Determination of the Efficiency and Kinetics of Biogas Production from Energy Crops through Nitrogen Fertilization Levels and Cutting Frequency

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The efficiency and kinetics of methane fermentation were evaluated for six energy crops when cultivated at three different nitrogen (N) fertilization levels, specifically, maize, sorghum, sunflower, triticale, reed canary grass (RCG), and Virginia mallow (VM). In the case of the perennials, RCG and VM, the impacts of individual swath and cutting frequency were examined. A new model for predicting the methane yield based on the substrate chemical composition was developed and validated. A raised N fertilization dose increased the biogas, methane yield, and the specific rate of their production. The highest increase in methane yield was observed in VM from 145 to 197 dm^3 kg^{-1} of volatile solids (VS) due to a 15% rise in biodegradability. This resulted from a decrease in the lignin content and favorable changes in the lignin to structural carbohydrates ratio. Moreover, in the case of perennials, more efficient biogas production was observed for the biomass collected at an earlier stage. The results in this investigation are important for the production of high-quality biomass for biogas plants, without competition for arable land areas with food and feed production.

Keywords: Methane fermentation kinetics; Nitrogen fertilization level; Reed canary grass; Virginia mallow; Biochemical Methane Potential (BMP) model

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INTRODUCTION

Energy crops have become the most relevant type of substrate for biogas production, due to their high methane yield, constant availability, and the possibility of easy storage in the form of silage. Furthermore, biomass of energy crops is homogenous and generally free from pathogens. Additionally, ensiled plant biomass does not undergo seasonal changes, in contrast to some kinds of waste (Drosg *et al.* 2013). This applies especially to maize (*Zea mays* L.), which is currently the most important substrate for biogas production in Central Europe (Herrmann 2013). However, its high proportion in biogas crop rotation systems (over 45%) carries a potential risk for negative environmental impacts (soil erosion, loss of biodiversity, and leaching of nitrate) as well as a low aesthetic value (Svoboda *et al.* 2013; Von Cossel *et al.* 2017). The diversity of biogas crop rotation systems is recommended to mitigate these negative impacts (Von Cossel *et al.* 2017). It is commonly understood that the cultivation of energy crops should not compete with arable land areas for food and feed production (Oleszek and Matyka 2017). Therefore, the achievement of a high biomass yield and simultaneously maintaining its good quality is a challenge today (Krzemińska and Oleszek 2016). High nitrogen (N) fertilization is frequently applied to elevate the yield of plants because this element is essential for proper plant development and growth. Wu *et al.* (1993) indicates that nitrogen is the most significant nutrient in increasing plant height. Moreover, nitrogen is an important part of chlorophyll, which is a molecule that absorbs solar energy for photosynthesis (Kaplan *et al.* 2016).

The issue of N fertilization has been explored in studies on biogas production, but mainly in the aspect of increasing biomass yield, and thus, biogas and energy productivity per unit area. Effect of N fertilizer doses on the chemical composition of energy crops, which could affect biogas production, appears to be neglected (Oleszek and Matyka 2017). There have been few studies on the influence of N fertilization levels on the efficiency of the methane fermentation process when it is used in the cultivation of energy crops as later substrates. Von Cossel *et al.* (2017) studied the effect of increased N fertilization levels on the methane fermentation of amaranth, and they did not state any significant influence on the specific methane yield and content of important biomass components such as lignin, nitrogen, and ash. In contrast, Kaplan *et al.* (2016) investigated the impact of three different nitrogen levels on the quality of maize as a feed for livestock, its digestibility, and its gas production during fermentation with rumen fluid. The results of the study showed that a raised N fertilization level increased the cobs/stems ratio and decreased the neutral detergent fiber (NDF) and acid detergent fiber (ADF) content in biomass. These chemical changes caused the increase in gas production and maize digestibility. Other reports on this issue are often divergent, and they do not explain the reasons for the recorded effects. One of the reports indicate that a decrease in the biogas yield from the silage of meadow plants is caused by raised nitrogen levels, which causes an increase in crude protein (CP) (Gröblinghoff and Lütke Entrup 2006). In contrast, Kacprzak *et al.* (2012) observed a decline in the specific biogas yield from reed canary grass (RCG) after the application of N fertilization at a dose of 120 kg ha^{-1}, compared to the lower doses of 40 and 80 kg ha^{-1}. The authors suggest that this finding is potentially caused by an increase in the lignin content. Massé *et al.* (2011) also notes a decrease in the specific biogas yield from RCG with an increase in nitrogen levels from 40 to 160 kg N ha^{-1}. As a potential reason of this phenomenon, Massé *et al.* (2011) states that the increase in proteins and lignin is caused by high nitrogen dose applications. The content of the mentioned components was not investigated in these papers. Additionally, these assumptions were contrary to the results of Kaplan *et al.* (2016) and Oleszek and Matyka (2017), who report a decline in the fiber fractions and lignin content caused by the highest nitrogen level application.

The dependence of biogas yield on the chemical components has been the subject of many studies. Many models have been developed that predict the methane yield using the chemical properties of feedstock. In many cases, lignin is considered the main inhibitor of methane production (Triolo *et al.* 2011; Dandikas *et al.* 2014; Thomsen *et al.* 2014). A negative correlation with biogas yield was also found for ash and proteins (Goliński and Jokś 2007). Nonetheless, there is no universal model for all of the substrates (Tsavkelova and Netrusov 2012).

In this study it was hypothesized that the N fertilization level and cutting frequency will significantly affect the methane fermentation efficiency and kinetics due to their influence on the chemical composition of the tested crops. Therefore, the goal of this study was to evaluate the impact of the N fertilization level of six energy crops: maize, sorghum, sunflower, triticale, reed canary grass (RCG), and Virginia mallow (VM), on the specific biogas and methane yield as well as on the kinetics parameters. In the case of RCG and VM, the impact of the individual swath and cutting frequency were also tested.

EXPERIMENTAL

Materials and Methods

Field experiments

Field experiments on this subject matter are described in detail by Oleszek and Matyka (2017). The tested plants were cultivated at the Experimental Station of Institute of Soil Science and Plant Cultivation in Osiny, Poland (N: 51 27´, E: 21 39´) and Jelcz-Laskowice, Poland (N: 51 2´ E: 17 21´) starting in 2012 through 2014 in a randomized complete block design (a "split-plot" system) with four replicates. Three doses of N fertilization in the form of ammonium nitrate, which is the fastest-acting form of nitrogen, were applied: 40, 80, and 160 kg N ha^{-1} in the case of sunflower (*Helianthus annuus* L. var. Kornelka), triticale (*x Triticosecale* Wittm. ex A. Camus. var. Leontino), reed canary grass (RCG) (*Phalaris arundinacea* L. var. Bamse), and Virginia mallow (VM) (*Sida hermaphrodita* L.); and doses of 80, 120, and 160 kg N ha^{-1} in the case of maize (*Zea Mays* L. var. Ułan) and sorghum (*Sorghum bicolor* L. var. Rona 1). The VM was harvested twice in a two-cut system (VM II C), and RCG was harvested twice and thrice in a two-cut (RCG II C) and a three-cut (RCG III C) system, and the differences between swaths were determined. After harvest, the plant material was combined, fragmented, and ensiled in plastic barrels with a volume of 5 L, and stored in the dark until their later use. Ensiling was conducted at ambient temperature for at least two months to ensure proper material preservation. To evaluate the effectiveness of ensiling, value of pH was determined. The sample of silage was blended with water in the proportion of 1:1 and filtered after 2 h. Subsequently, the pH was measured by CyberScan 6000 Series Meters (Eutech Instruments Pte Ltd, Singapore).

Methane fermentation

Methane fermentation was conducted according to the VDI 4630 (2006) protocol. Post fermentation sludge from a mesophilic, agricultural biogas plant that utilized maize silage, beet pulp, and whey was used as the inoculum. The inoculum was characterized by total solid (TS) content of 3.0%, a volatile solid (VS) content of 66.5% TS, and a pH of 7.5. The process parameters were as follows: temperature 37 °C, pH of approximately 7, total solids (TS) concentration of 40 g L^{-1}, substrate to inoculum ratio (S/I) of 1:1 (based on the VS), and a working volume of 0.8 L. The fermenters' content was mixed once a day, and the biogas volume and methane concentration were determined according to the method described by Oleszek *et al.* 2016. The fermentation was finished when the daily biogas volume was lower than 1% of the total biogas volume (total fermentation time (t_t)). The batch assays were performed in triplicate for each tested silage and the inoculum as a control. Next, the biogas yield of tested samples was corrected by subtraction of inoculum biogas yield.

Based on the chemical composition of the biomass investigated previously (Oleszek and Matyka 2017), the theoretical methane yield (TMY) and biodegradability (BD) were calculated as in Chen *et al*. (2014), examples of which are shown in Eqs. 1 and 2,

$$\text{TMY (dm}^3\text{ kg}^{-1}\text{ VS)} = 415 \times \text{CL} + 424 \times \text{HCL} + 727 \times \text{ADL} + 496 \times \text{CP} + 1014 \times \text{CF} + 415 \times \text{NFC} \quad (1)$$

$$\text{BD (\%)} = \text{EMY}/\text{TMY} \quad (2)$$

where EY is the empirical methane yield ($dm^3\ kg^{-1}$ VS), TMY is the theoretical methane yield ($dm^3\ kg^{-1}$ VS), CL is the cellulose (% TS), HCL is the hemicelluloses (% TS), ADL is the acid detergent lignin (% TS), CP is the crude protein (% TS), CF is the crude fat (% TS), NFC is the non-fiber carbohydrates (% TS), and BD is the biodegradability (%).

Statistical analysis

Statistical analysis was performed in STATISTICA 12 software (Stat Soft Inc., Tulsa, OK, USA). For all of the tested parameters, the mean and standard error (SE) from the three replications were determined. Both Shapiro-Wilk and Lillefors tests were used to evaluate the normality of the data, while Levene's test confirmed the equality of the variances. The significance of the differences between the tested energy crops and swaths within the same N fertilization level, as well as between the particular N fertilization level within one energy crop species and swath, were evaluated by a one-way analysis of variance (ANOVA) and Tukey's post hoc test. For determining the significance of the differences between all of the tested samples, the two-way ANOVA and the Tukey's post hoc test were applied.

The kinetic parameters, such as the length of the lag phase (λ), the specific biogas production rate (μ_m), and the theoretical maximum biogas yield after time t_t (A), were determined using non-linear estimation and the Gompertz equation, as shown in Eq. 3,

$$y = A\, exp\left\{-exp\left[\frac{\mu_m e}{A}(\lambda - t) + 1\right]\right\} \tag{3}$$

where y is the experimental biogas yield after time t ($dm^3\ kg^{-1}$ VS), A is the theoretical maximum biogas yield after time t_t ($dm^3\ kg^{-1}$ VS), λ is the length of the lag phase (d), μ_m is the specific biogas production rate ($dm^3\ kg^{-1}$ VS d^{-1}), t is the time (d), and e is the Euler constant = 2.71. The sample size was different for individual crops and depended on total time of the methane fermentation process (number of days multiplied by three replicates of batch test for each sample).

To explain the influence of the N fertilization level and swath on the efficiency and kinetics of the methane fermentation process, the correlation coefficients (R) between the biogas yield, methane yield, methane content or particular kinetics parameters, and all of the chemical properties were determined. Next, simple linear regression and successive stepwise regression analyses were performed with statistically significant variables. The relative root mean square error (RRMSE), the square of the sample determination coefficient (R^2), and the p value were used to assess the accuracy of the model.

The best model was validated based on the results previously presented by Oslaj *et al.* (2010), Menardo *et al.* (2012), Mahmood and Honermeier (2012), and Li *et al.* (2013), using scatter plots of the experimental methane yield (EMY) *versus* the predicted methane yield (PMY).

RESULTS

The results showed that both the N fertilization level and cutting frequency significantly determined methane fermentation efficiency and kinetics ($p < 0.05$). The species of energy crops had the highest impact on specific methane yield and kinetic parameters, which was reflected in the greatest F values from ANOVA (Tables 1 and 3).

Table 1. Biogas Yield, Methane Yield, Methane Content, and Biodegradability Depended on the Species and Nitrogen Fertilization Level

	EBY* (dm^3 kg^{-1} VS)	EMY (dm^3 kg^{-1} VS)	CH_4 in biogas (%)	TMY (dm^3 kg^{-1} VS)	BD (%)
Species					
Maize	471 ± 14 d**	272 ± 7 c	58 ± 1 d	437 ± 1 c	62.2 ± 1.5 b
Sunflower	334 ± 11 bc	160 ± 5 b	48 ± 1 a	484 ± 4 a	33.0 ± 0.7 e
Sorghum	562 ± 14 e	310 ± 7 d	55 ± 1 c	448 ± 1 b	69.2 ± 1.6 a
Triticale	262 ± 14 a	129 ± 5 a	49 ± 1 a	428 ± 1 d	30.2 ± 1.2 e
RCG II C	342 ± 8 bc	167 ± 4 b	49 ± 1 a	427 ± 2 d	39.2 ± 1.1 d
RCG III C	359 ± 8 c	176 ± 4 b	49 ± 0 a	426 ± 1 d	48.2 ± 1.6 c
VM	315 ± 18 b	165 ± 9 b	53 ± 1 b	345 ± 2 e	39.7 ± 2.6 d
p value	0.0000	0.0000	0.0000	0.0000	0.0000
F	132.15	203.12	57.55	2000.00	169.42
N Fertilization Level					
N I	352 ± 23 a	187 ± 15 a	53 ± 1 b	425 ± 8 b	43.5 ± 3.3 a
N II	371 ± 22 a	193 ± 13 a	51 ± 1 a	429 ± 9 a	45.1 ± 3.0 b
N III	410 ± 22 b	211 ± 14 b	50 ± 1 a	429 ± 9 a	49.3 ± 3.2 b
p value	0.0000	0.0000	0.0000	0.0002	0.0000
F	26.12	15.88	13.81	10.87	15.89
Species × N Fertilization Level					
Maize					
N I	470 ± 14 ab	275 ± 13 ab	59 ± 2 a	441 ± 0	62.5 ± 2.9
N II	429 ± 14 a	251 ± 6 a	58 ± 1 a	432 ± 1	58.1 ± 1.4
N III	514 ± 2 b	289 ± 4 b	56 ± 1 a	438 ± 0	65.9 ± 1.0
Sunflower					
N I	293 ± 6 a	143 ± 3 a	49 ± 0 b	470 ± 2	30.5 ± 0.6
N II	342 ± 7 b	171 ± 5 b	50 ± 0 b	491 ± 1	34.8 ± 1.0
N III	367 ± 2 b	166 ± 1 b	45 ± 0 a	490 ± 0	33.8 ± 0.2
Sorghum					
N I	528 ± 22 a	301 ± 10 a	56 ± 1 a	445 ± 1	67.6 ± 2.3
N II	565 ± 27 a	306 ± 14 a	54 ± 0 a	449 ± 1	68.0 ± 3.0
N III	592 ± 10 a	323 ± 14 a	55 ± 1 a	449 ± 1	72.1 ± 3.0
Triticale					
N I	242 ± 18 a	121 ± 14 a	53 ± 1 b	430 ± 3	28.1 ± 3.3
N II	251 ± 10 a	129 ± 3 a	48 ± 1 a	424 ± 1	30.4 ± 0.7
N III	292 ± 37 a	138 ± 8 a	45 ± 1 a	430 ± 2	32.1 ± 1.7
Reed Canary Grass II C					
N I	329 ± 11 a	164 ± 10 a	50 ± 1 a	429 ± 2	38.2 ± 2.2
N II	344 ± 17 a	165 ± 7 a	48 ± 0 a	431 ± 2	38.5 ± 1.8
N III	352 ± 17 a	173 ± 7 a	49 ± 1 a	422 ± 3	41.0 ± 1.8
Reed Canary Grass III C					
N I	332 ± 7 a	160 ± 1 a	48 ± 1 a	429 ± 2	43.6 ± 1.8
N II	369 ± 7 b	179 ± 3 a	49 ± 0 a	427 ± 1	50.7 ± 3.0
N III	376 ± 4 b	187 ± 2 a	50 ± 0 a	427 ± 1	50.2 ± 1.8
Virginia Mallow					
N I	267 ± 9 a	145 ± 3 a	54 ± 1 b	340 ± 4	34.3 ± 1.1
N II	298 ± 11 a	153 ± 6 a	51 ± 1 a	351 ± 1	35.0 ± 1.1
N III	380 ± 20 b	197 ± 12 b	52 ± 1 ab	245 ± 2	49.7 ± 1.4
p value	0.0543	0.0463	0.0001	0.0000	0.0082
F	1.96	2.02	4.47	13.11	2.72

*EBY - experimental biogas yield, EMY - experimental methane yield, TMY - theoretical methane yield, BD - biodegradability, RCG IIC, RCG IIIC - reed canary grass harvested in the two- or three-cut system, VM - Virginia mallow. **Means ± SE (n = 3) with different letters in the column differ significantly in Tukey test at $p<0.05$

Influence of the Nitrogen Fertilization Level on Biogas Production

The N fertilization positively influenced the biomass biodegradability, as well as the biogas and methane yield, wherein statistically significant differences were observed only after the highest N level application (Table 1). Despite the lack of statistically significant interactions between the N level and species ($p > 0.05$), the results of the post hoc test indicated that the influence of the N fertilization on the biogas yield was different for the same species of energy crop than for the other species.

In the case of sunflower and RCG IIIC, a significant increase in the biogas yield was observed at a moderate N level. The differences between the N level for sorghum, triticale, and RCG IIC were not statistically confirmed. In terms of maize, a significant difference was only observed between the medium and the highest N fertilization doses. Analogous relationships were observed for the methane yield.

The rise in the N fertilization level caused a general decrease in the methane content in the biogas for all the tested energy crops. However, the influence varied depending on the species of the plants (a significant interaction of the species × N level, $p > 0.05$). The results of the Tukey post hoc test confirmed the significant decrease in methane content in the biogas only for sunflower and triticale, and showed the lack of a clear trend for VM.

Influence of the Energy Crops Species on Biogas Production

Among all the tested crops, the highest biogas yield was exhibited by sorghum, but only for the medium N level was it significantly higher than that of maize (Table 1). The average biogas yield was observed with RCG, sunflower, and VM, while the lowest biogas yield was observed with triticale. The methane yield was less varied then the biogas yield. The highest value was noted for sorghum, which was slightly lower for maize, while the lowest was noted for triticale. There were no significant differences between sunflower, VM, RCG IIC, and RCG IIIC.

Significant differences between species occurred in terms of the methane content in the biogas. The majority of the methane was contained in biogas from the maize silage, and the least was in biogas from sunflower, triticale, RCG IIC, and RCG IIIC.

Influence of the Swath and Cut System on Biogas Production

Among all of the swaths of RCG, the highest biogas and methane yield was noted for the silage of the second swath of the three-cut system (II/III), and then for the silage of the first swath common in the two- and three-cut systems (I/II/III) (Table 2). A much lower biogas and methane yield was obtained from methane fermentation of the biomass collected in October (third swath of the three-cut system (III/III) and the second swath of the two-cut system II/II).

In the case of VM, higher biogas and methane production was observed from biomass collected at an earlier harvest date (I/II) than at the latest date (II/II). The lowest methane content in the biogas was noted during fermentation of the first swath (I/II), for both RCG and VM. This parameter increased along with the next swath, although for VM, it was not statistically significant. A two-way analysis of variance indicated a lack of interaction between the swath and N fertilization levels in the case of biogas and methane yield, for both RCG and VM. Nevertheless, the post hoc tests that were conducted separately for the swaths indicated that a statistically significant increase in the biogas and methane yield caused by N fertilization occurred only in the case of III/III of RCG and II/II of VM. For these silages, a significant influence of the N level on the CH_4 content was also demonstrated.

Table 2. Biogas Yield, Methane Yield, Methane Content, and Biodegradability Depending on the Nitrogen Level and Swath in the Case of RCG and VM

	EBY* (dm^3 kg^{-1} VS)	EMY (dm^3 kg^{-1} VS)	CH$_4$ in biogas (%)	TMY (dm^3 kg^{-1} VS)	BD (%)
RCG – Swath					
I/II/III	385 ± 7 c**	182 ± 3 c	48 ± 0 a	425 ± 1 c	42.9 ± 0.9 b
II/III	451 ± 14 d	224 ± 6 d	50 ± 0 ab	419 ± 2 b	53.4 ± 1.5 c
III/III	241 ± 14 a	121 ± 7 a	50 ± 1 ab	265 ± 4 a	45.5 ± 2.6 b
II/II	299 ± 14 b	152 ± 7 b	51 ± 1 b	429 ± 3 d	35.5 ± 1.6 a
p value	0.0000	0.0000	0.0156	0.0000	0.0000
F	73.90	74.70	4.23	2815.10	30.22
RCG - N Fertilization Level					
N I	320 ± 27 a	158 ± 12 a	50 ± 1 a	381 ± 23 a	41.3 ± 1.8 a
N II	355 ± 29 b	173 ± 14 ab	49 ± 0 a	390 ± 20 b	44.3 ± 2.7 b
N III	356 ± 22 b	179 ± 10 b	50 ± 1 a	383 ± 21 a	47.4 ± 2.4 c
p value	0.0176	0.0000	0.1866	0.0001	0.0041
F	4.80	5.92	1.80	13.60	6.96
RCG – Swath × N Fertilization Level					
I/II/III × N I	373 ± 6	176 ± 5	48 ± 2	425 ± 3	41.5 ± 1.1
I/II/III × N II	375 ± 11	178 ± 5	48 ± 0	426 ± 2	41.7 ± 1.2
I/II/III × N III	406 ± 5	193 ± 3	48 ± 0	425 ± 4	45.5 ± 1.0
II/III × N I	426 ± 12	206 ± 3	48 ± 1	415 ± 4	49.6 ± 0.8
II/III × N II	487 ± 32	240 ± 14	49 ± 0	421 ± 0	57.1 ± 3.3
II/III × N III	441 ± 5	225 ± 1	51 ± 1	421 ± 1	53.4 ± 0.3
III/III × N I	197 ± 8	98 ± 5	50 ± 0	252 ± 5	39.0 ± 1.1
III/III × N II	246 ± 21	120 ± 9	49 ± 1	278 ± 1	43.3 ± 3.3
III/III × N III	279 ± 6	144 ± 6	51 ± 1	265 ± 3	54.3 ± 2.8
II/II × N I	285 ± 26	151 ± 15	53 ± 1	433 ± 1	34.9 ± 3.5
II/II × N II	314 ± 25	153 ± 10	49 ± 1	435 ± 2	35.2 ± 2.4
II/II × N III	297 ± 32	153 ± 14	52 ± 4	420 ± 2	36.4 ± 3.4
p value	0.2134	0.1221	0.4930	0.0000	0.0368
F	1.52	1.90	0.93	8.20	2.73
VM – Swath					
I/II	357 ± 16 b	186 ± 9 b	52 ± 1 a	432 ± 1 b	43.0 ± 2.0
II/II	273 ± 28 a	144 ± 14 a	53 ± 2 a	426 ± 1 a	33.8 ± 3.3
p value	0.0018	0.0022	0.1986	0.0013	0.0034
F	16.01	15.03	1.85	17.5	13.27
VM - N Fertilization Level					
N I	267 ± 30 a	145 ± 11 a	55 ± 2 b	431 ± 2 a	33.6 ± 2.6
N II	298 ± 33 a	153 ± 19 a	51 ± 1 a	428 ± 2 a	35.6 ± 4.3
N III	380 ± 17 b	198 ± 10 b	52 ± 1 a	429 ± 2 a	46.1 ± 2.3
p value	0.0024	0.0036	0.0029	0.1826	0.0033
F	10.41	9.34	9.89	2.0	9.58
VM – Swath × Nitrogen Fertilization Level					
I/II × N I	318 ± 34	163 ± 13	52 ± 1	434 ± 2	37.6 ± 2.9
I/II × N II	365 ± 14	192 ± 11	52 ± 1	432 ± 1	44.3 ± 2.7
I/II × N III	388 ± 25	203 ± 14	52 ± 1	432 ± 2	47.1 ± 3.2
II/II × N I	215 ± 25	126 ± 12	59 ± 1	429 ± 3	29.5 ± 3.0
II/II × N II	230 ± 25	113 ± 11	49 ± 1	423 ± 1	26.8 ± 2.8
II/II × N III	373 ± 28	192 ± 17	51 ± 1	426 ± 1	45.2 ± 3.8
p value	0.0898	0.0723	0.0007	0.4323	0.0744
F	2.97	3.30	14.36	0.9	3.25

*EBY, EMY, TMY , BD, RCG, VM – see Table 1; I/II/III - first swath common for two- and three-cut system, I/II - first swath in two-cut system, II/II - second swath in two-cut system, II/III - second swath in three-cut system, III/III - third swath in three-cut system. ** See Table 1.

Swath III/III of RCG was characterized by an increase in CH_4 content, while swath II/II of VM was characterized by a decrease in CH_4 content as a result of the increased doses of N fertilizer.

The Kinetics of the Methane Fermentation Process

The results of methane fermentation assays indicated that the N level, the species of the energy crops, and the swath influenced the kinetics of the process. These relationships involved the total fermentation time t_t and the kinetics parameters, described by the Gompertz equation (Eq. 3), such as length of the lag phase (λ), specific biogas production rate (μ_m), and theoretical maximum biogas yield after t_t time (A).

A high correlation coefficient (in the range of 0.946 to 0.999) of the theoretical cumulative biogas yield after t time (y) and the experimental cumulative biogas yield testified to a good fit of the model. Furthermore, the value of the parameter A was close to the biogas yield obtained experimentally in methane fermentation assays (EBY) (Table 3).

The influence of the nitrogen fertilization level on the kinetics of methane fermentation

The N fertilization level significantly influenced only the theoretical maximum biogas yield after time t_t (A) and the specific biogas production rate (μ_m) for all of the tested energy crops ($p < 0.05$; Table 3). Application of the highest N fertilization dose caused a slight but statistically significant increase in the parameter μ_m. This result confirmed the positive impact of the N fertilization on the biomass decomposition in the methane fermentation process. Nitrogen fertilization did not significantly influence the length of the lag phase (λ) ($p > 0.05$). The exceptions were sunflower and VM, for which slight prolongation and shortening of the lag phase (λ) occurred, respectively. The total fermentation time (t_t) was extended by one day, as a result of the application of the highest level of N fertilizer, but it was not a statistically significant change. This dependence was specific to the plant species. For sunflower and RCG, a significant increase in t_t was observed, while for triticale there was a decrease with increasing doses of N. No significant differences were noted for maize, VM, or sorghum (Table 3).

The influence of the energy crop species on the kinetics of methane fermentation

The kinetics of methane fermentation were influenced by the energy crop species. The highest values of A were obtained for sorghum and maize, respectively. A substantially lower value for parameter A was noted for the other silages, between which there were no statistically significant differences within any N level (Table 3).

Additionally, the examined species differed in terms of the parameters of λ and μ_m ($p < 0.05$). The greatest μ_m was determined for maize, and was slightly lower for sorghum. The lowest biogas production rate was noted for triticale and RCG IIC because of the long total fermentation time t_t and the relatively low biogas yield. This finding demonstrates the weak digestibility of these silages.

The influence of the swath and cut-system on the kinetics of methane fermentation

Particular swaths of RCG differed significantly in terms of the values of the kinetics parameters ($p < 0.05$, Table 4). The highest maximum biogas production after t_t (A) was noted for II/III, as shown in Table 4. The kinetics parameters A, μ_m, λ, and the total fermentation time t_t, depended on the N fertilization level and swath in the case of reed canary grass and Virginia mallow, while they were the lowest for III/III. The lowest μ_m was observed in the case of II/II and III/III, and the highest was observed for II/III.

Table 3. Kinetics Parameters A, μ_m, λ, and Total Fermentation Time t_t, Depending on the Nitrogen Fertilization Level and Species

	A* (dm^3 kg^{-1} VS)	μ_m (dm^3 kg^{-1} VS d^{-1})	λ (d)	t_t (d)
Species				
Maize	475 ± 16 b**	31.0 ± 0.8 e	2.5 ± 0.2 b	28 ± 0 a
Sunflower	332 ± 13 a	14.0 ± 0.3 c	0.4 ± 0.2 a	39 ± 1 b
Sorghum	573 ± 11 c	22.3 ± 1.0 d	2.4 ± 0.3 b	43 ± 2 c
Triticale	321 ± 5 a	7.9 ± 0.8 a	3.9 ± 0.8 b	45 ± 1 c
RCG II C	339 ± 9 a	11.6 ± 0.4 b	0.4 ± 0.2 a	55 ± 1 d
RCG III C	358 ± 8 a	14.7 ± 0.6 c	2.6 ± 0.3 b	44 ± 1 c
VM	356 ± 19 a	12.5 ± 1.1 bc	2.4 ± 0.4 b	41 ± 0 b
p value	0.0000	0.0000	0.0000	0.0000
F	81.71	139.37	11.42	205.02
N Fertilization Level				
N I	363 ± 22 a	15.6 ± 1.9 a	1.7 ± 0.8 a	42 ± 2 a
N II	392 ± 19 b	15.9 ± 1.6 a	2.2 ± 0.3 a	42 ± 2 a
N III	425 ± 21 c	17.4 ± 1.7 b	2.4 ± 0.5 a	43 ± 3 a
p value	0.0000	0.0163	0.1028	0.0515
F	20.89	22.01	2.40	2.03
Species × N Fertilization Level				
Maize				
N I	474 ± 22 ab	31.5 ± 1.3 a	2.7 ± 0.3 a	29 ± 1 a
N II	428 ± 14 a	29.1 ± 1.6 a	2.2 ± 0.3a	30 ± 2 a
N III	523 ± 1 b	32.4 ± 1.1 a	2.6 ± 0.3 a	28 ± 1 a
Sunflower				
N I	282 ± 5 a	14.6 ± 0.6 a	0.0 ± 0.0 a	36 ± 3 a
N II	351 ± 6 b	14.0 ± 0.4 a	0.9 ± 0.2 b	36 ± 2 a
N III	363 ± 4 b	13.4 ± 0.2 a	0.3 ± 0.2 ab	44 ± 3 b
Sorghum				
N I	546 ± 21 a	20.3 ± 1.1 a	1.7 ± 0.2 a	44 ± 1 a
N II	569 ± 16 a	22.8 ± 3.1 ab	2.4 ± 1.0 a	43 ± 1 a
N III	603 ± 6 a	24.0 ± 1.0 b	3.0 ± 0.1 a	43 ± 1 a
Triticale				
N I	282 ± 14 a	6.4 ± 0.4 a	2.0 ± 1.0 a	49 ± 0 b
N II	323 ± 15 a	7.5 ± 0.2 a	4.0 ± 0.2 a	43 ± 1 a
N III	358 ± 46 a	10.0 ± 1.8 b	5.8 ± 2.2 a	42 ± 1 a
RCG II C				
N I	324 ± 11 a	12.2 ± 0.6 b	0.1 ± 0.0 a	53 ± 2 a
N II	343 ± 20 a	10.5 ± 0.4 a	0.3 ± 0.3 a	57 ± 3 ab
N III	349 ± 19 a	12.2 ± 0.8 b	1.0 ± 0.5 a	54 ± 3 b
RCG III C				
N I	333 ± 5 a	14.4 ± 0.2 a	2.5 ± 0.8 a	43 ± 1 a
N II	362 ± 17 a	15.7 ± 1.5 a	2.4 ± 0.5 a	44 ± 2 b
N III	378 ± 6 a	14.0 ± 1.0 a	3.0 ± 0.3 a	46 ± 2 b
VM				
N I	297 ± 3 a	10.1 ± 1.0 a	2.8 ± 0.3 b	41 ± 1 a
N II	370 ± 37 ab	11.5 ± 1.4 ab	3.3 ± 0.2 b	41 ± 1 a
N III	401 ± 17 b	16.0 ± 1.3 b	1.0 ± 0.5 a	42 ± 1 a
p value	0.1200	0.0513	0.0395	0.0000
F	1.63	1.98	2.09	14.52

*A is the maximal biogas production after t_t, t_t is the total fermentation time, μ_m is the specific biogas production rate, λ is the length of the lag phase, RCG IIC, RCG IIIC is the reed canary grass harvested in the two- and three-cut system, respectively, and VM is Virginia mallow. ** See Table 1.

The findings shown in Table 4 demonstrate a much better digestibility of the silage by the II/III swath in comparison with silages from biomass collected at a later date. The swath of II/III and III/III was characterized by the longest λ and simultaneously the shortest t_t. The longest t_t of 61 days was noted for the II/II swath (Table 4). Nitrogen fertilization did not influence the parameters A, μ_m, and λ of the methane fermentation of RCG, and only t_t slightly extended with increasing doses of N fertilizer.

Both swaths of VM differed significantly in terms of μ_m and λ (Table 4). A higher A and a longer t_t value were noted for the swath of I/II. An increasing N fertilization level resulted in an increase in A and t_t only in the case of II/II. With the increase in the N fertilization, the μ_m parameter also increased, although the differences were not statistically significant for individual swaths ($p > 0.05$), but only for the average of the two swaths. There were no statistically significant differences between the levels of N fertilization in the case of the λ parameter.

Correlation and Regression Analysis

Based on the results of a previous study of Oleszek and Matyka (2017) on the chemical composition of the tested crops, correlation and regression analyses were performed. The analysis of the correlation coefficients showed that non-fiber carbohydrates (NFC), the ratio of the sum of hemicelluloses and cellulose to lignin ((HCL + CL)/ADL), the volatile solids (VS), and the C/N ratio most strongly positively influenced the biogas production (Table 5). The strongest negative correlation with the biogas yield was stated for lignin (ADL), crude ash (CA), total nitrogen (N_{tot}), crude proteins (CP), and pH. A slightly weaker but also statistically significant correlation was noted for organic carbon (C_{org}) and HCL ($p < 0.05$, Table 5). There was no significant correlation with crude fat (CF) and cellulose (CL) ($p < 0.05$). Analogous results were obtained for the methane yield and parameter A because of its strong internal correlation with the biogas yield.

The methane content in biogas was directly proportional with the NFC, VS, and C/N ratio, and was inversely proportional with CP, CF, and pH. There were no significant correlations ($p > 0.05$) between the methane content and ADL, C_{org}, or HCL. The specific biogas production rate (μ_m) was negatively correlated with the ADL, CP, and pH. A positive correlation was stated between μ_m and VS, C_{org}, NFC, C/N, and the (HCL + CL)/ADL ratio.

Most of the tested chemical properties did not have a significant effect on λ and t_t ($p > 0.05$). The length of the lag phase (λ) was reduced by increases in TS, VS, C_{org}, and CF. The total fermentation time (t_t) was extended with a rise in the pH, TS, HCL, and ADL. An increase in the NFC and (HCL + CL)/ADL ratio caused the shortening of t_t.

Additionally, the dependence of the methane yield on the chemical composition of the tested energy crops was described by regression models. The regression linear trend of EMY *versus* particular variables is presented in Table 6.

Concerning the single variables, the most statistically significant model of methane yield was obtained using NFC and C/N ($p < 0.05$). Unfortunately, the model accuracy was relatively weak (RRMSE of 25.93 and 28.95, respectively). The multiple models with few independent variables proved to be better for the prediction of methane yield than the single models. The best parameters for the evaluation of the linear regression were obtained for the models based on HCL, ADL, NFC, CP, and their ratios. Figure 1 presents the correlation between the methane yield as calculated based on the model: $\text{PMY} = 20.3\ \text{HCL/ADL} - 24.2\ \text{CP/ADL} + 11.1\ \text{NFC/ADL} + 123.0$, and the methane yield obtained experimentally (EMY).

Table 4. Kinetics Parameters A, μ_m, λ, and Total Fermentation Time t_t, Depending on the Nitrogen Fertilization Level and Swath in the Case of Reed Canary Grass and Virginia Mallow

	A* (dm^3 kg^{-1} VS)	μ (dm^3 kg^{-1} VS d^{-1})	λ (d)	t_t (d)
RCG – Swath				
I/II/III	362 ± 9 c**	15.1 ± 0.8 b	0.1 ± 0.0 a	48 ± 1 b
II/III	449 ± 13 d	20.5 ± 1.3 c	3.7 ± 0.6 b	42 ± 1 a
III/III	262 ± 13 a	8.5 ± 0.7 a	4.2 ± 0.7 b	42 ± 0 a
II/II	315 ± 17 b	8.1 ± 0.3 a	0.8 ± 0.5 a	61 ± 1 c
p value	0.0000	0.0000	0.0000	0.0000
F	45.75	74.94	13.72	45.12
RCG - Nitrogen Fertilization Level				
N I	326 ± 21 a	12.4 ± 1.9 a	1.9 ± 0.8 a	47 ± 2 a
N II	356 ± 27 a	13.5 ± 2.0 a	1.9 ± 0.6 a	49 ± 3 b
N III	360 ± 20 a	13.3 ± 1.4 a	2.8 ± 0.7 a	49 ± 3 b
p value	0.0502	0.3286	0.3664	0.0193
F	3.40	1.17	1.05	3.15
RCG – Swath × Nitrogen Fertilization Level				
I/II/III × N I	346 ± 5	17.7 ± 0.4	0.2 ± 0.1	45 ± 2
I/II/III × N II	347 ± 14	14.2 ± 1.1	0.0 ± 0.0	50 ± 3
I/II/III × N III	392 ± 4	13.4 ± 1.3	0.0 ± 0.0	50 ± 3
II/III × N I	420 ± 9	19.4 ± 0.7	3.4 ± 1.6	42 ± 0
II/III × N II	486 ± 30	23.2 ± 3.2	3.1 ± 0.6	40 ± 0
II/III × N III	442 ± 10	18.9 ± 1.9	4.6 ± 1.0	45 ± 1
III/III × N I	234 ± 6	6.1 ± 0.6	4.0 ± 2.1	43 ± 1
III/III × N II	252 ± 27	9.8 ± 0.5	4.1 ± 1.1	42 ± 1
III/III × N III	300 ± 6	9.7 ± 0.2	4.4 ± 0.7	43 ± 1
II/II × N I	302 ± 26	6.6 ± 0.8	0.0 ± 0.0	60 ± 3
II/II × N II	338 ± 28	6.8 ± 0.7	0.5 ± 0.5	64 ± 4
II/II × N III	306 ± 38	11.0 ± 0.4	2.0 ± 1.1	58 ± 4
p value	0.2095	0.0320	0.9442	0.0466
F	1.54	2.82	0.27	10.02
VM – Swath				
I/II	433 ± 27 b	10.7 ± 0.9 a	3.0 ± 0.8 a	47 ± 0 b
II/II	279 ± 25 a	14.4 ± 2.0 a	1.8 ± 0.6 a	36 ± 0 a
p value	0.0000	0.0591	0.1781	0.0000
F	38.33	4.35	2.05	25.20
VM - Nitrogen Fertilization Level				
N I	297 ± 33 a	10.1 ± 1.4 a	2.8 ± 0.7 a	41 ± 3 a
N II	370 ± 65 ab	11.5 ± 1.6 ab	3.3 ± 1.1 a	41 ± 3 a
N III	401 ± 22 b	16.0 ± 2.3 b	1.0 ± 0.4 a	42 ± 2 a
p value	0.0144	0.0456	0.1041	0.1328
F	6.16	4.04	2.75	2.53
VM - Swath × Nitrogen Fertilization Level				
I/II × N I	362 ± 24	9.5 ± 1.8	2.8 ± 1.2	47 ± 0
I/II × N II	502 ± 56	11.0 ± 1.7	5.0 ± 1.3	47 ± 1
I/II × N III	436 ± 0	11.6 ± 1.8	1.1 ± 0.4	47 ± 1
II/II × N I	231 ± 21	10.7 ± 2.6	2.8 ± 1.0	35 ± 1
II/II × N II	239 ± 21	12.1 ± 3.1	1.6 ± 1.4	35 ± 1
II/II × N III	366 ± 33	20.5 ± 1.6	1.0 ± 0.7	37 ± 1
p value	0.0237	0.1583	0.1964	0.1328
F	5.20	2.16	1.87	2.53

*A, μ_m, λ, RCG, VM – see Table 3; I/II/III, I/II, II/II, II/III, III/III – see Table 2; **See Table 1

Table 5. Correlation Coefficients of the Biogas Yield, Methane Yield, Methane Content in Biogas, and Kinetics Parameters (*A*, μ_m, λ, and t_t) with Tested Chemical Characteristics

Characteristics	Biogas Yield	Methane Yield	Methane Content	*A***	μ_m	λ	t_t
TS	0.22*	0.25*	0.23*	0.15	0.23*	-0.25*	0.32*
VS	0.53*	0.53*	0.25*	0.52*	0.45*	-0.28*	-0.11
C_{org}	0.35*	0.32*	0.08	0.31*	0.23*	-0.33*	0.17
CP	-0.45*	-0.49*	-0.33*	-0.53*	-0.33*	-0.19	0.03
C/N	0.52*	0.52*	0.25*	0.54*	0.39*	0.04	0.04
CL	0.01	-0.08	-0.23*	0.03	-0.08	-0.19	0.19
HCL	0.33*	0.29*	0.01	0.33*	0.15	0.04	0.38*
ADL	-0.48*	-0.49*	-0.16	-0.37*	-0.64*	-0.09	0.63*
NFC	0.53*	0.64*	0.59*	0.51*	0.62*	-0.04	-0.54*
(CL + HCL)/ADL	0.56*	0.51*	0.04*	0.44*	0.59*	-0.11	-0.27*
CF	-0.00	-0.08	-0.32*	-0.07	0.01	-0.22*	-0.20
pH	-0.52*	-0.58*	-0.33*	-0.53*	-0.63*	-0.05a	0.48*

*Correlation statistically significant ($p < 0.05$), ** *A* is the maximal biogas production after t_t, t_t is the total fermentation time, μ_m is the specific biogas production rate, λ is the length of the lag phase R > 0.4, 0.4 < R > 0.2, R < 0.2

Table 6. Summary Statistics of Linear Regression Analysis

Variable	R^2	p	RRMSE	Equation
HCL	0.085	< 0.0053	32.43	PMY = 2.6 HCL + 133.7
C_{org}	0.104	< 0.0019	32.08	PMY = 2.9 C_{org} + 44.5
ADL	0.236	< 0.0000	29.63	PMY = -11.4 ADL + 268.1
CP	0.239	< 0.0000	29.59	PMY = -10.7 CP + 295.3
(CL + HCL)/ADL	0.257	< 0.0000	29.22	PMY = 9.5 (CL + HCL)/ADL + 113.0
C/N	0.271	< 0.0000	28.95	PMY = 3.1 C/N + 87.0
NFC	0.415	< 0.0000	25.93	PMY = 3.3 NFC + 128.8
(CL + HCL)/ADL, NFC	0.602	< 0.0000	21.50	PMY= 8.2 (CL + HCL)/ADL + 3.0 NFC + 69.2
(NFC + HCL)/ADL	0.603	< 0.0000	21.40	PMY = 11.0 (NFC + HCL)/ADL + 114.0
ADL, HCL, NFC	0.673	< 0.0000	19.60	PMY = -5.3 ADL + 4.1 HCL + 3.4 NFC + 79.4
(CL + HCL)/ADL, NFC, CP	0.729	< 0.0000	17.85	PMY = 9.2 (CL + HCL)/ADL + 2.3 NFC – 8.4 CP + 158.0
HCL/ADL, NFC/ADL, CP	0.793	< 0.0000	15.60	PMY = 15.8 HCL/ADL + 8.9 NFC/ADL – 7.1 CP + 176.4
HCL/ADL, NFC/ADL, CP/ADL	0.799	< 0.0000	15.37	PMY=20.3 HCL/ADL – 24.2 CP/ADL + 11.1 NFC/ADL + 123.0

Thirty-eight datasets from the literature were tested to validate the above model. The predicted values (PMY) *versus* the experimental values of the methane yield (EMY) from the various studies were plotted in Fig. 2. Additionally, the validation was performed for each source of datasets separately. The best prediction was obtained for the results of Mahmood *et al.* (2012) with an R^2 of 0.64.

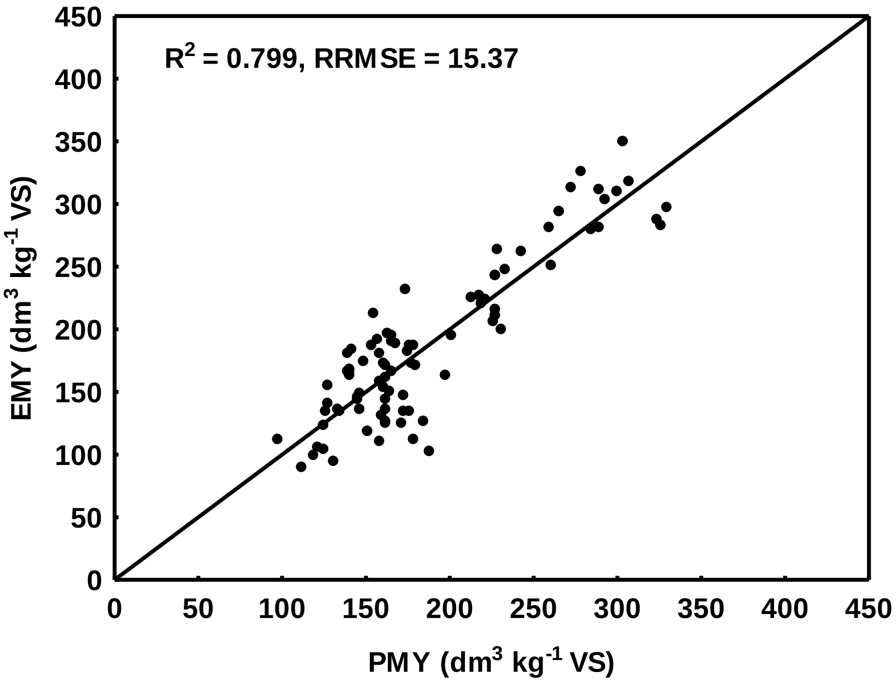

Fig. 1. EMY *versus* PMY obtained based on the model: PMY = 20.3 HCEL/ADL – 24.2 CP/ADL + 11.1 NFC/ADL + 123.0

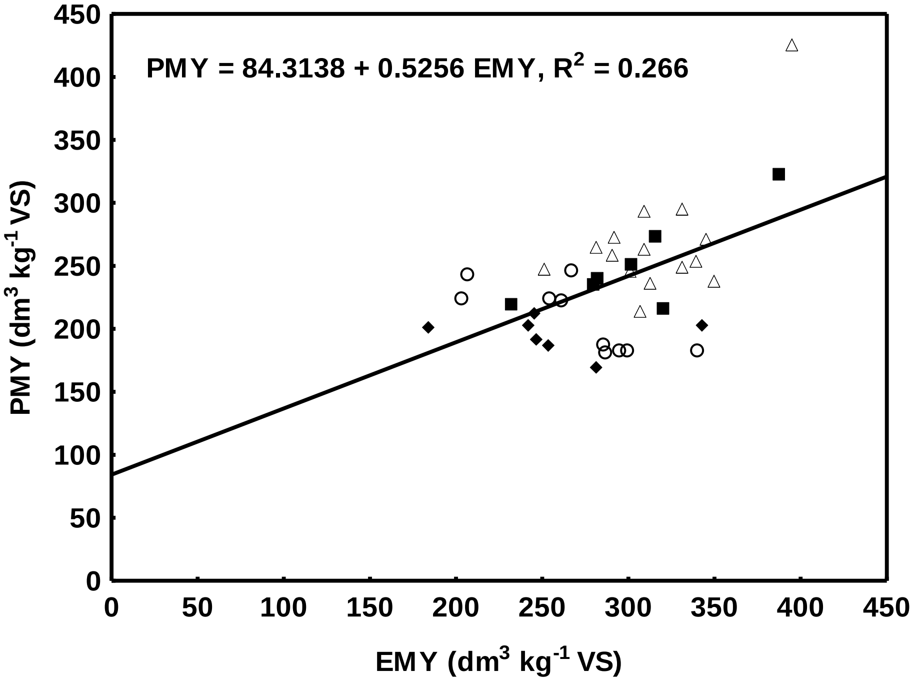

Fig. 2. Validation of the suggested model: EMY *versus* PMY and the linear trend; ◦ - Merando *et al.* 2012, ▪ - Mahmood *et al.* 2012, ♦ - Li *et al.* 2013, and Δ – Oslaj *et al.* 2010

DISCUSSION

The Influence of the Nitrogen Fertilization Level on Biogas Production

The results of the present study indicated that an increase in biogas and methane yield with increasing doses of nitrogen were consistent with the results obtained by Kandel *et al.* (2013), who investigated the effect of additional nitrogen, phosphorus, and potassium (NPK) fertilization after the first swath of RCG on biogas production from the biomass of the second swath. This study showed that the methane yield significantly increases with a decrease in ADL. Analysis of the correlation coefficient of the biogas and methane yield with particular chemical properties provided the basis for an explanation of the reasons for the positive influence of enhanced N levels on the efficiency of methane fermentation. Among the properties that are positively correlated with the biogas and methane yield, the (HCL + CL)/ADL ratio has a significant increase, and C/N is shown to decrease when the N level increases (Oleszek and Matyka 2017). In the case of properties that correlated negatively, an increase in the N level caused a decrease in the ADL and pH, while there was an increase in N_{tot} and CP. According to the above findings, the main cause of the increase in the biogas and methane yield resulted from rising N levels, which was primarily a decrease in the ADL as well as favorable changes in the proportion of lignocellulose components, as expressed in the (HCL + CL)/ADL ratio. Unfavorable changes, from the biogas production point of view, such as an increase in CP and particularly a decrease in the C/N ratio, could to some extent reduce the positive effect of improved digestibility of lignocellulose. The low pH of the silage from plants grown at the highest level of N fertilization was also noteworthy. Kaplan *et al.* (2016) confirms that the decrease in the pH of maize silage caused by increasing the doses of N fertilization increases the gas production in co-digestion with rumen fluid. This finding is in line with the findings of Prochnow *et al.* (2009), which states the close relationship between the silage quality and the biogas yield.

The influence of the N fertilization level on plant material quality, methane fermentation efficiency, and kinetics is probably associated with its impact on the morphological characteristics of plants, such as changes in proportion of leaves to stems and cobs to stems (in the case of maize) (Kaplan *et al.* 2016). As reported by Peyraud and Astigarraga (1998), N fertilization promotes the growth of succulent herbage that is low in cell wall content. In contrast, a low N fertilization level may accelerate the maturation and shortening of the growing season because the plants are forced to bloom (Kaplan *et al.* 2016). Jablonowski *et al.* (2017) and Kandel *et al.* (2013) stated that an increase in lignin follows maturation, which supports the authors' results of higher lignin content and lower methane fermentation efficiency associated with the lowest N fertilization level.

Influence of the Energy Crop Species on Biogas Production

Among the investigated energy plants, maize is the most often used substrate, especially in west and central Europe where it has high biomass yield (Oleszek *et al.* 2016). Additionally, the highest potential of methane production from maize is due to its low nutrient demand, high water-use efficiency, and high digestibility (Herrmann 2013; Rath *et al.* 2013). High biogas yield from maize silage that was obtained in the present study (471 ± 14 dm^3 kg^{-1} VS) resulted from favorable chemical properties, which are important for biogas production. As was reported by Oleszek and Matyka (2017), maize contains only a small amount of ADL and ash, but a large amount of NFC. Moreover, it was characterized by the highest ratio of (HCL + CL)/ADL among all of the tested species.

The average biogas yield of 471 ± 14 $dm^3 kg^{-1}$ VS was close to the results of Mursec *et al.* (2009) (362 $dm^3 kg^{-1}$ VS). Luna-delRisco *et al.* (2011) noted a methane yield of 296 ± 31 $dm^3 kg^{-1}$ VS, while Oslaj *et al.* (2010) obtained a biogas and methane yield in the range of 515 to 603 and 290 to 330 $dm^3 kg^{-1}$ VS, respectively, while conducting research on the efficiency of methane fermentation from 15 varieties of maize. Similar values were noted by Negri *et al.* (2014), who compared a few varieties that differed in the Food and Agriculture Organization of the United Nations number (FAO) (300 to 700) and stated that the biogas yield increases with increases in the FAO value. *Zea mays* var. *ułan*, which was tested in this study, has an FAO of 270, and is defined in Polish conditions as a medium-late variety. Amon *et al.* (2007b) investigated the effect of the harvesting dates on the maize methane yield, as well as the differences between the varieties. The methane yield was in the range of 268 to 366 $dm^3 kg^{-1}$ VS and decreased with the degree of maturity. However, it was associated with a rise in the biomass yield, and thus, the methane productivity per unit area.

The sunflower methane yield (160 $dm^3 kg^{-1}$ VS) proved to be much lower then was obtained by Mursec *et al.* (2009) (283 $dm^3 kg^{-1}$ VS), Nassab *et al.* (2011) (300 $dm^3 kg^{-1}$ VS), and Monlau *et al.* (2012) (192 $dm^3 kg^{-1}$ VS). The reason for the differences could have been due to the different chemical composition of the biomass used by the authors, which resulted from differences in the varieties, harvest data, methods of cultivation, pretreatment, storage, apparatus, and conditions of the methane fermentation process. For this reason, a comparison of the results of various laboratories is difficult (Kalač 2011). The relatively low biogas and methane yield obtained in the present study was probably due to the highest ADL content among all of the tested plants, which decreases the following ratio: (HCL + CL)/ADL (Oleszek and Matyka 2017). Additionally, high CA and low HCL values negatively influenced the biogas yield. The sunflower silage was distinguished by the highest content of CF, but it only weakly influenced the biogas production (R = 0.22).

The sorghum methane yield (301 to 323 $dm^3 kg^{-1}$ VS) was slightly higher than that noted by Barbanti *et al.* (2014), which was 262 $dm^3 kg^{-1}$ VS. Nonetheless, it should be mentioned that the authors investigated other varieties than those used in the present study. An investigation concerning the variety Rona 1 was conducted by Mahmood and Honermeier (2012), in which the highest results were obtained for the biogas and methane yield, of 721 and 387 $dm^3 kg^{-1}$ VS, respectively. Comparing the efficiency of the methane fermentation process of five sorghum varieties, the authors stated that the variety of Rona 1 was characterized by a significantly higher biogas yield than the others by an average of 200 $dm^3 kg^{-1}$ VS. A high biogas yield from sorghum silage is associated with high NFC content, and simultaneously, low ADL and CP content. Furthermore, sorghum was distinguished by the lowest CA and the highest VS as well as a high (HCL + CL)/ADL ratio (Oleszek and Matyka 2017).

The average biogas and methane yield RCG IIC, 342 and 167 $dm^3 kg^{-1}$ VS, as well as RCG IIIC, 359 and 176 $dm^3 kg^{-1}$ VS, turned out to be lower compared to the results of other authors (Seppälä *et al.* 2009; Kacprzak *et al.* 2012; Kandel *et al.* 2013). Nevertheless, similar relationships between the swaths were observed.

Oleszek and Matyka (2017) reported that RCG can be distinguished by the highest HCL and CL, causing a high ratio of (HCL + CL)/ADL, which was only slightly lower than in maize. Unfortunately, the low content of NFC and the relatively high content of ADL resulted in a weak biogas yield. Furthermore, the silages of RCG were characterized by an elevated pH. Proper pH of the silage that contains approximately 30% of the dry matter should not exceed 4.5 (Meeske *et al*. 2002).

In the last two years, there was an apparent increase in the number of studies on the biogas production from VM and its cultivation for silage (Nahm and Morhart 2018). The first attempts with biogas batch assays showed the higher biogas and methane yield (435 and 220 dm^3 kg^{-1} VS, respectively), compared with that obtained in the present study (Oleszek *et al.* 2013). Similar results were obtained several years later by Dębowski *et al.* (2017) of 381.39 and 166.61 dm^3 kg^{-1} VS, respectively, and Jablonowski *et al.* (2017), which were 419.5 and 204.2 dm^3 kg^{-1} VS, respectively. A lower biogas yield of 278 to 265 dm^3 kg^{-1} VS that was more consistent with the present study was obtained by Zieliński *et al.* (2013). In the present work, VM was distinguished by the lowest C/N and the highest CL (Oleszek and Matyka 2017), but the CL did not correlate with the biogas and methane yield. The property that could negatively influence the biogas production was a high pH of 4.8.

The lowest biogas yield was observed for triticale. As Oleszek and Matyka (2017) reported, silage of this energy crop was characterized by a low concentration of NFC, a high content of ADL and one of the lowest ratios of (HCL + CL)/ADL, which reflects low digestibility. Other authors obtained higher values of the biogas and methane yield. Negri *et al.* (2014) noted a biogas yield of 487 dm^3 kg^{-1} VS, and Amon *et al.* (2007a) noted a methane yield of 212 to 289 dm^3 kg^{-1} VS, depending on the harvest date. Moreover, they observed a significant decrease in the methane yield when delaying the harvest date. This fact and the high content of ADL could suggest that the triticale biomass in the present study was collected too late and at too high a degree of maturity.

Influence of the Swath and Cut System on Biogas Production

The negative correlations of the biogas yield with ADL, CA, and CP helped to explain the differences in the methane fermentation efficiency of certain swaths of RCG. The lowest biogas and methane yield was noted for the third swath of RCG collected in triplicate (III/III), due to the high CA and ADL content. However, the highest ADL was determined in the swath of II/II due to the high degree of maturity, which also had a significantly lower biogas yield than the swaths of I/II/III and II/III ($p < 0.05$). The swath of I/II/III is distinguished by a high ratio of (HCL + CL)/ADL and by the high content of CP and thus the low C/N ratio, which could cause the inhibition of methane fermentation by ammonia production (Wagner *et al.* 2013). The best biogas and methane yield was noted for the swath of II/III, and both were caused by the low content of CP and ADL as well as the high ratios of (HCL + CL)/ADL and C/N.

Mähnert *et al.* (2005) indicates that the frequency of cutting has a significant impact on the composition of crude fiber and the digestibility of organic matter, which as a consequence influences the biogas production. However, the results of the present study showed that despite the high biogas yield of the swath of II/III, the average biogas yield from RCG IIIC was not significantly different from RCG IIC ($p > 0.05$) because of the low biogas production from the swath of III/III.

The higher methane yield from the first swath (I/II/III) compared to the second swath (II/II) was confirmed by the results of Seppälä *et al.* (2009) and Kacprzak *et al.* (2012). In contrast, Kandel *et al.* (2013) did not observe significant differences between the methane yield of the first and second swath. However, a decline was shown in the methane yield with plant maturity. As the reason, they gave the decrease in the portion of leaves in the biomass during vegetation. The leaves contained less ADL and CL and were characterized by much higher methane yield than the stalks. The strong dependence of the methane yield on the maturity in the case of RCG provides the basis for explaining a higher methane yield obtained in the present study for the swath of II/III (harvested in August) than the swath of II/II (harvested in October). However, it should be noted that a harvesting delay is most often aimed at achieving a highest biomass yield, and thus, the productivity of methane and energy from the area unit.

Oleszek *et al.* (2014) determined a similar RCG biogas yield of 406 dm3 kg^{-1} VS. The authors stated that there is a higher methane production efficiency from the cultivated variety compared with the wild variety that originates from meadows. This was due to the much lower content of ADL and crystalline cellulose, which proves that agro-technical treatments, such as fertilization and systematic cutting, improve the digestibility and the biogas yield.

Among the two swaths of VM, a higher biogas and methane yield were noted for I/II, despite the much lower content of NFC and the higher ADL in its silage. The swath of I/II was also characterized by a lower ratio of (HCL + CL)/ADL compared with the swath of II/II, however, it simultaneously had a significantly higher C/N ratio ($p < 0.05$), which positively correlated with the biogas yield. These results were consistent with the findings of Jablonowski *et al.* (2017) in which a higher biogas yield from the first swath compared to second swath was also obtained, namely 419 and 269 dm^3 kg^{-1} VS, respectively.

Influence of the Chemical Properties on the Efficiency of Methane Fermentation

The influence of the biomass chemical composition was the subject of many previous studies. Most often the content of lignin was mentioned as a factor that strongly inhibited the methane fermentation process (Triolo *et al.* 2011; Li *et al.* 2013; Wagner *et al.* 2013; Dandikas *et al.* 2014; Godin *et al.* 2015). Tsavkelova and Netrusov (2011) as well as Wagner *et al.* (2013) report that the biodegradation of plant feedstock strongly depends on the ADL content, which does not decompose under anaerobic conditions, because the extracellular enzymes require oxygen to depolymerize (Triolo *et al.* 2011). In addition, lignin covers cellulose and hemicellulose chains and makes it difficult to break down (Zheng *et al.* 2014). The importance of this problem is evident by the scale of research studies on pretreatment methods that aim at improving the biodegradability of lignocellulose (Hendriks and Zeeman 2009; Zheng *et al.* 2014). The lower correlation of the methane yield and lignin (ADL) obtained in this work compared to other studies could have been due to the narrow range of ADL content in the tested crops (Tiolo *et al*. 2011).

The positive effect of NFC on the biogas yield was demonstrated by Godin *et al.* (2015), in which a moderately strong, positive correlation coefficient of methane yield from various grass with water soluble carbohydrates (R = 0.54) was recorded. In contrast to the present study, these authors found a positive correlation of biogas yield with the CP, whereas its correlation was negative with CL and HCL.

Nevertheless, in previous literature there are many reports on the negative influence of CP on biogas production (Goliński and Jokś 2007; Wagner *et al.* 2013). One of the reasons for the unprofitable effect of CP could be the ammonia production, which is the inhibitor of methane fermentation at too high a concentration (Wagner *et al.* 2013). Ammonia is formed especially at a low ratio of C/N.

While the decrease in ADL is always desired, the increase in the C/N ratio is beneficial only to an optimum range of 25 to 30 (Ward *et al.* 2008). This finding means that the influence of the concentration of N_{tot} and CP is dependent upon the C content.

Moreover, the correlation of biogas and C/N is not straightforward, and both too low and too high of values of this parameter are unfavorable.

However, this requires an explanation that the best biogas production was observed for the samples characterized by C/N exceeding an optimal value. It should be taken into account that the optimum C/N ratio is because methane fermentation microbes consume carbon thirty times more than nitrogen (Krishania *et al.* 2013). According to the above statement, the C/N ratio included only this amount of C and N, which is actually available for microorganisms. This finding means that in the case of low digestibility and availability of carbon, the actual C/N ratio can be considerably lower than the value calculated by the C_{org} content and the N_{tot} determined in the silage.

Additionally, it was assumed that improvement in the lignocellulose digestibility, due to the increasing N fertilization level, could increase in the presence of available C. In consequence, it might neutralize the drop in C/N that is caused by the rise in N content.

The methane content in the biogas proved to be less dependent on the chemical composition than biogas and methane yield. Generally, the values of CH_4 content fell within relatively narrow ranges, compared to biogas yield. Therefore, the methane yield might be high even at low CH_4 content in biogas. The NFC content was the only property of the biomass that moderately positively correlated with the CH_4 content (Table 5), but it was not dependent on the N level. This result was opposite to the observation of Kandel *et al.* (2013) of a lower CH_4 content in biogas from biomass with a higher digestibility and NFC content. In contrast, their results could justify the lower CH_4 content in biogas from plants that were cultivated at the highest N level, which was characterized by the best digestibility (the highest ratio of (HCL + CL)/ADL).

The decrease in the CH_4 content with increasing levels of nitrogen was explained by increases in the CF and CP (negative correlation with the CH_4 content). The positive correlation coefficient (R) between the methane content and NFC justified the high methane content obtained for sorghum, RCG, and VM.

The negative influence of CP and CF on the CH_4 content is contrary to the reports of Jacobi *et al.* (2012) and Prochnow *et al.* (2009), which regard the biogas of the highest CH_4 content from the proteins and lipid-rich substrates. However, Schittenhelm (2008), Wagner *et al.* (2013), and Kowalczyk-Juśko *et al.* (2015) note that the theoretical methane yield and methane content in biogas are often not confirmed in empirical results, due to differences in the digestibility and availability of the individual components. Wagner *et al.* (2013) explains that lipids are difficult to decompose in a fermenter, due to their low solubility in water. Furthermore, in the case of lipid-rich substrates, there is a risk of inhibition caused by an accumulation of long chain fatty acids (Schittenhelm 2008).

The multiple linear regression analysis allowed for the development of a model used for methane yield predictions that employs the chemical components of the biomass. The best developed model of methane yield that accounted for the ratio of HCL/ADL, NFC/ADL, and CP/ADL was characterized by the relatively high regression coefficient $R^2 = 0.799$ and quite favorable RRMSE of 15%. Additionally, the model was assessed using 38 datasets from the literature. The slope and intercept of the linear regression line of the PMY *versus* EMY plot was 0.526 and 84.3, respectively (Fig. 2). For comparison, the perfect fit was characterized by 1 and 0, respectively ($y = x$). The low slope of the regression line suggested that the model tended to underestimate the methane yield. The low R^2 of 0.266 for the datasets analyzed together was evidence of a weak prediction by the tested model, but it could also be the result of the application of various batch assay conditions. The validation procedure has shown that the model must be improved to increase the precision of the prediction of the methane yield. One of the best models to predict biochemical methane potential was developed by Thomsen *et al.* (2014). The model is based on a large dataset from literature and shows a high R^2-value of 0.96, but a slightly lower RRMSE of 19.7% compared to the present study.

The Kinetics of the Methane Fermentation Process

The analysis of the correlation coefficient showed that the increase in the specific biogas production rate (μ_m) due to increased doses of N fertilizer was caused primarily by the decrease in ADL, which led to an increase in the digestibility of the biomass. The strong negative influence on μ_m was also characteristic of the pH. The silage of the lower pH fermented faster and reached a higher biogas yield in a shorter amount of time. The low pH was evidence of good quality silage, while a pH that exceeded the optimal value could be the result of the elevated ADL content, which does not promote the ensiling. Jagadabhi *et al.* (2011) states that the low pH of substrates favors the methane fermentation process due to the fast hydrolysis step, for which the optimal pH is between 4 and 6.

The highest μ_m for maize and sorghum was associated with high NFC content as well as low ADL and CA content. The high C/N ratio was not less important. The lowest μ_m was noted for triticale and the II/II swath of RCG as a result of the high ADL content and the low (HCL + CL)/ADL ratio. Even though the sunflower was characterized by the lowest lignocellulose digestibility, its μ_m was not the lowest due to the high NFC content. Wahid *et al.* (2015) confirms the significant influence of the biomass digestibility on the specific biogas production rate μ_m.

The low correlation coefficient (R) for the length of the lag phase (λ) testified to the lack of influence of the chemical composition on this parameter. In contrast, the reduction in the total fermentation time (t_t) due to the increase in the NFC content and decrease in the ADL was noticeable.

For the μ_m, the positive effect of the drop of the substrate pH on t_t could be the result of faster and easier hydrolysis (Jagadabhi *et al.* 2011). In the present study, the total fermentation time (t_t) was in the range of 27 to 60 days, and was longest for triticale and RCG IIC, and was the shortest for maize. For comparison, Seppälä *et al.* (2013) noted a total fermentation time of the plants substrate in the range of 28 to 35 days, while Weiland (2006) gave a range of 60 to 90 days.

The reports that concern the application of the Gompertz equation (Eq. 3) for evaluating the methane fermentation kinetics have been rather scarce, but they have confirmed that this model is appropriate for the description of such processes. Yusuf *et al.* (2011) applied the Gompertz equation to compare the cumulative biogas yield from various types of manure mixed at different proportions. The authors obtained parameters that are close to the experimental biogas yield. The lag phase (λ) was notably longer than in the present study (8.6 days). In contrast, the specific biogas production rate (μ_m) was much lower (1.2 to 2.2 dm^3 kg^{-1} d^{-1}). However, it should be mentioned that the fermentation process was conducted at ambient temperatures, which were in the range of 28 to 33 °C. The authors observed that the parameter μ_m decreased with an increasing share of bovine manure in the mixture, which had a higher ADL content than the horse mixture. The authors stated that the highest μ_m was characteristic for the mixture of the most optimal value of C/N. These results are in accordance with the present study, where the greatest μ_m was noted for the highest N level associated with the lowest ADL content and the closest to the optimal C/N ratio.

Wahid *et al.* (2015) uses the Gompertz model to report a higher rate of biodegradation of biomass from the first swath of caraway and chicory, compared to its biomass from the second swath and that collected at the one-cutting system. The authors explain this in terms of the high content of the NDF and ADL fraction, which are associated with the high temperature and intensity of solar radiation in the later vegetation period.

CONCLUSIONS

1. The N fertilization positively influenced the BD, and thus the efficiency and kinetics of methane production.
2. These results were closely associated with favorable changes in the biomass chemical composition, such as a decrease in ADL and positive modification of the proportion of lignocellulose components expressed as the (HCL + CL)/ADL ratio.
3. For perennials, more efficient biogas production was observed for the biomass collected at an earlier stage.
4. The methane yield was successfully predicted by the ratios of HCL to NFC and CP to ADL. The validation showed that the model must be improved to increase the prediction precision.

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