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Investigation of the optimal percentage of green seaweed that may be co-digested with dairy slurry to produce gaseous biofuel

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HIGHLIGHTS

- The optimum mix of fresh *U. lactuca* is 25% by VS content with dairy slurry.
- The optimum loading rate is suggested as 2.5 kg VS m^{-3} d^{-1}.
- For stable operation it is suggested that management of trace elements is required.
- Critical parameters include high levels of chloride, calcium and VFA.
- Levels in excess of 75% *U. lactuca* are not recommended.

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ABSTRACT

Ulva lactuca, a green seaweed, accumulates on beaches and shallow estuaries subject to eutrophication. As a residue, and a macro-algae, it is a source of sustainable third generation biofuel. Production of biomethane from mono-digestion of *U. lactuca*, however is problematic due to high levels of sulphur and low ratios of carbon to nitrogen. Fresh and dried *U. lactuca* were continuously co-digested with dairy slurry at ratios of 25%, 50% and 75% (by volatile solid content) in 6 number 5 L reactors for 9 months. The reactors digesting a mix with 75% *U. lactuca* struggled to reach stable conditions. Volatile fatty acid levels of 14,000 mg l^{-1} were experienced. The levels of ammonia increased with percentage *U. lactuca* in the mix. Optimum conditions were observed with a mix of 25% fresh *U. lactuca* and 75% slurry. A yield of 170 L CH_4 kg^{-1} VS was achieved at an organic loading rate of 2.5 kg VS m^{-3} d^{-1}.

1. Introduction

1.1. The rationale for macro-algae as a source of biofuel

By 2020 according to The Renewable Energy Directive (European Commission, 2012a), 10% of energy use in transport should be renewable. In 2011 first generation biofuels provided for approximately 5% renewable energy supply in transport (RES-T) in the EU. In October 2012 an EC proposal (European Commission, 2012b) suggested limiting first generation food based biofuels to 5% RES-T. This limit was proposed to be raised to 6% in September 2013 (European Parliament, 2013) at which time it was also stipulated that advanced biofuels, such as sourced from seaweed, should represent at least 2.5% of RES-T by 2020.

Seaweed (or macro-algae) biofuels are deemed to be third-generation. They do not interfere with food production directly (they do not use food crops) or indirectly (they do not use agricultural land). From an energy perspective the differentiation between first, second and third generation biofuels can be noted with reference to potential gross energy yield per hectare. For example rape seed biodiesel (first generation) generates approximately 1350 L (44 GJ) of biodiesel per hectare per annum (Thamsiriroj and Murphy, 2009), willow biomethane (second generation biofuel produced through gasification) generates a gross energy yield of ca. 130 GJ ha^{-1} a^{-1} (Gallagher and Murphy, 2013). The yields per hectare of algae are not fully documented; however Christiansen (2008) stated that yields of 130t of kelp may be achieved per hectare. Allowing for 15% volatile solids and 330 L CH_4 kg^{-1} VS (Vanegas and Bartlett, 2013) the gross energy per hectare would be of the order of 230 GJ^{-1} ha^{-1} a^{-1}.

Ireland, with over 7500 miles of coastlines and direct access to the Atlantic Ocean offers itself as an ideal location to utilise macro-algae as a source of biofuel. Algae can be either cultivated in

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aquaculture farms or harvested from beaches or from the sea. *Ulva lactuca*, a green seaweed is a particular case in that it is a scourge to coastal environments that have long shallow bays which are subject to eutrophication. This has become more endemic in recent years in France, Denmark and Japan. It is seen as an algae bloom and can result in thousands of tonnes washing up on to beaches, forcing closures (Charlier et al., 2007). However the quantity of the bloom can lead to a cheap source of biofuel as it greatly reduces the harvesting costs.

1.2. Biomethane production from green seaweed

Anaerobic digestion (AD) is a relatively low energy input process which converts wet substrates to a gaseous biofuel. Germany has in excess of 7000 digestion facilities with substrates dominated by crops such as maize, cereals and grass (Murphy et al., 2011). Biogas produced from these systems which can have very good energy balances (Smyth et al., 2009) is never the less classified as first and second generation biofuel, and directly or indirectly compete with land for food production (EASAC, 2013). Production of biogas from macro-algae has not occurred in a commercial setting. The scientific literature on biogas from macro-algae, in particular *U. lactuca,* is very recent and relatively sparse. Most of the work relates to laboratory batch studies that do not give any indication of the operating conditions in continuous commercial operation of a bio-digester. Continuous co-digestion of *Ulva* sp. with pig or dairy slurry, respectively, was tested by Peu et al. (2011) and Sarker (2013). However, these studies did not focus on optimisation of mixtures of Ulva with co-substrates or the effect of varying the organic loading rates, which are essential parameters for continuous co-digestion. *U. lactuca* has been shown to have potential as an AD feedstock reaching yields of between 128 and 271 L CH_4 kg^{-1} VS (Allen et al., 2013a). *U. lactuca* has extremely low levels of lignin making it readily accessible for microbial digestion (Ventura and Castañón, 1998). However a crucial aspect of anaerobic digestion is the carbon to nitrogen (C:N) ratio; optimum values range from 20 to 30. *U. lactuca* has a C:N ratio less than 10 (Allen et al., 2013a). This can lead to problematic digestion due to excess levels of total ammonia nitrogen (TAN) which may inhibit methanogenesis. Co-digestion benefits from increased C:N ratios which aid digestibility and have been found to increase the level of digestibility for specific substrates (Lehtomäki et al., 2007). One method of increasing the C:N ratio is to co-digest with dairy slurry, which is characterised by a higher C:N ratio of above 20 (Seppälä et al., 2013) and in addition has a rich base of trace minerals, increasing digester efficiency (Yangin-Gomec and Ozturk, 2013).

U. lactuca also has a high sulphur content which can result in significant levels of hydrogen sulphide (H_2S) in the produced biogas (Percival and McDowel, 1968). H_2S is toxic and results in increased corrosion of equipment in biogas plants. High levels of dissolved H_2S can also act as an inhibitor to microorganisms of the AD process (Peu et al., 2011). Potential H_2S concentrations in biogas produced from a particular substrate can be forecasted by examining the carbon to sulphur ratio (C:S). The minimum recommended ratio is 40. Sulphur available for reduction or fermentation to H_2S is proportional to the biodegradable content of carbon in the substrate (Peu et al., 2012). A substrate with a C:S below 40 will tend to have larger accumulations of H_2S gas as experienced by seaweed digestion trails (Peu et al., 2012).

1.3. Aims and objectives

This paper builds upon previous work by the authors who evaluated co-digestion of Ulva and slurry in biomethane potential (BMP) assays operated in batch mode (Allen et al., 2013a). The aim of this paper is to assess the suitability of green seaweed in continuous long term co-digestion and to glean information on optimal operating parameters. The objectives are to establish:

(1) What is the optimal percentage of Ulva that may be co-digested with dairy slurry in a stable continuous anaerobic process?
(2) What is the optimal organic loading rate (OLR) for continuous co-digestion of Ulva and dairy slurry?
(3) What parameters are likely to lead to failure in digestion of green seaweed?

2. Methods

2.1. Materials

Approximately 300 kg of *U. lactuca* was sampled from Harbour view beach, Timoleague, Cork, Ireland in August, 2012. This was the same *U. lactuca* used in previous trials by the authors (Allen et al., 2013a). The seaweed was not washed. Drying was conducted by placing on airing tables with hot air passed up through the seaweed for 36 h at 80 °C. The seaweed was separated into 20 kg bags, frozen and stored at −20 °C.

Dairy slurry was collected from a dairy farm of 200 milking cows, in Cork, Ireland. The sampled slurry came from cows housed indoors, at the end of the lactation period. A significant quantity of slurry was collected and frozen in separate containers. Ulva and dairy slurry samples were defrosted prior to feeding of the digesters. All reactors were filled with the same inoculum. The inoculum used for the trials, was taken from a pilot scale reactor, fed only dairy slurry, which was operating in the same research lab. The inoculum was sieved through a 1 mm sieve and placed in each reactor and left to run for 1 week to remove residual gas which may contribute to biogas production. Biomethane potential (BMP) was previously assessed (Allen et al. 2013a) in a proprietary biomethane potential (BMP) system (Bioprocess AMPTS II system) as described in Section 2.2.2. The substrates are described in Table 1.

2.2. Methods

2.2.1. Analytical methods

Total solids (TS) and volatile solids (VS) were analysed and calculated by using standard methods (APHA, 2011). The pH was measured by a Jenway 3510 pH metre. The ratio of organic acid concentration to alkalinity (referred to as Fos:Tac) was carried out according to the Nordmann titration method using 0.1 N sulphuric acid with pH 5.0 and 4.4 endpoints (Nordmann, 1977). The ammonia concentration in each reactor was measured in terms of Total Ammonical Nitrogen (TAN) using Hach Lange CLK 303 cuvettes, with a 1:100 dilution of digestate using a Hach Lange DR3900 spectrometer to read samples. Free ammonia (NH_3) was calculated from a standardised equation relating the ammonia content to pH and temperature of the liquor (Banks and Heaven, 2013) total volatile fatty acid (tVFA) content was measured using gas chromatography (Agilent HP 6890 Series) equipped with a Nukol™ fused silica capillary column (30 m × 0.25 mm × 0.25 μm), argon as a carrier gas and flame ionisation detector. Samples were tested every second week for acetic, propionic, iso-butyric, butyric, iso-valeric, valeric, iso-caproic, caproic and enanthic acid. Ultimate analysis of each substrate and digestate was carried out using an EAC CE 4500 elemental analyser. Samples for ultimate analysis were oven dried at 105 °C for 24 h and were ground to <0.6 mm particle size. Trace element analysis was carried out by a commercial lab (Agrolab Labor GmbH) using standard methods (DIN, 2009, 2005). Salinity and conductivity were calculated using a VWR hand held C0310 monitor. These parameters were measured in conjunction with chloride