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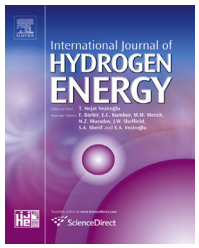

Hydrogen production using an anaerobic baffled reactor – Mass balances for pathway analysis and gas composition profiles

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ABSTRACT

This study investigated pathways for anaerobic hydrogen production from biomass at low pH values, also known as dark fermentation. A 200 l bench scale anaerobic baffled reactor with four internal compartments was used for hydrogen production from wheat starch. The liquid fermentation products and hydrodynamic characteristics were analyzed using high performance liquid chromatography, tracer studies, and gas analysis. A mean residence time of 29 h and a feed strength of 4 g_{COD}/l resulted in a total gas production of 230 l/d containing 42% hydrogen and 11% methane. The gas collected from the different compartments highly differed in composition showing a partial phase separation, with maximum H_2 concentrations of up to 60% observed in the first compartment. 49% and 44% of the total H_2 produced were derived during the formation of acetic and butyric acid respectively. Just 8% of the H_2 was produced during propionic acid synthesis. Concentrations up to 1 g/l lactic acid built by the bifidum pathway was also observed.

Introduction

Hydrogen is a key component in chemical industry, e.ġ. in crude oil processing or ammonia production, as well as in pharmaceutical and food production processes. Today, more than $5 \cdot 10^9$ kg hydrogen is produced worldwide, mainly by the steam reforming of methane [1]. Towards a sustainable future and a 100% renewable energy system, new processes for hydrogen production have to be developed to become compatible [2,3]. Besides the well known production by electrolysis, the biological conversion of biomass seems to offer promising options [4–7]. The microbial conversion of biomass for hydrogen production can be divided into the main process categories: photo- and dark fermentation, thermophyilic and enzymatic digestion. Dark fermentation comes with the advantage of using mixed cultures stabilized against contamination of biological species entering the process by

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the feed stream (favorable waste streams from other processes) [8]. Dark fermentation is also known as the acidogenesis step of the conventional anaerobic digestion (AD) [9].

Hydrogen production by anaerobic digestion has been discussed extensively in scientific papers during the last decades. Anaerobic digestion is already known to be an economical process for the treatment of complex waste streams, agricultural by-products, or energy crops for biogas production [10]. Biogas is a mixture of the main components: CO_2 and CH_4 with minor trace concentrations of NH_4, H_2, and H_2 S and other gases [11]. Today, the main use is for cooking when produced in small scale household digesters (mainly in developing countries) [12], combined heat and power (CHP) generation, and the production of substituted natural gas (SNG) by gas separation [13], or via the Sabatier process using hydrogen from renewable energy systems [14].

In recent years, the possibility of hydrogen production by anaerobic digestion has been increasingly discussed in scientific literature [15]. A wide range of studies have been performed using model substrates, such as sugar [16] or starch [17], up to very complex waste streams like agricultural waste [18,19] for demonstrating the feasibility of bio-H_2 production. H_2 production by dark fermentation is possible due to the nature of the anaerobic degradation of polymers via four steps: hydrolysis, acidogenisis, acetogenesis, and methanogenesis (see Fig. 1).

By lowering the pH value below 6.0–6.5, the methanogenic bacteria can be inhibited, thus H_2 production via the hydrolysis and acidogenesis steps can be released to the gas phase [17]. The H_2 is produced during the formation of the volatile fatty acids (VFA), for example acetic and butyric acid synthesis from glucose (as presented in equations (1) and (2)) [21]:

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 2CO_2 + 4H_2 \quad (1)$$

$$C_6H_{12}O_6 \rightarrow CH_3(CH_2)_2COOH + 2CO_2 + 2H_2. \quad (2)$$

Hydrogen plays a key role in anaerobic digestion: Released during the acidogenesis, it is consumed quickly by the acetoclastic/hydrogenotrophic methanogens producing CH_4 and CO_2 [22]. The presence of methanogens is the main disadvantage with the use of mixed cultures [23]. The molecular hydrogen dissolved in the liquid phase is oxidized by an enzyme called hydrogenases. Its activity decreases with decreasing pH, which is assumed to be the reason for inhibition of the methanogens at low pH [22].

The VFAs formed by the acidogenesis are degraded by the acetogenesis and methanogenesis to CH_4. This can be expressed by the general reaction [24]:

$$C_nH_aO_b + (n - a/4 - b/2)\,H_2O \rightarrow (n/2 - a/8 + b/a)\,CO_2 + (n/2 + a/8 - b/a)\,CH_4 \quad (3)$$

Furthermore, the H_2 and CO_2 process components present in the digestion reactor would also potentially react to form CH_4 [25]:

$$4H_2 + CO_2 \rightarrow CH_4 + H_2O. \quad (4)$$

With regards to the optimisation of proposed H_2 production using anaerobic digestion systems, the inhibition of this methanogenic step is therefore important to favor an accumulation of H_2 in the final gas phase.

In addition to the common fermentation VFAs (i. e. acetic, butyric, and propionic acid), the formation of another process intermediate, lactic acid is also of interest in this study. This is due to the fact that lactic acid formation has been reported to have a negative impact on H_2 production by its hydrogen neutral synthetic route [26].

In literature, the production of lactic acid can be explained by three hydrogen neutral pathways, the homofermentative (5), heterofermentative (6), and the bifidum (7) pathways [26]:

$$C_6H_{12}O_6 \rightarrow 2CH_3CHOHCOOH \quad (5)$$

$$C_6H_{12}O_6 \rightarrow CH_3CHOHCOOH + CH_3CH_2OH + CO_2 \quad (6)$$

$$2C_6H_{12}O_6 \rightarrow 2CH_3CHOHCOOH + 3CH_3COOH. \quad (7)$$

Although the conversion of the digested macromolecules to lactic acid intermediates would be preferentially limited for the proposed H_2 production via anaerobic digestion, lacitc acid can also be considered as a valuable chemical output with a lot of interest shown for its role in proposed biorefinery systems [27].

With regards to the reactor set-up used to facilitate the anaerobic digestion process, hydrolysis has often been carried out in continuous stirred tank reactors (CSTR) with low residence times due to its fast kinetics [28]. In recent years, upflow anaerobic sludge blanket reactors (UASBR) [29], packed bed reactors [30], and biotrickling reactors have been used for biohydrogen production [15]. The main difference of these systems compared to the CSTR being the fixation of the active biomass achieved by balancing the solid retention time (SRT) and hydraulic retention time (HRT). In conventional CSTRs both are the same, thus a wash-out of the bacterial consortium from the reactor when applying short (mean) residence times was encountered.

By using different compartments, the different phases of AD can be separated, i. e. the acidogenesis takes place in the first compartments, while the acetogenesis and methanogenesis steps occur place in the later compartments and at different pH [31]. Additional advantages with such systems are the simple and robust design without any moving parts [32] and good shock loading resistance [33].

For this study, an anaerobic baffled reactor (ABR) is used for H_2 production. The ABR system can simply be seen as a series of UASBRs. Considering such a series, it is possible to utilize the effluent from the H_2 producing stage for further methane production [34]. The common model for the ABR is a well fluidized sludge bed in the upflow section, where the main biological activity takes places. In the downflow, the sludge bed is settled and no biological activity is assumed to take place. Some models even neglect the volume of the sludge bed in the downflow section [32].

Thanwised et al. (2012) described the effects of hydraulic retention time on H_2 production and chemical oxygen demand removal from tapioca (a type of starch) wastewater using an ABR on lab scale (24 l). In their study, specific H_2 yields up to approximately 880 ml/(l·d) were observed. Inspired by that paper, we investigated the H_2 production from wheat starch in detail, using a 200 l bench scale ABR. This was carried out to provide more details on potential H_2

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