SELECTED EFFECTS OF ANAEROBIC SLUDGE COMPOSITION ON A BIOGAS PRODUCTION

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ABSTRACT
Intensification of biological treatment processes require more accurate both quantitative and qualitative assessment of a biogas production and factors affecting this process. Better energy recovery is of crucial importance in the overall sludge disposal, however it deeply depends on methane rich gas generation. Increased net biogas production and thus better energetic characteristics of the plant are recognized as the most important reasons to apply disintegration to the wasted activated sludge (WAS). Until now an assessment of efficiency of this process was done by steady state measurements of COD solubilisation, change of sludge flocs' size or change in a protein concentration. Results of tests and full-scale operation enlightened some specific problems which may occur in wastewater treatment plants where mesophilic fermentation of sludge was used as a stabilization method a significant decrease of a biogas production was proved. Operational procedure basing on a methanogenic activity respirometric tests was proposed and tested in full-scale design procedure.

INTRODUCTION

At present multi-phase biological reactors are most commonly applied facilities in municipal wastewater treatment. These reactors provide proper technical conditions to perform three main groups of processes in one technical facility as follows (Rybicki, 2009):

- Conversion of an organic matter contained in raw sewage into a biomass also its respiration products such as: carbon dioxide and water; discard of excess biomass is wasted from a system as so called wasted activated sludge (WAS);
- Incorporation of surplus amount of phosphorus into a biomass during consecutive exposure of a biomass to anaerobic and aerobic conditions;
- Conversion of an organic nitrogen and ammonia which are main nitrogen compounds in raw wastewater into their oxidized form: nitrites and nitrates (nitrification) and finally release a gaseous nitrogen into an ambient atmosphere (denitrification).

Main byproduct of contemporary wastewater appears to be a specific mixture of solid particles suspended in wastewater which contain solid particles which weren't decomposed during primary treatment (primary sludge – PS) and excess biomass from biological processes (WAS). This byproduct has significant potential as an energy source. A large amount of energy, in the form of electricity and oil, is used in municipal wastewater treatment plants (WWTPs). Reduction of fossil fuel consumption by municipal WWTPs should be based on production of renewable energy from biosolids, since large quantities of organic matter are included in biosolids. However, most biosolids are simply incinerated or landfilled so an anaerobic digestion (AD) is one of the most useful technologies for renewable energy production from biosolids (Lettinga 1996, Mizuta et al, 2011).The main aims of anaerobic sludge disposal are: biological sludge stabilization and recovery of highly energetic methane gas. Operational disadvantages of raw wastewater sludges are their hydrophilic character, high viscosity, odour emission and risk of biohazard. Anaerobic stabilization processes is converting sludges to biologically stable product for ultimate disposal, safe storage and use. Stabilization also reduces the odours, bacteria levels and amount of solids present in the sludge. Besides it is possible to recover an energy - thermal and/or electrical in an anaerobic process. During a methane fermentation approximately 50% of total organic matter content in sludge is decomposed producing a biogas (Cimochowicz-Rybicka 1999, Cimochowicz-Rybicka&Rybicki, 2011). The biogas is a mixture which content tends to vary depending mostly on sludge content. Gas composition is influenced by degradable matter content while produced gas volume depends mostly on an amount of mineralised organic matter content.

Anaerobic degradation

The microbial decomposition of complex organic substrates provides a source of energy and building materials to the bacterial cells which convert the organic material to carbon dioxide and methane. The anaerobic degradation of organic material has been described as a multi-step conversion of many, parallel, biochemical reactions. Many groups of anaerobic bacteria are involved in this process. Four main stages of this degradation can be distinguished (Cimochowicz-Rybicka, 1999):

a. hydrolysis of complex organic materials to soluble products (hydrolytic fermentative bacteria)
b. acidogenesis – generation of intermediary products such as short-chain fatty acids, (hydrogen producing and acetogenic organisms)
c. acetogenesis – acetate production (hydrogen-producing, hydrogen-consuming acetogenic organisms)
d. methanogenesis – methane production (methane-forming bacteria)

The nature and chemical composition of the substrates used in anaerobic digestion dictate the type and amount of the products. In case the chemical composition of the organic matter is known, the stoichiometric equation according to McCarty (Pavlostatis et al 1999; Cimochowicz-Rybicka,2000) can be used for the description of organic matter conversion to methane:

$$C_nH_aO_bN_c + (2n + c - b - 9sd/20 - ed/4)\ H_2O \rightarrow$$
$$d*e/8\ CH_4 + (n - c\ s*d/5 - de/8)\ CO_2 + sd/20\ C_5H_7O_2N + (c - sd/20)\ NH_4^+ + (c - sd/20)\ HCO_3^-$$

where: $d = 4n + a - 2b - 3c$,
s = fraction of waste converted to cells,
e = fraction of waste converted to methane for energy ($s + e = 1$),
$C_nH_aO_bN$ = empirical formula of waste being digested,
$C_5H_7O_2N$ = empirical formula of bacterial dry mass (VSS).

Methane production

All biochemical processes taking place within a living cell cause chemical structural changes accompanied by an energetic effects. These effects are strictly related to change of chemical potential of reacting substances. So two main types of such reaction can be recognised:

- exergonic which progress spontaneously causing decrease of total chemical potential of the system
- endergonic which cause increase of total chemical potential within the system so this type of reactions require to be supplemented by energy from outside of the system.

Methane generation is a final stage of organic matter decomposition in an anaerobic conditions resulting from its chemical structure : four-valent carbon atoms are saturated with four hydrogen atoms so a methane gas is most stable product of this process. Numerous bacteria species are specialised in methane production from different compounds (Ferry,1993; Cimochowicz-Rybicka

2000, Cimochowicz-Rybicka&Rybicki, 2009). Some of these bacteria species utilise substrates to cell growth and reproduction both as an energy source and as the sole carbon source. The catabolic pathways of methanogens are very complicated and usually they are presented as one of three groups: CO_2-reducing, methylotrophic and aceticlastic pathways as it was detailed in references .Most of the methane produced in nature originates from acetate. However, the some amounts of methane produced from the methyl group of acetate or reduction of CO_2 can vary depending on the presence of other metabolic groups of anaerobes and the environment, this acid decomposition can be described by following equation:

$$CH_3COOH \rightarrow CO_2 + CH_4 \qquad \Delta G^{o\prime} = -36 \text{ kJ/mol } CH_4 \qquad \text{(Eq-1)}$$

An acetate is a major substrate for methane production, only two genera of methanogenic acetotrophs - *Methanosarcina* and *Methanothrix* and a few species have been described.

MAIN FACTORS AFFECTING FERMENTATION GAS CHARACTERISTICS

Typical values being used for design purpose are based on specific unit volume of a gas which can be obtained from each of substrates, typical reference values are Table 1.

Table 1. The amount and gas composition produced in anaerobic digestion – typical values

Substrate	Gas amount [L/kg VSS]	Gas characteristic
Carbohydrates	790	50 % CH_4 50 % CO_2
Lipids	1250	68 % CH_4 32 % CO_2
Protein	700	71 % CH_4 29 % CO_2

These values in real –term conditions tend to vary as real sludge is a mixture of substrates in varying proportions. Gas production rates range from 750 - 1000 L of gas produced per kg volatile solids removed (or from 300 to 600 L of gas per kg of VSS delivered to digestion chamber. Biogas production in relation to COD is about 0.5 m^3/kg COD removed, corresponding to a methane production of 0.35 m^3 CH_4 per kg of COD removed (Grady et al. 1999, 2010; Cimochowicz-Rybicka 2000). Gas composition varies with sludge characteristics. Gas components include methane, carbon dioxide, hydrogen sulfide, nitrogen and hydrogen. The characteristic of digestion gas is generalized in Table 2.

Table 2. Typical characteristic of anaerobic digester gas

Constituent	Percentage fraction, %
Methane	55 - 75
Carbon dioxide	25 - 45
Hydrogen sulfide	0.01 - 1
Nitrogen	2 - 6
Hydrogen	0.1 - 2

Methane determine the heating value of the gas; carbon dioxide represents the stabilized carbon; hydrogen sulfide determines the corrosivity and odour potential of the gas.

Characterisation of components of fed and digested sludge

Data presented in Table 3 were obtained from lab tests on sludge from Nowy Sacz WWTP, results reflect 8 grab samples from 2010 year. Numeric data are average values from these samples.

Table 3. Characterisation of sludges and total solids components – grab samples

Parameter	Unit	Primary sludge	WAS	Digester chamber feed	Digested sludge
COD	mg O2/L	38000	46000	41000	17500
pH	-	5,3	6,7	6,3	7,5
TP	% of TS	1,1	3,0	1,9	-
TN	% of TS	4,6	7,8	6,8	12
VS	% of TS	88	79,5	81,1	66
TS	mg/L	32000	39000	37700	16500
TS structure					
Carbohydrates as percent of TS	% of TS	38	7	19	8
Proteins as percent of TS	% of TS	24	45	36	28
Lipids as percent of TS	% of TS	8	4	6	6
Inorganic as percent of TS	% of TS	12	18	15	50

Metal content in fed sludge

Authors presented papers concerning adverse impact of heavy metals excessive content on methane production (both overall volume of digested sludge and dynamics of the process). Presence of trivalent chromium in a fed sludge and its influence on digestion efficiency were presented (Cimochowicz-Rybicka, 1999, 2000). General statement of these investigation was that doses 200 and 500 mg Cr(III)/L[1] may cause decrease of a methane production of 20% as compared to the reference sample. Increase of inhibiting compound dose up to Cr(III) 1500 i 2000 mg Cr(III)/L led to 45% decrease of methane production. The concentration of Cr(III) equal to 3000 mg/L caused a

[1] 1 mg/L equals to 1 ppm

47 % decrease of methane production . Otherwise a methane is produced until entire organic matter is converted its reaction rate tends to decrease as the concentration of substrates drops being consumed by microorganisms.

However one should take into consideration that presence of trace metals is necessary to complete a process of methanogenesis, in general terms. Literature studies on cobalt , nickel and iron are usually based on proportional equations considering the removed COD as follows:

Authors investigation on grab sample from Kraków-Płaszów showed no problems related to lack of trace metals however in approx 15% of samples from Nowy-Sacz Wielopole WWTP proportions Me:COD were below the limit. It may be credited to significant input of food processing wastewater in overall composition of wastewater inflowing the WWTP.

Technical factors affecting characteristics of digester gas:

Temperature. The performance of anaerobic processes is significantly affected by operating temperature. The rate of biochemical reactions increase as temperature increase. Each group of methane-forming bacteria has an optimum temperature for growth. The digestion process can be performed in the one of the three ranges of temperature: psychrophilic $20^{o}C$ - $25^{o}C$, mesophilic $30^{o}C$ - $40^{o}C$, thermophilic $50^{o}C$ - $60^{o}C$.

pH. Anaerobic bacteria, especially the methane formers, are very sensitive to pH deviates. A pH range of 6.8 to 7.4 generally provides optimum conditions for the methanogens. pH can also affect the activity of the acidogenic microorganisms but the effect is less significant. A decrease in pH value increases the production of un-ionized volatile acids which become toxic to methanogenic bacteria but in case of pH above 8 the dissolved ammonia becomes toxic to these microorganisms.

Toxic substances. Anaerobic biodegradation process can be inhibited by two groups of chemicals: substances which are produced as process intermediates: e.g. volatile fatty acids and contaminations present in wastewater: light metal cations, heavy metals, ammonia, sulfide, oxygen, salt and organic compounds.

Table 5. Period of maximum methane production at various Cr(III) doses

Cr(III) dosage [mg/L]	Time of max CH4 production [hours]
control	approx. 96
200	120 - 144
500	144 - 168
1500	approx. 168
2000	to be repeated
3000	exceeds test period

It is visible that volume of methane decreases as the inhibitory dose rises , on the other hand a length of maximum productivity period extends with doses.

CONCLUSIONS

1. The methane production is inhibited at 200 mg Cr(III)/L and significantly decreases at above 1500 mg Cr(III)/L.
2. Results of tests showed an inhibitory effect not only as decrease of a reaction rate but also as change in real time necessary for stabilization of inhibitor containing sludge.
3. Observed changes may lead to more precise explanation of an inhibitory effect of Cr(III) on a methanogenesis. This testing method can be applied for examination of possible inhibition of a methanogenesis by various heavy metals.
4. Data obtained may be applied for design purposes in dimensioning closed digestion chambers at municipal wastewater treatment plants. Period of maximum gas production can be assessed with the use of this method and by the same a biomass efficiency can be measured.
5. During the batch test period, a high amount of methane was recorded in relation to the total fermentation gas production from all samples. This could prove the proper course of methanogenic processes in the tested samples.

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