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Investigating the Hydrolysis of Forage Maize Silage

The anaerobic conversion of biomass to methane can be divided into four degradation steps. The optimal process conditions for the hydrolysis and for acidogenesis differ from those for the subsequent acetogenesis and methanogenesis. The investigation presented here shows that optimizing the respective process conditions does not inevitably result in higher biogas yields.

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Keywords

Acidogenesis, biogas, hydrolysis, maize, maize silage, hydrogen

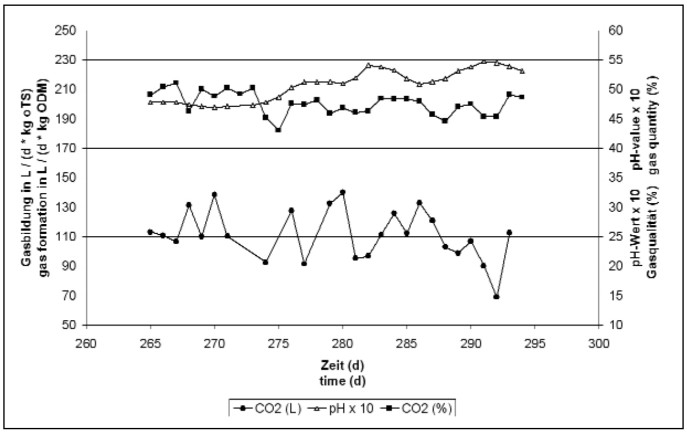

Fig. 1: Gradient of gas quality, quantity and pH-value during the conducted experiment

Lately the costs of the agricultural products have increased considerably, making the methane production from renewable raw materials increasingly uneconomically. At present, several possibilities which lead to the increase of the gas yields of the used substrates and therefore to a better utilisation of the used biomass are being pursued.

Biphasic fermentation

An approach already partially practiced in the agricultural biogas plants is the biphasic fermentation. In contrast to the currently common used single phased fermentation during which all four steps of the anaerobic fermentation take place in the same fermenter, in the biphasic fermentation the degradation process is separated into two parts. The hydrolysis, during which the macromolecules of the used substrates are being fragmented to monomers and also the acidogenesis, during which the previous generated monomers are being transformed into carboxylic acids, alcohols, carbon dioxide and hydrogen, take place in the first phase [5]. At this occurs the conversion of the anaerobic degradable nutrients, contained in the supplied substrates, into a liquid phase. Many of the microorganisms involved in the hydrolysis and the acidogenesis, called primary fermenters, achieve their metabolism optimum at a pH value of 5 to 6.3 [3]. The next conversion step, the acetogenesis also partially takes place in this first fermenter of the biphasic plant, often referred to as hydrolysis fermenter. The metabolism of the secondary fermenters is restricted here as a result of the high hydrogen partial pressure. In the last step of the process methane is being produced by the methanogenic microorganisms at a pH value of 6.8 to 8.2 out of hydrogen and carbon dioxide (about 28% of the methane), as well as out of acetic acid [3]. If all four steps of the process take place in the same digester, then the process conditions are being adapted for the last two steps, the acetogenesis and the methanogenesis, which are both limiting steps for the biogas production. This, however, restrains the potential efficiency of the first two process steps. A separation of the hydrolysis and acidogenesis from the acetogenesis and methanogenesis appears reasonable, not only because of the different pH optima. Information in literature shows that a higher methane content of the biogas can be achieved through the biphasic fermentation and that the whole process could take place in a steadier manner [4]. A biphasic fermentation should also lead to an avoidance of pH value fluctuations, which sensitively inhibit the methanogenesis [2]. The short doubling time of the primary fermenters of approximately 20 minutes to 1.5 days allows short retention times and therefore high substrate feeding during the hydrolysis and acidogenesis. The doubling time of the acetogenic and methanogenic microorganisms is in the range of 3.5 to 15 days, which requires far longer retention times [1]. When all four process steps take place in the same digester, then the relatively slow growth of the methanogenics restricts the possible retention time. The separation of the individual phases offers the possibility to achieve optimal process conditions for the respective phase.

Material und methods

This investigation concentrates on the first phase of the biogas process, the hydrolysis and the acidogenesis. The experiments have been carried out in two horizontal, continuously stirred and semicontinuously fed digesters with a capacity of 400 litres in the biogas laboratory of the Hohenheim University. Before the start of the experiment, the water filled digesters have each been inoculated with ten litres digesting substrate from a single phased driven biogas plant. The temperature of the fermentation is of 55°C. The digesters were supplied daily with 1.6 kg organic dry matter (ODM) in form of maize silage, which corresponds to a digester load of 4 kg ODM per cubic meter and day. The starting phase has been set aside and the experiments started immediately with a digester load of 4 kg VS. The adjustment of the pH value was possible through the addition of lime water based on burned lime (CaO). The quality (CO_2, CH_4) and quantity of the formed gas as well as the pH value of the digesting substrate were been daily measured. The addition of tap water limited the retention time to ten days. The maize silage and tap water proportion is around 1:7.

The effluent of the hydrolysis reactor was separated into a solid and a liquid fraction. We analysed both fractions from point of view of their methane production potential by adding liquid manure inoculums and by using the Hohenheim Biogas Yield Test (HBT) method. The used maize silage was displaced as a comparison variant in the same proportion with tap water, which made the volatile fatty acids, alcohols and other soluble substances, contained in the maize silage, disperse in the solution. The substrate was separated after 20 minutes of stirring. The methane production potential of the two fractions and of the untreated maize silage was ascertained. The determination of the specific gas yields occurred after an acid correction of the organic dry matter (ODM) content [6].

Preliminary results

The pH value in the digester dropped to 3.7, as a result of adding maize silage shortly after the start of the experiment. No gas formation took place in this first experimental period. The pH value could be stabilised between 4.6 and 5.5, only by adding burnt lime. The digester specific hydrolysis gas yield was over a period of three retention times at 0,866 m3/m3 d-1. The formed gas consisted out of an average 47.7 % carbon dioxide and contained no methane (*Fig. 1*). Externally conducted gas analyses showed that the undetermined gas amount (52,3 %) consisted almost exclusively of hydrogen. In the experimental plant 209.7 litres hydrolysis gas were produced per kg added volatile solids, which at a hydrogen percentage of 52,3% corresponds to an amount of 109,7 litres hydrogen per kg ODM. The acetic acid equivalent was in the liquid phase during the experimental phase described here at an average of 11450 ppm (*Table 1*).

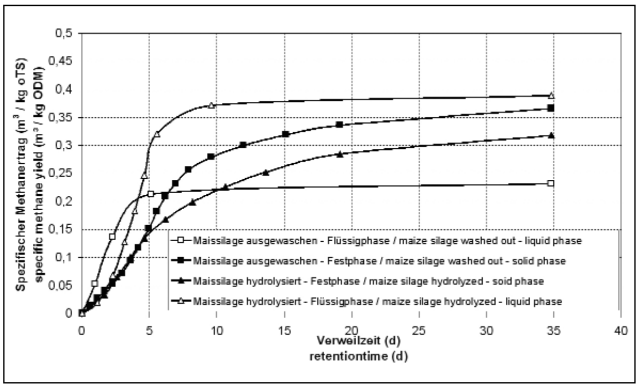

Fig. 2: Accumulated methane yield of effluent and not hydrolyzed maize silage; determination of dry matter content without considering volatile fatty acids

The methane production potential of the hydrolysed maize silage, the washed–out control variant and of the untreated control variant determined through the HBT method are presented in *Figure 2*. It shows that the substrate specific methane yield potential of the liquid phase after the hydrolysis is considerably higher than the one of the comparison variant in which only the soluble constituents of the maize silage were dispersed in solution. The solid phase of the hydrolysed effluent (~22% DM) measured had in contrast to the washed-out maize silage lower substrate specific methane yields. The specific methane yield of the hydrolysed maize silage was 0.394 m^3 / kg VS, under consideration of the absolute amount proportions and dry matter content, 21.4% lower than in the untreated control variant (0.418 m^3 / kg VS).

Discussion

The specific gas yield of the liquid phase of the effluent, the fatty acids content of the digesting substrate as well as the gas composition of the gas produced during the hydrolysis and the acidogenesis are prove of the the fact that during hydrolysis and acidogenesis the conversion of the solid biomass of the input substrate into organic acids, ethanol, carbon dioxide and hydrogen occurred. The absence of methane production was caused by the too low pH value (4.6 to 5.5) and that the methanogenic microorganisms had a too short retention time of merely ten days. The hydrolysis gas produced during the research period consisted of approximately equal parts of carbon dioxide and hydrogen. The hydrogen produced during the hydrolysis in a biphasic fermentation is not available for the methanogenic microorganisms of the second phase as an input substrate for the carbon dioxide reduction. The methane yield after the hydrolysis is expected to be around 6.9 % lower compared to an untreated maize silage as a result of the amounts of hydrogen produced in the research period and according to the stoichiometric relationship. Should biphasic fermentation improve the biomass degradation, then this reduction should be overcompensated to achieve an actual improvement of the specific methane yield. However, the specific methane yields of the effluents determined through HBT showed a reduction of 21.5 % compared to the untreated variant.

The partially higher biogas methane amounts observed in practical experience during a biphasic fermentation are not based on a proportionately higher methane production, but merely result from an absent ascertainment of the hydrolysis gas.

Table 1: Ferment acid pattern of the liquid phase of the effluent

ppm	Flüssigphase hydrolisiert	Flüssigphase ausgewaschen
Essigsäure	7637	1314
Propionsäure	686	143
Iso-Buttersäure	22	0
n-Buttersäure	3297	29
Iso-Valeriansäure	103	0
n-Valeriansäure	113	0
Capronsäure	1678	0
Milchsäure	363	1657
Ethanol	1100	786
1,2 Propandiol	0	143

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