Bioresource Technology 172 (2014) 349–355

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

The effect of trace element addition to mono-digestion of grass silage at high organic loading rates

David M. Wall [a,b,d], Eoin Allen [a,b], Barbara Straccialini [c], Padraig O'Kiely [d], Jerry D. Murphy [a,b,*]

[a] Environmental Research Institute, University College Cork, Cork, Ireland
[b] School of Engineering, University College Cork, Cork, Ireland
[c] Department of Agricultural, Food and Environmental Science, Perugia University, Perugia, Italy
[d] Animal & Grassland Research and Innovation Centre, Teagasc, Grange, Dunsany, Co. Meath, Ireland

HIGHLIGHTS

- Dairy slurry when co-digested with grass silage provided sufficient trace elements.
- Low addition of slurry (20% VS) exhibited stable VFA profiles and high SMYs.
- Mono-digestion of grass silage at high loading rates required trace element addition.
- Supplementation of cobalt, nickel and iron to mono-digestion increased SMY by 12%.

ARTICLE INFO

Article history:
Received 18 August 2014
Received in revised form 8 September 2014
Accepted 13 September 2014
Available online 20 September 2014

Keywords:
Trace elements
Biogas
Grass silage
Slurry

ABSTRACT

This study investigated the effect of trace element addition to mono-digestion of grass silage at high organic loading rates. Two continuous reactors were compared. The first mono-digested grass silage whilst the second operated in co-digestion, 80% grass silage with 20% dairy slurry (VS basis). The reactors were run for 65 weeks with a further 5 weeks taken for trace element supplementation for the mono-digestion of grass silage. The co-digestion reactor reported a higher biomethane efficiency (1.01) than mono-digestion (0.90) at an OLR of 4.0 kg VS m^{-3} d^{-1} prior to addition of trace elements. Addition of cobalt, iron and nickel, led to an increase in the SMY in mono-digestion of grass silage by 12% to 404 L CH_4 kg^{-1} VS and attained a biomethane efficiency of 1.01.

1. Introduction

1.1. Role of nutrients in anaerobic digestion

The role of nutrients in the anaerobic digestion process is a key aspect of digester performance and stability. Macronutrients (N, P, K, Na, Ca and Mg) are primarily associated with the digestate, and their potential role is as a fertiliser substitute or other valued added end products. They also act as important biological components in digestion systems. Micronutrients, or trace elements (TEs), are aligned to the operational performance of the reactor and any deficiency in such TEs can have a detrimental effect on potential biomethane yields. The bio-availability of TEs is primarily dependent on the chemical form in which they are present, and on the balance between individual macro-/micro-nutrients.

1.2. Benefit of trace elements in grass silage digestion

Grass silage, produced in excess of livestock requirements, is an essential substrate in the establishment of an anaerobic digestion industry in Ireland. In a previous paper by the authors (Wall et al., 2014), continuous mono-digestion of grass silage (termed R6 in the paper) was shown to give high specific methane yields (SMY) of 398 L CH_4 kg^{-1} volatile solids (VS) at an organic loading rate (OLR) of 3.5 kg VS m^{-3} d^{-1}. However, as the OLR was increased to 4.0 kg VS m^{-3} d^{-1}, the SMY decreased to 360 L CH_4 kg^{-1} VS; a drop of 12%. The system employed recirculation of effluent liquor (<25 g dry solids (DS) kg^{-1}) to ensure the reactor remained at a desirable solids content (<100 g DS kg^{-1}). This led to a shortened hydraulic retention time (HRT) of 19 days, which is postulated as a reason for the drop off in SMY.

To maintain high SMYs for mono-digestion of grass silage it is suggested that specific TEs be added to the reactor. Alternatively co-digestion with dairy cow slurry, an abundant agricultural resource in Ireland may be utilised. The addition of 20% dairy slurry

* Corresponding author at: Environmental Research Institute, University College Cork, Cork, Ireland.
E-mail address: jerry.murphy@ucc.ie (J.D. Murphy).

http://dx.doi.org/10.1016/j.biortech.2014.09.066
0960-8524/

(on a VS basis) to a grass silage fed digester (termed R5 in the paper) was shown to ensure maximum biomethane efficiency at an OLR of 4.0 kg VS m^{-3} d^{-1} (Wall et al., 2014). Biomethane efficiency is defined as the SMY in continuous digestion divided by the SMY from a biomethane potential (BMP) test. Thus in co-digestion, the SMY obtained from continuous trials matched the yields from a BMP test under optimum conditions.

It is postulated that TEs present in the grass-slurry mixture (R5) allowed a higher biomethane efficiency (1.01) to be achieved than mono-digestion of grass silage (R6) which achieved an efficiency of 0.90. However, as a potential anaerobic digestion co-substrate, slurry is high in water content, takes up a large proportion of reactor volume and at high concentrations can dilute the SMY of the digester.

1.3. Review of trace element additions in anaerobic digestion

Successful digestion of all biomass involves a sufficient concentration of both macronutrients and TEs (Takashima and Speece, 1989). Past literature has shown certain TEs, more specifically cobalt, nickel, molybdenum and selenium, are reported to be critical to process performance and any deficiency in such nutrients can inhibit methanogenesis (Schattauer et al., 2011). Other micronutrients such as cadmium, manganese, iron, zinc and copper are also accounted for in the digestion process but are generally thought to be abundant in most feedstocks (Schattauer et al., 2011). TEs in a digester serve as co-factors in enzymes directly involved with the degradation of the feedstock and in the formation of methane (Pobeheim et al., 2010, 2011). The unavailability of essential TEs in a reactor can upset digester stability and performance even when other process conditions remain under control (Demirel and Scherer, 2011).

The digestion process involves a complex matrix of both organic and inorganic matter and thus the bioavailability of certain TEs is often difficult to assess (Gustavsson et al., 2013). In general, the bioavailable nutrients represent only a fraction of the total amount measured in the medium (Oleszkiewicz and Sharma, 1990). Most of these TEs are present in the solid fraction of the substrate, whereas alkalinity and ammonia are more closely associated with the liquid phase (Zhang et al., 2011). Microbial communities in mono-digestion systems are said to have more issues with TE bioavailability than systems operating in co-digestion (Pobeheim et al., 2011). It is recommended that the process liquid effluent should be recirculated within the system as this can potentially increase the availability of the TEs (Jarvis et al., 1997). The addition of slurry residues to a digester has been recommended to alleviate concerns of TE deficiencies in a mono-substrate reactor (Braun et al., 2003; Seppälä et al., 2013). However, contrasting studies have suggested that slurry alone may not be enough to overcome such shortfalls (Schattauer et al., 2011). The addition of a low methane-yielding substrate such as slurry (<20 m^3 CH_4 m^{-3}) must be carefully balanced with the economic viability of the digester (Angelidaki and Ellegaard, 2003). Likewise, the supplementation of a digester with TEs needs to be done with care. Facchin et al. (2013) suggested that the addition of unneeded metals can have an adverse effect on methanogenesis. In a study examining a number of digesters across Europe, Schattauer et al. (2011) found great variations in TE concentrations ranging from 1–2 orders of magnitude.

The majority of past literature examining the role of TEs has focused on the digestion of food waste. This can be seen in the work of Zhang et al. (2011, 2012), Zhang and Jahng (2012), Banks et al. (2012), Jiang et al. (2012) and Facchin et al. (2013). These particular studies indicate a deficiency in TE for food waste digestion although this can potentially be rectified by the addition of element-rich supplements. However, recommended guidelines for concentrations of TE additions are generally not applicable to the digestion of crops since crops have quite different TE contents (Hinken et al., 2008). Previous literature on the availability of TEs in crops is limited, particularly when considering mono-digestion of grass. Jarvis et al. (1997) examined grass clover digestion and the requirements of methanogenic archaea for different TEs. It was reported that an increase in TE availability could potentially be achieved through recirculated process effluent. The same study indicated a critical cobalt concentration of 0.02 mg L^{-1}. Additions of cobalt provided a stimulatory effect on methanogenesis and thus higher methane yields were achieved. Another study, focused on the digestion of napier grass, showed that the addition of nickel, cobalt, molybdenum, selenium and sulphate solution (0.25 mg L^{-1}, 0.19 mg L^{-1}, 0.30 mg L^{-1}, 0.062 mg L^{-1} and 1.6 mg L^{-1}, respectively) enhanced methane yields by 40% and prevented volatile fatty acid (VFA) accumulation (Wilkie et al., 1986).

Although grass silage is a key feedstock in establishing an anaerobic digestion industry in Ireland, maize silage is the predominant substrate in central Europe. Pobeheim et al. (2010) looked at a synthetic model substrate for maize silage and the impact of essential TEs in mesophilic batch reactors. The study showed that the addition of a TE solution boosted methane yields by up to 30%, with nickel and cobalt the most significant components. Molybdenum was not found to have any significant effect. TE additions in semi-continuous reactors were also examined, again with a defined model substrate for maize (Pobeheim et al., 2011). Once more, nickel and cobalt were found to be limiting and deficiencies in these TEs caused an accumulation of organic acids. Concentrations of 0.6 and 0.05 mg kg^{-1} (fresh weight) of nickel and cobalt were recommended and allowed an OLR of 4.3 kg VS m^{-3} d^{-1} to be achieved.

Methanogenesis has two principal pathways – acetoclastic and hydrogenotrophic. The acetoclastic pathway refers to the conversion of acetic acid to methane and carbon dioxide while the hydrogenotrophic pathway refers to the formation of methane from hydrogen and carbon dioxide (Schattauer et al., 2011). TE non-availability is growth limiting to methanogens (Karlsson et al., 2012). Previous studies have shown that when the concentrations of both nickel and cobalt are sufficient, the microbial community will be dominated by acetogenic methanogens while hydrogenotrophic methanogens will thrive under a deficiency in these elements, resulting in VFA accumulation (Gustavsson et al., 2013).

1.4. Objectives

This study expands upon previous work undertaken by the authors (Wall et al., 2014) in assessing mono-digestion of grass silage and co-digestion of grass silage with dairy cow slurry in continuously stirred tank reactors (CSTR). Mono-digestion of grass silage (R6) saw a decreased SMY and reduced biomethane efficiency (0.90) at an OLR of 4.0 kg VS m^{-3} d^{-1}. The objective of this study was to develop comprehensive TE profiles to pinpoint specific TEs that may be supplemented to mono-digestion of grass silage to boost efficiency at high OLRs. This was assessed by comparing TE concentrations of R6 (100% grass silage) and R5 (co-digestion of grass silage with 20% slurry addition on a VS basis) at the same OLR over an operational timeframe of 70 weeks.

2. Methods

2.1. Grass silage

The grass silage used for the CSTR trial was a first-cut perennial ryegrass (*Lolium perenne*), harvested at an early inflorescence growth stage, and was obtained from the Animal and Grassland Research and Innovation Centre (Teagasc, Grange) in Dunsany, Co. Meath, Ireland. A period of 24 h was allowed for field wilting post-mowing. The silage was then ensiled in 1.2 m diameter × 1.2 m wide cylindrical bales wrapped in polyethylene stretch-film for 5 weeks.