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Hydrogen supersaturation in thermophilic mixed culture fermentation

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ABSTRACT

Hydrogen concentration is important for the metabolic distribution in mixed culture fermentation (MCF) but hydrogen supersaturation is often ignored. In this study, hydrogen supersaturation in thermophilic MCF was investigated online by a membrane inlet mass spectrometry. The results showed that with the increase of glucose loading rate (from 13.5 to 137.5 mmol/L/d) and the decrease of Reynolds number (from 12,900 to 3500), the hydrogen partial pressure (P_{H_2}) remained almost unchanged, but the hydrogen concentration in liquid (H_2^{aq}) increased from 0.82 to 1.27 and from 0.68 to 1.21 mmol/L, respectively. It demonstrated that hydrogen supersaturation occurred and the supersaturation ratio was between 1.7 and 3.0. Meanwhile, higher H_2^{aq} resulted in lower hydrogen yield, lower glucose degradation rate and higher mole ratio of ethanol/(acetate + butyrate). Thus, H_2^{aq} is more appropriate than P_{H_2} when discussing the H_2 role in MCF. Furthermore, the calculated K_La clearly illustrated that the required K_La values for maintaining low H_2^{aq} were order of magnitudes higher than the experimental ones. Therefore, hydrogen supersaturation is inevitable in practice and should be considered in MCF.

1. Introduction

With the emergence of petroleum crisis and environmental pollution, researchers pay more attention to cleaner and more reproducible biofuels [1]. Among these biofuels, hydrogen is an ideal energy carrier for its high energy density of weight (122 kJ/g) and carbon-free nature. Recently, the mixed culture fermentation (MCF) is recognized as one promising approach to realize resources recovery and valuable biofuels (such as hydrogen) and chemicals production [2–4]. H_2 concentration is one of the key factors to determine the metabolic distribution (chemicals) in MCF [5,6]. Until now, to enhance hydrogen yield, various methods have been proposed, such as the decrease of organic loading rate (OLR), vigorous stirring and gas stripping, but the hydrogen yields is still below the theoretical value (4 mol/mol_glucose) [4,7–9]. Hydrogen supersaturation is one reason for the low hydrogen yield [6,10].

Hydrogen supersaturation occurs if the hydrogen production rate in the system is higher than the liquid-to-gas transfer rate (K_La). Hydrogen supersaturation in mesophilic mixed culture fermentation has been reported [9,11]. For example, the hydrogen concentration in liquid (H_2^{aq}) was 3 times of that under equilibrium conditions according to Henry's Law in the hydrogen production reactor [11]. Meanwhile, high H_2^{aq} could promote hydrogen consumption by homoacetogens and other second metabolic reactions [10]. However, H_2^{aq} is seldom measured because the offline measurement varies in a wide range while online measurement is difficult to achieve [11]. Therefore, most studies ignored H_2^{aq} while used hydrogen

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partial pressure (P_{H_2}) as an index to discuss the hydrogen role in MCF, i.e. high P_{H_2} could inhibit H_2-generating hydrogenases activity, lead to higher NADH/NAD ratio, cause the metabolic shift to the reduced products (such as ethanol and lactate) and slow down the organic degradation rate [5,6,8,12,13]. If hydrogen supersaturation is common in MCF, H_2^{aq} should not be ignored. It could be a more proper factor than P_{H_2} to study the metabolic interactions.

Though there are general explanations about hydrogen supersaturation, the relationship between hydrogen supersaturation and operating conditions in MCF is still unclear. For example, the gas stripping was a common method to reduce hydrogen supersaturation and enhance hydrogen yield, but Kraemer and Bagley obtained a confusing phenomenon that the hydrogen supersaturation ratio (R_{H_2}) increased from 1.6 to 4.7 when nitrogen stripping was applied to decrease P_{H_2} from 0.6 atm to 0.09 atm [10]. It is well known that K_La is the global volumetric mass transfer coefficient from liquid to gas. It is a function of the gas nature, the liquid physiochemical and hydrodynamic properties, such as temperature and stirring velocity [14]. Therefore, K_La could provide the useful information about the relations between hydrogen supersaturation and operating conditions.

Recently, thermophilic MCF for hydrogen production gains more and more attention, attributed to its relative higher hydrogen yield, better substrate degradation rate and pathogenic organism destruction, etc [13,15,16]. Since the hydrogen transfer rate related to its diffusion coefficient in thermophilic MCF is higher than that under mesophilic condition, the hydrogen supersaturation is commonly ignored in thermophilic MCF. However, Ljunggren et al. recently demonstrated the occurring of hydrogen supersaturation in an extreme-thermophilic batch reactor (70 °C) with initial glucose concentration of 30 mmol/L [5]. This suggests that hydrogen supersaturation also occurs under thermophilic condition.

Therefore, in this work, hydrogen supersaturation in thermophilic MCF was online determined by a membrane inlet mass spectrometry (MIMS), which was recently used for the online determination of H_2^{aq} in mesophilic MCF processes [17,18]. Effects of OLR and stirring velocity on hydrogen supersaturation and metabolic distribution were investigated. Furthermore, the relationship between hydrogen supersaturation and K_La was proposed and utilized to elucidate the hydrogen supersaturation phenomenon under different operating conditions.

2. Materials and methods

2.1. The inoculum, reactor set-up and medium

The anaerobic sludge used in this study was collected from a UASB reactor treating citrate-producing wastewater. The inoculums were untreated and sparged with nitrogen (>99.99%) for 20 min before usage. The setup of continuously stirred tank reactor (CSTR) was shown in Fig. 1. The total volume was 2.0 L, and the working volume was 1.25 L. The temperature was maintained at 55 ± 0.5 °C with water bath. The hydraulic retention time (HRT) was initially kept at 12 days for 20 days to ensure the biomass activity at thermophilic condition. Then HRT gradually decreased to 16 h within 30 days. The pH was maintained as 5.5 ± 0.1 with 2 M NaOH. 5 g/L of glucose was the feeding concentration during the enrichment period. The reactor was shaken vigorously every week to detach the biofilm on the reactor walls.

The experiments were carried out in two runs. In the first run, different OLRs (1.6, 6.9, 11.8, 19.1 and 24.7 g/L/d, which were equal to 13.5, 38.3, 65.5, 106.0 and 137.5 mmol/L/d, respectively) were employed under the stirring velocity of 300 rpm. Different stirring velocities (120, 300, 450, 600, 800

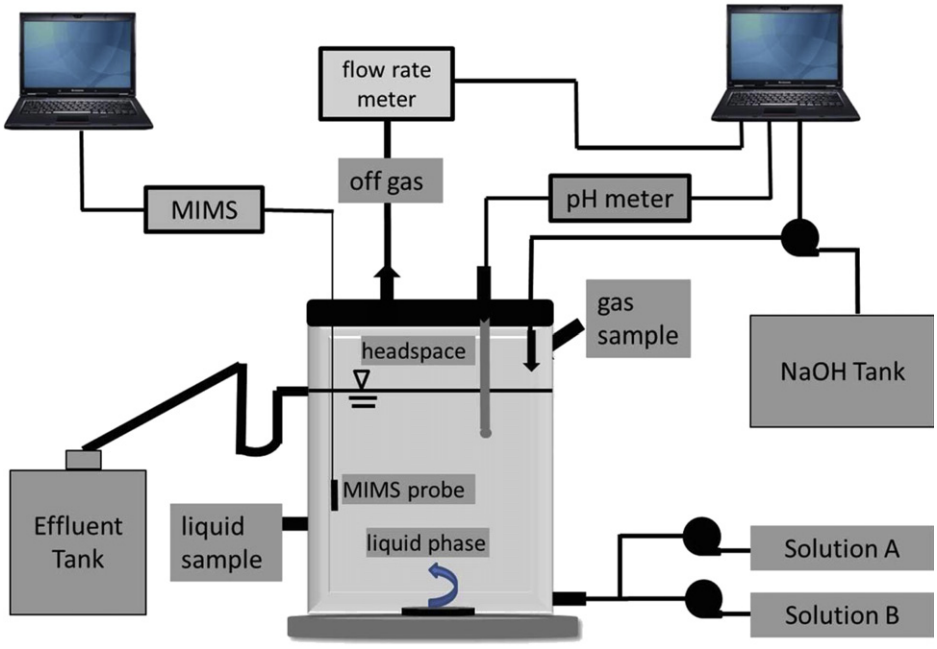

Fig. 1 – The set-up of thermophilic mixed culture fermentation reactor.