Testing the Biomethane Yield of Degradable Wastes of Meat Industry by BMP Test

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The optimal mix of solid waste from the meat industry (MI) for anaerobic digestion (AD) treatment can be selected by defining the biomethane potential (BMP test) of the waste in relation to the unit value of chemical oxygen demand (COD). In this paper, the BMP test of biodegradable wastes from MI has been performed. For the purposes of the experiment, two types of input substrates have been defined: manure (manure from cattle depots and transport vehicles for cattle transport) labeled as O1 and inedible offal, contents of the stomach, sludges from washing and cleaning, and the remains of meat defined as waste O2. According to the BMP test, mixtures of fresh inoculum (38 g), waste O1 and waste O2 in quantities of 1 g and 2 g have been tested, and the model for the selection of the best mix in terms of the biogas yield has been defined. Based on correlations of CH_4 and COD, mixture M1 (O1 : O2 = 80 : 20) is recommended, for treatment at the plant, because it has the highest yield of 256.16 mL CH_4 per unit value of COD.

Key words:
Testing of biomethane potential (BMP test), meat industry, mixture of meat industry waste, anaerobic digestion

Introduction

Bioenergy production using anaerobic digestion (AD) of solid waste (biowaste) such as waste sludge, cattle manure, crops, and other biomass is a widespread technology due to the very large number of requests coming from the market. Development and growth of this technology is primarily the result of an organized collection of certain types of solid waste from different industries that are presumed to have the potential for biogas production (biomethane).[1] The waste produced in the operation of meat production and processing has the potential to produce biogas using the AD process. This waste is accumulated in large quantities in the MI plants, and at the same time is very easy to collect, thus creating opportunities for the installation and development of these processes within the MI plants.[2] It is especially important to promptly treat MI waste because of its tendency to turn into "infectious waste" with the formation and expansion of a strong (characteristic) odor. This characteristic odor is a significant environmental problem for the population in the vicinity of MI plants. Therefore, the prompt disposal of the waste within the MI plants by the AD process equipment has additional, positive environmental significance for the microlocation of MI plants.

Within MI plants, biomethane as a product of the AD process can be used for the production of heat and electricity, and the resulting solid and liquid residues in the form of a digestate can be also used after compositing as fertilizers for agricultural land due to the high content of useful components (nitrogen, phosphorus) required for plant growth.[3–5] The production and use of biogas from biodegradable organic waste generated by the AD process represents significant potential to achieve energy-related, environmental and economic benefits.[2,3,6] Substrate composition is a major factor that affects the formation, development, and utilization of methane in the AD process.

In the last 40 years, a significant number of papers have been published[1] that deal with research into the potential of biomethane production using different types of solid waste. Some of the authors tried to investigate the physical and chemical analysis of solid waste, while others investigated the ratio of inoculum and substrate.[1,7,8]

The research presented in this paper represents a cross-section of two approaches: observation of biomethane yield (BMP test) in relation to the physical and chemical properties of solid waste (1), and addition of the basic waste from MI plant into reaction bottle (2), in two different volumes achieving variability of ratio of inoculum (38 g in the bottle) and the su bstrate (1 and 2 g).

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In order to select a mixture of the basic (tested) waste for the AD process, it is necessary to define the biomethane potential of basic waste in relation to the unit value of COD. The results of the experiment will be used to define the biomethane potential of different mixtures of basic waste. Based on that and on the amount of waste produced in a year, the most appropriate mix of available MI plant waste which is expected to give a maximum of biogas, would be selected.

The BMP test is used as the most relevant indicator for the assessment of biodegradability.[9] All activities of waste preparation for the realization of this pilot study were performed according to the requirements of standard methods for physical analysis and complete BMP test.[1,3,10,11]

For the purposes of this experiment, two types of input substrates were defined:

– O1-manure (manure from cattle depots and transport vehicles for cattle transport),

– O2-inedible offal (contents of the stomach, sludges from washing and cleaning, and the remains of meat).[12,13,14]

The mixture of fresh inoculum and waste O1, and the mixture of fresh inoculum and waste O2 in quantities of 1 and 2 grams were tested according to BMP test, and the model for selection of the best mix in terms of biogas yield was defined.

Materials and methods

Solid waste from MI Plant "Bajra" Travnik is believed to have high potential for biogas production and the waste is available throughout the year. Therefore, it was used as the substrate in this experiment. The estimated amount of waste from this MI plant is 1350 tons/year of waste O1 (Fig. 1a) and 350 t/y of waste O2 (Fig . 1b).[2]

Waste composition is decisive for the performance of AD. The aim of determining the biogas yield potential from certain types of waste, and their mutual ratio (mixture) with sludge from the municipal wastewater (inoculum) of Odžak,[1] was to achieve the most appropriate mixture from the aspect of biomethane production.

Fig. 1 – *Sample tests waste O1 (a) and O2 (b) from the meat industry*

[1]Odžak is a town in the north of Bosnia and Herzegovina.

Characterization of waste involves the testing of selected types of waste for proper management of the experiment and predicts potential toxic conditions during the real AD process.

Volatile fatty acids (VFA) and alkalinity were measured using the volumetric method (1-SMEWW, 5560 Organic and Volatile Acids, C. Distillation Method; 2-SMEWW, 2320 Alkalinity, B Titration Method), which is more suitable for the analysis of anaerobic wastewater and sludge. Laboratory analysis was performed on 5 waste samples: basic waste O1 and O2, waste mixtures M1 (O1 : O2 = 80 : 20), M2 (O1 : O2 = 50 : 50) and M3 (O1 : O2 = 20 : 80). Each sample was analyzed three times (with associated mean value and standard deviation).

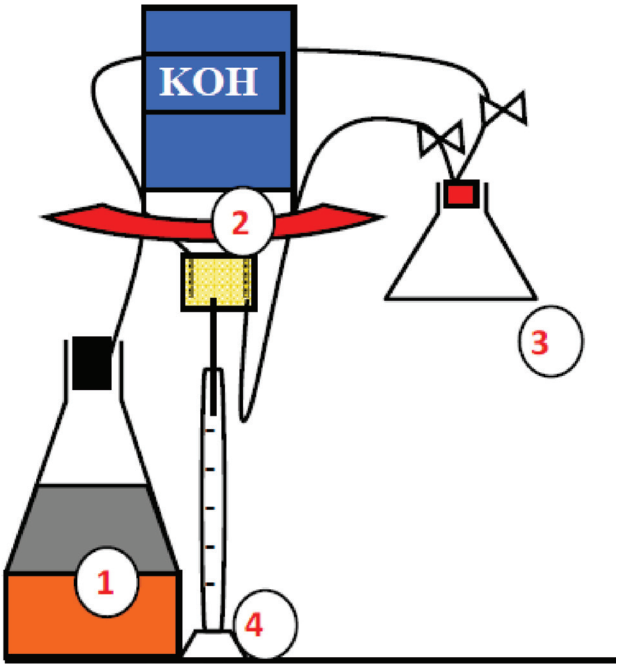
Methods and laboratory equipment

The most important information that could be obtained using the BMP test is: control of the activities of anaerobic sludge (inoculum), the minimum and maximum doses of waste that inoculum can degrade, and effect of influential pretreatments or enzymes on the flow of the anaerobic process. Therefore, this technique, with the previous characterization of waste, was applied to selected types of waste from MI.

BMP test defines the optimal mix of solid waste expressed as a concentration of chemical oxygen demand (COD) and the substrate (anaerobic sludge) to avoid excessive production of acid in the device for anaerobic treatment and to enable an easier transition to the first stage of production of methane.

BMP test was carried out in a special apparatus, made up of the 10 sample bottles filled with a mixture of anaerobic sludge and different amounts of waste from MI. The bottles were sealed and connected through a tube with a bottle filled with 1 liter of alkaline solution (3 % KOH), with the opening facing downwards. Another plastic tube was connected to the graduated cylinders. In order to protect the biodiversity of the solution from possible backflow of alkaline solution, one small bottle was placed between the sample bottles and the bottle of KOH. The whole apparatus was placed in a thermostat at a constant temperature of 36 ± 1 ºC (Fig. 2).[15,16]

All of the reaction bottles were filled with the same amount of inoculum (38 g), which corresponds to 10 % of volatile solids (VTS). The final volume of the reaction mixture was 200 mL. The tested parameters and a list of the equipment used with the corresponding reference measurement methods are given in Table 1.



1-reaction vessels filled with a mixture of different amounts of waste to be tested, 2-bottles filled with an alkaline solution of 3 % KOH (Mariotte bottle), 3-vessel safety, 4 measuring cup (measuring beaker)

Fig. 2 – *Setting of the experiment to determine biomethane potential of treated waste*

All analyses were carried out on the samples from solid to sludge consistency, and all these methods were adapted for the purpose of representative and more accurate results. Measurements of pH were carried out directly on the sample if it was of muddy consistency or with minimal addition of water if the sample was in solid state. The measurements were carried out with constant stirring. All other parameters of the quality of waste were analyzed from a solution containing 5 g of solid or sludge samples added in 1 liter of water.

Results and discussion

Results of physical and chemical analysis of waste

The objective of the waste characterization was to determine the ratio of COD:N:P, which will give an indication of the possibilities of AD treatment and the parameters that can indicate the presence of inhibitory conditions. Analysis of waste was carried out several times during the testing. Not all parameters were analyzed, only those which were significant from the research. Results of the analysis are shown in Table 2 and Table 3, only for sludge by alkalinity and VFA.

All analyzes and complete BMP test were performed at the accredited laboratories of the Institute of Hydrotechnics at the Sarajevo Faculty of Civil Engineering.

Based on the physical and chemical analysis of the waste and inoculum (sludge), the following can be concluded:

– The results of waste analysis are very reliable, because the standard deviation was acceptable in most cases, and these results could be used for the next phase (AD phase) in the bioreactor models,

– The sulphate and ammonia content is extremely low, reducing the possibility of creating toxic conditions during anaerobic process in the digesters,

– The pH value of the waste and sludge is neutral, thus reducing the possibility of creating toxic conditions during anaerobic process in the digesters,

Table 1 – *Equipment and methods of analysis used for waste and BMP-test*

Parameter	Equipment	Methods
Total solid (TS)	Scale, Laboratory Oven (Esco)	SMEWW, 2540 G. Total, Fixed, and Volatile Solids in Solid and Semisolid Samples
Volatile solids (VTS)	Scale, Laboratory Oven (Esco)	SMEWW, 4500+H+pH value
pH value	pH meter, magnetic headphones (Hanna instruments)	SMEWW, 4500-H+pH Value
COD	COD system (cookers, carboys for digestion cooling), automatic burette (Esco)	SMEWW, 5220 Chemical Oxygen Demand (COD)
VFA	Distillation system, automatic burette (Velp Seintifica)	SMEWW, 5560 Organic and Volatile Acids, C. Distillation Method
Ammonia	Distillation system, automatic burette (Velp Seintifica)	SMEWW, 4500-NH3 Nitrogen (Ammonia)
Organic nitrogen (N-org)	Distillation system, automatic burette (HACH)	SMEWW, 4500-NH3 Nitrogen (Organic)
Total phosphorus (TP)	Distillation system, automatic burette (Velp Seintifica)	spectrophotometric, IC
Alkalinity	pH meter, system for titration (Hanna Instr.)	SMEWW, 2320 Alkalinity, B Titration Method
Sulphide	Automatic burette (Esco)	SMEWW, 4500-S2“ Sulfide

Table 2 – *Analysis results – basic waste and their mixtures*

Parameter of waste (mixtures)	Sludge (inoculum)	O1	O2	M1 80(O1) : 20(O2)	M2 50(O1) : 50(O2)	M3 20(O1) : 80(O2)
	34	52	30	48	41	34
TS (%)	35	34	29	33	34	30
	35	55	30	50	44	35
Average value	**35**	**47**	**30**	**44**	**40**	**33**
Standard deviation (±)	1	11	1	9	5	3
	26	90	93	91	92	93
VTS (%)	27	88	95	90	92	94
	26	89	95	90	92	94
Average value	**26**	**89**	**95**	**90**	**92**	**94**
Standard deviation (±)	1	1	1	1	0	1
	66	595	245	528		550
COD (mg g^{-1})	68	670	193	514	380	472
	68	612	84	535	409	416
Average value	**67**	**626**	**174**	**526**	**395**	**479**
Standard deviation (±)	1	39	82	11	20	67
	0.108	2.320	0.506	1.856	1.584	1.328
TP (mg g^{-1})	0.074	1.630	0.614	1.732	1.500	1.476
	0.064	2.040	0.616	1.740	1.612	1.364
Average value	**0.082**	**1.997**	**0.579**	**1.776**	**1.565**	**1.389**
Standard deviation (±)	0.023	0.347	0.063	0.069	0.058	0.077
	0.192	3.600	1.200	1.600	2.080	0.192
Sulphide (mgS g^{-1})	0.184			1.920	2.080	0.184
	0.184					0.184
Average value	**0.187**	**3.600**	**1.200**	**1.760**	**2.080**	**0.187**
Standard deviation (±)	0.005			0.226		0.005
	0.45	3.81	1.62	2.02	1.68	1.68
Ammonia (mgN g^{-1})	0.34	3.70	1.46	2.02	1.74	1.62
	0.39	3.36	1.40			
Average value	**0.39**	**3.62**	**1.49**	**2.02**	**1.71**	**1.65**
Standard deviation (±)	0.06	0.23	0.12	0.00	0.04	0.04
	0.84	4.48	3.25	1.96	4.82	2.30
N-Kjeldahl (mgN g^{-1})	0.90	4.42	2.30	2.13	2.80	2.35
	0.78	3.64	2.97	0.00	0.00	0.00
Average value	**0.84**	**4.18**	**2.84**	**1.36**	**2.54**	**1.55**
Standard deviation (±)	0.06	0.47	0.49	1.18	2.42	1.34
pH value	**7.83**	**8.82**	**6.9**	**7.71**	**6.93**	**6.67**

Table 3 – *Analysis results – alkalinity and VFA of used sludge*

Parameter of waste (mixtures)	Sludge (inoculum)
Alkalinity (mg L^{-1})	4486
	4561
Average value	**4523**
VFA (mgCH3COOH g^{-1})	5000
	4400
Average value	**4700**

– The sludge has a very good nutrient content with the ratio COD : N = 560 : 7 (optimal ratio ranges from 400 : 7 up to 1000 : 7),

– Considerable concentrations of VFA in sludge have been found. At the same time insufficient concentrations of alkalinity were present. Ratio VFA/alkalinity is about 1, while the ideal theoretical value is 0.3.

Results and analysis of experimental studies of BMP tests

All settings of the BMP test for both types of waste with the inoculum, had similar amounts of charge, as stated below:

– The bottles with blank sample contained only anaerobic sludge that has a natural biogas production due to its decomposition, and that should be subtracted from the other tests,

– The test samples contained anaerobic sludge and 1 mL of acetic acid. This sample was used for investigating the activity of anaerobic sludge in contact with highly biodegradable substrate. The amount of 1 mL of acetic acid was taken on the basis of previous (similar) experiments and obtained pH value of sludge.

– The two tests were carried out with two replicates using the following combinations: inoculum plus 1 g of O1; inoculum plus 2 g of O1; inoculum plus 1 g of O2; inoculum plus 2 g of O2.

The exact composition of the reaction bottles contents, as well as the results of the complete BMP tests are presented in Table 4. Production of methane (CH_4) by the tested mixtures is shown in Fig. 3.

The BMP test on MI waste showed that the reaction bottles with acetic acid have yielded less methane than the blank samples. Such behaviour could be attributed to the following: small methanogenic activity due to gas leakage through the tube system, heavy gas load through a system of tubes, overload of inoculum with organic matter (acidification), or inactivity of the sludge. Inactivity of the sludge was rejected as a cause of this phenomenon because methanogens activity was observed in most of the reaction bottles. In fact, it is assumed that the cause was the inoculum highly loaded with organic matter. The inoculum contains significant concentrations of VFA and additional acetic acid causing a large load for anaerobic culture. At the same time, the alkalinity is not high enough to puffer the excess VFA. Therefore, it is assumed that there was acidification of anaerobic media (inhibitory conditions of AD). Recommendation for future experimental settings for this part of experiment would be to decrease the amount of acetic acid below 1 mL with successive monitoring of pH value of the mixture (eg. addition of 0.5 mL acetic acid in 10 mL of water, neutralized with NaOH).

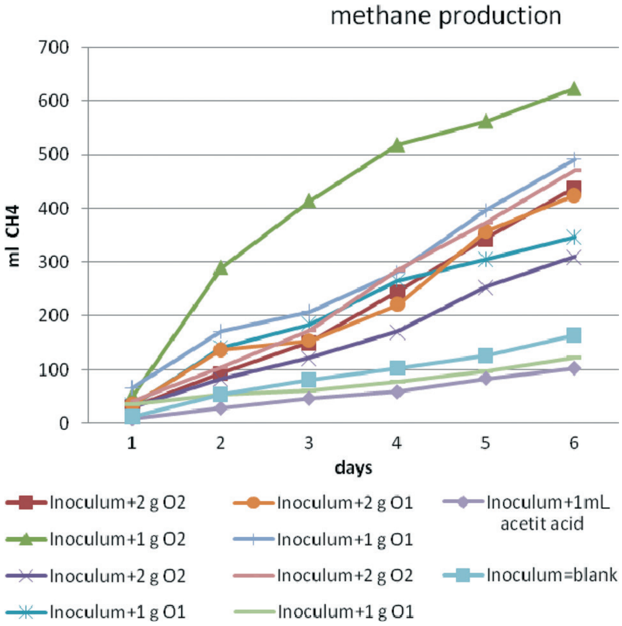


Fig. 3 – *Graphic view of production of methane per day per bottles*

During the experiment the decrease of methanogenic activity could not be observed. The entire KOH solution in most of the bottles was spent, so on the sixth day, the experiment was stopped. Exceptionally high methanogenic activity during AD is reported for both types of waste (O1 and O2).

Table 4 – *Methane production and COD as input parameter of BMP test*

Bottle	Bottle content	COD of the waste (g)	Input COD (g L^{-1})	Theoretical production of CH_4 (mL)	Total production of CH_4 (mL)	CH_4 production from substrate (mL)	Conversion (%)
1	Ino+2 g O2	0.348	1.74	121.8	438	273	62.3
2	Ino+1 g O2	0.174	0.87	60.9	–	–	–
3	Ino+2 g O2	0.348	1.74	121.8	310	145	46.8
4	Ino+1 g O1	0.626	3.13	219.1	–	–	–
5	Ino+2 g O1	0.626	3.13	219.1	424	259	61.1
6	Ino+1 g O1	1.252	6.26	438.2	492	327	66.5
7	Ino+2 g O2	0.174	0.87	60.9	471	306	65.0
8	Ino+1 g O1	1.252	6.26	438.2	122	–43	–35.2
9	Ino+1 mL acetic acid	1.07	5.53	374.5	103	–62	–60.2
10	Ino = blank	0	0	0	165	0	0.0

Within the first five days of the test, more than 50 % of the exposed COD waste was dissolved.

Further research activities could be focused on additional BMP tests, with reduced load of acetic acid to 2.5 COD L^{-1}. Also, the experiment can be started using 1.74 g COD L^{-1} for waste O2, and 5.0 g COD L^{-1} for waste O1. To obtain information about the maximum load of anaerobic process, it is necessary to repeat the experimental profile with large quantities of waste. This type of testing is sufficient to indicate the ratio of waste with the most productive methane.

Defining of biogas yield based on the results of the BMP test

Considering the results of the physical and chemical analysis and BMP test of the basic waste (O1 and O2), and based on their mutual comparison, a connection between the waste COD (mg) and methane production (mL) could be defined. Especially important is production of methane from the substrate, which is obtained as the difference between the total amount of methane produced at the end of the experiment and the background concentration of inoculum (165 mL). In order to find the appropriate link (correlation) between the COD and the production of methane, compared were the results for both types of waste and both quantities of substrates in the reaction bottle (Fig. 4).[17] It is clearly evident that, according to the COD, O2 waste produces a significantly higher amount of methane than waste O1.

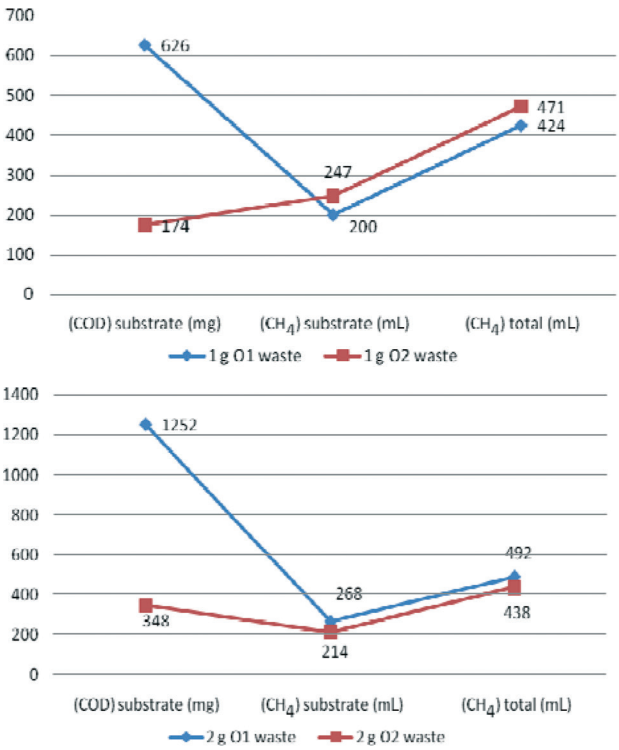


Fig. 4 – *Ratio of COD and CH_4 production of 1 and 2 g of waste*

After adding 1 g of waste to the reaction bottle (reducing the COD to the unit value of 1 mg), it could be observed that waste O1 produces 0.32 mL of methane, while in the same setting, waste O2 produces 1.42 mL methane mg^{-1} COD.

With the additions of 2 g of substrate to the reaction bottle, (taking into account the unit value of 1 mg of COD), waste O1 produces 0.214 mL CH_4 mg^{-1} of COD, while in the same setting, waste O2 produces 0.614 mL CH_4 mg^{-1} of COD.

Linear correlation between the two parameters, COD and CH_4 of the substrate and two different quantities of waste (1 and 2 grams) is given by the following equations:

$$\text{For 1 g:}\quad CH_4 = -0.104COD + 265.09 \tag{1}$$

$$\text{For 2 g:}\quad CH_4 = 0.059COD + 193.21 \tag{2}$$

It is also important to find a linear correlation between the COD and CH_4 of substrate and the two types of waste (equations 3 and 4):

$$\text{For O1:}\quad CH_4 = 0.108COD + 132 \tag{3}$$

$$\text{For O2:}\quad CH_4 = -0.445COD + 324.59 \tag{4}$$

In order to find the most optimal mixture (M1, M2 or M3), it is necessary to solve the set of equations indicated above, and choose the most efficient mixture from the aspect of biogas yield, taking into account the available amount of added waste. The result of eqs. (1) and (2) gives a yield of 0.497 mL CH_4 mg^{-1} COD, whereas the result of eqs. (3) and (4) gives a yield of 0.487 mL CH_4 mg^{-1} COD (selected value for the calculation mixture). According to these indicators, it is clear that there is a good match of biogas yield by type and amount of waste added. The resulting difference is attributed to the level of confidence of 95 %.

The mixture with the highest COD had the highest yield. This was mixture M1 with waste ratio being O1 : O2 = 80 : 20, with an average amount of COD of 526 mg/g (standard deviation ± 11). Also, the ratio of waste O1 : O2 was 3.85 (1330/350), which roughly confirms the selected mixtures M1 (80 : 20 = 4).

Conclusions

Based on the presented analysis and the experimental results, it can be concluded that the potential of biogas yield from organic waste in the conditions of the experiment (BMP test) directly correlates with COD of the waste. For the same conditions of BMP test, based on the established linear dependence of CH_4 and COD, biogas production of other types of waste mixture (defined mixtures M1, M2 and M3) can be calculated. Based on the results for the treatment of

AD installations for MI waste, a mixture of M1 (O1 : O2 = 80 : 20) is recommended because it had the highest COD of 526 mg COD, and the highest yield of 256.16 mL CH_4. According to this selection of waste mixtures (M1), based on the results of the BMP test, the annual production of methane from a related meat industry, based on the amount of 1700 tons per year, could be calculated. Production of methane is equal to the product of the amount of waste ($M1_{annual}$) COD_{M1} and unit production of CH_{4M1} (mL mg^{-1} COD). Based on the quantity of waste within the MI, total annual production of methane is 435 475 m^3.

Thus, important information for the correct selection of waste or mixture of wastes that can pass through the process of AD (Co-digestion) can be obtained by characterization of waste from the MI, based on physical and chemical analysis of waste.

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List of abbreviations

AD – Anaerobic Digestion
BMP – Biomethane Potential
COD – Chemical Oxidation Demand
Ino – Inoculum
MI – Meat Industry
M1, M2 and M3 – Appropriate Mix of Tested Wastes from the Meat Industry
O1, O2 – Tested Wastes of Meat Industry
TS – Total Solids
TVS – Total Volatile Solids
VFA – Volatile Fatty Acids

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