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Characteristics of Emissions from Municipal Waste Landfills

Ewelina Staszewska, Małgorzata Pawłowska
Lublin University of Technology

1. Introduction

Waste disposed at a landfill is a mixture of organic and inorganic waste with varying humidity and much heterogeneity. Approx. 75% of municipal waste is biodegradable organic material. Substances in waste have different 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 [7].

The main components of landfill gases are methane and carbon dioxide. Methane makes up approx. 45%-60% v/v, while carbon dioxide 40%-60% v/v. Landfill gases also contain small amounts of nitrogen, oxygen, ammonia, sulphides, hydrogen, carbon monoxide and less than one per cent of non-methane organic components (NMOC), also called non-methane hydrocarbons (NMHCs) (Table 1). 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 non-methane organic components have been identified [1, 7, 16]. 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 [13, 14, 16].

Table 1. Composition of gases released from waste landfills [6, 17, 18]
Tabela 1. Skład gazów uwolnonych ze składowisk odpadów [6, 17, 18]

Main components found in landfill gas			
Component	Typical value (% by volume)	Component	Typical value (% by volume)
Methane	45-60	NMOCs	0,01-0,6
Carbon dioxide	40-60	(non-methane organic compounds)	
Nitrogen	2-5		
Oxygen	0,1-1	Sulphides	0-1
Ammonia	0,1-1	Hydrogen	0-0,2
Trace components found in landfill gas			
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

Table 1. cont.
Tabela 1. cd.

Alcohols:		Ethers:	
Methanol	< 0.1-210	Dimethylether	0.02-<2
Ethanol	< 0.1->810	Methylethylether	<0.1-<2
Butan-1-ol	< 0.1-> 19	Diethylether	0.1-12
Other compounds:			
Acetone	< 0.1-3.4		
Tetrahydrofuran	< 0.1- <2		
Camphor	< 0.1-13		

2. Mechanism of biogas formation

Anaerobic fermentation is widespread in nature and it occurs for example in peat bogs, on sea bottom, in manure and at landfills. Organic matter is converted into biogas. Furthermore, certain quantities of fermented biomass form and heat is emitted. The biogas formation process, shown in Figure 1, involves hydrolysis, acidogenesis, acetogenesis and methanogenesis stages.

2.1. Hydrolysis stage

This stage involves the decomposition of insoluble organic compounds (carbohydrates, proteins, fats). Proteins are hydrolysed to amino acids, polysaccharides (including cellulose) to simple sugars and fats to polyhydroxy alcohols 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 [3, 11].

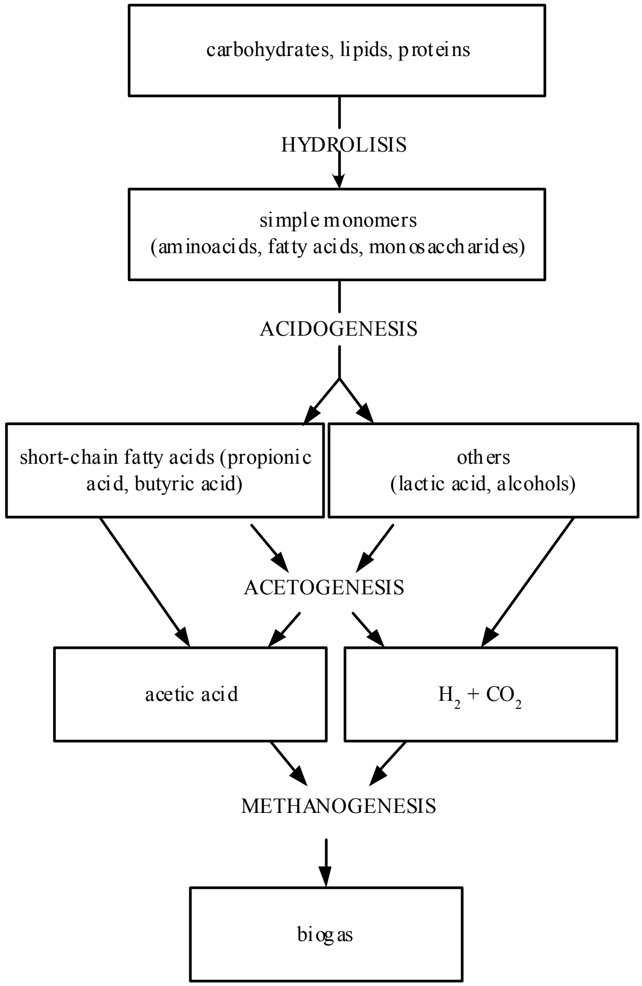

Fig. 1. Biogas formation process [9]
Rys. 1. Proces powstawania biogazu [9]

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), alcohols (methanol, ethanol), aldehydes, carbon dioxide and hydrogen. 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 can be shown as on Figure 2.

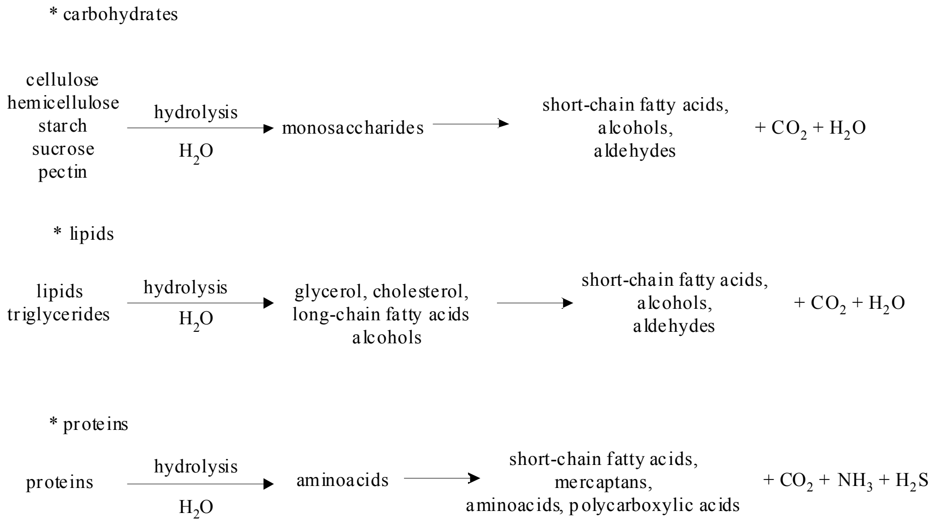

Fig. 2. Degradation of main organic compounds [10]
Rys. 2. Degradacji głównych związków organicznych [10]

2.3. Acetogenic stage (acetogenesis)

In this stage, 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, butyric acids 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 with hydrogen-consuming methanogenic organisms (syntrophy is the symbiosis of organisms, of which one generates and the other consumes hydrogen).

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 approx. 25% of acetate and 11% of hydrogen quantities generated during waste fermentation. The following genera of acetogenic bacteria are most widespread: *Syntrophobacter*, *Syntrophomona* [9, 11].

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:

- acetic acid (almost 70%)

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

- H_2 and 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

$$4\ CH_3OH \rightarrow 3\ CH_4 + CO_2 + 2\ H_2O$$
$$4\ CH_3NH_2 + 4\ H^+ + 2\ H_2O \rightarrow 3CH_4 + CO_2 + 4NH_4^+$$
$$2\ (CH_3)_2NH + 2H^+ + 2H_2O \rightarrow 3CH_4 + CO_2 + 2NH_4^+$$
$$2\ (CH_3)_2S + 2H_2O \rightarrow 3CH_4 + CO_2 + 2H_2O$$

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 [9, 11].

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 Figure 3 [9, 15].

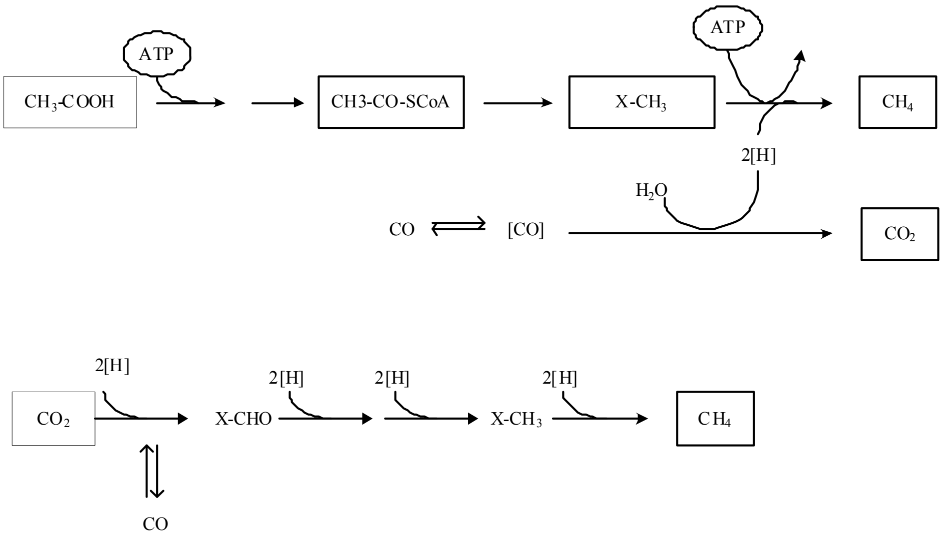

Fig. 3. Probable pathways for methane formation (based on [15])
Rys. 3. Prawdopodobne drogi tworzenia metanu (na podstawie [15])

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 rate of these bacteria is between 5 hours in the presence of carbohydrates to 72 hours during fat degradation. The optimum conditions for the growth of acidogenic microorganisms are pH of about 6 and temperature of about 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.

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 shown in Table 2 [11, 15].

Table 2. Selected species of methanogenic bacteria [11]
Tabela 2. Wybrane gatunki bakterii metanogennych [11]

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*

Acidic fermentation products can also be consumed by other groups of micro-organisms, 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 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 (parts per billion).

Hydrogen sulphide forms in anaerobic waste degradation from sulphur-containing amino acids or in the reduction of inorganic sulphur-containing compounds. Dissimilation sulphate reduction is a process in which bacteria use sulphates as electron acceptors in the 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 the solution as $H_2S_{(aq)}$ or HS^- . These forms are in equilibrium with $H_2S_{(g)}$ [8].

5. Ammonia formation

Proteins are the chief source of ammonia nitrogen. The process for the conversion of organic to inorganic nitrogen by heterotrophic bacteria is called ammonification. It is a two-stage process which involves enzymatic protein hydrolysis 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 (Figure 4) amino groups are released and 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 [2].

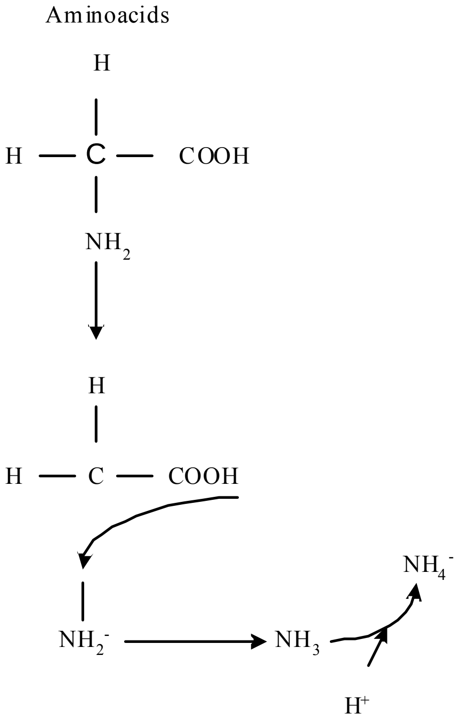

Fig. 4. Deamination process [2]
Rys. 4. Proces deaminacji [2]

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 old 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 from the start of storage.

Bacteria can produce methane in anaerobic conditions only. 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 [4, 5].

References

1. **Abushammala M.F.M., Basri N.E.A., Kadhum A.A.H.:** *Review on landfill gas emission to the atmosphere*. European Journal of Scientific Research 30 (3): 427-436, 2009.
2. **Berge N.D., Reinhart D.R.:** *The fate of nitrogen in bioreactor landfills*. Critical Reviews in Environmental Science and Technology 35: 365-399, 2005.
3. **Bhattacharyya J.K., Kumar S., Devotta S.:** *Studies on acidification in two-phase biomethanation process of municipal solid waste*. Waste Management 28: 164-169, 2008.
4. **Crawford J.F., Smith P.G.:** *Landfill technology*. London. Butterworths, 1985.
5. EPA, U.S. Environmental Protection Agency. *Solid waste disposal facility criteria – technical manual*. EPA 530-R-93-017, 1993.
6. EPA, U.S. Environmental Protection Agency. *Compilation of Air Pollutant Emissions Factors, AP-42, Fifth Addition, Volume 1: Stationary Point and Area Sources. Section 2.4 – Municipal Solid waste Landfills,* 1995.
7. EPA, U.S. Environmental Protection Agency. *Frequently Asked Questions About Landfill Gas and How It Affects Public Health, Safety, and the Environment* http://www.epa.gov/landfill/docs/faqs-3.html, 2008.
8. **Erses A.S., Onay T.T.:** *In situ heavy metal attenuation in landfills under methanogenic conditions*. Journal of Hazardous Materials B99: 159-175, 2002.

9. **Głodek E., Kalinowski W., Janecka L., Werszler A., Garus T., Kościanowski J.:** *Acquisition of agricultural biogas and its use as an energy source.* Opole's Transfer Innovation Centre in the range of building materials and renewable energy sources (Project number Z/2.16/II/2.6/16/06), 2007.
10. **Janosz-Rajczyk M.:** *Selected process units In environmental engineering*. Czestochowa: University of Technology Publishers, 2004.
11. **Jędrczak A.:** *Biological waste processing*. Warsaw: Polish Scientific Publishers PWN, 2007.
12. **Lewicki R.:** *The Monitoring of Landfill Gas*. Lodz: OBREM, 1991.
13. **Molina M., Rowland F.S.:** *Stratospheric sink for chlorofluoromethanes – chlorine atomic – catalysed destruction of ozone*. Nature 249: 810-812, 1974.
14. **Nikiema J., Bibeau L., Lavoie J., Brzezinski R., Vigneux J., Heitz M.:** *Biofiltration of methane: an experimental study*. Chemical Engineering Journal 113: 111-117, 2005.
15. **Schlegel H.G.:** *General Microbiology*. Warsaw: Polish Scientific Publishers PWN, 2003.
16. **Scheutz C., Bogner J., Chanton J.P., Blake D., Morcet M., Aran C., Kjeldsen P.:** *Atmospheric emissions and attenuation of non-methane organic compounds in cover soils at a French landfill*. Waste Management 28: 1892-1908, 2008.
17. **Tchobanoglous G., Theisen H., Vigil S.:** *Integrated Solid Waste Management, EngineeringPrinciples and Management Issues*. New York: McGraw-Hill Inc. pp. 381-417, 1993.
18. **Williams P.T.:** *Waste Treatment and Disposal*. England: John Wiley& Sons Ltd., 2005.

Charakterystyka emisji ze składowisk odpadów komunalnych

Streszczenie

Ilość gazu z odpadów zależy od właściwości odpadów (skład i wiek) i wielu czynników środowiskowych (zawartość tlenu, wilgotność, temperatura). Wyższa zawartości odpadów organicznych na składowisku prowadzi do zwiększonego wytwarzania, przez bakterie odpowiedzialne za degradację, gazów takich jak: dwutlenek węgla, metan, azot lub siarkowodór. Wyższa zawartość odpadów chemicznych przyczynia się do powstawania niemetalowych związków organicznych wskutek parowania lub reakcji chemicznych.

Większa ilość gazu jest uwalniana z odpadów w wyniku degradacji bakteryjnej, parowania i reakcji chemicznych, gdy odpady składowane są przez okres krótszy niż 10 lat, w stosunku do odpadów przechowywanych dłużej niż 10 lat. Największa emisji gazów ze składowisk odpadów występuje 5-7 lat po rozpoczęciu składowania.

Bakterie wytwarzają metan tylko w warunkach beztlenowych. Im wyższa zawartość tlenu, tym dłużej odpady są rozkładane przez bakterie tlenowe w pierwszym etapie. Jeżeli odpady są luźno ułożone występuję większa dostępność tlenu. Tym samym bakterie tlenowe żyją dłużej i produkują dwutlenek węgla i wodę przez dłuższy okres. Jeżeli odpady są składowane ściśle wówczas bakterie beztlenowe, które produkują metan, rosną szybciej i nie są zastępowane przez bakterie tlenowe.

Ponad 40% wilgotności (w oparciu o wilgotną masę odpadów) przyczynia się do szybszego uwolnienia gazu ze składowisk odpadów. Spowodowane jest to korzystnym wpływem wilgotności na rozwój bakterii i transport substancji odżywczych w składowisku.

Wysoka temperatura zwiększa aktywność bakterii, co prowadzi do zwiększenia emisji gazów ze składowisk odpadów. Niższe temperatury obniżają aktywność bakterii. Ze względu na ciepło emitowane podczas procesów degradacji bakteryjnej, temperatura w składowisku wynosi od 25 do 45°C [4, 5].