Andrade, Diana and Weber, Andreas

Biogas from grassland biomass: Recommendations for the optimization of the degradation process

In practice often difficulties with control and stability of the anaerobic fermentation of grassland material occur. The elevated protein content leads to high concentrations of ammonium in the reactor during biogas process. In this study, the substrate mixtures with grassland with a C/N-ratio ≥ 22, a cell wall content below 500 g kg^{-1} VS and a good silage quality were better suited for the production of biogas. In the continuously experiments the optimum operating parameters for a stable degradation process were the mesophilic digester temperature and an organic loading rate of 2.5 kg VS m^{-3} d^{-1} with a grass silage content of 50 % of VS.

Keywords
Biogas, grassland biomass, ammonia, substrate mixture, C/N-ratio

Abstract
Landtechnik 68(5), 2013, pp. 339–343, 5 figures, 1 table, 7 references

Alternative use of grassland biomass no longer required in future as forage for livestock feed is a central factor to the conservation of the cultural landscape in Bavaria. In a feasibility study by the Bavarian State Institute for Agriculture (LfL) it was established that in 2020, depending on the scenario, 165,000 to 200,000 ha of grassland and 71,000 ha of arable forage area would no longer be required for livestock forage and would therefore be available for alternative use [1]. So far, however, growth from grassland has been hardly ever used as main substrate in biogas plants. In practice, experiences so far with anaerobic fermentation of grassland biomass indicate that process management is difficult, with unreliable long-term process stability. As a rule, the high protein content in this substrate leads to a high ammonium concentration during anaerobic degradation. In association with operating temperature and pH, ammonia is released during the fermentation and this can have an inhibitory effect on the microorganisms in the anaerobic degradation process.

At the LfL Institute for Agricultural Engineering and Animal Husbandry (ILT) various aspects influencing biogas process stability were systematically investigated in trials. The influence of cutting length, operation temperature, silage quality and C/N ratio were investigated in continuous flow trials under increasing organic loading rates in order to analyse the conditions for an optimal process.

Materials and methods

In 21 continuous flow trials carried out according to VDI 4630 biogas production, highest possible organic loading rate, and process stability in anaerobic fermentation of different types of grassland growth material were investigated either as mono fermentation or as a mixture with other regionally typical substrates (**Table 1**). The experiments took place in one-stage fermenters (28 l). The reactors were operated as continuous stirred tank reactors. Every reactor included gas meter and gas collection sack from which the gas composition per 4.0 l of collected biogas volume was automatically recorded.

Used as standard inoculum for the continuous flow trials, was the standard biocenosis applied at the ILT [2]. This was harvested from a 3.5 m^3 pilot plant that has for several years been permanently fed with the same substrate (3 kg VS m^{-3} d^{-1} from 80 % cattle dung and 20 % dairy cow TMR). The hydraulic retention time was < 20 days.

For every increase in organic loading rate, and during critical phases of the fermentation, the following chemical parameters of digester contents were recorded:

- Total solids (TS)
- Volatile solids (VS)
- pH
- Content ratio of volatile organic acids (VOA) and carbonate buffers (TIC) (VOA/TIC)
- Organic volatile fatty acids (VFA)
- Ammonium

The substrates fed into the digester were analysed for their TS, VS, pH, VFA, carbon (C_{org}), nitrogen (N_{org}) and van Soest fractions.

Table 1

Compilation of the investigated substrates and the experimental setup in the continuously test

Einflussfaktor ***Factor***	**Varianten** ***Trials***	**Substrate** ***Substrates***	**Charakterisierung** ***Characterization***
Betriebstemperatur *Operating temperature*	mesophil (38 °C)/*mesophilic (38 °C)* thermophil (55 °C)/*thermophilic (55 °C)*	Grassilage *grass silage*	TS[1] = 26 % FM[1] oTS[1]/*VS*[1] = 89 % TS FFS[1]/*VFA*[1] = 12 g · kg^{-1} FM C/N[1] = 11
Schnittlänge *Cutting length*	mesophil (38 °C)/*mesophilic (38 °C)* Schnittlänge/*cutting length:* → kurz/*short 4 mm* → lang/*long 15 mm*	Grassilage *grass silage*	kurz/*short 4 mm* TS[1] = 33 % FM[1] oTS[1]/*VS*[1] = 89 %TS FFS[1]/*VFA*[1] = 23 g · kg^{-1} FM C/N[1] = 16 lang/*long 15 mm* TS[1] = 34 % FM[1] oTS[1]/*VS*[1] = 89 % TS FFS[1]/*VFA*[1] = 4 g · kg^{-1} FM C/N[1] = 16
Silagequalität (Die Silagequalität wurde anhand der Futtermittelbewertung für die Tierhaltung festgestellt) *Silage quality* *(A good silage quality was determined according to the criteria for animal feed)*	mesophil (38 °C)/*mesophilic (38 °C)* → *gute Qualität: keine Buttersäure in der Silage* *good quality: no butyric acid in the silage* → *schlechte Qualität: hoher Buttersäuregehalt in der Silage* *bad quality: high butyric acid content in the silage*	Grassilage *grass silage*	gute Qualität/*good quality* TS[1] = 35 % FM[1] oTS[1]/*VS*[1] = 89 % TS FFS[1]/*VFA*[1] = 7 g · kg^{-1} FM C/N[1] = 20 schlechte Qualität/*bad quality* TS[1] = 23 % FM[1] oTS[1]/*VS*[1] = 89 % TS FFS[1]/*VFA*[1] = 17 g · kg^{-1} FM C/N[1] = 21
C/N-Verhältnis bei der Monovergärung *C/N-ratio in monodigestion*	mesophil (38 °C)/*mesophilic (38 °C)*	Kleesilage *clover silage* Grassilage *grass silage*	Kleesilage/*clover silage* TS[1] = 35 % FM[1] oTS[1]/*VS*[1] = 89 % TS FFS[1]/*VFA*[1] = 7 g · kg^{-1} FM C/N[1] = 20 Grassilage/*grass silage* TS[1] = 30 % FM[1] oTS[1]/*VS*[1] = 91 % TS FFS[1]/*VFA*[1] = 10 g · kg^{-1} FM C/N[1] = 16
C/N-Verhältnis bei der Substratmischung *C/N-ration in substrate mixture*	mesophil (38 °C)/*mesophilic (38 °C)* Angaben in Prozent an der insgesamt zugeführten Menge an oTS[1] *In percent of the total amount supplied to VS*[1] a. Gras/*grass* 70 %, Mais/*maize* 30 % b. Gras/*grass* 50 %, Mais/*maize* 50 % c. Gras/*grass* 95 %, Wdü[1]/*manure*[1] 5 % d. Gras/*grass* 50 %, Mais/*maize* 25 %, Grünroggen/*green rye* 25 % e. Gras/*grass* 50 %, Mais/*maize* 25 %, Weizenstroh/*wheat straw* 25 %	Grassilage *grass silage* Maissilage *maize silage* Rindergülle *cow manure* Grünroggensilage *green rye silage* Weizenstroh *wheat straw*	Mischung/*mixture* – C/N[1] a. 19 b. 22 c. 16 d. 22 e. 23

[1] TS: Trockensubstanz/*total solids*, FM: Frischmasse/*fresh mass*, oTS: organische Trockensubstanz/*VS: Volatile solids,* FFS: organische flüchtige Fettsäuren/*VFA: Volatile fatty acids*, C/N: C/N-Verhältnis/*C/N-ratio*, Wdü: Rindergülle/*cow manure*

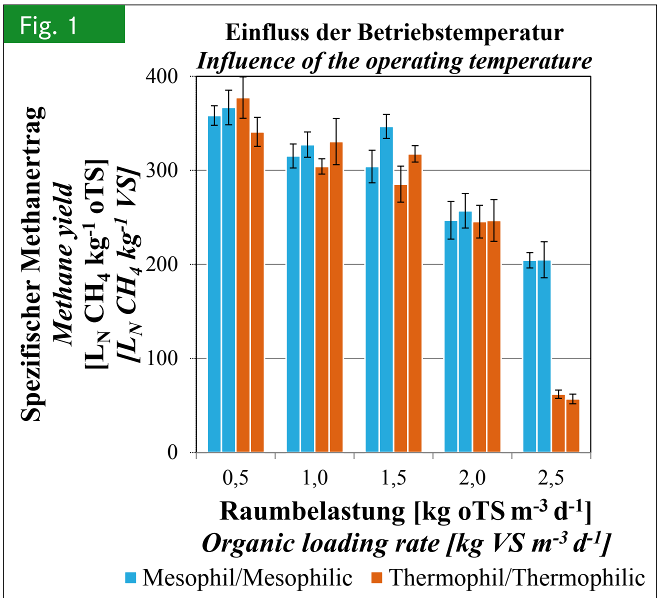
Results and discussion

The continuous flow trials clearly confirmed the inhibitory effect of ammonia during the fermenting of grassland biomass. The toxic effect of ammonia in biological systems is recognised [3]. Anaerobic fermentation trials confirm that from 560 mg NH_3N l^{-1} there is a halving of methane production [4].

Influence of operating temperature

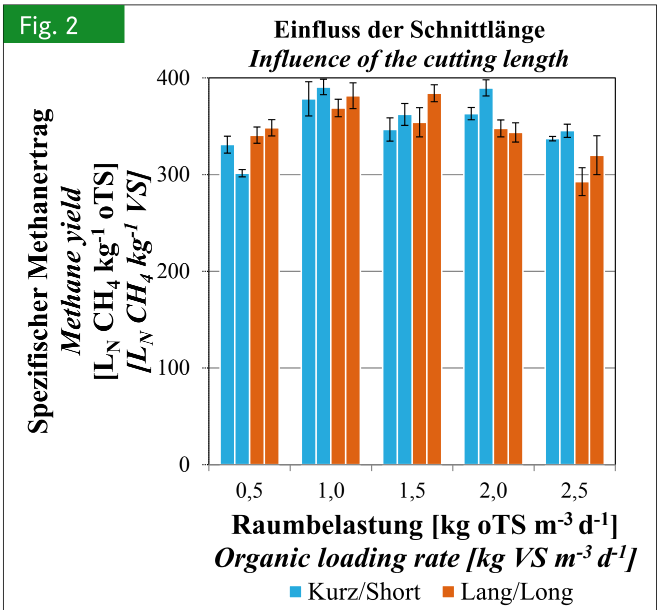
In the continual flow trials the influence of operating temperature on the biogas process during fermentation of grassland biomass could be demonstrated. Under mesophilic conditions, the degradation process was markedly more stable and resilient than under thermophilic conditions (**Figure 1**). This difference

Fig. 1



Methane yield of the trials in the continuously experiment: Influence of operating temperature

Fig. 2



Methane yield of the trials in the continuously experiment: Influence of silage cutting length

was attributed to the ammonia concentration produced by thermophilic organisms as a result of high operation temperatures. The calculated ammonia contents [5] were very high from the start in the thermophile fermenting processes (> 1.5 g kg^{-1} FM), while mesophilic systems were only able to achieve this level at end of trial with a high organic loading rate. Under thermophilic conditions inhibition of the degradation process was recorded from a level of 700 mg NH_3 N l^{-1} [6].

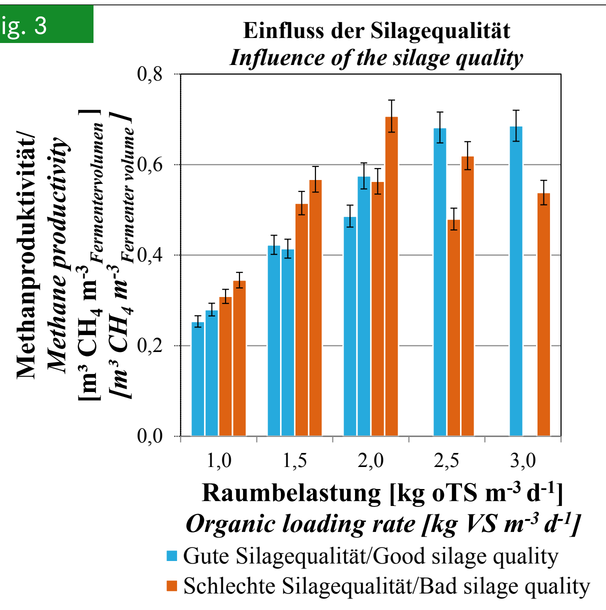
Influence ofcutting length

No influence on methane yield from grass silage cutting length was apparent in the continuous flow trials with monofermentation. Methane production was the same with all variants. The highest methane yield was achieved with an organic loading rate of 0.5 to 1.5 kg VS m^{-3} d^{-1} (**Figure 2**). On the other hand, particle size can have an effect on the viscosity of the digester suspension and/or the degradation kinetics under continuous flow conditions. It is reported from practical experiences that both of these effects can lead to reductions in vulnerability to foam reformation or of stratification in the digester. Because of this, susceptibility to disruptions and agitation system energy requirements could be reduced. In this aspect, however, there remains need for further research.

Influence of silage quality

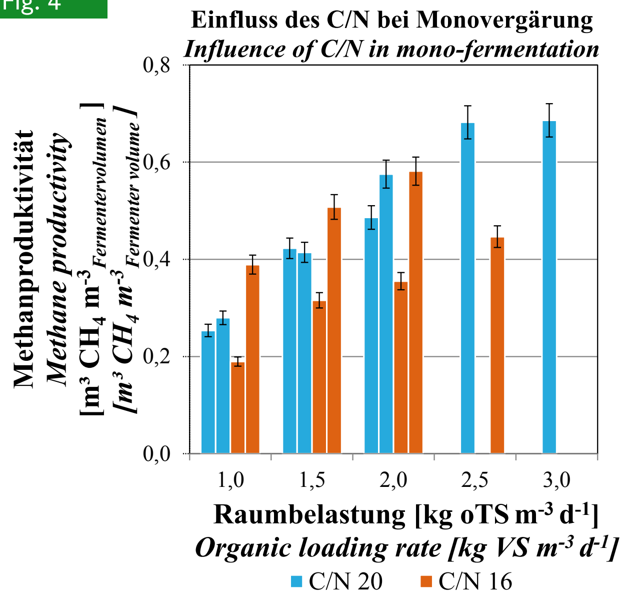
A dependable substrate conservation is crucial to biogas production. Although, contrary to silage for feeding stock, quality parameters such as palatability measured on the butyric acid content play only a subordinate role [7]. In continuous flow trials the influence of silage quality on methane production was investigated. The effect of poor silage quality (higher butyric acid content) on the biogas process was clearly discernable from an organic loading rate of 2.0 kg VS m^{-3} d^{-1}. The deterioration of methane productivity (minus 19 %) and of the substrate degradation was more marked than that of the variant with good ensiled material (**Figure 3**). Despite this, the application of poorly ensiled material during lower organic loading rates had a positive effect in the short-term. The higher concentration of VFA in the substrate with the poor silage quality was in part further fermented as hydrolysed material. Additionally, the stimulation of the hydrolysis and acidification phases resulted in a rapid reduction of pH level which in turn reduced the proportion of ammoniacal nitrogen. These conditions minimised the toxic ammonia effect in the process. For this reason it is possible that using poorly ensiled grassland growth over a

Fig. 3



Methane productivity of the trials in the continuously experiment: Influence of silage quality

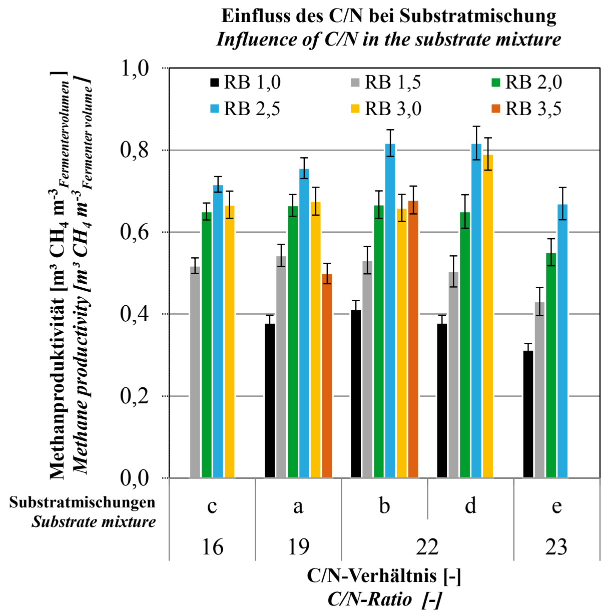
Fig. 4



Methane productivity of the trials in the continuously experiment: Influence of the C/N ratio in the mono-fermentation

C/N: C/N-Verhältnis/ C/N-ratio

Fig. 5



a. 70% Gras/*Grass* - 30% Mais/*Maize*
b. 50% Gras/*Grass* - 50% Mais/*Maize*
c. 95% Gras/*Grass* - 5% Rindergülle/*Cow manure*
d. 50% Gras/*Grass* - 25% Mais/*Maize*- 25% Grünroggen/*Green rye*
e. 50% Gras/*Grass* - 25% Mais/*Maize* - 25% Weizenstroh/*Wheat straw*

Angaben in Prozent an der gesamten zugeführten Mengen an oTS
In percent of the total amount supplied to VS

RB: Raumbelastung in kg oTS m^{-3} d^{-1}
Organic loading rate in kg VS m^{-3} d^{-1}

Methane productivity of the trials in the continuously experiment: Influence of Influence of the C/N ratio in the substrate mixtures

short period of time would be suitable when there is evidence of hydrolysis and acidification phase inhibition, i.e., when a disruption of biogas production and lower fatty acid concentration in the digester of the biogas plant is determined.

Influence of the C/N ratio

The influence of the C/N ratio in the grassland biomass was investigated as a key parameter for biogas process stability. With the monofermentation variants in the continuous flow trials a stable methane production was achieved up to an organic loading rate of 1.5 kg VS m^{-3} d^{-1} with a C/N ratio = 16, which was markedly less than the variant with C/N = 20. Also, the methane productivity from the C/N = 16 variant was weaker than where the C/N ratio was higher (**Figure 4**).This reached the maximum performance of 0.58 m^3 CH_4 $m^{-3}{}_{digester\ volume}$ with an organic loading rate of 2.0 kg VS m^{-3} d^{-1}. The degradation process was more stable and markedly more resilient than with the high C/N ratio. With the variant C/N = 20 the methane yield was stable up to an organic loading rate 2.0 kg VS m^{-3} d^{-1}. The highest achieved methane productivity of 0.68 m^3 CH_4 $m^{-3}{}_{digester\ volume}$ was achieved with an organic loading rate of 2.5 and 3.0 kg VS m^{-3} d^{-1}.

Clearly identified as main reason for process disruption was an unfavourable C/N ratio in the substrate, in that the variants with lower C/N ratios (= 16) landed earlier at their loading limits. As a result, positive effects could be observed from the different substrate mixtures. The substrate mixtures with a C/N ratio between 19 and 22 demonstrated high process efficiency up to an organic loading rate of 2.0 kg VS m^{-3} d^{-1}, biomass degradation of 74 % and methane productivity of 0.66 m^3 $CH_4 m^{-3}{}_{digester\ volume}$ (**Figure 5**). The degradation performance began to slow down with the increase in organic loading rate. The substrate mix with wheat straw (C/N = 23) showed a marked reduction in substrate conversion of approx. 52 % between the organic loading rates 2.5 and 3.0 kg VS m^{-3} d^{-1}. The digestibility of the substrate mixture with this variant had a negative effect on process stability, despite lower nitrogen input. The variants with low C/N ratio (< 23) demonstrated a marked reduction in methane productivity with every increase in organic loading rate (**Figure 5**). As a result, ammonia concentration in the digester had a negative effect on biogas production.

The variant with cattle manure (**Figure 5**, mixture c) showed similar performance as far as methane production was concerned as the comparable monofermentation variant (**Figure 4**, C/N = 16). At the end of the trial with an organic loading rate of 3.0 kg VS m^{-3} d^{-1} the digester with the farmyard manure showed a slight improvement in methane production. However, the first signs of a process disruption were already to be seen. Through the addition of cattle manure the degradation process could be supported to a certain extent. The biogas production with the farmyard manure variant was stable over a longer period. A marked concentration of acids first occurred later on in the process compared with the monofermentation procedure.

Looking at the complete trial showed that the cattle manure helped through the daily addition of water involved. In this variant the TS value remained under 10 % over a longer period. The liquid improved the dissolving rate of certain nutrient compounds that were available as salts in the system. In this context, according to experiences so far, the addition of farmyard manure in the fermentation of grassland biomass can be approved of from the process biological aspect.

Alongside a favourable C/N ratio, a low proportion of difficult to digest fractions (cell wall components) in the grassland biomass is also important in the assessment of process stability. In the research report presented here conditions were optimal for biogas production with a cell wall content (sum of hemicellulose, cellulose and lignin) in the grassland growth mixture at under 500 g kg^{-1} VS and with an organic loading rate of 2.5 kg VS m^{-3} d^{-1} under mesophilic conditions. The investigated mixtures b and d with a C/N ratio > 22 satisfied these criteria.

Conclusions

The continuous flow trials conducted clearly confirm the inhibitory effect of ammonia in the fermentation of substrate with a high content of grassland material. Stable process conditions were achieved in mesophilic operation. Clearly identified as main cause of disruptions in the biogas process were unfavourable C/N ratios in the substrate in that the variants with a C/N ratio < 22 reached their biological limit early. Based on the results, positive effects through the different substrate mixtures were observed. A stable degradation process could be demonstrated up to an organic loading rate of 2.5 kg VS m^{-3} d^{-1} with a grass silage proportion of 50 % on a VS basis. At the same time there has been so far no indication that cutting length has any significant influence on methane production in this respect. The negative effect of poor silage quality on the biogas process could be confirmed in this investigation.

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Authors

Dipl.-Ing. M. Sc. Diana Andrade is scientific researcher at the Institute for Agricultural Engineering and Animal Husbandry (ILT),
Dr. agr. Andreas Weber is manager of the working group Biogas Technology and Residue Management at the Bavarian State Institute for Agriculture (LfL), Am Staudengarten 3, 85354 Freising,
e-mail: diana.andrade@lfl.bayern.de

Acknowledgement

This research work was financially supported by the Bavarian State Ministry for Food, Agriculture and Forestry.