

## Influence of Silage Additives on Methane Yield and Economic Performance of Selected Feedstock

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### ABSTRACT

Ensiling is an appropriate way of preserving feedstock for anaerobic digestion. Biological and chemical silage additives were used to improve silage quality and to prevent silage losses due to aerobic instability. Lab-scale experiments were conducted using alfalfa, grass and maize. Silages without additives and with chemical and biological additives were compared to the fresh material as well. The effect of silage additives was investigated using batch anaerobic digestion tests and comparing the results on an organic dry matter basis as well as on a hectare basis. In an economic assessment the costs of silage additives were compared to the additional proceeds which can be achieved from improving digestibility and preventing silage losses. In many cases the costs of additive application exceeds the additional income from surplus methane formation. Nevertheless, in case of aerobic instability of opened silos the additional income can over-compensate the costs of the application of chemical additives. There seems to be some evidence that there is a correlation between organic acid content of silages and methane yield on organic dry matter basis.

**Keywords:** maize, alfalfa, grass, anaerobic digestion, methane hectare yield, silage losses, acetic acid fermentation

### 1. INTRODUCTION

Silage additives are applied to enhance ensiling velocity and to prevent silage losses during ensiling, storage and after the opening of the silo. Common silage additives are either based on their chemical activity – propionate, benzoate, nitrite or hexa-methylene tetra-amine - well known as preservatives or on the biological activity of propionic and lactic acid forming bacteria. The latter are distinguished in homo-fermentative and hetero-fermentative species (Woolford and Pahlow, 1997). Homo-fermentative bacteria convert C6-sugars solely into lactic acid whereas hetero-fermentative species produce lactic acid and carbon dioxide at equal shares as well as traces of acetic acid or ethanol. Well-known species of the homo-fermentative bacteria are *Lactobacillus plantarum*, *Pediococcus acidilactici*, *P. pentosaceus*, *Enterococcus faecium*, *L. delbrueckii*, *L.casei*, and *L. rhamnosus*. Commonly available hetero-fermentative bacteria are *L. brevis* and *L. buchneri* (Woolford and Pahlow, 1997).

Up to now silages have been used exclusively as animal feed. Only recently and due to the aim of providing energy from biogenic resources crops are increasingly used as feedstock for anaerobic digestion. Hence, it becomes necessary to preserve these crops for year round usage

after harvest. It seems to be obvious that ensiling is the best way to achieve this goal. In a first instance the same rules applying for the quality of animal feed silages apply for biogas silages as well: high lactic acid concentration and thus, low pH-value, prevention of infestations of chlostridae, and entero bacteria, prevention of silage losses, aerobic stability after opening of the silo, etc. After opening of the silo numerous microbes can lead to an increase in pH-value and temperature of the silage as well as to a reduction of free available sugars. Loss of carbon dioxide and temperature increase determine net energy loss (Driehuis and Oude Elferink, 2000).

If silages are used as feedstock for anaerobic digestion the question of losses might be answered different to the situation in animal feeding. Dry matter losses due to the formation of other organic acids are not comparable to losses of digestible material. The loss of dry matter might be compensated by an improved digestibility of the crops. Hence, it becomes important to compare methane yields on a hectare basis as well.

Silages which turned out to be fermented to acetic acid stage rather than to the lactic acid one and hence, are inappropriate for animal feed are still a good or even very good feedstock for anaerobic digestion. It can further be concluded that high acetic acid concentration might even enhance methane formation as acetic acid is a precursor of methane (Banemann *et al.*, 2007).

There are a number of investigations which worked on the difference in methane yield of silages and fresh material. Only a few reports considered the effects of silage additives, some of these with a strong focus on grass as a specific crop, (Herrmann *et al.*, 2007; Herrmann *et al.*, 2008; Idler *et al.*, 2007; Knický, 2005; Lehtomäki, 2006; Neureiter *et al.*, 2005; Pakarinen *et al.*, 2008; Plöchl and Heiermann, 2006). And there are no reports which assess the economic benefit or loss of the application of silage additives if the silages are used as feedstock for anaerobic digestion.

In order to assess effects of silage additives on methane yield and economic performance of silages in anaerobic digestion lab-scale experiments were conducted with maize, alfalfa and grass treated with a selection of silage additives chemical as well as biological ones.

## 2. MATERIALS AND METHODS

### 2.1 Crops and ensiling

The investigations were conducted with alfalfa (*Medicago sativa*), grass (mixed stand), and maize (*Zea mais* var. Aurelia) (Table 1). The grass stand was a mixed stand with major species *Lolium perenne* minor species were *Alopecurus pratensis*, *A. geniculatus*, *Phleum pratense*, *Poa pratensis*, *P. trivialis*, and *Festuca pratensis*. The material was harvested in northwest Germany in 2006. At the laboratories of LWK Niedersachsen<sup>1</sup> the fresh material was chopped to a length of 30 to 40 mm and in the case of maize to 8 mm in average. The chopped material was analysed und ensiled using different silage additives and for control without additive. In addition, a share of fresh chopped material was stored at -18° C. Ensiling was carried out in lab-scale silo of 1.5 litres volume with three replicates (Figure 1). Silos were locked with glass lids, using a rubber seal and a metal spring to ensure air impermeability and to achieve anaerobic conditions in the silos. They were kept shut for 90 days and stored at 20° C, in case of the grass the period was extended to 180 days. In order to prove gas-tightness of the silos they were weighed regularly. After opening the silos were again weighed to measure anaerobic gas losses. Afterwards the

<sup>1</sup> LWK Niedersachsen (Chamber of Agriculture Lower-Saxony, Oldenburg) is a state agency for investigation and extension service in agriculture of the State of Lower Saxony, Germany

material was analysed for its physical and chemical properties and stored at  $-18^{\circ}\text{C}$  for further investigation.

Table 1: Properties of fresh material (harvested in 2006)

Parameter		alfalfa	grass	maize
Dry matter	[% FM]	26.8	24.2	29.5
Organic dry matter	[% DM]	79.8	89.9	96.2
Sugars	[% DM]	1.6	14.3	9.2
Crude protein	[% DM]	17.5	13.6	6.9
Crude fibre	[% DM]	28.1	23.4	19.3
Starch	[% DM]	n/a	n/a	24.8
Nitrate	$[\text{mg}\cdot\text{kg}_{\text{DM}}^{-1}]$	800	912	n/a

n/a = not available



Figure 1: Lab-scale silos

Silage additives used in this investigation are based on biological agents, homo-fermentative as well as hetero-fermentative bacteria, and on chemical agents. Both commercially available products as well as products recently developed were applied (Table 2).

Table 2: Silage additives properties, application recommendations and prices

Silage additive	principal agent	principal effect	crop applied to	application	price
Kofasil <sup>®</sup> liquid	sodium nitrite, hexa-methylene tetra-amine	inhibition of enterobacteria and chlostridia	alfalfa, grass	3.0 l·t <sub>FM</sub> <sup>-1</sup>	1.35 €l <sup>-1</sup>
Mais Kofasil <sup>®</sup> liquid	sodium benzoate, sodium propionate	inhibition of moulds and yeasts	maize	4.0 l·t <sub>FM</sub> <sup>-1</sup>	1.50 €l <sup>-1</sup>
Kofasil <sup>®</sup> life	homo-fermentative lactic acid bacteria, propionic acid bacteria	support of lactic acid formation, propionic acid as preservative	alfalfa	6.7 g·t <sub>FM</sub> <sup>-1</sup>	135 €kg <sup>-1</sup>
Kofasil <sup>®</sup> lac	homo-fermentative lactic acid bacteria	support of lactic acid formation	maize	5.0 g·t <sub>FM</sub> <sup>-1</sup>	180 €kg <sup>-1</sup>
Kofasil <sup>®</sup> stabil	sodium benzoate, potassium sorbate	inhibition of moulds and yeasts	maize	2.0 l·t <sub>FM</sub> <sup>-1</sup>	2.50 €l <sup>-1</sup>
MSB 1	homo-fermentative lactic acid bacteria	support of lactic acid formation	grass	n/a	n/a
MSB 2	homo-fermentative lactic acid bacteria	support of lactic acid formation	grass	n/a	n/a

n/a = not available

Each variant – crop x silage additive – as well as control and fresh material were investigated in three replicates (Table 2).

## 2.2 Aerobic stability of silages

The silages of alfalfa and maize were also investigated for their aerobic stability. According to (Honig, 1986) aerobic stability was assessed. The investigation is conducted at 25 °C. An increase of silage temperature of 3°C above ambient temperature marks the moment of aerobic instability.

## 2.3 Anaerobic digestion batch tests

Methane formation potential of crops was determined in batch-tests. Therefore, 1000 ml of inoculum diluted with additional 500 ml water, for each experiment, was given to 2 litre polyethylene-flasks. These were kept at 35° C (mesophilic conditions) in a climatic chamber with air circulation for 1 day. After acclimatisation material to be investigated was added and flasks were stored for a period of approximately 35 days at mesophilic conditions. The flasks were locked with a rubber plug and attached to a gas bag via a PVC tube. The gas bag could be detached at a stop-valve and attached to a gas meter in order to determine the gas volume formed. The gas was further collected and if volume exceeded 400 ml the gas was analysed for methane, carbon dioxide and hydrogen sulphide content. Biogas was measured from flasks containing only inoculum in three replicates as control. Methane formation was finally determined from biogas formation and methane content of biogas, corrected by the value of

methane formed in control and related to organic dry matter (ODM) of material to be investigated.

## 2.4 Analytical parameters and methods

Fresh material and silages were analysed for dry matter (DM) by drying at 105° C. Out of dry matter crude protein, crude fibre, sugars and ash content were determined by near infrared spectroscopy (NIRS). Ash was, additionally, determined by heating up to 550° C. Dry matter minus ash gives organic dry matter. Buffer capacity was determined after elutriating the material in water and titration with 0.1 n lactic acid until pH drops below 4.0. Nitrate was analysed using the filtrate after extracting the dry and ground material with calcium chloride by continuous-flow photometry. Organic acids were determined from membrane filtered aqueous extract by ion chromatography. Ammonium nitrogen was measured potentiometric with gas-sensitive ammonium electrode from sodium alkaline aqueous extraction. The pH values of the materials were measured with a pH-electrode from a calcium chloride suspension.

Dry matter and organic dry matter values used throughout this paper are modifications of the determined values (dv) by regarding the loss of volatile organic compounds during dry matter determination (Weissbach and Kuhla, 1995):

$$\begin{array}{ll} \text{for maize silages} & DM = 2.22 + 0.960DM_{dv} \\ \text{for other silages} & DM = 2.08 + 0.975DM_{dv} \end{array}$$

## 2.5 Methane yield per unit area

In order to assess the net effect of the silage additives tested it is necessary to balance the methane yield on a hectare basis ( $M_{ha}$ ). These are obtained from combining silage losses both in closed silos and during aerobic exposition ( $L_{DM}$ ), methane yield per fresh matter ( $M_{FM}$ ), and crop yields ( $Y_{FM,ha}$ ):

$$M_{ha} = Y_{FM,ha} \cdot \frac{M_{FM}}{100} \cdot (100 - L_{DM} [\%])$$

The average crop yields (maize 41  $t_{FM} \cdot ha^{-1}$ ; alfalfa and grass per cut 12  $t_{FM} \cdot ha^{-1}$ ) are based on medium soil conditions and were taken from Hanff *et al.* (2005).

## 2.6 Economic assessment

The economic assessment is based on the assumption of an average biogas plant where biogas is converted to electricity and heat via a combined heat and power unit (CHP). The CHP is assumed to be of 500 kW electric capacity with an electrical conversion efficiency of 0.36 and thermal conversion efficiency of 0.42. Further it is assumed that the CHP runs for 8000 hours per year. According to German legislation for renewable electricity there is a difference in fee for electricity if excess heat is consumed by external processes. Therefore two variations are distinguished: (A) no use of excess heat and (B) 80 % of excess heat can be used. Considering a start of operation in 2006 and according to the German Act of Renewable Energies (BMU, 2004) variation A leads to a fee of 0.156 €/per kilowatt hour (kWh) fed to the electricity grid. In case of variation B the fee achieved equals 0.172 €/kWh<sup>-1</sup>.

The costs of applying silage additives are oriented to the application recommendations of the manufacturers and the average of the range of current market prices (Table 2).

### 3. RESULTS

#### 3.1 Alfalfa

The fresh material was only moderately wilted (DM is 26.8 % of FM) and relatively poor in sugars and nitrate. The low sugar content of 1.6 % of DM as well as a high crude protein content of 17.5 % DM indicate for a minimum dry matter content of 43 % to achieve a butyric acid free fermentation (Weissbach, 2002). Neither the natural covering with lactic acid bacteria nor the additives applied were able to reduce pH to sufficient values inhibiting the development of spoilage organisms. In terms of feed quality these silages were of lowest quality containing large amounts of acetic acid, butyric acid and ammonium-N whereas lactic acid was completely decomposed (Table 3). The loss of dry matter ranged between 6.1 % (Kofasil<sup>®</sup> liquid) and 11.4 % (control) compared to the fresh material (Figure 2). All alfalfa silages remained aerobic stable after opening of the silo, which is due to the low sugar content and the high concentrations of acetic acid and butyric acids.

Table 3: Properties of alfalfa silages after 90 days storage

Parameter [ $\text{g}\cdot\text{kg}_{\text{FM}}^{-1}$ ]	control	Kofasil <sup>®</sup> liquid	Kofasil <sup>®</sup> life
pH	5.63	4.89	5.52
Dry matter	256	273	275
Lactic acid	n/d	12.01	4.40
Acetic acid	11.49	9.36	12.93
Butyric acid	9.27	0.11	0.00
Methanol	1.05	0.85	1.05
Ethanol	1.36	0.38	2.89
Ammonium-N [% total-N]	24.6	12.5	19.3

n/d = not detectable

Methane yields<sup>2</sup> on organic dry matter basis of alfalfa silages ranged from 201.5  $\text{m}_\text{N}^3\cdot\text{t}_{\text{ODM}}^{-1}$  (Kofasil<sup>®</sup> life) to 226.4  $\text{m}_\text{N}^3\cdot\text{t}_{\text{ODM}}^{-1}$  (control). The methane yield of the non-ensiled material lay in between this range with 214.3  $\text{m}_\text{N}^3\cdot\text{t}_{\text{ODM}}^{-1}$ . The methane content of all alfalfa tests ranged from 58.5 % to 61.1 % (Figure 3).

<sup>2</sup> All methane values are given in standard  $\text{m}_\text{N}^3$  which refer to standardised conditions of 0° C air temperature, 1013 hPa air pressure and 0 % relative humidity

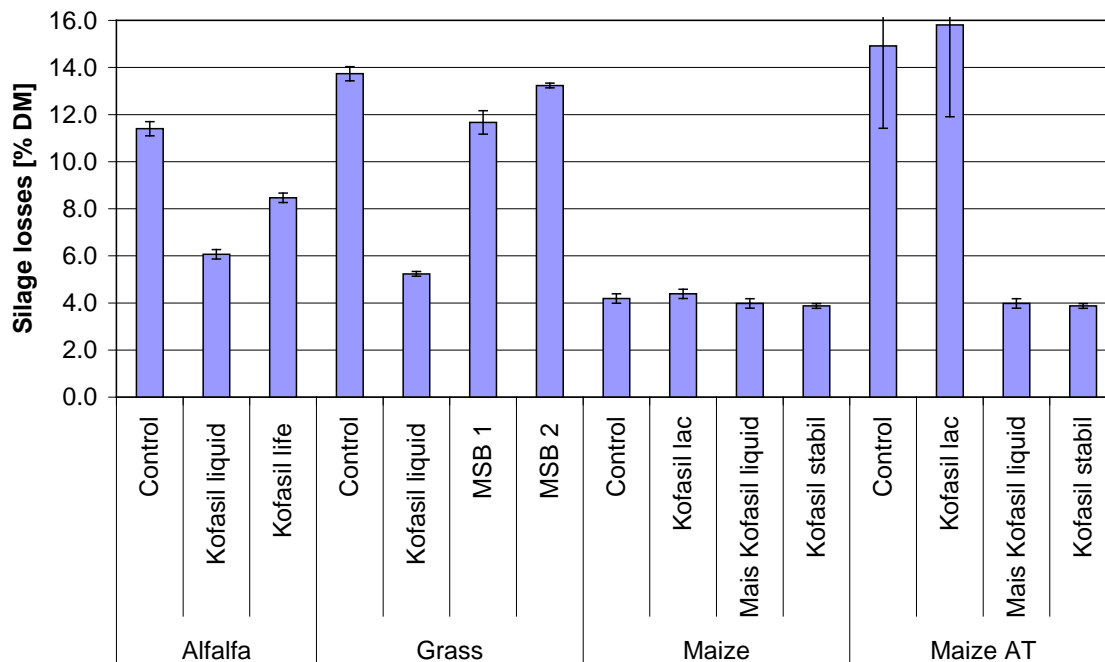


Figure 2: Dry matter losses during silage period and in case of maize after aerobic treatment (Maize AT) including losses due to re-heating after opening of the silo.

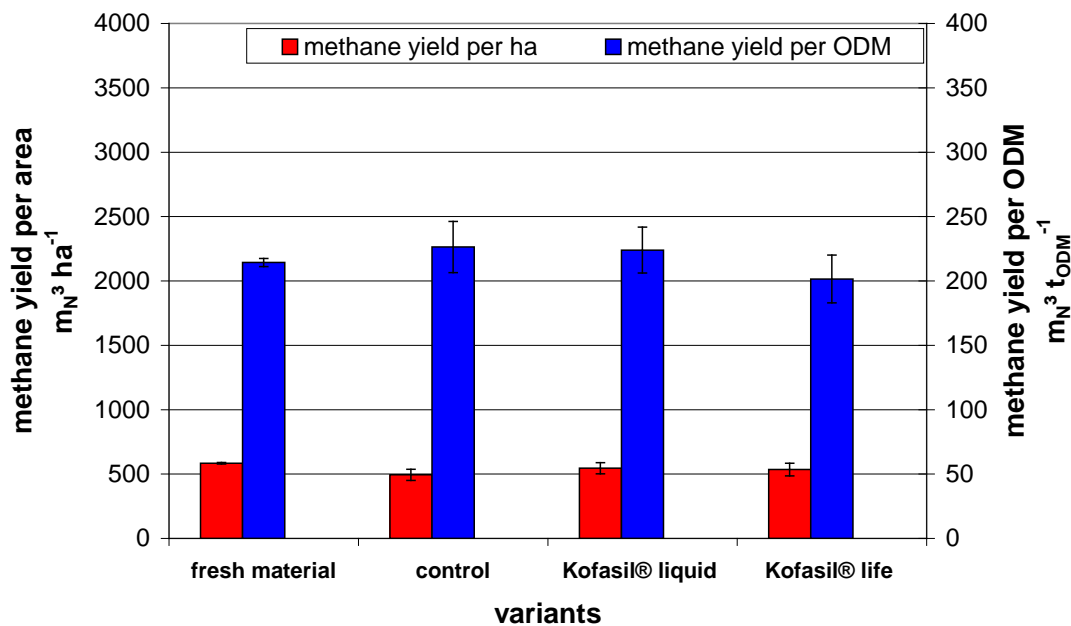


Figure 3: Methane yields on ODM basis and on hectare basis of alfalfa, fresh material and silages

The methane yields on hectare basis modified this picture as silage losses and different dry matter contents compensated lower methane yields on organic dry matter basis (Figure 3). The non-ensiled material had the largest hectare yield with  $584.5 m_N^3 \cdot ha^{-1}$ , the control the smallest



with  $494.1 \text{ m}_N^3 \cdot \text{ha}^{-1}$ . Both silages with additives showed medium values of  $545.3 \text{ m}_N^3 \cdot \text{ha}^{-1}$  and  $535.4 \text{ m}_N^3 \cdot \text{ha}^{-1}$ , respectively, i.e. smaller losses and higher methane hectare yields compared to the control and thus, proceeds could be increased. Nevertheless, the high costs of the chemical additive could not be compensated by this additional income. In contrast, the cost of the biological additive was exceeded by the proceeds in the order of 100 to 150 % (Figure 4).

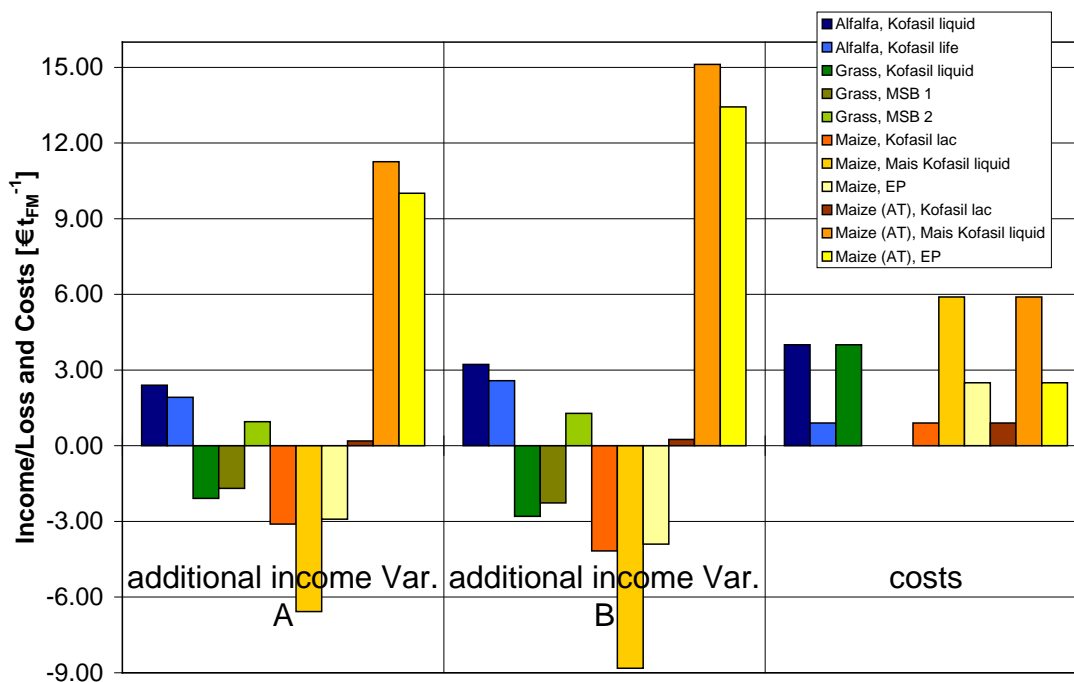


Figure 4: Additional income compared to control (distinguishing variation A without selling heat and variation B with selling heat) and costs for the application of silage additives.

### 3.2 Grass

The fresh material was only moderately wilted, but had considerable high sugar contents. Although a good fermentability was expected the silages, with exception of the one Kofasil® liquid added, showed relatively high acetic acid concentrations after 180 days of storage (Table 4). The high pH values indicate that lactic acid was degraded in favour of acetic acid. High acetic acid concentrations, degraded lactic acid and low butyric acid values indicate clostridia as the main spoilage organism. Clostridia produce acetic acid instead of butyric acid if there are sufficient nitrate levels.

Silage losses of control and of these applied with lactic acid bacteria amounted to 11.7 % to 13.7 % of the original dry matter. The silage treated with the chemical additive had moderate losses of 5.2 % (Figure 2).



Table 4: Properties of grass silages after 180 days storage

parameter [ $\text{g}\cdot\text{kg}_{\text{FM}}^{-1}$ ]	control	Kofasil® liquid	MSB 1	MSB 2
pH	5.23	4.20	4.97	5.03
dry matter	173	205	179	178
sugars	1.63	11.75	0.86	2.15
lactic acid	4.41	6.54	5.19	5.00
acetic acid	14.03	2.62	9.77	13.71
butyric acid	0.09	0.02	0.09	0.02

Methane yields on organic dry matter basis contrasted to the silage losses. The silage with the lowest dry matter loss had the lowest methane yield ( $251.9.0 \text{ m}_N^3\cdot\text{t}_{\text{ODM}}^{-1}$ ), followed by the non-ensiled material ( $267.2 \text{ m}_N^3\cdot\text{t}_{\text{ODM}}^{-1}$ ). Control and silages treated biologically had significantly higher methane yields with  $373.7 \text{ m}_N^3\cdot\text{t}_{\text{ODM}}^{-1}$ ,  $337.6 \text{ m}_N^3\cdot\text{t}_{\text{ODM}}^{-1}$ , and  $369.8 \text{ m}_N^3\cdot\text{t}_{\text{ODM}}^{-1}$ , respectively (Figure 4). Silage losses and ODM methane yields compensated each other, thus the methane hectare yields were almost equal between all variants and ranged from  $532.7 \text{ m}_N^3\cdot\text{ha}^{-1}$  to  $599.2 \text{ m}_N^3\cdot\text{ha}^{-1}$  (Figure 5).

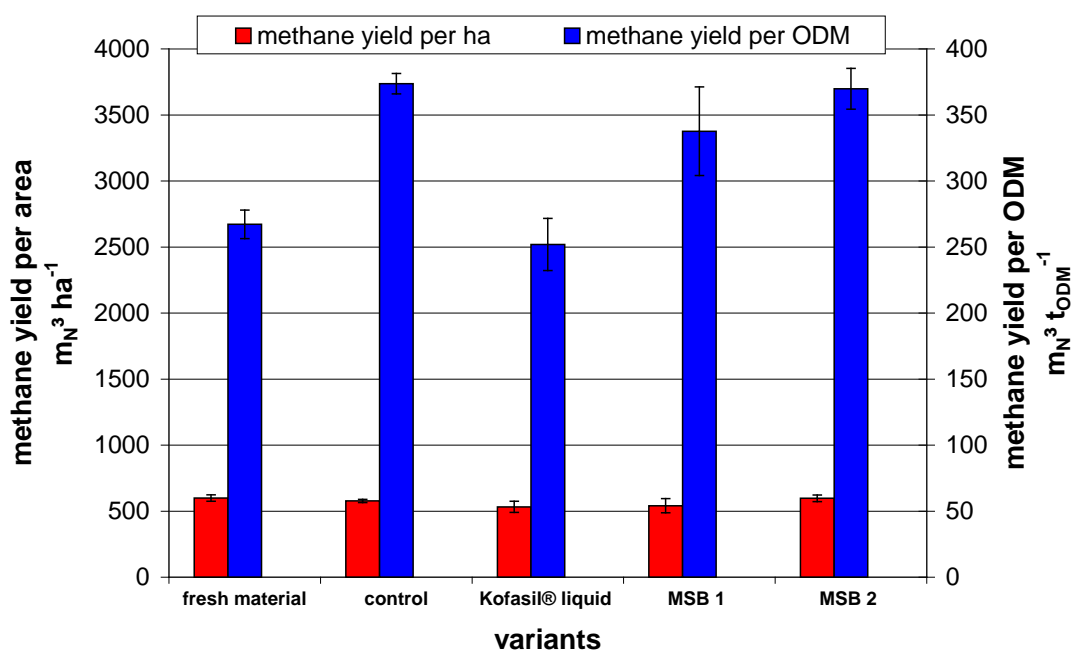


Figure 5: Methane yields on ODM basis and on hectare basis of grass, fresh material and silages. Although the differences in methane hectare yields are small, two of the treated variants had a moderately lower performance as the control and hence, could not achieve additional income neither in variation A nor in variation B. Only one variant of lactic acid bacteria treated silage could gain additional proceeds of approximately  $1 \text{ €t}_{\text{FM}}^{-1}$  (Figure 4). For the chemical treatment the actual loss compares to  $4 \text{ €t}_{\text{FM}}^{-1}$  additional costs. As for the lactic acid bacteria no prices were available it can only be approximated that it might be in the range of  $0.80$  to  $1.50 \text{ €t}_{\text{FM}}^{-1}$  and thus, might be close to the expected additional income in the best case.

### 3.3 Maize

Dry matter content of the fresh material was 29.5 % of FM, sugar content was typical for maize, although the starch content was only 24.8 % of DM, which may reflect the very dry climatic conditions of the year 2006. All silages, independent on silage additives, showed very good fermentability. Lactic acid contents ranged from 5.07 g·kg<sub>FM</sub><sup>-1</sup> to 5.89 g·kg<sub>FM</sub><sup>-1</sup> which was reflected in pH values of 3.81 to 3.83. Acetic acid contents (1.61 g·kg<sub>FM</sub><sup>-1</sup> to 2.21 g·kg<sub>FM</sub><sup>-1</sup>) were considerably low as well as ethanol contents (0.67 g·kg<sub>FM</sub><sup>-1</sup> to 0.79 g·kg<sub>FM</sub><sup>-1</sup>). Silage losses ranged from 3.9 % to 4.4 % on a dry matter basis (Table 5). This very uniform picture changed completely after exposure of the silages to aerobic conditions. Both control and silage treated with Kofasil<sup>®</sup> lac showed considerable aerobic instability and hence, large losses of material (10.7 % DM to 11.4 % DM) during 3 days after a 4 day period of apparent stability. Silages treated with Mais Kofasil<sup>®</sup> liquid and Kofasil<sup>®</sup> stabil remained aerobic stable and had no losses during the total period of 7 days (Figure 2). The control showed moderate decrease in acetic acid and increase in propionic acid during aerobic phase. The Kofasil<sup>®</sup> lac treated silage had a considerable decomposition, and hence loss, of acetic acid during that period (Table 5). The chemically treated silages showed an increase in acetic acid concentration due to the activity of acetic acid bacteria converting ethanol and lactic acid available in the silages.

Table 5: Properties of maize silages after 90 days storage and after aerobic treatment – total loss of aerobic treatment is the sum of both values

Parameter [g·kg <sub>FM</sub> <sup>-1</sup> ]	control	control	Kofasil <sup>®</sup>	Kofasil <sup>®</sup>	Kofasil <sup>®</sup>	Kofasil <sup>®</sup>	Kofasil <sup>®</sup>	Kofasil <sup>®</sup>
	AT	AT	lac	lac	Mais	Mais	stabil	stabil
				AT	liquid	liquid	AT	AT
pH	3.83		3.81		3.82		3.81	
Dry matter	268		273		274		276	
Dry matter loss [%]	4.2	10.7	4.4	11.4	4.0	0.0	3.9	0.0
Lactic acid	5.89		5.07		5.14		5.46	
Acetic acid	1.61	2.27	2.21	1.29	2.00	3.41	2.01	3.24
Propionic acid		0.38		0.05		0.22		0.05
Butyric acid	n/d		n/d		n/d		n/d	
Methanol	n/d		n/d		n/d		n/d	
Ethanol	0.67	0.12	0.79	0.14	0.74	0.64	0.77	0.59
Ammonium-N [% total-N]	6.3		5.6		4.4		4.9	

n/d = not detectable

Methane yield on organic dry matter basis of the Mais Kofasil<sup>®</sup> liquid silage was significantly lower (308.2 m<sub>N</sub><sup>3</sup>·t<sub>ODM</sub><sup>-1</sup>) than of all other variants (319.7 m<sub>N</sub><sup>3</sup>·t<sub>ODM</sub><sup>-1</sup> to 324.7 m<sub>N</sub><sup>3</sup>·t<sub>ODM</sub><sup>-1</sup>), whereas the control showed significantly the highest value (364.2 m<sub>N</sub><sup>3</sup>·t<sub>ODM</sub><sup>-1</sup>). Methane contents of the biogas ranged from 55.4 % to 56.8 %. The methane contents of the biogas from the silages after aerobic storage remained in this range, but there was a considerable change in the methane yields (Figure 6). There was a sizeable decrease in methane yield of control (281.3 m<sub>N</sub><sup>3</sup>·t<sub>ODM</sub><sup>-1</sup>) and of biologically treated variant (292.7 m<sub>N</sub><sup>3</sup>·t<sub>ODM</sub><sup>-1</sup>). The variant treated with Kofasil<sup>®</sup> stabil also decreased in ODM methane yield (308.0 m<sub>N</sub><sup>3</sup>·t<sub>ODM</sub><sup>-1</sup>) whereas there was an increase in methane yield of the second chemically treated variant (330.7 m<sub>N</sub><sup>3</sup>·t<sub>ODM</sub><sup>-1</sup>).

Looking on the silages before aerobic treatment methane yields on hectare basis reflected the picture of the ODM methane yields. In the case of the control ( $3616 \text{ m}_N^3 \cdot \text{ha}^{-1}$ ), there is compared to the fresh material ( $3558 \text{ m}_N^3 \cdot \text{ha}^{-1}$ ) even an over-compensation of the silage losses due to the high ODM methane yield (Figure 6). The losses of aerobic instability lead to significant changes of the hectare methane yield of the control ( $2643 \text{ m}_N^3 \cdot \text{ha}^{-1}$ ) and the Kofasil<sup>®</sup> lac variant ( $2657 \text{ m}_N^3 \cdot \text{ha}^{-1}$ ), whereas the Kofasil<sup>®</sup> stabil variant could almost remain its hectare yield ( $3404$  and  $3374 \text{ m}_N^3 \cdot \text{ha}^{-1}$ , respectively) and the Mais Kofasil<sup>®</sup> liquid variant ( $3136$  and  $3465 \text{ m}_N^3 \cdot \text{ha}^{-1}$ , respectively) could even enhance its hectare methane yield (Figure 6).

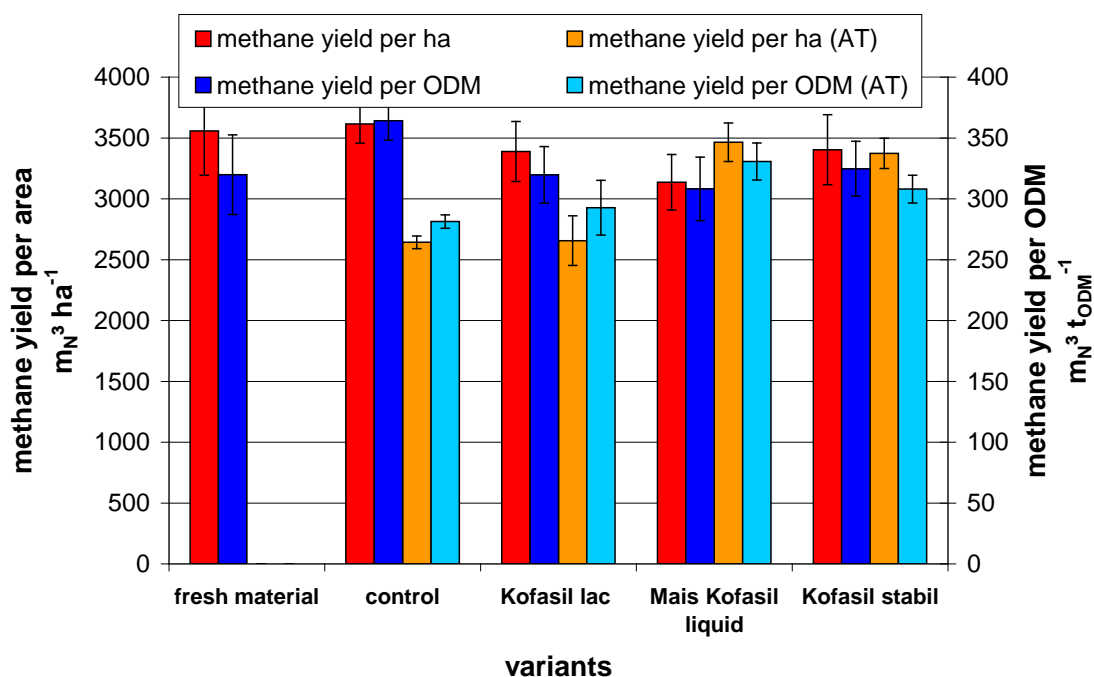


Figure 6: methane yields on ODM basis and on hectare basis of maize, fresh material and silages and of silages four days after opening of the silo (maize AT)

According to the very good performance of the control variant all treated variants decreased in income (Figure 4). If the losses due to aerobic instability are accounted there is almost no difference between control and the biologically treated variant. In contrast, the chemically stabilised variants showed a substantial increase in proceeds, which significantly exceeds the costs for silage additive application (Figure 4).

### 3.4 Methane yield and acetic acid concentration

Furthermore the question should be answered if there is a relation between acetic acid concentration and methane yield on organic dry matter basis. In Figure 7 ODM methane yield is displayed against acetic acid concentration for each variant. In the case of grass and maize after aerobic treatment (AT) there is an increase of methane yields with increasing acetic acid concentrations. E.g. methane from grass silage, which showed the strongest impact, increased from  $250 \text{ m}_N^3 \cdot \text{t}_{\text{ODM}}^{-1}$  to  $370 \text{ m}_N^3 \cdot \text{t}_{\text{ODM}}^{-1}$  while acetic acid concentration increased from  $2.6 \text{ g} \cdot \text{kg}_{\text{FM}}^{-1}$  to  $14.0 \text{ g} \cdot \text{kg}_{\text{FM}}^{-1}$ . In the case of maize before aerobic treatment this cannot be observed which might be due to the fact that both, acetic acid concentrations and methane yields, are very close

together for all variants. The alfalfa variants did also not show a clear trend. But if the ODM methane yields are compared to the total sum of acids (lactic acid, acetic acid, propionic acid, butyric acid) in the silages there is an obvious trend for all silages investigated (Figure 8).

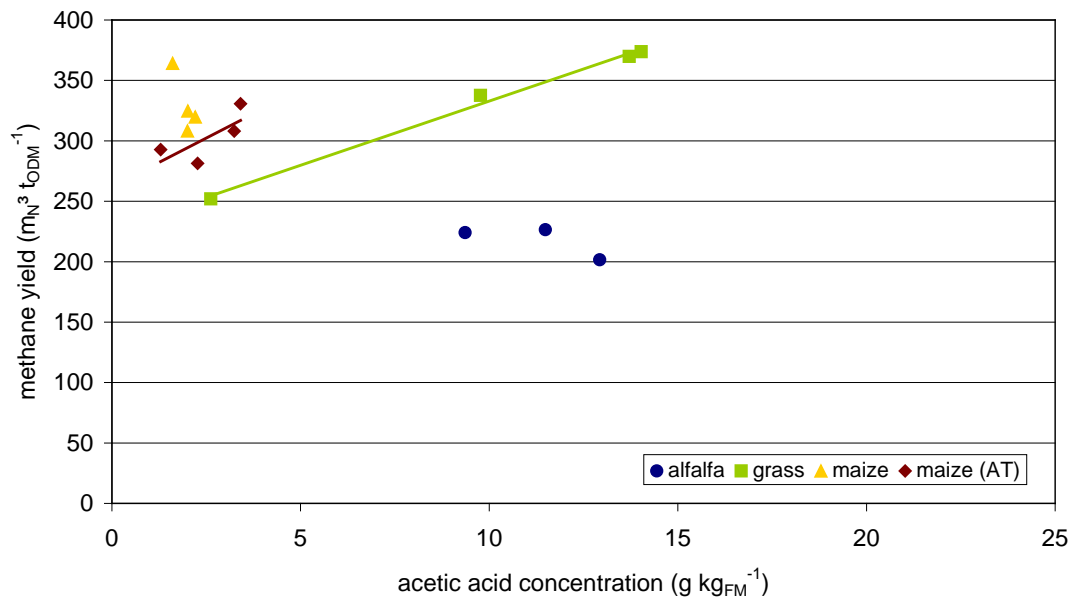


Figure 7: Relationship between acetic acid and ODM methane yield of different silages

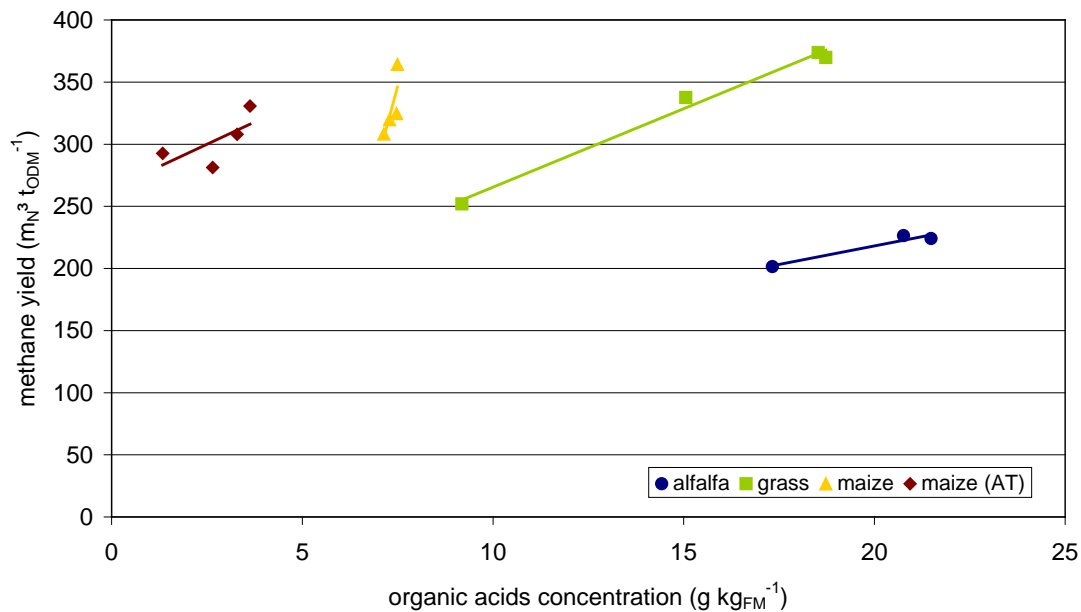


Figure 8: Relationship between sum of organic acids and ODM methane yield of different silages

#### 4. DISCUSSION

The fresh materials of alfalfa as well as of grass were not in an appropriate condition for ensiling. Content of dry matter and sugar were in both cases not sufficient to neither produce enough

lactic acid nor prevent other spoilage. Hence, the quality of the control silages was poor and considerable silage losses occurred. These losses could be decreased to a certain degree by the application of additives containing either pure lactic acid bacteria or in mixture with propionic acid bacteria. It can be assumed that these bacteria lead to an enhanced decrease in pH and thus, a more rapid inhibition of spoilage organisms. The application of the chemical additive affects directly the growth of spoilage organisms. As a consequence the losses could be decreased to values only moderately above minimum values of silage losses (Ruppel *et al.*, 1995).

Maize, in general, is very easy to ensile. Hence, silage additives will be used to prolong aerobic stability rather than to enhance silage quality. The maize, used in this experiment, was ideal for ensiling and showed minimum losses of 4 % DM, ideal pH values of 3.8 and excellent lactic acid concentration. Therefore it could not be expected that the application of silage additives would lead to any enhancements in the silage quality. But this silage quality is not a guarantee for stability under aerobic conditions. In contrast to the chemical treated silages, the control and the biological treated ones had enormous losses after the opening of the silos. The chemical additives could radically depress the development of yeasts and moulds and kept the silages stable for more than 7 days. This is longer than could be expected. Even the 4 days of stability of the control and the biological treated is noticeable compared to values obtained in an extensive series on aerobic stability (Kaiser and Piltz, 2002). Already after 3 days more than 60 % of the silages showed considerable reheating. The number of days of aerobic stability is not predictable as there are many factors enhancing the instability: compression, availability of convertible substances, dry matter content, degree of infestation with yeasts, moulds, and acetic acid bacteria, etc. The aerobic stability achieved with the application of the chemical additives will be very important in the cases where the consumption rate of the silo is too low, compaction was insufficient and diffusion into the silo becomes possible or the silo cannot be in the vicinity of the biogas plant and the feedstock has to be transported and stored under aerobic conditions for a number of days.

The methane yields on ODM basis range from 200 to 375  $\text{m}_\text{N}^3 \cdot \text{t}_{\text{ODM}}^{-1}$ , with alfalfa at the lower end and maize and grass at the higher end and compare quite well with the findings of other authors (Amon *et al.*, 2007; Amon *et al.*, 2004; Heiermann and Plöchl, 2004; Lehtomäki, 2006; Neureiter *et al.*, 2005; Oechsner *et al.*, 2003; Plöchl and Heiermann, 2006; Prochnow *et al.*, 2005). Whereas the methane yields on a hectare basis (500 to 600  $\text{m}_\text{N}^3 \cdot \text{ha}^{-1}$  for alfalfa and grass and 3000 to 3500  $\text{m}_\text{N}^3 \cdot \text{ha}^{-1}$  for maize) range at the lower end. But one has to consider that the hectare yields for alfalfa and grass are only for one cut and one can expect to usually have two to three cuts.

The findings of other authors (Herrmann *et al.*, 2007; Herrmann *et al.*, 2008; Idler *et al.*, 2007; Lehtomäki, 2006; Neureiter *et al.*, 2005) that there is, in general, an increase in ODM methane yield of ensiled material compared to fresh material is supported by the findings of this investigation. This increase in methane yields ranged from a few  $\text{m}_\text{N}^3 \cdot \text{t}_{\text{ODM}}^{-1}$  to almost 100  $\text{m}_\text{N}^3 \cdot \text{t}_{\text{ODM}}^{-1}$  and can be linked to the formation of additional organic acids.

The addition of silage additives has considerable effect on the quality of silages if the fresh material is difficult to ensile. i.e. sugar content is low, or dry matter content is high and difficult to compress. But the improved silage quality and hence increased methane yield per hectare does not compensate, in general, the cost of silage additives. This is different if the silage is prone to aerobic deterioration, as in the cases already described above. Under these circumstances silage additives can prevent aerobic reheating and hence aerobic silage losses. These silage losses can

result in decreases in methane hectare yields of  $700 \text{ m}_N^3 \cdot \text{ha}^{-1}$  or 20 % of the control. Hence, the costs for additives, ranging from 2 to 6  $\text{€t}_{\text{FM}}^{-1}$ , will be reimbursed by an additional income of 13 to 15  $\text{€t}_{\text{FM}}^{-1}$ .

The further very interesting question in the context of this investigation is whether the quality demand on silage as feedstock for biogas is comparable to the quality standard of silage as animal feed and which silage parameters influence the methane yield. In the case of the grass silage and the maize silage after aerobic treatment there is a clear relationship between acetic acid concentration of fresh matter and ODM methane yield. Although this correlation has been stated by other authors (Banemann *et al.*, 2007) it is yet not clear what is the underlying mechanism. The assumption that applying acetic acid as precursor of bio-methanation is certainly not sufficient as the amount of acetic acid formed during the process is several times larger than the amount of acetic acid applied with feedstock. Furthermore, it is recognised that the formation of acetic acid is not the bottle neck of the whole process (IWA, 2002). Not an answer but another hint that there might be a link between organic acids at all in the silage and the ODM methane yield can be seen looking on the results of alfalfa. There is no clear correlation between acetic acid concentration and ODM methane yield, but taking into consideration the relationship between the sum of all acids (lactic acid, acetic acid, propionic acid, and butyric acid concentrations in fresh matter) and the ODM methane yield there is an obvious trend. This trend could also be observed for the other silages investigated. As a consequence both high-quality silage as well as mis-fermented silage in terms of animal feed might be appropriate for biogas feedstock as long as there is a high concentration of organic acids.

## 5. CONCLUSIONS

Considering the above mentioned findings the aim of silage additives would be to prevent silage losses rather than to improve ensiling velocity and quality. This can also be clearly seen considering the methane yield on a hectare basis. Here silage additives have a real advantage preventing infestation with yeasts, moulds and other spoilage organisms. In the case of maize there is clear advantage in avoiding aerobic instability. Thus the best additive would be one that enhances the presence of organic acids and decreases the risk of aerobic losses. In this context there is also the question to be regarded whether the application of additives is economically applicable or not. The analysis of the economic assessment of this study shows clearly that in many cases the costs of additive application exceeds the additional income of surplus performance. On the other hand, the results also demonstrated that it is possible to obtain considerable economic benefits as e.g. the application of the EP. The question whether silage additives could produce improved digestability is not yet answered, although there are hints that increased concentrations of organic acids increase specific methane yields. Hence, it seems necessary to continue basic research on the effects of ensiling on the methane yield of crops and to further develop silage additives selective for the ensiling of biogas feedstock.

## 6. ACKNOWLEDGEMENTS

The experiments underlying this paper were financed by ADDCON EUROPE GmbH. The authors wish to thank Ms. Dr. Kalzendorf from the Chamber of Agriculture Lower-Saxony, Oldenburg for the preparation of the silages.

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