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Increased loading rates and specific methane yields facilitated by digesting grass silage at thermophilic rather than mesophilic temperatures

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HIGHLIGHTS

- Thermophilic digestion of grass allowed for high loading and specific methane yield.
- Reduced viscosity properties at 55 °C facilitated mixing and fermentation of grass.
- Stable digestion at 4 g VS L^{-1} d^{-1} and 46 days retention yielded 381 L CH_4 kg VS^{-1}.
- Biomethane efficiencies were highest at loading rates of 3 and 4 g VS L^{-1} d^{-1}.
- A loading rate of 7 g VS L^{-1} d^{-1} was feasible without recirculation of liquor.

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ABSTRACT

This study was conducted to advance the understanding of thermophilic grass digestion. Late harvested grass silage was fermented at thermophilic conditions at increasing organic loading rates (OLR). Stable digestion took place at an OLR between 3 and 4 g VS L^{-1} d^{-1}. This enabled specific methane yields (SMY) as high as 405 L CH_4 kg VS^{-1}. An accumulation of volatile fatty acids (VFA), accompanied by a gradual deterioration of pH, FOS/TAC (ratio of VFA to alkalinity) arose at an OLR between 5 and 7 g VS L^{-1} d^{-1}, yet inhibition did not occur. SMY decreased with reduced retention time ranging between 336 and 358 L CH_4 kg VS^{-1} at OLR 7 and 5 g VS L^{-1} d^{-1} respectively. The biomethane efficiencies remained high (92–103%) at corresponding retention times. Comparative results indicated a superior performance with respect to higher loading and SMY as compared with mesophilic conditions.

1. Introduction

Ireland's temperate climate provides ideal conditions for grass production and grazing based livestock systems. Grass silage surplus to livestock requirements has been identified as a potential source for biomethane production in Ireland (McEniry et al., 2013; Murphy and Power, 2009; Wall et al., 2013). In respect of Ireland's EU 2020 targets, 1.1% of grassland co-digested with the majority of slurry from dairy cows could satisfy 10% of renewable energy supply in transport (Wall et al., 2013). Furthermore, grass as a renewable gaseous transport fuel gives at least a 50% better net energy yield per hectare than the next best indigenous European liquid biofuel system (Smyth et al., 2009).

Grassland not suitable for grazing or forage, such as roadside plantings, green wastes, nature conservation biomass or fallow land is a valuable source of substrate for anaerobic digestion. Those resources are typically only harvested once or twice a year at an advanced growth stage and exhibit a lignocellulosic composition. The more complex form of this biomass includes for enhanced fractions of lignin and hemi-cellulose, locking accessibility to easily degradable carbohydrate fractions. This results in a more incomplete fermentation and reduced rates of degradation at standard conditions. Possible technologies to break up the lignocellulosic structure and facilitate accessibility to easy degradable fractions include for substrate specific mechanical, chemical, biological, sonic or thermal treatment methods. Current research in increasing yields include for assessment of: chemical treatment with acids; biologically treatment with enzymes; hydrolysis pretreatment; and change in pH or temperature (Amnuaycheewa et al., 2016; Kumar et al., 2015; Wall et al., 2016).

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The potential for grass digestion systems has been extensively examined at mesophilic temperatures in Ireland (Allen et al., 2016; Nizami and Murphy, 2010; Nizami et al., 2012; Singh et al., 2011; Thamsiriroj et al., 2012; Wall et al., 2014a; Wall et al., 2014b). Yields from 349 to 451 L CH_4 kg VS^{-1} have been obtained depending on harvest date and maturity. Other studies suggest methane yields of 253–394 L CH_4 kg VS^{-1} for mesophilic mono and co-digestion of various grass species (Koch et al., 2009; Mähnert et al., 2005; Seppälä et al., 2009; Xie et al., 2011).

Managing sustainable grass digestion systems, through maximum possible loading rates, whilst generating a high specific methane yield, remains a critical design challenge. Xie et al. (2011) achieved stable co-digestion of grass silage with pig manure, however mono-digestion failed. Thamsiriroj et al. (2012) investigated long-term operation of mesophilic grass mono-digestion and suggested a limit of 3 g VS L^{-1} d^{-1}. Mechanical failure was manifested when this loading rate was exceeded. This was mainly attributed to insufficient mixing caused by enhanced viscosity and a dry solids (DS) level rising above 12%. Wall et al. (2014b) assessed the optimisation of digester performance with increasing organic loading rates for mesophilic mono and co-digestion of grass silage. Recirculation of liquid effluent was incorporated to maintain a dry solids content below 12% in the reactor. Optimum conditions were assessed for grass mono-digestion at an organic loading rate (OLR) of 3.5 to 4 g VS L^{-1} d^{-1}. Despite the benefits of grass digestion, it remains a challenging substrate for anaerobic digestion, in particular if no dilution, co-digestion or recirculation of liquor occurs. The high fibre and total solids content impacts negatively on the prevailing viscosity in the reactor. This is the main reason why loading rates exceeding 4 g VS L^{-1} d^{-1} in grass mono-digestion have not been reported in literature.

However, an increase in temperature mitigates those limiting effects due to improved kinetic properties, increased enzyme activity, reduced viscosity, higher substrate utilisation and growth rates of bacteria (Mähnert, 2007). The correlation of loading and dry solids on viscosity, based on mesophilic and thermophilic digestion of maize, rye and sugar beet silage was outlined in detail by Mähnert (2007). An increase in loading provoked a significant gain in viscosity at mesophilic temperatures. However, at similar dry solids content in the reactor the thermophilic reactor displayed a lower viscosity. For 100% maize digestion the apparent viscosity at 7% DS accounted for 0.6 Pa s at mesophilic (35 °C) digestion and 0.2 Pa s for thermophilic (55 °C) digestion. The greater the loading rate and dry solids content, the more distinct this difference became.

Table 1
Characteristics of the substrate grass silage (harvest 24th June).

Parameters		Grass silage
pH		4.6
Dry solids (DS)	g kg^{-1}	199
Volatile solids (VS)	g kg^{-1}	181
VS/DS	g kg^{-1}	910
Neutral detergent fibre (NDF)	g kg^{-1} DS	716
Acid detergent fibre (ADF)	g kg^{-1} DS	400
Dry solids digestibility (DSD)	g kg^{-1} DS	555
Crude protein	g kg^{-1} DS	148
Water soluble carbohydrate	g kg^{-1} DS	71
C:N ratio		26.5
Cadmium	mg kg^{-1}	<0.19
Cobalt	mg kg^{-1}	<0.29
Copper	mg kg^{-1}	1.95
Iron	mg kg^{-1}	106.5
Manganese	mg kg^{-1}	11.1
Molybdenum	mg kg^{-1}	1.16
Nickel	mg kg^{-1}	0.70
Selenium	mg kg^{-1}	<0.19
Zinc	mg kg^{-1}	6.50

The relevant gap in the state of the art is that though the advantages of thermophilic systems have been widely described, there is no literature on assessing thermophilic digestion of late cut grass silage at increasing organic loading rates and comparing to mesophilic digestion. The innovation in this paper is that it:

- Assesses the biomethane potential (BMP) of late cut grass silage at a range of retention times at thermophilic temperatures.
- Contrasts BMP values at thermophilic and mesophilic temperatures.
- Assesses the specific methane yield (SMY) of late cut grass silage in continuous thermophilic digestion at increasing loading rates.
- Assesses the ratio of the SMY to the BMP at thermophilic temperature ranges at the same retention times.

2. Materials and methods

2.1. Inoculum and substrate

The inoculum was obtained from a full scale thermophilic digester based on manure and crops operating at an OLR of 7 g VS L^{-1} d^{-1}. The feedstock was a first-cut perennial ryegrass (*Lolium perenne*), harvested on the 24th June (a late growth stage for Ireland) to address the utilisation of a more mature and lignocellulosic substrate. The wilted grass was ensiled for 5 weeks in 1.2 m diameter cylindrical bales wrapped in polyethylene foil and subsequently repacked into stretch-film wrapped 25 kg bales. The particle size of the grass silage was further reduced with a heavy duty mincer to a size between 5 and 10 mm. It was stored at a temperature of −20 °C until fed to the anaerobic reactors. The characteristics of the substrate grass silage (harvest 24th June) are indicated in Table 1. The delayed time of harvest influenced the digestibility of the silage, reflected by increased neutral detergent fibre (NDF) and acid detergent fibre (ADF). As a result, dry solids digestibility (DSD) remained at lower levels than normal for Irish first cut grass silage.

2.2. Nutrient supplementation

The grass silage contained trace element metals such as Co (Cobalt), Cu (Copper), Fe (Iron), Ni (Nickel), Mn (Manganese), Mo (Molybdenum), Ni (Nickel), Se (Selenium) and Zn (Zinc) in the range of 0.19–11.2 mg L^{-1} (Table 1). Some of the key trace elements for anaerobic digestion (such as Co, Mo, Ni and Se) were undersupplied and partly below the detection limit as suggested by others (Banks et al., 2012; Lemmer et al., 2010; Pobeheim et al., 2011; Thamsiriroj et al., 2012; Voelklein et al., 2016; Wall et al., 2014a). Thamsiriroj et al. (2012) and Wall et al. (2014a) found positive effects in supplementing deficient elements such as cobalt, iron and nickel to grass digestion trials. The selected concentrations for supplementation of trace elements in this experiment followed the supplementation levels in operation at the full scale digester (where the inoculum was sourced) and coincided with concentrations most frequently applied and recommended values from literature (Banks et al., 2012; Lemmer et al., 2010; Pobeheim et al., 2011; Thamsiriroj et al., 2012; Voelklein et al., 2016; Wall et al., 2014a). Levels of 0.5 mg L^{-1} Co, 500 mg L^{-1} Fe, 5 mg L^{-1} Mo, 5 mg L^{-1} Ni and 0.5 mg L^{-1} Se were added to the feedstock. In the present study Co was added in the form of $CoCl_2{\cdot}6H_2O$, Fe as $FeCL_3{\cdot}6H_2O$, Mo as $H_{24}Mo_7N_6O_{24}{\cdot}4H_2O$, Ni as $Cl_2Ni{\cdot}6H_2O$ and Se as Na_2SeO_3. Adequate amounts of iron were added to precipitate emerging hydrogen sulphate to iron sulphur compounds and maintain increased bioavailability of the trace elements in the reactor.