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Hydrogen production dynamic during cheese whey Dark Fermentation: New insights from modelization

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ABSTRACT

The modelization of non methanogenic anaerobic environments can be particularly challenging owing to the variability of the metabolic products. In particular, both hydrogen production and consumption take place at the same time due to the simultaneous occurrence of Dark Fermentation (DF) and homoacetogenis. The goal of this study is to investigate the kinetic and thermodynamic aspects of the biochemical pathways involved in the fermentation of ultrafiltered cheese whey; to this aim, a continuous digester was operated under three different Hydraulic Retention Times (6, 9 and 12 h) and fixed pH (5.5). A mathematical model, based on a variable stoichiometry approach, was implemented and calibrated; the proposed model allowed the determination of the parameters governing the most relevant pathways, namely homoacetogenesis and butyric and ethanol-type DF.

A special focus was given to the quantification of the hydrogen turnover rate; the model proved to be an effective tool, in addition to widely adopted techniques such as microbial and isotopic analysis, for obtaining a deeper comprehension of the crucial aspects governing the non-methanogenic process.

Introduction

Hydrogen is a secondary source of energy, whose final product of combustion is sole water; because of the absence of carbon dioxide emissions, hydrogen is commonly considered as a clean energy carrier, capable to store and supply energy [1]. Several technologies can be employed to produce hydrogen; thermochemical processes, such as pyrolysis, gasification and steam reforming are commonly applied using both renewable (organic waste, sewage sludge, wood) and non-renewable sources of energy (raw materials, methane, plastic waste). Another option consists in water electrolysis, an energy intensive process where the energetic requirement is generally supplied by the electric grid [2,3].

Biological processes for hydrogen production, such as DF, photofermentation and microbial electrolysis, are based on a wide range of renewable sources; among other organic substrates, agricultural and agro-activities waste represent a challenging opportunity for circular economy development

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strategies [4]. In this view, cheese whey could represent an important renewable source to exploit, considering that global production of liquid whey from cheese and casein amounts to over 180 million ton., accounting for over 80% in volume of processed milk [5]. Indeed, cheese whey output contains also 8.6 million ton. of lactose, a very important source of carbohydrates [6].

Lactose is a disaccharide consisting of one molecule of glucose and one molecule of galactose [7]. Hydrogen production from lactose/glucose-rich substrates can be achieved via light dependent and light independent microbial pathways [4]; the former consists in photofermentation whereas the latter encompasses DF and microbial electrolysis. These processes are based on the activity of heterotrophic microorganisms, which are capable to transform the organic matter, namely glucose, in short chained compounds and hydrogen. DF is the conversion of glucose into Volatile Fatty Acids (VFAs), hydrogen and alcohols under anaerobic conditions; unless an electron transport chain is artificially introduced in the anaerobic environment, glucose and VFAs oxidation proceeds via dehydrogenation [8], thus generating a large amount of hydrogen. There are three possible types of fermentation, that is, butyric-type, propionic-type and ethanol-type [9,10]. The fermentation process is governed by several factors, such as pH, hydrogen partial pressure and the concentration of fermentation metabolites, comprised of lactic, propionic, butyric and acetic acids and ethanol; all these compounds are produced in various proportions to keep a proper $NADH/NAD^+$ ratio, which determines the fermentation-type designation [10].

The hydrogen yield is correlated to the stoichiometry of the metabolic pathways; according to Ghimire et al. [11], glucose DF can be accomplished following four hydrogen producing pathways, three hydrogen unfavourable pathways and one hydrogen consuming pathway. The maximum theoretical specific yield corresponds to 4 mol H_2 mol^{-1} glucose and is achieved when glucose is converted directly to acetate; nevertheless, this specific production is hard to achieve [12], owing to the simultaneous occurrence of the other pathways. In addition to hydrogen production, an hydrogen-consuming process, referred to as homoacetogenesis, can take place when DF is fullfilled at low pH [13], thus reducing the substrate-to-hydrogen conversion rate.

Mathematical modelization is an effective tool to predict the production of biogas in an anaerobic digester; the most comprehensive model is the Anaerobic Digestion Model n° 1 (ADM1) [14], developed by the IWA task group. The ADM1 accounts for 19 biochemical processes involved in the conversion of organic matter in a biogas flow comprised of methane, hydrogen and carbon dioxide; nevertheless, with regard to the fermentative pathways, only 4 acids (valeric, propionic, butyric and acetic) are considered, whereas other compounds potentially involved in DF, such as caproate, lactate, pyruvate, ethanol, etc. are disregarded. Their omission is due to their relatively low concentration in most anaerobic digesters and their limited impact on methane yield [14]; however, these compounds should be included when modelling intermediates and hydrogen production in the DF process [15].

In the literature, several models have been proposed to simulate the DF of organic substrates under varying operational conditions. García Gen et al. [15] proposed a methodology to implement the fermentation of glycerol, ethanol and lactate in the ADM1 to extend its application to the co-digestion of multiple substrates. Hinken et al. [16] incorporated the lactic acid fermentation into the ADM1 to simulate the performance of an Up-flow Anaerobic Sludge Blanket (UASB) reactor treating wastewater originated from the wheat starch industry; the same approach was followed by Satpathy et al. [17,18] for the co-digestion of food waste and cattle manure in a continuous reactor with an Hydraulic Retention Time (HRT) of 18 days. Thamsiriroj et al. [19] suggested that lactic acid is a primary parameter to model for grass silage digestion. Pradhan et al. [20] built an ADM1-based model for simulating the hydrogen production from the glucose fermentation operated by the marine bacterium *Thermotoga neapolitana;* the model ecompassed the pyruvate and lactate pathway for the glucose catabolism.

The main issue to address in the mathematical modelization is the stoichiometry of the reactions taking place in the anaerobic environment; the fermentation pathways are highly impacted by the operational conditions of the digestion (temperature, pH, HRT, stirring velocity) and the accumulation of the metabolic products, in particular hydrogen and VFAs. Thermodynamic aspects are the main driver of the metabolic pathways; catabolic reactions are very close to thermodynamic equilibrium and therefore small changes in environmental condition can affect the stoichiometry of the fermentation process to a large extent [21]. In particular, the Gibbs free energy of acetogenesis reactions can turn positive when either the metabolic products concentration or the hydrogen partial pressure exceed a certain value [22], thus determining a shift in the fermentation pathways.

Based on these premises, Rodríguez et al. [23] suggested to include a thermodynamic control in the modelization of the reactions taking place in the anaerobic environment. Penumathsa et al. [24] proposed a modified version of the ADM1 for sucrose fermentation in a continuous digester run at HRT of 12 h; in this model the stoichiometry matrix was modified as a function of undissociated acid concentrations.

In the literature, the need for exploring the kinetic and thermodynamic aspect of hydrogen production and consumption in a non methanogenic environment was emphasized by several authors [13,25]. Dinamarca et al. [25] addressed the importance to perform this kind of investigations in continuous flow reactor. Antonopoulou et al. [26] developed a variable stoichiometry model – comprehensive of homoacetogenesis - for sweet sorghum extract DF and the calibration was based on batch tests. Alexandropoulou et al. [27] proposed a novel approach for continuous DF modelization, assuming different kinetic parameters for each sugar consuming pathway and fixed stoichiometric coefficients.

The scope of this study was to investigate the DF of cheese whey, from a mechanistic point of view, addressing the variability of the metabolic products and the ratio between hydrogen production and uptake ought to homoacetogenesis. To this aim, a modified version of the ADM1 model, based on a variable stoichiometry approach, has been developed. A continuous fermentative digester was conducted under varying HRTs (6, 9 and 12 h); the pH value was kept at a