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Various additives for improving dark fermentative hydrogen production: A review

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ABSTRACT

Hydrogen production via dark fermentation has been widely considered as a promising strategy for clean energy generation. In addition, a wide variety of organic wastes can be used as feedstock for hydrogen production in dark fermentation, thus providing an added advantage of waste recycling. However, the process of dark fermentation is essentially restricted by the low yield of hydrogen. In recent years, the supplementation of additives has drawn increasingly interests as the process intensification approach, owing to its capacity to improve process performance and the advantages of ease of operation and low energy consumption. This paper critically reviews the recent advances in the use of additives in dark fermentation based on 90 relevant publications. In the present review, the used additives are divided into five categories according to their roles in dark fermentation, including metal additives (metal monomers, metal ions and metal oxides), additives for microbial immobilization, L-cysteine, augmenting microbes, and enzymes. The impact of these additives on hydrogen fermentation performance and corresponding functional mechanisms were explained in detail. Meanwhile, the optimal dosage for each additive was discussed. Furthermore, this review also briefly discussed recent advances in the "addition" of various processes to hydrogen fermentation. Finally, based on a deep analysis of results in these publications, concluding remarks and some suggestions for future work were proposed.

1. Introduction

About 80% of total energy used today is based on fossil fuels [1]. Excessive use of fossil fuels will deplete these limited fossil energy resources [2]. In addition, the combustion of fossil fuels can cause serious adverse impact to the environment [3]. For these reasons, almost all countries worldwide have made significant efforts to seek for alternative energy sources which are renewable and environmentally friendly. Hydrogen has been widely regarded as a promising energy source for the future [4]. Hydrogen is a clean fuel with only water as the combustion product and can be easily used in fuel cells for producing electricity [5]. In addition, hydrogen has a much higher energy density of 141.9 MJ/kg in comparison with other fuels, such as ethanol (29.9 MJ/kg), methane (55.7 MJ/kg), natural gas (50 MJ/kg), and biodiesel (37 MJ/kg) [6].

At present, most of hydrogen is produced from fossil fuels and water electrolysis [7]. However, these conventional hydrogen production processes are usually unsustainable, energy consuming and cost-intensive. Therefore, there is an urgent need to develop a sustainable way for producing hydrogen. In this sense, dark fermentation has gained widespread attention as a promising strategy due to its low operating cost, fast reaction rate, low energy demand, and simple operation conditions [8,9]. More attractively, this process can directly utilize a versatile range of organic wastes for producing hydrogen, such as wastewater, sewage sludge, food waste, agricultural waste and forestry waste [10–12], which could simultaneously achieve the production of renewable hydrogen and the utilization of organic waste.

Despite the advantages mentioned above, the process of dark fermentation is usually restricted by the low yield of hydrogen [13]. So far, hydrogen yields reported in most studies have been lower than 2 mol/mol-glucose [14]. Consequently, most investigations have concentrated on process intensification techniques to enhance the hydrogen yield in the last decades. Various methods have been applied to improve the efficiency of dark fermentation. First, some researchers have investigated various pretreatments (e.g. ultrasound, acid and enzyme pretreatments) to increase the bioavailability of complex organic substrates [15–17]. Second, some researchers have optimized the operation conditions (such as hydraulic retention time and temperature) for facilitating the work of hydrogen-producing bacteria [18–21]. Third, some researchers have co-fermented various substrates with

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complementary characteristics to synergistically enhance their utilization efficiency in dark fermentation [22–24]. Furthermore, some other researchers have selected effective hydrogen-producing bacteria or applied the genetic modification of already characterized strains for the optimization of this process [25,26]. So far, some bibliographic reviews addressing above intensification approaches already exist in the literature [15,26–32].

Besides aforementioned approaches, the supplementation of additives has drawn increasingly attentions as the process intensification approach in recent years. Additives can facilitate the microbial growth and enzymatic activity in dark fermentation, thereby leading to the enhancement of process performance [33–35]. Furthermore, from an application viewpoint, using additives seems to be more feasible compared with other intensification approaches (e.g. pretreatment) owing to its advantages of simple operation and low energy consumption. However, current literature reviews have mainly devoted to summary the progresses of other intensification approaches, such as pretreatment, co-fermentation and the optimization of operation conditions, while less attention has been paid to the topic of using additives in dark fermentation. This motivates us to conduct a comprehensive overview with a specific focus on the roles of additives in dark fermentation.

This review critically summarizes the recent advances in dark fermentation using different types of additives based on 90 relevant publications from 2001 to 2018, which aimed to present the achievements and progress in the topic. The optimal dosages for various additives and their corresponding functional mechanisms are analyzed in detail. Furthermore, the addition of various processes to hydrogen fermentation was also briefly discussed. Finally, some concluding remarks and suggestions for future work were proposed.

2. Methods

The literatures used in this review were mainly collected from the scientific data bases of Web of Science, Google Scholar and Science Direct via keyword search. Various keyword groups were comprised of several words including “dark fermentation”, “hydrogen fermentation”, “fermentative hydrogen production”, “biohydrogen”, “additive” and “supplement”. Considering that the aforementioned search strategy could possibly exclude relevant literatures, an additional search process was carried out with more detailed keywords one by one, including “trace metal”, “iron”, “nickel”, “magnesium”, “sodium”, “calcium”, “immobilization”, “L-cysteine”, “bioaugmentation” and “exogenous enzyme”. For the additional search, these mentioned keywords were also connected to the words of “dark fermentation”, “hydrogen fermentation”, “fermentative hydrogen production” or “biohydrogen”.

Relevant literatures were selected by carefully reviewing the abstract of the references filtered in the screening process. The relevance of full texts of pre-selected literatures was confirmed using the available online data bank. Then, the selected literatures were read carefully to extract the useful information related to substrate, inoculum, fermentation conditions, process performance, and additives and their functional mechanisms. Meanwhile, the extracted information was listed in the table in order to facilitate the subsequent analysis and discussion. Reported data in the selected literatures were carefully analyzed to evaluate the role of additives on hydrogen fermentation. In addition, special attention was paid to the optimal dosage of each additive, because it usually differed from literature to literature.

3. Various additives used in dark fermentation

Dark fermentation for hydrogen production is a complicated biological process with the essence of transforming organic substrate into hydrogen [36]. In this process, protons (H^+) can act as electron acceptors to neutralize the electrons generated by microbial oxidation of substrate, consequently generating hydrogen. Generally, hydrogen fermentation process begins with the breakdown of carbohydrate derived sugars to pyruvate, producing the reduced form of NADH via the glycolytic pathway. Then, there are three possible pathways for the production of hydrogen. For the first pathway, intermediate pyruvate is converted to acetyl-CoA and formate, and then formate is further converted to hydrogen and CO_2 with the catalysis of formate-hydrogen lyase. This fermentation pathway usually exists in facultative anaerobes. For the second pathway, intermediate pyruvate is converted to acetyl-CoA and CO_2, producing reduced ferredoxin. The reduced ferredoxin then transfers electrons to the hydrogenase, finally producing hydrogen. For the third pathway, the NADH generated during the glycolytic pathway can be oxidized to generate hydrogen, probably catalyzed by a NADH dependent hydrogenase. The last two fermentation pathways usually exist in strict anaerobes. Meanwhile, acetyl-CoA generated from pyruvate decomposition is commonly converted into some soluble metabolite products, such as acetate, butyrate and ethanol. Various types of microbes have the ability to produce hydrogen via dark fermentation, such as *Clostridium* sp., *Enterobacter* sp. and *Bacillus* sp. [37]. In addition, there are various types of enzymes involving in the fermentation process to accelerate the rate of relevant biochemical reactions, such as dehydrogenase, hydrogenase and pyruvate ferredoxin oxidoreductase [7]. According to the characteristics of these microbes and enzymes, the main purpose of additives is to promote microbial growth, and improve the metabolic activity of fermentative bacteria and the catalytic activity of key enzymes, thereby causing the higher hydrogen yield, more rapid hydrogen production rate and better process stability.

Recently, additives have attracted more and more research interests in the field of dark fermentation. Fig. 1 illustrates the number of article published on the topic of using additives in dark fermentation from 2001 to 2017. It can be seen from Fig. 1 that the number of article published presents a continuous increase trend during the past 17 years. All these studies were performed in laboratory scale, and most of fermentation experiments were carried out under *meso*philic conditions. The studied substrates include glucose, xylose, sucrose, cellulose, starch, organic fraction of municipal solid waste (OFMSW), food waste, lignocellulose, wastewater and sewage sludge (Fig. 2A). Among which, glucose, sucrose and wastewater were the most three studied substrates, which accounted for 32.9%, 20% and 17.7%, respectively (Fig. 2A). In addition, the used additives in dark fermentation can be divided into five categories, including metal additives (metal monomers, metal ions and metal oxides), biomass immobilization carrier (i.e. additives for biomass immobilization), L-cysteine, augmenting microbes, and enzymes (Fig. 3). Among these additives, metal ions, biomass immobilization carrier and metal oxides were the most three studied ones,

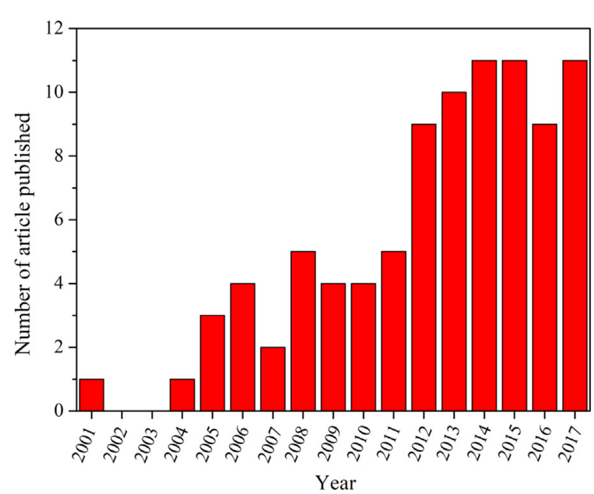

Fig. 1. Number of article published on the topic of using additives in dark fermentation from 2001 to 2017 (The data in pie-chart are calculated based on 90 relevant publications in the reviewed literature).