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Review

Methane fermentation process for utilization of organic waste

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A b s t r a c t. Biogas is a renewable and sustainable energy carrier generated *via* anaerobic digestion of biomass. This fuel is derived from various biomass resources and depending on its origin it contains methane (40-75%), carbon dioxide (20-45%) and some other compounds. The aim of this paper is to present the current knowledge and prospects of using the methane fermentation process to dispose of various types of organic wastes as well as conditions and factors affecting the methane fermentation process.

K e y w o r d s: biogas, methane fermentation, organic waste utilization

INTRODUCTION

Due to the negative impact of conventional energy production methods on the environment as well as running out of fossil fuels, more and more importance is put on the development of renewable energy. Since earliest times biomass was used by humans as a basic source of energy. In many parts of the world, including Poland, methane fermentation process has been currently regarded as the prospective source of renewable energy and very good way for organic waste utilization. Among various types of wastes, the sewage sludge, municipal waste, food industry waste and agricultural waste are most important substrates in methane fermentation process (Budzianowski, 2012; Igliński *et al.*, 2011).

The municipal wastes production forecast included in the National Plan of Wastes Management (2010) indicates that the amount of biodegradable wastes which should be subjected to recovery and neutralization in Poland (apart from landfilling) will reach the level of approx. 2.5 mln Mg in 2010, 3.5 mln Mg in 2013, and 3.6 mln Mg in 2018. It is expected that in Poland will increase the use of installations for mechanical and biological wastes processing (MBP), including those based on the methane fermentation process. The process of organic recycling is based on production of biogas and digested product – post-fermentation sludge (Ministry of Environment, 2008).

The agricultural biogas-plants developmental program prepared by the Ministry of Agriculture and Rural Development (2009) points to the production potential of national agriculture. It is assumed that at first the liquid and solid animal excrements and agricultural and food industry wastes will be used. The basic benefits of this solution include, apart from acquisition of energy from biogas, are as follows: elimination of substances which may cause soil acidification, considerable limitation of microorganisms which may induce diseases of plants, increase in the value of digested wastes and their improved digestibility, additional source of incomes for livestock farms or arable farms.

It is estimated that 1 m^3 of liquid animal excrements may yield on average 20 m^3 of biogas, whereas 1 m^3 of solid manure – as much as 30 m^3, with energy value of approx. 23 MJ m^{-3}. The potential of biogas production from animal excrements in Poland amounts to approx. 3 310 mln m^3 (Cebula and Latocha, 2005).

Simultaneously with the use of these resources, crops cultivation is expected to grow, with focus on plants used as energy crops that can be converted to biogas. This will provide raw materials enabling the production of approx. 5-6 billion m^3 of biogas annually. One biogas-plant producing annually approx. 3.5-3.8 mln m^3 of biogas, constitutes an equivalent of approx. 2.5 mln m^3 of high-methane natural gas. From 1 ha of arable land, 10-20 t of biomass are collected, which is equal to 5-10 t of coal (Arbon, 2002; Naik, 2010).

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To obtain about 1 kWh of electrical energy and 1.25 kWh of thermal energy, the following amounts of raw materials constituting a basis for energy production from renewable sources are needed: 5-7 kg of biomass wastes, 5-15 kg of municipal solid wastes, 8-12 kg of manure and organic wastes and 4-7 m^3 of municipal wastes.

The central issue of biogas-based power generation is the availability of cheap feedstock in sufficient quantity. There are several sources of valuable feedstock for biogas production of municipal, agricultural and industrial origin (Budzianowski, 2010; Budzianowski and Chasiak, 2011). They include sewage sludge, animal residues, energy crops, grasses, organic sorted wastes, landfilled wastes, *etc*. The development of biogas production creates an additional demand on organic feedstock, which otherwise have limited availability, thus increasing feedstock prices and enhancing the development of a feedstock market (Budzianowski, 2012).

Implementation of modern technologies of energy production is expected to half CO_2 emissions till 2050 (IPCC, 2009). In Poland as much as around 254 mln t of carbon dioxide are emitted through combustion of hard and brown coal while the admissible limit of CO_2 emissions granted by the European Commission was around 208 mln t in 2008. Therefore, there is an urgent need to develop low-emission technologies of energy production that will contribute to providing the energetic and ecologic safety. Because of numerous advantages, the biomass may become the principal raw material used in production of alternative fuels, in particular second generation fuels such as bioethanol, biogas and BTL. According to UE directive (Directive 2003/30/EEC) from 1 mln hectare of energy crops it can be derived around 65 TWh of energy accumulated in primary fuels. Application of biogas derived this way for production of electric energy and heat may reduce the annual emissions of CO_2 by around 57 mln t. This fuel is harmless for the natural environment because carbon dioxide emissions to the atmosphere during its combustion are equivalent to CO_2 absorption by plants during photosynthesis (Borkowska and Stępniewska, 2011; Chandra *et al.,* 2012).

The aim of this paper is to present the current knowledge and prospects of using the methane fermentation process to dispose of various types of organic wastes. Also conditions and factors affecting the methane fermentation process are described.

ORGANIC WASTES

Characteristics and categories of organic wastes

For many enterprises, the possibility of wastes management in biogas-plants will cause reduction of costs connected with their utilization. Pursuant to mandatory regulations, many wastes from agricultural and food industry, such as slaughter residue, including the content of animal rumen, blood, fat residue and fish wastes must be utilized pursuant to regulations on handling the environmentally hazardous wastes (IEA, 2006). Landfilling is prohibited in this case. Also animal excrements cause a serious problem for many farmers. Agricultural use of such wastes according to mandatory regulations will be largely limited. Since 2008 farmers have been obliged to collect and store fermented and unfermented liquid manure in tight, covered containers for six months (EC, 2007). Therefore, the possibility to convert these wastes in biogas-plants is an attractive solution for them.

Anaerobic digestion of animal excrements alone is ineffective. Decisive for the usefulness of the raw materials for biological processing is the structure, content of biodegradable organic compounds, nutritive ingredients, hydration and environmental pH (Karakashev *et al.*, 2005; Lyberatos and Skiadas, 1999).

Therefore, it is reasonable to supplement these wastes with various organic substrates (co-substrates) available on the local market. These may be wastes from vegetable and animal production, food industry, as well as biomass of specialist crops. The use of co-substrates enables appropriate loading of the digestive chamber, improves the methane digestion process kinetics because of the suitable coal to nitrogen ratio, and increases its efficacy and economic viability. Currently, most popular approach is co-fermentation of organic fraction of municipal wastes with sewage sludge. Properties of organic waste materials that can be used in the methane fermentation process are presented in Table 1 (Cebula and Latocha, 2005). Apart from the above mentioned wastes, biogas may be produced also from materials that have been used as fodder *eg* sugar beet pulp from sugar factories or wastes from breweries (Classen *et al.*, 1999). The wastes suitable for anaerobic digestion processing are presented in Fig. 1.

Sewage sludge

Sewage sludge occurs in municipal and industrial waste treatment plants and is a by-product of the wastes treatment process. There are different types of sludge: preliminary sludge *ie* a suspension precipitated in the preliminary sedimentation tank, excess sludge which occurs during biological treatment; post-coagulation sludge *ie* a suspension formed in the chemical treatment process (Maiti *et al.*, 1992).

The quantity and quality of sludge depend on physicochemical characteristics of wastewater and technological system of the waste treatment plant (Singh and Agrawal, 2008; Włodarczyk *et al*., 2012). The mass of sludge depends on a technology of waste treatment. The sludge which by volume constitutes 3% of wastes contains over a half of the whole load of effluents flowing in crude wastewater. Their utilization expenditures constitute approx. 50% of total costs related to the operation of waste water treatment plant (Wang *et al.*, 2008).

The common features of all types of sludge are: high hydration – 93-99%, high content of organic compounds, easy putrefaction, and occurrence of biogenous fertilizer compounds (nitrogen, phosphorus) (Sousa *et al.*, 2011).

T a b l e 1. Characteristics of organic waste materials for methane fermentation process (Cebula and Latocha, 2005)

Substrates	Dry matter content (%)	Content of dry organic matter (DOM) (% d.m.)	Theoretical biogas profitability		
			from 1 kg DOM (dm^3)	from 1 Mg fresh matter (m^3)	Methane concentration (%)
Cattle slurry	10.0	68.5	801	55	55
Pig slurry	7.5	82.0	815	50	58
Chicken manure	27.0	67.0	773	140	58
Malt sprouts	92.0	93.0	600	514	58
Molasses	77.0	93.0	600	514	58
Rotary fresh	23.7	95.3	581	131	59
Rotary pickled	26.2	95.0	559	139	60
Rotary dry	90.0	95.2	602	516	60
Beet leaf silage	15.0	79.1	627	74	56
Barley straw	86.0	93.7	427	344	52
Potato waste	88.3	94.2	732	609	52
Flax waste	88.6	93.4	681	563	59
Linseed cake	89.9	93.6	698	587	60
Thin cake	8.6	91.8	756	60	58
Cake from rapeseed 15% of oil	91.0	93.2	722	612	63
Residue after rape extraction	88.6	92.1	633	516	61
Dry grass	86.0	91.9	393	311	52

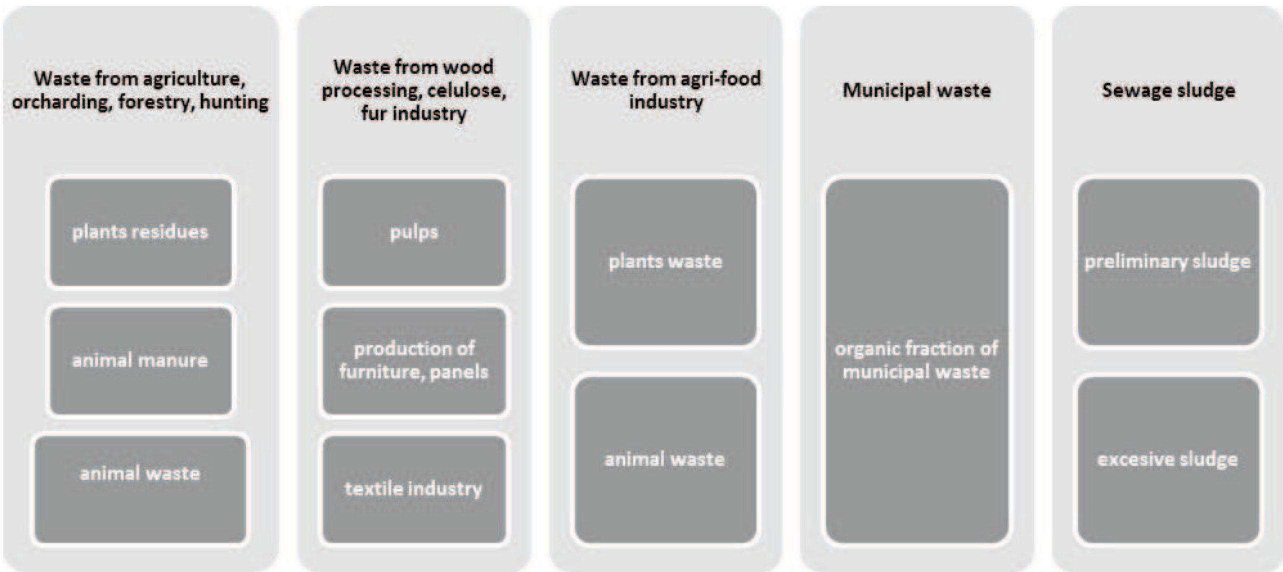

Fig. 1. Ttype of wastes suitable for methane fermentation process.

The content of mineral and organic pollutants in the preliminary sludge amounts to approx. 1-2 % of solid substance. Excess sludge contains mainly organic pollutants, in the amount of 2% of solid substance (Ren, 2004). Apart from fertilizer components, sewage sludge contains also toxic substances. The most important of them are organic compounds of chlorine: polychlorinated dibenzodioxins (PCDD), polychlorinated dibenzofurans (PCDF), polychlo- rinated biphenyls (PCB) and heavy metals. The total amount of adsorptive organic compounds of chlorine in sludge must not exceed 500 mg kg^{-1} of the sludge solid substance (Grothenhuis, 1991; Rosik-Dulewska, 2002; Verstraete *et al.*, 2002).

Sewage sludge forms a specific environment which consists of viruses, bacteria, fungi, parasitic invertebrates and their eggs. They include both pathogenic species, harmful for humans, and saprophytic microorganisms inert in sanitary respect. According to Pepper *et al.* (2006), sewage sludge usually contains the following species of bacteria: *Escherichia coli, Salmonella typhi*, *Clostridium botulinum*, *Vibrio cholerae*, *Mycobacterium tuberculosis.* The most difficult to eliminate are the eggs of parasitic nematodes, human round worm *Ascaris lumbricoides* and dogs roundworm *Toxocara canis*.

Classical methods of sludge treatment do not completely eliminate the pathogenic organisms, they merely reduce their number and vitality. Sewage sludge may be composted or processed anaerobically. Owing to a high content of nitrogen in sludge, the composting process requires addition of appropriately structure-forming materials rich in carbon. More advisable is methane digestion of sludge (Jędrczak, 2007).

In 2000 year 359.8 thousand t of sludge solid substance were produced, while in 2007 over 486.0 thousand t of solid substance (NPWM, 2010). According to the National Plan of Waste Management (2010), during 2010-2018 the amount of sludge will increase from 612.8 thousand t of solid substance to 706.6 thousand t of solid substance (Fig. 2). There are different sewage sludge utilization methods in Poland: 35.3% of the sludge has been temporarily stored in waste treatment plants, 21.4% – earmarked for land reclamation, including the land for agricultural purposes, 20.8% – on landfill sites, 17.6% – used in agriculture, 4.6% – earmarked for production of compost and manurial preparations, and 0.3% has been processed thermally (Central Statistical Office, 2009).

In recent years more and more attention has been paid to the methods which reduce the amount of sludge released into the environment. Implementation of Directive – 99/31/EC on waste landfilling is the Decree of the Minister of Economy and Labour of 12nd June 2007, introducing from 1st January 2013 a ban on disposing unprocessed sludge on landfills other than the dangerous waste landfill site. Therefore, an important purpose of sludge processing is its stabilization and volume reduction. Sludge can be stabilized using many processes, such as: composting, digestion, drying and incineration (Pepper *et al.*, 2006; Singh and Agrawal, 2008).

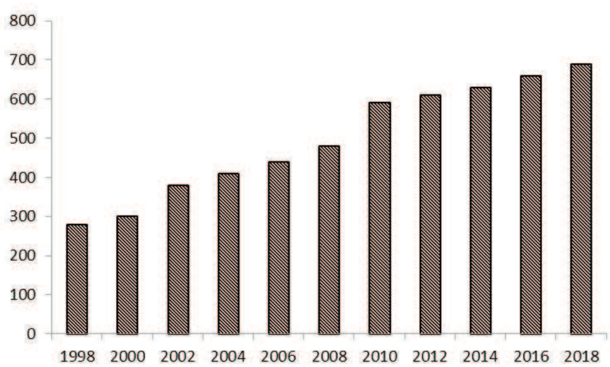

Fig. 2. Sludge production in the years 1998-2018 (thousand t) (National Plan of Waste Management, 2010).

Composting provides stabilization of organic compounds, disinfection and reduction of mass and hydration of sludge. Owing to the content of organic substance, nutrients and mineral elements the sludge may be used as a fertilizer characterized by good soil-forming properties. Subjected to this process is dewatered sludge that is mixed with *eg* straw or sawdust where the content of solids ranges from 40 to 50%, whereas hydration ranges respectively from 60 to 50%. The 26:1 ratio of organic carbon to nitrogen is required. A limitation in the use of the composting process is the requirement of chemical analysis of each portion of sludge earmarked for agricultural use and the need to lagoon the compost in winter or summer (Kosobucki *et al.*, 2000).

More advisable is the methane fermentation of sludge (Davidsson *et al.*, 2008). The sludge stabilization technology in the methane digestion process is well developed and widely used. In various countries the percentage of sludge subjected to this disposal method ranges between 30 and 70% of produced sludge. Anaerobic digestion provides reduction of unpleasant odour and elimination of pathogenic microorganisms and parasites (Nishio, 2007).

Digester gas arising from sludge processing contains approx. 60% of methane, 30% of carbon dioxide, water vapour and approx. 1-2% of hydrogen sulphide. Sewage sludge may be digested together with other wastes in the digestion process. More and more often used is sludge digestion jointly with biowastes (McMahon *et al.*, 2004). The main effects of such solution are following: increased production of biogas, higher degree of organic substance decomposition, lower concentration of toxic substances and higher concentration of fertilizer compounds in the digested sludge (Byrant, 1979; Griffin *et al.*, 2000).

Wastes coming from farming, food and agricultural industry

Increasing knowledge of microbiological and biochemical conversions within methane fermentation entails extension of the types of applied substrates and increased efficiency of the process. Figure 3 presents the different types of organic waste from agriculture and agro-food industry suitable for methane fermentation process.

Largely developed in recent years was the work related to biomass biodegradation (Sakar, 2009). Only 1-2% of reproducible biomass produced within a year is used in industry as food articles, substrates for paper-making industry and as a source of organic compounds. With development of biotechnology, also the possibilities of biological processing of raw materials hitherto not used increase. These comprise lignocellulosic materials which are waste products of agriculture, food industry, paper-making industry and municipal refuse.

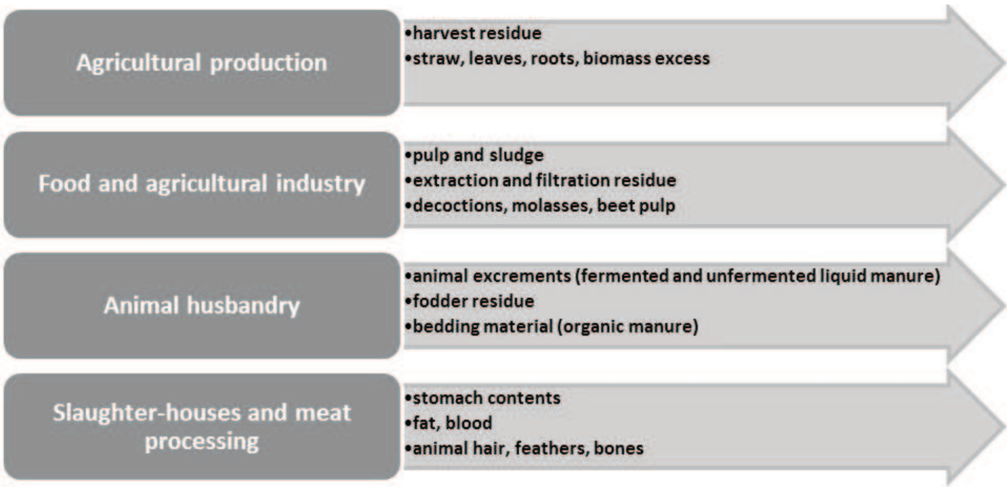

Fig. 3. Origin of farming and food and agricultural industry wastes.

Most of the food and agricultural industry wastes contain all components necessary for the development of microorganisms, such as: carbohydrates (cellulose, hemicelluloses, starch), proteins, fat, nutrients, microelements and vitamins. To provide an appropriate composition of nutrients, the composition of substrates for the fermentation process should be properly selected, which assures a high efficiency of the process with respect to biogas production. Numerous advantages arise from the use of the methane fermentation technology in agricultural wastes disposal: elimination of 'agriculturally hazardous' compounds from fertilizers, such as organic acids which may cause repulsive odour and diseases of plants, increased fertilizer value of wastes owing to the improved digestibility of the compounds, prevention of microbiological contamination of ground waters, prevention of water eutrophication through the reduction of surface flow, recovery and use of biogas (Ledakowicz and Krzystek, 2005).

Municipal wastes

Municipal wastes arise in households and infrastructure facilities, such as those related to trade, services, education, crafts, tourism, market places *etc*. According to Central Statistical Office (2009), 9 350 000 Mg of municipal wastes were produced in Poland in 2008. The municipal wastes consist of: kitchen wastes, paper and cardboard, plastics, textiles, glass, metals, mineral wastes, dangerous wastes *etc*. (Central Statistical Office, 2009). Municipal wastes may be divided into three groups: biodegradable wastes (kitchen refuse, paper, cardboard, green wastes); combustible wastes (plastics, packages, textile wastes); inert wastes (glass, mineral wastes, metals).

The content of wastes fractions varies with the region, type of buildings and specificity of households. Municipal wastes may be subjected to biological processing. Biodegradable wastes constitute approx. 40% of the total production of municipal wastes (Central Statistical Office, 2009).

Council Directive 99/31/EC on landfills, enacted on 16.07.1999, obligates Poland to reduce the amount of landfilled biodegradable municipal wastes, as compared to their mass produced in 1995, by 25, 50 and 65%, till 2010, 2013 and 2020, recpectively.

Subjected to the methane fermentation process may be biowastes which constitute a selected fraction of municipal wastes or mixed wastes. Biowastes sorted at source are the basic raw material for the production of high quality fertilizer appearing as a product of methane fermentation and biogas. The usefulness of biowastes for digestion depends mainly on the content of wastes rich in lignocellulose which is a hardly degradable compound under anaerobic conditions. The high lignocellulose content in plant wastes like branches and bark makes them less apt for degradation (Verstraete *et al.*, 2002).

Methods of organic wastes disposal and management

Wastes disposal consists in subjecting the wastes to biological, physical or chemical processes aimed at changing their condition so that they no longer create any risks for human life and health or for the environment. The wastes disposal processes comprise: landfilling on dumping sites, treatment in soil and earth, surfacial retention *eg* dumping the wastes on small sludge fields or lagoons, thermal conversion and biological processing of wastes (Kathiravale and Yunus, 2008).

One of the basic trends of operation is an intense increase in the use of both biological and thermal methods of municipal wastes conversion. Limitation of landfilling of biodegradable wastes is associated with the need to construct technological equipment for their processing: composting plants for organic wastes, set for mechanical and biological processing of wastes, installation for digestion of wastes (organic or mixed) and municipal wastes thermal processing plants (Ministry of Environment, 2008; NPWM, 2010).

Composting is a process which consists in a low-temperature aerobic decomposition of organic substance mainly by microorganisms (Slater and Frederickson, 2001). Wastes composting consists of three basic technological phases: preparation of wastes for composting, appropriate composting, and treatment of wastes. The actual composting process consists of three phases: mineralization, humification and stabilization. Composting is the most prevalent method of organic wastes disposal. Advantages of this process are following: decrease in the amount of landfilled wastes, assuring the wastes sanitary cleanliness, recirculation of organic components occurring in wastes, formation of compost which is a valuable fertilizer and structure-forming material (Jędrczak, 2007).

Methane fermentation is a process conducted under anaerobic conditions, in closed chambers at 35-55°C. The process products are: biogas and natural organic fertilizer. The usefulness of this process for organic wastes disposal is presented in further parts of the article. The main purposes of the methane fermentation process are presented in Fig. 4.

Subjected to incineration may be the wastes of low humidity content. Because of a high amount of humidity and low combustion heat, organic wastes are not subjected to thermal treatment (Weiland, 2010).

In 2014-2018 the recovery of energy from packaging wastes useless for recycling is expected to increase through their combustion in municipal wastes incineration plants. This refers mostly to plastic wastes, multi-material wastes including plastics, paper and metal foils and thin aluminium foils as well as those consumer packages exhibiting high calorific value and coming from households, for which the product residue is a barrier in recycling (NPWM, 2010).

Landfilling is a predominant form of municipal wastes disposal in Poland; over 90% of wastes mass falls to landfills. Because of the insufficiently developed system of wastes separation or lack of separation, also organic wastes are dumped on landfills. This results in reduced time of the landfill use, the landfill nuisance related to the production and migration of biogas, and occurrence of highly polluted effluents. Modern landfills for wastes have some drainage systems to carry off biogas and effluents. Biogas is used for production of electrical and thermal energy, whereas effluents are referred to the waste treatment plant.

Generation and migration of biogas on landfills create hazards not only for the environment but also for humans. Biogas may get into the atmosphere or buildings, creating hazards connected with: self-ignition and explosion, increased greenhouse effect, toxic effects on humans and animals, necrosis of plants because of limited access of oxygen to the roots (McMahon *et al.*, 2004). The biogas production in methane fermentation process can be associated with potential greenhouse gases reduction (Budzianowski, 2011). It is a very important for environment protection sector.

LEGAL CONDITIONS OF WASTE DISPOSAL

There are a number of legal regulations indicating that the preferred method of biodegradable waste disposal is their selective collection aimed at organic recycling. The main legal act governing the wastes management in Poland is the Act on Wastes of April 27, 2001 (Official Journal of Laws, 2001). This document defines wastes as substances and items which the owner gets rid of, intends to get rid of or is obliged to get rid of. Biodegradable wastes comprise those which undergo aerobic or anaerobic degradation with a contribution of microorganisms.

Another document is the National Plan of Wastes Management (2010). This document presents the activities which will enable to form an integrated wastes management assuring environmental protection, considering the present and future technical, organizational possibilities and economic conditions. The long-term tasks within the NPWM

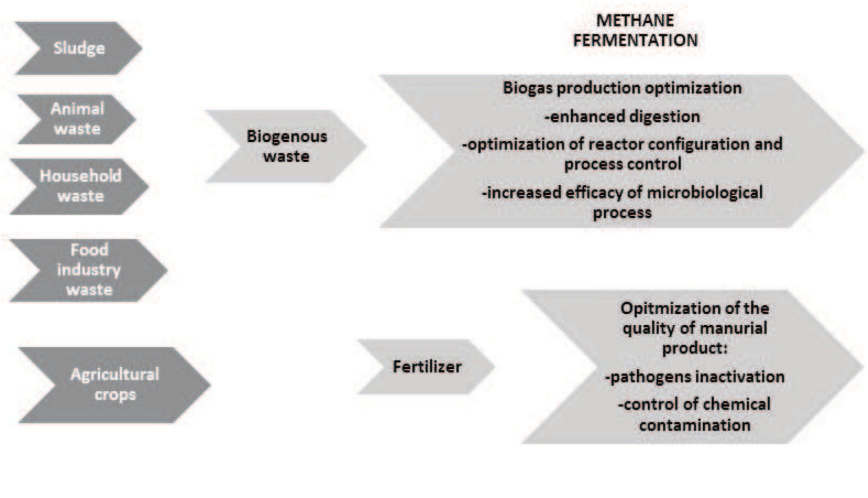

Fig. 4. Basic aims of methane digestion.

(2010) include: improvement of municipal wastes management systems, development of selective collection of wastes, implementation of modern technologies of recovery and disposal of wastes.

The Renewable Energy Development Strategy (2001) approved by the Polish Parliament onAugust 23, 2001 is the most important document for development of renewable sources of energy in Poland. The document presents the objectives and conditions of the development of renewable energy till 2020. The strategy assumes an increase in the share of energy from renewable sources in Poland fuel-energy balance up to 14% by 2020.

The directive on wastes – Council Directive No. 75/442/EEC (1975) establishes the general rules of dealing with wastes in the European Union countries. This document determines the hierarchy of wastes handling which aims at prevention of wastes formation, reduction of their quantity and hazardousness, and their recovery and re-use.

The directive on earth landfills for wastes – Council Directive No. 99/31/EC of April 26, 1999, defines the biodegradable waste as all waste undergoing aerobic or anaerobic decomposition. The directive determines adopting by the Member States of a strategy of limiting biowastes earmarked for landfilling. Pursuant to this document, by 2016 the quantity of biodegradable municipal wastes which are dumped on landfills must be decreased to 35% of weight units, as compared to 1995.

Energy for the Future: Renewable Energy Sources. White Paper for Community Strategy an Action Plan was published by the European Commission in November 1997. This document presents the European Union states energy policy priorities which comprise: increased competitiveness of the sector of renewable sources of energy in the European Union; environmental protection, assuring the safety and diversity of energy supplies.

Conditions and factors affecting the process of methane digestion

The methane digestion process is characterised by high sensitivity to external factors and has to be fully controlled. For correct course of methane digestion, appropriate environmental requirements for methane bacteria have to be met. Efficiency of the process depends on many factors and parameters, including: temperature, presence of oxygen, reaction, nutrients and toxic substances as well as retention time and the reactor substrate load.

ENVIRONMENTAL PARAMETERS

Oxygen belongs to the key elements deciding of the methane formation process. Access of oxygen to bioreactor inhibits the production of methane. It affects the rate of microorganisms growth and physiology of cells *ie* the type, efficiency and production of specific metabolites (Nishio, 2007). Methanogenic bacteria are obligatory anaerobes and even the lowest amount of oxygen (0.01 mg l^{-1}) stops their growth. In the initial phases of methane fermentation the bacteria which are facultative anaerobes (*Streptococcus*, *Enterobacterium*) grow and use oxygen, thereby creating advantageous conditions for the growth of methane bacteria (Jędrczak, 2007).

Also temperature is one of the most important parameters affecting the methane fermentation process (Varel *et al.*, 1980). Anaerobic degradation of organic matter may be conducted in a vast range of temperatures (10-60°C). The temperature is not so important for the bacteria which conduct hydrolysis, owing to high adaptability of these microorganisms to the conditions in which the process is conducted. However, it is particularly important for methanogenic bacteria, due to a limited temperature resistance of their protein structures (Mashaphu, 2005). Once the process temperature is established, bacterial cultures adapt to it and any change may cause inhibition of methanogenic phase and domination of acidic phase. During operation of fermentation chambers, the stability of temperature is required and its amplitude cannot be higher than 2°C a day.

The amount of biogas arising from anaerobic decomposition largely depends on the process temperature. At higher temperatures the organic matter decomposition is faster, at the same time more biogas is produced (Sanchez *et al.*, 2000). At 10°C, from 1 kg of dry organic mass, approx. 275 dm^3 of biogas is obtained, while at 20°C – 380 dm^3, and at 30°C as much as 480 dm^3. The efficiency of termophilic digestion (from -55 to -65ºC) is increased by 25-30% compared to mesophilic conditions (30-40°C), at the same time under these process conditions the lower growth of biomass is observed (Scherer *et al.*, 2000) along with a high degree of post-digestion sludge hygienization which is not provided by mesophilic digestion. However, because of the high costs of heating and maintaining of appropriate temperature, the thermophilic methane fermentation is rarely used in Poland.

Furthermore, the environmental reaction significantly affects the efficiency and stability of methane formation. Changes in pH reflect variable phases of waste decomposition (Sanchez *et al.*, 2000). The pH value is determined by a buffer system which depends on the presence, in the digested mass, of weak acids (carbonic acid, organic acids, hydrogen sulfide) and weak bases (ammonium hydroxide). The pH decides of the solubility of organic and inorganic compounds and about correct functioning of microorganisms. The optimum value of pH for bacteria conducting hydrolysis and conversion of monomers into simple organic acids ranges between 5.2 and 6.3. Methane bacteria require constant neutral conditions: pH between 6.8 and 7.2, and even small changes in pH cause disturbances in their reproduction. The optimal pH for the processes of anaerobic waste decomposition ranges between 6.7 and 7.5 (Bryant, 1979; Lyberatos and Skiadas, 1999).

The content of nutrients is another factor significantly affecting the course of the process of methane fermentation. For metabolic conversions of organic substance by microorganisms, the presence of a number of mineral components (C, H, O, N, K, S), especially nitrogen and phosphorus, is essential. These elements are extremely important, because nitrogen is contained in cellular proteins, and phosphorus is a component of high energy compounds (Cooper *et al.*, 1994; Lanyon *et al.*, 1985; Sanchez *et al.*, 2000). Apart from the above mentioned elements, for correct development of microorganisms the soluble forms of potassium, sodium, iron, magnesium and calcium are necessary, as well as trace elements (molybdenum, manganese, copper, zinc, cobalt, selenium and tungsten) in dissolved form (Zeikus, 1977). Typical substrates, such as: agricultural wastes, sewage sludge, and biowastes usually contain appropriate amounts of the mentioned elements.

Furthermore, decisive of a stable course of the process are appropriate proportions between carbon and the other elements which assure appropriate metabolism of microorganisms and consequently – decay of organic matter (Gonzalez-Avalos and Ruiz-Suarez, 2001). Because of a low energetic efficiency of anaerobic metabolism, the increase in bacterial biomass is relatively low and does not exceed 10%, therefore the demand of biogenic elements is relatively low (Wable and Randall, 1994). The structure of hypothetical cellular substance $C_5H_9O_3N$ indicates that approx. 11% weight nitrogen is needed for the bacterial cell synthesis. The phosphorus demand is estimated as 15-25% of the demand of nitrogen (Lanyon *et al.*, 1985; Zeikus, 1977). Particularly important is the C:N ratio which in wastes should vary between 10:1 and 16:1. The C:N ratio is the function of availability of carbon and nitrogen in substrates. Digestion may be effective even if this ratio reaches 90, because not all organic carbon and nitrogen occurring in the raw material are available during biodegradation. If the C:N ratio is too low, an excess of nitrogen may give rise to formation of ammonia which even in low concentrations inhibits the growth of bacteria. The optimum N:P:S ratio is 7:1:1 (Jędrczak, 2007).

The content of water in wastes significantly affects the growth of microorganisms in the digested mass. Water is the basic component of living organisms (Gonzalez-Avalos and Ruiz-Suarez, 2001). It affects the structure and properties of wastes and is necessary for the transport of raw materials and metabolites. The minimum level of humidity in wastes required to conduct the processes of biological decomposition of wastes is very low. Decomposition of wastes may be observed even at approx. 20% humidity. Effective waste stabilization requires the maintenance of humidity at the level of 60-70%. Besides, acidic bacteria grow faster at a low humidity of wastes, which may become an inhibiting factor in relation to methanogenic bacteria population. The maximum content of solid substance in substrates should not exceed 40%. At a lower content of water some phenomena may occur which disturb the correct course of biological process (Ministry of Environment, 2008).

The size of waste particles also significantly affects the intensity of their biological decomposition processes. A decrease in the size of particles enables the growth of microorganisms on a larger surface of wastes, besides it increases the effectiveness of the exchange of water and nutrients, consequently accelerating the process of waste decomposition (Montalvo *et al.*, 2005). In result, the decrease in the size of waste particles causes an increase in the rate of the first stage of digestion – hydrolysis and contributes to increased production of gas. A negative effect of the particles comminution is an increase in specific resistance of digested wastes (dewatering) (Jędrczak, 2007).

Mixing of biomass determines the correct course of the process of digestion due to: assuring a homogeneous course of the processes in the whole volume of biomass, maintenance of uniform temperature, maintenance of equal consistency, improved degassing and decrease in the amount of dissolved carbon dioxide, prevention of biomass thickening in result of released oversludge water. The basic parameters of the process of mesophilic methane fermentation are presented in Table 2 (Miksch and Sikora, 2010).

T a b l e 2. Basic parameters of the process of mesophilic methane fermentation (Miksch and Sikora, 2010)

Parameter	Optimum value	Extreme value
Temperature (°C)	30-35	25-40
Reaction (pH)	6.8-7.4	6.2-7.8
Oxidation-reduction potential (mV)	-520 to -530	-490 to -550
Alkalinity (g $CaCO_3$ m^{-3})	2000-3000	1000-5000
Volatile organic acids (g CH_3COOH m^{-3})	50-500	2000

Toxic substances – inhibitors of the process

Microorganisms accounting for the course of the digestion process are very sensitive to chemical substances which may be introduced to the fermenter in supplied substrates or may arise as intermediate products during their decomposition. These substances are called the process inhibitors. The effect of the presence of inhibitors may be an evident decrease in daily production of biogas, and in extreme cases – complete inhibition of transformations within the process (Bryant, 1979; Classen *et al.*, 1999).

The scale of the effects of toxic compounds on methanogenic bacteria and digestion process depends on their concentration, form of occurrence, dissociation degree and presence of other inhibitors. We should emphasize that undissociated forms exhibit toxic effects at a much lower concentration, as compared to dissociated forms.

Many studies aimed at determining the proper living conditions in the anaerobic digestion environment refer to the effects of toxic substances (Anderson *et al.*, 2006; Denman *et al.*, 2007; Goel *et al.*, 2009; Mathers and Miller, 1982; Tezel *et al.*, 2006). The toxic components for anaerobic microorganisms may be both substances supplied from outside and those arising in excessive amounts in the cellular metabolic processes (Kumar *et al.*, 2009).

The impact of these substances is differentiated. Some cause the cellular wall destruction, other adversely affect the protoplasm or enzymes participating in metabolism (Van Nevel and Demeyer, 1992). The toxic substances introduced into the process in biomass comprise: cations of metals: Mg^{2+}, Ca^{2+}, Na^{+}, K^{+}, Pb^{2+}, Cd^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}; anions: cyanides CN^{-}, carbonates CO_3^{2-}, sulfides S^{2-}; organic compounds: fodder additives, disinfectants, disinsectants, chemotherapeutic agents, pesticides, surfactants, oxygen, chlorine and such substances as: quinine, potassium chlorate, chloroform, atropine, strychnine (Jędrczak, 2007; Kumar *et al.*, 2009).

Ionic forms of heavy metals exhibit strong toxic effects for microorganisms through inhibition of important metabolic enzymes. Toxic organic compounds, such as detergents, pesticides, solvents and medicinal drugs largely inhibit the growth of methane bacteria. Metabolites released during digestion may become inhibitors of the process when the concentrations allowing their usage as substrates in consecutive phases of the process are exceeded. Of the products of conversions occurring in the fermentor, the following exhibit toxic effects: volatile fatty acids, hydrogen sulfide, ammonia, hydrogen (Guan *et al.*, 2006; Kumar *et al.*, 2009).

Organic acids are products of acidic phase of the methane digestion process. Volatile acids, such as: acetic, propionic and butyric acids exhibit toxic effects on the digestion environment when their concentration in the digested suspension is too high. Most toxic for anaerobic microorganisms are long-chain fatty acids, such as oleic and stearic acids. Although they are degradable, they inhibit the production of methane (Dohme *et al.*, 2004; Machmuller and Kreuzer, 1999). In the case of an excessive increase in the concentration of volatile fatty acids, the so called 'refraction' of methanogenic phase *ie* methanogenesis occurs. Toxic effects were found most of all in the case of protonated forms of acids the share of which grows with decreased pH. For anaerobic cultures, also long-chain fatty acids, such as stearic and oleic, are toxic. These acids are degradable, but they inhibit the formation of methane. So far, microorganisms adaptation to toxic effects of fatty acids has not been found (Boone *et al.*, 1993). The share of protonated forms of acids was found to increase with a decrease in pH. The decrease in pH by unit causes a ten-fold increase in the share of the molecular form, as compared to the total amount of acid. It was found out that allowable concentration of volatile fatty acids in digested wastes should not exceed 2000 mg of CH_3COOH dm^{-3}. Assumed as optimum concentrations of volatile acids are 100-500 mg of CH_3COOH dm^{-3} (Jędrczak, 2007).

Also the impact of sulphur compounds on methanogenesis is complex. Toxic concentrations of sulfates have not been analysed in literature in detail. Most frequently a value higher than 200 mg SO_4^{-} dm^{-3} is presented. Sulfides and hydrogen sulfide may be introduced to digestion with wastes or may be formed in result of reduction of sulfates or decomposition of amino acids containing sulphur. Methane bacteria tolerate the concentration of sulfides between 50 and 100 mg dm^{-3}, and their content amounting to approximately 5 mg dm^{-3} may even stimulate the production of methane (Karhadkar *et al.*, 1987). Besides, while determining allowable concentrations of heavy metals in anaerobic processes of treatment, we should also take into account the presence of sulphur compounds. Approximately 1.8 to 2.0 mg dm^{-3} of heavy metal ions are precipitated, in the form of sulfides, by 1.0 mg dm^{3} of ions S^{-3}. The toxicity of heavy metals depends upon the concentration of the various chemical forms that they may take under anaerobic conditions at the present temperature and pH (Ahring and Westermann, 1983).

Hydrogen sulfide arises from decomposition of organic sulphur compounds (cystine, cysteine, methionine) and in the process of sulfates reduction by bacteria *eg Desulfovibrio desulfuricans*. Inhibiting effects of hydrogen sulfide is displayed at 25-50 mg dm^{-3} concentrations, and complete termination of the production of methane occurs at the concentration of 200-300 mg dm^{-3}. The toxic effects of hydrogen sulfide are increased with decreased pH value (Karhadkar *et al*., 1987).

The mechanism of toxic effects of hydrogen sulfide remains unknown as yet. Hypotheses of inhibiting effects of H_2S: a high concentration of hydrogen sulfide is toxic for methanogens, trace elements (Ni, Co, Mo, Fe), indispensable for the growth of methanogenic bacteria, form with sulfides hardly soluble compounds, unavailable for these microorganisms and reduction of sulfates constitutes a competition for methanogenic bacteria (Kumar *et al.*, 2009).

Hydrogen sulfide exhibits the highest toxicity in its molecular form. Inhibiting effects of hydrogen sulfide on the digestion process occurs at the molecular form concentration of 25-50 mg dm^{-3}, whereas the complete inhibition occurs at the concentration equal to 200 mg dm^{-3}. Hydrogen sulfide may form with heavy metals hardly soluble sulfides the precipitation of which on the one hand is advantageous, because it leads to decreased concentration of hydrogen sulfide and heavy metals which in excessive amounts are toxic for anaerobic microorganisms (McCartney and Oleszkiewicz, 1991). On the other hand some trace elements (Ni, Co, Mo, Fe), indispensable for bacteria growth, may become unavailable for them (Feng *et al.*, 2010).

Ammonia is formed during anaerobic decomposition of organic nitrogen compounds such as: proteins, amino acids, urea, and constitutes the basic source of nitrogen in wastes. The problem of its toxic effects occurs in raw materials digestion processes with a high content of protein. In excessive amounts it may be toxic for anaerobic bacteria. Ammonia is hazardous to the growth of methanogenic bacteria. The concentration of ammonia is increased when the alkaline reaction is increased and the concentration of OH^- ions is increased. A high concentration of NH_3 may lead to inhibited process of biogas production (Hansen *et al.*, 1999). A state of nitrogen balance in the digestion mass is extremely important, because ammonia (NH_3) was found to be over 20 times more toxic than ammonium ion. In neutral environment (pH=7) the ionic form dominates and only 1% of nitrogen occurs in the form of free ammonia, while at pH 8 over 5% is in an undissociated form. Ammonia inhibits the methane bacteria growth through inactivation of the enzyme connected with methane synthesis and through the disturbance in the acid-alkaline balance resulting from the diffusion of this compound into the cells (Gallert and Winter, 1997). More hazardous for methanogenesis than ammonia are nitrates (V) which for most anaerobic bacteria play the role of electron acceptor, thereby contributing to accumulation of nitrates (III) in the environment, decrease in the production of hydrogen, increase in the release of carbon monoxide (IV) and in turn, in an intensive growth of non-methanogenic bacteria. Formation of ammonia disturbs also the acid-base balance of the environment, causing a strong alkalization which inhibits the growth of methanogenic bacteria while a decrease in pH reduces toxic effects of ammonia due to its protonation (Borja *et al.*, 1996; Gallert and Winter, 1997). We should emphasize that low concentrations of ammonium ions in the digested raw material (50-200 mg N dm^{-3}) stimulate methanogenic activity. Free ammonia inhibits the growth of methanogenes at a concentration higher than 80-100 mg dm^{-3}, and kills them above 150 mg dm^{-3}. Resistance of methanogenic bacteria to toxic effects of ammonia increases during free adaptation of microorganisms to higher concentrations of ammonia (Strik *et al.*, 2006).

McCarty (1964) in his research found out that at ammonia nitrogen concentrations from 1.5 to 3.0 g dm^{-3} and pH above 7.0 the digestion is inhibited, whereas above 3.0 g dm^{-3} – ammonia becomes toxic irrespective of the pH value. The amount of environmental pH is important because the balance between it and ammonium ions is sensitive to pH changes. Free ammonia, toxic for the process concerned, is released at high pH values (Chen *et al.*, 2008). But some studies demonstrate that after an appropriate adaptation the bacteria can tolerate higher concentrations of ammonia. Kroeker *et al.* (1979) examined a substrate containing urea and acetic acid. They found out that the production of methane was decreasing at ammonia concentrations above 2.0 g dm^{-3}, but even at 7.0 g dm^{-3} the process was not inhibited completely.

Nitrates are more hazardous than ammonium ions. Their concentration above 150 mg dm^{-3} is considered to be toxic. On the other hand Winfrey and Zeikus (1977) indicate that in lake water even at the concentration of 10 mg NO_3^- dm^{-3} methanogenesis is inhibited. At the same time they did not find inhibition of the process in bottom deposits of lakes even at concentrations of 10 000 mg NO_3^- dm^{-3}. It is possible when denitrification occurs and molecular nitrogen is released into the atmosphere. We could generally say that the impact of nitrogen compounds on the digestion process is complex and depends on many factors, such as: pH, concentration and type of pollutants, form of nitrogen and adaptation of bacteria capability to remove hazardous compounds.

A relatively high impact on anaerobic digestion is also that of the concentration of cations: Ca^{+2}, Mg^{+2}, K^+, Na^+. At low concentrations of the salts of these metals a stimulating effect occurs, but at higher concentrations there may be inhibition, till it stops completely (Chen *et al.*, 2008; Krylova *et al.*, 1997; McCarty and McKinney, 1961).

Many studies (Borja *et al.*, 1997; Gonzales-Gil *et al.*, 2002; McCue *et al.*, 2003; Stergar *et al.*, 2003) refer to determination of the impact of aldehydes, unsaturated ketones, phenols and other organic compounds on methane fermentation. Their authors demonstrated that an evident (over 50%) deterioration of digestion effects was observed at the following concentrations of the compounds selected for the studies: acrylaldehyde – 20-50, formaldehyde – 50-100, crotonaldehyde – 50-100, diethylamine – 100, and phenol – 300-1 000 mg dm^{-3}. Inhibiting effects of these compounds were increased at concentrations of volatile acids, present in the substrate, exceeding 500 mg CH_3COOH dm^{-3}. According to Quayle (1972), allowable concentration of formaldehyde in the substrate amounts to 0.2% per dry mass. On the other hand Meinck and Stoof (1975) state that microorganisms may be adapted to its concentration equal even to 15% of dry mass. Few studies refer to the effects of antibiotics on the course of anaerobic processes. According to Fischer *et al.*, (1981), chlorotetracyclines do not exhibit adverse effects on methanogenesis. Similarly Sanz *et al.*, (1996) indicate that erythromycin, penicillin and streptomycin in the amount of 1 000 μ dm^{-3} do not inhibit biological decomposition. The authors concluded that most of the antibiotics normally used in livestock farms will not drastically affect biogas production if used at recommended concentrations. A similar conclusion was also drawn by Massé *et al.* (2000) who studied the effect of antibiotics on psychrophillic anaerobic digestion of swine manure.

Aliphatic alcohols exhibit bactericidal effects at different concentrations, starting from 100 mg dm^{-3}; the longer their chain, the higher the toxic effect (Alves *et al.*, 2001; Shin *et al.*, 2003). Also unsaturated long-chain fatty acids may evidently inhibit the process of digestion at concentrations of mmol dm^{-3}. The toxicity of these compounds grows with increased degree of their unsaturation (Pereira *et al.*, 2003).

The toxicity of the compounds depends also on the dissociation degree. The undissociated compounds exhibit toxic effects even at low concentrations, whereas dissociated – at higher concentrations. The presence of heavy metals in the substrate reduces toxic effects of hydrogen sulfide (O'Flaherty *et al.*, 1998). However, nickel, cobalt, molybdenum and selenium constitute stimulators of methanogenic bacteria (Kayhanian and Rich, 1995).

RECAPITULATION

The amount of wastes in Poland is constantly increasing, causing also an increase in the importance of correct management of wastes and interest in methods of rendering them harmless. The growing amount of produced biodegradable wastes, the need to eliminate odours and a great emphasis put on the development of renewable sources of energy largely contribute to increased interest in methane digestion as a method of rendering the wastes harmless.

Another cause of the development of the technology of anaerobic disposal of wastes are legal regulations in Poland and the European Union, which place a special emphasis on environmental protection and renewable energy. The obligations resulting from the National Plan of Wastes Management, connected with limited landfilling of biodegradable wastes and increased use of energy from renewable sources, according to the Renewable Energy Development Strategy, also pose a significant premise for the development of technologies based on methane digestion. A significant asset of anaerobic technologies is the possibility of simultaneous rendering wastes harmless and production of biogas counted among renewable sources of energy.

The technologies of anaerobic processing of wastes enable to render harmless the qualitatively different wastes which are the charge material. These comprise, among other, agricultural wastes, food industry wastes, sewage sludge or municipal wastes. Currently pending are the studies on combined digestion of wastes coming from different sources to obtain biogas containing a high amount of methane.

In recent years the interest in the possibility of anaerobic disposal of organic wastes has grown significantly. In the world, especially in Europe, new facilities arise which are specialized in wastes biodegradation using the methane digestion process.

The use of the methane digestion technology in rendering the wastes harmless brings about many benefits, both for the wastes management and for the environment. The methane digestion process largely reduces emission of methane into the atmosphere; being processed into electrical energy, methane is one of the main greenhouse gases. The use of biomethane as a renewable source of energy diminishes the use of fossil fuels *ie* brown coal or petroleum. Methane digestion technologies contribute to sustainable management of (agricultural, industrial, municipal) wastes, limiting their landfilling. Another benefit is the use of the digestion sludge in agriculture, which is associated with the return of nutritive components to the soil, improvement of its structure and decreased use of mineral fertilizers, which minimizes the water eutrophication effect.

One of the most important factors limiting the intensive development of methane digestion technology are high investment costs connected with the construction of a biogas plant and its correct, failure-free operation. In last years appropriate economic instruments in the form of preferential loans or subsidies were introduced to imopove financial sector of biogas production and would help in development of these technologies also in Poland.

From the conducted analyses in Poland the following conclusions could be drawn:

– Methane fermentation process is one of the most important method for biodegradation and utilization different organic waste.
– There are many feedstocks for sustainable biogas production in Poland, included sewage sludge, waste from farming, food and agricultural sector.
– Biogas energy sector could stimulate development of agro-food industry by increase the role of agrobiogas production not only in Poland, but also in other EU countries.

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