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Chemical composition and methane yield of maize hybrids with contrasting maturity

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ABSTRACT

Maize (Zea mays L.) is the most important substrate for biogas production in Germany. This study was conducted to determine the influence of harvest date and hybrid maturity on the yield and quality of maize biomass for anaerobic methane production. In 2004 and 2005, maize hybrids of widely contrasting maturity were grown on a loamy sand soil (Haplic Luvisol) near Braunschweig, Germany. Whole-plant yield was determined several times after female flowering and the biomass analysed for nutrient composition. The specific methane yield (SMY) was measured using 201 batch digesters. In both experimental years, the late energy maize prototypes had a lower concentration of fat and protein, but higher concentration of ash, detergent fibre, and lignin as compared with the climatically adapted medium-early hybrids. Despite substantially different nutrient concentration among the maize hybrids, no clear-cut association existed between chemical composition and specific methane yield. Contrary to the medium-early hybrids, the late hybrids attained both maximum specific methane yield and maximum methane hectare yields at the final harvest date. In the very long growing season of 2004, the highest individual methane yield of 9370 N m³ ha⁻¹ was obtained by the hybrid with the latest maturity used in the study. It appears that late energy maize, which can take full advantage of the growing season, is better suited for biogas production, provided that the whole-plant dry matter concentration is high enough to produce good quality silage. © 2008 Elsevier B.V. All rights reserved.

1. Introduction

Agricultural biogas production is a fast growing market in many European countries. In Germany, the number of operating biogas plants increased from 274 in 1995 to about 3200 in the middle of 2006 (Weiland, 2006, 2007). This development was promoted by the adoption of the Renewable Energy Sources Act (EEG) in the year 2000, and particularly after its amendment in 2004 (BMJ, 2004). The EEG guarantees compensatory payments for a period of up to 20 years per biogas plant and provides an extra financial bonus for the use of plant biomass. Such new markets for agricultural bioenergy not only allow the introduction of new crops and cropping systems but also enable the recycling of nutrients (Anex et al., 2007).

Because of its high methane yield per hectare, and the ease of mechanisation and integration into the farm organisation, maize is a highly competitive energy crop. Consequently, more than 90% of the German agricultural biogas plants use maize silage as fermentation substrate (Weiland, 2007). Under the favourable economic conditions of the EEG, the German energy maize acreage is expected to expand from 156,000 ha in the year 2006 to 1.7 million ha by the year 2015 (Gömann et al., 2007). To cope with the growing market for biogas maize, special energy maize breeding programs aim at increasing the dry matter biomass yield to $30 \text{ t} \text{ ha}^{-1}$ (Landbeck and Schmidt, 2005). Future energy maize hybrids will be larger sized and later maturing than today's silage maize hybrids. Besides a high dry matter yield, energy maize for biogas production should also have a high specific methane yield (SMY) and a dry matter concentration >28–30% to avoid seepage loss during ensiling.

In assessing the methane production potential of maize, it seems obvious to fall back on forage quality parameters. However, substantial differences exist in the requirements on maize as biogas substrate and as cattle feed. While high methane yields are aimed at in biogas plants, ruminal methane production is ecologically harmful and thus undesirable. In addition, to maximise methane production, biomass remains in the biogas plant over 60–90 days, whereas the retention time of silage maize in the rumen lasts for only about 24 h (Herrmann and Taube, 2006).

Only inconsistent results are available from the few studies aimed at determining the optimal chemical composition and the most favourable maturity index and harvest date for maximizing the specific methane yield in the biogas fermenter. Eder et al. (2005) observed a significant correlation between methane production





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and in vitro digestibility of organic matter (IVDOM) but there was no clear correlation with other important quality parameters in animal nutrition such as enzyme-soluble organic substance (ELOS) and starch concentration. According to Amon et al. (2007), methane production of maize is a function of protein, fat, cellulose (CEL), and hemicellulose (HEM) concentration of the whole-plant biomass. Although the starch level does not seem to play an important role for obtaining energy from anaerobic digestion of plant biomass, Eder et al. (2005) postulate a minimum whole-plant dry matter starch concentration of 20% and Amon et al. (2007) conclude that further research is needed to clarify the role of starch for methane production.

The present investigation aims at answering the questions (1) whether maize hybrids with widely contrasting maturity differ in quality parameters presumably relevant for methane production, (2) how these factors change over the season and (3) what ideal biogas maize should look like.

2. Materials and methods

2.1. Experimental site and weather conditions

The trials were conducted during 2004 and 2005 on the institute's experimental fields ($52^{\circ}17'N$, $10^{\circ}26'E$, altitude 75 m) located near Braunschweig in the North German Plain. The site is characterised by an annual mean precipitation of 627 mm and a mean air temperature of 9.1 °C. The experimental fields were situated on a loamy sand soil classified as Haplic Luvisol (FAO, 1997). The soil has a water-holding capacity of 120 mm of which 96 mm is plant available. The weather data were recorded at the Agrometeorological Research Station of the German Weather Service located within a distance of 1 km from the experimental fields. The average air temperature between April and October amounted to 14.1 °C in 2004 and 14.5 °C in 2005. Air temperatures during this 7-month growing period exceeded the long-term average by 0.6 °C in 2004 and 1.1 °C in 2005. Rainfall from sowing to final harvest amounted to 391 mm in 2004 and 296 mm in 2005.

2.2. Experimental layout and crop management

Commercial silage maize hybrids of widely contrasting maturity were used in each of the two experimental years. The set of hybrids used in 2004 consisted of Gavott (S 250, KWS), Mikado (ca. S 500, KWS) and Doge (ca. S 700, KWS), with the maturity index (BSA, 2007) and breeders given in brackets. The 2005 set consisted of Flavi (S 250, Caussade), PR36K67 (S 350, Pioneer), and once more Mikado. Although not adapted to the cool climate of Northern Germany, Doge and Mikado were chosen to represent energy maize prototypes. In 2005, Doge was substituted by PR36K67 because the whole-plant dry matter concentration of 25% at the final harvest in 2004 was critically low for the production of good quality silage. The hybrids were arranged in a randomised complete-block design with four replications. The plots consisted of eight 20 m long rows with 0.75 m row spacing. Winter barley was the preceding crop in each of the 2 years. Sowing was performed on 22 April 2004 and 28 April 2005. A density of 10 plants m^{-2} was established in each year. Nitrogen fertilizer was applied at a rate of 180 kg N ha⁻¹ as calcium ammonium nitrate directly before sowing. Weeds were controlled through postemergence application of a tank-mix of Artett (each 375 g a.i. ha⁻¹ terbuthylazine and bentazone) and Motivell (40 g a.i. ha⁻¹ nicosulfuron). Irrigation was practiced to assure that plant available soil water in the upper 60 cm of the soil would not fall below 50% of its maximum during the entire growing season. Therefore, eight irrigations with a total of 85 mm and twelve irrigations with a total of 145 mm were applied in 2004 and 2005, respectively. Irrigation scheduling was based on PR2 profile probes in 2004 and ML2x probes in 2005 (both from Delta-T Services, Cambridge). Uniform water supply was assured by pressure compensated drip lines (Netafim Ltd., Tel Aviv) with a 30-cm dripper distance. The well-irrigated experimental plots analysed in this study were part of a larger irrigation experiment.

2.3. Data acquisition in the field and laboratory

2.3.1. Agronomic characteristics

Twenty plants from each plot were manually harvested at eight dates in 2004 and six dates in 2005. Harvesting started at silking of the earliest hybrid and additional harvests followed at 2-week intervals in 2004, and about 3-week intervals in 2005. In 2004, the first harvesting date was on 27 July (96 days after sowing, DAS). and the final harvest on 2 November (194 DAS). The corresponding figures for 2005 were 19 July (83 DAS) and 25 October (180 DAS). Because of the substantial maturity differences, the hybrids were in different developmental stages at each sampling. Very early harvesting dates were practiced in order to monitor maturity dependent changes in quality characteristics and yield. After the shoot fresh weight of the 20-plant sample was determined, eight plants were chopped to provide material for dry matter determination, chemical analyses, and biogas tests. Duplicate subsamples (ca. 500 g) were dried at 105 °C to a constant weight, and reweighed to determine subsample dry weights. Another 250g subsample was oven dried for 1 h at 100°C, and then for 72 h at 70°C, ground using a Brabender laboratory mill with 1 mm grid, and stored in gaseous nitrogen for later chemical analyses. Two 4 kg subsamples were stored at -20 °C for later measurement of specific methane yield. At the final harvest date in 2004, ten additional plants were separated into leaves, stems (including leaf sheaths and tassels), grains, and combined rachis and husks. The dry weight of each plant fraction was determined as described above for the whole-plant sample. At each sequential harvest, plant height was measured on four plants per plot from the soil surface to the base of the tallest leaf. The leaf area index (LAI) was determined using the SunScan canopy analysis system (Delta-T Devices, Cambridge) connected to a beam fraction sensor. Sixteen LAI measurements within each plot were taken once every week around noon by positioning the SunScan probe at a ca. 45° angle across two rows directly above the soil level. The beginning of female flowering was defined as the date when 50% of the plants within a plot exhibited silk emergence.

2.3.2. NIR spectroscopy and chemical analyses

Near-infrared reflectance spectroscopy (NIRS) was used to predict the concentration of ash, fat, protein, water-soluble carbohydrates (WSC), starch, and the cell-wall fractions neutral detergent fibre (NDF), acid detergent fibre (ADF), and acid detergent lignin (ADL). The predicted values of NDF, ADF, and ADL concentration were used to estimate hemicellulose by subtracting ADF from NDF and cellulose by subtracting ADL from ADF. Samples were scanned with a Foss NIR-Systems scanning monochromator (Model 6500, Silver Spring, MD) in the range of 1100-2500 nm at 2 nm intervals. The prediction equations used for analysing the maize samples from the present study were based on calibration samples collected from time harvest studies of whole-plant maize quality conducted at the institute from the years 2000 through 2003. They were updated with additional samples from the current study identified by the Infrasoft International (ISI, Port Matilda, PA) NIRS 3 v. 4.0 software program 'Select' as being outside the spectral characteristics of the previous calibration population. Results from analyses of the calibration set were used to develop

prediction equations by modified partial least squares regression (Shenk and Westerhaus, 1991). Overfitting was restricted by means of cross-validation.

The samples in the calibration set were subjected to standard wet chemical analyses as briefly described below. The volatile solids (VS) concentration was measured as the weight lost during incineration at 550 °C in a muffle furnace and is thus estimation for the organic matter present in the sample. The ash concentration was determined as the residue after incineration. Fat was extracted for 6 h with petroleum ether in a Soxhlet apparatus after prior HCl hydrolysis. The protein concentration ($N \times 6.25$) was determined with an automated FP-2000 LECO analyser (LECO Corporation, St. Joseph, MI). The anthrone colorimetric method was used for determining the WSC concentration and starch was determined by the Ewers polarimetric method. In determining NDF, ADF, and ADL, the laboratory procedures given by Goering and van Soest (1970) were followed.

2.3.3. Specific methane yield

The methane production from whole-plant maize samples was determined by laboratory batch tests carried out in duplicate in 201 glass bottles at 37 °C using inoculum from anaerobically digested material of a preceding batch experiment. The total volume of biogas was determined using a drum-type gasmeter and the methane concentration was measured by infrared absorption. The volume of accumulated CH₄ production over time was converted to normal conditions, i.e. norm litre (NI) per kg of volatile solids at 0 °C and 1013 mbar.

2.4. Data analysis

For all measured and calculated data, separate analyses of variance (ANOVAs) were carried out for each year and harvest date using the PLABSTAT program (Utz, 2005). In these ANOVAs, hybrids were considered fixed effects and replications random effects. When *F*-ratios were significant (P < 0.05), LSD values at that level were used to compare treatment means. To study the relation between the specific methane yield as dependent variable and the concentration of various nutrients as potential predictors, a multiple regression analysis was performed using the SPSS statistical analysis package (SPSS, 1993). SPSS was also used to calculate Pearson correlations between all pairs of variables.

3. Results

3.1. Plant development and dry matter distribution

Because of their sensitivity to chilling, the late energy maize prototypes Doge and Mikado displayed a slower early growth in each year as compared with the climatically adapted medium-early hybrids. However, this developmental delay was overcompensated through superior canopy development later in the season. The hybrids reached maximal plant heights of 248, 274, and 288 cm for Gavott, Mikado, and Doge in 2004 and 225, 260, and 292 cm for Flavi, PR36K67, and Mikado in 2005, respectively. The maximal LAI values were 5.6, 9.1, and 8.6 m² m⁻² for Gavott, Mikado, and Doge in 2004 and 5.5, 8.0, and 9.4 m² m⁻² for Flavi, PR36K67, and Mikado in 2005, respectively.

At the final harvest in 2004, the maize hybrids significantly (P < 0.01) differed in the relative proportion of the various plant parts (Fig. 1). The fraction of vegetative plant parts (leaves and stems) considerably increased with increasing maturity of the hybrid. In relation to the total dry weight, the leaf plus stem fraction made up 36% for Gavott, 49% for Mikado, and 59% for Doge.



Fig. 1. Proportion of various plant fractions as percentage of whole-plant dry matter biomass for three maize hybrids with contrasting maturity at the final harvest date in 2004. Within plant fractions, means followed by different letters are significantly different (P < 0.05).

3.2. Nutrient composition

The whole-plant dry matter concentration in each year was markedly different among the hybrids (Fig. 2). The higher the maturity indices of the hybrids were, the lower the dry matter concentration at the final harvest. Maximum values for whole-plant dry matter concentration were 39.0%, 34.8%, and 25.0% for Gavott, Mikado, and Doge in 2004 and 38.7%, 29.7%, and 22.4% for Flavi, PR36K67, and Mikado in 2005, respectively.

The ash concentration in both years decreased during plant development (Fig. 3). There was a tendency towards higher ash concentration with later maturity of the hybrids. The ash concentrations of the hybrids were insignificantly different at the final harvest dates. In each year, the fat concentration of all hybrids increased towards the end of the growing season. The differences in whole-plant fat levels among the hybrids were more pronounced at the later developmental stages. The protein levels decreased almost consistently from the first to the last harvesting date. No significant differences in protein concentration occurred among the hybrids at the later samplings.

The WSC concentration followed a peak function for all maize hybrids studied (Fig. 4). In 2004, the maximum WSC concentrations



Fig. 2. Dry matter concentration of the whole-plant biomass as a function of days after sowing for maize hybrids with contrasting maturity in 2004 and 2005. Least significant differences (P<0.05) for each sampling date are presented by vertical bars if the ANOVA showed significant *F*-values.



Fig. 3. Concentration of ash, fat, and protein in the whole-plant biomass as a function of days after sowing for maize hybrids with contrasting maturity in 2004 and 2005. Vertical bars present least significant differences (P < 0.05) for each sampling date if the ANOVA showed significant *F*-values.

for Gavott, Mikado, and Doge were attained at 110, 138, and 153 DAS, respectively. In 2005, the WSC concentrations of Flavi, PR36K67, and Mikado peaked at 103, 118, and 137 DAS, respectively. In each year, the succession of silking of the various hybrids coincided with the initiation of starch synthesis. The increase of whole-plant starch concentration corresponded with a decreasing WSC concentration.

At most harvesting dates, the concentration of the fibre components HEM, CEL, and ADL increased with later hybrid maturity (Fig. 5). At the final sampling date, the hybrids' fibre concentrations were significantly different for HEM in 2004, for CEL in 2004 and 2005, but not for ADL.

3.3. Methane yields

Typical cumulative methane production curves were obtained from the laboratory batch tests for all hybrids and sampling dates (Fig. 6). The period of substantial and almost linear increase in methane production lasted about 10 days. On average, 90% of the maximal methane production was attained after 22 days. The velocity of digestion differed among hybrids and sampling dates. It took 30 days for Flavi to reach the 90% level at 180 DAS in 2005, but only 18 days for Gavott at 153 DAS in 2004.



Fig. 4. Concentration of water-soluble carbohydrates (WSC) and starch in the wholeplant biomass as a function of days after sowing for maize hybrids with contrasting maturity in 2004 and 2005. Vertical bars present least significant differences (P<0.05) for each sampling date if the ANOVA showed significant *F*-values. Arrows denote the initiation of female flowering.

In 2004, the specific methane yields varied from $287 \text{ Nl} (\text{kg VS})^{-1}$ for Gavott at 124 DAS to 419 Nl (kg VS)⁻¹ for Doge at 180 DAS (Fig. 7). In 2005, the respective range was $282 \text{ Nl} (\text{kg VS})^{-1}$ for PR36K67 at 118 DAS to 379 Nl (kg VS)⁻¹ for Flavi at 137 DAS. Averaged across hybrids and harvest dates, methane production amounted to 335 Nl (kg VS)⁻¹ in 2004 and 334 Nl (kg VS)⁻¹ in 2005. While the late maturity hybrids had maximum specific methane production at the latest sampling date in each experimental year, the mediumearly hybrids had already peaked at the second to last sampling date.

In 2004, the highest methane yield of $9370 \,\mathrm{Nm^3} \,\mathrm{ha^{-1}}$ was attained by Doge, followed by Mikado with $7719 \,\mathrm{Nm^3} \,\mathrm{ha^{-1}}$, and Gavott with $7453 \,\mathrm{Nm^3} \,\mathrm{ha^{-1}}$. In 2005, the hybrids Mikado, PR36K67, and Flavi had similar methane yields of 8610, 8254, and 8262 $\,\mathrm{Nm^3} \,\mathrm{ha^{-1}}$, respectively. In accordance with the specific methane yield, the maximum methane hectare yields were attained at the final sampling date, except for Gavott and Flavi, which had already peaked at the second to last date.

3.4. Relationship between biomass quality parameters

The specific methane yield was not significantly (P < 0.05) related with any of the nutrients studied (Table 1). The highest correlation of r = 0.911 (P < 0.01) was observed between the concentration of fat and starch. Starch concentration was negatively correlated with both WSC (P < 0.05) and cellulose (P < 0.01) concentration. The multiple regression analysis showed that the overall regression (R = 0.55 and $R^2 = 0.30$) was statistically not significant (P < 0.05). Furthermore, none of the individual predictor variables made statistically significant contribution. Thus, specific methane yield could not be predicted at levels significantly above chance from the nutrient parameters studied.



Fig. 5. Concentration of hemicellulose (HEM), cellulose (CEL), and acid detergent lignin (ADL) in the whole-plant biomass as a function of days after sowing for maize hybrids with contrasting maturity in 2004 and 2005. Vertical bars present least significant differences (P < 0.05) for each sampling date if the ANOVA showed significant *F*-values.

4. Discussion

4.1. Chemical composition and methane yield

After female flowering, the maize ear becomes an important sink organ. The non-structural carbohydrates are translocated from the vegetative plant parts to the developing grains where they are used for starch synthesis. This close interrelationship between WSC and starch concentration is evident from Table 1 and Fig. 4. In all hybrids, the starch level started to increase at the beginning of the generative phase, while at the same time the WSC level began to decrease. Because of the late initiation of reproductive sinks in the energy maize prototypes Doge and Mikado, a relatively large portion of photosynthetic energy remained as WSC in the stover (Figs. 1 and 4).

The specific methane yields of $282-419 \text{ Nl} \text{ CH}_4 \text{ (kg VS)}^{-1}$ obtained in this study are comparable with other reports in the literature (Eder et al., 2005; Kaiser et al., 2005; Amon et al., 2007; Tatah et al., 2007). In the present study, the specific methane yields of the late maturity hybrids largely increased with sampling date, whereas the climatically adapted medium-early hybrids attained their maximum methane production at an earlier date. The same tendency was observed by Schumacher et al. (2006) in a harvest



Fig. 6. Accumulated methane production over time for anaerobically digested whole-plant samples of maize hybrids with contrasting maturity harvested at different times after sowing in 2004 and 2005. Vertical bars represent ± 1 S.E. of the mean where these exceed the size of the symbol. NI, litre at 0 °C and 1.013 bar; VS, volatile solids.

date experiment with a broad maturity spectrum of the maize hybrids.

The major organic plant compounds differ in their theoretical specific methane yield from anaerobic fermentation. The methane potential of carbohydrates, proteins, and lipids amounts to 415, 496, and 1014 Nl (kg VS)⁻¹ (Angelidaki and Sanders, 2004). Because of the high energy density of lipids, oil plants should attain particularly high specific methane yields. However, these theoretical expectations are not supported by empirical studies. In a comparison of several energy crops, Oechsner et al. (2003) obtained the lowest methane yield of 2301 CH₄ (kg VS)⁻¹ from the oil crop sunflower (*Helianthus annuus* L.). Furthermore, in a study by Amon (2006), maize produced substantially higher specific methane yields than sunflower.



Fig. 7. Specific methane yield, yield of volatile solids, and hectare yield of methane as a function of days after sowing for maize hybrids with contrasting maturity in 2004 and 2005. Vertical bars present least significant differences (P < 0.05) for each sampling date if the ANOVA showed significant *F*-values. No least significant differences are shown for methane yield because sample mixtures of the four replicates were analysed. NI and N m³, litre and cubic meter at 0 °C and 1.013 bar; VS, volatile solids.

Because of similar findings from feeding experiments with ruminant animals, a short excursus seems worthwhile at this point. Ruminant research recently has focussed on methane suppression because methane production is not only a serious source of feed energy loss, but methane as a greenhouse gas also contributes to global warming. Increasing the fat concentration by supplementing diets with long-chain polyunsaturated fatty acids (LCPUFAs) as prevalent in oil plants such as sunflower, significantly reduced methane emission of lambs (Machmüller et al., 2000) and cattle (Beauchemin et al., 2007). Medium-chain fatty acids (MCFAs) too are effective in reducing ruminant methanogenesis (Dohme et al., 2000). While both MCFAs and LCPUFAs have a direct toxic effect on rumen methanogens, the LCPUFAs also indirectly reduce methane emission by inhibiting ruminant fibre degradation (Palmquist and Jenkins, 1980; Van Nevel and Demeyer, 1988; Matsumoto et al., 1991). Processes similar to those described for the rumen are not expected to be of importance in agricultural biogas plants because they mostly use maize silage as fermentation substrate. Maize silage has only a very low concentration of 2.5–3.5% fat in the dry matter. A different situation may exist in biogas plants fed with waste grease and slaughterhouse offal. It should be noted however, that the functionality of biogas plant and rumen are not directly comparable. While fat degradation in the rumen ends with the hydrolysis of triglycerides and the biohydrogenation of unsaturated fatty acids, the entire fat degradation in the biogas plant takes place in a single-stage fermenter.

In earlier fermentation studies with various biomass substrates, Klass (1984) as well as Zauner and Künzel (1986), did not find evidence for an association between chemical composition and methane yield. Klass (1984) reasoned that the same component in two substrates, such as cellulose, may not have precisely the same molecular structure and consequently may differ in degradability.

According to Eder et al. (2005), a minimum starch concentration of about 20% in the maize dry biomass is necessary to obtain high methane yields. Contrary to this assumption, in the present study satisfactory specific methane yields were already achieved at the first sampling date (Fig. 7) when virtually no starch was present in the plant dry matter (Fig. 4). Furthermore, despite lower levels of fat and protein, but higher levels of detergent fibre and even lignin, the late energy maize prototypes had similar maximal specific methane yields like the climatically adapted medium-early hybrids (Fig. 7).

4.2. Optimal harvest date for biogas production

In this study, the specific methane yield averaged across hybrids consistently increased between 124 and 180 DAS in 2004 from 311 to 369 Nl CH₄ $(kgVS)^{-1}$ and between 118 and 180 DAS in 2005 from 309 to 342 Nl CH_4 (kg VS)⁻¹ (Fig. 7). An exception was the hybrid Flavi, which at the final harvest in 2005 exhibited a substantially reduced methane production. This exception may be caused by reduced substrate degradability, because the dry matter concentration of Flavi had reached 39% at the latest sampling date. The methane hectare yields of the late energy maize prototypes Doge and Mikado in the present study increased until the final harvest date. In accordance with these findings, Oechsner et al. (2003) also observed a consistent increase of the specific methane yield towards maturity. In contrast, Amon et al. (2007) found a general decrease in the specific methane yields towards maturity in a time harvest study with a large number of early to late maturing maize hybrids in Austria. In that study, the hybrids with early and medium maturity already attained their maximum methane yield per hectare at the milk or wax ripeness stage. The late maturity hybrids on the contrary had the highest methane hectare yields at full ripeness, because the strongly increasing yield of volatile

Table 1

Correlation matrix for eight biomass quality parameters determined at different developmental stages of maize hybrids with contrasting maturity in 2004 and 2005

Parameter ^a	SMY	Protein	Fat	Starch	WSC	HEM	CEL	
Protein	-0.192							
Fat	0.104	-0.144						
Starch	0.262	-0.326	0.911**					
WSC	-0.148	-0.332	-0.520**	-0.390*				
HEM	0.034	0.272	0.473*	0.360	-0.042			
CEL	-0.032	0.545**	-0.451*	-0.528**	0.007	0.259		
Lignin	0.248	-0.538**	0.101	0.132	0.149	0.242	0.165	

Significant at *P < 0.05 and **P < 0.001.

^a SMY, specific methane yield; WSC, water-soluble carbohydrates; HEM, hemicellulose; CEL, cellulose.

solids towards maturity overcompensated the decreasing specific methane yields.

4.3. What should the ideal biogas maize look like?

The increasing use of maize as a biogas substrate raises questions concerning the morphology and chemical composition of the ideal energy maize. Degenhardt (2005) recommends using maize for biogas production that matures only slightly later (maximal 50 FAO units) than the forage maize typically grown at a given location. He stresses that breeding should aim at improving the presently low fat and protein levels because of their higher specific methane yields in comparison with carbohydrates. Landbeck and Schmidt (2005) hypothesise that new breeding approaches are essential to significantly improve the dry matter biomass yield up to $30 \text{ t} \text{ ha}^{-1}$. These authors in a special energy maize breeding program aim at increasing the vegetative biomass by delaying ear formation through the introduction of short-day genes from Latin America. The late maturity hybrids resulting from this program will certainly not have complete ear fill. Such incomplete ear development may not be essential for maximising total dry matter yield in areas of low solar irradiance and cool autumn temperatures such as the northern USA, Canada, and northern Europe, because grain development in source-limited environments exceeds the photosynthetic capacity of the stover (Coors et al., 1997). In addition, the large stem is a strong alternative sink that may compensate for the late onset of ears and prevent a negative feedback of leaf photosynthetic rate due to assimilate concentration in the leaves (Allison and Watson, 1966; Tollenaar, 1977). It has been demonstrated in the USA that the introgression of exotic germplasm can be used to elevate both yield and (via improved NDF digestibility) forage quality of adapted silage maize germplasm (Nass and Coors, 2003). The appropriateness of the breeding approach of Landbeck and Schmidt (2005) is also supported by the study of Amon et al. (2007) showing that whole-plant maize has higher methane production than corn cob mix (CCM), grain, and stover. These authors speculate that the broad spectrum of nutrients present in the whole-plant is crucial for methane production.

Herrmann and Taube (2007) presume that enhanced lodging resistance, necessary in hybrids with improved plant height and biomass yield, requires more lignocellulose in the stem and may thus reduce digestibility. However, in the present study, the energy maize prototypes Doge and Mikado, in spite of significantly greater plant height and mostly higher cellulose and lignin concentration, in no case produced lower specific methane yields than the shorter sized hybrids. This may be attributable to the fact that the complexity of the bonding within the cell-wall carbohydrate complex increases towards physiological maturity (Morrison et al., 1998), and that the stover cell-wall fraction of immature energy maize is more easily accessible to microbial fermentation.

5. Conclusions

Currently, divergent views exist among agronomists and breeders concerning the maize ideotype for biogas production. Methane production in the present study was not negatively affected by the comparatively low starch and high fibre concentration of late energy maize prototypes as compared with adapted medium-early hybrids. In addition, the energy maize prototypes produced higher methane yields per hectare than the adapted hybrids. There exists potential for further increasing the methane yield, because the energy maize prototypes do not yet take full advantage of the growing season due to their chilling sensitivity.

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References

- Allison, J.C.S., Watson, D.J., 1966. The production and distribution of dry matter in maize after flowering. Ann. Bot. 30, 365–381.
- Amon, T., 2006. Optimierung der Methanerzeugung aus Energiepflanzen mit dem Methanenergiewertsystem. In: Berichte aus Energie- und Umweltforschung 80/2006. Austrian Federal Ministry of Transport, Innovation and Technology, Wien.
- Amon, T., Amon, B., Kryvoruchko, V., Zollitsch, W., Mayer, K., Gruber, L., 2007. Biogas production from maize and dairy cattle manure—influence of biomass composition on the methane yield. Agric. Ecosyst. Environ. 118, 173–182.
- Anex, R.P., Lynd, L.R., Laser, M.S., Heggenstaller, A.H., Liebman, M., 2007. Potential for enhanced nutrient cycling through coupling of agricultural and bioenergy systems. Crop Sci. 47, 1327–1355.
- Angelidaki, I., Sanders, W., 2004. Assessment of the anaerobic biodegradability of macropollutants. Rev. Environ. Sci. Biotechnol. 3, 117–129.
- Beauchemin, K.A., McGinn, S.M., Petit, H.V., 2007. Methane abatement strategies for cattle: lipid supplementation of diets. Can. J. Anim. Sci. 87, 431–440.
- BMJ, 2004. Gesetz f
 ür den Vorrang Erneuerbarer Energien. Available at: http://www.bundesrecht.juris.de/eeg_2004/ (verified March 17 2007).
- BSA, 2007. Beschreibende Sortenliste für Getreide, Mais, Ölfrüchte, Leguminosen (großkörnig), Hackfrüchte (außer Kartoffeln). Deutscher Landwirtschaftsverlag, Hannover, Germany.
- Coors, J.G., Albrecht, K.A., Bures, E.A., 1997. Ear-fill effects on yield and quality of silage corn. Crop Sci. 37, 243–247.
- Degenhardt, H., 2005. Optimierung des Biogasertrages durch angepasste Maissorten und richtiges Anbaumanagement. CD-ROM computer file. In: Proceedings of the First International Energy Farming Congress, Papenburg, Germany, March 2–4 2005. Kompetenzzentrum Nachwachsende Rohstoffe, Werlte, Germany.
- Dohme, F., Machmüller, A., Wasserfallen, A., Kreuzer, M., 2000. Comparative efficiency of various fats rich in medium-chain fatty acids to suppress ruminal methanogenesis as measured with RUSITEC. Can. J. Anim. Sci. 80, 473–482.
- Eder, J., Papst, C., Eder, B., Krützfeldt, B., Oechsner, H., Mukengle, M., 2005. Aktuelle Ergebnisse aus dem Energiepflanzenanbau–Leistungspotenziale, Pflanzenbau und Fruchtfolgen. In: Proceedings of the First Einbecker Energiepflanzen Kolloquium, December 7–8 2005. KWS Saat AG, Einbeck, Germany.
- FAO, 1997. FAO/UNESCO Soil Map of the World. Revised legend, with corrections and updates. World Soil Resources Report 60, FAO, Rome. Reprinted with updates as Technical Paper 20, ISRIC, Wageningen, The Netherlands.
- Goering, H.K., van Soest, P.J., 1970. Forage fiber analysis. Agricultural Handbook, vol. 379. USDA-ARS, U.S. Gov. Print. Office, Washington, DC.
- Gömann, H., Kreins, P., Osterburg, B., Breuer, T., 2007. Nutzungskonkurrenzen durch die Förderung von Biogas und anderen Energieträgern. Agrarspectrum 40, 135–150.
- Herrmann, A., Taube, F., 2006. Die energetische Nutzung von Mais in Biogasanlagen—Hinkt die Forschung der Praxis hinterher? Berichte über Landwirtschaft 84, 165–197.
- Herrmann, A., Taube, F., 2007. Masse oder Verdaulichkeit? Verlagsbeilage Saatgut-Magazin der DLG Mitteilungen 1, 2–3.
- Kaiser, F., Schlattmann, M., Gronauer, A., 2005. Methane yield of various energy crops tests at laboratory scale and transferability to full-scale application. In: Proceedings of the Seventh International Conference on Construction, Technology, and Environment in Farm Animal Husbandry, Braunschweig, Germany, March 2–3 2005, pp. 355–360 (in German, with English abstract).
- Klass, D.L., 1984. Methane from anaerobic fermentation. Science 223, 1021-1028.
- Landbeck, M., Schmidt, W., 2005. Energy maize—goals, strategies and first breeding successes. CD-ROM computer file. In: Proceedings of the First International Energy Farming Congress, Papenburg, Germany, March 2–4 2005. Kompetenzzentrum Nachwachsende Rohstoffe, Werlte, Germany.
- Machmüller, A., Ossowski, D.A., Kreuzer, M., 2000. Comparative evaluation of the effects of coconut oil, oilseeds and crystalline fat on methane release, digestion and energy balance in lambs. Anim. Feed Sci. Technol. 85, 41–60.
- Matsumoto, M., Kobayashi, T., Takenaka, A., Itabashi, H., 1991. Defaunation effects of medium-chain fatty acids and their derivates on goat rumen protozoa. J. Gen. Appl. Microbiol. 37, 439–445.
- Morrison, T.A., Jung, H.G., Buxton, D.R., Hatfield, R.D., 1998. Cell-wall composition of maize internodes of varying maturity. Crop Sci. 38, 455–460.
- Nass, L.L., Coors, J.G., 2003. Potential of exotic × adapted maize germplasm for silage. Maydica 48, 197–206.
- Oechsner, H., Lemmer, A., Neuberg, C., 2003. Feldfrüchte als G\u00e4rsubstrat in Biogasanlagen. Landtechnik 58, 146–147.

Palmquist, D.L., Jenkins, T.C., 1980. Fat in lactation rations. Rev. J. Dairy Sci. 63, 1–14. Schumacher, B., Böhmel, C., Oechsner, H., 2006. Welchen Energiemais wann ernten für die Biogasgewinnung. Landtechnik 61, 84–85.

Shenk, J.S., Westerhaus, M.O., 1991. Population structuring of near infrared spectra and modified partial least squares regression. Crop Sci. 31, 1548–1555.

SPSS, 1993. SPSS Base System. Release 6.0. SPSS Inc.

- Tatah, E., Gaudchau, M., Honermeier, B., 2007. The impact of maize cultivar and maturity stage on dry matter, biogas and methane gas yields. Mitt. Ges. Pflanzenbauwiss. 19, 196–197.
- Tollenaar, M., 1977. Sink-source relationships during reproductive development in maize. A review. Maydica 22, 49–75.
- Utz, H.F., 2005. PLABSTAT. A computer program for statistical analysis of plant breeding experiments, Institute of Plant Breeding, Seed Science,

and Population Genetics. Version 3A. Available at: http://www.unihohenheim.de/plantbreeding/software/plabstat/plabstat_manual_eng.pdf (verified March 17 2007).

- Van Nevel, C.J., Demeyer, D.I., 1988. Manipulation of rumen fermentation. In: Hobson, P.N. (Ed.), The Rumen Microbial Ecosystem. Elsevier Applied Science, London, pp. 387–443.
- Weiland, P., 2006. Biomass digestion in agriculture: a successful pathway for the energy production and waste treatment in Germany. Eng. Life Sci. 6, 302–309.
- Weiland, P., 2007. Biogas—Stand und Perspektiven der Erzeugung und Nutzung in Deutschland. Agrarspectrum 40, 111–122.
- Zauner, E., Künzel, U., 1986. Methane production from ensilaged plant material. Biomass 10, 207–223.