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Anaerobic conversion of hydrogen and carbon dioxide to fatty acids production in a membrane biofilm reactor: A modeling approach

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HIGHLIGHTS

- A new model for syngas fermentation in MBfR was proposed and tested.
- Uncertainty of the four estimated parameters was explored by sensitivity analysis.
- Impacts of key process parameters on MBfR performance were assessed.

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ABSTRACT

Biological conversion of gaseous compounds (e.g., H_2/CO_2) into valuable liquid fuels or chemicals using mixed culture is a promising technology, which could be effectively and efficiently implemented in a membrane biofilm reactor (MBfR) with gas being supplied from inside of membranes. In this study, a model integrating multiple production pathways of fatty acids (including acetate, butyrate, and caproate) was developed and tested using reported mixed culture experimental data from a lab-scale MBfR fed with 60% H_2 and 40% CO_2. The uncertainty of the four estimated model parameters was explored by a sensitivity analysis. With the developed model, the impacts of key process parameters (i.e., gas supply and hydraulic retention time (HRT)) on the performance of the MBfR converting H_2/CO_2 to fatty acids were then investigated. The results show that a high HRT is imperative for chain elongation to produce a higher proportion of caproate with a higher added value. A proper gas supply should be provided to favour the speciation of biological gas conversion products as well as to fully exploit the conversion capacity of the MBfR. The findings of this work provide useful information for a better understanding and further applications of this MBfR technology for mixed culture syngas fermentation.

1. Introduction

While anaerobic digestion of organic wastes mainly aims at methane production, there has been substantial emergence that focuses on more targeted reactions to generate biomaterials of a higher value [1], such as fatty acids, ethanol, and butanol. The produced short-chain fatty acids (acetate (C2) and butyrate (C4)) are important precursors for biofuel production [2–4]. Liquid biofuels (e.g., ethanol and butanol) offer significant advantages in comparison with gas products (H_2 and CH_4), which include a high energy intensity and easy storage and transportation [4]. Among them, medium-chain fatty acids (e.g., caproate (C6) and caprylate (C8)), which possess a chain of 6–12 carbons and a lower oxygen/carbon ratio than acetate and ethanol, are generally regarded as more valuable industrial commodities and more suitable precursors for liquid biofuels or biochemicals. Therefore, other than a valorisation process, the conversion of organic wastes to fatty acids also represents an important alternative to deal with the growing global energy demand.

However, direct and complete biological conversion of organic wastes is difficult due to the significant amount of non-biodegradable matter contained, such as lignin which accounts for 10–35% of the entire biomass [5–7]. The lignin content of biomass could be effectively utilized through gasification, which is commonly practiced for resource recovery and yields synthetic gas (syngas) as a mixture of H_2, CO, and CO_2. Syngas could then be used further as a feed stock for the production of useful biochemicals such as acetate and butyrate by either chemically-catalysed conversion (e.g., Fischer-Tropsch (FT) synthesis) or biological conversion routes (known as syngas fermentation) [8]. Nevertheless, FT synthesis is still not popularized and widely

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adopted due to its process complexity and relatively low efficiency. In contrast, biologically-catalysed generation of liquid biofuels or biochemicals via syngas fermentation is more efficient and requires less energy input [9]. Other merits include a higher tolerance for impurities such as sulfur compounds, a wider range of usable H_2, CO, and CO_2 mixture, and a lower operating temperature and pressure [10].

So far, the production of acetate from syngas (e.g., CO_2 and H_2) has been well studied [11–13], and the produced acetate could be converted to longer carboxylates such as butyrate and caproate through microbially-mediated chain elongation [14,15]. Chain elongation is achieved through the reverse β-oxidation pathway, which includes acetate elongation to butyrate via acetyl-CoA and butyrate elongation to caproate via butyl-CoA [15,16]. *Clostridium kluyveri* is the best-known microbe capable of carrying out the well described reverse β-oxidation pathway [16–18]. Chain elongation processes not only add value to the final fermentation products but also improve their downstream processing, which remains a key issue to be addressed for syngas fermentation [1]. Pervaporation, electrodialysis, and solvent based extraction [19] are commonly proposed to refine the mixed products from syngas fermentation, and larger molecular weight products are generally more readily extracted and separated [20]. Chain elongation is therefore highly desired in order to reduce the operational cost associated with syngas fermentation.

One of the main challenges that restrict the application of syngas fermentation is the low solubility of hydrogen in the water phase as well as its poor gas-to-liquid mass transfer efficiency and rate [21], which govern the process rate. Mechanical augmentation such as gas circulation and liquid agitation could potentially promote the gas transfer process in fermentation reactors. However, these techniques are usually energy-intensive and faced with scale-up difficulties. The membrane biofilm reactor (MBfR) technology is particularly suitable for delivering gas with low solubility (e.g., H_2 and CH_4), which has been applied to hydrogen-based denitrification [22,23] and methane-based denitrification [24–27], and could be utilized similarly for syngas fermentation. Since the gaseous substrate (i.e., syngas in this case) is supplied directly through gas-permeable and bubbleless membranes, its transfer could be enhanced greatly and controlled flexibly by pressure adjustment. Functional microorganisms could naturally attach to and proliferate on the membrane surface, and the produced fatty acids (e.g., C2, C4, and/or C6) could diffuse to the bulk liquid and be collected afterwards, as delineated in Fig. 1. The decoupling of hydraulic retention time (HRT) and solid retention time (SRT) ensures a high biomass concentration, which also ensures good resilience of the MBfR to environmental changes. Proving this concept, Zhang et al. [4,13] observed high productions of fatty acids (C2, C4, and/or C6) in the MBfRs fed with syngas containing 60% H_2 and 40% CO_2. However, more work is of imperative need, in order to render a more comprehensive understanding of this technology as well as to better facilitate its future implementation.

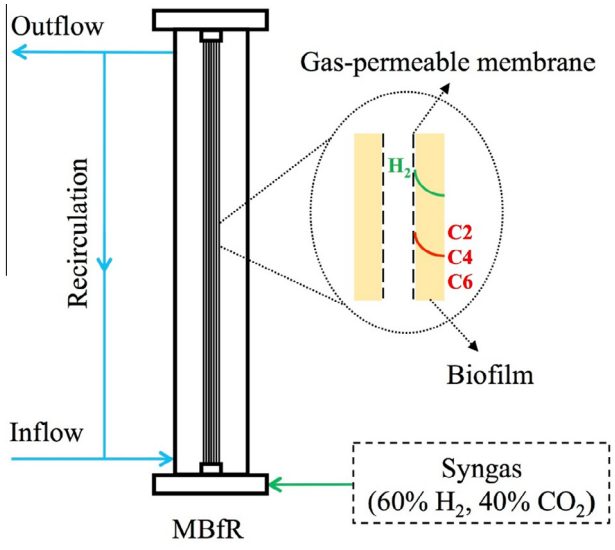

Fig. 1. The schematic diagram of membrane biofilm reactor (MBfR) performing mixed culture syngas fermentation.

Mathematical modeling serves as a useful and reliable tool to probe into emerging technologies and significantly reduces the workload related to process evaluation or optimization. To our knowledge, mathematical model is currently not available to describe syngas fermentation processes for fatty acids production, especially in MBfR systems. Therefore, in this work, we developed and tested a modeling approach which integrates multiple production pathways of fatty acids (i.e., C2, C4, and C6) using reported mixed culture experimental data obtained from a lab-scale MBfR fed with 60% H_2 and 40% CO_2. With the developed model, the impacts of key process parameters (i.e., gas supply and HRT) on the performance of the MBfR converting H_2/CO_2 to fatty acids were then investigated. The results of this work are expected to provide useful information for a better understanding and further applications of this MBfR technology for syngas fermentation.

2. Materials and methods

2.1. Model development

Production of both short-chain and medium-chain fatty acids from H_2 and CO_2 by mixed microbial culture in a hollow-fiber MBfR has previously been demonstrated experimentally [4]. In the MBfR, H_2 and CO_2 were supplied through gas-permeable membranes, which also served as biofilm support, to the base of the biofilm, as shown in Fig. 1. The hydrogen was for 100% utilized within the biofilms attached on the outer surface of the hollow-fiber membrane. Based on the experimental observations and the known metabolisms, Zhang et al. [4] revealed the production of acetate, butyrate, and caproate from syngas containing 60% H_2 and 40% CO_2 could be described by Eqs. (1)–(4):

$$4H_2 + 2CO_2 \rightarrow C_2H_3O_2^- + H^+ + 2H_2O \ (\text{at pH } 7.0,\ \Delta G^{0'} = -95 \text{ kJ mol}^{-1}) \quad (1)$$

$$C_2H_3O_2^- + 6H_2 + 2CO_2 \rightarrow C_4H_7O_2^- + 4H_2O \ (\text{at pH } 7.0,\ \Delta G^{0'} = -143 \text{ kJ mol}^{-1}) \quad (2)$$

$$3C_2H_3O_2^- + 2H^+ + 4H_2 \rightarrow C_6H_{11}O_2^- + 4H_2O \ (\text{at pH } 7.0,\ \Delta G^{0'} = -97 \text{ kJ mol}^{-1}) \quad (3)$$

$$C_4H_7O_2^- + 6H_2 + 2CO_2 \rightarrow C_6H_{11}O_2^- + 4H_2O \ (\text{at pH } 7.0,\ \Delta G^{0'} = -143 \text{ kJ mol}^{-1}) \quad (4)$$

It should be noted that caproate could be elongated from either acetate (Eq. (3)) or butyrate (Eq. (4)) or both. However, the Gibbs free energy of Eq. (4) (−143 kJ mol^{-1}) is higher than that of Eq. (3) (−97 kJ mol^{-1}) [4], which means Eq. (4) would be favoured under same condition. This thermodynamic approach has been widely adopted to determine the most significant and feasible pathways involved in chain elongation [14,16,28]. Moreover, sequential chain elongation from acetate to caproate via butyrate has been well studied and clearly defined for *Clostridium kluyveri* [14,29]. Therefore, for simplicity, chain elongation for caproate