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Biohydrogen and biomethane production sustained by untreated matrices and alternative application of compost waste

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ABSTRACT

Biohydrogen and biomethane production offers many advantages for environmental protection over the fossil fuels or the existing physical-chemical methods for hydrogen and methane synthesis.

The aim of this study is focused on the exploitation of several samples from the composting process: (1) a mixture of waste vegetable materials ("*Mix*"); (2) an unmatured compost sample (ACV15); and (3) three types of green compost with different properties and soil improver quality (ACV1, ACV2 and ACV3). These samples were tested for biohydrogen and biomethane production, thus obtaining second generation biofuels and resulting in a novel possibility to manage renewable waste biomasses.

The ability of these substrates as original feed during dark fermentation was assayed anaerobically in batch, in glass bottles, in order to determine the optimal operating conditions for hydrogen and/or methane production using "*Mix*" or ACV1, ACV2 or ACV3 green compost and a limited amount of water.

Hydrogen could be produced with a fast kinetic in the range 0.02–2.45 mL H_2 g^{-1} VS, while methane was produced with a slower kinetic in the range 0.5–8 mL CH_4 g^{-1} VS. It was observed that the composition of each sample influenced significantly the gas production. It was also observed that the addition of different water amounts play a crucial role in the development of hydrogen or methane. This parameter can be used to push towards the alternative production of one or another gas.

Hydrogen and methane production was detected spontaneously from these matrices, without additional sources of nutrients or any pre-treatment, suggesting that they can be used as an additional inoculum or feed into single or two-stage plants. This might allow the use of compost with low quality as soil improver for alternative and further applications.

1. Introduction

The exhaustion of fossil fuels and global warming are strong motivating factors for alternative fuels research. This makes it necessary to find alternative energy sources that are renewable and environment friendly (Powan and Danvirutai, 2014).

Many countries are interested in sustainable renewable energy sources such as geothermal and wind power, small-scale hydropower, solar energy, biomass energy, tidal and wave power (Berndes et al., 2003). Cellulosic biomass is a promising source due to its abundance and low cost (Dongmin and Hongzhang, 2007). Currently, biomass contributes about 12% of the world energy supply, while in many developing countries it contributes 40–50% energy supply. Biomass research is recently receiving increasing attention because of the probable waste-to-energy application (Ni et al., 2006). For instance, 150 Gt of vegetable biomatter generated globally every year can produce about 1.08×10^{10} GJ energy (Larminie and Dicks, 2000).

Biomass includes a large variety of materials generated by sunlight, such as agricultural wastes from farming and wood processing or dedicated bioenergy crops. The use of energy crops for fuel production has some drawbacks and there is a concern that they might indirectly cause an increase in the food price thus contributing to the global food crisis (Mei Guo et al., 2010). In line with these concerns, the latest amendment to the EU renewable energy

Abbreviations: AD, anaerobic digestion; TOC, total organic content; VS, volatile solids; MSW, municipal solid waste; OFMSW, organic fraction of municipal solid waste; VOAs, volatile organic acids; LOI, loss on ignition.

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directive (EU, 2009) introduces a limit to the contribution made from liquid biofuels produced from food crops, such as those based on cereals and other starch rich, sugars and oil crops (Browne et al., 2013). Therefore the attention has been redirected to the production of second generation biofuels, utilising biomasses derived from the carbonaceous waste of human activities, animal farming and agriculture as renewable natural resources for energy recovery (Muzenda, 2014).

Converting waste biomass into gaseous fuels, electricity and especially hydrogen (H_2) and methane (CH_4) is possibly the most efficient way of biomass utilisation and waste management (Ni et al., 2006).

Biohydrogen and biomethane could be produced from a large variety of organic substrates or biomasses by dark fermentation and anaerobic digestion (AD), respectively. The microorganisms transform biodegradable substrates into H_2, biogas and stabilised solid residues (Roati et al., 2012).

Biological H_2 production from organic matter is considered one of the most promising alternatives for sustainable green energy production. Dark fermentative H_2 production is a process in which strict or facultative anaerobic bacteria use organic compounds to produce H_2 in the absence of a light source. This process may have other environmental benefits such as the use of organic waste materials as the raw carbon source (Zu and Beland, 2006; Morra et al., 2014). The AD under oxygen-free conditions is most commonly applied to transform the organic matter into biogas. Biogas is a mixture of mostly CH_4 and carbon dioxide (CO_2). The microbial anaerobic conversion to biomethane is a process for both effective waste treatment and sustainable energy production (Wilkie, 2008).

The biohydrogen and biomethane production process could become sustainable in dedicated plants, the best performances being expected in a two-stage reactor plant. In a two-stage digestion, the first step involves loading material into a digestion tank where hydrolysis, acetogenesis and acidogenesis occur and a first stream of hydrogen and CO_2 can be produced and collected. The resulting digestate is then introduced into the methanogenic reactor for biogas/biomethane production. The two-stage process results in fast and efficient formation of biogas in the second stage with CH_4 concentrations up to 85%. Biohydrogen deriving from the first stage can be used directly in combustion engines for transportation or after purification in fuel cells to produce electricity (Kapdan and Kargi, 2006). The biomethane can be used *in situ* in a cogeneration system, it can be sent to national natural gas network or it can be used as a renewable biofuel in the automotive sector (Cucchiella et al., 2015). The combination of the two streams of hydrogen and methane generated in the two-stage plant can also be exploited as biohythane (Liu et al., 2013). H_2 and CH_4 production in a two-stage plant can utilise various types of substrates, for example residual materials and agricultural, food, farm and industrial wastes. In these types of plants, in both stages, the use of a source high in anaerobic microbes to start up anaerobic system is called inoculation. The type, quality and quantity of inoculum (or seed) are critical to the performance of the anaerobic digester. The most common seeds are various pure (Li and Chen, 2007; Kvesitadze et al., 2012) or mixed microbial cultures (De Gionnis et al., 2013). The second type seems to be preferred because the system would be cheaper to operate, easier to control and capable of digesting a variety of feedstock materials; some examples are anaerobic sludge from full-scale digesters, granular sludge, waste activated sludge, cattle manure (Guo et al., 2014; Zhang et al., 2007; Fan et al., 2006), and vegetable kitchen waste compost (Lee et al., 2010).

There are different types of compost: green compost (ACV) is made from tree and yard wastes, crop residues and other wastes of plant origin; brown compost (ACM) is obtained from municipal organic wastes, kitchen and canteen wastes, animal manure.

To date and to our knowledge, no study has yet been devoted to the use of ACV or of low quality green compost to produce H_2 and CH_4 via dark fermentation.

This study examined anaerobic fermentation of three different types of not pre-treated mature green composts (ACV1, ACV2 and ACV3), immature compost in bioxidation phase (ACV15) and raw material mixture of composting process ("*Mix*") by observing alterations in H_2 and CH_4 content utilising different amounts of water. The test was done in small scale and in batch condition and these studies were performed under mesophilic conditions. The research aims at evaluating the possible alternative use of compost, and in particular of low quality batches unsaleable as soil improvers, as feedstock in industrial plant for H_2 and CH_4 productions.

2. Material and methods

2.1. Waste biomass samples

Waste biomasses at different maturation state from composting process were provided and collected from the company Agri New Tech, located in Torino, Italy.

The composting process is the standard protocol that is commercially used by the company. Briefly, plant biomass was crushed to a maximum size of 10 mm and composting piles were prepared. Piles dimensions were 5 m large and 3 m high. Piles were turned once every 7 days for approximately 1–2 months, until temperature rose over 50°C (degradation phase). After that, piles were turned once every 15 days for another 1–3 months until completely mature. The entire process lasted for a minimum of 3 months.

The samples were collected in different periods and analysed immediately after collection (with the exclusion of ACV3): green compost (ACV3) in January 2013; mixture of green wastes (sample defined as "*Mix*") in December 2013; early composted wastes (ACV15) in January 2014 after 15 days from the start of composting process; green composts (ACV1 and ACV2) in February 2014.

The most relevant characteristics of each sample are reported in Table 1. The pH was measured according to the international standard CEN EN 13037:2011. The quality as fertilizers have been defined according to the fulfillment of national standards (D.Lgs. 75/2010) and internal quality standards developed by Agri New Tech.

Mix is the raw material of composting process used in this study; it is a complex matrix made by green wastes including a part of cellulosic material from pruning of trees and a part of leaves and grass clippings collected in the province of Torino from private and public gardens.

ACV15 is a sample collected during the composting process, 15 days after the starting of composting process (during the bio-oxidation phase). It is a transition biomass.

Table 1
Main characteristics of the compost samples used in this study. Data for ACV3 refers to its initial composition, before storage.

	Mix	ACV1	ACV2	ACV3
Initial moisture (%)	24.0	20.7	48.0	14.0
LOI (%)	98.12	42.79	36.88	42.79
pH	3.77	7.25	7.33	7.25
Total nitrogen (%)	0.195	0.716	0.991	0.716
Volatile solids (g VS/kg)	657	680	203	680
TOC (%)	39	11	17	11
Kjeldahl N (mg kg^{-1})	2400	650	5700	650
C/N ratio	200	15.4	17.2	15.4
Sifting (mm)	100	12	10	12