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# Effects on the biogas and methane production of cattle manure treated with urease inhibitor



**BIOMASS &** BIOENERGY

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## ABSTRACT

Urease inhibitors are in general known as potential measure for reducing ammonia emissions in dairy and cattle housing systems. Due to the application of the urease inhibitor on the exercise areas within a housing system the inhibitor is "mixed" with cattle manure and this "mixture" remains unchanged during manure storage. In Germany, a large part of the total stored cattle manure is utilized as a substrate in biogas plants. Therefore, the aim of the current study was to test if different concentrations of urease inhibitor mixed with typical cattle slurry will have any (negative) effects on the biogas and methane yield. The Hohenheim Biogas Yield Test (HBT) was used to determine if the biogas and methane production of cattle manure is influenced by the admixture with urease inhibitor. Altogether, four urease inhibitor concentrations (0%, 0.1%, 1% und 10% of total Kjeldahl nitrogen) were tested in the HBT experiments with two different substrates, cattle manure and cellulose, as a reference, in repetitions each. The average biogas and methane production of cellulose was 740 L<sub>N</sub>/kg<sub>ODM</sub> and 403 L<sub>N</sub>/kg <sub>ODM</sub> and of cattle manure  $471 L_N/kg_{ODM}$  and 295  $L_N/kg_{ODM}$ . Both substrates treated with urease inhibitor showed no significant change in the biogas and methane production compared to the untreated ones. The use of urease inhibitors to reduce ammonia is harmless from the view of biogas plants. © 2015 Elsevier Ltd. All rights reserved.

#### 1. Introduction

Nitrogen is an essential nutrient for plants. A part of this nitrogen is present in manure as gaseous ammonia. Emissions of ammonia (NH<sub>3</sub>) lead to environmental damage of the ecosystem caused by acidification and eutrophication. NH3 also has adverse health effects to humans and animals [1–4]. Due to the environmental and indirect greenhouse effect, NH<sub>3</sub> reduction is more and more a focus of national and international policy [5-14]. Germany has committed in Gothenburg protocol [7] and in the European national emission ceilings guidelines 2001/81/EG Ref. [15] to reduce the annual emission of NH<sub>3</sub>. To comply with the national emission ceilings, a reduction of NH<sub>3</sub> emissions is necessary. Significant NH<sub>3</sub> emissions occur from housing floors, slats, manure pits, and exercise areas.

The urease-catalyzed hydrolysis is the cause of the NH<sub>3</sub> emissions in animal husbandry. One possibility to reduce NH<sub>3</sub> emissions is the use of urease inhibitors, which inhibit the reaction of urease and thus the release of  $NH_3$  [16,17]. The use of urease inhibitors in livestock farming has been investigated in several studies [18–25] but commercial implementation in dairy farm practice was not realized. The practical use of an inhibitor (inhibitor K) at three different dairy farms during normal operation was carried out [26]. This inhibitor showed

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the highest ammonia reduction potential in laboratory studies [27].

When the urease inhibitor serves to reduce ammonia emissions in practice, the urease inhibitor (2.5 mg/m<sup>2</sup>) needs to be applied daily to the whole exercise area of a dairy facility [26], thus manure is treated with the inhibitor. This manure is often used as a substrate for biogas plants in Germany.

In Germany, 7515 biogas plants existed in 2012. Approximately 7900 plants were estimated for the year 2014 [28]. The majority of these plants use agricultural residues and renewable raw materials for biogas production. In 2012, renewable raw materials (52.8%) and animal excrement (43.1%) such as liquid manure and solid manure dominated the mass-referred use of substrate (Fig. 1). The cattle manure was the majority among the livestock manure with 68% [29]. In Fig. 1 is shown additionally a detailed illustration of the mass-referred use of different livestock manures.

Cattle manure as substrate in biogas plants is widespread in Germany. The Renewable Energy Sources Act [30] promoted the use of livestock manure in small biogas plants (up to an electrical output of 75 kW), if at least 80% of the amount of substrate is manure.

In literature only one study by Reinhardt-Hanisch [25] dealt with the influence of urease inhibitors (inhibitor D) on the biogas production. This inhibitor D had no influence on the biogas and methane production at three different concentration levels.

The anaerobic fermentation of biomass is the basis of biogas production, where different types of microorganisms are involved. When the urease inhibitor is mixed with the manure (biogas substrate) the urease inhibitor should have no adverse influence on these important microorganisms. Therefore the aim of this study was to determine the influence of a novel urease inhibitor (inhibitor K) on the biogas and methane production.

# 2. Material and method

### 2.1. Hohenheim Biogas Yield Test (HBT)

The Hohenheim Biogas Yield Test (HBT) is based on Helffrich and Oechsner [31] and is carried out in compliance with German Standard Procedure VDI 4630 [32]. The HBT simulates biogas production of a biogas plant. A glass syringe (retort



Fig. 1 – Mass-referred substrate use in biogas plants and mass-referred substrate use of livestock manure in Germany 2012 [29].

sampler) with a volume of 100 ml is used as a fermenter (Fig. 2). The content of the retort sampler consists of inoculum, the substrate, and the biogas formed. For quality control, the HBT laboratory of the Institute of Agricultural Engineering (University of Kiel, Germany) takes part regularly in round-robin tests of the Association for Technology and Structures in Agriculture (KTBL).

The filling process of the HBT was the same for each retort sampler. First 30 ml of the inoculum was filled into sampler and weighed out. Then the weighed substrates (manure = 6 g  $\pm$  0.2; cellulose = 0.3 g  $\pm$  0.003) were filled into the sampler (scales: Kern ALJ 160 4 M,  $\pm$  0.2 mg). The inoculum and the substrate were mixed by gentle shaking. The existing air in the retort sampler was pushed out by the lubricated stopper (sliding + sealing coating: Baysilone, medium viscosity). The sampler was closed using a tube clip and the filling level was noted. Then the sampler was placed in a motor-driven rotor (two rotations per minute) which ensured a constant mixing of the retort sampler over the entire experimental period. The placement of the sampler carried out according to Stoffers [33] to avoid random effects.

The experimental setup (motor-driven rotor) was located in an incubator to guarantee a constant temperature of 38 °C ( $\pm$ 1 °C). The experiment ended after 35 days, which allowed the comparison with the studies of Reinhardt-Hanisch [25].

The biogas quantity was detected as many times as necessary (reading: daily to once weekly). The proportion of methane in the biogas was determined each time biogas was vented with an advanced Gasmitter<sup>®</sup> (AGM 10, Sensors Europe). The measurement was based on the non-dispersive infrared principle (NDIR). The measuring range of the gas analyzer was between 0% and 100% with an accuracy of  $\pm 2\%$  of the measuring range. For the correction of the readings, the temperature of the incubators and the current local air pressure of the laboratory were recorded using a weather station (TFA Dostmann  $\pm 1$  °C;  $\pm 3$  hPa).

## 2.2. Experimental setup

The inoculum was digested sewage sludge which contained the required bacteria for fermentation originating from the wastewater treatment plant Kiel-Bülk (Strande, Germany). The inoculum was coarsely sieved (<1 mm) and previously stored for 7 days at 38 °C to decrease its own gas production. According to the Association of German Engineers [32] for testing the activity of sewage sludge (guideline no. 4630) a reference substrate must be performed with each test whose specific biogas



Fig. 2 – Retort sampler with glass syringe (1), stopper
(2), fermentations substrate (3), vent for gas analysis
(4), tube clip (5), graduation 1/1 (6), gas chamber (7), sliding and sealing coating (8) [32].

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