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Correcting the Dry Matter Content of Maize Silages as a Substrate for Biogas Production

During the process of determining DM content in silages, volatile compounds (fermentation acids and alcohols) are lost. Therefore, the DM content measured in the conventional way has to be corrected afterwards. If that is not done correctly or precisely enough, calculations on nutrient contents, as well as specific biogas yields will be false, causing experimental data to be misleading. A sufficiently exact calculation of the volatile compounds is only possible with a full chemical analysis of all the fermentation acids and alcohols contained in the silages. In order to apply the analysis results from maize silages, an improved equation for DM correction is recommended here.

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Keywords

Biogas, maize silage, dry matter, correction for volatile compounds

The need of correction of dry matter (DM) content of silages for the loss of volatile compounds during drying has been used for a long time in feed analysis. However, this procedure has not been common in the evaluation of silages, used as substrate for biogas production. In the VDI-guideline 4630 "Fermentation of Organic Materials" [3], which was published in 2005, the remark is given that the content of organic dry matter determined in the conventional way and used without consideration of the content of volatile compounds "…constitutes a falsified reference variable with regard to the determined biogas potential…". But this VDI-guideline [3] does not offer sufficiently exact recommendations for complete determination of these losses.

Recent experimental data published by Mukengele and Oechsner [2] showed that the often reported apparent increase of the biogas yield in silage, compared to green forage which it was made from, can mainly be explained by missing or incomplete correction of the DM content of silage. Some experimental results, which described an increase of the biogas yield as a consequence of the use of certain silage additives, might also be explained in a similar way.

The authors [2] used equations for the correction of DM content given by Weissbach and Kuhla [5]. Those are based on experimental data previously published by Berg and Weissbach [1, 4]. However, the measure of volatility of individual alcohols could not be determined in these investigations, due to a lack of appropriate analytical methods for separation (gas chromatography).

Special bacterial silage inoculants have recently been recommended for improving aerobic stability of maize silages, in particular of those intended to be used in biogas production. These silage additives modify the ensiling fermentation pattern. Beside higher acetic acid concentrations, treated silages also contain higher levels of 1,2-propanediole than untreated silages. This study is aimed at elucidating the volatility of alcohols (especially such with two hydroxyl groups) which are formed in silage, and at proposing an improved equation for the correction of DM content of maize silage.

Materials and methods

In total 117 samples of maize silages were taken from farm silos and analysed. All silages had been stored in silos for at least six months. Silages were analysed for all potentially volatile fermentation acids and alcohols as well as for pH. DM content was determined by the official German method used in feed evaluation. According to this method, samples are subjected to preliminary drying at 60…65 °C to constant weight and subsequent final drying at 105 °C for three hours.

Table 1: Concentration for potentially volatile fermentation products in maize silage (n = 117)

	Content (g kg^{-1} FM) Mean	Range	Standard deviation	Frequency of occurence* %
Acids				
Acetic acid	9.98	2.62 …19.16	3.40	100
Propionic acid	0.28	0.05 … 1.74	0.33	100
Isobutyric acid	0.01	0 … 0.15	0.03	16
Butyric acid	0.09	0 … 1.24	0.15	62
Isovaleric acid	0.06	0 … 0.16	0.04	78
Valeric acid	0.01	0 … 0.07	0.02	9
Caproic acid	0.01	0 … 0.13	0.03	21
Lactic acid	15.20	3.76 …26.01	3.75	100
Alcohols				
Ethanol	5.80	0.10 …13.16	3.21	100
Propanol	0.25	0 … 3.24	0.52	50
Butanol	0	0 … 0.08		1
1,2-Propanediol	0.70	0 … 6.83	1.07	92
2,3-Butanediol	0.08	0 … 0.49	0.10	52

* samples with ≥ 0.05 g kg^{-1}FM

	Acetic acid	Propionic acid	Butyric acid**	Lactic acid
Content in silage (g kg^{-1} FM)				
Mean	13.7	0.4	0.1	12.9
Range	8.2…19.2	0.1…1.0	0…0.5	9.5…20.5
Standard deviation	2.8	0.3	0.1	2.6
Content in drying residue (g kg^{-1} FM)				
Mean	0.63	0.02	n. d. *	11.9
Range	0.36…0.92	0…0.05		8.7…17.3
Standard deviation	0.16	0.02		2.3
Volatilization (%)				
Mean	95	97	100	8
Range	95…96	91…100		3…16
Standard deviation	0.4	3.3		3.8

* not detectable; ** butyric acid and higher homologues

Table 2: Volatilization percentage of fermentation acids from maize silages (n = 20)

	Ethanol	Propanol	1,2-Propanediol	2,3-Butanediol
Content in silage (g kg^{-1} FM)				
Mean	5.7	0.4	2.6	0.1
Range	2.9…9.3	0…1.6	1.5…6.8	0…0.4
Standard deviation	2.2	0.4	1.4	0.1
Content in drying residue (g kg^{-1} FM)				
Mean	0.02	n. d.*	0.61	n. d.*
Range	0…0.04		0.20…1.82	
Standard deviation	0.02		0.42	
Volatilization (%)				
Mean	100	100	77	100
Range	99…100		70…86	
Standard deviation	0.3		5.0	

* not detectable

Table 3: Volatilization percentage of alcohols from maize silages (n = 20)

From the farm silage pool, 20 samples were selected, which had relatively high contents of 1,2-propanediol and 2,3-butanediol, respectively. In those silages, all potentially volatile fermentation products were measured also in the residues after final drying (three hours at 105 °C). Subsequently, volatility was calculated from the difference between the contents of each fermentation product in the fresh and in the dried samples.

Results and discussion

All silages were of good fermentation quality. DM content ranged between 224 and 492 g kg^{-1} (mean = 337 g kg^{-1}). Almost all silages had a pH between 3.5 and 4.0 (mean = 3.8). *Table 1* summarizes means and parameters of variability for all individual potentially volatile compounds which were detected in maize silages.

Acetic acid was determined to represent the vast proportion of all short chain fatty acids, which are know to be highly volatile. However, its content varied extremely. Propionic acid was also detected in all silages, but at markedly lower concentrations. Butyric acid and other higher homologues (valeric and caproic acids) were found in traces only. Lactic acid, which is known to be less volatile, was measured at typical levels but showed unexpected high variability. Alcohols were mainly composed of ethanol. Its content was also extremely variable. Other simple alcohols (propanol and butanol) occurred in very low concentrations and were detected at low frequency. This applies also for 2,3-butanediol, which was found in traces only. On the contrary, 1,2-propanediol was detected in more than 90 % of all maize silages, and in some at substantial concentration.

The analytical data of the 20 selected silages and their drying residues are shown in *Tables 2 and 3*. In order to enable the comparison between fresh matter (FM) and drying residue, all data are expressed in g per kg FM. The results on volatility of acids are in good agreement with earlier studies [1, 4]. Acetic acid was found to be volatile at 95 %. This value can be considered as practically constant and can be used for all other short-chain fatty acids, produced in maize silage with its typical low pH. Under the drying conditions described above, the mean volatility of lactic acid was found to be 8 %, which agrees with earlier findings [1, 4]. The assumption that all simple alcohols are fully volatile [5] could also be confirmed.

For the first time it was possible to determine the volatility of 1,2-propanediol. The average volatility of this compound was found to be 77 %. It varied in a relatively small range and proved to be unaffected by the concentration of this alcohol in silages. The concentrations of 2,3-butanediol were too small for determining its volatility.

In summary, it can be stated that the percentages of volatilization of the individual fermentation products in maize silage – in contrast to their concentrations – are nearly constant at defined drying conditions. Therefore, the mean percentage of volatilization of the individual compounds can be generalized and used for correction of DM content on the basis of analysed fermentation pattern of maize silage. The validity of percentages of volatilization determined here, however, strictly depends on drying conditions as described in this study.

Conclusions and recommendations

Maize silages contain substantial amounts of volatile organic compounds, which have gas forming potential and must not be neglected in measuring the specific gas yield potential. Concentrations of these volatile acids and alcohols in silages are extremely variable between silages. Therefore, a complete analysis for fermentation products in silages is absolutely necessary if the specific gas yield is determined by fermentation tests. Simplified methods of DM correction in silages based on average concentrations of volatile compounds, which are only influenced by the DM level, are inappropriate for this purpose.

The following equation for calculating the corrected DM content (DMc) of maize silages based on the non-corrected DM content (DMn) measured by oven drying is recommended:

$$DM_c = DM_n + 0.95\ FA + 0.08\ LA + 0.77\ PD + 1.00\ OA\ [\text{g kg}^{-1}\ \text{FM}]$$

where is:

FA = fatty acids (C2 … C6)
LA = lactic acid
PD = 1,2-propanediol
OA = other alcohols (C2 … C4, including 2,3-butanediol)

All values are to be put into the equation in the dimension g per kg fresh weight.

The equation is valid only for defined drying condition (preliminary drying at 60…65 °C; final drying three hours at 105 °C).

As a consequence of DM correction, all other analytical parameters, which are expressed on DM basis, have also to be corrected. Those which are directly measured in the dried sample and usually expressed as percent of DM_n (e. g. crude ash) must be multiplied with the quotient DM_n/DM_c. Difference fractions (e. g. organic matter) have to be calculated once more by using the values expressed as percent of DM_c.

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