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Low temperature calcium hydroxide treatment enhances anaerobic methane production from (extruded) biomass

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HIGHLIGHTS

- Methane production is improved by low temperature (10 °C) $Ca(OH)_2$ treatment.
- $Ca(OH)_2$ post-treatment after extrusion further enhances the biogas production.
- Temperature effect of $Ca(OH)_2$ treatment is less critical after extrusion.
- Fast extrusion is more energetically favourable for biomass pretreatment.

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ABSTRACT

$Ca(OH)_2$ treatment was applied to enhance methane yield. Different alkali concentration, incubation temperature and duration were evaluated for their effect on methane production and COD conversion efficiency from (non-)extruded biomass during mesophilic anaerobic digestion at lab-scale. An optimum $Ca(OH)_2$ pretreatment for grass is found at 7.5% lime loading at 10 °C for 20 h (37.3% surplus), while mild (50 °C) and high temperatures perform sub-optimal. $Ca(OH)_2$ post-treatment after fast extrusion gives an additional surplus compared to extruded material of 15.2% (grass), 11.2% (maize straw) and 8.2% (sprout stem) regarding methane production. COD conversion improves accordingly, with additional improvements of 10.3% (grass), 9.0% (maize straw) and 6.8% (sprout stem) by $Ca(OH)_2$ post-treatment. Therefore, $Ca(OH)_2$ pretreatment and post-treatment at low temperature generate an additional effect regarding methane production and COD conversion efficiency. Fast extrusion gives a higher energy efficiency ratio compared to slow extrusion.

1. Introduction

Over the past decades, lignocellulosic biomass has become an increasingly important renewable resource for biogas and biochemicals. Today, grass is as yet unused for this despite its wide availability in temperate regions. Grass can be available from nature, agriculture and roadside clipping, although the latter is less attractive due to the impurities which require prior removal steps before further processing can take place. By considering the economic and environmental impacts, previous study has also shown that grass is a suitable feedstock for biogas production (Prochnow et al., 2009). Next to grass, maize straw and sprout stem are of major interest due to the big scale plantation of the crops, hence a potential input for energy and chemical production.

Depending on the type of feedstock, 40–65% of the chemical oxygen demand (COD) of typical plant biomass is converted to biogas when digested without pretreatment (Weiland, 1993), whereas digestate exiting the anaerobic digester can be composted and thereby returned as fertilizer and soil improvement to arable land, the effective economic value tends to be low. The biodegradability of plant biomass is limited due to the recalcitrant nature of lignin and its structural carbohydrates. Therefore, pretreatment decreasing particle size and hydrolysing (part of) the lignocellulosic biomass is considered critical. While the effects of different pretreatment methods with various feedstock on anaerobic digestion have been compared (Carlsson et al., 2012), chemical alkali treatment and thermo-mechanical extrusion are the main focuses of this study.

Chemical pretreatment typically aims at depolymerisation of the biomass. The approaches most commonly researched are the use of acids, bases and peroxides. Alkali substances have been found the most promising for soft wood (Mosier et al., 2005) and it has been shown to be able to remove lignin and release acetate groups from hemicellulose, increasing the vulnerability of the hemicellulose and cellulose structures to enzymatic attack (Chang and Holtzapple, 2000). Among these, sodium hydroxide is

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the most effective, but the chemical is costly when applied on large scale. Therefore, $Ca(OH)_2$ seems to be an alternative worthwhile investigating, as it relies on the same working principle but is 8–10 times cheaper. However, its effectiveness does require an adequate temperature and contact time. Thermo-chemical pretreatments are often carried out at high temperature (80–120 °C) (Gonzalez et al., 2013; Sierra et al., 2009), while mild (50 °C) and ambient (21 °C) temperatures have also been investigated (Xu et al., 2010). However lower temperature ranges such as 10 °C mimicking the ambient temperature of north and central Europe for extensive time intervals have not been tested before. This could be interesting, as calcium hydroxide has a different property where the solubility of the chemical increases with decrease in temperature (Grieve et al., 2011).

Combination of alkali and extrusion have also been investigated in the past by Kang et al. (2013) for ethanol production and Zhang et al. (2012) for glucose yield. Sodium hydroxide was added before the extrusion, resulting in an increase of 20–60% glucose yield versus untreated corn stover. In contrast to alkali treatment, extrusion is a thermo-mechanical operation which results in reduction of biomass particle size as well as depolymerisation of lignin, hemicellulose and cellulose. The process involves compression at the centre of a barrel and expansion at the end, which breaks down the biomass structure due to the shearing, friction and pressure release. To our knowledge, the effect of $Ca(OH)_2$ has not yet been tested on extruded biomass. Moreover, the combination of alkaline treatment after extrusion (alkaline post-treatment) is novel, although the alkaline treatment could benefit from the increase in surface ratio of the extruded biomass. As both pretreatments have different working principles, added value is expected.

The objective of the current study is to investigate the optimal effect of $Ca(OH)_2$ in terms of a broad temperature range, duration and concentration for methane conversion on biomass. Furthermore, this study wants to pinpoint if $Ca(OH)_2$ after extrusion of biomass is still effective in giving a methane surplus. In the first phase $Ca(OH)_2$ dosing was optimized using a CCD (Central Composite Design) in terms of temperature, duration and lime loading for grass. Secondly, the effect of extrusion on three biomass (grass, maize straw and sprout stem) was determined. Finally $Ca(OH)_2$ was applied on these extruded biomass to estimate the additional effect of combined (mechano-thermo-chemical) treatment. The energy input for extrusion of biomass was also measured and related to the energy surplus obtained from extra methane production to assess the energetic feasibility of the pretreatment process.

2. Methods

2.1. Materials

Biomass including maize straw, grass (from landscape, extensive management) and sprout stem (*Brassica oleracea convar. oleracea var. gemmifera*) were harvested during October 2012 and kindly provided by Inagro vzw (West Flanders, Belgium). All biomass was manually size reduced to less than 5 mm with scissors before storage. Grass, used for the $Ca(OH)_2$ Central Composite Design (CCD) experiment was stored in vacuum bags at 4 °C until usage. For the extrusion test, biomass was stored in vacuum bags at −20 °C until usage.

2.2. Pretreatment and post-treatment

2.2.1. Pretreatment of grass with $Ca(OH)_2$

A 3 factor 3 level Central Composite Design (CCD) (Box et al., 1978) was carried out to determine the optimum condition for grass pretreatment with $Ca(OH)_2$. Alkali loadings, times and temperatures were arrayed using central composite design. Controls without $Ca(OH)_2$ addition or extrusion were included. All $Ca(OH)_2$ treatments were charged with a water loading of 10 g water per g total solid (Chang et al., 1997). Design Expert® 9.0.2.0 (Statease, Inc. Minneapolis, USA) was used to generate the experimental runs and the experimental data was analysed using response surface methodology (RSM) (Box et al., 1978). Experiments were carried out in two triplicated blocks. In total, 15 conditions were tested, including the centre point. The control (non-treated) was run simultaneously in triplicate. One way analysis of variance (ANOVA) was used to test the variation in mean values of methane produced and the fitness of model for increase in methane production.

2.2.2. Extrusion and $Ca(OH)_2$ post-treatment of grass, maize straw and sprout stem

A pilot scale twin-screw extruder (model MSZK, Laborextruder 4 kW, Lehmann Germany) was kindly provided by Bioliquid (Raalte, the Netherlands). About five kilograms of fresh biomass (grass, maize straw and sprout stem respectively) were extruded at fast rate (60 rpm and 90 °C) and slow rate (15 rpm and 60 °C). The temperature rise was purely due to the friction between the screw and the biomass during the extrusion operation and no extra heating was applied. Non-extruded controls were included for each biomass. Part of the extruded biomass were further post-treated with 7.5% $Ca(OH)_2$ at low temperature (10 °C) and mild temperature (50 °C) for 24 h.

2.3. Biochemical methane potential (BMP) test

BMP test was carried out to investigate the effect of the pretreatments on methane yield from the feedstock. The inoculum was acquired from a 200 m^3 co-digestion plant (Inagro vzw) digesting cow manure and grass, assuring the inoculum was well adapted for plant feedstock. The batch assays were set up with reference to the protocol from VDI 4630 (2006). Glass reactors of 500 mL were filled with 300 mL of inoculum, and a corresponding amount of lignocellulosic biomass to achieve a loading ratio of 0.5 g VS inoculum per g VS feedstock. Negative controls (inoculum without feedstock) were also included. The biogas produced was collected in graduated glass cylinders filled with an acidified barrier solution (sulphuric acid at pH 2). The BMP test was carried out at 37 °C and lasted 30 days to evaluate the pretreatment efficiency. Both gas production and gas composition were measured two to three times weekly and the values were normalized to standard temperature and pressure (STP). The rate of biomethanation is represented as the ratio between total methane production of the treated biomass and the total methane production of the untreated control at day 5.

For experiments with $Ca(OH)_2$ pretreatment and post-treatment, the pH was not adjusted prior to digestion as this incurs an unrealistic cost towards application. Moreover, the buffering capacity of the sludge was able to maintain the pH between 7 and 8 throughout the digestion period. The $Ca(OH)_2$ pretreatment and post-treatment were carried out in triplicate hence only one BMP test was performed on each replicate. Extrusion was run in batch for grass, maize straw and sprout stem respectively, and hence BMP was tested in triplicate for each batch of biomass. COD conversion efficiency is calculated based on the ratio of COD converted into methane versus initial feedstock COD, with assumption that 1 g of COD gives 350 mL of methane.

2.4. Kinetic modelling

A first-order kinetic model – modified Hill model, was used to model the methane production (Kiely et al., 1997). The model