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Effect of HRT on hydrogen production and organic matter solubilization in acidogenic anaerobic digestion of OFMSW

M.A. Romero Aguilar, L.A. Fdez-Güelfo, C.J. Álvarez-Gallego, L.I. Romero García *

Department of Chemical Engineering and Food Technology, Faculty of Science, University of Cádiz, 11510 Puerto Real, Cádiz, Spain

HIGHLIGHTS

- The maximum hydrogen production is reached at 1.9-days HRT.
- The maximum solubilized organic carbon concentration is reached at 1.9-day HRT.
- The ratio ASC/DOC allows further interpretation of process limitations.

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ABSTRACT

The main objective of this work has been to analyze the effect of hydraulic retention time (HRT) on the hydrogen production from the organic fraction of municipal solid waste (OFMSW) coming from a full-scale mechanical–biological-treatment (MBT) plant. Furthermore, it has also been studied, simultaneously, the effect of HRT on the solubilization of organic matter.

Experiments were conducted in an anaerobic continuous stirred tank reactor (CSTR) operating at thermophilic-dry conditions (55 °C and 20% in total solids concentration respectively). A decreasing sequence of nine HRTs, from 15 days to 1.5 days, was imposed to evaluate its influence on the hydrogen production (HP), the specific hydrogen production (SHP) and the solubilized organic matter expressed in form of acidogenic substrate as carbon (ASC), dissolved organic carbon (DOC) and dissolved acid carbon (DAC).

The results have shown that the best results were obtained at 1.9-day HRT with a feeding regime of twice a day (type-C). At these conditions, the HP and the SHP was 1.077 L $H_2/L_{reactor}$ day and 24.3 mL H_2/g VS_{added}, respectively. Maximum concentrations obtained of solubilized organic matter were: 1201 mg/L for ASC, 1936 mg/L for DOC and 735 mg/L for DAC.

As novelty, the parameter ASC and, specially, the ratio ASC/DOC have shown to be adequate for analyzing and interpreting the behavior of the process and, concretely, to determine if hydrolysis and acidogenesis are coupled (stable process) or decoupled (transitory stage).

1. Introduction

The current generation of municipal solid waste (MSW) and the high consumption rate of fossil fuels are environmental problems typical of areas with high population density. Nowadays, the MSW generation represents a serious problem since most of them are deposited in landfills causing negative environmental effects. In Spain, 588 kg *per capita* are annually collected and this amount is increasing every year [1]. On the other hand, the current reserves of fossil fuels are being depleted very fast due to the growing energy needs [2].

In this sense, many works demonstrated the possibility of coupling hydrogen generation with the use of several organic substrates including waste materials (such as MSW), industrial wastewaters and agro-industrial wastes. This generation of hydrogen from wastes may simultaneously offer environmental and economic benefits in order to meet the growing demand for renewable energy [3–5].

Among these works, anaerobic digestion (AD) processes are considered one of the best options to treat MSW since they may

Abbreviations: AD, anaerobic digestion; ASC, acidogenic substrate as carbon; CSTR, continuous stirred tank reactor; DAC, dissolved acid carbon; DOC, dissolved organic carbon; HP, hydrogen production; HRT, hydraulic retention time; MBT, mechanical–biological-treatment; WWTP, wastewater treatment plant; MW, molecular weight; OFMSW, organic fraction of municipal solid waste; OLR, organic loading rate; SHP, specific hydrogen production; TCD, thermal conductivity detector; TS, total solids; VFA, volatile fatty acids; VS, volatile solids; MSW, municipal solid waste.

* Corresponding author. Tel.: +34 956016379; fax: +34 956016411.
E-mail address: luisisidoro.romero@uca.es (L.I. Romero García).

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solve two problems at once: to reduce the pollution caused by its deposition and, simultaneously, it is possible to produce a clean alternative fuel (hydrogen) through its treatment. It must be noted that the hydrogen is considered one of the most promising energetic vectors of the future due to its lack of environmental impact and its ability to be used in fuel cells. In fact, the role of replacing fossil fuels has been commonly assigned to this gas in order to base the future on the "*hydrogen economy*" [6,7].

In particular, it has been reported that the two-stage AD, versus the traditional single-stage AD process, allows to differentiate the biofuel production (bio-hydrogen, bio-methane or both (biohythane)), improving the overall yield of gas and allow higher methane levels in the biogas generated in the second reactor and decreasing its purification cost. However, today most of full-scale biogas plants in Europe are operating on single-stage process and, hence, the two-stage technology remains unusual in this field [8,9]. This fact may be mainly due to that the process stability of the *dark fermentation* (acidogenic stage of the AD) and the maximization of bio-hydrogen production yields are still uncertain.

In recent literature, complex substrates have been often used in dark fermentation process for hydrogen production, such as OFMSW, sewage sludge, wheat straws or sugar beets, generally mixed with different inoculums such as sewage sludge, anaerobically digested sludge from wastewater treatment plants (WWTPs) or cow and pig manures. Either, the improvement of the hydrogen generation implies that the bioactivity of hydrogen-consumers bacteria (homoacetogens and hydrogenotrophic methanogens) of these inoculums must be inhibited and, in this case, it may be expected that the anaerobic treatment of biowaste will present a suitable potential to generate this gas.

In order to inhibit the hydrogen consumers, the system should be operated at low hydraulic retention times (HRTs), to promote the washing-out of methanogens, and a pH around 5.5.

HRT is a critical design parameter since it determines the microbial/substrate reaction time and thus the removal efficiency of the substrate. Values of HRT between 8 and 12 h are considered suitable for continuous hydrogen production from solubilized organic matter [12]. The use of high-solids anaerobic digestion was originally developed to reduce liquid management issues with agricultural wastes [13], but also offers opportunity for high volumetric production rates [14,15] due to higher substrate concentrations.

Besides, in order to select the acidogenic bacteria from the overall microbiota and to reach the inhibition of hydrogen-consumers bacteria it is very important to establish pH values near to 5.5 which inhibits growth of methanogens but is considered optimum for acidogenic bacteria [16]. Therefore, pH may be considered another basic control parameter of the dark fermentation.

About the hydrogen yield, it generally ranges from 16.26 L H_2/kg VS_{added} for sewage sludge [10] to 257 L H_2/kg VS_{added} of household wastes [11] even if at extreme thermophilic temperature. In this context it was demonstrated that, in general, the carbohydrate-rich feedstock presents higher hydrogen yields. In relation to the best conditions of the AD for enhance the hydrogen production, it is very important to highlight that in the case of food waste, similar to the OFMSW, the acidogenesis stage in thermophilic regime of temperature (55 °C) shows greater volumetric production rates and efficiencies versus the mesophilic (35 °C) option [12]. In addition, the most common type of bioreactor used for hydrogen production by dark fermentation is the continuous stirred tank reactor (CSTR) [17].

According to the above statements, the main aim of this study has been to enhance the hydrogen production from OFMSW coming from a full-scale mechanical–biological-treatment (MBT) plant by means of dark fermentation at thermophilic-dry conditions in a laboratory-scale CSTR. To reach this general objective, the HRT was studied and its effect on the solubilized organic matter was also analyzed. In addition, new indirect parameters (Acidogenic Substrate as Carbon, ASC and Dissolved acid Carbon, DAC) recently published has been used for a better understanding of the hydrolytic and acidogenic phases behavior in the dark fermentation of OFMSW.

Finally, it must be noted that the AD process for waste stabilization, as it was mentioned before, is very attractive option in management of organic solid wastes and, hence, a lot of full-scale biomethanization plants are operating today around the world. However, this research is focused on the thermophilic-dry acidogenic anaerobic digestion (dark fermentation) of the OFMSW with high particle size (15 mm) coming from a full-scale MBT plant, which is an innovative aspect of the paper.

2. Materials and methods

2.1. Continuous stirred tank reactor (CSTR)

A 10-L CSTR (5.5 L of working volume) without biomass recycling was used (Fig. 1). From a thermostatic water bath (7 L of volume), hot water was pumped through the jacket of the reactor to maintain the thermophilic conditions (55 °C). The reactor was equipped with a discharge ball valve and several input/output ports located at the top: a stirring paddle (stirring rate of 12 rpm), biogas outlet and feed inlet.

In this type of reactor, each HRT has been calculated by a fixed inflow rate. In this sense, a decreasing sequence of nine HRTs, from 15 days to 1.5 days, was imposed to evaluate the influence of this parameter on the organic matter solubilization rate, the hydrogen daily generation and the specific hydrogen production (SHP). Each HRT was maintained three periods in order to reach stable operation.

In addition, the feeding regime was modified according to the decreasing sequence of HRT imposed to the system (Table 1). In this sense, the feeding regime was increased as the HRT was decreased in order to minimize microorganism washing-out at short HRTs. In the last case, higher feeding frequencies are necessary to minimize that the washing-out induced by semicontinuous regime

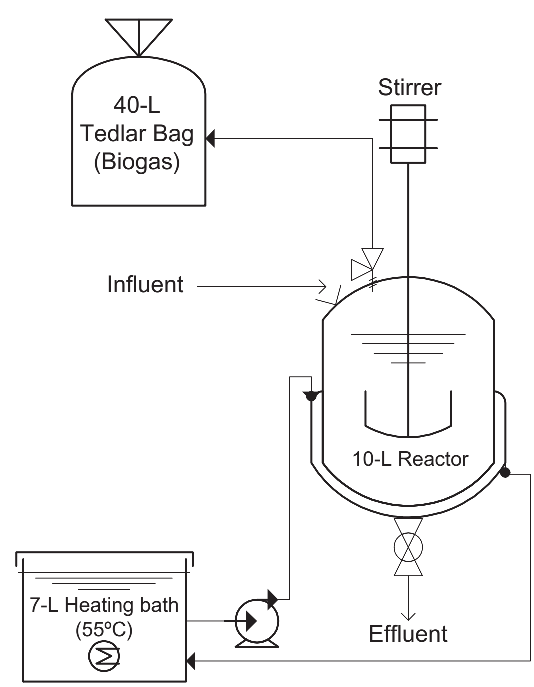

Fig. 1. Diagram of the laboratory-scale CSTR.