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Mixed culture fermentation of synthesis gas in the microfiltration and ultrafiltration hollow-fiber membrane biofilm reactors

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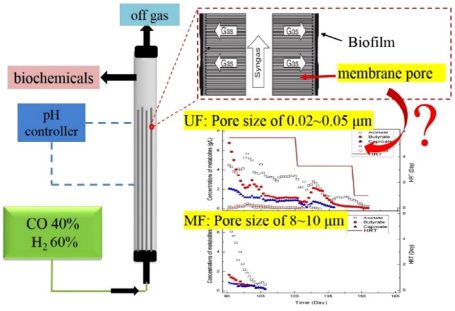
GRAPHICAL ABSTRACT



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ABSTRACT

The effects of pore sizes on the in-situ utilization of synthesis gas (syngas, H_2 and CO) mixed culture fermentation (MCF) in the hollow-fiber membrane biofilm reactor (HfMBR) are not clear. Thus, the ultrafiltration (R1) and microfiltration (R2) HfMBRs were constructed. Syngas was totally consumed within the formed biofilm in R1; contrarily, it accumulated notably in R2. In the batch mode of R1 and R2, volatile fatty acids (VFAs) of acetate, butyrate and caproate were the main metabolites, but the production rate of total VFA in R1 (61.9 mmol-C/(L·d)) was higher than that of R2 (27.6 mmol-C/(L·d)). In the continuous mode, the R1 performance was much better than that of R2, and the biofilm in R2 was even washed out. Furthermore, *Clostridium* (30.0%) was the main genus in the enriched biofilm of R1, which converted syngas to VFAs. Thus, the ultrafiltration membrane shall be the suitable candidate for syngas MCF.

1. Introduction

Exploring the environmental friendly technologies to produce biochemicals and biofuels, such as acetate and ethanol, from the organic wastes of biomass and sludge are gaining more and more attentions in the last decades (He et al., 2014; Kan et al., 2016). But, the direct conversion of organic wastes by the biological processes is difficult and a significant amount of non-biodegradable material remains in the

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effluent. For example, most of the degradable cellulose and hemicellulose in the biomass are packed with lignin that are resistant to microbial degradation (Abubackar et al., 2011). And several methods including acid-based methods and hydrothermal processing are proposed to remove lignin and hemicelluloses (Dai et al., 2018; Jönsson and Martín, 2016). Gasification to synthesis gas (syngas, mainly CO and H_2) provides an alternative technology for the utilization of these recalcitrant organic wastes (Latif et al., 2014). The produced syngas could be furthermore converted to volatile fatty acids (VFAs, including acetate, butyrate and caproate, etc.) and biofuels (such as ethanol) by mixed culture fermentation (MCF) (Ge et al., 2015; He et al., 2018; Latif et al., 2014).

The poor aqueous solubility of H_2 and CO is one major limiting factor in syngas fermentation (Esquivel-Elizondo et al., 2017; Lee et al., 2016). High impeller speed is commonly suggested to provide high gas/liquid mass transfer coefficient, but it can also lead to high-power consumption and may inhibit bacterial activity (Henstra et al., 2007; Zhao et al., 2014). Recently, He et al. (2018) used porous sponge scouring pad to promote CO transferring to the liquid and biofilm formation in the reactor, and the maximal concentrations of caproate, heptylate, and caprylate were 0.22, 0.21, and 0.14 g/L, respectively. Increasing the specific gas-liquid interfacial area can diminish poor gas solubility. In the hollow-fiber membrane biofilm reactor (HfMBR), H_2 permeates from inside of the membrane lumen and is directly consumed by biofilms naturally attached on the outer surface of the hollow-fiber membrane (Zhang et al., 2013b). Zhang et al. demonstrated the in-situ H_2 consumption (100%) in a mesophilic HfMBR, in which the concentrations of caproate (0.98 g/L) and caprylate (0.42 g/L) were higher (Zhang et al., 2013b). Several researchers also show that the microporous or nonporous membranes are useful for reduction or oxidation NO_3^-, ClO_4^- and other contaminants with H_2, O_2 and CH_4-based membrane biofilm reactors (Luo et al., 2015; Xie et al., 2017). Meanwhile, the membrane reactor also presents other advantages, such as small reactor footprint and easy scale-up (Martin and Nerenberg, 2012). However, research on the biochemicals production from syngas in HfMBR is rarely reported.

On the other hand, microfiltration (the pore size between 0.1 and 10 μm) and ultrafiltration (the pore size between 0.01 and 0.1 μm) membranes are the common materials in membrane bioreactors for wastewater treatment (Holloway et al., 2015; Peter-Varbanets et al., 2009). Till now, most of the studies focus on the microfiltration membrane with the pore size of 0.1–0.2 μm in HfMBRs (Lai et al., 2016; Wang et al., 2017). Several workers found that membrane pore size could affect the gas utilization, for example, poor CO solubility in the aqueous phase occurred as the reactors using large pore sizes (20 μm) such as column diffuser and sparger (Munasinghe and Khanal, 2010). In bacteria-free reactors, Orgill et al. (2013) used O_2 as the gaseous mass transfer agent and found that the nonporous polydimethylsiloxane hollow-fiber membrane provided the highest volumetric mass transfer coefficient (1062 1/h), followed by the trickle-bed reactor (421 1/h) and stirred tank reactor (114 1/h). Yasin et al. (2014) determined the CO mass transfer using hollow fiber membrane with pore size of 0.1 μm and found that mass transfer coefficient (k_{La}) increased from 63.7 1/h to 135.7 1/h as the inlet pressure increased from 37.2 kPa and 93.8 kPa.

Consequently, the pore size in MF and UF membranes shall be an important factor for biofilm attachment and metabolites production in syngas fermentation. In our former works, the membrane pore size was mainly 0.01 μm in HfMBR (Wang et al., 2017; Wang et al., 2018b). But, to the best of our knowledge, such studies of higher pore sizes (above 0.01 μm) are rarely reported on syngas (CO and H_2) fermentation in HfMBR. Thus, the aims in this work were to 1) construct the hollow-fiber membranes (MF of 8–10 μm and UF of 0.02–0.05 μm) biofilm reactors and compare the metabolites production; 2) reveal the dominant bacteria in HfMBR biofilm by the Illumina MiSeq high-throughput sequencing. Consequently, it is expected that the outcomes would benefit to choose the suitable membrane in HfMBR for syngas MCF in future.

2. Materials and methods

2.1. HfMBR setup and operational conditions

Two HfMBRs were configured with the ultrafiltration (R1, pore size 0.02–0.05 μm) and microfiltration (R2, pore size 8–10 μm) hollow-fiber membranes (PureSea Spring Membrane Technology Co. Ltd, China), respectively, in which the working volume and total membrane surface area were same, and were 420 mL and 0.016 m^2, respectively. Syngas of 60% H_2 and 40% CO were fed into HfMBR. The inlet gas pressures of R1 and R2 were manually adjusted by the regulator and were monitored by a gas-pressure gauge (Hua Yitong Electromechanical Equipment Co. Ltd, Nanjing, China). Recirculation pump provided an inner loop within the flow of 60 L/h. pH was controlled at 6 ± 0.1 by a pH controller with 1 M NaOH and temperature was controlled at 35 ± 1 °C by a water bath. The medium was fed to the reactor with a peristaltic pump (Longer pump, Baoding, China).

Two HfMBRs were inoculated with anaerobic sludge (60 mL) collected from an anaerobic digester, which was the same as that of Wang et al. (2017). The reactors were initially supplemented with 10 mmol/L Bromoethane sulfonate (BES) to inhibit methanogenesis. The whole experimental processes of R1 and R2 were divided into batch and continuous modes. R1 and R2 were initially run in the batch mode, in which 90% medium was removed from the reactor at day 53, and the fresh medium without BES was added. At day 90, the continuous mode began, the medium with no BES added was fed to the reactors. The reactor performance of R1 was investigated under different HRTs (5.5, 3.3, and 1 days), in which 4 cycles were operated for each experiment. Whereas, the biofilm in R2 was washed out under the HRT of 5.5 days, and the experiment was stopped at day 107. The composition of medium was the same as that of Zhang et al. (2013b).

2.2. Chemical analysis and scanning electron microscopy (SEM) image of biofilm

The gas and liquid samples were determined every day. The concentrations of VFAs, ethanol and butanol were measured using a gas chromatograph (Agilent 7890, CA). The samples were filtered with 0.45 mm microfiltration membrane and then acidified with 3% (v/v) formic acid before analysis. The contents of H_2, CO_2, CO, and CH_4 in the headspace were analyzed using a gas chromatograph (Lunan model SP7890, CN). The biofilms of R1 (day 153) and R2 (day 108) after the continuous experiments were analyzed by SEM (SIRION 200, FEI, USA) and the details of the method were described by Zhang et al. (2013b).

2.3. Data analysis

Statistical analysis was carried out with the SPSS 20.0 package. The bivariate correlation method was used to check the influences of microfiltration and ultrafiltration membrane on VFAs production. The one-way ANOVA method was used to check the effect of HRT on the CO consumption rate in R1.

2.4. DNA extraction and high throughout sequencing

The biofilms of R1 (day 153) and R2 (day 108) after the continuous experiments were first detached from the outer surface of the hollow-fiber membrane and then collected in phosphate-buffered saline (PBS). DNA samples of inoculum, R1 biofilm and R2 biofilm were then extracted from PBS using the PowerSoil DNA Isolation Kit (MO BIO, USA). The primers used to target the V3-V4 regions of both bacterial and archaeal 16S rRNA genes were identified as 341F and 806R (Sundberg et al., 2013). The entire sequencing process was performed at the Novogene Institute (Beijing, China). The sequencing data of inoculum, R1 biofilm and R2 biofilm in the current study were archived in NCBI Sequence Read Archive with accession numbers of SRR6370522,