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Biogas from wastes of pumpkin, marrow and apple

V. Dubrovskis[*] and I. Plume

Latvia University of Agriculture, Faculty of Engineering, Institute of Energetics, Cakstes blvd 5, LV 3001 Jelgava, Latvia
[*]Correspondence: vilisd@inbox.lv

Abstract. A lot of vegetables and fruits, which have been grown in Latvia or were imported from foreign countries, become waste, often due to unconformity to the marketing standards or biodegradation process fouling during storage. Waste biomass piles emissions during storage that contributes~~s~~ to global warming. It is appropriate to use such biomass as raw material for anaerobic digestion. This article shows the results of studies on evaluation of suitability of vegetable and fruit waste biomass for the production of biogas. Anaerobic digestion was investigated in 0.75 L digesters, operated in batch mode at a temperature of 38 ± 1.0 °C. The average biogas yield per mass unit of dry organic matter added (DOM) from digestion of pumpkin biomass was 1.095 L g^{-1}_{DOM} and the specific methane yield was 0.422 L g^{-1}_{DOM}. Average biogas yield from digestion of marrow biomass was 0.768 L g^{-1}_{ODM} and the methane yield was 0.274 L g^{-1}_{DOM}. Average biogas yield from digestion of apple biomass was 1.020 L g^{-1}_{DOM} and the methane yield was 0.451 L g^{-1}_{DOM}. All investigated wastes can be a very good source for biogas production. Anaerobic digestion may be a solution to treat waste biomass from food production facilities or supermarkets.

Key words: anaerobic digestion, pumpkins, marrows, apple, biogas, methane.

INTRODUCTION

The world is going through an era of rapidly diminishing fossil energy resources. It is therefore necessary to increase the usage of the renewable energy resources and, in first order, to recover the energy content of different organic wastes. Organic wastes, e.g. sewage sludge, vegetable residues, damaged products, whey, grain screenings and other residues from crop production, undergo biodegradation process, especially if stored in piles, so producing greenhouse gases and contributing to climate change.

The production of biogas is one of the most nature's friendly and prospective alternative energy technologies, and development of this technology will continue. Effectiveness of biogas production in Latvia will increase also for the benefits obtained from an environmental point of view, due to reduced GHG emissions and minimised losses of plant nutrients from manure. Fermented animal manure can serve better for substitution of commercial fertilisers, compared to unfermented manure, due to slower mineralization process and a better plant nutrients C: N ratio. Fermented manure can be applied directly for fertilization of crops in plants growing phase.

The use of cheaper raw materials will allow replacing the expensive corn silage. The effective operation of biogas plant will enable the use so far un-used organic wastes from cities and surroundings energy production and to reduce the usage of the fossil energy resources.

Governmental aid measures for biogas plant~~s~~ construction and electricity selling tariff facilitate~~s~~ the rapid development of biogas technologies in the last decade in Latvia resulting in 59 running biogas plants in year 2017. Any organic substances can be used for anaerobic fermentation process, and organic wastes are the most appropriate resources for anaerobic fermentation (Buffiere et al, 2006). In rural areas, such wastes can be manure, food residue, crop residue, municipal organic waste, sewage sludge, plant green biomass and other organic wastes sources from industry.

Raw material sources from large agricultural or food processing enterprises are suitable for biogas production (Hansen et al., 2004). Processing of biomass wastes in an environmentally friendly way is mandatory for every large enterprise, according to the Law On Pollution, Amendment 1, if production of such enterprises comply with the following conditions (The Saeima, 2001):

- pig farm with more than 2,000 places for pigs;
- pig farm with more than 750 places for sows;
- poultry farm with more than 40,000 places for poultry;
- fruit and vegetable processing plant with a capacity of more than 300 t d^{-1};
- animal raw materials (other than exclusively milk), with a finished product production capacity greater than 75 t d^{-1};
- milk production facilities with daily milk supply of more than 200 t d^{-1};
- slaughterhouses with a carcass production capacity greater than 50 tonnes per day

EC directives demand, that food processing plants, while producing biogas, must fulfil the necessary requirements for sanitation of some wastes. The technology for pre-treatment of slaughterhouses wastes and wastes originating from animal products for biogas production should include pasteurisation equipment requiring heating to 70 °C for 1 hour for 100% destruction of pathogenic micro-organisms.

All substrates or raw materials for biogas production are divided into the basic substrates and the additional substrates (co-substrates). Base substrates are manures produced in farm and additional substrates are usually different crops, plants by-products and food industry waste.

If the biogas plant is located nearby to the city, usage of manure is not desirable due to unpleasant odour. However, utilization of some other basic substrates produced in or nearby to the cities, e.g. sewage sludge, milk processing wastes, should be processed in biogas plant built at site of wastes origin to minimize the transport expenses and to improve environmental conditions, including odour.

Biogas volume obtained from a various raw materials is different (Baader et al., 1978; Angelidaki, I. et al, 2009). Researchers working with similar raw materials have obtained different results. Biogas volume depends on the substrate composition, on anaerobic conditions, organic matter (OM) and other factors (Chen et al., 1984). One of the most important factors that determine~~s~~ the potential of biogas production is the organic matter content and its composition, and especially the content of three main OM groups (Fernandez et al., 2001) carbohydrates, methane content of biogas can be determined using the Buswell-Symons formula (Symons, 1933, Liebetrau et al., 2016).

In practice, biomass is never fully degraded in fermentation processes; therefore, investigations should be carried out, in order to assess the methane potential for each specific biomass. Different methodologies are used for such the investigations. For investigation of the methane potential we have used a methodology similar to that described in a method guide used in Germany (Kaltschmitt & Hartmann, 2009; Kaltschmitt, 2010). In practice, many of the biogas plants digestate sample analyses reveal a still too high organic matter content.

The biogas and methane potential of abundant pumpkins, marrows and apples or of rotten fruits in Latvia has not been studied up till now. Such data were missing also in review information provided by German researchers (Becker, 2007).

The aim of this study is therefore the investigation of the potential of biogas production from vegetable processing plant residues and wastes: non-standard pumpkins, marrows and apples. The second aim is to investigate the effect of addition of a catalyst MF3. Positive results can give confidence to biogas plant owners on the feasibility of utilisation of mentioned biomass in biogas co-generation plants for electricity and heat production.

The results of the studies may be used throughout Latvia, where it is possible to work with the raw materials investigated during this study. The results of this study can be used also for calculation of the actual dose of biomass to be daily filled in biogas reactors.

MATERIALS AND METHODS

Materials, equipment and methods

Damaged pumpkin, marrow and apples were used in this study, Figs 1–3.

Figure 1. Pumpkin biomass.

Figure 2. Vegetable marrow biomass.

Figure 3. Chopped apple biomass.

Representative biomass samples were taken and their chemical composition was analysed using the standardized methodologies ISO 6496: 1999. Dry matter content, the organic matter content and the ashes content were investigated for the three raw materials and for the used inocula. Analyses were done using standard methods. The volume of biogas production was studied using laboratory equipment consisting of 16 bioreactors.

Each group of raw materials (pumpkin, marrow or apple biomass) and the inocula (fermented cow manure) were weighed and mixed together carefully. The inocula for digestion experiments of the three substrates and for control bioreactors was digester effluent of a continuously working bioreactor having inside almost completely biodegraded manure.

Study assays contained 20 g of the respective biowastes and 500 g inoculum in each of 14 bioreactors with a volume of 0.72 L. As references (controls) only 500 mL inoculum was placed in 2 bioreactors. An anaerobic fermentation temperature of 38 ± 0.1 °C was maintained inside the bioreactors during batch mode incubations.

1 mL of Metaferm MF3, a commercial catalyst for advancement of the anaerobic digestion process was added into R6-R9 bioreactors. Metaferm contains multiple ferments, micronutrients and B-group vitamins. The true composition of MF3 is not known due to proprietary rights of the producing company.

Dry matter, ashes and organic dry matter content was determined for every biomass mixture before filling of substrates into the bioreactors. All 16 bioreactors were placed into a large thermostat for anaerobic fermentation processing during 21 days. Accuracies of measurements were as following: ± 0.2 g for inocula and substrate weight (using scales Kern KFB HAS 16 KO2); ± 0.001 g for biomass dry matter, organic matter and ashes weight; ± 0.02 pH for pH (using instrument PP-50); ± 0.05 L for gas volume (using low flow gas meter) and ± 0.1 °C for temperature inside the thermostat (Memmert model).

Gases were collected in gas bags with a volume of 2 litres positioned outside of reactor and connected with reactors by plastic pipes. Gases volume measurements and gases content analyses were provided regularly during fermentation period. Biogas volume measurement was provided by Bioprocess control low flow gas meter, and normalized biogas volume (at standard pressure and temperature) was calculated. Biogas composition (CH_4, CO_2, O_2 and H_2S) was determined with a gas analyser GA 2000. Dry matter was determined by specialized unit Shimazy at temperature 105 °C, and ashing of samples was provided in oven Nabertherm at temperature 550 °C according to standard heating program.

All the substrates were weighed, dry matter, ashes and organic matter content measured after finishing of the anaerobic fermentation process. Standard error was calculated for each group of digesters using the standardized data processing tools.

RESULTS AND DISCUSSION

The results of the analyses of the raw materials before anaerobic fermentation are listed in Table 1.

The results of the analyses of the digestate in each bioreactor after anaerobic fermentation are shown in Table 2.

Raw biomass of pumpkins, marrows and apples have a low dry matter and organic dry matter content (Table 1), and are appropriate for biogas production, due to their high content of sugars and juice. The degradation rate of DOM was calculated using the data of the average organic dry matter content in raw biomass and of inocula before fermentation (Table 1) and data of the average DOM content in finished substrate (Table 2). Average dry organic matter (DOM) content in the finished substrate with pumpkins was 4.12 g and the average degradation rate was calculated as 54.92%. It is probable that some minor portion of DOM of the inocula still continues biodegradation in the anaerobic fermentation process. Average DOM in the finished substrate with marrow and inoculum was 5.01 g and the average degradation rate was calculated as 43.52%.

Table 1. The results of the analyses of raw materials

Bio reactor	Raw material	pH	TS, %	TS, g	Ashes, %	DOM, %	DOM, g	Weight, g
R1, R16	IN500	7.12	1.83	9.15	21.09	78.91	7.22	500
R2-R5	IN500 + P20		10.47	2.09	8.48	91.52	1.92	20
		7.11	2.16	11.24	18.68	81.32	9.14	520
R6-R9	IN500 + P20 + MF3		10.47	2.09	8.48	91.52	1.92	20
		7.13	2.16	11.24	18.68	81.32	9.14	521
R10-R12	IN500 + M20		9.0	1.8	8.48	91.52	1.65	20
			2.11	10.95	19.00	81.00	8.87	520
R13-R15	IN500 + A20		14.53	2.91	3.25	96.75	2.81	20
		7.12	2.32	12.06	16.84	83.16	10.03	520

Abbreviations: TS – total solids, DOM – dry organic matter (applied to organic dry matter of raw material to be investigated), IN – inoculum; P – pumpkin; M – marrow; A – apple; MF3 – commercial additive MF3 in volume of 1 mL.

Table 2. The results of the analyses of the digestate

Bio reactor	Raw material	pH	TS, %	TS, g	Ashes, %	DOM, %	DOM, g	Weight, g
R1	IN500	7.15	1.02	5.08	37.57	62.43	3.17	498.5
R16	IN500	7.15	1.03	5.13	37.62	62.38	3.20	499.0
R2	IN500 + P20	7.21	1.17	6.04	31.3	68.7	4.15	516.5
R3	IN500 + P20	7.23	1.16	5.99	31.25	68.75	4.12	516.4
R4	IN500 + P20	7.24	1.16	5.99	31.3	78.70	4.12	516.5
R5	IN500 + P20	7.20	1.15	5.94	31.20	68.80	4.09	516.6
R6	IN500 + P20 + MF3	7.21	1.10	5.68	24.8	75.20	4.27	516.8
R7	IN500 + P20 + MF3	7.30	1.08	5.59	23.68	76.32	4.27	518.0
R8	IN500 + P20 + MF3	7.37	0.92	4.77	19.64	80.36	3.83	518.6
R9	IN500 + P20 + MF3	7.35	1.12	5.80	23.49	76.51	4.43	517.5
R10	IN500 + M20	7.36	1.27	6.54	22.3	77.70	5.08	515.3
R11	IN500 + M20	7.15	1.25	6.44	22.27	77.73	5.01	515.5
R12	IN500 + M20	7.16	1.24	6.39	22.26	77.74	4.97	515.6
R13	IN500 + A20	7.19	1.47	7.59	22.15	77.85	5.91	516.6
R14	IN500 + A20	7.18	1.48	7.65	22.15	77.85	5.95	516.7
R15	IN500 + A20	7.18	1.49	7.70	22.20	77.80	5.99	516.8

Average DOM in the finished substrate with apple biomass was 5.95 g and the average degradation rate of organic dry matter was 40.68%.

Results confirm~~s~~ that pumpkin, marrow or apple biomass contains some substances that facilitates the bacteria growth resulting in better utilisation of other raw materials also, e.g. some residual organics of the inocula.

Methane and biogas yields from bioreactors with pumpkin, marrow and apple biomass are shown in Table 3.

Table 3. Produced biogas and methane

Bio reactor	Raw material	Biogas, L	Biogas, L g^{-1}_{DOM}	Methane, max %	Methane, L	Methane, L g^{-1}_{DOM}
R1	IN500	0.0			0.0	
R16	IN500	0.0			0.0	
R2	IN500 + P20	2.4	1.25	53.2	0.917	0.478
R3	IN500 + P20	1.9	0.99	58.8	0.751	0.391
R4	IN500 + P20	2.2	1.15	53.8	0.762	0.397
R5	IN500 + P20	1.9	0.99	61.8	0.809	0.421
Average R2-R5			1.095 ± 0.060			0.422 ± 0.040
R6	IN500 + P20 + MF3	2.1	1.093	52.9	0.738	0.384
R7	IN500 + P20 + MF3	2.0	1.042	64.1	0.869	0.452
R8	IN500 + P20 + MF3	2.1	1.093	62.0	0.944	0.492
R9	IN500 + P20 + MF3	1.9	0.99	51.8	0.604	0.315
Average R6-R9			1.055 ± 0.047			0.411 ± 0.078
R10	IN500 + M20	1.3	0.788	53.4	0.462	0.280
R11	IN500 + M20	1.2	0.727	54.6	0.434	0.263
R12	IN500 + M20	1.3	0.788	56.5	0.460	0.279
Average R10-R12			0.768 ± 0.026			0.274 ± 0.010
R13	IN500 + A20	3.0	1.068	67.9	1.342	0.478
R14	IN500 + A20	3.0	1.068	64.4	1.306	0.464
R15	IN500 + A20	2.6	0.925	70.0	1.158	0.412
Average R13-R15			1.020 ± 0.072			0.451 ± 0.033

Abbreviations: L g^{-1}_{DOM} – litres per 1 g organic dry matter (applied to organic dry matter of investigated raw material).

The obtained results are indicating a high efficiency of anaerobic degradation. Such good biomass degradation by micro-organisms can be explained by the beneficial chemical composition of substrates (high content of sugars and juice) for biogas production and by the buffering effect of the inocula during co-fermentation.

A high average specific methane volume of 0.422 L g^{-1}_{DOM} was obtained from pumpkins, calculated as methane volume released per 1 g initial organic dry matter. Less specific methane volume of 0.274 L g^{-1}_{DOM} was obtained from vegetable marrow. This may be explained by the fact that the vegetable marrow samples have relatively thick peels, which were difficult to degrade by bacteria. The highest specific methane volume of 0.451 L g^{-1}_{DOM} was obtained from apple biomass. The relatively high average methane content in the biogas from apples is explained by the fact that the raw material contains a lot of juice and sugars. From bioreactors containing pumpkins biomass and 1 mL of the additive MF3 the specific methane volume was 2.7% less compared to that obtained from bioreactors with pumpkins biomass but without the additive. This shows that the additive MF3 may contain some component(s) impairing the functioning of bacteria.

The volume of biogas and methane obtained from each bioreactor containing pumpkins biomass is shown in Fig. 4.

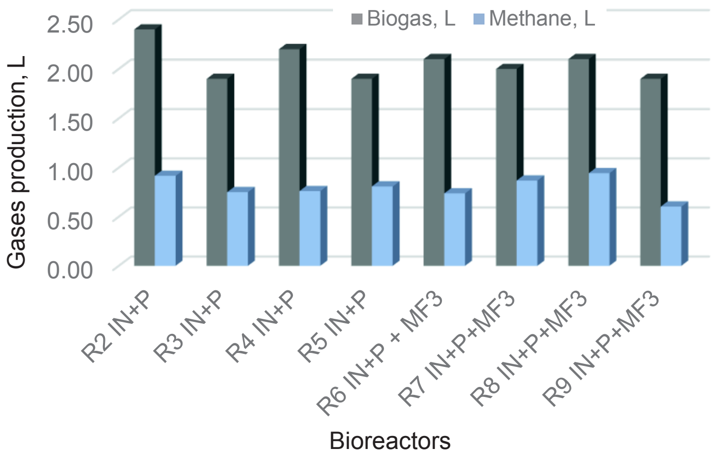

Figure 4. Volume of biogas and methane obtained from bioreactors with pumpkins biomass.

The specific volume of the biogas and methane per 1 g organic matter of raw biomass released from each bioreactor with pumpkins is shown in Fig. 5.

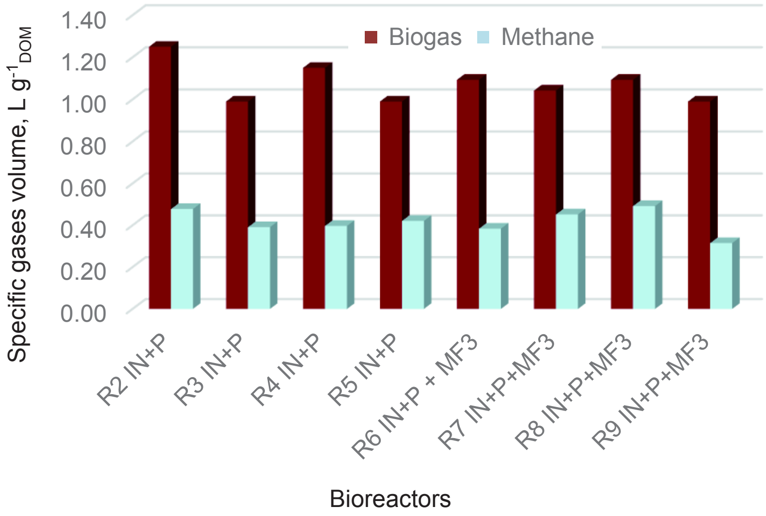

Figure 5. Specific volume of the biogas and methane released from each bioreactor with pumpkins biomass.

The maximal methane content in biogas from each bioreactor with pumpkins is shown in Fig. 6.

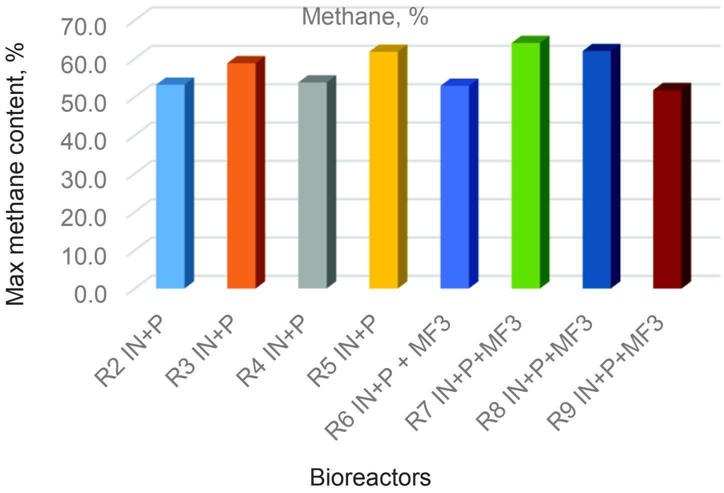

Figure 6. Maximal methane content in biogas from bioreactors with pumpkins biomass.

The biogas and methane volumes from each bioreactor containing marrow or apple biomass are shown in Fig. 7.

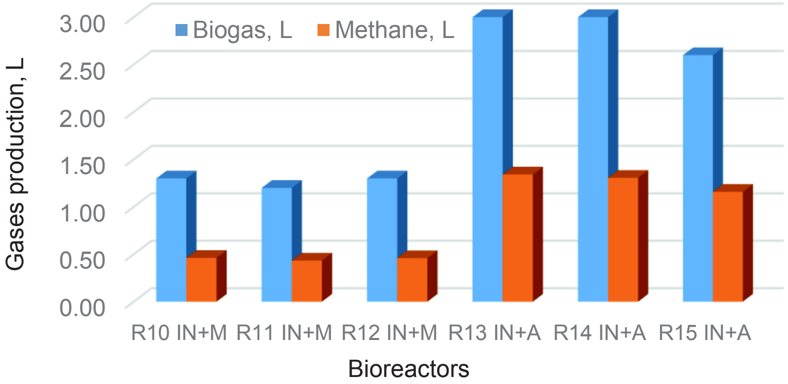

Figure 7. Volumes of biogas and methane obtained from bioreactors with marrow and apple biomass.

The specific volume of the biogas and methane released from each bioreactor containing marrow or apple biomass is shown in Fig. 8.

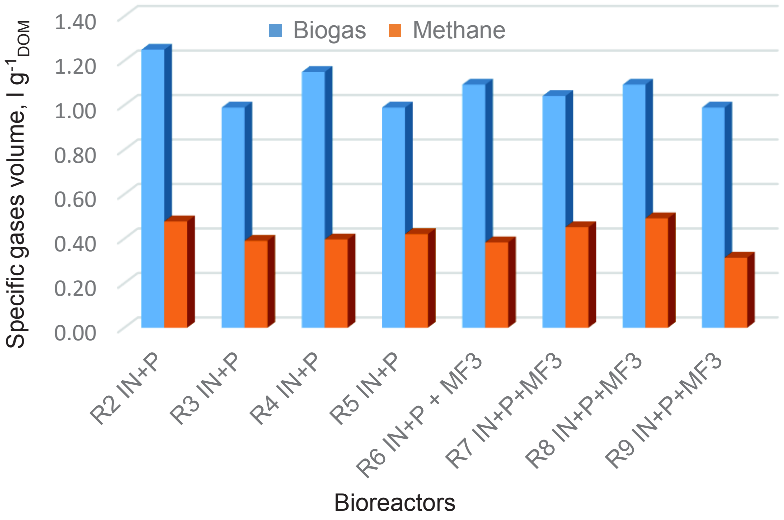

Figure 8. Specific volumes of the biogas and methane released from bioreactors with marrow or apple biomass.

The maximal content of methane in biogas from each bioreactors containing marrow or apple biomass is shown in Fig. 9.

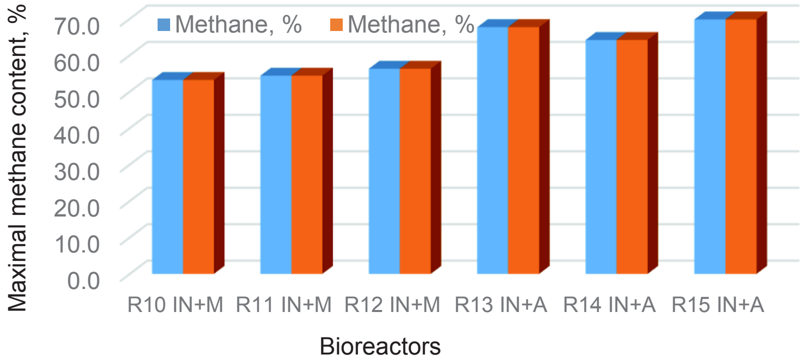

Figure 9. Maximal methane content in biogas from each bioreactor with marrow or apple biomass.

CONCLUSIONS

Pumpkin biomass is recommended for utilisation in biogas co-generation plants due to the high specific methane yield of 0.422 L g^{-1}_{DOM} on average.

The average specific methane yield from marrow biomass was 0.274 L g^{-1}_{DOM}.

The highest average specific methane yield was obtained from apple biomass and was 0.451 L g^{-1}_{DOM}. This was 6.4% or 39.2% higher as compared to the specific methane yield obtained from pumpkin or vegetable marrow biomass respectively.

Results of investigations show that pumpkin, marrows and apples biomass are good raw materials for biomethane production.

Addition of 1 mL MF3 results in lowering of the specific methane volume by 2.7% compared to that obtained from pumpkins biomass without this additive. It is proposed that the additive MF3 may contain some component(s) impairing the activity of bacteria.

Results of our investigations shows that co-substrates (raw materials) with a high content of sugars added to fermented cattle manure apparently "induce" additional biodegradation of finished digestate, therefore partial return of such the substrates into the cogeneration plant bioreactor can be regarded as useful.

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REFERENCES

Angelidaki, I, Alves, M, Bolzonella, D, Borzacconi, L, Campos, J.L., Guwy, A.J Kalyuzhnyi, S, Jenicek, P. & van Lier, J.B. 2009. Defining the biomethane potential: proposed protocol for batch assays. *Water Science & Technology* **59**(5), 927–934.

Baader, B., Done, E. & Brenndorfer, M. 1978. Biogas in theory and practice. *KTBL-Schrift.* 229, p. 133 (In German).

Becker, C. 2007. Faustzahlen Biogas. *Kuratorium für Technik und Bauwesen in der Landwirtschaft (KTBL)*, Darmstadt, p. 181 (In German).

Buffiere, P., Loisel, D., Bernet, N. & Delgenes, J.P. 2006. Towards new indicators for the prediction of solid waste anaerobic digestion properties. *Water Sci. Technol*. **53**(8), 233–241.

Chen, T.H., Day, D.L., Pfeffer, J.T., Bryant, M.P. & Vanderholm, D.H. 1984. Kinetic parameters of thermophilic digestion of swine manure. *Trans. ASAE* **27**, 1491–1498.

Fernandez, B., Porrier, P. & Chamy, R. 2001. Effect of inoculum, substrate ratio on the start-up of solid waste anaerobic digesters. *Water Sci. Technol*. **44**(4), 103 –108.

Hansen, T.L., Schmidt, J.E., Angelidaki, I., Marca, E., Jansen, J.C., Mosbæk, H. & Christensen, T.H. 2004. Measurement of methane potentials of solid organic waste. *Waste Manag*. **24**(4), 393–400.

Kaltschmitt, M. & Hartmann, H. 2009. Energy from biomass – basics, techniques and procedures. 2. Aufl, Springer-Verlag, Berlin, Heidelberg, p. 135 (In German).

Kaltschmitt, M. 2010. Methodenhandbuch, Leipzig, p. 93 (In German).

Liebetrau, J., Pfeiffer, D. & Thran, D., editors. 2016. Collection of methods for biogas, p. 210.

Symons, G.E. & Buswell, A.M. 1933. The Methane Fermentation of Carbohydrates. *J. Am. Chem. Soc.* **55**(5), 2028–2036.

The Saeima. 2001. Law On Pollution, Annex 1, *Latvijas Vēstnesis* **51**(2438), online *http://likumi.lv/doc.php?id=6075,* accessed 24.01.2017.