



## Review

# A review of dark fermentative hydrogen production from biodegradable municipal waste fractions

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## ABSTRACT

Hydrogen is believed to play a potentially key role in the implementation of sustainable energy production, particularly when it is produced from renewable sources and low energy-demanding processes. In the present paper an attempt was made at critically reviewing more than 80 recent publications, in order to harmonize and compare the available results from different studies on hydrogen production from FW and OFMSW through dark fermentation, and derive reliable information about process yield and stability in view of building related predictive models. The review was focused on the effect of factors, recognized as potentially affecting process evolution (including type of substrate and co-substrate and relative ratio, type of inoculum, food/microorganisms [F/M] ratio, applied pre-treatment, reactor configuration, temperature and pH), on the fermentation yield and kinetics. Statistical analysis of literature data from batch experiments was also conducted, showing that the variables affecting the H<sub>2</sub> production yield were ranked in the order: type of co-substrate, type of pre-treatment, operating pH, control of initial pH and fermentation temperature. However, due to the dispersion of data observed in some instances, the ambiguity about the presence of additional hidden variables cannot be resolved. The results from the analysis thus suggest that, for reliable predictive models of fermentative hydrogen production to be derived, a high level of consistency between data is strictly required, claiming for more systematic and comprehensive studies on the subject.

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## 1. Introduction

In Europe, anaerobic digestion of biodegradable residues has received renewed attention by the scientific and technical community over the last decade (Mata-Alvarez et al., 2000; Mata-Alvarez, 2002; De Baere, 2003; Bolzonella et al., 2006; Karagiannidis and Perkoulidis, 2009), especially for the organic fraction of municipal solid waste. This is due to several reasons that stem

from the EU legislative framework, which has set specific constraints on landfilling of biodegradable wastes, maximization of materials recycling as well as enhancement of energy production from renewable sources.

Numerous investigators (Han and Shin, 2004a; Liu et al., 2006; Gómez et al., 2006, 2009; Ueno et al., 2007; Chu et al., 2008; Wang and Zhao, 2009; Lee et al., 2010b; Dong et al., 2011) demonstrated that if fermentation of biodegradable organic substrates is appropriately operated in a two-staged mode, separation of the acidogenic and methanogenic phases can be accomplished: while acidogenesis produces hydrogen and carbon dioxide as the gaseous products and releases VFAs into the liquid solution, methanogenesis allows for final conversion of the residual biodegradable organic matter from the first stage into methane and carbon dioxide. Considering that H<sub>2</sub> has the highest calorific value per unit weight of any known fuel and an improved acidogenic phase has been reported to result in enhanced biogas yield in the second stage, separating the phases of the anaerobic digestion process would increase the energy efficiency overall (Liu et al., 2006; Lee and Chung, 2010; Dong et al., 2011). Furthermore, proper processing of the digestate to yield a valuable final product for use as a soil

*Abbreviations:* AR, aged refuse; COD, chemical oxygen demand; CSTR, continuous stirred tank reactor; F/M, food/microorganisms; FW, food waste; HRT, hydraulic retention time; HST, heat shock treatment; MEC, microbial electrolysis cell; MFC, microbial fuel cell; OLR, organic loading rate; OFMSW, organic fraction of municipal solid waste; OMW, olive mill wastewater; PBR, packed bed reactor; PS, primary sludge; SBR, sequencing batch reactor; SRT, solids retention time; SS, sewage sludge (mixture of primary and secondary sludge); TOC, total organic carbon; TS, total solids; TKN, total Kjeldahl nitrogen; UASB, upflow anaerobic sludge blanket; VFAs, volatile fatty acids; VS, volatile solids; WAS, waste activated sludge.

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amending material would contribute to improved environmental sustainability of management of biodegradable organic residues.

A number of potentially suitable residual substrates have been evaluated for biohydrogen generation potential through dark fermentation. Among these, fractions of municipal solid waste such as food waste (FW) and the broader mixture of materials known as organic fraction of municipal solid waste (OFMSW; basically FW combined with non-recoverable paper residues) may represent relatively inexpensive and suitable sources of biodegradable organic matter for H<sub>2</sub> production, mainly due to their high carbohydrate content and wide availability (Okamoto et al., 2000; Lay et al., 2003; Kim et al., 2004, 2011a; Liu et al., 2006; Li et al., 2008a,b; Zhu et al., 2008; Wang and Zhao, 2009; Nazlina et al., 2011).

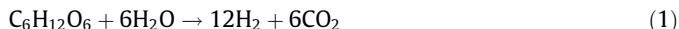
Hydrogen production via fermentation involves either facultative or strict anaerobic bacteria. The various metabolic pathways that may establish can either be promoted or inhibited, depending on the adopted operating conditions, which govern the production of specific volatile fatty acids (VFAs) and alcohols including acetate, propionate, butyrate, lactate and ethanol. In carbohydrates fermentation, the acetate and butyrate pathways involve the production of, respectively, 4 and 2 mol of molecular hydrogen per mol of glucose degraded. However, propionate, ethanol and lactic acid can also be produced in mixed bacterial cultures, adversely affecting H<sub>2</sub> production: propionate is a metabolite of a H<sub>2</sub>-consuming pathway, while ethanol and lactic acid are associated with zero-H<sub>2</sub> pathways (Guo et al., 2010a). The question as to how to achieve optimal H<sub>2</sub> generation while keeping treatment costs low and producing an effluent suitable for further treatment is probably the main technical issue to be addressed. To this regard, operational parameters including temperature, pH, reactor configuration, substrate concentration and organic loading rate should be the subject for optimization of process efficiency. Recent literature studies on H<sub>2</sub> production from FW and OFMSW through dark fermentation have focused on a broad range of operating conditions, implicitly denoting that for full-scale application of the process a better understanding of the influence of the relevant process parameters is still required.

The aim of this manuscript is to present an updated overview of H<sub>2</sub> production from FW or OFMSW through dark fermentation, based on more than 80 recent related publications. Although a number of review papers has been published on fermentative H<sub>2</sub> production from various biodegradable wastes, to the authors' knowledge a critical overview of literature studies with a specific focus on FW/OFMSW is still missing. The analysis conducted in the present study was focused on the following issues: (a) type of inoculum and applied pre-treatment, (b) type of fermentation reactor, (c) organic loading rate (OLR), (d) solids retention time (SRT), (e) temperature and pH. Since the numerous literature studies on this subject have adopted different approaches focusing on several specific aspects of the fermentation process, the reported results are diverse and sometimes even conflicting. On account of this, an effort was made in the present manuscript to statistically analyzing literature data to derive information on the relative importance of the main parameters of concern, as well as on their potential mutual relationships.

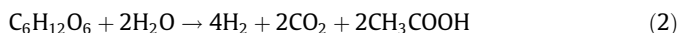
## 2. Process yield and conversion efficiency

An important issue related to fermentative hydrogen production from biodegradable wastes involves how to appropriately evaluate and express process efficiency. To this regard, the expected hydrogen production yield may be conveniently converted into a parameter representing the conversion efficiency attained upon fermentation, which may in turn be expressed either in terms

of mass or energy units. The concept of conversion efficiency derives from the existence of a fermentation barrier to hydrogen production from organic substrates, which may be elucidated considering the conversion of a simple carbohydrate such as glucose. If the complete conversion reaction to hydrogen is taken into account (Eq. (1)), it turns out that theoretically 12 mol H<sub>2</sub> can be extracted from 1 mol of glucose:



However, this reaction is energetically unfavorable with respect to biomass growth and would also only occur at extremely low H<sub>2</sub> concentrations, so that the real conversion potential is in fact lower than this theoretical value. At the best, the optimized conversion of glucose into hydrogen is limited to acetate production and is therefore practically limited by the existence of an upper threshold – the so-called Thauer limit (Thauer et al., 1977) – of 4 mol H<sub>2</sub>/mol glucose (Eq. (2)). As a result, only one third of the theoretical hydrogen production can be achieved in practice, since part of the reducing equivalents in the original substrate remains as acetate.



In practice, however, organic intermediates also act as electron scavengers, which gives rise to the production of more reduced fermentation products compared to acetate, including propionate, butyrate and longer aliphatic acids, lactate, formate, alcohols and ketones, with an associated decrease in the H<sub>2</sub> generation yield. In case the butyrate fermentation pathway is established, the conversion efficiency is reduced to 2 mol H<sub>2</sub>/mol glucose:



It has also been shown (Nath and Das, 2004; Davila-Vazquez et al., 2008; Hallenbeck and Ghosh, 2009) that, since in nature fermentation processes have been optimized not to produce hydrogen but to sustain microbial growth, hydrogen represents a waste of energy during metabolism and is therefore preferentially recycled within the metabolic pathways. As a result, a number of reduced products are formed to sustain microbial cell synthesis, including ethanol, butanol, butyrate and lactate, which allow for NADH re-oxidation. This explains how in real practice, even under optimal process conditions, conversion efficiencies to H<sub>2</sub> of higher than 15% of the original electrons in the substrate are hardly attained (Angenent et al., 2004).

On account of the considerations above, the conversion efficiency may be calculated on a mass basis as follows:

$$E_m = \frac{\text{mol H}_2 \text{ produced/mass of substrate}}{\text{Theoretical mol H}_2 \text{ produced/mass of substrate}} \times 100 \quad (4)$$

Table 1 reports conversion efficiency data according to the definition provided above, as derived from different literature sources.

The hydrogen production efficiency may alternatively be evaluated from an energetic perspective, considering the fraction of the total energy content of the substrate recovered in the form of hydrogen, as expressed by Eq. (5):

$$E_e = \frac{\text{Energy content of the H}_2 \text{ produced}}{\text{Energy content of the original substrate}} \times 100 \quad (5)$$

Assuming 2888 kJ/mol glucose and 242 kJ/mol H<sub>2</sub> (Dong et al., 2009b) as the lower heating values of glucose and hydrogen, energy conversion efficiencies of 33.5% and 16.8% are calculated if the acetate (Eq. (2)) or butyrate (Eq. (3)) fermentation pathways are assumed to occur, respectively.

Alternatively, the amount of energy converted into hydrogen may also be derived considering the COD equivalent of H<sub>2</sub>, which is equal to 16 g COD/mol H<sub>2</sub>; accordingly, if the specific hydrogen production is expressed per unit mass of input COD, it may be easy

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