Bioconversion of syngas into biofuels and chemicals

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Introduction

In order to ensure a more sustainable world, fuels and platform chemicals, traditionally produced from non-renewable resources and fossil feedstocks, need to be obtained from more environmental-friendly sources such as biomass, solid waste or industrial effluents, among others. Biomass and waste can be gasified to yield synthesis gas (syngas), composed to a large extent of different amounts of carbon monoxide, hydrogen, as well as some carbon dioxide, depending on the gasification conditions (Kennes and Veiga, 2013). Acetogenic bacteria, mainly clostridia, have the ability to metabolize such gas mixtures, in different ratios to produce valuable commercial products. Some industrial waste gases, *e.g.* effluents from steel industries, do actually also have a similar composition and can be used as suitable substrates for such bioconversion processes as well (Abubackar et al., 2011). Increasing interest has been shown very recently, over the past few years, in such bioprocesses as suitable alternative for the production of fuels, platform chemicals or biopolymers, among others from waste or biomass, among others. Since carbon dioxide can be used as a substrate, this process does also allow to mitigate greenhouse gas pollution.

Material and Methods

Gas treatment or gas fermentation can be performed in many different types of bioreactor configurations (*e.g.*, biofilters, biotrickling filters, membrane bioreactors, stirred tank bioreactors, ...) (Kennes and Veiga, 2001). The data presented here have all been obtained in stirred tank bioreactors, with continuous gas feed while applying either continuous or batch conditions for the aqueous nutrient phase.

All experiments were performed in BIOFLO110 or BIOFLO120 bioreactors (New Brunswick Scientific, NJ, USA), inoculated with acetogenic bacteria and fed CO-rich syngas, while using a similar, but slightly different, aqueous phase depending on the metabolites to be produced, *e.g.* ethanol, higher alcohols, acetic acid, biopolymers. The exact composition of such media and more detailed operating conditions can be found in recent literature (Abubackar et al., 2016; Fernández-Naveira et al., 2017; Lagoa-Costa et al., 2017).

Gas phase compounds were analyzed by GC while soluble metabolites were measured and quantified by HPLC, and biomass growth was evaluated spectrophotometrically (Abubackar et al., 2016; Fernández-Naveira et al., 2017a).

Results and Discussion

Several examples and experimental data are given hereafter on the production of different metabolites.

Production of ethanol

Although the production of acids, mainly acetic acid, from gases (CO, CO_2, H_2) has been reported in several acetogenic bacteria, the production of alcohols has only been observed in a few strains so far. The studies reported here were performed with *Clostridium autoethanogenum* as biocatalyst. Ethanol is an interesting (bio)fuel that can be obtained through anaerobic gas fermentation in a two step process, similarly as in the ABE fermentation with carbohydrates as substrates (Fernández-Naveira et al., 2017b). This two-step process starts with an acetogenic period followed by a solventogenic one. Acetogenesis takes place at near neutral or slightly acidic pH, while solventogenesis is stimulated under acidic conditions. During the first step, gases are converted to acetic acid mainly, together with biomass growth. In this experiment, at constant pH 5.75 once the maximum concentration of acids had been reached and started levelling off, the pH was decreased to 4.75 resulting in the conversion of the organic acid into ethanol. If this pH shift strategy is applied in the form of continuous sequential cycles of high and low pH, then a higher final alcohol concentration can be reached (Table 1).

Production of higher alcohols

Clostridium carboxidovorans can not only produce ethanol, but also higher alcohols (*e.g.*, butanol, hexanol) through gas fermentation, in a similar way as the conversion of such gases to ethanol by *Clostridium autoethanogenum*. Following a similar strategy as described above for *Clostridium autoethanogenum*, it was observed that after applying one cycle of high/low pH, a mixture of ethanol, butanol and hexanol was obtained,

Table 1. Highest concentrations of acids (acetogenesis) and ethanol (solventogenesis) reached after three cycles of high/low pH, through gas fermentation in continuous gas-fed bioreactors.

pH	Highest acetic acid concentration (g/L)	Highest ethanol concentration (g/L)
5.75 (acetogenesis)	3.59	4.59
4.75 (solventogenesis)	-	7.14

with highest concentrations found for the short chain alcohols (Table 2). It was elucidated that the metabolic pattern consisted first in an acetogenic step with conversion of the gases to acetic, butyric and hexanoic acids followed by their conversion into the respective C2, C4 and C6 alcohols.

Table 2. Highest concentrations of alcohols found through gas fermentation in continuous gas-fed bioreactors.

Metabolites	Final concentrations (g/L)
Ethanol	2.77
Butanol	1.88
Hexanol	0.85

Production of organic acids and other bioproducts

Several acetogenic bacteria produce organic acids such as acetic acid as sole end metabolite. Studies were performed, among others with *Clostridium aceticum* and *Acetobacterium woodii*, on the optimization of such process in continuous bioreactors. Besides, as already suggested above, in *Clostridium autoethanogenum* the bioreactor´s operating conditions can be optimized in order to produce either ethanol or acetic acid. Experiments were performed in order to favour acetic acid production. Then the latter was used for its conversion to biopolymers (PHA). Two reactors were used, with anaerobic syngas conversion in the first one, followed by aerobic fed-batch assays for the conversion of organic acids (acetic acid) to PHA. All the acetic acid, available from the first bioreactor, appeared to be converted to PHA while ethanol remained as a suitable biofuel.

Production of metabolites with genetically engineered strains

Preliminary studies show that metabolites that cannot be produced by parent strains, because of energetic barriers, can be produced by engineered acetogenic strains in bioreactors.

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