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Fatty acids production from hydrogen and carbon dioxide by mixed culture in the membrane biofilm reactor

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ABSTRACT

Gasification of waste to syngas (H_2/CO_2) is seen as a promising route to a circular economy. Biological conversion of the gaseous compounds into a liquid fuel or chemical, preferably medium chain fatty acids (caproate and caprylate) is an attractive concept. This study for the first time demonstrated *in-situ* production of medium chain fatty acids from H_2 and CO_2 in a hollow-fiber membrane biofilm reactor by mixed microbial culture. The hydrogen was for 100% utilized within the biofilms attached on the outer surface of the hollow-fiber membrane. The obtained concentrations of acetate, butyrate, caproate and caprylate were 7.4, 1.8, 0.98 and 0.42 g/L, respectively. The biomass specific production rate of caproate (31.4 mmol-C/(L day g-biomass)) was similar to literature reports for suspended cell cultures while for caprylate the rate (19.1 mmol-C/(L day g-biomass)) was more than 6 times higher. Microbial community analysis showed the biofilms were dominated by *Clostridium* spp., *such as Clostridium ljungdahlii* and *Clostridium kluyveri*. This study demonstrates a potential technology for syngas fermentation in the hollow-fiber membrane biofilm reactors.

1. Introduction

There is a general trend in developing processes to efficiently convert waste organic compounds into new resources. To minimize operational costs and deal with variations in environmental and feedstock parameters, mixed culture fermentation (MCF) has been proposed as a promising approach to realize resources recovery and valuable biomaterials production, such as fatty acids, ethanol, bioplastics and hydrogen (Agler et al., 2011; Kleerebezem and van Loosdrecht, 2007). The produced fatty acids (acetate, butyrate, etc.) are also important precursors for liquid biofuels production (Agler et al., 2011; Steinbusch et al., 2008). Compared to gas products (H_2 and CH_4), liquid biofuels (ethanol, butanol, etc.) offer much more advantages, such as high energy density, easy storage and transportation. Recently, Steinbusch et al. proposed a direct production of medium chain fatty acids (caproate and caprylate) from acetate and ethanol/H_2 by mixed cultures (Steinbusch et al., 2011). Medium chain fatty acids, that have a longer carbon chain and lower O/C ratio (oxygen/

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carbon ratio) than acetate or ethanol, are considered to be much more suitable precursors for biofuels or biochemical by granting higher energy density.

The conversion of organic waste by biological processes is difficult and a significant amount of non-biodegradable material remains in the effluents (Xu and Lewis, 2012). For example, Hartmann et al. reported that in an anaerobic digester for the treatment of municipal solid waste, the achieved reduction of volatile solids (VS) was just about 70% (Hartmann and Ahring, 2005). The lignocellulose is the most abundant renewable organic material on the earth, but most of the degradable cellulose (40–50%) and hemicellulose (20–40%) in the biomass is packed with lignin (10–40%) that is resistant to microbial degradation (Abubackar et al., 2011). It was shown that the waste sludge can be converted to syngas as a mixture of H_2, CO and CO_2 for the benefit of solid residues treatment and energy production (Judex et al., 2012). Therefore gasification is suggested as a good alternative for the resource recovery. The produced syngas can be converted to chemicals in a Fischer-Tropsch synthesis. However, after decades of development this route is still rather complicated and the biological conversions can be potentially more efficient. The production of acetate from syngas (for example, H_2 and CO_2 in Eq. (1)) is a well-known biological process (de Kok et al., 2012; Ni et al., 2011). Also the chain elongation of acetate by H_2/CO_2 has been described as microbiological mediated processes, such as butyrate (Eq. (2)) and caproate production (Eq. (3) and Eq. (4)).

$$4H_2 + 2CO_2 \rightarrow C_2H_3O_2^- + H^+ + 2H_2O; \text{at pH7.0}, \Delta G_r^{0\prime} = -95\text{kJ/mol} \quad (1)$$

$$C_2H_3O_2^- + 6H_2 + 2CO_2 \rightarrow C_4H_7O_2^- + 4H_2O; \text{at pH7.0}, \Delta G^{0\prime} = -143\text{kJ/mol} \quad (2)$$

$$3C_2H_3O_2^- + 2H^+ + 4H_2 \rightarrow C_6H_{11}O_2^- + 4H_2O; \text{ at pH7.0}, \Delta G^{0\prime} = -97\text{kJ/mol} \quad (3)$$

$$C_4H_7O_2^- + 6H_2 + 2CO_2 \rightarrow C_6H_{11}O_2^- + 4H_2O; \text{at pH7.0}, \Delta G^{0\prime} = -143\text{kJ/mol} \quad (4)$$

As proposed by Nie et al. and de Kok et al., homoacetogens can be used to consume H_2 and CO_2 in fermentation processes which could prevent hydrogen formation and increase the acetate yield (de Kok et al., 2012; Ni et al., 2011; Nie et al., 2008). When firstly acetate is produced directly from syngas, it can be combined with a process proposed by Steinbuch et al. converting the produced acetic acid to long chain fatty acids (Steinbusch et al., 2011). These have not only better fuel value then e.g. bioethanol but are also easier to separate from the fermentation medium (Agler et al., 2012; Steinbusch et al., 2011). Therefore, the medium chain fatty acids produced in mixed culture fermentations from H_2 and CO_2 could offer better biofuel production and lower operating cost.

The low solubility of hydrogen in the water phase (around 1.6 mg/L at 1 atm H_2 at 298 K) is the main challenge for its utilization (Rittmann, 2007). Vigorous stirring and gas circulation are the common methods to promote the gas transferring from headspace to liquid solution in the gas fermentation reactor, which has a high energy requirement and is hard to scale up (Abubackar et al., 2011; Henstra et al., 2007; Hussain et al., 2011; Nie et al., 2008). The hollow-fiber membrane biofilm reactor (HFMBR) (Rittmann, 2007) is recently considered as an elegant and attractive technology, in which gas permeates from inside of the membrane lumen and is directly consumed by biofilms naturally attached on the outer surface of the hollow-fiber membrane without loss of gas through bubble formation, as shown in Fig. 1. The high specific exchange surface area of HFMBR also promotes a high volumetric gas transfer rate, increases the product generation rate and reduce the investment cost (Henstra et al., 2007; Hussain et al., 2011). Meanwhile, as biofilms naturally formed on the outer surface of the hollow-fiber membrane, it could be resilient to the environmental stress, allowing low growth rates and avoiding the microorganisms washout in planktonic state (Hussain et al., 2011; Rittmann, 2007). Actually, HFMBR has already been evaluated for reduction or oxidation of NO_3^-, ClO_4^- and other contaminants with H_2 or O_2, in which the gas utilization efficient was close to 100% (Lee and Rittmann, 2002; Martin and Nerenberg, 2012; Sahinkaya et al., 2011).

Until now there were no reports on fatty acids production from H_2 and CO_2 in hollow-fiber membrane bioreactors. In a recent overview of technologies for biomass-derived syngas fermentations, the hollow-fiber membrane biotechnology was indicated as a highly promising approach (Munasinghe and Khanal, 2010). Therefore, the objective of this work was to investigate the *in-situ* fatty acids production from hydrogen and CO_2 by mixed cultures in a hollow-fiber membrane biofilm reactor. Theoretically methane could be produced in such systems. Bromoethane sulfonate (BES), a methanogenic specific inhibitor, can be consumed in mixed cultures at pH 7.0 (Steinbusch et al., 2011). Methanogenic activity is reported to be inhibited at a pH lower than 6 at mesophilic temperatures (Luo et al., 2011). Therefore, in this work pH was controlled at 6.0 to reduce methanogenic activity in the long-term operation. The evolution of fatty acids production, such as acetate, butyrate, caproate and caprylate, was discussed and the microbial community attached on the hollow-fiber membrane was analyzed.

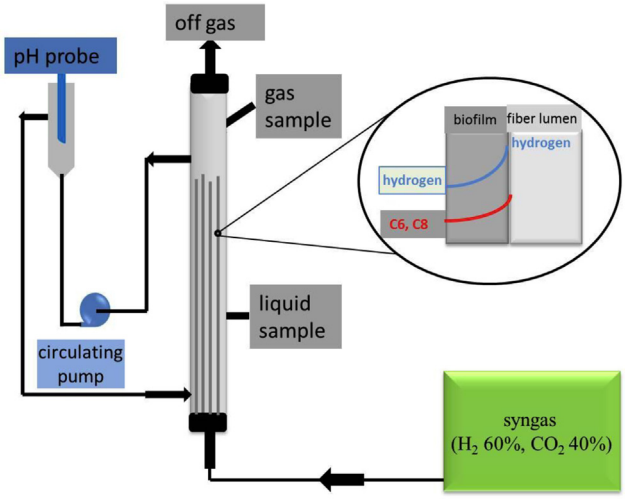

Fig. 1 – The set-up and biofilm image of hollow-fiber membrane biofilm reactor.