IOP Conference Series: Earth and Environmental Science

PAPER • OPEN ACCESS

Effect of long-term storage of cattle manure on its energy potential and biodegradability

To cite this article: I V Miroshnichenko *et al* 2024 *IOP Conf. Ser.: Earth Environ. Sci.* **1390** 012010

IOP Conf. Series: Earth and Environmental Science **1390** (2024) 012010 doi:10.1088/1755-1315/1390/1/012010

Effect of long-term storage of cattle manure on its energy potential and biodegradability

I V Miroshnichenko[1*], A S Oskina[2], V A Lomazov[1, 3], D N Klyosov[1] and A V Lomazov[4]

[1]Belgorod State Agricultural University named after V. Gorin, 1, Vavilova, Mayskiy, Belgorod Region, 308503, Russia
[2]University of Hohenheim, 9, Garbenstr., Stuttgart, 70599, Germany
[3]Belgorod State National Research University, 85, Pobedy, Belgorod, 308015, Russia
[4]Financial University under the Government of the Russian Federation, 49, Leningradskiy, Moscow, 125167, Russia

*E-mail: imiroshnichenko_@mail.ru

Abstract. In recent years in Russia, due to the complicated geopolitical situation in some border areas, biogas plants have been considered not only as waste utilization facilities, but also as reserve energy sources, which are safer than traditional - nuclear power plants. In this context, the development of an algorithm for the flexible operation of a biogas plant is particularly relevant, which gives rise to the need to study the stability of the system under the influence of different unfavourable factors. In this work, the influence of long-term storage of cattle manure on its energy potential and biodegradability is studied. The specific methane yield in the test variant with manure stored for 10 months before anaerobic fermentation was 1.41±0.55 ml/g oDM, which is 6.23 times lower than in the test variant with fresh manure; the methane content of manure after long-term storage is 9.66 times lower and the degree of decomposition of its organic matter is 2.72 times lower compared to similar indicators of manure processed without preliminary storage. However, the specific biogas yield from long-term stored manure is 1.66 times higher than the control, which indicates intensive formation of other gases. Thus, long-term storage has a negative impact on the energy potential of cattle manure; if it is necessary to process it in a biogas plant, it is advisable to combine it with more energy-intensive raw materials.

1. Introduction

In Russia, due to the availability of cheap fossil energy sources, biogas technologies are of interest mainly as a method of waste utilization. Increasing the share of biogas in the overall energy balance allows to reduce the specific ecological footprint per unit of commodities and to reduce the negative impact on the environment by reducing the share of organic waste disposal. Nevertheless, the use of biogas as an energy source can solve various problems in the following ways:

- developing new energy resources to meet growing human needs;
- reducing energy shortages in remote rural areas without access to traditional energy systems;
- ensuring sustainable industrial development while reducing the technogenic impact on the environment;
- increase sustainability of the energy generation process, contributing to the reduction of the energy intensity of products, thus increasing their demand and competitiveness;

- finding additional opportunities for cooperation with other sectors of the economy [1].

The majority of research in the field of biogas technologies is aimed at improving the efficiency of biogas plants. Recently, the issue of increasing their efficiency, ensuring their operational stability and flexibility of the processes taking place in them has become more and more urgent, since excessive gas formation is as economically unprofitable as insufficient gas formation: it indicates irrational consumption of substrate, excessive gas is burned in the emergency flare of the plant without producing useful energy. Within the framework of biogas plant stabilization, issues of regulation of technological parameters and selection of substrates are considered in such a way that biogas production and composition are maintained at a constant level. Flexibility of biogas plant operation is a characteristic that is particularly important for a reserve energy source, i.e. the ability to effectively supplement or replace the main energy sources if necessary [2, 3, 4, 5, 6, 7, 8].

In recent years, the tense and unstable political situation in some border areas of Russia has created an urgent need to reconsider certain aspects of economic and security activities. Biogas plants are now considered not only from the point of view of waste utilization and reduction of anthropogenic pollution, but also as a reserve energy source. Moreover, in the current geopolitical situation, such energy facilities are safer than traditional - nuclear - power plants. In this regard, it is necessary to develop an algorithm for flexible operation of a biogas plant, which leads to the need to study the stability of the system under the influence of unfavourable factors - for example, when using substrates stored for a long time.

Cattle manure is a valuable fertilizer and raw material for biogas production. However, when manure is stored for more than 6 months, its organic matter content decreases significantly due to the activity of microorganisms. This organic matter is converted into carbon dioxide, methane, ammonia and other substances. In addition to polluting the air with greenhouse gases and odours, this reduces the value of manure not only as a fertilizer but also as an energy source [9, 10].

Gas emissions are the main source of carbon and nitrogen losses during open-air manure storage. According to Shan N. et al. (2019), when pig manure is stored for 60 days in summer, the losses of total carbon and total nitrogen are 62 and 41% (of the mass fraction of dry matter), respectively. At the same time, the main losses of nitrogen occur in the first days of storage, while carbon losses occur later in the storage period [11].

To reduce methane emissions, many researchers recommend storing solid manure at lower temperatures or acidifying liquid manure. [9, 10]. Compared to other methods, acidification to pH 5.5 is optimal because it reduces methane emissions from pig and cattle manure during storage by 95-99% and 65-99%, respectively. The use of other chemicals, such as antimicrobial and oxidizing agents, can also significantly reduce methane emissions, and the combination of acidification with physical and chemical treatments has a cumulative or synergistic effect [12].

S. Im et al. (2020) found that when the storage temperature of solid manure (with a dry matter mass fraction above 30%) is reduced from +35°C to +20°C and below for 80 days, methane emissions from the manure are more than halved and the degree of decomposition of organic matter is reduced by more than 3.6 times. Reduced decomposition of organic matter at low temperatures results in a 1.72-fold increase in methane production potential [13].

The decrease of dry matter, organic matter, nitrogen and phosphorus content in processed manure (effluent) after storage and the temperature dependence of these parameters are reported by Yan J. et al. (2023) [14]. If the effluent is stored at +10°C for 180 days prior to use as a fertilizer, additional treatment is required due to the increased phytotoxicity of the effluent resulting from the accumulation of high concentrations of ammonium nitrogen, volatile fatty acids, phenolic compounds and salts. Temperature is the key factor that determines the change in effluent characteristics during storage and can affect microbial activity and microbial community development, as well as gas emissions (mainly methane, carbon dioxide, nitrous oxide, ammonia and hydrogen sulfide) that determine the change in effluent characteristics [13, 15].

Due to the high organic loading rate of the bioreactors or the short retention time of the substrate in the reactor, a significant fraction of the organic matter in the feedstock remains undegraded [16]. Noncompletely degraded organic matter not only has a negative impact on the environment as a pollutant, but when applied to soil it can also be phytotoxic due to the release of heat during the degradation of rapidly degradable substances [17, 18, 19] and excessive respiration of soil microflora, causing immobilization and denitrification of nitrogen [20]. In addition, incompletely anaerobically fermented raw materials still contain high concentrations of ammonia nitrogen, volatile fatty acids, phenolic compounds and salts, which can have negative effects on plants [21, 22].

Ólafsdóttir S. S. et al. (2023) found that pasteurization of pig manure and acidification with sulfuric acid contribute to the reduction of methane emissions during storage at relatively low temperatures (around +4°C). However, they have different effects on the biogas productivity of the substrate during its further anaerobic fermentation: pasteurization increases the specific methane yield (SMY) by 16-35% and acidification reduces the SMY by 6-23% compared to untreated manure. Further studies by these authors show that storage itself has a positive effect on the methane yield of thermally treated manure at the subsequent stage of anaerobic fermentation. The authors attribute this to the increased availability of nutrients to the methanogenic microflora, with an increase in the rate of hydrolysis, resulting in an increase in the rate of methanogenesis [23].

The aim of this work was the investigation of the effect of long-term storage of cattle manure on its energy potential and biodegradation by anaerobic fermentation.

2. Materials and methods

The research substrate was cattle manure – fresh and after 10 months of storage in an open pit at +5+20°C – and inoculum from a working biogas plant. The mass fraction of dry matter (DM) and organic matter (oDM) in the studied substrate was determined according to the procedure described in the literature [24].

To investigate the biogas potential of the substrate in the laboratory biogas plant, a batch experiment was carried out according to [25]. Glass vessels with a working volume of 300 ml each were used as bioreactors. Heating to +37±0.2°C was performed in a water bath, and mixing was performed using magnetic stirrers. Biogas was collected in gas holders, its volume was determined weekly using a sealed graduated glass tube with piston and its composition was determined using an Optima-7 Biogas analyzer. The gas volume was adjusted to normal conditions using the equation (1).

$$V_0=(P*V*T_0)/(T*P_0), \quad (1)$$

where: V_0 – volume of dry gas under normal conditions, ml; V – measured gas volume, ml; P – gas pressure at the time of measurement, mbar; P_0 – atmospheric pressure at normal conditions; P_0 = 1013 mbar; T_0 – air temperature at normal conditions; T_0 = 273 K; T – biogas temperature, K.

The duration of the experiment was 35 days. Reactor loading rates were calculated so that the ratio of inoculum oDM to substrate oDM was 1.5-2 to 1. The inoculum was pre-filtered through a sieve with a pore size of 2 mm.

The degree of organic matter degradation of the substrates was calculated according to [24] using the equation (2):

$$M_{biogas} = V_{biogas} * (1.96 * (C_{CO_2} / 100) + 0.73 * (C_{CH_4} / 100)) \quad (2)$$

where: M_{biogas} – mass of biogas, mg; V_{biogas} – biogas volume, mL; C – concentration of the detected gases in the gas mixture, %; 1.96; 0.73 – density of the detected gases respectively, mg/mL.

All variants were tested in three repetitions. The obtained results were processed by the method of variation statistics according to [26] using Microsoft Excel program. The data are presented as mean value and arithmetic mean error (M±m). The result was considered reliable at P≥0.95*, P≥0.99**, P≥0.999***.

3. Results and discussion

Table 1 shows the composition of the initial substrates and inoculum.

Table 1. Composition of raw materials.

Raw material	DM, %	oDM, % of DM
Fresh cattle manure	5.29±0.03	73.83±0.55
Cattle manure after storage	8.62±0.082	81.24±1.55
Inoculum	3.01±0.03	66.91±1.20

In our experiment, the mass fractions of dry matter and organic matter in manure did not decrease during storage, on the contrary, they increased slightly. This is probably due to the loss of moisture and a certain proportion of elements included in the composition of the gases released - presumably ammonia, carbon dioxide and methane.

Taking into account the oDM content of the starting material and the recommendations on the ratio of substrate to inoculum oDM given in [25], 60.79 g of fresh cattle manure and 239.21 g of inoculum were added to each reactor of the control variant, 37.27 g of cattle manure after 10 months of storage and 262.73 g of inoculum to each reactor of the experimental variant and 300 g of inoculum to each reactor of the "zero" variant.

Table 2 shows the energy potential of the variants without correction for the "zero" variant, i.e. from a mixture of substrate and inoculum in the reactor. As the specific methane yield of the substrate was significantly lower than that of the inoculum in two out of three reactors of the experimental variant, it was not possible to make a correction for this variant.

Table 2. Energy potential of the variants (without correction).

Variants (substrates)	Gross yield, mL		Methane content, %	Specific yield, mL/g oDM	
	biogas	methane		biogas	methane
Control (fresh manure)	335.50±24.83	63.07±3.82	18.84±0.47	46.60±3.45	8.76±0.53
«Zero» variant (inoculum)	67.94±11.94	6.96±1.22	10.24±0.00	11.23±1.97	1.15±0.20
Treated (manure after storage)	588.67±187.77	11.12±4.32***	1.95±0.34***	74.45±23.75	1.41±0.55***

***P≥0.999

It was found that the gross and specific biogas yield is higher from manure stored for 10 months (experimental variant), but the gross and specific methane yield is significantly lower here - by 51.95 mL and 7.35 mL/g oDM, respectively, or by 5.67 and 6.23 times, respectively.

The energy potential of cattle manure in our experiment is much lower than in the work of other researchers. In the study by Tariq M. et al. (2023), the specific biogas yield from cattle manure using inoculum in the form of ruminant intestinal waste was 239 mL/g oDM [27]. In Cárdenas A. et al. (2021), the specific methane yield from cattle manure ranged from 0.084 to 0.203 mL/g oDM during summer storage (extensive fermentation for 40 weeks) and up to 0.002 ml/g oDM during winter storage (extensive fermentation for 20 weeks) [28].

In anaerobic fermentation of cattle manure without inoculum, Wi J. et al. (2023) had a specific methane yield of 54.3±1.7 mL/g oDM [29].

In relation to 1 kg of manure in natural weight, the methane yield in our experiment was 0.95 and 0.13 L in the control and experimental variants, respectively, which is much lower than the results obtained by Im S. et al. (2020), which ranged from 25 to 43 L/kg of manure [13].

In a study by Møller H. B. and Moset V. (2015), the specific methane yield from cattle manure during 225 days of fermentation at +35°C ranged from 217 to 348 L/kg oDM, but the mass fractions of DM and oDM in the material they tested were higher than in our experiment, ranging from 7.03 to 14.82 and 80.45 to 85.92 %, respectively [30].

In our experiment, the amount of methane formed in the experimental variant was the smallest - 16.91% less than in the control (table 2), while the amounts of oxygen and other gases released from it exceeded the control by 4.61 and 15.14 % respectively (table 3). Hydrogen sulfide was released almost 10 times more in the experimental variant than in the control variant, but in all variants the values of this indicator are small and do not exceed 0.00053±0.00028 ppm.

Table 3. Gas formation during anaerobic fermentation of cattle manure, M±m.

Variant	Carbon dioxide		Hydrogen sulfide, ppm	Oxygen		Other gases	
	mL	%		mL	%	mL	%
Control (fresh manure)	16.2±0.739	4.86	0.00005±0.00002	35.06±3.38	10.45	221.06±17.19	65.89
«Zero» variant (inoculum)	2.31±0.41	3.40	0.00014±0.00002	6.93±1.22	10.20	51.75±9.09	76.16
Treated (manure after storage)	11.90±4.30	2.02	0.00053±0.00028	88.64±28.93	15.06	477.01±153.72	81.03

Thus, in our experiment, long-term storage of manure had a negative effect on its energy potential - probably a significant part of the nutrients was lost with gas emissions; according to Qu Q. and Zhang K. (2021), gas emissions are the main pathways of nutrient loss during storage [31]. The methane yield was very low in all the variants studied compared to the results obtained by other researchers - the influence of the breeds and diets of the animals from which the material for the studies was obtained cannot be excluded [30, 32].

The methane content in the biogas in our experiment did not exceed 18.84±0.47% in all variants - therefore the biogas obtained is not combustible and these substrates should be used for energy purposes in a mixture with more energy-intensive raw materials, including their use as inoculum in the processing of substrates rich in nitrogenous compounds. For example, Wi J et al (2023) found that anaerobic co-fermentation of pig and cattle manure avoids the inhibition caused by the accumulation of ammonia and volatile fatty acids and increases methane yields [29].

The highest biogas production in all variants was observed during the first week of the experiment (figure 1). The further decrease in the intensity of gas formation in the control variant was smooth, in the experimental variant there was some growth of this indicator during the fourth week of the experiment. By the end of the fifth week of the experiment, gas formation was practically at a standstill in all variants.

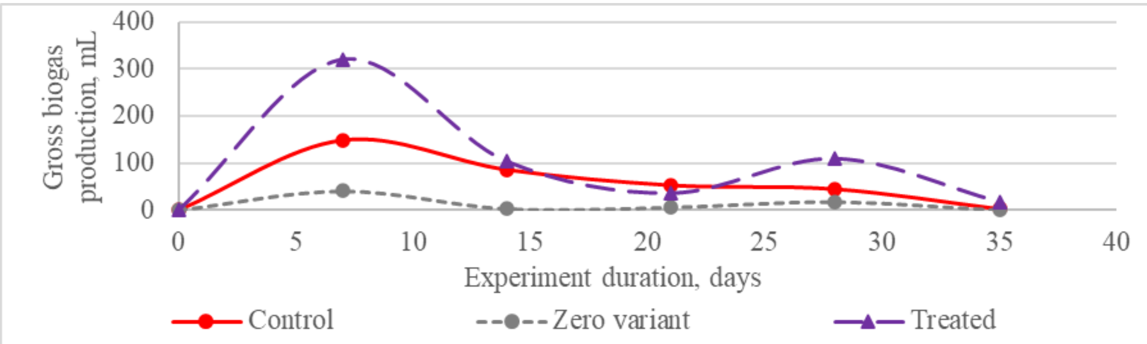

Figure 1. Kinetics of biogas production.

The most intensive methane formation in the control variant was observed during the first week of the experiment, then it began to decrease steadily and stopped at the end of the fifth week (figure 2). In the experimental variant, the intensity of methane synthesis had a wave-like character: during the first two weeks, the volume of methane formed was approximately the same, at the end of the third week the intensity of its formation decreased significantly, during the fourth week it increased again and at the end of the experiment methane formation stopped.

The degree of organic matter decomposition was low in all variants and was 1.08±0.06 % in the control variant and 0.40±0.15 % in the experimental variant, which was 0.68 % (or 2.72 times) significantly lower than in the control variant (P≥0.95). In the "zero" variant, the degree of organic matter decomposition was 0.16±0.03 %. In the works of other authors, this indicator is much higher - about 15.10% in Wi J., Lee S. and Ahn H. (2023) when processing manure after 6 months of storage and 27% in Tariq M. et al. (2023) who used fresher manure and bacterial inoculum [27, 29].

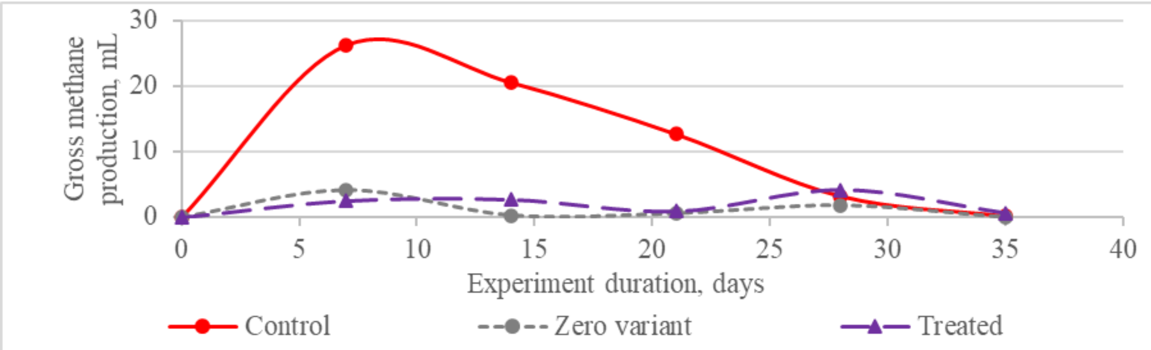

Figure 2. Kinetics of methane production.

4. Conclusion

In our experiment it was found that prolonged storage of cattle manure has a negative effect on its energy potential. The specific methane yield in the variant with manure stored for 10 months before anaerobic fermentation was 1.41±0.55 mL/g oDM, which was 6.23 times lower than in the variant with fresh manure; the methane content was 9.66 times lower (1.95±0.34 vs. 18.84±0.47 %). The degree of decomposition of its organic matter in the biogas plant was 0.40±0.15 % - 2.72 times lower than the same indicator for manure processed without pre-storage. However, the specific biogas yield from pre-stored manure is 1.66 times higher, which indicates more intensive formation of other gases - oxygen and probably gaseous nitrogen compounds.

The resulting biogas is non-flammable, and if it is necessary to use such substrates for energy purposes, it makes sense to combine them with more energy-intensive raw materials, including their use as inoculum in the processing of nitrogen-rich substrates to reduce the inhibitory effect of biogas synthesis intermediates formed by the microbial consortium of the biogas plant reactor.

Acknowledgments

The research was supported by the Russian Science Foundation (RSF) project No. 24-21-00059, https://rscf.ru/project/24-21-00059/.

References

[1] Ishkov A G, Pystina N B, Akopova G S and Yulkin G M 2014 *Territorija Neftegaz* **5** 130-7

[2] *Status of the Flexibilization of Biogas Plants* Specialist (2021) Agency for Renewable Raw Materials Retrieved from: https://biogas.fnr.de/biogas-nutzung/stromerzeugung/stand-der-flexibilisierung-von-biogasanlagen

[3] *SARR Collects Real-Time Data on Flexible Biogas Electricity Feed-In* Specialist Agency for Renewable Resources Retrieved from: https://biogas.fnr.de/service/presse/presse/aktuelle-nachricht/fnr-erhebt-echtzeitdaten-flexibler-biogas-stromeinspeisung

[4] Barchmann T, Mauky E, Dotzauer M, Stur M, Weinrich S, Jacobi H F, Liebetrau J and

Nelles M 2016 *Agricultural Engineering* **71(6)** 233-51
[5] Weinrich S, Mauky E and Liebetrau J 2018 *Process Flexibility at Biogas Plants 27th Biogas Forum Bavaria* (Munich: Technical University of Munich, Leipzig: German Biomass Research Center) pp 1-37
[6] Purkus A, Gawel E, Szarka N, Lauer M, Lenz V, Ortwein A, Tafarte P, Eichhorn M and Thraen D 2018 *Energy, Sustainability and Society* **8** 18
[7] Daniel-Gromke J, Kornatz P, Dotzauer M, Stur M, Denysenko V, Stelzer M, Hahn H, Krautkremer B, von Bredow H and Antonow K 2020 *Guidelines for Making Electricity Supply More Flexible in Biogas Plants (LF Flex): Final report* (Leipzig: German Biomass Research Center) pp 200
[8] Lomazov V A, Mironov A L, Lomazova V I, Miroshnichenko I V and Petrosov D A 2021 *IOP Conference Series: Earth and Environmental Science* **659** 012111
[9] Petersen S O, Andresen A J and Eriksen J 2012 *Journal of Environmental Quality* **41** 88-94
[10] Regueiro I, Coutinho J and Fangueiro D 2016 *Journal of Cleaner Production* **131** 296-307
[11] Shan N, Li H, Li J-Zh, Ee Ling N, Ma Y, Wang L-G and Chen Q 2019 *Journal of Integrative Agriculture* **18(1)** 190-200
[12] Ambrose H W, F R Dalby, A Feilberg and Kofoed M V W 2023 *Biosystems Engineering* **229** 209-45
[13] Im S, Petersen S O, Lee D and Kim D-H 2020 *Waste Management* **101** 35-43
[14] Yan J, Chen X, Wang Z, Zhang Ch J, Meng X, Zhao X, Ma X, Zhu W, Cui Z and Yuan X 2023 *Waste Management* **159** 1-11
[15] Wang Y, Zhu Z P, Li X R, Yang J, Liang L, Sui Q, Wang B and Dong H 2021 *Journal of Cleaner Production* **319** 128560
[16] Monlau F, Kaparaju P, Trably E, Steyer J P and Carrere H 2015 *Chemical Engineering Journal* **260** 377-85
[17] Stehel V, Vochozka M, Marouskova A, Shawl J and Kolar L 2018 *Energy Sources A* **40** 301-5
[18] Wang G, Yang Y, Kong Y, Ma R, Yuan J and Li G 2022 *Journal of Hazardous Materials* **421** 126809
[19] Yague M R and Lobo C 2020 *Spanish Journal of Soil Science* **10** 248-56
[20] Antonio Alburquerque J, de la Fuente C and Pilar Bernal M 2012 *Agriculture, Ecosystems & Environment* **160** 15-22
[21] Nkoa R 2014 *Agronomy for Sustainable Development* **34** 473-92
[22] Torrisi B, Allegra M, Amenta M, Gentile F, Rapisarda P, Fabroni S and Ferlito F 2021 *Waste Management* **131** 201-13
[23] Ólafsdóttir S S, Jensen C D, Lymperatou A, Henriksen U B and Gavala H N 2023 *Journal of Environmental Management* A **325** 116456
[24] Pfeiffer D and Dittrich-Zechendorf M 2012 *Collection of Biogas Measuring Methods: Methods for Determining Analytical and Process-Describing Parameters in the Biogas Sector* (Leipzig: German Biomass Research Center) pp 1-151
[25] *VDI 4630:2006-04 Fermentation of Organic Materials – Characterisation of the Substrate, Sampling, Collection of Material Data, Fermentation Tests* 2006 (Düsseldorf: AoGE-Society for Energy and Environment) pp 1-132
[26] Plokhinsky N A 1970 *Biometrics* (Moscow: Moscow State University Publishing House) pp 1-367
[27] Tariq M *et al.* 2023 *BioEnergy Research* **16** 1913-21
[28] Cardenas A, Ammona C, Schumacher B, Stinner W, Herrmann C, Schneider M, Weinrich S, Fischer P, Amona T and Amona B 2021 *Waste Management* **121** 393-402
[29] Wi J, Lee S and Ahn H 2023 *Bioengineering (Basel)* **10(4)** 432
[30] Moller H B and Moset V 2015 *Methane Emissions from Liquid Manure Storage – Influence of Temperature, Storage Time, Substrate Type and Anaerobic Digestion* (Tjele: Aarhus University) pp 1-20

[31] Qu Q and Zhang K 2021 *Atmosphere* **12** 1156
[32] Yohaness M T 2010 *Biogas Potential from Cow Manure – Influence of Diet: Master Thesis* (Uppsala: Swedish University of Agricultural Sciences) pp 1-51