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Effects of carbohydrate, protein and lipid content of organic waste on hydrogen production and fermentation products

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ABSTRACT

Organic waste from municipalities, food waste and agro-industrial residues are ideal feedstocks for use in biological conversion processes in biorefinery chains, representing biodegradable materials containing a series of substances belonging to the three main groups of the organic matter: carbohydrates, proteins and lipids. Biological hydrogen production by dark fermentation may assume a central role in the biorefinery concept, representing an up-front treatment for organic waste capable of hydrolysing complex organics and producing biohydrogen. This research study was aimed at evaluating the effects of carbohydrate, protein and lipid content of organic waste on hydrogen yields, volatile fatty acid production and carbon-fate. Biogas and hydrogen productions were linearly correlated to carbohydrate content of substrates while proteins and lipids failed to produce significant contributions. Chemical composition also produced effects on the final products of dark fermentation. Acetic and butyric acids were the main fermentation products, with their ratio proving to correlate with carbohydrate and protein content. The results obtained in this research study enhance the understanding of data variability on hydrogen yields from organic waste. Detailed information on waste composition and chemical characterisation are essential to clearly identify the potential performances of the dark fermentation process.

1. Introduction

Petroleum, coal and natural gas are currently the main available sources of energy, fuels, chemicals and polymers. An alternative to the dependency on finite fossil fuels to meet energy and material requirements is represented by the use of renewable energy sources and biomass for both the production of bio-fuels and bio-products. The concept expressing the possibility to derive energy and commodities from organic materials is defined as biorefinery (Yang et al., 2015; Kamm and Kamm, 2004).

Organic waste from municipalities, agro-industrial residues and food waste are ideal feedstocks to be used in a biorefinery processes, representing biodegradable materials containing a series of substances belonging to the three main groups of organic matter: carbohydrates (simple sugars and polysaccharides), proteins and lipids. A series of value-added bioproducts can be produced from these organics by means of biological or thermo-chemical processes, including biofuels, chemicals, commodities, biopolymers and bioplastics (Kiran et al., 2014; Pham et al., 2015; Tuck et al., 2012).

Limits on landfill disposal of biodegradable organic materials and green house gas emission reduction targets established by the European Union may represent a incentive for a new challenge in the field of waste management: the use of industrial processes to simultaneously dispose waste and produce energy or commodities from no longer reusable or recyclable materials, in a scheme of circular economy (Cossu, 2012, 2009). The biorefinery concept fits well with this new perspective: wastes are not simply treated before final disposal but are used to produce bio-fuels, bulk chemicals, biopolymers or bioproducts for further industrial or commercial applications.

Biological hydrogen production by dark fermentation may assume a central role in the use of organic waste in a biorefinery concept (Alibardi et al., 2014). Dark fermentation may be applied as an up-front treatment for organic waste, agro-industrial residues or food waste in view of its ability to: (i) hydrolyse biodegradable complex organic to short chain fatty acids and alcohols; (ii) produce gaseous biohydrogen and carbon dioxide; (iii) hydrolyse organic nitrogen to ammonium nitrogen. The benefits of this approach would be a biologically optimised hydrolytic pre-treatment producing at the same time hydrogen (to be used as a bio-fuel, stored for energy conservation/balance or used as reactant in different chemical processes) and other important bulk chemicals for further uses.

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The dark fermentation process is influenced by numerous parameters, including briefly: substrate types, substrates ratio in co-digestion processes, type and origin inocula, pre-treatments applied to substrates and inocula, temperature, pH, micro-nutrient availability, reactor configuration and management procedures. These factors produce a considerable effect on hydrogen fermentation yields from organic waste resulting in a large variability of data reported in scientific literature (De Gioannis et al., 2013; Wang and Wan, 2009; Ni et al., 2006).

Waste composition is one of the fundamental characteristics to be taken into account in a proper comparison of hydrogen yields (Alibardi and Cossu, 2015). Carbohydrate-rich substances are reported to have higher hydrogen yields than protein- and lipid-rich substrates (De Gioannis et al., 2013; Kobayashi et al., 2012; Okamoto et al., 2000). The fermentation of lipids produces glycerol and long chain fatty acids (LCFAs). LCFAs inhibit anaerobic bacteria as they adhere to the cell wall and decrease the efficiency of nutrient transportation (Dong et al., 2009). The degradation of proteins to organic acids occurs by means of three pathways: the Stickland reaction, oxidative deamination from sole amino acid and reductive deamination from sole amino acid. The first reaction controls almost 90% of degradation, the second, with hydrogen as one of the products, is thermodynamically unfavourable and requires extremely low values of hydrogen partial pressure, whereas the third one is favourable and is hydrogen consuming (Dong et al., 2009). Although the presence of proteins may enhance the fermentation process by providing necessary nutrients for cell growth (Bai et al., 2004), the degradation of amino acids involves hydrogen-consuming reactions. Varying chemical waste compositions may therefore result in inconstant hydrogen yields. Few studies to date have specifically evaluated the effects of chemical composition of substrates on dark fermentation process performances. Bai et al. (2004) focused on the effects of protein on hydrogen yields in batch conditions from mixtures of glucose or starch, as source of carbohydrate, and peptone as source of protein. The Authors reported highest hydrogen yields at glucose and peptone concentrations of 3000 and 2000 mg/l as Chemical Oxygen Demand (COD), respectively, thus suggesting an optimal glucose to peptone ratio of 1.5 gCOD/gCOD. When starch was used as source of carbohydrate, highest hydrogen yields were obtained at starch and peptone concentrations of 4000 and 1000 mgCOD/l, respectively, thus resulting in a different optimal starch to peptone ratio of 4 gCOD/gCOD. Other Authors observed the effect of a variable substrate chemical composition on hydrogen production during co-digestion studies. Kim et al. (2004) evaluated different mixtures of food waste, as source of carbohydrate, and sewage sludge, as source of protein, during co-digestion batch tests for hydrogen production. The highest hydrogen yields were obtained for mixtures made up of 81–87% of food waste and 19–13% of sewage sludge on volatile solids (VS) basis (food waste to sewage sludge ratio between 0.8 and 0.9 gVS/gVS) at VS concentrations in the digestion liquid ranging from 0.5% to 5%. The Authors reported that the enhanced hydrogen yield was due to a balanced carbohydrate to protein ratio of 1.66 g COD/gCOD. Boni et al., (2013) evaluated optimal co-digestion conditions of food waste with slaughterhouse waste, a protein- and lipid-rich substrate. The Authors reported improved hydrogen productions when the digestion mixture comprised 60–70% of slaughterhouse waste and 30–40% food waste (% of raw weight). This condition corresponds to a food to slaughterhouse waste ratio of 0.2 as gVS/gVS and a carbon to nitrogen ratio (C/N) equal to 5.5 gC/gN (both calculated from data reported in the article) while content of COD, carbohydrate, protein or lipid of the mixture was not reported.

The reported results indicate therefore that optimal conditions are not univocal and more detailed information on the chemical composition of substrates is required for data comparison and definition of optimal process conditions. Waste composition and chemical characterisation of organic waste from municipalities are not constant over time and this variability greatly affects hydrogen yields (Alibardi and Cossu, 2015). Studies should therefore be undertaken to evaluate how the variable contents of carbohydrates, proteins and lipids present in organic waste are associated to hydrogen yields, and whether synergistic or antagonistic effects exist between these three main groups of organics. Moreover, within the concept of hydrogen biorefinery, where different fermentation products of commercial interest could be obtained in addition to hydrogen (Sarma et al., 2015), it is equally fundamental to assess how chemical composition of feeding substrates influences fermentation products.

The aim of this research study was to evaluate the effects of the chemical composition of organic waste, in terms of carbohydrate, protein and lipid content (as percentage of total solids – %TS), on hydrogen potential productions from a dark fermentation process. The study also aimed at evaluating how chemical waste composition affects volatile fatty acid (VFAs) production and the fate of organic carbon.

2. Materials and methods

2.1. Organic waste samples

Organic waste samples were prepared from food products with the aim of using reproducible substrates capable of simulating both organic waste and industrial food waste.

Four different fractions of organic waste were defined: meat-fish-cheese (MFC), fruits (F), vegetable (V), bread-pasta (BP). The fraction MFC was composed of raw chicken breast, tuna chunks in brine and butter; the fraction F was composed of apple-banana mousse; the fraction V was composed of lyophilized minestrone soup; the fraction BP was composed of bread crumbs and raw pasta. Raw composition of the four fractions is reported in Table 1.

Eight different organic waste mixtures (Mix 1 to Mix 8) were prepared by mixing the four fractions MFC, F, V, and BP. Mix 1 to Mix 4 were prepared in order to obtain a growing lipid content, a constant protein content and a decreasing carbohydrate content. Mix 5 to Mix 8 were prepared in order to obtain a growing protein content, constant lipid content and decreasing carbohydrate content. Raw composition of the eight mixtures is reported in Table 1.

After preparation all samples were shredded in a kitchen mill to create a homogeneous substrate. All samples were characterized for the following parameters: Total Solid (TS), Volatile Solid (VS), Total Organic Carbon (TOC), Total Kjeldahl Nitrogen (TKN). To provide for a detailed assessment of the type of organics present in any substrate and to confirm the predetermined composition of the eight mixtures, the following groups of organics were analysed: lipids, proteins, carbohydrates, hemicellulose, cellulose, non structural carbohydrates (NCS), starch, free sugars, sucrose, glucose. Data on the physical and chemical characterisation of all substrates are reported in Table 2. The chemical compositions of the eight mixtures were chosen within ranges reported in literature (Alibardi and Cossu, 2015; Lund Hansen et al., 2007; Garcıa et al., 2005; la Cour Jansen et al., 2004).

2.2. Dark fermentation batch tests

To evaluate the effects of a variable chemical composition of organic waste on the dark fermentation process, laboratory scale batch tests were performed on the four fractions (MFC, F, V, BP) and eight mixtures (Mix 1 to Mix 8) previously described. Dark