Machinery & Energetics. Journal of Rural Production Research. Kyiv. Ukraine. 2020, Vol. 11, No 3, 135-141
ISSN 2663-1334 (print), ISSN 2663-1342 (online), www.journals.nubip.edu.ua/index.php/Tekhnica

http://dx.doi.org/10.31548/machenergy2020.03.135

УДК 621.078-048.34

BIOTECHNOLOGY OF CO-FERMENTATION OF SUGAR BY-PRODUCTS WITH TYPICAL AGRICULTURAL SUBSTRATES

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Speciality of article: 162 – biotechnology and bioengineering.

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Article history: Received – April 2020, Accepted – August 2020.
Bibl. 10, fig. 3, tabl. 0.

Abstract. Anaerobic digestion (AD) is a promising option for the environmentally friendly recycling of agricultural by-products. However, overloading of the digester with sugar, starch or protein might cause inhibition of the anaerobic processes. The aim of the present project was to investigate the influence of sugar beet by products on biogas yield from a typical mixture of energy crops and animal manure.

The investigated substrates have been: cattle slurry, maize, sorghum and grass silage, sugar beet pulp e (SBP) and sugar beet tail silage (SBT). The difference between untreated SBT to processed SBP. All substrates were digested in 1 l eudiometer-batch digesters at 37.5°C during 28 to 38 days. The specific methane yield of mixtures and various substrates exanimated. The experiments showed that edition of sugar beet by product to energy crop and slurry mixture results in high methane yield even the achieved methane yield of the mixture was lower the expected.

Key words: anaerobic digestion, biogas, methane yield, by-products, sugar beet pulp, sugar beet tail, potato peel pulp, potato fruit water.

Introduction

Except of the present project, little work on AD and methane yield of by-products from the sugar and starch industry has been done [1].

The low pH value and the high protein and sugar contents in these substrates may cause an acidification of the digester and therefore an inhibition of the methane production [2].

Formulation of problem

To avoid this danger in biogas plants, these by-products need to be investigated in laboratory experiments and the development of important process parameters has to be recorded [3-5].

Analysis of recent research results

The most important parameters to indicate a possible inhibition of the AD process are: pH, volatile fatty acids and ammonia concentration [6-9]. Beside these process parameters, it is also important to have knowledge about the development of the biogas composition (methane, hydrogen sulphide and carbon dioxide) during the AD [10].

Purpose of research

The objectives of the present project were to determine the suitable volume and the co-fermentation effects of sugar beet by products within the mixture of other agricultural substrates and manure for biogas production.

Results of research

Substrates. Sugar beet pulp (SBP) and sugar beet tail (SBT) were collected as silages from the AGRANA Zucker Ges.m.b.H. in Tulln, Austria. The proofed mixture of agricultural substrates consists of cattle slurry, maize and sorghum was collected on the Farms in Lower Austria.

Inoculum. Active sludge from a commercial biogas plant in Lower Austria (table 1) was used as inoculum. The substrates of the biogas plant were vegetables, maize silage and sunflower silage. The inoculum was collected from the last part of the horizontal fermenter into a 50 l heatable container. Before sampling the transport container was filled with argon to insure anaerobic conditions inside.

Table 2 shows the nutrient content of the inoculum. In the course of the AD experiment in the laboratory, the specific methane potential of the inoculum was measured as well. The inoculum showed a low specific methane potential of only 15 l_N (kg VS)$^{-1}$.

Determination *of methane potential (Experiment A).* The present study included 14 experimental variants. There of six variants were explored in mono digestion.

Sugar by-products were analyzed as silage an as dried material. To determine the co-fermentation effects of sugar by-products 6 mixtures with different content (30, 50 and 70% DM) of SBP and SBT were also digested. In the course of the experiment the fermentation process was detailed monitored to recognize any inhibitions or co-fermentation effects of different variants.

Table 1. Parameters of the biogas plant from which the inoculum was taken

Parameter	
Digester type	Horizontal plug flow digester
Digester	1 mixing tank 193 m^3 4 horizontal plug flow digesters 160 m^3 each 1 vertical second stage digester 1885 m^3 1 storage tank (uncovered) 4825m^3
Digested substrates	Energy crops, vegetables
Temperature in the digester	37°C
∅ hydraulic retention time	15 days h. digester + 55 days second stage
Electrical output	330 kW
Energy production	2 475.000 kWh a^{-1}

Anaerobic digestion experiments - Determination of the biochemical methane potential. The biochemical methane potential of the by-products was determined in 1 l eudiometer-batch digesters at 37.5°C. The experiments were carried out in accordance with VDI 4630 [xx] and DIN 38 414-8. Prior to AD, samples of all substrates were analysed for pH, DM, VS, crude protein, crude lipids, crude fibre, crude ash, N-free extracts, nitrogen and carbon using standard analysing procedures according to VDLUFA Band II.I [xx] and VDLUFA Band III. The gross energy content was measured with a calorimeter. The substrates were digested together with 350 g inoculum. That means on average the DM ratio between substrate and inoculum was 1:3. The DM content in the digesters with SBP and SBT ranged from 3.8 to 4.0%, the DM content in the digesters with PP, PPP and PFW from 3.0 to 3.1%. DM.

Each eudiometer consists of six digesters connected to equilibrium vessels, with a septum for gas extraction (fig. 1). The digesters were placed on magnetic stirrers in a tempered water bath. Specific methane yield from each substrate was measured in three replicates. During AD, the digester content was mixed for 10 minutes every 30 minutes. Biogas was collected in gas-collection tubes connected to the digesters. The amount of biogas produced was monitored every day. Biogas quality (methane, hydrogen sulphide and ammonia) was analysed six times during the experiments. Methane (CH_4) concentration in the biogas was measured using a NDIR analyser (Dräger X-am 7000, Dräger Safety, Lübeck, Germany) with an accuracy of ± 1-3% of the measurement reading. Before each measurement, the analyser was calibrated with CH_4 calibration gas containing 60% CH_4 and 40% CO_2. NDIR readings were validated at regular intervals with gas chromatographic analysis. Hydrogen sulphide (H_2S) and ammonia (NH_3) concentration in the biogas were analysed with the NDIR analyser in combination with Dräger tubes (accuracy ± 5-10% and 10-15% of the measurement reading, respectively). The biogas and methane production from the inoculum alone was also measured and subtracted from the biogas and methane production from the digesters containing the substrates and inoculum. The specific biogas and methane yields were calculated on the basis of norm conditions: 273 K and 1013 mbar and are given in norm litre per kg of volatile solids (l_N kg VS). In addition, the coefficient of energy efficiency of AD (η) was calculated for each substrate. This coefficient relates the produced methane energy to the gross energy of the substrate.

To control the quality and stability of the fermentation process, measurements of pH were done every second to third day and volatile fatty acids were measured twice during the experiment, at the beginning and at the end using gas chromatography. The fatty acid spectrum examined was C1-C6: acetic acid (HAC), propionic acid (PRO), iso butyric acid (i-BUT), butyric acid (n-BUT), iso valeric acid (i-VAL), valeric acid (n-VAL) and caproic acid (CAP).

Statistical data analysis. Statistical data analysis was carried out using the software package SPSS (version 12.0, SPSS Inc. 2006). In a first step, the descriptive statistics were done, determining means, standard deviations and frequency distributions of the data. Differences in the specific biogas and methane yields were tested with a pair wise comparison of regression parameters by the Tukey-HSD-Test and T-Test. The level of significance was set to 0.05.

Volatile fatty acid concentrations and pH during anaerobic digestion. The AD process of all substrates was carried out under optimal mesophilic conditions. The average temperature was 37.5°C and the pH values in the experiments ranged between 7.29 and 7.85. Average pH values and concentrations of volatile fatty acids at the beginning and at the end of the AD are shown in Table 5 and 6.

Table 2. Nutrient content of inoculum

Substrate	XP	XL	XF	XA	XX	N	C	GE	C/N	pH	DM	VS
	% DM	% DM	% DM	% DM	% DM	% DM	% DM	MJ kg^{-1} DM			% FM	% DM
Inoculum	14.5	0.8	10.0	47.2	27.5	6.3	27.7	18.0	4.4	7.4	2.4	52.8

XP = crude protein, XL = crude lipids, XF = crude fiber, XA = crude ash, XX = N-free extracts, N = nitrogen, C = carbon, GE = gross energy, DM = dry matter, FM = fresh matter, VS = volatile solids.

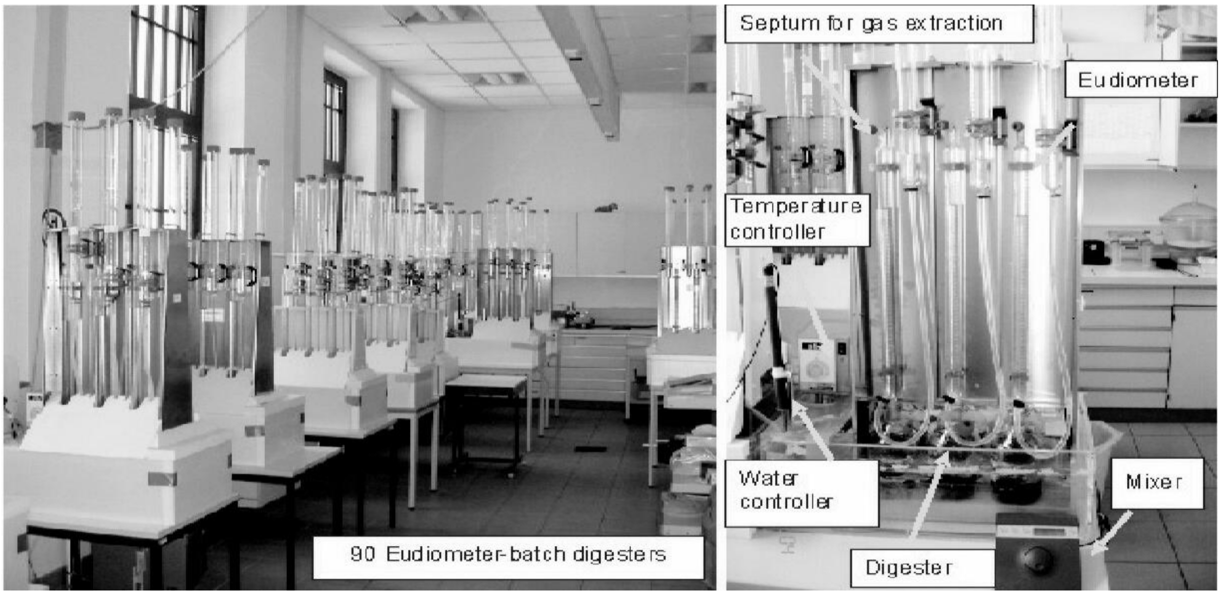

Fig. 1. Eudiometer-batch digester system.

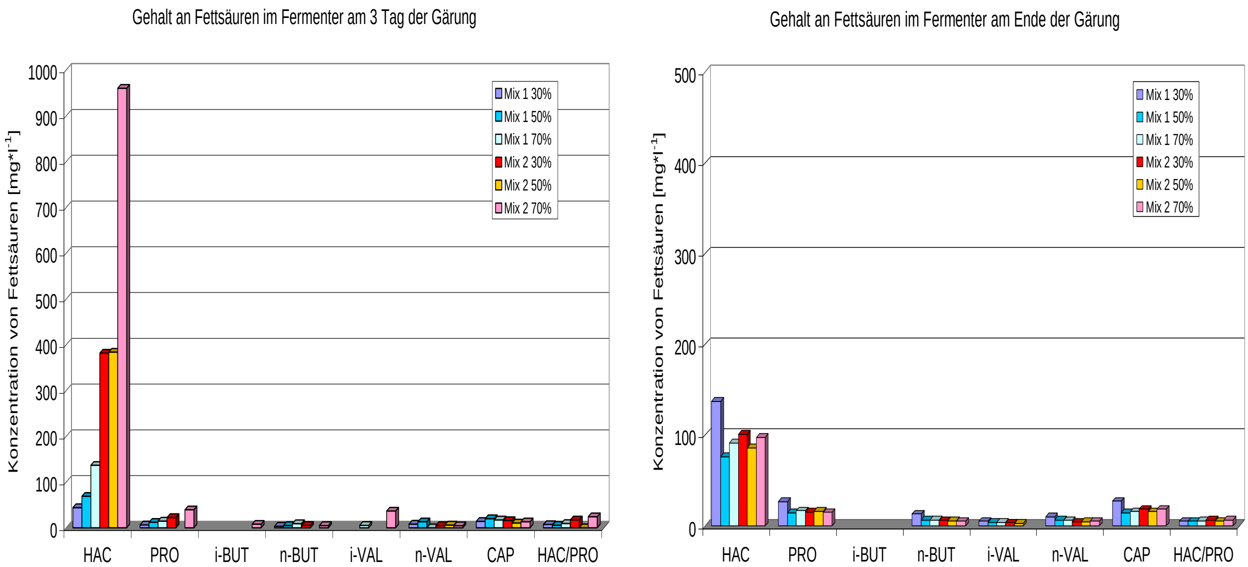

Fig. 2. Concentration of fatty acids in the fomenters to begin and to the end of digestion.

For SBP and SBT, at the beginning of the experiment the pH was 7.29 and 7.85, respectively (table 5). At the end of the experiment the pH for SBP and SBT was 7.34 and 7.79, respectively. That means during the whole experiment, the pH was lower in the digesters with SBP compared to digesters with SBT. From the beginning to the end of the experiment, the concentrations of acetic, propionic and butyric acid decreased in the digesters with SBP from 969 to 96.7, 113 to 4.2 and 8.8 to 0 mg l^{-1}, respectively. For SBT the values decreased from 791 to 58.0, 114 to 4.7 and 11.0 to 0 mg l^{-1}, respectively. The high concentrations of acetic and propionic acid at the beginning of AD are typical for the batch digester experiments. The low concentrations of acetic and propionic acid at the end of AD is a sign that the AD was not inhibited and the substrates were almost completely digested.

The pH was in all experimental variants in the range of 7.1 at the beginning of fermentation to 7.7 to 8.2 at the end of fermentation. Thus, there was optimum pH environment for the bacteria in the fermenters in experiment from the perspective of the. The optimal environment for the bacteria to a pH is between 6.4 and 8.0 (VDI 4630). If the pH is outside this range, there may be a worse gas yield and gas composition with a higher CO_2 content.

According to Wellinger, the AD runs optimal if the concentration of acetic, propionic and butyric acid is less than 1000, 200 and 50 mg l^{-1}, respectively and the value for HAC/PRO lies between 5 and 10. When the total concentration of volatile fatty acids exceeds 3000 mg l^{-1} or the propionic acid concentration becomes higher than 300 mg l^{-1}, an inhibition of the AD can take place. In the present experiments, except for PFW, the measured acetic acid concentrations were less than 1000 mg l^{-1} (fig. 1).

However, with SBT the total concentration of volatile fatty acids did not exceed 3000 mg l^{-1} and with none of the substrates a propionic acid concentration higher than 300 mg l^{-1} was measured. This demonstrates that in the present experiments the AD should not be inhibited.

Composition of the produced biogas. Table 3 displays the average composition of the biogas produced.

Six times during the experiment the concentration of methane, hydrogen sulphide and ammonia were measured.

The differences between the variants were not significant because the composition of the produced biogas varied during the experiments.

In both experiments the concentrations of methane, hydrogen sulphide and ammonia increased during the first five days, then were more or less stable for the following 20 days and slightly decreased towards the end of the experiments.

The present data are comparable with literature data. With regard to the by-products of sugar beet processing, SBP had higher concentrations of methane, hydrogen sulphide and ammonia compared to SBT (table 3).

Table 3. Concentration of methane (CH_4), hydrogen sulphide (H_2S) and ammonia (NH_3) in the biogas.

Variant	CH_4-Content			H_2S- Content			NH_3- Content		
	%	n	±	%	n	±	%	n	±
cattle slurry	53.0	7	8.,8	267	6	112	26	3	11
maize	55.1	7	3.7	214	6	58	29	3	16
sorghum	57.2	7	4	213	6	49	29	3	13
grass	57.6	7	4.2	281	6	149	32	3	30
pressed beet pulp silage	50.9	7	7.1	321	6	74	37	3	11
beet-tail silage	49.6	7	5	174	6	100	30	3	7
Mix 1 30%	56.7	7	3.7	209	6	23	33	3	1
Mix 1 50%	57.0	7	2.9	362	6	51	35	3	4
Mix 1 70%	57.3	7	3.3	176	6	97	32	3	10
Mix 2 30%	53.6	7	5.4	358	6	118	16	3	8
Mix 2 50%	54.7	7	7	387	6	45	16	3	13
Mix 2 70%	55.0	7	7.3	350	6	82	17	3	10
pressed and dryed beet pulp silage	46.2	7	12.8	250	6	127	41	3	38
dryed beet-tail silage	54.2	7	5.1	355	6	99	31	3	20

Table 4: Specific biogas and methane yield

Variante	Biogas yield [Nl *(kg oTS)-1]			Methane yield [Nl *(kg oTS)-1]		
	Av	n	St.div	Av	n	St.div
cattle slurry	249	3	2.6	132	3	0.5
maize	782	3	86.8	431	3	42.5
sorghum	608	3	26.8	348	3	14.9
grass	668	3	15.5	385	3	9
pressed beet pulp silage	845	3	33.3	430	3	18.1
beet-tail silage	970	3	68.7	481	3	32.4
Mix 1 30%	372	3	27.1	211	3	16.1
Mix 1 50%	405	3	15.5	231	3	8.1
Mix 1 70%	517	3	9.2	296	3	16.1
Mix 2 30%	668	3	24.0	358	3	10.2
Mix 2 50%	707	3	23.3	387	3	14.3
Mix 2 70%	812	3	50.0	447	3	24.9
pressed and dryed beet pulp silage	641	3	21.4	296	3	13.2
dryed beet-tail silage	506	3	27.9	274	3	14.9

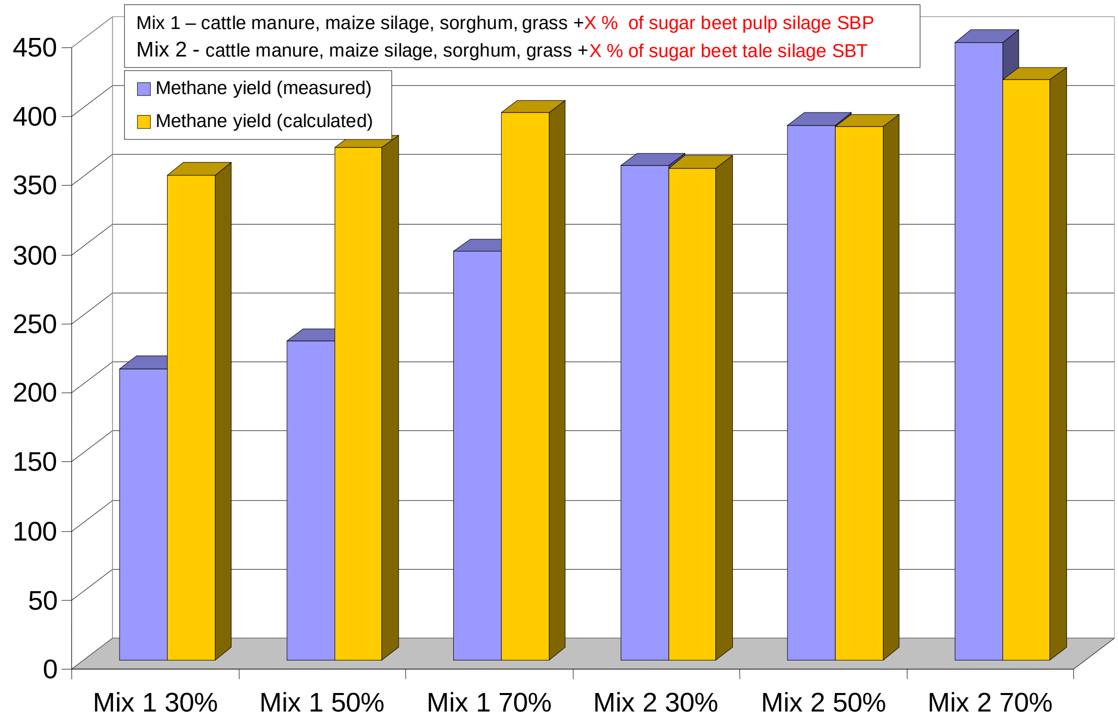

Fig. 2. Measured und calculated methane yeild of agricultural substrates (determination of co- fermentation effects)

As we can see the average methane concentration of grass and sorghum was higher then from the other substrates. The drying of sugar beet pulp silage reduced the methane content. It could be caused by the evaporation of fatty acids during drying process. The Mixtures with SBP shown a little higher methane content in biogas compared to the mixtures with SBT.

Specific biogas and methane yields as well as energetic efficiency of the investigated substrates. Specific biogas and methane yield of by-products of sugar beet processing (Experiment A). The specific biogas and methane yield of the sugar by-products: sugar beet pulp silage (SBP) and sugar beet tail silage (SBT) were measured over 30 days. The measurements were carried out until the specific methane yield per day was less than 1% of the cumulative specific methane yield.

The specific biogas and methane yields of SBP and SBT were significantly different (table 3). With SBT the specific biogas and methane yields were higher. On average a specific methane yield of 481 l_N (kg VS)$^{-1}$ was measured for SBT, whereas for SBP the specific methane yield was 430 l_N (kg VS)$^{-1}$. In the literature similar values were reported. For sugar beet silage gave the methane yields between 400 and 468 l_N kg^{-1} VS.

Table 4 also gives results for η, the energetic efficiency. For SBP on average 87.4% of the gross energy was converted to methane energy. The average value for SBT was 88.5%. SBT silage showed the highest methane yield of 480 Nl CH 4 (kg VS)$^{-1}$. The lowest methane yield was achieved from cattle manure. The standard deviation of the average methane yield for the SBP-silage, meadow and Sudan grass silage was significantly lower than of SBT silage and corn silage. This indicates a different homogeneity of the samples.

In the literature we found, for SBP silage a specific methane production potential of 400 NL CH_4 per kg VS. SBT silage for a specific methane production potential of 96 m³ / t FM is, 52% CH4, 17% TS and 75 m³ / t FM indicated (no indication TS). The specific methane yield from cattle manure, maize and grass silage were also in the folding back from the fields of literature.

The efficiency of methane digestion was calculated in accordance with the methane yield and the gross energy content in the biomass. It was 24% for cattle manure, 84% for maize, 64% for sudan grass, 73% in meadow grass, 85% for SBP silage and 89% for SBT silage. The efficiency of methane fermentation shows the energy recovery and fermentability of constituents of biomass in anaerobic fermentation process. The formula is described in chapter "Material and Methods. "

To identify the optimal mixture ratio of SBP silage and SBT silage in the mixture of cow manure, corn silage, to see Sudan grass and grass silage, were digested separately and in the mixtures. The measured specific biogas and methane yields with the standard deviation of three replicates are shown in Table 4. As shown in table 4, the biogas and methane yield of the mixtures increased with increasing amount of sugar by-products in the mixture.

Determination of co-fermentation effects. To clarify the cofermentations effects caused by the addition of SBP and SBT silage to the mixtures of cattle manure, maize silage, Sudan grass and meadow grass the substrates were digested in the mixture were digested in the mixture and separately. Based on the determined specific methane yields of the individual separately digested components and their content in the mixtures the expected specific methane yields were calculated.

Figure 2 shows the measured specific methane production potential of the mixtures 1 and 2 with different proportions of sugar beet by-products compared to the expected specific methane yield of these mixtures. As we can see in the fig 6 there was now co-fermentation effect achieved. The lower achieved as calculated specific methane yield of the mixtures with SBP silage could be possibly caused by reduced activity of cellulolytic bacteria, and thus lower recovery of nutrients from corn, Sudan grass and meadow grass silage. In animal nutrition we know that allowance of slightly soluble carbohydrates (sugars and starches) in ruminants may reduce the digestibility of other nutrients, particularly of protein and crude fiber. This decrease is referred to as "general digestive depression". According to primarily the cellulotic bacteria (cellulotische activity) coul be inhibited. This could explain the reduced actual methane yield of the mixtures with SPB silage.

The mixtures of Group 2 with SBT silage showed only slight co-fermentations effects. The addition of 70% of the ZR-top silage, resulted maximal additional methane yield of 6%. Optimal mixing ratios:

Conclusions

1. The fermentation of all variants was uniformly and stably without significant inhibition of methane fermentation. With increasing content of SBP silage in the mixture the specific methane production potential of the mixture increased. The addition of SBT silage (70% of DM fraction) to the mixture of energy crops and manure resulted in comparison to the mono-digestion of the substrates – in a slightly higher methane yield as calculated. In other mixtures there was no co-fermentations effects achieved or they were even negative. For recommendations of the suitability of the ZR-pulp silage as performance-enhancing additive for biogas production, it is reasonable to test the transferability of the present test results in continuous experiments at laboratory scale.

2. Drying of sugar beet by-products. The effect of drying of sugar beet-pulp silage and silage on top of their methane potential was tested in the present experiment compared to the non getrocknenten ensiled biomass. The results indicate that the drying of pulp silage-ZR and ZR-top silage to reduce the methane production potential of 30 and 43% resulted. The drying process causes the steaming out of free volatile fatty acids, which were formed during the ensiling process and can thus reduce the methane production potential of biomass.

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БІОТЕХНОЛОГІЯ КОФЕРМЕНТАЦІЇ ЦУКРОВИХ ПОБІЧНИХ ПРОДУКТІВ ІЗ ТИПОВИМИ СІЛЬСЬКОГОСПОДАРСЬКИМИ СУБСТРАТАМИ

Є. О. Дворник

Анотація. Анаеробне виварювання - багатообіцяюча можливість для нешкідливої для навколишнього середовища рециркуляції сільськогосподарських побічних продуктів. Однак, перевантаження систематизатора з цукром, крохмалем або білком могла б викликати заборона анаеробних процесів. Мета існуючого проекту полягала в тому, щоб дослідити вплив цукрових буряків продуктами на врожаї біогазу від типової суміші енергетичних зернових культур і гною.

Досліджені підстави були: рідкий гній рогатої худоби, кукурудза, сорго та силос трави, цукрові буряки перетворює в м'яку масу і силос гички цукрових буряків (SBT). Різниця між невилікуваним SBT до обробленого SBP. Всі підстави були переварені в 1 l систематизатора eudiometer-партії в 37,5 °C протягом 28-38 днів. Певний урожай метану сумішей і різних підстав екс-жвавий. Експерименти показали, що випуск цукрових буряків продуктом до енергетичного урожаю і шламових результатами суміші в високому метані поступається, навіть досягнутий урожай метану суміші був нижчим за очікуваний.

Ключові слова: анаеробне виварювання, біогаз, метан, побічні продукти, м'якоть цукрових буряків, бадилля цукрових буряків, картопля.

БИОТЕХНОЛОГИЯ КОФЕРМЕНТАЦИИ САХАРНЫХ ПОБОЧНЫХ ПРОДУКТОВ С ТИПИЧНЫМИ СЕЛЬСКОХОЗЯЙСТВЕННЫМИ СУБСТРАТАМИ

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Аннотация. Анаэробное вываривание – многообещающая возможность для безвредной для окружающей среды рециркуляции сельскохозяйственных побочных продуктов. Однако, перегрузка систематизатора с сахаром, крахмалом или белком могла бы вызвать запрещение анаэробных процессов. Цель существующего проекта состояла в том, чтобы исследовать влияние сахарной свеклы продуктами на урожае биогаза от типичной смеси энергетических зерновых культур и навоза.

Исследованные основания были: жидкий навоз рогатого скота, кукуруза, сорго и силос травы, сахарная свекла превращает в мягкую массу и силос ботвы сахарной свеклы (SBT). Различие между невылеченным SBT к обработанному SBP. Все основания были переварены в 1 l систематизаторе eudiometer-партии в 37,5°C в течение 28-38 дней. Определенный урожай метана смесей и различных оснований экс-оживлен. Эксперименты показали, что выпуск сахарной свеклы продуктом к энергетическому урожаю и шламовым результатам смеси в высоком метане уступает, даже достигнутый урожай метана смеси был ниже ожидаемого.

Ключевые слова: анаэробное вываривание, биогаз, метан, побочные продукты, мякоть сахарной свеклы, ботва сахарной свеклы, картофель.

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