inflammable gas from decaying organic matter in the 17th century (van Brakel 1980). Volta is generally recognized to have first isolated methane. He concluded as early as 1776 that the amount of gas that evolves is a function of the amount of decaying vegetation. In 1894, Gayon, a student of Pasteur, fermented manure at 35°C and obtained 100 L of methane per m³ of manure. Toward the end of the 19th century, methanogenesis was found to be connected to microbial activity. Béchamp (1868) named the “organism” – apparently, a mixed community – responsible for methane production from ethanol. In 1876, Herter reported that acetate in sewage sludge was converted stoichiometrically to equal amounts of methane and carbon dioxide (cited from Zehnder et al. 1982). As early as 1896, gas from sewage was used for lighting streets in Exeter, England. Then, in 1904, Travis put into operation a new, two-stage process, in which the suspended material was separated from the wastewater, and was allowed to pass into a separate “hydrolyzing” chamber. Söhngen (1906) was able to enrich two distinct acetate utilizing bacteria, and he found that formate, hydrogen and carbon dioxide could be precursors for methane. Buswell and co-workers identified anaerobic bacteria and investigated the conditions that promote methanogenesis. Research focused also on the fate of nitrogen in anaerobic digestion, the stoichiometry of the reaction and the production of energy from farm and industrial wastes (Buswell and Neave 1930; Buswell and Hatfield 1936). Barker and his group performed basic biochemical studies of methanogenic archaea (then methane bacteria) and contributed significantly to the field (e.g., Pine and Barker 1956).

In Europe, biogas use has been promoted in several campaigns since the 1970s, and currently experiences a new boom. In particular, if national policies support the production of biogas by subsidies, considerable increases in plant numbers are observed. The approach, however, was often focused on agro-industrial use of energy crops in large plants and technologically sophisticated constructions. This often led to problems in terms of cost/benefit imbalances. Johansson and Azar (2007) have further shown that renewable bioenergy production based on specialized agricultural crop production will compete with the food production sector and lead to exploding food prices. This is of major concern, particularly in the less developed countries.

4.1.2 Asia

The use of biogas has a long history in Asia and dates back many centuries. There is evidence that biogas was used for heating bath water in Assyria during the tenth century BC. Marco Polo mentions the use of covered sewage tanks, a practice that

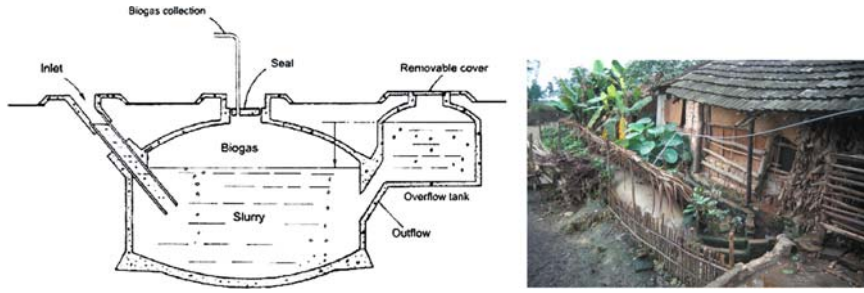


Fig. 4.1 Scheme of Chinese dome digester (*left*) and view of a small-scale manure digester in Vietnam (*right*; Foto: E. Schreckensperger)

probably goes back 2,000–3,000 years in ancient China (Chawla, 1986). India has also a quite long history of biogas development. The first unit, usually referred to in literature, is a biogas unit at a lepers asylum near Mumbai installed in 1859. The primary function seems to have been sewage treatment, but the gas was used for lighting. In China, by the end of the 19th century, simple biogas digesters had appeared in the coastal areas of southern China. Guorui invented and built an 8-m³ biogas tank in the 1920s which formed the basis for the establishment of a successful company. *Chinese Guorui Biogas Digester Practical Lecture Notes* was published in 1935, the first monograph on biogas in China and in the world. This was the first wave of biogas use in China. The second wave of biogas use in China originated in Wuchang in 1958 in a campaign to exploit the multiple functions of biogas production, which simultaneously solved the problems of manure disposal and improvement of hygiene. The third wave of biogas use occurred between the late 1970s and early 1980s when the Chinese government enforced biogas production as an effective use of natural resources in rural areas. Biogas production was considered not only to provide energy, but also to contribute to environmental protection and improvement of hygiene. Some six million digesters were set up in China, and the “China dome” digester became the standard construction, which is followed to the present day (Fig. 4.1) for small-scale domestic use. China’s *2003–2010 National Rural Biogas Construction Plan* is aimed at increasing the biogas use by a total of 50 million small-scale plants by 2010, which is 35% of all farm households.

4.1.3 Numerical Tools and Current Technologies

In parallel to the progress in biogas technology, numerical tools have been developed to analyze, understand, and simulate processes catalyzed by anaerobic microorganisms. Anaerobic digestion is a multi-step degradation process in which metabolites are transferred from one functional group of microbes to the other.

In the late 1960s and 1970s, first attempts in biokinetic modeling of anaerobic digestion processes focused on the rate-limiting process step (e.g., O'Rourke 1968; Graef and Andrews 1974; Lyberatos and Skiadas 1999) which needs to be defined for specific process conditions and substrates. Subsequently, more complex models have been developed in order to describe the digester behavior and inhibit the impacts by unionized volatile fatty acids (VFA), -acetate and -ammonia (e.g., Hill and Barth 1977; Moletta et al. 1986). The inclusion of hydrogen partial pressure as a key process parameter (Mosey 1983; Costello et al. 1991) contributed to the interactive process. Additional improvements (e.g., Angelidaki et al. 1993; Siegrist et al. 1993) led to the development of IWA's widely acknowledged Anaerobic Digestion Model ADM1 (Batstone et al. 2002a). It represents a generic description of digestion processes for various substrates like sewage sludge and manure, and considers seven functional groups of microbes (in total, more than 30 state variables) and employs more than 100 parameters (Fig. 4.2). The only nutrient that is balanced by ADM1 is nitrogen which is released as ammonia from degraded organic matter (Wett et al. 2006). Recent knowledge on methanogenesis and the involved microbiota is summarized in Chaps. 1 and 3 (Insam et al. 2010; Braun et al. 2010).

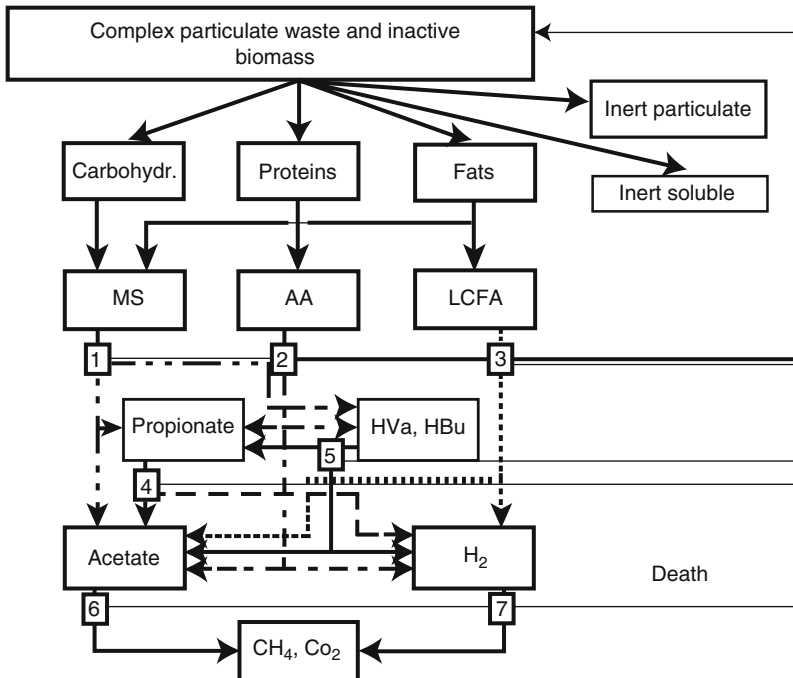


Fig. 4.2 The Anaerobic Digestion Model ADM1 considers seven groups of organisms which catalyze the following biochemical processes: (1) acidogenesis from sugars, (2) acidogenesis from amino acids, (3) acetogenesis from LCFA, (4) acetogenesis from propionate, (5) acetogenesis from butyrate and valerate, (6) aceticlastic methanogenesis, and (7) hydrogenotrophic methanogenesis (Batstone et al. 2002b)

4.2 The BIO4GAS-Approach

4.2.1 *The Development of an Idea*

To summarize the historical development of biogas technology till date, basically two systems of agricultural biogas plants have been established which differ significantly in size, application, and in terms of safety and general technological standards:

- Huge number of small-scale plants in developing countries for cooking gas production (energy self-sufficient households)
- Agro-industrial plants for electrical power generation (typically, >100 kW) based mainly on energy crops (renewable energy production)

The range of biogas plants between these two basic types has often been seen as economically not feasible while latest funding programs in Central Europe target smaller plants based mainly on manure as substrate. In an attempt to design a small-scale reactor for the use of agricultural wastes, in particular liquid manure, a new reactor type and mixing system called BIO4-GAS technology evolved (Wett et al. 2007). The driving factors are as given below.

1. it is known that biogas production based on agricultural and other wastes is the approach with the best performance in terms of mitigation of greenhouse gas emissions. Therefore, the size of the BIO4GAS plants should fit the size of a wide range of farms
2. often, individual planning of biogas plants makes them too costly in terms of construction and maintenance; our aim was to develop a reactor that works without any electromechanical parts inside and to reduce the construction costs by a standardized or serial implementation

The 4-chamber design was derived from a biogas plant that has been in operation since 40 years at a farm in Buch (Tyrol, Austria) (Wackerle 2005). The layout is now formed by two concentric cylinders (Fig. 4.3). The inner cylinder and the outer ring contain two chambers, each separated by baffles. During operation the substrate is pumped to chamber 1 (K1) and biogas production starts, mainly in chamber 1. Since the construction is gas-tight, gas pressure of the head space of chamber 1 displaces the liquid manure below the baffle to K2 and drives a gas-lift in K2. The gas lift also serves as a pipe-heat-exchanger for heating the reactor. The chamber K1 is also heated and mixed by a thermo-gas-lift which is driven by pressurized air injected for the desulfurization of the generated biogas. Deposits in K1 and K2 are avoided by periodical opening of a relief valve causing an oscillation and a concurrent recycle flow between K1 and K2. The determination of the optimal layout was supported by numerical models (Fig. 4.4).

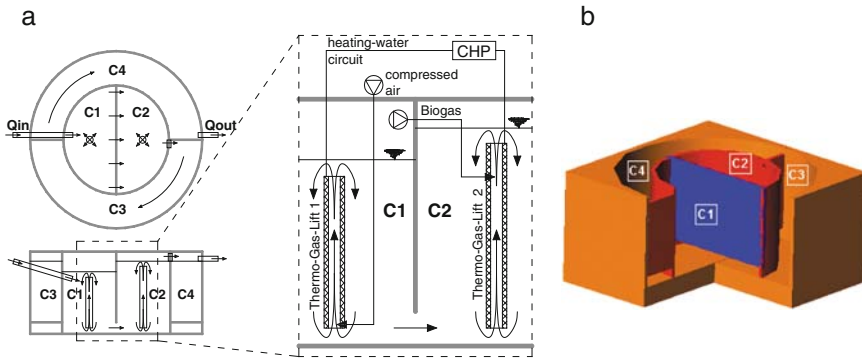


Fig. 4.3 Scheme of the BIO4GAS pilot plant with concentric shape and thermo-gas-lifts employed for heating, mixing, and desulfurization

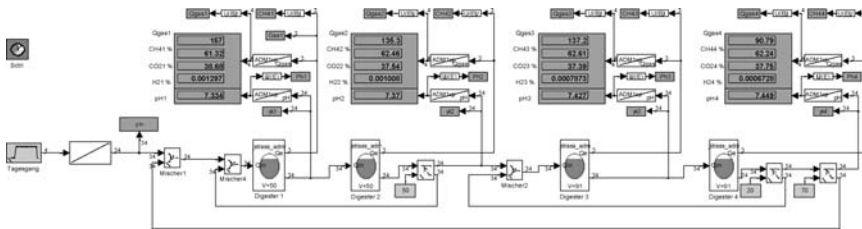


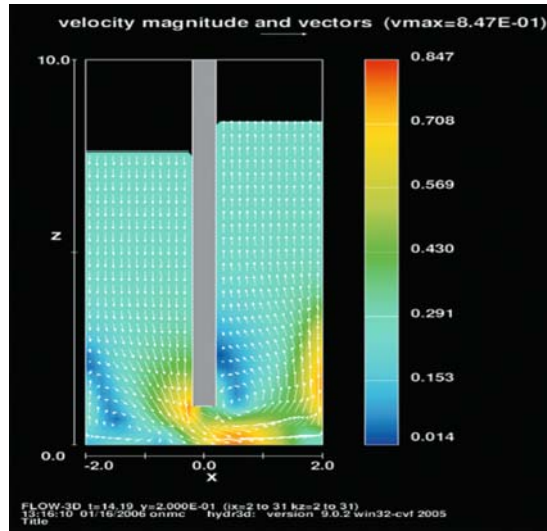
Fig. 4.4 Four-chamber system represented by serial ADM1 digesters, edited in the SIMBA-environment for the simulation of gas production in individual chambers (Wett et al. 2007)

4.2.2 Mixing and Agitation

As described above, the gas pressure is used in a twofold manner to mix the content of the reactor: Chambers K1 and K2 are individually mixed by a vertical flow induced by the thermo-gas-lifts. Rising bubbles of the injected air in K1 and biogas in K2, respectively, and heat convection reduce the density of the water column in the lift pipe, resulting in a moderate but continuous upflow current.

The difference in water level between chamber K1 and K2 represents the pressure head driving the gas-lift. A pneumatic pressure relief valve is used for a sudden equalization of the pressure difference causing an oscillation of the water columns in K1 and K2. The periodic oscillation flow shows velocity peaks at the bottom opening (Fig. 4.5), which mobilizes the occasionally heavy sludge layers. Additionally, the counterflow seeds more mature biomass back to the first chamber. Both the vertical flow from the gas-lifts and from the pressure oscillation provide sufficient turbulence to prevent stratification of the liquor in the reactor. For substrates with severe bulking sludge, an additional stirrer at the water surface for reliable scum destruction is suggested.

Fig. 4.5 CFD-simulation (computational fluid dynamics) of the equalization flow after the pressure relief valve between headspace of chamber K1 and K2 has been opened (colors indicating velocity magnitude and arrows directions of flow)



Several authors (e.g., Vavilin and Angelidaki 2005; Speece et al. 2006) have suggested that high mixing intensity and duration have an adverse effect on the biogas production rates in agricultural biogas plants. The sheering forces are supposed to disrupt the important spatial proximity of volatile fatty acid degrading bacteria and hydrogen-utilizing methanogens. It is generally recognized that syntrophic growth of different bacterial and archaeal species is important, and sheering forces may hamper the necessary biofilm and aggregate formation (e.g., Wu et al. 1996). The BIO4GAS approach attempts to reduce the sheering forces as much as possible, yet ensuring a sufficient substrate mixing.

4.2.3 Heating

Continuous vertical flow through the thermo-gas-lifts ensures an efficient heat transfer via the pipe walls. The actual heating medium is water circulating between the double-walled lift-pipes and the co-generation unit where the biogas is burned. The coupled heat-power system has been installed in a pre-fabricated container module hosting the complete electrical- and safety-equipment. The heat produced is distributed to three consecutive heat cycles at the following steps of hierarchy: Fermenter heating requires about one third of the heat flow and shows highest priority. The next is the external consumer, and only unused excess heat will be eliminated by an emergency cooler at the roof-top of the container. A further advancement means the installation of a boiler for redundant gas conversion, replacing the flare so that even during failure or servicing of the combined heat and power plant (CHP) unit, the thermal energy of the biogas may be used.

Table 4.1 Growth conditions of Thiobacilli

Species	pH [-]	Temperature [°C]
<i>Acidithiobacillus</i>		
<i>A. albertensis, ferrooxidans</i>	2–4	30–35
<i>A. caldus</i>	1–3.5	32–52
<i>A. thiooxidans</i>	2–4	25–30
<i>Halothiobacillus</i>		
<i>H. halophilus</i>	7	30–32
<i>H. hydrothermalis</i>	7.5–8	35–40
<i>H. kellyi</i>	6.5	37–42
<i>H. neapolitanus</i>	6–8	25–30
<i>Thermithiobacillus</i>		
<i>T. tepidarius</i>	6–8	40–45
<i>Thiocalivibrio</i>		
<i>T. denitrificans, nitratus</i>	10	25–30
<i>T. versutus</i>	10–10.2	25–30
<i>Thioalcalimicrobium</i>		
<i>T. aerophilum</i>	9–10	25–30
<i>Thiomicrospira</i>		
<i>T. chilensis</i>	7	32–37
<i>T. crunogena</i>	7–8	28–32
<i>T. frisia</i>	6.5	32–35
<i>T. kuenenii</i>	6	29–33
<i>T. peliphila</i>	6–8	25–30
<i>T. thyasirae</i>	7–8	35–40
<i>Thiobacillus</i>		
<i>T. aquaesulis</i>	7.5–8	40–50
<i>T. denitrificans, thioparus</i>	6–8	25–30
<i>Thiomonas</i>		
<i>T. cuprina</i>	3–4	30–36
<i>T. intermedia, T. perometabolis</i>	5.5–6	30–35
<i>T. thermosulfata</i>	5.2–5.6	50–52.5

Source: Robertson (2004)

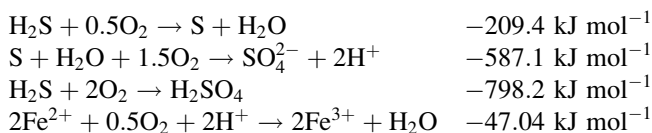
Microorganisms in the digester show a broad range of optimum growth conditions as Table 4.1 exemplifies for Thiobacilli (temperature optima between 25 and 52.5°C). According to Karakashev et al. (2005), the microbial diversity is higher in mesophilic than thermophilic reactors. Diversity, however, does not seem to be related to methane production rates. Pender et al. (2004) compared the microbial communities in mesophilically and thermophilically operated reactors, with and without the addition of sulfate. The reactor biomass sampled during mesophilic operation, both in the presence and absence of sulfate, was characterized by a predominance of *Methanosaeta* spp. In contrast, in the 55°C reactor an archaeon closely related to *Methanocorpusculum parvum* was dominant, when sulfate was added, *Methanobacterium thermoautotrophicum* was dominant and reactor performance decreased. The sensitivity of the acetoclastic methanogens, dominated by *Methanocorpusculum parvum*, demonstrated the fragile nature of this thermophilic ecosystem which was particularly sensitive to sulfide inhibition. An issue that has not yet adequately been addressed is the even temperature distribution within

reactors. Since methanogenesis is usually retarded in the temperature range between 40 and 50°C, a suboptimal temperature range for both mesophilic and thermophilic microorganisms, any reactor design should aim at an even temperature distribution. This is ensured in the BIO4GAS reactor by mixing and heating, accompanied by a good thermal insulation.

4.2.4 Hydrogen Sulfide Oxidation

Anaerobic digestion involves the breakdown of organic matter in an oxygen-free environment. The biogas produced contains, besides methane and carbon dioxide, hydrogen sulfide (H₂S) which is of major concern not only because of odor nuisance, but mainly because of its destructiveness to engines by impacting corrosion and oil viscosity. The concentration of H₂S in the biogas produced from chicken manure and molasses may be as high as 4,000 mg m⁻³. Post-treatment of the biogas could be avoided by oxidation of H₂S in the reactor which can be accomplished or at least reduced by offering good conditions for the growth of sulfur oxidizing bacteria.

Sulfur oxidizing bacteria, also known as Thiobacilli, were reclassified by Kelly and Wood (2000), forming three genera, *Acidithiobacilli*, *Halothiobacilli*, and *Thermothiobacilli*. Besides reduced sulfur compounds as an electron donor, like H₂S, the presence of an electron acceptor like oxygen is necessary. In nature, Thiobacilli grow in the boundary layer of anaerobic sediment and aerobic water body. Many Thiobacilli are obligate or facultative autotrophs, using carbon dioxide as their only C source. A major product of H₂S oxidation is elementary sulfur. The elementary sulfur is precipitated and in biogas plants one can always find yellow sulfur excretions (Fig. 4.6). Besides reduced sulfur compounds, Thiobacilli also oxidize Fe²⁺ and form Fe³⁺, and are thus responsible for metal corrosion (Brock and Gustafson 1976):



Sulfate production, as the second oxidation step, is promoted at excess oxygen conditions (Janssen et al. 2009) and causes acidification and high oxygen demand. Munz et al. (2009) point out that high pH, around 9, represents an even stronger drive for sulfate production. Fuseler et al. (1996) have shown that sulfur is not necessarily a stable intermediate but can be object to disproportionation to sulfate and hydrogen sulfide. Nevertheless moderate oxygenation (ca. 0.05 g O₂ g⁻¹ COD) of anaerobic sludge environments does not lead to significant sulfate production (van der Zee et al. 2007). Obviously, sulfur production is difficult to measure due to its precipitation and attachment to surfaces, and therefore, needs to be estimated



Fig. 4.6 Surface of gas-dome and manhole cover of an agricultural biogas plant coated by precipitated elemental sulfur from biological H_2S oxidation (Foto: F. Wackerle)

from the total S balance gap. Zee et al. demonstrated that sulfide oxidation rates increased during long-term micro-aerobic operation which resulted in very low sulfide concentration in the biogas.

In agricultural biogas plants, desulfurization of the biogas is accomplished mainly in the fermenter gas space. For this purpose, small amounts of air (approximately, 5–10% of the produced biogas) are added. As in all biological processes, the availability of surfaces for bacterial settlement is most important. In the BIO4GAS technology, the admixed air fulfils a double purpose. First, the air is pressed into the reactor at the bottom of the thermo-gas-lift and thus aids the mixing of the substrate by the ascending gas bubbles. And second, majority of the formed biogas is produced in chamber 1, and is forced to move along the subsequent three chambers before it is tapped at the rear end of chamber 4. Thus, the gas has a very long passage way allowing the Thiobacilli to act. The efficiency of H_2S oxidation is demonstrated by an operational data during the start-up period when measured H_2S concentrations dropped below 200 ppm (Fig. 4.7). While the methane concentration tends to increase along the flow path through the chambers (range around 50%), the injected air (oxygen) is used up by oxidation processes.

Oechsner (1998) investigated 52 biogas plants and found that in 54% and 15% of all plants the H_2S concentration exceeded 500 ppm and 2,000 ppm, respectively. This showed that biological desulfurization did not work optimally in most cases. The explanation may be a lack of suitable surface, a passage for the gas that is too short, or a suboptimal temperature. In particular, non-insulated covers may have surface temperatures below the optimum for many Thiobacilli (see Table 4.1).

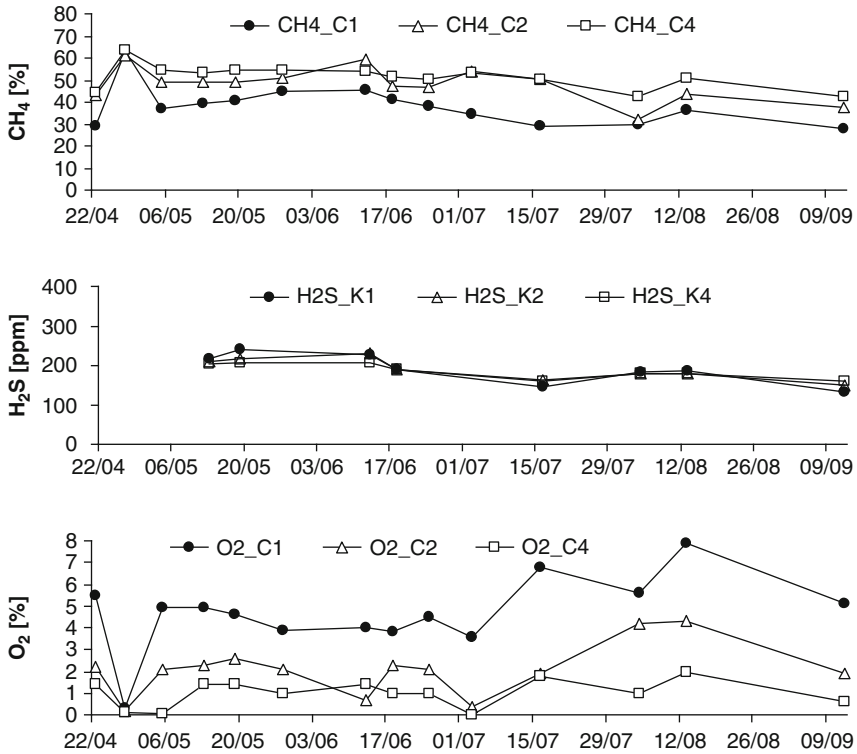


Fig. 4.7 Spatial and temporal concentration profiles of CH₄, H₂S, and O₂ along the flow-path through the head-space of BIO4GAS chambers C1, C2, and C4 of the demonstration plant in Rotholz

4.3 Conclusions

Production of biogas from organic wastes is successfully used in millions of small-scale reactors in Asia, while high-tech biogas plants in the Megawatt range are efficiently operating in many countries worldwide. Yet, medium-scale plants with a power range of 10–100 kW seem to experience a dilemma: state-of-the-art technology is too expensive in construction and maintenance, while environmental regulations and safety standards do not allow to upsize simple solutions known from developing countries. With the BIO4GAS technology, a solution has been found that optimizes the workplace of microbes in medium-scale Biogas plants.

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