Agronomy Research **16**(4), 1642–1648, 2018
https://doi.org/10.15159/AR.18.172

Suitability of Common nettle (*Urticadioica*) and Canadian goldenrod (*Solidagocanadensis*) for methane production

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Abstract. Support for biogas production in Latvia was decreased. There is an urgent need to investigate the suitability of various inexpensive renewable biomass resources for energy production. Also, itis necessary to explore the possibilities to improve the anaerobic fermentation process with the help of various catalysts. Biocatalyst Metaferm produced in Latvia was used in previous studies with other biomass and showed increase in biogas and methane production. The article shows the results of studies on biogas (methane) production from chopped fresh Common nettle (*Urtica dioica*) and Canadian goldenrod (*Solidago canadensis*) biomass and effect of catalyst Metaferm in anaerobic fermentation process. The anaerobic digestion process was performed in 0.75 L laboratory digesters, operated in batch mode (38 ± 1.0 °C, 35 days). The average specific biogas or methane production per unit of dry organic matter added (DOM) from Common nettle was 0.709 L g^{-1}_{DOM} or was 0.324 L g^{-1}_{DOM} respectively. Average specific biogas or methane volume produced from chopped Canadian goldenrod in anaerobic fermentation was 0.548 L g^{-1}_{DOM} or 0.267 L g^{-1}_{DOM} respectively. Average biogas or methane yield from digestion of chopped Common nettle with 1 mL Metaferm was 0.752 L g^{-1}_{DOM} or 0.328 L g^{-1}_{DOM} respectively. Average specific biogas or methane yield from anaerobic fermentation of chopped Canadian goldenrod with 1 mL Metaferm was 0.624 L g^{-1}_{DOM} or 0.276 L g^{-1}_{DOM} respectively. Adding of catalyst Metaferm increases methane yield from chopped nettle or Canadian goldenrod by 1.2% or 3.4% respectively. All investigated biomass resources can be used for methane production.

Key words: anaerobic digestion, biogas, Canadian goldenrod, methane, nettle.

INTRODUCTION

In recent years, several measures have been implemented in Latvia to reduce the support for biogas production, such as the introduction of a 9% profit margin, without taking into account large initial capital investments and high interest rates on bank loans. Raw material prices have also increased. The financial situation of the producers of biogas has deteriorated and some owners have already ceased operation of biogas plant. Therefore, the use of new, inexpensive raw biomass would be very important for them.

There are land areas in Latvia that are not well managed. Such areas were overgrown with wild plants, e.g. with Common nettle and, more recently, with Canadian goldenrod. Canadian Golden alpine or Canadian goldenrod (*Solidago canadensis*) is the species within *Curculidae* family that has a natural distribution area in North America, but now it is spread as invasive plant across Europe, including Latvia. In Latvia, this plant is spreading widely, forming dense groups in lawns, set-aside lands, along railways and roads. The Canadian goldenrod is a perennial herb with a height of 70–150 cm. A lot of leaves are located on the stem densely up to hop cones, which is quite dense with yellow flowers. The plant blooms from July to September (Klavins, 2018).

Common nettle or Stinging nettle (*Urtica dioica*) is a perennial Common nettle family herb (60–170 cm in height). This is one of the best–known herb within nettle's genus. The natural spread area is Europe, Asia, North Africa and North America. Common nettles, when in contact with humans or other animals, injects histamine and other chemicals into the skin, causing burning pain. The roots are long, yellowish. Leaves are ellipsoidal with linear bracts and are richly covered with pitchforks. The herb has lot of flowers that manifestly exceeds the length of the leaf stalk. The plant blooms from June to October (Klavins, 2018).

There is less literature data on the use of Common nettles for the production of biogas. Some (Statistics handbook Austria, 2005; Cropgen, 2011) show that nettles are a good raw material providing 120–420 m^3 t^{-1} per unit of dry organic matter or 605–3,780 m^3 ha^{-1} per year. Lehtomaki (2006) calculated that 3,000–5,000 m^3ha^{-1} of methane per year could be obtained from Common nettles or 30–50 MWh ha^{-1} energy per year. Other authors (Wellinger et al., 2013) have reported dry matter yield 6–10 t_{DM} ha^{-1}, methane 2,200–3,600 m^3 ha^{-1} per year, and energy 21–35 MWh ha^{-1} per year.

Information on use of Canadian goldenrod for biogas production also can be found in literature (Oleszek & Krzeminska, 2017).These authors analyse the suitability of common goldenrod plants as mono–substrates and co–substrates for biogas production. Furthermore, the role of bioactive compounds included in the biomass of this plant species was investigated. The results showed that the common goldenrod species produces lower biogas and methane yields than maize silage. The methane yield from Goldenrod was 127 L kg^{-1}_{DOM}, from maize silage 241 L kg^{-1}_{DOM} and from Goldenrod with maize silage 214L kg^{-1}_{DOM}. However, the anaerobic fermentation of Goldenrod and maize mixture(1:1) resulted in approximately 9.5% higher biogas yield and 16.6% higher methane yield compared to the theoretical yields estimated for two mono–substrates. A statistically significant increase in biogas production efficiency resulted from more favourable C : N ratio and by the influence of bioactive compounds contained in Canadian Goldenrod biomass. The addition of Goldenrod crude extract into maize silage caused 30% increase in the biogas yield approximately. This effect may be associated with a positive impact of biologically active substances on microorganisms or with a decrease in redox potential of the fermenting mass.

Several publications have documented the biogas yields from invasive varieties of *S. canadensis* and *S. gigantea* (Seppälä et al., 2013). These studies stated that these species are productive and cheap substrates that are worthy of interest. Generally, to achieve the highest profitability in biogas production, low–cost substrates with high methane potential are selected. Cultivated or wild perennials are increasingly considered for this purpose and can be an additional source of feedstock for biogas plants. Desirable features of wild perennials are high yield at low soil fertility requirements. To avoid competition with land for food and feed production, fallows for cultivation of perennials could be considered due to its large areas, which are estimated at 8.3 Mha (million hectare) in EU–15 by year 2030 (Seppälä et al., 2013). Such lands are overgrown mostly by invasive plants (such as goldenrods), which are characterised by great tolerance to habitat conditions. As stated by (Young et al., 2011), insufficient research has been conducted on existing (non-cultivated) bioenergy sources (such as invasive plant species) from non-crop agricultural land areas.

Metaferm, created and produced in Latvia is substance, which induce biological processes. Metaferm contain multi enzymes, microelements and B group vitamins as well growing stimulators. Our previous studies shows that use of catalyst Metaferm has a positive effect on methane yield in anaerobic fermentation process of some biomass (Dubrovskis & Plume, 2015).

The aim of this study is to evaluate the suitability of Canadian goldenrod and Common nettle as substrates for biogas production and clarify whether the addition of biocatalyst Metaferm (made in Latvia) in substrates leads to positive effect. Furthermore, the role of bioactive compounds included in this plant biomass should be clarified.

MATERIALS AND METHODS

The methodology described below and similar with German VDI 4630 guideline and the German Methodenhandbuch Energetische Biomassenutzung (Thran, 2010) were used for the present study.

Freshly (15.09.2017) picked from meadow near our laboratory samples of Common nettle and Canadian goldenrod (whole plants without roots) were finely (2–10 mm chunks) chopped and used for anaerobic fermentation experiments. Average samples were taken and it's the chemicals compositions were determined in the LUA laboratory according to the standardized methodology ISO 6496:1999. For each group of raw materials an average sample was taken and the total dry matter, organic dry matter and ashes content were measured.

The analysis were performed according to standard methods. Each group's raw material was thoroughly weighed carefully. All bioreactors (volume of 0.75 L) were filled with the same amount (500.0 g) of inoculums (digestate from a continuous working laboratory bioreactor with almost finished cows manure). Two bioreactors were filled with inoculums only as control. The others bioreactors were filled in with inoculums and biomass sample (20.0 g) with/without catalyst Metaferm (see Table 1).

Chopped Common nettles (20.0 g) (15% flowers, 56% leaves and 29% stalks) were filled in bioreactors R2-R5 (without Metaferm), and in bioreactors R6–R8 (with 1 mL Metaferm). Chopped Canadian goldenrods (20.0 g) (17% flowers, 64% leaves and 19% stalks) were filled in bioreactors R9–R11 (without Metaferm), and in bioreactors R12–R15 (with 1 mL Metaferm).

Bioreactors were filled with substrate and placed in a heated chamber (Memmert model). Gas from each bioreactor was directed into separate storage gas bag located outside the heated chamber.

Dry matter (TS) and organic dry matter (DOM) was determined by investigation of initial biomass sample weight and dry weight by using scales Shimazu at 105 °C and by investigation of ashes content help by furnace (Nabertherm model) burning the samples at 550 °C according to special heating cycle. All substrates were prepared, carefully mixed, and all sealed bioreactors were put in heated chamber in same time before anaerobic digestion. Composition of gases collected in storage bag was analysed with the gas analyser (GA 2000 model). The percentage of oxygen, carbon dioxide, methane and hydrogen sulphide were registered. Substrate pH value was measured before and after finishing of anaerobic fermentation process, using pH meter (PP–50 model) with accessories. Scales (Kern KFB 16KO2 model) was used for weighting of substrate before anaerobic processing and for weighting of digestate after finishing of fermentation process.

The accuracy of the measurements was ± 0.025 L for gas volume, ± 0.1 °C for temperature and ± 0.02 for pH. Methane (CH_4), carbon dioxide (CO), oxygen (O_2) and hydrogen sulphide (H_2S) content in biogas was measured periodically. Weights Kern FKB 16KO2 with accuracy ± 0.2 g was used for measurement of total weight of substrates, and the unit Shimazu with accuracy ± 0.001 g was used for weighting of biomass samples to obtain total solids and dry organic matter content.

Fermentation process was provided with single filling in batch mode until biogas emission ceases (35 days). Final digestate was weighed, and dry matter and ashes were investigated to determine organic dry matter content. Total biogas and methane production values were calculated using the biogas normal volumes and quality parameters obtained from gas collected in the gas storage bag for each bioreactor (Becker et al 2007).

Experimental data were recorded in the experimental log and also stored in computer.

RESULTS AND DISCUSSION

The data on sample analysis and on amount of biogas and methane produced was estimated for all 16 bioreactors, and average results were calculated.

The results of raw material analyses before anaerobic digestion are shown in Table 1.

Weight of raw material in Table 1 is provided with error value depending on accuracy of respective weight measuring instrument used. Weight of total solids (TS) and dry organic matter (DOM) in Table 1 is provided with accuracy ± 0.001 g.

Table 1. Results of analysis of raw materials

Bioreactor	Raw material	Weight g	pH	TS %	TS g	ASH %	DOM %	DOM g
R1; R16	IN	500 ± 0.2	7.69	2.01	10.050	19.61	80.39	8.079
R2–R5	CN	20 ± 0.001		21.81	4.362	20.83	79.17	3.453
R2–R5	IN+CN	520 ± 0.2	7.35	2.77	14.412	19.98	80.02	11.532
R6–R8	IN+CN+MF	521 ± 0.2	7.36	2.78	14.483	19.99	80.01	11.588
R9–R11	CG	20 ± 0.001		34.33	6.866	8.99	91.01	6.249
R9–R11	IN+CG	520 ± 0.2		3.20	16.916	13.77	86.23	14.328
R12–R15	IN+CG+MF	521 ± 0.2		3.20	16.682	13.79	86.21	14.382

Abbreviations: TS – total solids; ASH – ashes; DOM – dry organic matter; IN – inoculums; CN – Common nettle; CG – Canadian goldenrod; MF – Metaferm.

Both inoculum substrates in control bioreactors (R1, R16) have low dry matter content as almost finished digestate were used for inoculums.

As it can be seen from the raw material (Table 1) Canadian goldenrod biomass has a relatively high dry matter and organic dry matter content. This is explained due to the fact that the stems part of the plant was also used, and this part has less moisture content compared to the fresh leaves or flowers. The Common nettle biomass had higher moisture content, because their stem contains more juice. The natural proportions (by the weight) of the three main components of the plant – stem, leaves and flowers – were observed during filling in each bioreactor.

This raw material, containing a lot of organic dry matter and also juice, is well suited for biogas production. Biogas and methane yields from Common nettle and Canadian goldenrod are shown in Table 2.

Table 2. Biogas and methane yields from Common nettle and Canadian goldenrod

Reactor	Raw material	Biogas, L	Biogas, L g^{-1}_{DOM}	Methane, aver. %	Methane, L	Methane, L g^{-1}_{DOM}
R1	IN500	0.00	0.00	0.00	0.00	0.00
R16	IN500	0.20	0.025	8,00	0.016	0.020
R2	IN500+CN20	2.50	0.724	37.71	0.943	0.273
R3	IN500+CN20	2.20	0.637	50.23	1.105	0.320
R4	IN500+CN20	2.40	0.695	48.06	1.154	0.334
R5	IN500+CN20	2.70	0.781	47.38	1.277	0.370
	Aver. R2–R4	**2.45**	**0.709**	**45.85**	**1.120**	**0.324**
	± st.dev.	**± 0.21**	**± 0.06**	**± 5.56**	**± 0.14**	**± 0.04**
R6	IN500+CN20+MF1	2.50	0.724	45.02	1.124	0.326
R7	IN500+CN20+MF1	2.60	0.752	43.75	1.137	0.329
R8	IN500+CN20+MF1	2.70	0.781	42.13	1.137	0.329
	Aver. R5–R8	**2.60**	**0.75**	**43.60**	**1.133**	**0.328**
	± st.dev.	**± 0.10**	**± 0.03**	**± 1.45**	**± 0.01**	**± 0.01**
R9	IN500+CG20	4.20	0.672	44.79	1.882	0.301
R10	IN500+CG20	3.40	0.544	42.83	1.461	0.233
R11	IN500+CG20	3.30	0.528	49.62	1.636	0.262
R12	IN500+CG20	2.80	0.448	60.94	1.708	0.273
	Aver. R9–R11	**3.43**	**0.548**	**49.55**	**1.67**	**0.267**
	± st.dev.	**± 0.58**	**± 0.09**	**± 8.11**	**± 0.17**	**± 0.03**
R13	IN500+CG20+MF1	3.90	0.62	42.79	1.670	0.267
R14	IN500+CG20+MF1	3.80	0.608	47.04	1.789	0.286
R15	IN500+CG20+MF1	4.00	0.640	42.81	1.71	0.274
	Aver. R12–R15	**3.90**	**0.624**	**44.21**	**1.723**	**0.276**
	± st.dev.	**± 0.10**	**± 0.02**	**± 2.45**	**± 0.06**	**± 0.01**

Note: Biogas and methane values for bioreactors 2–15 with fresh source biomass are provided with already subtracted average biogas and methane values obtained from reactors 1 and 16.

Abbreviation: L g^{-1}_{DOM} – litres per 1 g dry organic matter added (added fresh organic matter into inoculum).

Usually, pre-shredding of raw material significantly increases methane yields. This could be explained by the fact that the raw materials studied were better distributed by the anaerobic digestion process because the microbial access to the raw material was better. Compared to literature (Lehtomaki, 2006), the methane yield from Common nettles is medium (Table 2).

Methane production from the Canadian goldenrod was much higher, compared to results reported by Polish researchers (Oleszek & Krzeminska, 2017). This is explained by fact that Polish researchers used silage from Canadian goldenrod.

Specific biogas and methane gases volumes obtained from bioreactors R2–R15 are presented in Fig. 1.

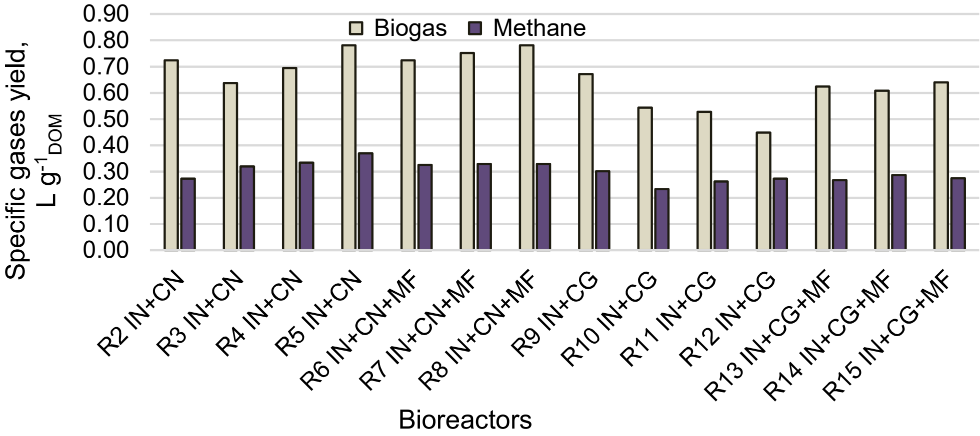

Figure 1. Specific biogas and methane yields from bioreactors filled with Common nettles and Canadian goldenrods.

The figure shows the best methane yield from bioreactor R5. It can be explained with better microbes association in used inoculum filled in this bioreactor.

Average methane volumes and methane percentage in biogas for groups of bioreactors with Common nettle and Canadian goldenrod biomass are shown in Fig. 2.

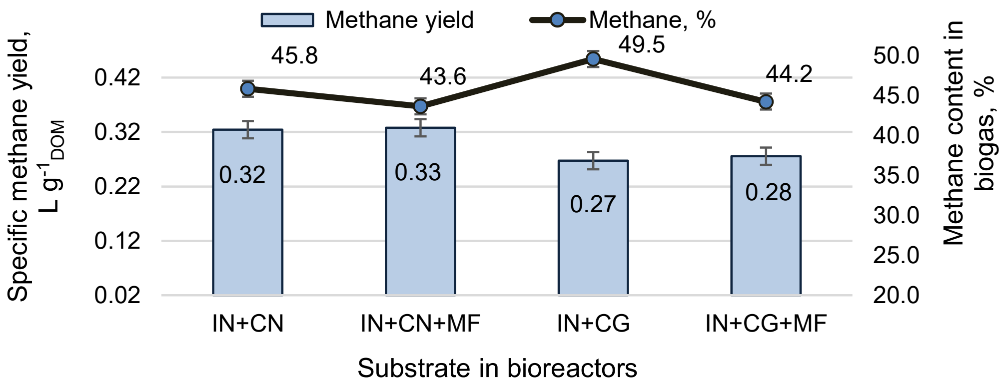

Figure 2. Average specific methane yields and methane percentage for groups of bioreactors with Common nettle and Canadian goldenrod substrates without and with added Metaferm.

Fig. 2 shows the average methane content in biogas from Common nettle biomass in biogas was 45.8% and the average methane content in biogas from Canadian goldenrod was 49.5%. These are lower methane contents compare with often used in biogas plants raw materials (for example maize silage).These contents are higher for both plants, if used Metaferm. It can be explained by the fact that there used fresh raw materials.

The total methane yield from Common nettle with Metaferm was higher by 1.2% compared to Common nettle substrate without Metaferm. A slight increase could be explained by the fact that there are already enough bioactive substances in the substrate without Metaferm. Adding of 1 mL catalyst Metaferm to substrate with Canadian goldenrod increased methane yield by 3.4%.

CONCLUSIONS

The average specific methane yield from Common nettle biomass substrate was 0.324 L g^{-1}_{DOM}. The result is good, similar that obtainable from maize silage. It convinces that fresh Common nettle can substitute maize silage for some month's period in summer. The average specific methane yield from Canadian goldenrod biomass was 0.267 L g^{-1}_{DOM}, which is better than from manure, but expectations in improving of high methane production were not met.

The addition of Metaferm increased the specific methane yield slightly. Using this biocatalyst for Common nettle and Canadian goldenrod fresh biomass cannot be economically. Such level of increased methane yield in Latvian conditions do not justify the application costs of Metaferm.

The results of the study show that nettle and Canadian goldenrod can be used as raw materials for the production of methane.

In future studies, it would be desirable to clarify the effect of different pre-treatment (treatment with acids, bases, chrushing degree) methods on the anaerobic fermentation of investigated biomass.

ACKNOWLEDGEMENTS. This work has been supported by the Latvian National Research Programme LATENERGI.

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