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CHARACTERISTICS OF EMISSIONS FROM MUNICIPAL WASTE LANDFILLS

Biogas is formed by the methanogenic anaerobic bacteria which decompose organic substances. Processes occurring during fermentation of methane involve conversion of organic compounds with various oxidation levels to gaseous final products, mainly methane and carbon dioxide. The process of biogas formation involves the following stages: hydrolysis, acidogenesis, acetogenesis and methanogenesis. The composition and quantity of biogas depend mainly on the chemical composition of organic compounds being fermented, maintenance of fermentation conditions and substrate residence time in the reactor. Biogas generated in the fermentation process is utilised mainly for generation of power and heat.

1. INTRODUCTION

In accordance with the Intergovernmental Panel of Climate Change (IPCC) one of the most important threats to wellbeing of human civilization is climate warming due to anthropogenic emission of greenhouse gases. A mitigation measure which has to be taken requires multidimensional approach based on sustainable development concept [1, 2].

Sustainable development is a pattern of resource use that aims to meet human needs while preserving the environment so that these needs can be met not only in the present, but also for generations to come. The term was used by the Brundtland Commission who defined sustainable development as the one that *meets the needs of the present without compromising the ability of future generations to meet their own needs* [3]. To ensure the survival of human civilisation, it is necessary to introduce considerable changes in almost all its aspects: resource management [4], world economy [4–6], pattern of manufacturing of goods [7, 8] and lifestyle [9, 10].

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One of particular problems is climate change which is an inevitable and urgent global challenge with long-term implications for the sustainable development of all countries. Warming of climactic system is expected to impact the availability of basic necessities like freshwater, food security, and energy. The links between climate change and sustainable development are strong. While climate change has no boundaries, poor and developing countries, particularly those low developed, will be among those most adversely affected and least able to cope with the anticipated shocks to their social, economic and natural systems. The Earth's average surface temperature has increased by 0.76 °C since 1850. The IPCC projects that, without further action to reduce greenhouse gas emissions, the global average surface temperature is likely to rise by a further 1.8–4.0 °C this century. Even the lower end of this range would take the temperature increase since pre-industrial times above 2 °C, the threshold beyond which irreversible and possibly catastrophic changes become far more likely.

Human activities that contribute to climate change include in particular the burning of fossil fuels, agriculture and land-use changes like deforestation. These cause emissions of carbon dioxide (CO_2), the main gas responsible for climate change, as well as of other greenhouse gases (GHG). These gases remain in the atmosphere for many decades and trap heat from the sun in the same way as the glass of a greenhouse. To bring climate change to a halt, global greenhouse gas emissions must be reduced significantly. Therefore, there is urgent need to decrease emission of greenhouse gases to mitigate climate warming. The most important is reduction of CO_2 emission from energy sector.

The only alternatives to fossil fuels, presently accounting for over 80% of global primary energy, are nuclear energy and various forms of renewable energy. Nuclear energy today provides less that 6% of world energy, and official forecasts do not see its share increasing much in coming decades, mainly because of its high costs and political problems. Other alternatives such as lowering atmospheric CO_2 emissions by carbon capture and storage from fossil fuel use, or capturing CO_2 directly from the atmosphere would either have limited global impact or entail heavy energy costs, if implemented at the needed scale [11]. Like geoengineering, these approaches do not address fossil fuel depletion. Many researchers thus argue that removable energy will have to replace fossil fuels as the dominant global energy source in the coming decades.

However, carbon dioxide is not the only trace gas which is responsible for in climate change. Methane is another one which some have estimated to be over a third as much as that of carbon dioxide. Gas from natural sources, cows and other ruminants, and natural sources where natural decomposition by fermentation produces methane, all contribute to the blanketing which is the cause of the greenhouse effect. However, human activity is also responsible for a lot of methane gas production and Municipal Solid Waste Landfills (MSWL) have in turn been recognized to be a source of greenhouse gases which is contributing to the atmospheric build-up.

However, the magnitude of the landfill gas contribution to the greenhouse effect have been uncertain, and the subject of some debate. But, as time goes on, the evidence becomes stronger, and the fact of climate change is now accepted by the vast majority of scientists working in this field. Thus, it appears that landfill gases make an important net contribution to the greenhouse phenomenon. Therefore better understanding of landfill gases formation may help to decrease their emissions from landfill sites.

Table 1

Composition of gases released from waste landfills (after [18–20])

Main components			
Component	Typical value [vol. %])	Component	Typical value [vol. %]
Methane	45–60	Ammonia	0.1–1
Carbon dioxide	40–60	NMOCs	0.01–0.6
Nitrogen	2–5	Sulphides	0–1
Oxygen	0.1–1	Hydrogen	0–0.2
Trace components			
Component	Concentration range [mg/m^3]	Component	Concentration range [mg/m^3]
Alkanes		Alkenes	
Propane	< 0.1–1.0	Butadiene	< 0.1–20
Butanes	< 0.1–90	Butenes	< 0.1–90
Pentanes	1.8–105	Pentadienes	< 0.1–0.4
Cycloalkanes		Cycloalkenes	
Cyclopentane	< 0.2–6.7	Limonene	2.1–240
Cyclohexane	< 0.5–103	Other terpenes	14.3–311
Methylcyclopentane	< 0.1–79	Methene	<0.1–29
Halogenated compounds		Aromatic hydrocarbons	
Chloromethane	< 0.1–1	Benzene	0.4–114
Chlorofluoromethane	< 0.1–10	Styrene	< 0.1–7
Dichloromethane	< 0.1–190	Xylenes	34–470
Chloroform	< 0.1–0.8		
Chlorobenzene	< 0.1–2.1		
Esters		Organosulphur compounds	
Ethyl acetate	< 0.1–64	Carbonyl sulphide	< 0.1–1
Methyl butanoate	< 0.1–15	Carbon disulphide	< 0.1–2
Ethyl propionate	< 0.1–136	Methanethiol	< 0.1–87

A mixture of organic and inorganic wastes is disposed at a landfill with varying humidity and much heterogeneity. Approximately 75% of municipal waste is biodegradable organic material. Substances in waste have various decomposition rates. Food waste is most readily degraded. Garden waste forms a group with medium half-life (5 years). Paper, cardboard, wood and textile waste decomposes slowly (half-life of 15 years), while plastics and rubber are not degraded at all [12]. A number of factors affect the quantity of gases formed at landfills and their composition, such as waste type and age, quantity and type of organic components, waste humidity and temperature. Landfill gases form in microbiological processes, as a result of evaporation or in chemical reactions [13].

The main components of landfill gases are methane and carbon dioxide. Methane makes up ca. 45–60 vol. %, while carbon dioxide 40–60 vol. %. Landfill gases also contain small amounts of nitrogen, oxygen, ammonia, sulphides, hydrogen, carbon monoxide and less than 1% of non-methane organic components (NMOC), also called non-methane hydrocarbons (NMHCs) (Table1). Some of them have strong, pungent odour, such as hydrogen sulphide. Non-methane organic components (NMOC), such as volatile organic compounds (VOC) and hazardous air pollutants (HAP), may react under the influence of sunlight and form smog. More then 200 NMOC have been identified [13-15]. Among the landfill gases, carcinogenic substances such as benzene chloride and vinyl chloride may be harmful to the life of the staff and residents of neighbouring areas, while chlorofluorocarbons (CFCs) or hydrochlorofluorocarbons (HCFCs) contribute to ozone layer depletion and climate change [15–17].

2. MECHANISM OF BIOGAS FORMATION

Anaerobic fermentation is widespread in nature, occurring for example in peat bogs, on sea bottom, in manure and at landfills. Organic matter is converted into biogas [21].

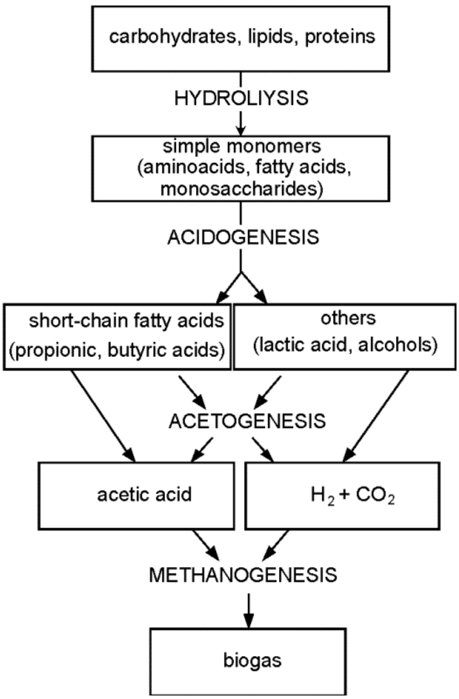

Fig. 1. Scheme of the process of biogas formation (after [22])

Furthermore, certain quantities of fermented biomass form and heat is emitted. The process of biogas formation (Fig. 1) involves such stages as hydrolysis, acidogenesis, acetogenesis and methanogenesis.

2.1. STAGE OF HYDROLYSIS

This stage involves the decomposition of insoluble organic compounds (carbohydrates, proteins, fats). Proteins hydrolyse to amino acids, polysaccharides (including cellulose) to simple sugars, and fats to polyhydroxyalcohols and fatty acids. The quantity of hardly degradable polymers such as cellulose, lignins, non-degradable fats, proteins and carbohydrates is considered the hydrolysis rate limiting step. In the anaerobic fermentation of solid waste as little as 50% of organic substances are decomposed. The rest of complex organic substances are not biodegraded due to the lack of specific depolymerisation enzymes resulting from the absence of specific organisms which secrete various extracellular enzymes [23, 24].

2.2. ACIDOGENIC STAGE (ACIDOGENESIS)

In this stage, facultative acidogenic bacteria convert chemical substances dissolved in water, including hydrolysis products, to short-chained organic acids (C_1–C_6) (formic, acetic, propionic, butyric, valeric acid), alcohols (methanol, ethanol), aldehydes and carbon dioxide and hydrogen.

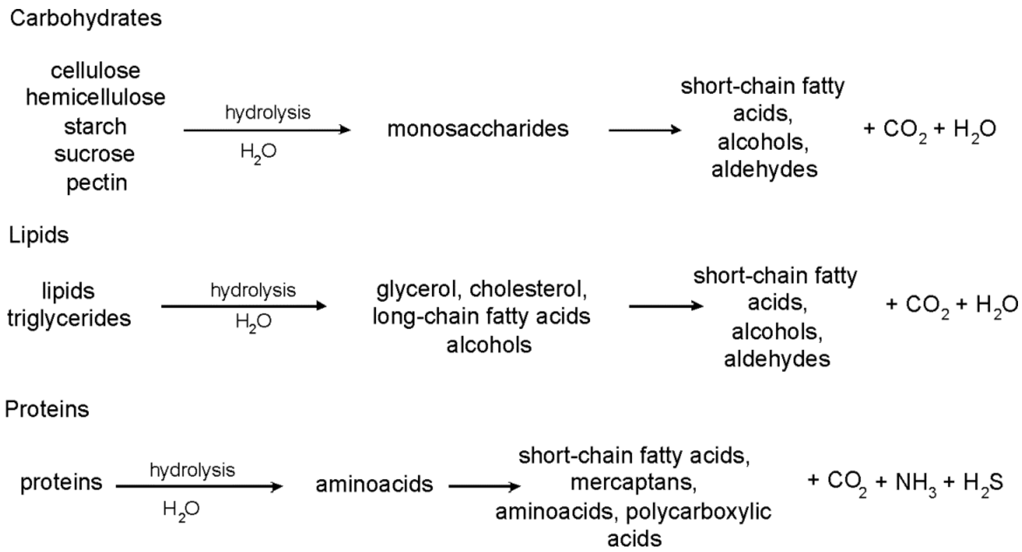

Fig. 2. Scheme of degradation of respective groups of compounds during acidogenesis (after [25])

Acidogenic bacteria include for example: *Clostridium*, *Bacteroides*, *Ruminococcus*, *Butyrylvibrio*, *Escherichia coli*, *Bacillus*, *Bifidobacterium*. Bacteria involved in acidic fermentation are obligate or facultative anaerobes. Considering the classification of substrates with respect to their structure, the degradation of respective groups of compounds has been shown in Fig. 2.

2.3. ACETOGENIC STAGE (ACETOGENESIS)

During acetogenesis, ethanol and volatile fatty acids (C_3–C_6) are converted by acetogenic bacteria to CO_2 and H_2. For example, the decomposition of propionic acid, butyric acid and ethanol to acetic acid may involve the following reactions:

$$CH_3CH_2COO^- + 3H_2O \rightarrow CH_3COO^- + H^+ + HCO_3^- + 3H_2$$

$$CH_3CH_2CH_2COO^- + 2H_2O \rightarrow 2CH_3COO^- + H^+ + 2H_2$$

$$CH_3CH_2OH + H_2O \rightarrow CH_3COO^- + H^+ + 2H_2$$

The reactions occur only if hydrogen is removed from the system and its partial pressure is maintained at a low level. Therefore, acetogenesis occurs only with the syntrophy* of acetogenic organisms with hydrogen-consuming methanogenic organisms. Hydrogen may be used in the formation of acetic acid from carbon dioxide and hydrogen:

$$2HCO_3^- + H^+ + 4H_2 \rightarrow CH_3COO^- + 4H_2$$

or at the methanogenesis stage. Acetogenesis determines biogas formation efficiency. Reactions of higher organic acids at this stage contribute to approximately. 25% of acetate and 11% of hydrogen generated during waste fermentation. The following genera of acetogenic bacteria are most widespread: *Syntrophobacter*, *Syntrophomona* [22, 23].

2.4. METHANOGENIC STAGE

Methanogenic organisms form the last element of the anaerobic food chain which, as discussed before, starts with polysaccharides (cellulose, starch), proteins and lipids and involves fermentation bacteria: 1) bacteria responsible for cellulose fermentation to succinate, propionate, butyrate, lactate, acetate, alcohols, CO_2 and H_2, 2) acetogenic bacteria responsible for the fermentation of the former to acetate, formate, CO_2 and H_2. These products, acetates and alcohols are substrates for methanogenic organisms. Methane forms from the following substrates:

*Syntrophy is the symbiosis of organisms, of which one generates hydrogen and the other consumes it.

- acetic acid (almost 70%)

$$CH_3COO^- + H_2O \rightarrow CH_4 + HCO_3^-$$

- H_2, CO_2 and formate

$$HCO_3^- + 4H_2 + H^+ \rightarrow CH_4 + 3H_2O$$

$$4HCOO^- + H^+ + H_2O \rightarrow CH_4 + 3\ HCO_3^-$$

- methanol, methylamine or dimethyl sulphide

$$4CH_3OH \rightarrow 3CH_4 + CO_2 + 2H_2O$$

$$4CH_3NH_2 + 4H^+ + 2H_2O \rightarrow 3CH_4 + CO_2 + 4NH_4^+$$

$$2(CH_3)_2NH + 2H^+ + 2H_2O \rightarrow 3CH_4 + CO_2 + 2NH_4^+$$

$$2(CH_3)_2S + 2H_2O \rightarrow 3CH_4 + CO_2 + 2H_2O$$

It was found based on stoichiometric relationships that almost 70% of methane forms in the reduction of acetates, even though a few bacterial species only are able to produce methane from acetates, while almost all known methanogenic bacteria can product methane from hydrogen and carbon dioxide [22, 23].

Biochemical transformations of CO_2 and H_2 to methane and acetate to methane and CO_2 occur with various enzymes and prosthetic groups, found so far in methanogenic organisms only. The probable pathways for methane formation from acetate and from hydrogen and carbon dioxide are shown in Fig. 3 [22, 26].

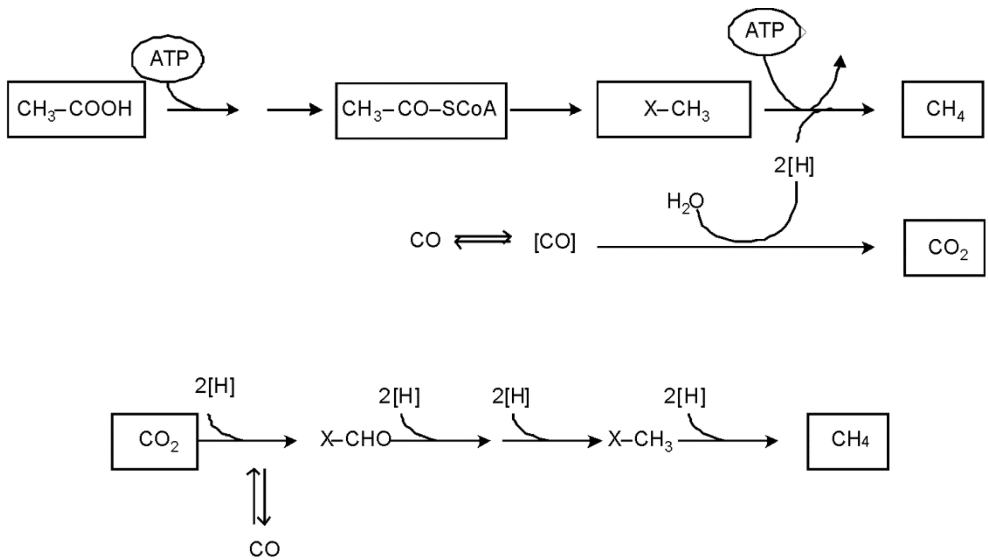

Fig. 3. Probable pathways for methane formation (based on [26])

3. CHARACTERISTICS OF MICROORGANISMS

Three groups of microorganisms contribute to biogas formation: acidogenic, acetogenic and methanogenic bacteria. The first two stages are dominated by both obligate anaerobes (*Bacillus*, *Pseudomonas*, *Clostridium*, *Bifidobacterium*) and facultative anaerobes (*Streptococcus*, *Enterobacterium*). Some acidogenic bacteria are obligate anaerobes (*Aerobacter*, *Alcaligenes*, *Clostridium*, *Escherichia*, *Lactobacillus*, *Micrococcus*, *Flavobacterium*). The growth rates of these bacteria are from 5 h in the presence of carbohydrates to 72 h during fat degradation. The optimum conditions for the growth of acidogenic microorganisms are pH of ca. 6 and temperature of ca. 30 °C. Products of the acidogenic stage (butyric and propionic acids and alcohols) are converted by acetogenic bacteria (*Syntrophomonas* and *Syntrophobacter* sp.). The acetates and hydrogen which form can be used by methanogenic bacteria. The latter may grow only if hydrogen is consumed by hydrogen producing organisms. The cooperation between hydrogen producing and hydrogen consuming bacteria is called interspecies hydrogen transfer. Hydrogen is also removed by homoacetogenic bacteria in the process of acetate formation from CO_2 and H_2. However, the process does not occur in typical fermentation conditions.

Table 2

Selected species of methanogenic bacteria (according to [23])

Genus	Species
Methanobacterium	*M. bryantii* *M. formicicum* *M. thermoautotrophicum*
Methanobrevibacter	*M. arboriphilus* *M. ruminantium* *M. smithi*
Methanococcus	*M. vannielii* *M. volta*
Methanogenium	*M. wariaci* *M. marisnigri*
Methanomicrobium	*M. mobile*
Methanospirillum	*M. hungatei*
Methanosarcina	*M. barkeri*
Methanotrix	*M. soehngenii*

Methanogenic bacteria are all *Archaeobacteriales*. They are obligate anaerobes with any air quantities being lethal. Approximately 40 strains of methanogenic bacteria have been isolated. They are divided into two groups: acetic acid consumers and H_2/CO_2 consumers. Methanogenic bacteria have a form of rods (*Methanobacterium*), spirals (*Methanospirillum*) or coccidia (*Methanococcus*, *Methanosarcina*). Optimum temperature for methanogenesis is in a range of 35–45 °C and optimum pH is 7. Selected species of methanogenic bacteria are presented in Table 2 [23, 26].

Acidic fermentation products can also be consumed by other groups of microorganisms such as sulphate or nitrate reducing bacteria. The presence of the first group of bacteria leads to the presence of hydrogen sulphide in the biogas, while the other contributes to the presence of ammonia.

4. HYDROGEN SULPHIDE FORMATION

Due to the presence of hydrogen sulphide, landfill gases have a peculiar odour of rotten eggs. The unpleasant odour is perceptible even at very low concentrations. Some people with a very low odour perception level can detect sulphide at concentrations as low as 0.5 ppb). Hydrogen sulphide forms during anaerobic waste degradation from sulphur containing amino acids or due to reduction of inorganic sulphur containing compounds. Dissimilation sulphate reduction is a process in which bacteria use sulphates as electron acceptors in oxidation of organic matter. Bacteria of genera *Desulfovibrio* and *Desulfotomaculum* are classified as sulphate reducing bacteria (SRB).

Hydrogen sulphide is usually the first sulphur product of bacterial degradation of sulphur containing organic compounds. Part of the hydrogen sulphide formed passes to biogas; however, most is dissolved in twaters as $H_2S_{(aq)}$ or HS^-. These forms are in equilibrium with $H_2S_{(g)}$ [27].

5. AMMONIA FORMATION

Proteins are the chief source of ammonia nitrogen. The process of conversion of organic to inorganic nitrogen by heterotrophic bacteria is called ammonification. It is a two-stage process which involves hydrolysis of enzymatic protein to amino acids by aerobic and anaerobic microorganisms, followed by deamination and fatty acid fermentation leading to the formation of carbon dioxide, ammonia nitrogen and volatile fatty acids. During deamination (Fig. 4) amino groups are released and the form ammonia or ammonium ions.

Ammonia is not a greenhouse gas and, therefore, it is not so harmful to the environment as methane. However, exposure to the gas may lead to certain adverse health effects. Ammonia has pungent odour and may be irritant to the respiratory system. In addition, ammonia may dissolve in the skin protective layer and form ammonium hydroxide, a corrosive substance which causes skin irritation [28].

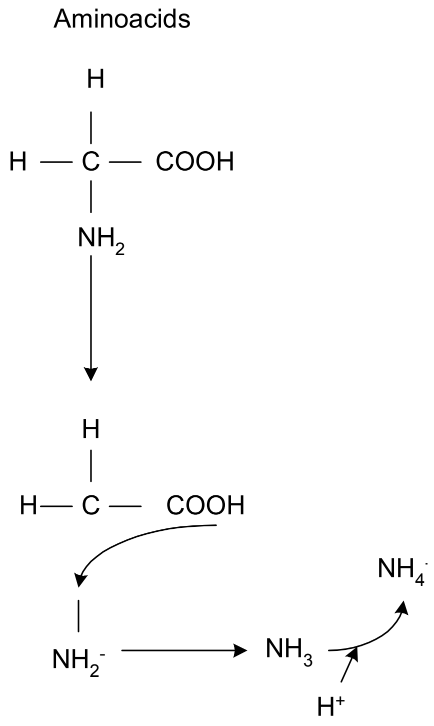

Fig. 4. Deamination process [28]

6. SUMMARY

The quantity of landfill gases depends on the properties of waste (composition and age) and multiple environmental factors (oxygen content, humidity, temperature). Higher content of organic waste at a landfill leads to the increased generation of gases, such as carbon dioxide, methane, nitrogen or hydrogen sulphide, by bacteria responsible for degradation, while higher content of chemical waste contributes to the formation of NMOCs due to evaporation or chemical reactions.

More gases are released from waste stored for less than 10 years as a result of bacterial degradation, evaporation and chemical reactions than from that stored for more than 10 years. The highest emission of gases from landfills occurs 5–7 years after the start of storage.

Bacteria can produce methane only in anaerobic conditions. The higher the oxygen content, the longer waste is decomposed by aerobic bacteria at the first stage. If waste is loosely packed, better oxygen accessibility is ensured and, consequently, aerobic bacteria live longer and produce carbon dioxide and water for a longer period. If waste is compacted, anaerobic bacteria which produce methane grow more rapidly, to be later replaced by aerobic bacteria.

More than 40% humidity (based on wet waste matter) contributes to more rapid gas release from landfills. This is caused by the favourable effect of humidity on bacterial growth and transport of nutrients throughout the landfill.

High temperature increases bacterial activity which, in effect, leads to higher emissions of gases from landfills. Lower temperatures reduce bacterial activity. Due to the heat emitted during bacterial degradation processes, landfill temperatures are 25–45 °C. It was found that the quantity of NMOCs being released doubles with each 8 °C temperature increase [29, 30].

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