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Hybrid Process for Bio-hydrogen and Methane Production from Hydrogenic Effluent: A Mini Review

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ABSTRACT

Hydrogenic effluent is the effluent from the bio-hydrogen production process via dark fermentation. It mainly consists of volatile fatty acids, residual sugars, and organic solid residues with a high chemical oxygen demand (COD), which prohibits direct discharge to the environment. Therefore, a post-process after dark fermentation to utilize the organic substances in the hydrogenic effluent is needed to complete the organic conversion and reduce the COD load. This review discussed the use of organic substances in the hydrogenic effluent to produce bioenergy, including bio-hydrogen, through photo fermentation and microbial electrolysis cells, and to produce methane by anaerobic digestion. Furthermore, the advantages and disadvantages of using hydrogenic effluent to generate bio-hydrogen and methane and the challenges and future perspectives on utilizing the hydrogenic effluent are discussed.

Keywords: Dark fermentation; Hydrogenic effluent; Ph oto fe rmentation; Microbial electrolysis ce lls; Two-stage anaerobic digestion

INTRODUCTION

Recently, the drastic depletion of fossil fuels and environmental deterioration have driven toward more sustainable energy (Arpia et al. 2021). Renewable energy is considered a promising alternative energy source to mitigate the energy scarcity and environmental problems caused by fossil sources, such as greenhouse gas (GHG) emissions (Abraham et al. 2020). Due to these criteria, worldwide efforts are focused on searching and producing renewable energy from renewable feedstocks (Basak et al. 2020). As a result, renewable energy resources play an important role in the transition towards sustainable and clean energy production.

Among the various alternative clean fuels, hydrogen is a carbon-neutral energy carrier because its combustion generates only water as a reaction product with a high energy yield of 122 kJ/g, which is 2.75 times greater than that of hydrocarbon fuels (Mohan et al. 2013). Hydrogen can be produced from various materials, pathways, and technologies (Dawood et al. 2020). Conventional hydrogen production technologies include steam reforming of natural gas (methane), gasification of coal, catalytic decomposition of natural gas, and partial oxidation of heavy hydrocarbons. However, these technologies are energy-intensive and not always environmentally friendly because all fossil fuel processes generate a high amount of carbon dioxide (CO_2) emissions (Lui et al. 2020). Among these conventional techniques, dark hydrogen fermentation from renewable resources is more promising, attractive, and sustainable because it can use renewable resources as feedstock (Balachandar et al. 2013). Dark fermentation is a biological process in which microorganisms utilize carbohydrates, mainly glucose, as the preferred carbon source to produce hydrogen under anaerobic fermentation conditions (Nath & Das 2004). However, the low process yield and incomplete conversion of organic biomass are two major limitations for commercial dark fermentative hydrogen production (Ghimire et al. 2015). Dark fermentation can enhance the process efficiency and substrate conversion by applying optimal fermentative conditions (e.g., pH and temperature), substrate pretreatment, inoculum selection, and nutrient supplementation. However, dark fermentation has a maximum hydrogen yield of only 33% (on sugars) (Gomez et al. 2011). Additionally, the hydrogenic effluent left over after the fermentation process could not be discharged directly into the environmental system due to its low pH and high chemical oxygen demand (COD) (Reungsang et al. 2016). Therefore, the post-process after dark fermentation for utilizing the hydrogenic effluent should be applied to complete the conversion of organic substances.

This review briefly describes the processes for utilizing hydrogenic effluent. The advantages and disadvantages of each process are also discussed. Challenges and perspectives to improve the utilization and recycling of hydrogenic effluents were also addressed.

HYDROGENIC EFFLUENT

Hydrogenic effluent, a waste residue from a dark fermentation process, mainly contains volatile fatty acids (VFAs), organic solid residues, and residual sugars (Jomnonkhaow et al. 2021; Nualsri et al. 2016). VFAs are linear short-chain fatty acids consisting of two to six carbon atoms, including acetic, propionic, iso-butyric, butyric, iso-valeric, valeric, and caproic acids (Wainaina et al. 2019). The types and concentrations of VFAs vary depending on the substrate, inoculum, and fermentative conditions, such as pH and temperature. High concentrations of VFAs and other components of hydrogenic effluents have been reported. For example, total VFAs and total soluble metabolite products (SMPs) of 12.4-16.4 and 16.2-24.1 g COD/L, respectively, were detected in hydrogenic effluent from the dark fermentation of sugarcane syrup (Nualsri et al. 2016). Hydrogenic effluents obtained from hydrogen fermentation of Napier grass contained total SMPs in the range of 5.7-6.1 g-SMPs/L (Jomnonkhaow et al. 2021). These high amounts of VFAs can be value added by being used as the substrate to produce bio-hydrogen by photo fermentation, microbial electrolysis cells (MECs), and methane by anaerobic digestion (AD). An overview of the utilization of hydrogenic effluent to produce bio-hydrogen and methane is presented in Figure 1.

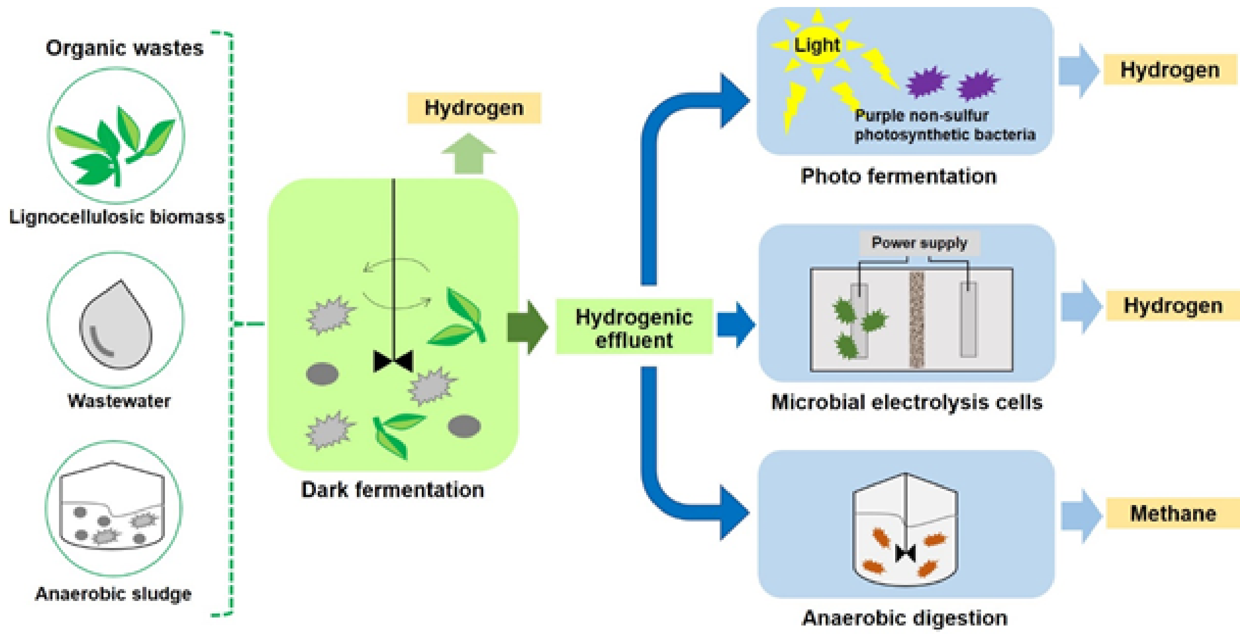

FIGURE 1. The overview of the process for utilizing hydrogenic effluent

PHOTO FERMENTATION

Photo fermentation is the process by which purple non-sulfur photosynthetic bacteria (PNSB) carry out anaerobic photosynthesis using light as an energy source for the synthesis of hydrogen (Ghimire et al. 2015). PNSB can use various kinds of organic acids, such as acetic acid, butyric acid, and succinic acid, as carbon sources to produce hydrogen. Argun and Kargi (2011) reported that the maximum hydrogen yield and maximum light conversion efficiency of PNSB were 80% and 9.3%, respectively, depending on the carbon source. The advantages of photo fermentation are the excellent conversion of organic acid wastes to hydrogen, as expressed by the hydrogen yield, COD removal efficiency, and potential waste treatment. Thus, photo fermentation can be a good post-treatment for bio-hydrogen production from dark fermentation. Moreover, there are some drawbacks of PNSB, including low light conversion efficiencies, high energy demand, and economic issues of large areas, which are needed for anaerobic photobioreactors (Dalena et al. 2017; Hallenbeck 2013; Mishra et al. 2019).

MICROBIAL ELETROLYSIS CELLS (MECS)

MECs are technologies that use microorganisms to catalyze reactions to produce hydrogen at the anode and/or cathode (Liu et al. 2005). In MECs, microorganisms oxidize organic matter and convert it into protons, CO_2, and electrons. These electrons are transported to the anode and flow from the anode to the cathode via an electrical circuit containing a power supply. At the cathode, electrons combined to protons evolved from the oxidation of the organic matter to produce hydrogen (Jeremiasse et al. 2010). In MECs, to drive hydrogen production from acetate under standard biological conditions (25 °C, 1 bar pressure, and pH 7), 0.14 V has to be applied (Logan et al. 2008). The main advantage of the MECs process is its low energy consumption, since an applied voltage as low as 0.2 V is considered to be necessary for microbial electrohydrogenesis to produce hydrogen (Hu et al. 2009), whereas the theoretical minimum voltage of 1.23 V is required for water electrolysis (Rozendal et al. 2007). However, a disadvantage of the MEC system is the pH gradient created from the use of membranes to separate the cathode and anode compartments (Rozendal et al. 2007). The pH gradient increased the theoretical voltage required to operate the MECs. A way to protect the pH gradient is to remove the membrane; however, removal of this membrane may cause a substrate/product crossover, resulting in undesired side reactions and products (Hamelers et al. 2010).

TWO-STAGE DARK FERMENTATION AND METHANE PRODUCTION

The microbial metabolite products from dark fermentative hydrogen production can be further converted into methane by the function of various microorganisms in the AD process. The two-stage fermentation process may become an economically feasible alternative to treat residual organic wastes and biomass, as well as to reduce pollution. Moreover, the production of methane at end products can increase the total energy recovery gained from organic biomass conversion and make the dark fermentation process more industrially viable (Tapia-Venegas et al. 2015)

The concept of a two-stage process can be employed in high-solid substrates such as lignocellulosic biomass, food waste, and wastewater. The operation and function of each stage may vary depending on the characteristics of the feedstock and inoculum (Rajendran et al. 2020). The integrated production of hydrogen and methane by two sequential reactors: the first reactor is operated by dark fermentation to produce hydrogen, and the second reactor is an AD reactor for methane production (Ghimire et al. 2015). In some industrial AD reactors where hydrogen is not harvested, the first reactor corresponds to an acidogenic/hydrolytic reactor where VFAs are generated before further conversion to methane in a second methanogenesis reactor (Escamilla-Alvarado et al. 2014; Willquist et al. 2012).

This two-stage process has several advantages. First, a two-stage process has been reported to improve the stability and robustness of the methanogenesis process. In addition, the process can be performed with a higher organic loading rate than the one-stage methanogenesis process (Ke et al. 2005). Second, the physical separation of both reactors makes it possible to operate the individual process under optimal conditions to maximize the production yield and easily control the processes (Tapia-Venegas et al. 2015). Third, hydrogen production coupled with AD yields hythane, which is a mixture of hydrogen (10%–25% by volume) and methane (75%–90% by volume) (Kumari & Das 2019; Liu et al. 2013). Hythane is an environmentally friendly fuel that can help reduce greenhouse gas emissions. The addition of hydrogen can increase the H/C ratio of the hythane. Moreover, the addition of hydrogen to methane can improve the narrow flammability range of methane during combustion. Furthermore, it can reduce the combustion duration and improve the heat efficiency, thereby increasing the biogas efficiency and flame speed (Dong et al. 2020; Liu et al. 2013). Finally, two-stage hydrogen and methane production are widely applied to increase the energy yield from biomass conversion. Dong et al. (2020) evaluated the potential for hythane production from rice straw using two-stage anaerobic fermentation. The maximum hydrogen yield of 225.1 mL H_2/g sugar was obtained from the first stage of dark fermentation, whereas the maximum methane yield of 112.8 mL CH_4/g sugar attained from the second stage AD. The hythane reached 337.9 mL hythane/g sugar. The energy conversion efficiency of hythane fermentation was 10.4%, which was 22.8% and 190.5% higher than that obtained from single hydrogen and methane fermentation, respectively.

The advantages and disadvantages of the utilization of hydrogenic effluent via photo fermentation, MECs to produce hydrogen, and the two-stage AD process to produce methane are presented in Table 1.

FUTURE PERSPECTIVE AND CHALLENGES

The presented information showed that hydrogenic effluent can be successfully used to produce hydrogen and methane. Biofuels can be produced from VFAs, as well as pharmaceuticals, petrochemicals, cosmetics, and chemicals (Wainaina et al. 2019). However, it should be noted that VFAs in hydrogenic effluent are mixed VFAs, which are less valuable than the pure form of individual acids (Aghapour Aktij et al. 2020). Thus, methods for the recovery and purification of VFAs are necessary to add the values to the VFAs. VFA recovery and purification can be achieved through a variety of techniques, including precipitation (Tao et al. 2016), adsorption, ion exchange (Rebecchi et al. 2016), distillation (Kumar et al. 2006), membrane processes (Ravishankar et al. 2021), and combined techniques (Aghapour Aktij et al. 2020). Each technique has its advantages and disadvantages. The major disadvantage of every technique is the requirement for high energy and capital investment for processing (Aghapour Aktij et al. 2020). Therefore, a search for cost-effective and sustainable techniques to recover and purify VFAs is needed. Moreover, the development of a process that can maximize VFA concentrations should be explored.

CONCLUSIONS

The post-process after dark fermentation by utilizing hydrogenic effluent has the advantage of completing the organic conversion and generating bio-energy in the form of hydrogen and methane. VFAs, such as acetic acid, butyric acid, and succinic acid, can produce hydrogen via

TABLE 1. The advantage and disadvantage of the utilization of hydrogenic effluent via photo fermentation, microbial electrolysis cells (MECs), and two-stage anaerobic digestion process

Method	Advantages	Disadvantages	References
Photo fermentation	(i) High conversion of organic acids to hydrogen (ii) High chemical oxygen demand removal efficiency (iii) Wide spectral light energy can be used	(i) Low light conversion efficiency (ii) High energy demand (iii) Economic issues of photobioreactor covering large areas	Dalena et al. (2017); Hallenbeck (2013); Mishra et al. (2019)
MECs	Low energy requirements	Undesired pH gradient	Hu et al. (2009); Hamelers et al. (2010)
Two-stage anaerobic digestion	(i) Improve the stability and robustness of the methanogenesis reactor (ii) Possible to operate the individual reactor under the optimal condition (iii) Easy to control the process (iv) Hydrogen coupled with methane represents an interest by producing hythane (v) High conversion of organic waste (vi) Economically feasible alternative for treating residual organic wastes	Long-time operation of the methanogenesis process	Ke et al. (2005); Tapia Venegas et al. (2015); Kumari and Das (2019); Liu et al. (2013)

photo fermentation, MEC, and methane by the AD process. However, organic acids from hydrogenic effluent in the pure form of individual acids are more valuable than the mixed form. Thus, technologies for the recovery and purification of VFAs from hydrogenic effluents should be considered. Furthermore, the fermentation process that maximizes VFA production should be examined.

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DECLARATION OF COMPETING INTEREST

None

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