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Biogas production on dairy farms: A Croatia case study

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Summary

In order to determine the differences in the production and composition of biogas as well as the quality of digested residue from anaerobic digestion of the raw materials generated by dairy farms in Croatia, investigations were undertaken in the biogas laboratory facility of the Faculty of Agriculture. The investigated raw materials were: dairy manure, corn silage, haylage and equal-measure mix (1/3) of all raw materials. For each substrate, three runs of experiments were performed with the same overall hydraulic retention time (40 days) and temperature of digestion (35 °C) in mesophilic conditions. The investigations found that the most efficient production of biogas was from corn silage. As for biogas composition, it was acceptable in all investigated samples both in energy and environmental terms. Digested residues, which are mildly alkaline, have low dry matter content. About 70 % of dry matter content is organic. On the basis of N:P:K analysis and the analysis of biogenic elements values and heavy metal values, it can be concluded that digested residues of all input raw materials can be used in agricultural production.

Key words: anaerobic digestion, dairy farms, biogas, digested residue

Introduction

In the EU countries thousands of anaerobic digestion-based biogas plants have been installed during the past two decades with the aim of biofuel production for cogeneration plants, i.e., electrical energy and heat generation in combined energy conversion processes. Out of total generated thermal and electrical energy, 10 to 30 percent is plant's own use i.e., this share of energy is used for the plant's operation and for meeting the energy needs of a farm where the plant is located. The remaining electrical energy is delivered to power distribution operators and heat is delivered to consumers in the vicinity of the farm (Krička at al., 2006; FNR, 2008; Comino et al., 2009). Biogas can be produced from a wide range of crops, organic wastes and from the most commonly used animal manure and, thus, it enables high flexibility and can be adapted to the special needs of different locations and farm management. On average, biogas consists of 55-80 % CH_4, 20-45 % CO_2 with trace amounts of H_2S and other impurities (Truong LVA, 2005), which makes it an acceptable fuel in energy and environmental terms. In the context of animal farming, as one of the most important activities within the agricultural sector, the dairy industry is recognized as a vast untapped source for thermal and electrical energy as well as the largest agricultural source of greenhouse gas (CH_4) emissions (Weiske et al., 2006). Anaerobic digestion (AD) of dairy manure holds promise as a means to simultaneously reduce greenhouse gas emissions and to produce energy and power while also remediating potential environmental concerns such as odour and air/water quality (Frear et al., 2011).

Animal farming is an activity which is present in the whole territory of Croatia, with cattle breeding as its most wide-spread branch. In 2010, there were 87 registered farmers keeping more than 100 cows, which makes 24875 livestock units overall. In terms of geographical distribution, the most of large farmers are located in the Osječko-baranjska County. It is important to emphasize that in Croatia there are

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44 560 registered dairy farmers, but 96 percent of these farmers keep less than 15 cows each, while the most of the family farms (90 %) keep less than 10 cows. Only 10 percent of the Croatian dairy farms keep more than 10 animals (HPA, 2010; Priručnik za bioplin (Biogas Manual), 2008). Given the described situation in the Croatian dairy farming sector it seems difficult to obtain a viable and cost-efficient biogas production in Croatia. However, taking into account the investigations performed by Kulišić and Par in 2008 and by Pukšec and Duić in 2010, a significant energy value of dairy manure can be identified when calculating the potentials of biogas production from this raw material in the Croatian regions. Moreover, according to Kulišić and Par (2008), the potential of national biogas production can be theoretically estimated at 0.7-2.1 PJ/year provided that there are sufficient quantities of this raw material available for biogas production in commercially oriented farms only.

Corn silage and haylage are raw materials indispensable in modern animal farming, especially in dairy production systems at cattle farms. However, these two raw materials are not only sources of high-quality animal feed but they can also be used as energy raw materials for biogas production. Thus, the addition of corn silage and haylage, as co-substrates in anaerobic digestion of dairy waste, could potentially help to overcome the problems of low content of solids and low biogas yield of dairy manure. The use of corn silage or haylage as rich organic co-substrates in anaerobic digestion has been tested for a number of waste streams such as organic solid wastes and concentrated animal manure (Arroquy et al., 2005; FNR, 2008). After anaerobic digestion, the digestate is a valuable fertilizer for agricultural crops. However, to guarantee the maximum recovery value of organic wastes, the residual product i.e., biogas residue should have a meaningful purpose and optimal benefits derived from its production. The application of residue as a fertilization agent that is recycled back to arable land ensures that crops receive the majority of the essential nutrients required for growth (Hill et al., 2001; Callaghan et al., 2002), i.e., that soil fertility is conserved (Boualllagui et al., 2003), and the soil structure and humus balance is improved (Basiliko and Yavitt, 2001), thus promoting a closure of the natural nutrient and energy cycles. As opposed to fertilization by means of non-digested organic substances in the agriculture, research has proved the digested fertilizers to have a more immediate effect, due to the fact that after the digestion process, the nutrients are already mineralized and plants can use them more effectively. Therefore, the use of biogas residue as an alternative should not only close the global nutrient cycle, but should also indirectly reduce greenhouse gas emissions to the atmosphere by decreasing needs for inorganic fertilizers and new landfill sites (Voća et al., 2005; Arthurson, 2009).

Therefore, this paper will investigate the production and composition of biogas from dairy manure, corn silage and haylage and from the mixture of these materials. It will also deal with the quality of digested residue as a biofertilizer produced from dairy manure in the anaerobic digestion process.

Material and methods

Laboratory investigations were carried out at the Faculty of Agriculture in Zagreb; the samples were taken from three dairy farms in the Osječko-baranjska County. In addition to manure, these farms use corn silage and haylage from their own animal feed production as input co-substrates for biogas production. The samples (packed in 10-L buckets) were transported immediately to the laboratory and stored in a refrigerator at approximately 4 °C. Before being put into the reactor, the corn silage and haylage material was cut into 2~3 cm pieces. Each reactor had a 3-liter capacity and contained 1800 mL of total liquid, including 600 mL of inoculum. Anaerobic digestion of dairy manure, corn silage and haylage and co-digestion of mixture of 1/3 of dairy manure, 1/3 of corn silage and 1/3 of haylage was conducted on laboratory scale, where active sludge from treated waste water in the Zagreb area was used as inoculum. For each substrate, three runs of experiments were performed with the same overall hydraulic retention time (40 days) and temperature of digestion (33 °C). The samples for analysis were taken immediately after the process of anaerobic digestion conducted on a laboratory scale. The biogas produced during anaerobic digestion of the investigated raw materials was collected in a graduated glass column (on a daily basis) and analyzed (at the end of the anaerobic digestion process) in a gas chromatograph equipped with a thermal conductivity detector (CP-3800) after calibration with a standard gas mix containing CO_2, H_2S and CH_4, which were the components detected in the biogas (HRN EN ISO 6974-4:2008). Furthermore, the chemical analysis of the digested residue was conducted by means of several different chemical procedures. pH was measured directly in the sample by a pH-meter with a combined electrode. Electrical conductivity (EC) was determined by use of a conductometer MA5964 with a combined electrode. Total nitrogen was measured according to Kjeldahl (Kjeltec system 1026 Distilling Unit); ammonia nitrogen (NH_3-N) was measured by means of Nesler reagent method according to Jackson (1958) spectrophotometrically at the wavelength of 436 mm. Phosphorus was measured by means of the molybdate-blue method on a UV/VIS spectrophotometer PU 8600, potassium and sodium were measured flame-photometrically, and all the other elements (Ca, Mg, Mn, Zn, Cu, Fe, Pb, Cd) were measured spectrometrically by use of atomic absorber (Jackson, 1958). Sample burning was carried out in a Milestone ETHOS D microwave oven (2001) according to the procedure "Milestone application notes for microwave digestion". The analysis of variance (ANOVA) and correlation analysis were performed by use of the SAS software package. The least significant differences (LSD) among mean values were calculated at $\alpha<0.05$ confidence level. A value of p less than or equal to 0.05 was considered to indicate statistically significant differences.

Results and discussion

After the preparation of the samples from the dairy farms, all four input raw materials surveyed in this paper, i.e., dairy manure, corn silage, grass clover mixture haylage, and a mix of these materials, underwent a series of suggested chemical and physical analyses. The values of cumulative production and composition of biogas obtained from the anaerobic digestion process are presented in Fig. 2 and Table 1.

During the first 4-5 days of the anaerobic digestion process, no biogas was produced. However, after the day five the production started to grow exponentially. Moreover, according to the obtained curves, this trend would have continued even after the forty-day digestion process. After this forty-day digestion process, corn silage proved to be the most appropriate raw material for biogas production, with cumulative production of more than 4500 mL/L. The lowest biogas potential was found to be that of dairy manure, measured at approximately 2800 mL/L of biogas. According to the investigations carried out by FNR 2008, Bruni et al., 2010, corn silage was also identified as the most acceptable raw material for biogas production. Also, a review of literature sources on biogas production from manure digestion, including dairy manure, confirmed that there was a very wide divergence in biogas production quantities, ranging from 380 to 3000 mL/L (Karim et al.,

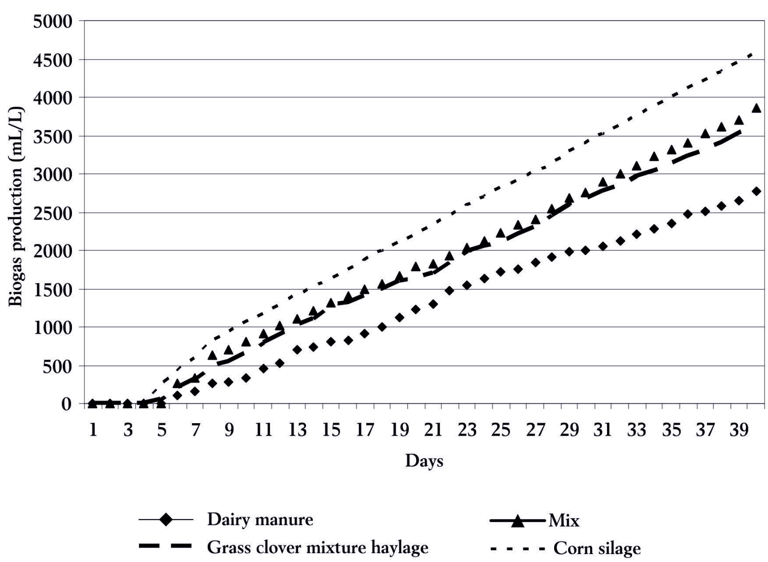

Figure 1. Cumulative biogas production from anaerobic digestion of investigated raw materials

Table 1. Biogas composition in the analyzed raw materials

Substrate	CH_4 (%)	CO_2 (%)	H_2S (ppm)
Dairy manure	52.47	49.08	1243
Haylage	54.45	45.04	1546
Silage	59.07	46.84	1785
Mix	55.98	48.57	1954

2005; Umetsu et al., 2006, Xiaojiao et al., 2012). Such wide divergences in biogas production could be interpreted as a result of acclimatization of microorganisms. Haylage and raw material mix give, in average, between 2100 and 5100 mL/L (Uzodimna and Ofoefule, 2009; Xiaojiao et al., 2012) and the analyzed productions of 3500 and 4000 mL/L of biogas fully comply with literature sources. Apart from production, it is important to analyze the composition of biogas (Table 1) in order to define the values of obtained biogas in energy and environmental terms. The two main components of biogas are CH_4 and CO_2, as products of the simple organic compounds conversion by methanogenic bacteria. An overview of literature data on biogas composition of the investigated raw materials enabled to establish the contents of NH_4 and CO_2 at 50-65 % and 38-48 % respectively (Kimberly, 2007; Herout et al., 2011). Comparison of the analyzed data with the literature showed slight discrepancies in concentration of CO_2 generated from dairy manure and from the raw material mix. In addition to CH_4 and CO_2, H_2S also represents a significant component of biogas, primarily because of its damaging environmental impact. However, found quantity of 1243-1954 ppm does not imply a significantly detrimental H_2S content in biogas. The analyzed values are fully in accordance with the literature data, which quote average H_2S values of 1114-2554 ppm (Kimberly, 2007; Herout et al., 2011).

When defining the quality of a biofertilizer, as a by-product of anaerobic digestion, it is necessary to carry out laboratory analyzes. Table 2 shows the obtained values of the investigated digested residues.

If achieve an optimal production of methanogenic bacteria and fast and efficient decomposition of digested material in to methane and carbon dioxide wants to be achieved, it is necessary to try to achieve a value of digested material as neutral as possible. However, according to Liu et al. (2008), an optimal pH ratio would be between 6.5 and 7.5. Since the investigations found digested residues' reactions to be in a range from mildly alkaline (materials mix, silage) to neutral (manure, haylage), it can be concluded that pH value is within the allowed limits. The aim of electrical conductivity (E.C.) determination of the digested residues is to identify total quantity of salt in the solution, because of possible consequences of soil salinization through fertilizers. In electrical conductivity determination, different types of conductometers were used, most of which represent a modified "Wheatstone's bridge" (Voća et al., 2005). The analyses discovered that dairy manure had higher E.C., which leads to conclusion that anaerobic digestion of dairy manure will give a biofertilizer of somewhat higher quality compared to other substrates. Al-Masri (2001) and Suárez Quiñones (2012) analyzed different digested residues and found that the E.C. values were in a range from 1.5 to 3.4 mS/cm. At the same time, Al-Masri (2001) stressed that E.C. decreased in relation to percentage of lingocellulose raw material in the digester. The same case is with the pH value, as it is corroborated by our investigations. High moisture content usually facilitates the anaerobic digestion. However, it is difficult to maintain the same availability of water throughout the digestion cycle (Hernandez-Berriel et al., 2008). It has been reported that the highest methane production rates occur at 60-80 % of humidity (Bouallagui et al., 2003). The analysis of the digested residues found similar moisture content values (97.92-99.34 %) in all of the investigated samples. Therefore, it can be concluded that the investigated substrates have increased moisture contents, but it did not affect the biogas production and its composition in any significant way. Also, the contents of organic and mineral matter in the investigated samples were determined by ash analysis. Uzodimna and Ofoefule (2009) and Chouchene (2012) state that the percentage

Table 2. The means of the chemical analyses results of the digested residue samples

	Dairy manure	Corn silage	Hay	Mixture	p value
pH directly	7,06a	4,51c	7,00a	5,03b	***
E.C. mS/cm	4,41a	3,32b	3,13b	3,12b	**
% dry matter (105 °C)	2,08a	1,91ab	0,66c	1,63b	***
% moisture	97,92a	98,09a	99,34a	98,37a	NS
% ash (550 °C)	14,75b	6,25d	25,00a	9,63c	***
% N - total/dry matter	0,62b	3,13a	3,84a	3,08a	***
% C organic	47,00ab	50,15a	42,00b	51,45a	**
C/N ratio	76a	16b	11c	17b	***
% P_2O_5 (d.m)	0,70c	0,95b	1,58a	0,91b	***
% K_2O	1,01b	1,15b	2,95a	1,01b	***
% Ca	0,60b	0,09d	2,28a	0,19c	***
% Mg	2,20a	0,47c	2,12a	0,88b	***
% Na	0,13b	0,08c	0,41a	0,10bc	***
mg/kg Zn	90,42a	30,96d	36,24c	43,11b	***
mg/kg Cu	20,12a	9,75c	15,43b	10,11c	***
mg/kg Fe	597,25a	520,07b	221,45d	350,97c	***
mg/kg Ni	4,13a	0,63c	0,95b	0,70c	***
mg/kg Mo	1,54a	1,14c	1,34b	1,47c	***
mg/kg Pb	0,82a	0,29b	0,11c	0,25b	***
mg/kg Cd	0,13a	0,05c	0,07bc	0,09b	*
mg/kg As			Below sensitivity		
mg/kg Hg			Below sensitivity		
mg/kg Co	0,03a	0,01a	0,01a	0,02a	NS

shares of ashes in different digested residues range from 6.25 to 25.00 percent, which fully corroborates the consistency of the conducted analyses. In order to determine if the samples of the investigated digested residues are suitable for use as fertilizers in agricultural production, the respective ratios between basic biogenic elements, nitrogen, phosphorous, and potassium have been calculated. The obtained results are as follows: in corn silage this ratio is 3.29:1:1.21; in dairy manure 0.88:1:1.44; in haylage 2.43:1:1.86; and in the mix of materials it is 3.38:1:1.10. For example, specific ratio of the nutrients in wheat is 1.2:1:1.5; in potato it is 1:1:1.8; while in grass this ratio is 2.4:1:1 (Kaltwasser, 1980). The mentioned ratios enable to conclude that digested residues can meet the plants' needs for all elements analyzed here. The other conclusion is that nitrogen content in corn silage, haylage and the mix is increased. In general, biofertilizers have a narrow C/N ratio, mainly from 10:1 to 15:1 (Voća et al., 2005). In the investigated raw materials obtained from digested residues, minor discrepancy of C/N ratio was found in corn silage and in the mixture, while in dairy manure this discrepancy was much larger (76:1). This can be explained by a significantly higher content of urea in the sample before anaerobic digestion. In investigations of the identical digested residue (dairy manure), Kavacik and Bahattin (2010) also determined an increased C/N ratio of 40:1. Furthermore, it is difficult to monitor the quantities of the most important biogenic elements in digested residues when establishing the possible qualities of the fertilizer as such. So, the analysis was made for quantities of calcium (0.09-2.28 %), magnesium (0.47-2.20 %) and sodium (0.08-0.41 %) in digested residues. On the basis of the obtained results, which are in accordance with the data determined by Jeyabal and Kuppuswamy (2001), it can be found that the values of biogenic elements in the investigated fertilizers are moderate and are suitable for application in the agricultural production as fertilizers. Also, in order to determine the degree of environmental acceptability of these fertilizers, the analyzed fertilizers were compared with the values set by the Ordinance on organic production of plants and plant products (Official Gazette 91/2001). The prescribed limit values of heavy metals are as follows: Cd 07 mg/kg; Hg 0.7 mg/kg; Pb 70 mg/kg; Mo 10 mg/kg; As 10 mg/kg; Co 50 mg/kg; Ni 42 mg/kg; Cu 70 mg/kg; Cr 70 mg/kg and Zn 210 mg/kg. As shown in Table 2, the determined quantities of the above mentioned heavy metals in all samples of digested residues were found in concentrations below the allowed limits and, as such, they meet the requirements set by the Croatian regulations and are suitable for application in crop production. According to the mentioned Ordinance the by-products of any production, such as digested residue - liquid litter in this case, can be applied on agricultural surfaces only under condition that they have been analyzed and properly monitored by experts. In addition to manure analysis, it is necessary to carry out an analysis of the soil in order to determine the quantities of liquid manure needed.

Conclusion

The conducted anaerobic digestion of the investigated samples was stable and, as a result, it produced biogas in satisfactory quantities and of satisfactory composition. The chemical analysis discovered a mild alkaline reaction in all investigated samples. Such reaction was presumably caused by increased concentrations of calcium. Thus, it can be concluded that pH is within the allowed limits. Low dry matter content was determined (except for household waste). Namely, water content in total mass was about 90 %. Out of total dry matter, about 70 % was organic matter, which resulted in high organic carbon content. By monitoring the major biogenic elements (Ca, Mg and Na) it could be determined that their concentrations in all investigated samples are moderate, and it should be emphasized that they are the highest in the sample obtained from household organic waste. The same applies to manganese content as well. The analysis of heavy metals (Zn, Cu, Fe, Pb, Cd) have brought to the conclusion that they are within the limits set under the Ordinance on organic production of crops and crop products in the Republic of Croatia (OG 91/2001). The heavy metal content is within the allowed limits in all investigated samples. Since such digested residue is used as fertilizer in organic agriculture, it can be determined that the found N:P:K ratio meets the requirements of such production methods. If the digested residues are used in crop production and grass cultivation, no additional residue processing is required.

Proizvodnja bioplina na mljekarskim farmama: primjer Hrvatska

Sažetak

S ciljem utvrđivanja razlika u produkciji i sastavu bioplina kao i kvaliteti fermentiranog ostatka nakon anaerobne fermentacije sirovina s farmi muznih krava u Hrvatskoj, provedena su istraživanja na bioplinskom laboratorijskom postrojenju na Agronomskom fakultetu. Sirovine u ovom istraživanju bile su goveđi gnoj, kukuruzna silaža, sjenaža i mješavina jednakih omjera (1/3) svih sirovina. Svaka istraživana sirovina analizirana je u tri ponavljanja, u jednakom vremenskom razdoblju (35 dana) i temperaturi fermentacije (35 °C), pri mezofilnim uvjetima. Provedenim istraživanjima utvrđeno je da se produkcija bioplina najbolje ostvarivala kod kukuruzne silaže, dok je njegov sastav, s energetsko-ekološkog stajališta, bio prihvatljiv u svim istraživanim uzorcima. Fermentirani ostatci, koji su blago alkalni, sadrže niske udjele suhe tvari od koje je približno 70 % organska tvar. Analizom N:P:K, vrijednostima biogenih elemenata i teških metala može se zaključiti da se fermentirani ostatci svih ulaznih sirovina mogu primijeniti u poljoprivrednoj proizvodnji.

Ključne riječi: anaerobna fermentacija, farme muznih krava, bioplin, fermentirani ostatak

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