PRODUCTION OF BIOGAS THROUGH ANAEROBIC CO-FERMENTATION OF CATTLE SLURRY WITH BISCUIT WASTE

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Abstract

The paper presents the results of the model of anaerobic co-fermentation of cattle slurry with biscuit waste. It was confirmed that the waste from the food industry is a valuable biogas substrate. The highest specific production of methane (0.49 $m_N^3 \cdot kg_{VS}^{-1}$) was achieved in the co-fermentation of 20 wt% biscuit waste with cattle slurry. The feed mixture contained 22 wt% of total solids. The biscuit waste has the specific production of biogas 0.66 $m_N^3 \cdot kg^{-1}$ and the specific production of methane 0.38 $m_N^3 \cdot kg^{-1}$.

Keywords: biscuit waste, cattle slurry, anaerobic co-digestion

1 INTRODUCTION

Anaerobic digestion [1-5] is a biochemical process with a positive energy balance. The aim is to transform the organic material to energy-profitable products. Combining this process with agriculture is very advantageous thanks to huge amounts of biological waste that are generated in this area [6-7]. The resulting biogas brings an unlimited perspective of the future use on the energy market [8]. A wide range of various biologically degradable wastes is created in the food industry, which is largely landfilled. The Directive No. 1999/31/EC on the landfill of waste [9] imposes on member states the duty to reduce the amount of biologically degradable waste landfilled to 75% of the weight of this type of waste created between 1995 and 2010, to 50% of the weight by 2013, and to 35% not later than by 2020. Although the Czech Republic can use a four-year postponement in the fulfilment of these limits, it will not avoid future problems in complying with the requirements of the directive. Only a small part of biowaste from the food manufacturing industry is used for feeding purposes, and only a small part is used for biogas production, as well. This waste has long been considered only as a material for disposal, not as a potential for side raw materials of a high value. Waste generated from confectionery production is classified in *Group 2, Paragraph (h)* according to *Annex 1* to *Decree No. 453/2008 Coll.,*[10], which stipulates "the types, methods of utilization, and parameters of biomass for purposes of supporting the generation of electricity from biomass". This waste may be processed by agricultural BGSs classified both in the category of anaerobic processes AF2 and in the category *AF1*. The requirement of hygienization pursuant to *Regulation (EC) No. 1774/2002* [11], or pursuant to *Decree No. 341/2008 Coll. of the Ministry of the Environment "on biowaste",* respectively, does not apply to this waste [12].

Currently, an increasing tendency for operators of agricultural biogas and other stations are bypassing companies that classifies biowaste from the production of confectionery and similar food for the production of feed additives. Nowadays biogas stations are trying to use these biowaste without distinguishing whether the biowaste is suitable or unsuitable. This can gradually jeopardize supplies of valuable feed additives to farmers, although demand in farming decreases due to a decline. In the case of biscuit waste, it is not probably a bad thing.

The objectives of this article are to verify the potential and efficiency of low-high solids mesophilic anaerobic digestion of biscuit waste and determine the specific production of biogas and methane. For our model experiment, we selected the biscuit waste with the waste catalogue number 02 03 04 – materials unsuitable for consumption or processing. The confectionary plant generates more than 60 tonnes/month of this waste; a small portion of the waste only is used in different ways (e.g. for feeding).

2 MATERIALS AND METHODS

The cattle slurry (reference substrate and inoculum) was delivered for the experiment from the biogas station Pustějov I. It is a classical agricultural biogas station using the wet anaerobic process, and with the installed electric power of 0.5 MW. The biscuit waste was delivered for the experiment by the Czech confectionery company Emco Ltd. The dry matter of the waste contained mainly extractable nitrogen-free substances (69.9%), starch (38%) and lipids (18.5%). The contents of carbohydrates, proteins, and other nitrogen substances were very low. At this time biscuit waste serves primarily as a valuable additive in feed mixtures, but due to the gradual reduction of agricultural production the biscuit meal and other valuable feed are becoming waste increasing the range that is removed/disposed of in landfills. The European Union mandates to reduce the biodegradable waste going to landfills. No mechanical or physical treatment of biowaste was used. The parameters of one sample of inoculum and one sample of the substrate can be found in Table 1 (measured in the external laboratory MORAVA).

Table 1: Parameters of inoculum and substrate

Parameter	**Symbol, Unit**	**Inoculum (low-solids digestate)**	**Biscuit waste**
Hydrogen exponent	pH-H_2O, -	7.1	5.81
Total solids (105°C)	TS, wt %	7.7	94.2
Volatile solids (Loss on ignition, 550°C)	VS, $\%_{TS}$	80.0	98.6
Total organic carbon	TOC, $\%_{TS}$	39.8	46.6
Total nitrogen	N, $\%_{TS}$	4.4	1.4
Ammonia nitrogen	N_{NH4+}, $\%_{TS}$	0.95	0.02
Total phosphorus	P, $\%_{TS}$	0.9	0.28
Total sulphur	S, $\%_{TS}$	0.5	0.06
Crude Ash	CA, $\%_{TS}$	20.0	1.42
Crude lipids	CL,$\%_{TS}$	4.0	18.5
Crude fiber	CF, $\%_{TS}$	20.5	1.4
Crude protein	CP, $\%_{TS}$	2.7	1.3
Carbohydrates	CH, $\%_{TS}$	2.3	23.2
Starch	ST, $\%_{TS}$	0.9	38.3
Nitrogen compounds	NC, $\%_{TS}$	46.0	1.4
Nitrogen-free compounds extracted	NFE, $\%_{TS}$	9.5	69.9
C/N ratio	C/N, -	11.5	600.0

Note: *pH of aqueous extract, total organic carbon (TOC) is approximately equal to total carbon*; NFE ($\%_{TS}$) = 100-(NC+CL+CF+CA); C/N ratio = TOC/(N-N_{NH4+})*

3 EXPERIMENTAL PART

A laboratory fermenter with a leading volume of 0.06 m^3 and continuous stirring was used to carry out long-term tests of continuous mesophilic anaerobic co-digestion (Figure 1). The average digestion temperature was kept at 40±2 °C with a continuous run of the low-speed stirrer (24 min^{-1}). The measurements of biogas production were carried out with laboratory drum-type gas flow meters and the composition of the biogas was measured daily using a mobile analyser with IR and electrochemical sensors. No mechanical or physical treatment of biowaste was used. The input mixtures of biowaste with cattle slurry were always prepared in a spare amount from 3 to 5 days while hydrolysis and acidification partially occurred (at laboratory temperature of 22±3°C).

The test was divided into two periods. In the first period, the content of the biscuit waste in the feed mixture with cattle slurry was 10 wt. %, in the second period, it rose to 20 wt. %. After each digestion test, average values of the parameters, characterizing the input mixture, digestate, biogas and process itself, were calculated.

4 RESULTS AND DISCUSSION

Period A: Co-fermentation of cattle slurry with 10% of biscuit waste

In the period A, the mean amount of 0.071 $m_N^3 \cdot d^{-1}$ of biogas, containing 57 vol. % of methane, was produced through the co-fermentation of the input mixture having the volumetric weight of approx. 1020 $kg \cdot m^{-3}$, mean pH of 4.6, total solids content of 15%, volatile solids content of 13.5%, average daily dose of 0.001 $m_N^3 \cdot d^{-1}$, the volumetric load of fermenter of 1.63 $kg_{VS} \cdot m^{-3} \cdot d^{-1}$, and the theoretical hydraulic retention time of 85 days. The mean total solids content obtained in the reactor was 6.0%. Calculated on the actual co-substrate (biscuit waste), the specific biogas production value was 0.660 $m_N^3 \cdot kg^{-1}$ and the specific methane production value was 0.375 $m_N^3 \cdot kg^{-1}$. The co-substrate volatile solids methane production was 0.404 $m_N^3 \cdot kg_{VS}^{-1}$.

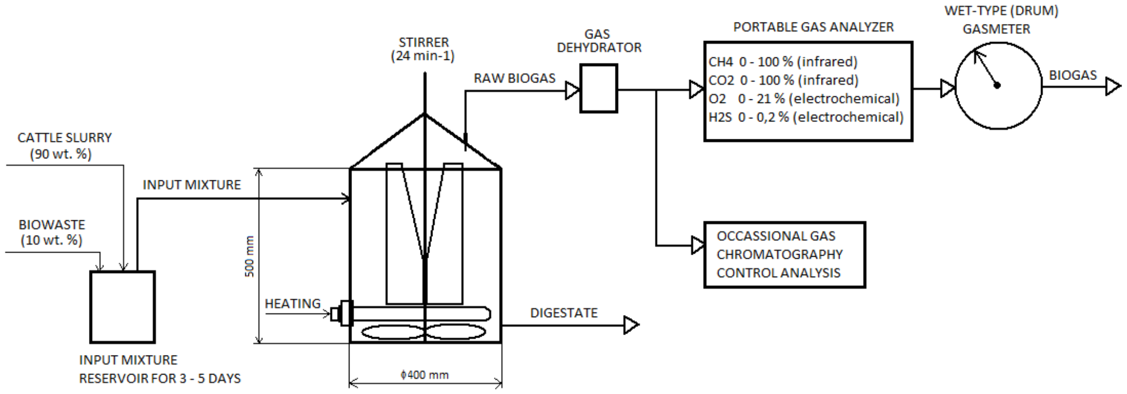

Figure 1: Layout of laboratory apparatus

Period B: Co-fermentation of cattle slurry with 20% of biscuit waste

In this period, the mean amount of 0.111 $m_N^3 \cdot d^{-1}$ of biogas, containing 60 vol. % of methane, was produced through the co-fermentation of the input mixture having the volumetric weight of approx. 1024 $kg \cdot m^{-3}$, mean pH of 4.7, total solids content of 22.4%, volatile solids content of 21.0%, average daily dose of 0.001 $m_N^3 \cdot d^{-1}$, the volumetric load of fermenter of 2.26 $kg_{VS} \cdot m^{-3} \cdot d^{-1}$, and the theoretical hydraulic retention time of 95 days. The mean total solids content obtained in the reactor was 6.0%. A marked increase of biogas production was observed within 2 days. Calculated on the actual co-substrate (biscuit waste), the specific biogas production value was 0.684 $m_N^3 \cdot kg^{-1}$ and the specific methane production value was 0.412 $m_N^3 \cdot kg^{-1}$. The co-substrate volatile solids methane production was 0.443 $m_N^3\ kg_{VS}^{-1}$.

The course of fermentation temperature, total solids content in the reactor, the digestate solids loss on ignition, the daily production of biogas and the average dry methane content are shown in Figure 2.

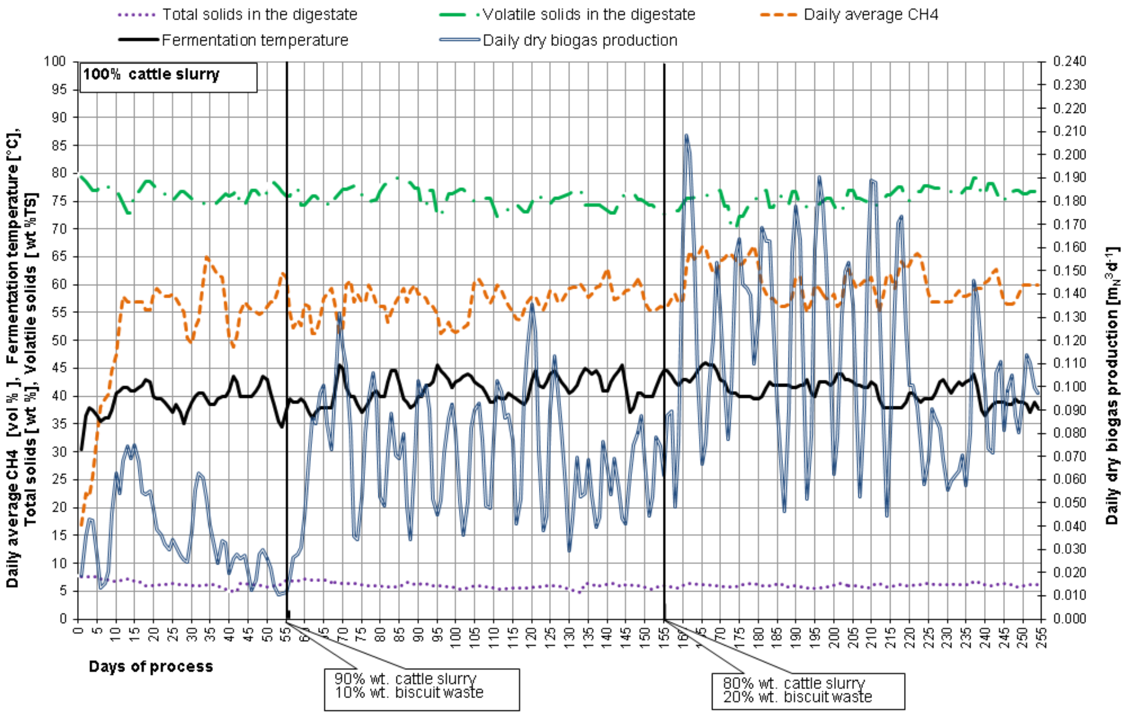

Figure 2: Course load and biogas production

Biogas production intensity

Compared to the period A, the biogas production rose by 56% in the period B, while the volumetric portion of methane remained virtually preserved at 60%, i.e. the methane production intensity rose approx. by 67%. At the same time, however, it was clear that the process efficiency decreased in the period B.

Gasification *efficiency*

In the period A, more biodegradable solids were present so that 12% of the feed went to biogas. In the period B, almost 21% of the feed went to biogas.

For a more detailed analysis, the sample of digestate was taken from the period A. Limited budgets did not allow to take the digestate from the period B.

The digestate sample from the period A with the chemical composition (content of combustible materials in solids higher than 25% mass and content of total nitrogen in solids higher than 0.6% mass) is suitable for fertilization of the agricultural land according to Regulation No. 271/2009 Coll., [13] Addendum 1, Table 2c), as amended. On average the digestate contained 5.4 % mass of total solids. The average content of the organic materials in solids was higher than 49% mass (74.7% mass). The content of total carbon was formed by organic carbon (41.5%). Half of the content of total nitrogen (approx. 7.4% mass of solids) is formed by ammonia nitrogen. The nitrate nitrogen content was relatively negligible. Approx. 1.6% mass of total solids is formed by phosphorus. Sulphur formed 0.7 % mass of total solids.

The measured values show that the digestate from the model test did not meet the allowed limits for risk elements (Cd, Pb, Hg, As, Cr, Mo, Cu, and Zn) with the solids content of max. 13% mass acc. to Regulation No. 271/2009 Coll., [13] as amended. The problem was only with the risk element Cu. The concentration of Cu was higher than 250 $mg.kg^{-1}{}_{TS}$ (495 $mg\cdot kg^{-1}{}_{TS}$). The presence of copper was caused by the $CuSO_4$ solution which is used for disinfection of cattle hooves. The analysed digestate met the quality parameters (max. humidity 98.0% mass, min. total nitrogen as N re-calculated for a dried sample 0.3% mass, and pH in the range of 6.5 to 9.0) of re-cultivation digestates according to *Regulation No. 341/2008 Coll.,* [12] *Addendum 5, Table 5.3, as amended*, without any problems. The digestate met the demands on the limits of risk elements and materials in the re-cultivation digestate according to *Regulation No. 341/2008 Coll.,* [12] *Addendum 5, Table 5.1, as amended,* for *Group 2* and *Class III* with the max limit of 500 $mg\cdot kg^{-1}$ for copper and max limit of 1500 $mg\cdot kg^{-1}$ for zinc. This means that this material can be used for the recultivation of landfill for hazardous waste according to the *Norm No. 83 8035* [14].

5 CONCLUSIONS

Biscuit wastes can be easily processed using wet anaerobic digestion. It was confirmed that the waste from the food industry is a valuable biogas substrate. Almost the whole dry matter of the waste is biologically degradable. The highest specific production of methane (0.493 $m_N^3\cdot kg_{VSp}^{-1}$) was achieved in the co-fermentation of 20% wt. biscuit waste with cattle slurry. The feed mixture contained 22 wt.% of total solids. The biscuit waste has the specific production of biogas 0.66 $m_N^3\cdot kg^{-1}$ and the specific production of methane 0.38 $m_N^3\cdot kg^{-1}$.

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REFERENCES

[1] WARD, A. J., HOBBS, P. J., HOLLIMAN, P. J., JONES, D. L. Optimisation of the anaerobic digestion of agricultural resources. *Bioresource technology.* 2008, **99**(17), 7928-7940 .

[2] MATA-ALVAREZ J, MACÉ S, LLABRÉS P. Anaerobic digestion of organic solid wastes. An overview of research achievements and perspectives. *Bioresource technology.* 2000, **74**(1), 3–16.

[3] ZHANG C, XIAO G, PENG L, SU H, TAN T. The anaerobic co-digestion of food waste and cattle manure. *Bioresource technology.* 2013, **129**, 170–176.

[4] FANG C, BOE K, ANGELIDAKI I. Anaerobic co-digestion of by-products from sugar production with cow manure. *Water research.* 2011, **45**(11), 3473–3480.

[5] PAGÉS DÍAZ J,PEREDA REYES I,LUNDIN M, SÁRVÁRI HORVÁTH I. Co-digestion of different waste mixtures from agro-industrial activities: kinetic evaluation and synergetic effects. *Bioresource technology.* 2011, **102**(23), 10834–10840.

[6] WEILAND P. Anaerobic waste digestion in Germany - status and recent developments. *Biodegradation.* 2000, **11**(6), 415-421.

[7] MTUI GYS. Recent advances in pretreatment of lignocellulosic wastes and production of value added products. *African Journal of Biotechnology.* 2009, **8**(8), 1398-1415.

[8] COMINO E, RIGGIO V A, ROSSO M. Biogas production by anaerobic co-digestion of cattle slurry and cheese whey. *Bioresource technology.* 2012, **114**, 46–53.

[9] DIRCTIVE, L. Council Directive 1999/31/EC of 26 April 1999 on the landfill of waste. *Official Journal,* L 182. 1999, 1–19.

[10] Decree No. 453/2008 Coll., which stipulates the types, methods of utilization, and parameters of biomass for purposes of supporting the generation of electricity from biomass. (in Czech).

[11] Commission Regulation (EC) No 1774/2002 of the European Parliament and of the Council of 3 October 2002 laying down health rules concerning animal by-products not intended for human consumption.

[12] Decree No 341/2008 Coll., on details on biodegradable waste disposal. (in Czech)

[13] Regulation no. 271/2009 Coll., down requirements for fertilizers. (in Czech)

[14] Czech Office for Standards, Metrology and Testing. Landfill for hazardous waste ČSN 83 8035. Prague: Czech Office for Standards, Metrology and Testing.