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DYNAMICS OF METHANE FERMENTATION PROCESS AND RETENTION TIME FOR DIFFERENT AGRICULTURAL SUBSTRATES

Summary

A hydraulic retention time (retention) also known as HRT is one of the most important parameter in biogas plant exploitation. In practice, there are many substrates with different HRT used in agricultural biogas plant which makes difficulties in fermentation process optimization. The aim of this study was to investigate and compare the efficiency of biomethane production and to determine the dynamics of the fermentation process expressed by reaching 60, 80, 90 and 100% of HRT. The results showed very big differences in efficiency of methane production as well as HRT duration between analyzed substrates. The total fermentation period (100% of HRT) for investigated substrates amounted average 31,5 day (range: 21-41 days). However production of last 10% of methane average out 28%. It proves very low dynamics of fermentation process in the last phase.
Key words: *biogas plants, agricultural substrates, methane fermentation process, retention time, experimentation, Poland*

1. Introduction

Along with the constant development of civilization and improvement of the material situation of the society, especially in the developed and developing countries, it is more visible an increase of energy consumption. This trend requires the delivery of more and more increasing amounts of energy for the population ever [1]. This can be achieved by using two basic options in order to satisfy the energy demands. The first one is to increase the production and then combustion of fossil fuels. This process is not favorable to the environment since it causes its significant devastation. The second way is to increase the share of energy from renewable sources. This action will help to keep energy level obtained from fossil fuels at a constant level, or even reduce it in order to limit the negative changes in the environment [2]. One type of the renewable energy sources is its extraction from biomass in biogas plants. In these installations from bio-wastes or intentionally prepared agricultural substrates through the methane fermentation the biogas can be obtained [3]. Biogas is a mixture consisting mainly of methane and carbon dioxide. Obtained gas mixture can easily be converted into electricity, heat, or, if necessary, to obtain pure methane similar to that found in natural gas. It is obvious that the more biogas in the shortest period of time will be produced the more energy will be gained [4]. In consequence this yield allows the biogas plant to achieve higher incomes from energy sale.

Although the biogas production under anaerobic conditions is the process naturally occurring, it is possible to some extent be influenced. It can be achieved primarily through the proper selection of the substrates [5] i.e. an attempt to achieve synergy effect and ensuring their adequate preparation for the trial. More important factor before supplying the substrate into the fermentation chamber affecting the efficiency should be their purification and fragmentation. Purification is a process that allows to separate from the substrates mixture such part which is undesirable. It concerns all kinds of impurities such as mineral fraction, plastics, glass, etc. Fragmentation is conversion process of raw materials into smaller pieces with a fixed diameter which will increase the efficiency of fermentation itself and prevent the interferences occurring in the process [6]. The fragmentation and other pre-treatment techniques (e.g. use of ultrasound, steam explosion or extrusion) allow for a significant acceleration of fermentation processes organic making an organic matter of the substrate more accessible for fermentation bacteria [7]. Extremely important parameter characterizing the efficiency of the methane production process is a hydraulic retention time (retention) also known as HRT. This parameter determines the average residence time of the substrates in fermentation chamber of the biogas plant. The longest retention time is required for the hard decomposable substances in fermentation process, such as cellulose, hemicellulose or lignin [8]. Decomposition of the substrates rich in these materials is time-consuming, thereby the efficiency of the process is significantly limited. Substrates positively affecting the efficiency of the anaerobic digestion are those rich in carbohydrates, fats and proteins [9]. Taking into account these dependences the determination of retention time seems to be an important parameter informing about the changes dynamics of methane fermentation process. In a further stage the knowledge of this parameter allows to estimate the optimal choice of substrates in order to increase the amount of produced energy and eliminates possible effects of inhibitors that prolong the process [10]. In practice, the substrates used in Polish biogas plants have very different length of HRT, which size can vary by as much as several hundred percent. However, for proper investment planning of the biogas plant as well as the calculation of its technical parameters is important to consider both the biogas efficiency of the substrates and its fermentation period [11].

In practice, the substrates fermentation until they are completely fermented is not used because final fermentation period which is characterized by a small amount of produced biogas can be very long. [12]. However it requires the construction of the very large digesters and dramatically increases the cost. Hence the real retention time in the fermentation chamber does not exceed 90% of HRT.

In case when the tank with digested pulp is hermetic and allows to collect the biogas then HRT may be reduced to 80%.

The aim of this study was to investigate and compare the efficiency of biomethane production and to determine the dynamics of the fermentation process expressed by reaching 60, 80, 90 and 100% of HRT. The authors were focused on the analysis of the content of the produced methane as this biogas component determines the efficiency of the fermentation process.

2. Methodology

The Experiments were carried out in the years 2011-12 in Ecotechnology Laboratory located at the Poznan University of Life Sciences (PULS). They were based on a modified German standard norm DIN 38 414, while the physico-chemical analyzes of the substrates were based on the Polish Standards. Analytical procedures concerning the bio-waste have been developed in the laboratory during several research projects funded by the European Union 6th Framework Programme and Polish Ministry of Science and Higher Education in the years 2006-12.

Substrates and inoculum

The common substrates used for the biogas production in Poland have been tested, such as: cattle slurry, cattle manure, swine slurry, swine manure, maize silage, beet pulp, brewers' grains, maize straw, distillery decoction, slaughter waste, turkey manure, tomatoes waste.

It should be noted that maize silage before the fermentation process was crushed to a grain size 0-5 mm (using a chopper), since in such form it will be used in summer 2013 in the new opening PULS biogas plant, in Przybroda. Such a pre-treatment aims in acceleration of the fermentation process. The digested pulp from working Polish biogas plant was used as inoculum.

Fermentation position

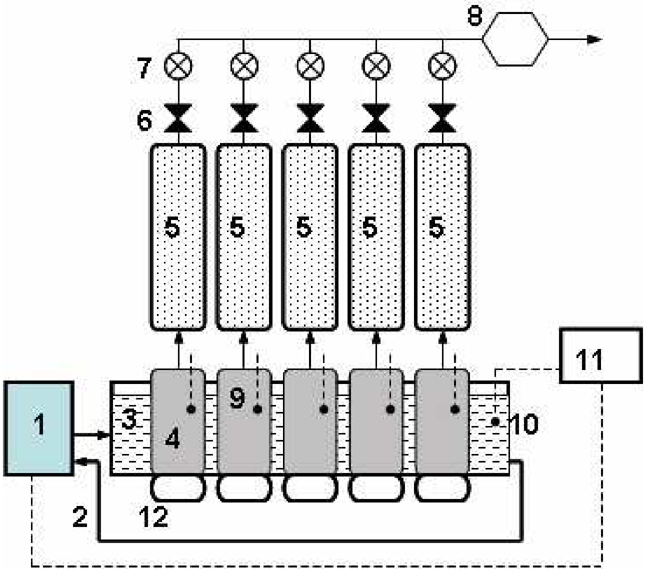
The experiments were carried out in 21-chamber fermenters for methane fermentation. Simplified diagram of this position is shown in Figure 1. These reactors are commonly used in order to investigate the biogas efficiency of many biosubstrates.

In order to conduct the experiments there were used two-liter glass reactors constructed in the Ecotechnology Laboratory. Due to achievement of anaerobic conditions and inoculum additive the ideal conditions for methane fermentation have been created. In order to run the process under mesophilic conditions, the reactors were placed in a temperature-controlled aquariums of 39°C, to achieve the typical conditions for most of the agricultural working biogas plants. The biogas produced in each reactor was stored in measured cylinders filled with barrier liquid (a substance with reduced solubility of gases). Each test was performed in 3 replications.

Solid samples

Prepared for the fermentation samples were analyzed in terms of physical and chemical parameters. The most important of these was pH, which optimum in fermentation process ranges from 6.8 to 7.5. Then the substrates were tested for the content of ammonium nitrogen.

This analysis is important because if the concentration of N-NH4+ in the mixture prepared for fermentation exceeds 2.7 g/dm3 then strong inhibition of the process takes place [14]. Was used for CP-411's pH meter from Elmetron firm was used for pH measurements. In addition it has been done the analysis of the content of dry matter and dry organic matter of the analyzed samples. This was necessary to determine the biogas efficiency of the substrates per ton of dry matter and dry matter of organic substrate. While conducting experiments used for the following Polish Standards: for dry matter PN-75 C-04616/01, pH - PN-90 C-04540/01 and dry organic matter PN-Z-15011-3. Nitrogen was determined by the Kjeldahl method.



Source: own study

Fig. 1: Scheme of biofermentor for biogas production research (5-chamber section): 1 – water heater with temperature regulator, 2 – insulated conductors of calefaction liquid, 3 – water coat with temp. 36-38°C, 4 – biofermentor with charge capacity 2 dm^3, 5 – biogas reservoir, 6 – cutting off valves, 7 – gas flow meters, 8 – gaseous analyzers (CH_4, CO_2, NH_3, O_2, H_2S), 9 – pH sensors, 10 – temperature sensor, 11 – steering – recording central station, 12 – charge magnetic mixers

Gaseous samples

The volume of produced gas was checked every 24 h. Gas analyzes were performed on a gas analyzer MSMR-4 of ALTER S.A. It consisted of a number of electrochemical factors (heads Mg-72 and Mg-73) for checking the concentration of the following gases: methane, carbon dioxide, oxygen, hydrogen sulfide and ammonia. Analysis of biogas composition was performed for each 1 liter of produced gas. This was due to the characteristics of the measuring apparatus, for which 1 dm^3 was the minimum volume to carry out this analysis.

Gas sensors were characterized by the following measuring range: CH_4 0-100%, CO_2 0-100%, O_2 0-25%, H_2S 0-2000 ppm and NH_3 0-2000 ppm. The calibration took place at weekly intervals with the calibration gases supplied by Air Products of the following parameters: 65% CH_4, 35% CO_2 (in a mixture). 500 ppm H_2S and 100 ppm NH3. The oxygen sensor was calibrated with synthetic air. The biogas productivity was calculated in specially written biogas calculator (the MS Office Excel). Analyzing the resulting graphs it was possible to analyze the current accuracy of the process.

3. Research results

Summary results for the production efficiency of the biogas and biomethane are presented in Table.

Table. The results of production efficiency of biogas and methane based on fresh and dry mass and dry organic mass

Sample	Methane concentration [%]	Cumulative methane [m³/t FM[1]]	Cumulative biogas [m³/t FM]	Cumulative methane [m³/t DM[2]]	Cumulative biogas [m³/t DM]	Cumulative methane [m³/tODM[3]]	Cumulative biogas [m³/tODM]
Cattle slury	54,30	20,89	24,07	172,63	198,95	207,98	239,70
Cattle manure	53,41	22,32	27,65	160,19	198,42	203,08	251,55
Swine slury	44,71	2,17	4,68	124,90	269,02	230,99	497,43
Swine manure	55,00	66,59	111,14	236,14	394,18	292,26	487,77
Maize silage	52,86	136,96	247,96	331,34	600,07	349,07	632,01
Beet pulp	54,08	75,96	125,85	350,10	580,03	361,45	598,84
Brewers' grains	54,40	79,69	134,74	362,60	613,10	379,49	641,66
Maize straw	49,05	204,85	418,24	228,99	467,52	255,85	522,37
Distillery decoction	55,44	29,19	49,59	412,13	700,22	463,02	786,77
Slaughter waste	63,06	303,12	461,42	632,55	962,76	662,92	1009,12
Turkey manure	51,63	90,11	168,38	157,80	294,89	190,06	355,17
Tomatoes waste	45,74	46,71	102,79	301,52	663,50	325,91	717,18

[1]FM – Fresh Matter, [2]DM – Dry Matter, [3]ODM – Organic Dry Matter *Source: own study*

As it is shown in Table 1, considerably highest biogas and methane efficiency from 1 tonne of fresh mass is in case of slaughter wastes (respectively 461 and 303 m³/t). Unexpectedly high biogas efficiency (418 m³/t DM) was observed in case of maize straw silage but it was caused with a high content of dry mass of the sample used in the experiment. In spite of the low content of biomethane in the produced biogas, (49%) of the amount of produced CH_4 was only less than 205 m³/t DM). In turn low efficiency of pig slurry is connected with its very high dilution. The studies of numerous attempts of pig slurry conducted in the Ecotechnology Laboratory clear show that under Polish conditions usually does not exceed 3% of the content of dry mass, which is the average level of 2-fold lower than in German households.

The course of fermentation process for one of the analyzed substrates regarding daily measurements of produced methane and other biogas ingredients is shown in Figure 2.

However, due to the need of realization the study aim and determination it was necessary to convert the obtained daily results of biomethane production into cumulative emission. It was achieved through adding together the results of the daily biomethane production, previously converted to the production value of tonne of dry substrate mass. It was necessary in order to compare with each other substrates of varying humidity. The scheme of cumulative production of the substrate for one of the tested substrates is shown in Figure 3.

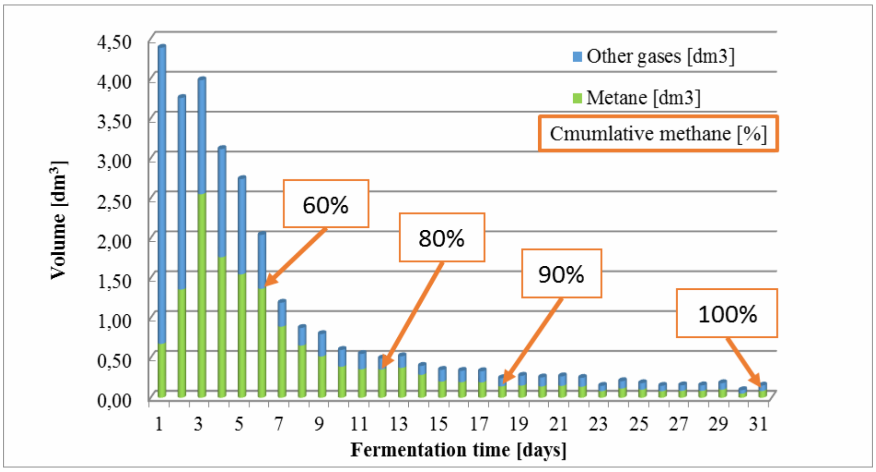


Fig. 2. Changes of the intensity of produced methane and other gases during experiments *Source: own study*

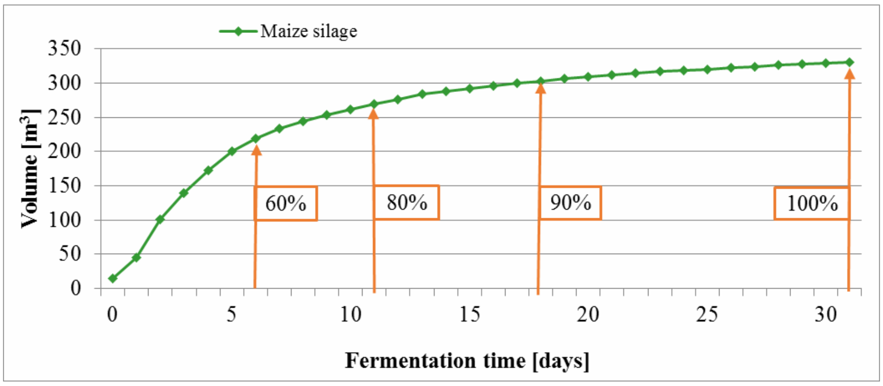
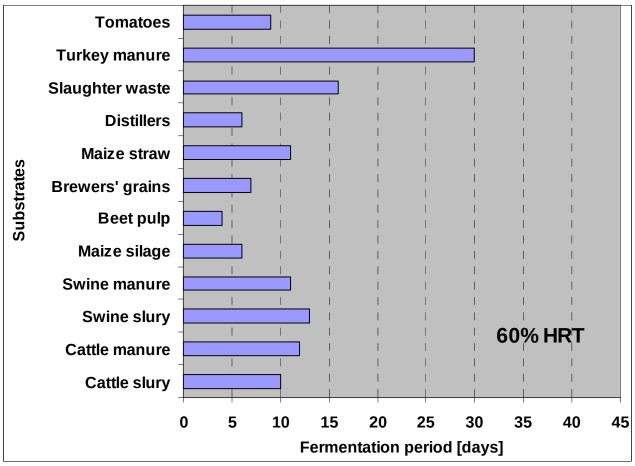


Fig. 3. Scheme of biomethane cumulative production for fermentation of maize silage *Source: own study*

This period proportionally increases even when the threshold of 90% HRT is moved until the end of fermentation (100% of HRT).

Figure 3 shows clearly how detrimental to the operation of biogas plants is extending of the fermentation period above 90% of HRT, because it requires the construction of the digesters with a much larger capacity. Meanwhile, the profit of additional few percent more of obtained biomethane does not reimburse the costs of construction of larger tanks, which along with technical equipment are often even more than half of the biogas plant cost.



Source: own study

Rys. 4. Time to reach 60% of HRT for the tested substrates

Figure 4 shows very large differences in the dynamics of fermentation process of particular substrates. The mean time to reach 60% of HRT for tested substrates was 11.3 days. However, if turkey manure will be excluded from this statement (for which the excess of ammonia nitrogen was an inhibitor of the process), the average time of fermentation was only 9.5 days.

On the other hand, taking into account five tested manures and slurries the level of 60% of HRT mean was achieved on 15.2 days. This reflects the relatively low growth rate of the fermentation of manure. It is worth noting that in the range of 0-60% of HRT the fastest fermentation process was in the case of sugar beet pulp and distillery stillage and (which is surprisingly enough) in the case of the crushed maize silage.

The results of time to achieve 80% of the fermentation efficiency are shown in Figure 5.

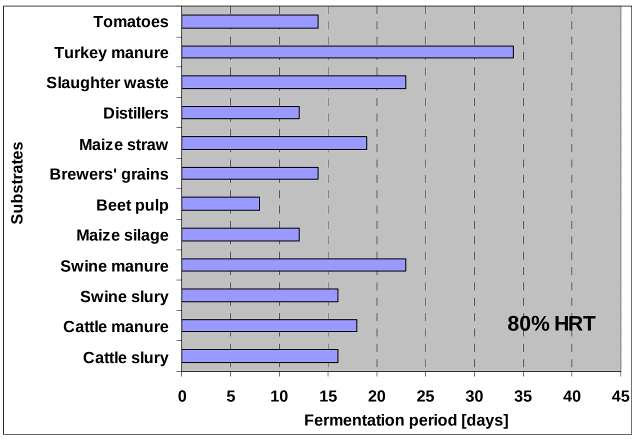


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Fig. 5. Time to reach 80% of HRT for the tested substrates

Average fermentation time, after which the tested substrates reached 80% of the total yield was 17.4 days. Excluding the slowest fermenting turkey manure it was 15.9 day. Also in this case, the average manure fermentation time is longer than the other substrates and amounts 21.4 day. It is worth noting that maize straw silage reaches 80% of HRT faster than slaughterhouse waste. From the point of view of exploitation of biogas plant it is particularly important to achieve a threshold level of 90% of fermentation efficiency. Those results for tested substrates are shown in Figure 6.

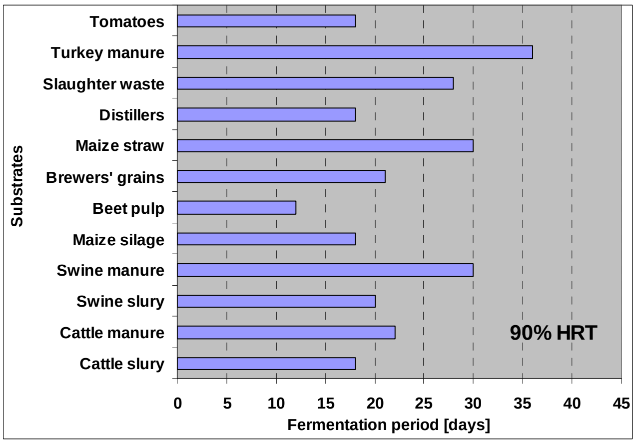

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Fig. 6. Time to reach 90% of HRT for the tested substrates

The mean time to reach 90% of HRT for the tested substrates was 22.6 days and for the same animal wastes 25.2 day. Such a long period contrasts with the results for sugar beet that reach 90% of the fermentation efficiency already on day 12. It is worth noting that in each case of tested slurries this time is a few days shorter than for analyzed manures (Fig. 6). This indicates that for acceleration of degradation processes the manures should be subject to the appropriate pre-treatment - such as fragmentation in the chopper.

Total fermentation time of tested substrates is shows Fig. 7.

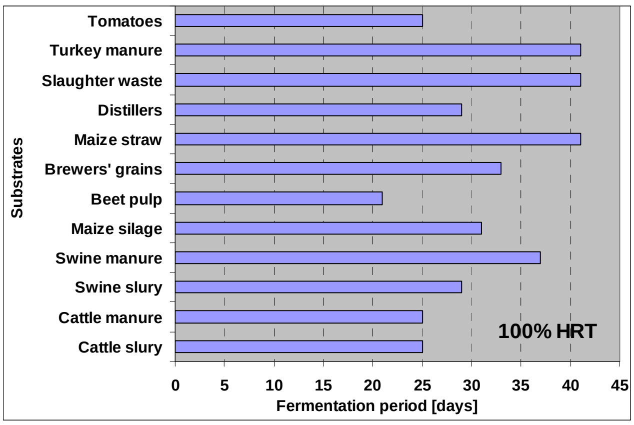

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Fig. 7. Total fermentation time (100% of HRT) for investigated substrates

The results presented in Figure 7 show very big differences in the length of the fermentation process of the tested substrates. For three investigated substrates (turkey manure, slaughterhouse waste and silage maize) it was o 41 days, while for sugar beet pulp only 21 days. The longest period of transition from 90 to 100% of HRT was noted for maize silage and slaughterhouse waste and it was 13 days. Average for the tested substrates, this fermentation period (passage from 90 to 100% of HRT) was 8.9 days. Meanwhile average time of total fermentation of investigated substrates amounted 31,5 day. It means that production of last 10% of biomethane (from 90 up to 100% of HRT) lasted average 28% of the time of total fermentation.

4. Conclusions

On the basis of conducted research the following conclusions have been obtained:

1. Substrates used in the experiments showed very big differences in efficiency of methane production. Definitely the highest methane production (both expressed in production from fresh mass as well as dry and organic dry mass) was obtained for slaughterhouse waste. Also the methane concentration in the obtained biogas was the highest in case of slaughterhouse waste.
2. Very low methane efficiency from fresh mass of pig slurry is related to very low content of dry mass which is a very common problem in Polish farms.
3. Huge differences in the dynamics of fermentation process of the particular substrates have been stated. Mean time for 60% HRT for natural manures amounted 15,2 day, while for the rest of the substrates usually amounted below 10 days.
4. The total fermentation period for investigated substrates amounted average 31,5 day (range: 21-41 days). However production of last 10% of methane average out 28%. It proves very low dynamics of fermentation process in the last phase.

5. References

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