PRODUCTION OF BIOGAS FROM GRASS AT VARIOUS PRE-TREATMENT AND ANAEROBIC FERMENTATION TEMPERATURES UNDER INFLUENCE OF MAGNETIC FIELD

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Abstract. Biogas production from agricultural biomass is declining in Latvia, as stricter regulations propose restriction of using energy crops, e.g. maize silage, by 2030. An alternative to energy crops can be grass overgrowth biomass from abandoned areas, municipal or domestic green areas and protected areas such as roadsides, areas under power lines and others. The biomass of grass contains lot of lignocellulose, which slowly decomposes during the anaerobic fermentation (AF) process. The aim of the study was to investigate the influence of pretreatment of grass by freeze-thawing cycle at a low temperature -15 ºC or -23 ºC on methane yield. Also, influence of various mesophilic temperatures 25; 33 and 38 ºC on production of biomethane was investigated during the AF process. Some bioreactors (volume 0.75 L) with grass biomass were added magnetic powder (MP) and/or fitted with a pair of magnets for providing of weak magnetic field (WMF). Results of the experimental setup 1 shows the increase in specific methane 68 or 75% if the grass biomass is pretreated at -15 ºC and -23 ºC in double freeze-thawing cycle. The highest specific methane yield 0.313 $L \cdot g_{VS}^{-1}$ was observed from grass biomass pretreated at -23 ºC, that was 100% higher compared to control. Results of setup 2 show high specific methane 0.202 $L \cdot g_{VS}^{-1}$ from the group of bioreactors with added MP 1.0 g, moderate methane yield 0.188 $L \cdot g_{VS}^{-1}$ under influence of WMF 3.6 µF and the highest methane yield 0.234 $L \cdot g_{VS}^{-1}$ from combined application of MP 2.0 and WMF 3.6 µF which 24%, 15% and 44% respectively, compared to control (grass without MP addition and WMF application).

Keywords: anaerobic fermentation; pretreatment, magnetic powder, magnetic field.

Introduction

Production of biogas in anaerobic fermentation (AF) is considered as an advanced method for utilizing of biomass residues in an environmentally friendly way for energy and fertiliser production. Since 2017, the number of biogas plants in Latvia has decreased due to reduced state support for the purchase of electricity produced by biogas CHP plants, as well as due to restrictions on the use of energy crops for biogas production. There is an urgent need to find alternative sources of biomass to replace energy crops, such as maize, in biogas plants with locally available biomass. An alternative can be grass biomass, which is available from uncultivated agricultural areas, various hedgerows, from strips under power lines, along roads, parks, yards, lawns, and other areas.

Grass biomass is widely used to produce biogas. However, the potential for methane production is relatively low compared to energy crops. The specific methane potential of switchgrass harvested in winter is 140 $mL \cdot g^{-1}$ or switchgrass harvested in summer is 205 $mL \cdot g^{-1}$ that is by 53% or 31% lower respectively compared to methane potential of maize silage [1].

Biodegradability and biomethane potential (BMP) may be lowered by the high content of cellulose, hemicellulose, and lignin in grass biomass. It is investigated that the content of cellulose, hemicellulose and lignin in switchgrass grown without nitrogen biofertilizer and harvested in two cuts was 32.3% cellulose, 31.4% hemicellulose and 4.2% lignin. Dry matter yield of unfertilised switchgrass was 9.5 $t \cdot ha^{-1}$ in 2012 [2].

To increase biogas production and decrease hydraulic retention time (HRC) of grasses in the biodegradation process, different biomass pretreatment methods are developed including chemical (acid or alkali chemicals) or physical (e.g. thermal, ultrasound, microwave) or their combination. Experimental investigation of milled grass sample (0.425–0.850 mm) shows increase of Soluble Chemical Oxygen Demand and Soluble Carbohydrate contents by 98.6% and 236.9% respectively, after dilute acid pretreatment combined with ultrasound treatment. The hydrogen yield reached 42.2 $mL \cdot g^{-1}$ dry grass after the combined treatment, that was 311.7%, and 35.0% and 190.0% higher compared to the control, individual acid, and ultrasound pretreated groups, respectively [3].

Pretreatment of grass waste using combined ionizing radiation- acid treatment for enhancing fermentative hydrogen production resulted in hydrogen yield 68 $mL \cdot g^{-1}$ grass, which was by 161.5%, 112.5% and 28.3% higher than those for the control, ionizing radiation pretreated and acid pretreated groups, respectively. SCOD and soluble polysaccharide contents of grass waste increased by 1.6 and

2.91 times after the combined pretreatment, respectively. The volatile solid (VS) removal increased from 13.9% to 25.6% by the combined pretreatment [4].

Comparison of reduction of lignin and hemicellulose contents after pre-treatment with acid and alkali chemicals was provided for grass lawn (GL) biomass. The experimental results obtained showed that the treatment with acids led to higher hemicellulose solubilization, while lignin removal from the solid matrix was achieved using the treatment with NaOH. The highest methane yields 427.07 $L \cdot kg_{VS}^{-1}$ or by 25.7% higher compared to untreated GL was observed from grass lawn biomass pretreated with alkaline at the highest NaOH concentration (20 g per 100 g total solids). Thermal treatment of GL at 80 or 120 ºC gives methane yield 340.72 or 383.7 $L \cdot kg_{VS}^{-1}$ respectively, which was by 0.8% or 13.5% higher compared to untreated GL [5].

Pretreatment methods above require high consumption of materials and energy. Freeze-thawing of lignocellulosic biomass may be more cost effective compared to thermal pretreatment. Study [6] has shown that natural freeze-thawing (NFT) of maize stover for 21 days with solid:liquid ratio of 1:6 gives the best methane yields of 253 $mL \cdot g_{VS}^{-1}$ and VS reduction of 58.6%, which are 40.5% and 27.4% higher than untreated maize stalks, respectively.

Freezing-thawing pretreatment was used also on wheat straw, and the freezing time was studied in terms of methane production [7]. Three kinetic models were used to predict the efficiency of anaerobic digestion. Modified Gompertz model and the logistic function model are satisfactory and have high R^2 values. The logistic function model has the best fit with the result with a lower RMSE value. All three kinetic models show that pretreatment using freezing-thawing shortens the start-up time of anaerobic fermentation. However, there is no significant increase found in total methane production from wheat straw using freezing-thawing pretreatment.

The use of permanent magnetic fields can be considered as a particularly low-energy method, both for the pre-treatment of lignocellulosic biomass or for improving the fermentation process itself. Treatment of a single extruded wheat straw substrate (8.4 mm length of particles) with a 1.8 mT permanent magnetic field increases the biogas yield, providing the same amount of biogas as a five-fold extrusion, but with 4.28 times less energy consumption and a 5.5% increase in the biomethane yield compared to the control [8].

Increase in biogas and methane production during anaerobic digestion (AD) also was observed during application of magnetic nanoparticles directly in the post-digestate [9]. Biochemical methane potential (BMP) tests were performed on the municipal WWTP post-digestate with four different magnetic nanoparticles in 1 L bioreactors during a 30-day period at 40 ºC. The highest biogas yield (400 mL per day) and methane yield (100% CH4) was attained with 2 g magnetic nanoparticles composed of Fe_2O_4-TiO_2 as compared to the biogas production (350 mL/day) and methane yield (65% CH_4) in the control.

Effects of different magnetic factors such as the effect of the static magnetic field, magnetic nanoparticles or combined use of the magnetic field and magnetic nanoparticles were investigated for anaerobic digestion of municipal dewatered sludge [10]. Methane yield from application of the magnetic field, magnetic nanoparticles or combined use of the magnetic field and magnetic nanoparticles was higher by 48.0%, 96.2% or 98.8% compared to control (sludge) respectively.

Similar effect was observed in the swine manure-fed digester supplemented with micron-sized zero valent iron (ZVI) under influence of a weak magnetic field (WMF) [11]. Treatments that included ZVI only or combined use of WMF with ZVI increased the CH_4 production by 77.0 or 124.5%, respectively.

The purpose of this study is to investigate the effect of freeze-thawing pre-treatment of grass biomass in combination with the application of a weak magnetic field during the anaerobic digestion (AD) process at different mesophilic temperatures and the effect of addition of magnetic powder in substrate on biogas and methane production.

Materials and methods

The grass biomass for the study was collected in a household during lawn mowing in August 2023. After collecting, grass samples were divided in 3 parts, and stored in a freezer at temperatures + 1 ºC, -15 ºC and -23 ºC. Before the anaerobic digestion experiment, the frozen herbal biomass was subjected to a double freeze-thaw procedure with a freezing period not less than 24 h. Grass samples stored at + 1 ºC were used as controls for the freezing effect study.

Permanent magnets were used on opposite sides of each glass bioreactor. The magnetic field was applied by placing a magnet on opposite sides of each bioreactor with the north pole (N) facing the south pole (S) of the magnet on the opposite side of the reactor. Increase of the magnetic field was provided by use of two or three pairs of permanents magnets. The study was carried out in two configurations.

Experimental setup 1 consisted of 3 groups of reactors in which the biogas and methane yields were determined depending on the grass biomass fermentation temperature (25 ºC, 33 ºC and 38 ºC). Each of 3 groups consist of 6 subgroups including one subgroup with inoculums (500 g), one subgroup with inoculums and grass biomass addition stored at temperature + 1 ºC, two subgroups with inoculums and grass biomass addition stored at temperature -15 ºC or -25 ºC and subjected to a freeze-thaw cycle pre-treatment, and two subgroups with inoculums and grass biomass exposed to a permanent magnetic field, Table 1.

Table 1

Setup 1 of bioreactors for investigating the grass at different fermentation temperatures

Reactor No	Components, g	TF, ºC	TPR, ºC	WMF, µF
R1, R16	IN500	25	+20	0
R2-R4	IN500 + G25	25	+1.0	0
R5-R7	IN500 + G25	25	-23	0
R8-R10	IN500 + G25	25	-15	0
R11-R12	IN500 + G25 + WMF0.8	25	+1.0	0.8
R13-R14	IN500 + G25 + WMF1.6	25	-23	1.6
R21-R36	IN500	38	+20	0
R22-R24	IN500 + G2	38	+1.0	0
R25-R27	IN500 + G20	38	-23	0
R28-R30	IN500 + G20	38	-15	0
R31-R32	IN500 + G20 + WMF0.8	38	+1.0	0.8
R33-R34	IN500 + G20 + WMF1.6	38	-23	1.6
R41, R56	IN500	33	+20	0
R42-R45	IN500 + G20	33	-23	0
R46-R47	IN500 + G20 + WMF0.8	33	+1.0	0.8
R48-R49	IN500 + G20 + WMF1.6	33	-23	1.6
R50-R51	IN500 + G20	33	-15	0
R53-R55	IN500 + G20	33	+1.0	0

Abbreviations: TF – temperature of the anaerobic fermentation process; TPR – pretreatment (freezing) temperature or temperature of storage of grass biomass before the fermentation process; WMF – weak magnetic field; IN – inoculums; G – grass biomass.

All reactors were fermented in batch mode at constant temperatures (Table 1) during a 30-day period until release of biogas ceases.

Experimental setup 2 consisted of 2 bioreactors filled with 500 g of inoculum (IN – fermented cow manure) and 20 bioreactors filled with 500 g IN and 15 g of grass (G) biomass composed of 7.5 g of grass biomass with a storage temperature + 1 ºC and 7.5 g of grass biomass with a storage (freezing) temperature of -15 ºC. The group of bioreactors with IN500 + G15 was divided in 10 subgroups including one subgroup without addition of magnetic powder (MP) and without influence of weak magnetic field (WMF), 3 subgroups with MP (0.5, 1.0 or 2.0 g), 3 subgroups with application of constant WMF (1.2, 2.4 or 3.6 µF) and 3 subgroups with combined MP (0.5, 1.0 or 2.0 g) addition and WMF (1.2, 2.4 or 3.6 µF) application. Configuration of pairs of permanent magnets for both experimental setups is shown in Fig. 1.

Magnetic field inductance was measured in the central part of the bioreactors using the electromagnetic radiation tester EMF01 (±0.01 µF).

Before anaerobic fermentation, inoculums and grass biomass were analysed for the total solid (TS) content in automated (drying-weighting) unit MOC-120H, accuracy ± 0.001 g in the standard cycle at 120 ºC.

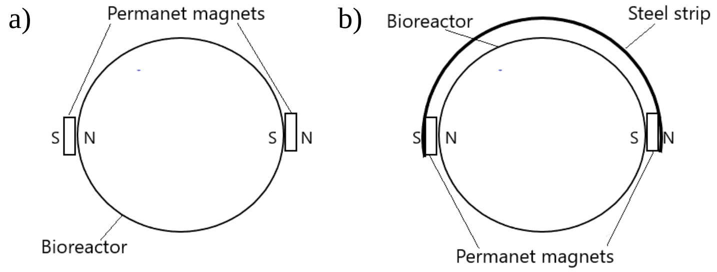

Fig. 1. **Magnet configuration in experimental setups of bioreactors:** a – setup 1; b – setup 2

Volatile solid content (VS) was determined by aching of dried samples in the oven (model Memmert) at 550 ºC using the standard aching cycle. Standard mathematical operations were used for calculation of the sample TS and VS content.

The material of added magnetic powder in bioreactors was carbon steel powder with the size of particles < 0.05 mm. Magnetic field source – permanent magnets, arranged in pairs, used magnetic flux densities are shown above (Table 1).

The specific gas (biogas, methane, hydrogen, etc.) volume produced per 1 g of the added biomass calculates as follows [12]:

$$V_{GA} = \frac{V_{GS} - V_{GIN}}{M_{VSA}}, \tag{1}$$

where V_{GA} – specific volume of gases produced per 1 g volatile solids (VS) of added biomass, $L \cdot g_{VS}^{-1}$;
V_{GS} – volume of gases produced from VS of substrate in the anaerobic fermentation (AF) process, L;
V_{GIN} – volume of gases produced from VS of inoculum in the AF process, L;
M_{VSA} – mass of volatile solids (VS) in added biomass, $L \cdot kg_{VS}^{-1}$.

Gas sampling bags (Tedlar type) positioned outside the thermostats containing bioreactors were used for gas collection. Gas volume was measured by a flow meter (Ritter drum-type) and gas composition was analysed bya gas analyser (model Gasboard 3200L, accuracy ± 1.0%).

Substrate pH value was measured in the bioreactor before and after the AF process, using the pH meter (model HI 8424, accuracy ± 0.01).

All reactors were fermented in batch mode at constant temperature 38 ºC during a 30-day period until production of biogas ceases. Specific biogas and methane volumes were measured by help of gas bags and a gas flowmeter. Gas volumes from the added biomass obtained in the AF process were calculated for every reactor according to equation (1).

In both experimental setups, every group has 2-3 bioreactors, and the average value and standard deviation of the measurement results were calculated using standard statistical tools.

Results and discussion

Analyses of grass biomass before the AF process were following – total solid (TS) content: 24.1%; volatile solids (VS): 18.8%; ash: 5.24%.

Average specific methane volumes calculated for subgroups of bioreactors with grass biomass in the first experimental setup 1 are shown in Fig. 2.

Pretreatment of grass biomass using the freezing-thawing cycle or under a weak magnetic field results in increase of the specific methane yield in all bioreactors compared to control (grass without pretreatment in the freeze-thawing cycle and without the influence of the magnetic field). The high specific methane yield 0.286 or 0.274 $L \cdot g_{VS}^{-1}$ was observed at the AF process temperature 38 ºC during the fermentation of grass biomass pretreated in a double freeze-thaw cycle at -23 ºC or -15 ºC that was higher by 75% or 68% respectively, compared to grass without free-thawing pretreatment. The highest specific methane yield 0.313 L·g_{VS}^{-1} was observed at the AF process temperature 38 ºC under the influence of the magnetic field 1.6 µF that was higher by 100%, compared to control.

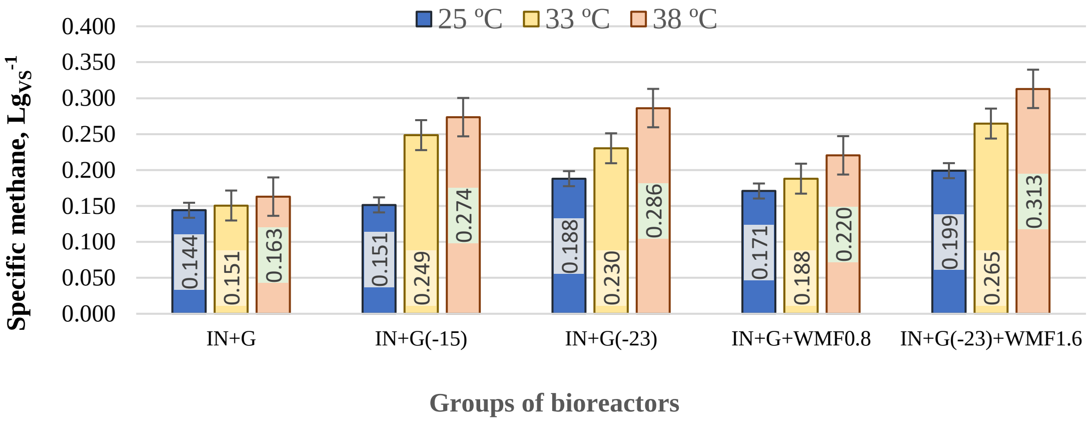

Fig. 2. **Specific methane output in dependence on pretreatment and AF temperatures:**
IN – inoculums; G(-15) – grass biomass with pretreatment at -15 ºC;
WMF1.0 – weak magnetic field 1.0 µF

Average specific methane volumes and methane content in biogas for groups of bioreactors in the experimental **setup 2** are shown in Fig. 3.

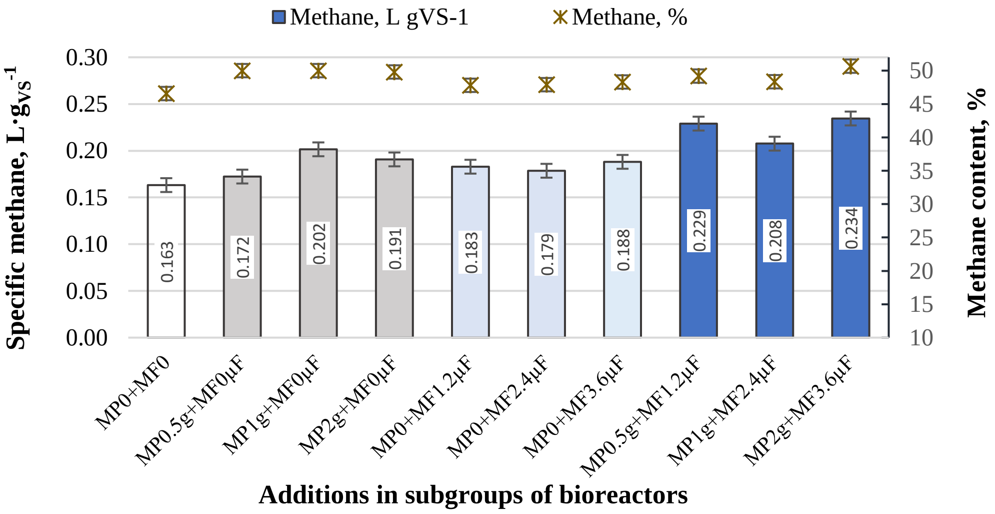

Fig. 3. **Effect of addition of magnetic powder and magnetic field on specific methane yield:**
MP0.5g – magnetic powder 0.5 g; WMF1.2 – weak magnetic field 1.2 µF

All bioreactors with added magnetic powder (MP), applied weak magnetic field (WMF) or combination of both increase the biogas and methane output. Among the subgroups of bioreactors with added magnetic powder, the highest specific methane yield of 0.202 L·g_{VS}^{-1} was observed with MP 1.0 g, an increase of 24% compared to the control. Of the bioreactor groups with applied magnetic field, the highest specific methane yield was 0.188 L·g_{VS}^{-1} at WMF 3.6 µF, an increase of 15% compared to the control. The highest methane yield 0.234 L·g_{VS}^{-1} was observed from the group of bioreactors with combined application of MP 2.0 and WMF 3.6 µF, which is 44% higher compared to control (grass without addition of MP and without application of WMF).

Conclusions

1. Pretreatment of grass biomass at the temperature -15 ºC or -23 ºC results in increase of the specific methane yields in all bioreactors, with the highest yield 0.286 L·g_{VS}^{-1} for pretreatment at -23 ºC (75% increase).

2. Combined pretreatment at the temperature -23 ºC with applied weak magnetic field (WMF) 1.6 µF results in 0.313 $L \cdot g_{VS}^{-1}$ or 100% higher compared to control.
3. In the experimental setup 2 (with a closed magnetic circuit), addition of magnetic powder (MP) in grass substrate increases the specific methane yield in all bioreactors, with the highest average yield 0.202 $L \cdot g_{VS}^{-1}$ with addition of 1.0 g MP, which is 24% above control, but application of a WMF 3.6 µF increases the specific biomethane yield to 0.188 $L \cdot g_{VS}^{-1}$ which is 15% above control).
4. The highest average specific methane yield in the experimental setup 2 was observed from the group of bioreactors with combined application of MP 2.0 with WMF 3.6 µF, which is higher by 24% compared to control (grass without MP or WMF application).

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Author contributions

Conceptualization, I.P. and E.A; methodology, I.P. and E.A., software, L.P., validation, L.P; investigation, E.A. and L.P., data curation, E.A. and L.P., writing – original draft preparation, I.P and E.A., writing – review and editing, I.P and V.D; visualiWzation, L.P., financial management, V.D. All authors have read and agreed to the published version of the manuscript.

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