



Characterisation of anaerobic digestion substrates regarding trace elements and determination of the influence of trace elements on the hydrolysis and acidification phases during the methanisation of a maize silage-based feedstock



Nwagbo Christpeace Ezebuio¹, Ina Körner*

Hamburg University of Technology, Eissendorfer Straße 42, D-21073 Hamburg, Germany

ARTICLE INFO

Article history:

Received 18 August 2016
Received in revised form 14 November 2016
Accepted 24 November 2016
Available online 25 November 2016

Keywords:

Anaerobic digestion
Hydrolysis
Acidification
Nickel
Cobalt
Selenium
Molybdenum
Factor interactions
Volatile fatty acids

ABSTRACT

Anaerobic digestion (AD²) is a well-known pathway in bioenergy production but it could become more efficient. There is a poor understanding of the impacts of trace elements (TEs³) on substrate hydrolysis, which is a limiting step for energy production during AD. Hence, selected substrates were analysed for determining the TEs contents and other properties that are connected with TEs activities. The results showed a wide variation in TEs concentration, and also suggest that the TEs composition may be unfavourable for an optimum substrate hydrolysis. Therefore, AD investigations were carried-out using 1-L glass reactors in mesophilic batch mode with a maize silage-based feedstock (MSF⁴) as an exemplary AD substrate. The experimental set-up was based on a factorial design with Ni, Co, Se, Mo and VFA as factors and hydrolysis and acidification rate (HAR⁵) as response. The objectives were to qualitatively evaluate the influences of substrate characteristics on HAR, to determine the main and interaction effects of TEs and VFA concentrations on HAR and to optimise TEs configuration at different VFA levels. The response surface model and the desirability function were applied for data analyses. Certain Ni and Mo concentrations as well as the VFA*Mo interaction improved HAR at VFA levels of 10 and 120 mmol/L. At VFA levels ≥ 200 mmol/L, Co*Se interaction was significantly beneficial, while Co*Mo interaction significantly decreased the HAR. In conclusion, TEs supplementation can enhance substrate HAR during AD but the efficiency will depend on the process VFA concentration.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Anaerobic digestion (AD) for methane production, also known as methanisation, enables the conversion of biodegradable bioresources into methane-containing biogas. The process also produces digestate, which may be used as biofertilizer. AD occurs

in consecutive steps. It starts with hydrolysis of substrate carried out by extracellular enzymes into sugars, amino acids and long chain fatty acids and proceeds to acidogenesis that involves the fermentation of sugars and amino acids into alcohols and organic acids. The last two steps include acetogenesis by obligate hydrogen producing acetogens that produce, CO₂, H₂ and acetic acids, and methanogenesis that involves hydrogenotrophs and aceticlastic microbes that do the final transformations into CH₄ and CO₂, which are the main components of biogas [1]. In this publication the first part of the cascade involving hydrolysis and acidogenesis is considered with the focus on TEs impacts, since weak substrate hydrolysis connected with acidification often makes the whole AD process slow and inefficient. However, TEs are also relevant for optimum acetogenesis and methanogenesis, and these are discussed in more detail in another publication by one of the

* Corresponding author.

E-mail addresses: christpeace201@yahoo.com (N.C. Ezebuio), i.koerner@tuhh.de (I. Körner).

¹ National Biotechnology Development Agency, Umar Musa Yar'Adua Expressway, P.M.B. 5118 Wuse, Abuja, Nigeria.

² Anaerobic digestion.

³ Trace elements including nickel, cobalt, selenium and molybdenum.

⁴ Maize silage-based feedstock.

⁵ Hydrolysis and acidification rate.

authors, where it is shown that the optimum TE settings could increase methane production by more than 20% [2].

1.1. Overview of the enzymatic processes involved in hydrolysis and acidification in AD

In order to maximise the methane production, the hydrolysis rate of a substrate needs to be optimised during AD. Hydrolysis is initiated by the attack of the hydroxyl (OH^-) group from a water molecule (H_2O) on a substrate. The transfer of the OH^- from H_2O could be driven by physicochemical means, or supported by the enzymes of hydrolytic bacteria [3]. Important physicochemical factors of hydrolysis include the substrate composition and pH, while the biochemical factors include the concentrations of the hydrolytic enzymes and enzyme-substrate interactions [4]. Hydrolytic enzymes or hydrolases could solubilise AD substrates inside (intracellular) or outside (extracellular) the cell of microorganisms. The important hydrolases of AD are extracellular enzymes and include lipases, glucosidases and proteases [1,3]. The extracellular enzymes released by microorganisms during AD could either be adsorbed to polymeric compounds or dispersed freely in the inoculum [3,5]. The results of enzymatic degradation activities are, amongst others, organic acids. The types can be manifold, e.g. propionate and butyrate, and are generally referred to as volatile fatty acids (VFA) [1]. If VFA are not transformed in the subsequent steps of methanisation, they could accumulate and limit the efficiency of the AD process. This investigation involves hydrolysis and acidification steps of AD, and the hydrolysis and acidification rate (HAR) is the experimentally determined response parameter that was evaluated.

1.2. The importance of TEs for HAR

The active sites of the enzymes of hydrolysis (hydrolases) generally consist of amino acids, but may also contain one or two divalent metal ions [6]. Such metal-containing enzymes are called metalloenzymes (MEs). The metals are necessary in order to catalyse the transformation of the substrates. They may be needed only in traces and are called trace elements (TEs). TEs such as Ni, Co, Se and Mo have been reported by many authors as playing important roles during different stages of AD [7,8]. The hydrolytic potential of MEs varies with the number of coordinating divalent metal ions. According to Frey and Hegeman [9], the hydrolytic effect of two divalent metal ions is twice as high as that of a single divalent metal ion.

Metals and elements with known hydrolytic potentials include calcium (Ca), magnesium (Mg), zinc (Zn), nickel (Ni), cobalt (Co), selenium (Se), molybdenum (Mo), and iron (Fe) [3,9]. These metals are often contained in AD substrates in variable concentrations, but could also be supplemented if considered deficient during AD. However, although AD plants operate worldwide in practice, with more or less success, the handling of these metals can still be considered as a “black-box-system”. Whether the metals with hydrolytic potentials are contained in AD substrates as natural constituents or introduced by supplementation, they may be biologically unavailable due to some unwanted biological processes occurring during AD. For example, the redox reaction between Fe and S to precipitate iron (II) sulphide (FeS) is facilitated by anaerobic bacteria; and the interaction between precipitated FeS and TEs results in the formation of insoluble FeS-metal complexes [10,11], and therefore the TEs become inactive and are not useable for HAR, although contained in the substrate. The influence of such processes on the availability of metals and other elements is important because the formation of insoluble complexes may result in the unavailability of TEs of biological importance [12].

Hence, adsorption or complexation of these TEs with insoluble precipitates will reduce the biochemical efficiency of AD processes.

1.3. Further parameters of influence on HAR

In addition to S, Fe and the potentially resulting FeS-TEs interactions, carbon (C) and nitrogen (N) contents have also been reported to influence substrate hydrolysis due to their impact on pH and buffering capacity [13]. Particularly important is the influence of C/N on the formation of ammonia and ammonium ratio ($\text{NH}_3/\text{NH}_4^+$), hydrogen carbonate ion (HCO_3^-) and volatile fatty acids (VFA) [13,14]. According to Mata-Alvarez [13], VFA as intermediate products of hydrolysis and acidification may accumulate and inhibit further substrate hydrolysis. This suggests that substrates with high content of easily hydrolysable C may produce large VFA concentrations and inhibit further substrate hydrolysis. In this context, the types of C-containing compounds in the substrate are relevant and may vary widely in relation to degradability. Aromatic compounds such as lignin are for instance, non-degradable under anaerobic conditions, whereas monomeric sugars are easily hydrolysable. This listing of parameters of influence cannot be considered as comprehensive for AD. For instance, other manifold inhibitors can be problematic for AD. An actual review on inhibitors of AD has been reported by Chen et al. [15]. In this article, we emphasised the important substrate parameters that can influence TE interactions only.

The sensitivity of the hydrolysis and acidification phases of AD to substrate characteristics such as C, N, S, Fe and TE contents implies that poor HAR could reduce the efficiency of the entire AD process [13]. Consequently, understanding the characteristics of AD substrates will enable the evaluation of process modifications required to improve the rate of hydrolysis and the conversion of the products of hydrolysis into VFA without VFA-related inhibition. Enhancing substrate HAR during AD from the perspective of substrate characteristics and of the hydrolytic potentials of TEs is a challenge. Little is known about the relationships between substrate characteristics such as C, N, S and Fe, the interactions between different TEs, and the interaction between TEs and the different phases of AD. Therefore, this research aims to investigate the characteristics of selected AD substrates, and explore the catalytic potentials of TEs in relation to substrate hydrolysis and reduction in VFA-related inhibition of hydrolysis during AD. To do this, it is necessary to investigate which TE composition and concentrations (configurations) can enhance hydrolytic processes. Equally important is the finding of the optimum TE configurations, and the interaction effects of TE configurations at different levels of VFA accumulation (pre-acidification levels). Consequently, the specific objectives of this research include the determination of the following:

- TE contents and other substrate characteristics of selected AD substrates that could influence substrate HAR;
- Relationship between TEs and HAR at various pre-acidification (VFA) levels using maize silage-based feedstock (MSF) as exemplary substrate; and
- TE compositions and concentrations that can minimise VFA-related inhibition during substrate hydrolysis and significantly enhance substrate HAR at various pre-acidification levels.

Whereas this manuscript focuses on some substrate characteristics and the influences of TEs on substrate hydrolysis and acidification phases of AD, it is a part of a broader investigation that covers the influences of TEs on the other AD phases of acetogenesis and methanogenesis as well. The analyses under the broader investigations include Michaelis-Menten kinetics for the determination of the mechanisms of TE effects during AD, change in

Download English Version:

<https://daneshyari.com/en/article/6477353>

Download Persian Version:

<https://daneshyari.com/article/6477353>

[Daneshyari.com](https://daneshyari.com)