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Identification of synergistic impacts during anaerobic co-digestion of organic wastes

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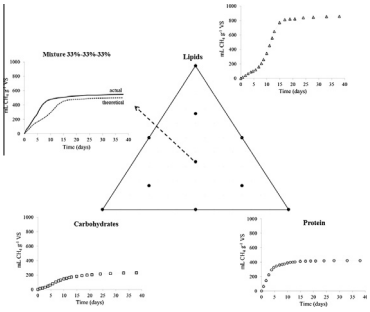
HIGHLIGHTS

- Pure and slaughterhouse carbohydrate, protein, and lipid substrates were tested.
- Modelling was used to quantify the impact of mixing substrates.
- LCFA inhibition was substantial and detrimental with a K_I of 1.3 g VS L^{-1}.
- Co-digestion did not increase ultimate biodegradability.
- Co-digestion mitigated LCFA inhibition, mainly through dilution.

GRAPHICAL ABSTRACT



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ABSTRACT

Anaerobic co-digestion has been widely investigated, but there is limited analysis of interaction between substrates. The objective of this work was to assess the role of carbohydrates, protein and lipids in co-digestion behaviour separately, and together. Two sets of batch tests were done, each set consisting of the mono-digestion of three substrates, and the co-digestion of seven mixtures. The first was done with pure substrates – cellulose, casein and olive oil – while in the second slaughterhouse waste – paunch, blood and fat – were used as carbohydrate, protein and lipid sources, respectively. Synergistic effects were mainly improvement of process kinetics without a significant change in biodegradability. Kinetics improvement was linked to the mitigation of inhibitory compounds, particularly fats dilution. The exception was co-digestion of paunch with lipids, which resulted in an improved final yield with model based analysis indicating the presence of paunch improved degradability of the fatty feed.

1. Introduction

Cattle slaughterhouses process meat for human consumption, animal by-products (e.g. meat, bone and blood meal, tallow and skin) and generate a large variety of solid and liquid waste (Cuetos et al., 2008). The latter represents 5–10% of the total animal weight depending on the degree of further processing of the slaughtered animals, with the majority of waste being cattle paunch, or undigested feed (Jensen et al., 2013). Cattle slaughterhouse waste (SHW), which includes multiple waste streams such as stomach and intestinal content, fat, manure, blood and rendering residues, has emerged as an industrial waste with strong potential to recover energy and nutrient resources through waste management. SHW is considered a good substrate for anaerobic digestion, however, the composition of SHW is highly variable with methane yields ranging between 230 and 700 mL CH_4 kg^{-1} VS (Edström et al., 2003; Cuetos et al., 2008; Hejnfelt and Angelidaki, 2009; Zhang and Banks, 2012). Anaerobic treatment

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of SHW also includes risks associated with the high concentration of ammonia (NH_3) and/or long chain fatty acids (LCFA), potential inhibitors of the methanogenic activity (Cuetos et al., 2008). Ammonia inhibition is related to its capacity to diffuse into microbial cells and disruption of cellular homeostasis (Kayhanian, 1999), whereas LCFAs adsorb onto the cell membrane, interfering with membrane functionality (Palatsi et al., 2009; Chen et al., 2008). Since ammonia is a by-product of protein acidification and LCFAs are an intermediate product from the degradation of fat, oil and grease, slaughterhouse wastewater as well as other high-value wastes are high-risk, with inhibition being directly linked to the composition. Nevertheless, process instability and inhibition may be minimised through anaerobic co-digestion, which uses the degradation properties of a mixture of wastes to mitigate or dilute specific compounds (Mata-Alvarez et al., 2011).

Anaerobic co-digestion (AcoD) is a process where two or more substrates with complementary characteristics are mixed for combined treatment. AcoD has been reported as a feasible solution to overcome ammonia and LCFA inhibition and to improve the methane yield of SHW digestion. SHW have been successfully co-digested with biowaste (Zhang and Banks, 2012), manure (Hejnfelt and Angelidaki, 2009) and mixture of biowaste and manure (Edström et al., 2003; Murto et al., 2004; Alvarez and Lidén, 2008; Cuetos et al., 2008). In AcoD, the improvement in methane production is mainly a result of the increase in organic loading rate (Astals et al., 2013); however, when possible, it is important to choose the best co-substrate and blend ration in order to: (i) favour positive interactions, i.e. synergisms, macro- and micro-nutrient equilibrium and moisture balance; (ii) dilute inhibitory or toxic compounds; (iii) optimise methane production and (iv) enhance digestate stability (Astals et al., 2011; Mata-Alvarez et al., 2011). Even though all these factors should be considered, the decisions on the ratio between wastes had been typically simplified to the optimisation of the carbon-to-nitrogen (C/N) ratio, where optimum reported values vary from 20 to 60 (Alvarez et al., 2010; Mata-Alvarez et al., 2014; Wang et al., 2012). At the present time, there is limited knowledge about how waste composition (carbohydrates, protein and lipids) influences AcoD performance or whether interactions between substrates enhance or attenuate inhibition thresholds, degradation rates, or biogas yields on individual substrates. The degradation of carbohydrates, protein and lipids occur by different metabolic pathways, with varying rates and methane yields (Angelidaki and Sanders, 2004) and therefore knowledge about the influence of the substrate macro-composition would enhance the understanding and utility of potential and/or novel AcoD applications.

Reliable AcoD modelling is required to predict, in a clear and quantifiable manner, the effect of mixing two or more wastes in a digester and remove potentially negative impacts from mixing based on random or heuristic decisions (Astals et al., 2011; Mata-Alvarez et al., 2011). In addition, a better mechanistic understanding of how different feeds mix may reduce the time and costs associated with laboratory experiments as well as improve co-substrate selection and dose rates (Mata-Alvarez et al., 2014). Models are also useful to estimate important biochemical parameters such as biodegradability, hydrolysis rate and inhibition constant, which are critical in AD design, performance and troubleshooting (Batstone et al., 2009; Jensen et al., 2011). Recent nonlinear parameter estimation methods can provide quantitative and rigorous analysis of the impacts of AcoD (Batstone et al., 2003, 2004).

The aim of the present study was to identify the interactions (synergisms and antagonisms) between carbohydrates, protein and lipids that take place during anaerobic co-digestion, focusing on process kinetics and anaerobic biodegradability of the substrates for a mechanistic model-based understanding of AcoD. This aims at identifying AcoD opportunities and, consequently, improving the anaerobic digestion of slaughterhouse and other similar wastes.

2. Methods

2.1. Chemical analytical methods

Analyses of the total fraction were performed directly on the raw samples. For analyses of the soluble fraction, the samples were centrifuged at 4000 *g* for 5 min and then the supernatant was filtered through a 0.45 μm PES Millipore® filter. Total solids (TS) and volatile solids (VS) were measured according to standard methods procedure 2540G with minor modifications (APHA, 2005). Specifically, samples were dried overnight, at least 16 h, in a Clayson OM1000ME oven set at 103 °C and afterwards samples were volatilised in a BTC 9090 muffle furnace (heating ramp from room temperature to 550 °C and held for 3 h). Total chemical oxygen demand (CODt) and soluble chemical oxygen demand (CODs) were measured using Merck COD Sprectroquant® test, range 500–10000 mg L^{-1}, and by a SQ 118 spectrophotometer (Merck, Germany). Volatile fatty acids (acetic, propionic, butyric and valeric) and ethanol were analysed by an Agilent 7890A gas chromatograph equipped with a Phenomenex ZB-FFAP column (15 m length, 0.53 mm internal diameter and 1.0 μm film) and a flame ionization detector. The chromatograph oven program was as follows: hold 2 min at 60 °C, ramp to 240 °C at 20 °C min^{-1}, and hold 2 min. Injector and detector temperature was set at 220 °C and 300 °C, respectively; 12.5 mL min^{-1} of high purity Helium at 8.6 psi was used as carrier gas. Nitrogen and phosphorous ions (NH_4^+, NO_2^-, NO_3^-, PO_4^{3-}), total Kjeldahl nitrogen (TKN) and phosphorous (TKP) were determined by a Lachat Quik-Chem 8000 flow injection analyser using the methods (QuickChem®) developed by the instrument provider (Lachat Instruments, US). Metals ions were determined by an inductively coupled plasma optical emission spectrometer (ICP-OES) Perkin Elmer Optima 7300 DV, which uses 15 L min^{-1} of high purity Argon as plasma gas. Prior to plasma analysis, samples were digested (15 min at 200 °C) with 10% nitric acid in a MARS Xpress microwave. Total and soluble carbohydrates were analysed by the anthrone method using glucose as standard (Smith et al., 1985). Total and soluble protein was determined by the bicinchoninic acid method using bovine serum albumin as standard (Raunkjær et al., 1994). Oil and grease were determined by a Wilks Enterprise, Inc. InfraCal TOG/TPH analyser, where S-316 was used as extraction solvent.

2.2. Biochemical methane potential test

Biochemical methane potential (BMP) tests were carried out according to Angelidaki et al. (2009) in 240 mL glass serum bottles at mesophilic temperature. All tests contained 120 mL inoculum, the amount of substrate that met an inoculum to substrate ratio (ISR) of 2 (VS-basis) and deionised water, added to make up the total test volume to 160 mL. Bottles were flushed with 99.99% N_2 gas for 1 min (4 L min^{-1}), sealed with a rubber stopper retained with an aluminium crimp seal and stored in temperature-controlled incubators (37 ± 1 °C). Tests were mixed by inverting once per day. Blanks containing inoculum and no substrate were used to correct for background methane potential in the inoculum. All tests and blanks were carried out in triplicate, and all error bars indicate 95% confidence in the average of the triplicate. Biogas volume was measured by manometer at the start of each sampling event. Accumulated volumetric gas production was calculated from the pressure increase in the headspace volume (80 mL) and expressed under standard conditions (0 °C, 1 bar). At each sample event, the biogas composition (CH_4, CO_2 and H_2) was determined