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Utilization of food waste for fermentative hydrogen production

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1 Introduction

Current imperative global issues such as petroleum depletion and global warming are leading to new developments in fuel markets all over the world [1]. Interest in the development of renewable energy to reduce the reliance on fossil fuels and achieve sustainable development in energy consumption is increasing [2, 3]. Hydrogen is a promising alternative to fossil fuels because it is clean and renewable [4]. The energy yield of hydrogen is 122 kJ/g, which is 2.75 times higher than fossil fuel [5]. Moreover, hydrogen can be directly used to produce electricity via fuel cells [6]. Therefore, hydrogen is considered to be a promising energy carrier of the future.

The best-known industrial ways of hydrogen production are steam reformation of natural gas, coal gasification and splitting water with electricity [7, 8]. However, these industrial processes could also release carbon dioxide and other greenhouse gases and pollutants as byproducts [9]. Recently, biological hydrogen production has attracted considerable attention since it could deal with the conversion of low cost residues or organic waste/wastewater to hydrogen [10, 11]. Biological hydrogen production processes are considered to be more environmentally friendly and less energy intensive compared to thermochemical and electrochemical processes [12]. Generally, biological hydrogen production can be divided into two categories: photosynthesis and dark fermentation [13]. Dark fermentation seems to be a more feasible biotechnology for hydrogen production than photosynthesis due to lower energy consumption and no light limitation [14]. However, the low hydrogen production rate and high cost are the dominant obstacles for large-scale dark fermentative hydrogen production [15]. Utilization of raw waste/wastewater as substrate for fermentative hydrogen production (such as food waste) could effectively enhance the economic benefit which is regarded as a promising solution [16].

Food waste is a promising raw material for biofuel production because of its high organic content and availability. It mainly consists of starch, protein and fat which are good carbon sources for fermentative hydrogen production [17]. Fermentative bacteria hydrolyze and ferment carbohydrates, protein and lipids to volatile fatty acids which are then further converted into acetate, carbon dioxide and hydrogen by acetogenic bacteria [18]. Hydrogen and ATP are produced by fermentative bacteria such as *Clostridium* sp. during the degradation process. The limiting factor for biohydrogen production from food waste is the hydrolysis rate [19]. Kim et al. [20] found that heat-pretreated food waste could accelerate the hydrolysis rate of food waste and produce high biohydrogen yield when compared to untreated food waste. Similarly, sonication of food waste with heat and without inoculum was applied by Elbeshbishy et al. [21] for biohydrogen production. This research showed that pretreatment of food waste could enhance biohydrogen production efficiency and therefore can be regarded as an important parameter influencing biohydrogen production. Enzymatic hydrolysis could release nutrients (such as glucose and free amino nitrogen) from food waste with the advantage of a high hydrolysis rate and mild reaction conditions [22, 23].

Therefore, this chapter presents an updated review on dark fermentative hydrogen production from food waste. The analysis performed in the present chapter was focused on the following issues: (1) metabolic pathway of fermentative hydrogen production, (2) characteristics of food waste affecting the performance of fermentative hydrogen production, (3) pretreatment of food waste for fermentative hydrogen production.

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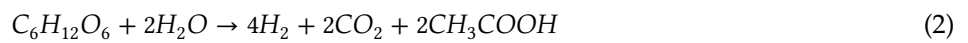
2 Metabolic pathway of fermentative hydrogen production

2.1 Process yield and conversion efficiency

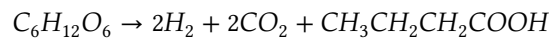
The concept of conversion efficiency derives from the existence of a fermentation barrier to hydrogen production from organic substrates. If the complete conversion reaction to hydrogen is taken into account (Eq. (1)), it is concluded that theoretically 12 mol hydrogen could be generated from 1 mol glucose [24, 25].



However, this reaction is energetically unfavorable with respect to biomass growth and would occur only with extremely low hydrogen concentration. The optimal conversion of glucose into hydrogen is limited by acetate production. As a result, one third of the theoretical hydrogen production can be achieved in practice because part of the reducing equivalents in the original substrate remains as acetate (Eq. (2)) [26].



In practice, organic intermediates act as electron scavengers, which give rise to the production of more reduced fermentation products compared to acetate, including propionate, butyrate and ethanol, with an associated decrease in the hydrogen yield. In case the butyrate fermentation pathway is established, the conversion efficiency is reduced to 2 mol H_2 /mol glucose (Eq. (3)) [27].



2.2 Metabolic pathway for fermentative hydrogen production

The carbohydrate must undergo liquefaction by extracellular enzymes before being taken up by acidogenic bacteria. The rate of hydrolysis is a function of several factors, such as pH and temperature [28, 29]. After that, soluble organic components, including the products of hydrolysis, are converted into organic acids, ethanol, hydrogen and carbon dioxide by acidogens (Figure 1). The products of acidogenesis are then converted into acetate, hydrogen and carbon dioxide [30].

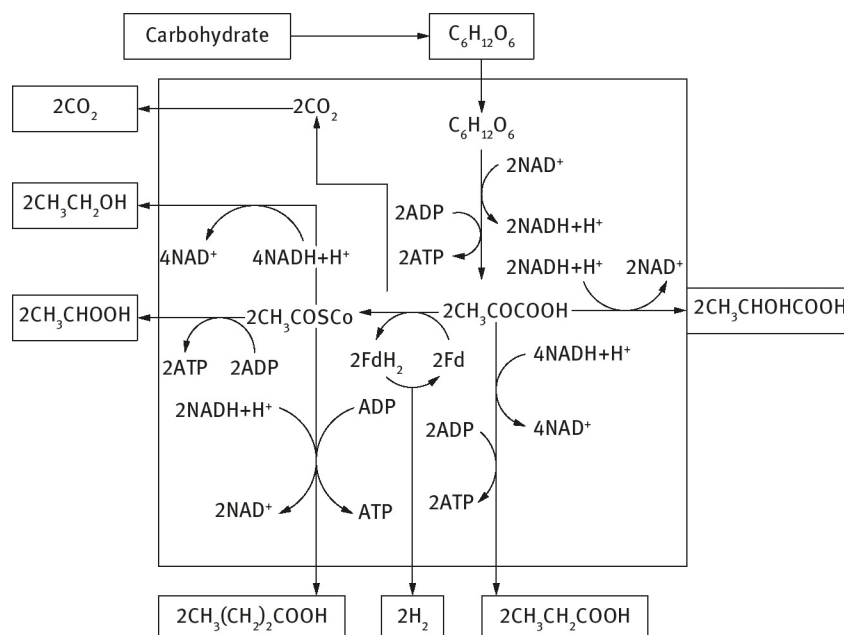
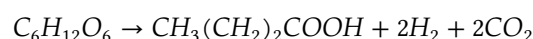


Figure 1: Metabolic pathway and byproducts in fermentative hydrogen production [58].

Fermentative hydrogen production is carried out by anaerobic acidogenic bacteria with highly diverse fermentation characteristics and hydrogen production capabilities. Performance of fermentative hydrogen production depends on a number of parameters, such as pH, temperature, and organic loading rate [31–33]. The variations of parameters would lead to various microbial communities which finally result in diverse fermentation types [34]. There are four main fermentation types in the anaerobic acidogenesis, namely acetate type fermentation, butyrate type fermentation, ethanol type fermentation and propionate type fermentation [35–37]. Many microbial communities exhibit acetate fermentation with acetate as the major product (Eq. (4)). The major products of propionate type fermentation are propionate and acetate (Eq. (5)), while the products of ethanol type fermentation are ethanol and acetate (Eq. (6)). As for butyrate type fermentation, butyrate and acetate are the primary fermentation products (Eq. (7)).



Equations (4)–(7) show that hydrogen is produced from acetate, butyrate and ethanol type fermentations. Propionate type fermentation could not generate hydrogen. However, propionate type fermentation is concurrent with other fermentation types capable of producing hydrogen in a mixed microbial community [38, 39]. Therefore, hydrogen could also be generated from anaerobic fermentation when the production of propionate is still high.

In many papers, butyrate type fermentation is considered as the most common pathway for fermentative hydrogen production. Relative research about ethanol type fermentation remains deficient. Based on the equilibrium of the NADH/NAD⁺ ratio inside the bacteria cell, Ren et al. [40] proposed that the ethanol type pathway induced at pH 4.5 is a better and more stable metabolic pathway than the butyrate type pathway induced at pH 5.0. Although the theoretical yield of hydrogen is 2 mol hydrogen/mol glucose in butyrate type fermentation (Reaction 7), which is same as that of the ethanol type fermentation (Reaction 6), butyrate type fermentation lacks the stability for NADH accumulation because part of the produced NADH can be utilized rapidly by cellular synthesis or converted to hydrogen and NAD⁺ under the presence of acetyl-CoA [41]. So, the butyrate production pathway has the potential to change to the butanol production pathway, where hydrogen may be consumed [42, 43]. Conversely, it can be inferred from Figure 2 that ethanol type fermentation is able to preserve a balance of NADH + H⁺/NAD⁺. The carbohydrate is first degraded to glucose which is further converted to pyruvate (CH₃COCOOH). Pyruvate is oxidized to CH₃COSCoA by depletion of NAD⁺ with molecular hydrogen and carbon dioxide generation. In order to keep sequential production of hydrogen, the metabolism product NADH + H⁺ must be utilized to regenerate NAD⁺ to compensate for equilibrium between the NADH + H⁺ and NAD⁺ by the reaction of the ethanol-acetate pathway [44]. This fermentation pathway can reduce acidic terminal products by producing neutral matter of ethanol and make the acidogenic fermentation process favorable for hydrogen production [45]. This shows that ethanol type fermentation can obtain better stability and no pH regulation was required for this fermentation during the whole operation process. Therefore, ethanol type fermentation is the optimal choice for maximum hydrogen production by mixed culture [46–48]. Despite the potential advantages, further deep studies are worth doing to examine the metabolic pathway using genetic modification of hydrogen-producing bacteria and further clarify in more detail the control strategy of ethanol type fermentation.

3 Biohydrogen production from food waste

There are two main ways of biological hydrogen production from carbohydrate: dark fermentation and photosynthesis [49]. The major substrates used for dark fermentation are simple sugars, such as glucose and sucrose. However, the substrates used for photosynthesis are organic acids, such as acetate and butyrate [50]. Dark fermentation is considered to be a more feasible biotechnology for hydrogen production than photosynthesis due to lower energy consumption and no light limitation [51]. However, the low hydrogen production rate and high cost are the dominant obstacles for large-scale dark fermentative hydrogen production [52]. Utilization of raw waste/wastewater as substrate for fermentative hydrogen production (such as food waste) could effectively enhance the economic benefit which is regarded as a promising solution [53].

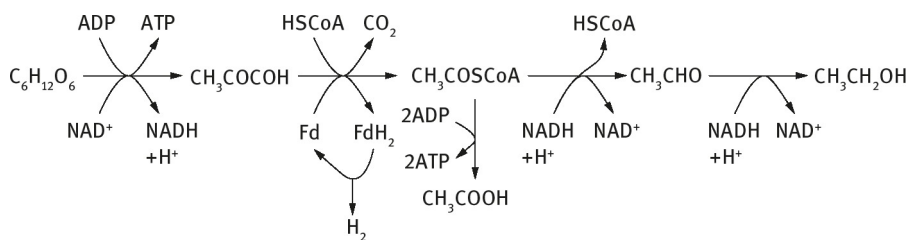


Figure 2: Amended ethanol type fermentation route by acidogenic bacteria [22, 33].

Food waste is one of the most severe environmental problems all over the world [54]. Over a billion tons of food waste is generated per year which accounts for 33% of annual global food production [55]. Therefore, disposal and utilization of food waste is becoming one of the major global challenges. Food waste consists mainly of starch and protein which make food waste an economical source for biofuel production [56]. Utilization of food waste for hydrogen production could not only solve the food waste problem, but also produce an alternative energy source simultaneously [16, 57]. However, nutrients stored in food waste are in the form of macromolecules (such as starch and protein) which have to be broken into utilizable forms (glucose and free amino nitrogen) before being utilized by microorganisms for fermentative hydrogen production [24, 58]. Generally, there are two main stages in fermentative hydrogen production from food waste (hydrolysis and fermentation). Separate hydrolysis and fermentation is the process in which food waste is first hydrolyzed by pretreatments to obtain micro-molecules. Then, the nutrients solution is subjected to dark fermentation for hydrogen production. The hydrolysis stage of complex substrate is the rate limiting step in most of the bioprocesses [59]. However, hydrolysis of food waste in a separate process could overcome this problem. The operating conditions in pretreatment can be optimized to get the maximum food waste to nutrients solution conversion rate [60].

3.1 Carbohydrate

Food waste is considered to be a suitable substrate for fermentative hydrogen production since it is rich in carbohydrate. The carbohydrate has to be hydrolyzed by hydrolytic bacteria to produce simple sugars, such as glucose and sucrose, before being utilized as substrate for fermentative hydrogen production. The product of carbohydrate hydrolysis mainly depends on the microorganisms present in the culture broth. The speed of carbohydrate hydrolysis is faster than that for lipid and protein. Lay et al. [61] indicated that the yield of hydrogen production from carbohydrate rich substrate is 20 times higher than using lipid and protein rich substrate. Sagnak et al. [62] applied both acid and heat treatments to get monomeric sugar for fermentative hydrogen production. Han et al. [63] added glucoamylase and protease to the food waste before hydrogen production to increase the efficiency of starch and protein hydrolysis.

3.2 Fats

Oils are sources of lipids in food waste [16]. The presence of lipids in anaerobic fermentation could lead to flotation and mass transfer problems. The process of fermentative hydrogen production from lipid hydrolysis would be slower than carbohydrate hydrolysis because of the ability of hydrogenotrophic methanogens to consume hydrogen-producing bacteria [34]. Therefore, it is acknowledged that lipids are not suitable to be utilized as the sole substrate for fermentative hydrogen production.

3.3 Protein

Food waste contains significant amounts of protein which are polypeptides formed by joining covalently linked amino acid [53]. The hydrolysis of protein is performed to produce amino acids by proteases excreted by microorganisms. Then, the amino acids are further utilized to generate volatile fatty acids, carbon dioxide and hydrogen. The speed of protein hydrolysis is slower than carbohydrate and lipid hydrolysis. Therefore, it is not suitable to use protein as sole substrate for fermentative hydrogen production.

4 Pretreatment of food waste for fermentative hydrogen production

Depending on the food waste structure, pretreatment could be applied in single or multiple steps, including physical, chemical and enzymatic pretreatments. Physical pretreatment is related to size reduction or the contribution of a physical force to decompose the food waste structure. Chemical pretreatment is usually applied in severe acidic or alkaline conditions. Enzymatic pretreatment could be accomplished at ambient operation conditions with higher conversion rate and yield.

4.1 Physical pretreatment

Physical pretreatment of food waste could reduce the size of food waste by physical forces without chemicals or microorganisms [51]. Comminution is the most common physical pretreatment. The main objective of physical pretreatment is to improve the available surface area by reducing the substrate size. It enables a more efficient chemical or microbial hydrolysis of the substrate matrix and decreases hydrolytic enzyme limitations. Physical pretreatment is one of the most common ways applied in fermentative hydrogen production from food waste. Reducing the size of food waste by mechanical comminution is an energy intensive process which could be achieved by different devices, such as shredders and grinders.

4.2 Chemical pretreatment

Chemical pretreatment is the process to depolymerize the food waste using chemicals [28]. The goal of chemical pretreatment is to enable enzymatic access to fermentable sugars by breaking down the macromolecules into micromolecules. Acid and alkaline are the most commonly applied chemical pretreatment. Dilute acid hydrolysis includes HCl, H₂SO₄, and HNO₃. Dilute acid hydrolysis can be accomplished at 100–250°C, 0.5–30 min with 0.5–3% acid concentrations [55]. The main disadvantages of acid hydrolysis are the toxic byproducts, such as furfural, which would inhibit the performance of hydrogen production in the fermentation step.

4.3 Enzymatic pretreatment

Food waste could be used as substrate for fermentative hydrogen production after physical or chemical pretreatment processes [10]. However, it has been observed that physical or chemical pretreatment could require intensive energy, chemicals and severe operation conditions leading to wastewater and toxic byproduct formation. Therefore, the selection of an environmental friendly and sustainable process is of great importance. Enzymatic pretreatment is regarded as an alternative option to physical and chemical pretreatment of food waste.

Microorganisms, such as fungi (*Aspergillus awamori* and *Aspergillus oryzae*) and some bacteria (*Clostridium thermocellum*), can produce glucoamylase and protease which could degrade macromolecules (starch and protein) to release fermentable nutrients from food waste [31]. Compared to physical and chemical pretreatments, enzymatic pretreatment could operate under mild condition without toxic byproduct formation. Glucoamylase could degrade starch into glucose which can further be utilized as substrate for fermentative hydrogen production. Meanwhile, protease could hydrolyze protein into free amino nitrogen (FAN). Usually, food waste pretreatment starts with physical size reduction followed by diverse combinations of chemical and enzymatic processes.

Table 1: Comparison of the performance of hydrogen production from food waste.

Substrate	Microorganisms	Reactor type	H ₂ yield (ml H ₂ /g VS _{added})	References
Food waste (grain, vegetables, meats and fish)	Sewage sludge	Continuous	205	[3]
Sonicated food waste	No inoculum	Batch	97	[62]
Food waste	<i>Clostridium-rich</i> composts	Batch	77	[61]
Food waste	<i>Escherichia cloacae</i>	Batch	52	[30]

Food waste	Sewage sludge	Continuous	165	[12]
Food waste	Anaerobic digester	Packed-bed reactor	249	[24]
Food waste	sludge			
	<i>Biohydrogen-</i>	Batch	294.47	[63]
	<i>bacterium R3</i>			

VS_{added} : volatile solid_{added}.

5 Performance of biohydrogen production from food waste

Table 1 summarizes the comparison of the performance of fermentative hydrogen production from food waste. Lee and Chung [35] conducted a cost analysis of hydrogen production from food waste using two-phase hydrogen/methane fermentation and suggested that the abundance and low cost of food waste makes it economically more feasible than the other sources for H_2 production. Han et al. [63] developed a novel combination bioprocess of solid-state fermentation (SSF) and fermentative hydrogen production from food waste. Food waste was first utilized in solid-state fermentation by *Aspergillus awamori* and *Aspergillus oryzae* to produce glucoamylase and protease, respectively, which were used to hydrolyze food waste to obtain the food waste hydrolysate rich in glucose and free amino nitrogen (FAN). Then, the food waste hydrolysate was used as substrate for fermentative hydrogen production by heat pretreated sludge. The best hydrogen yield (52.4 ml H_2 /g food waste or 294.47 ml H_2 / VS_{added}) was achieved at food waste mass ratio of 5%. The proposed combination bioprocess could effectively accelerate the hydrolysis rate, improve raw material utilization and enhance hydrogen yield.

6 Prospects and challenges of fermentative hydrogen production from food waste

Recently, fermentative hydrogen production from food waste has attracted great attention. According to the UN Food and Agriculture Organization, around 1.3 billion tons of food is wasted per year. Food waste, which is comprised mainly of starch, protein and fat, becomes a feasible source for fermentative hydrogen production. A survey was carried out to predict the development of the fermentative hydrogen production sector worldwide. It was found that China would get the largest fermentative hydrogen production market, following by the US, Japan, and India. Additional research is required to improve the efficiency of fermentative hydrogen production from food waste. It is hoped that the limitations to fermentative hydrogen production from food waste can be solved in the near future.

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