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States and challenges for high-value biohythane production from waste biomass by dark fermentation technology

Zhidan Liu [a], Chong Zhang [b], Yuan Lu [b], Xiao Wu [b], Lang Wang [b], Linjun Wang [b], Bing Han [c], Xin-Hui Xing [b,*]

[a] College of Water Resources and Civil Engineering, China Agricultural University, Beijing 100083, China
[b] Department of Chemical Engineering, Tsinghua University, Beijing 100084, China
[c] National Institute of Clean-and-Low-Carbon Energy (NICE), Beijing 102209, China

HIGHLIGHTS

- Hythane ($H_2 + CH_4$) has attracted growing attention as clean vehicle fuel.
- We review the progress of bioH_2 and bioCH_4 fermentation in the past ten years.
- We discuss the feasibility of biohythane output from bioH_2 and bioCH_4.
- This review is intended to provide a state-of-the-art insight to biohythane.

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ABSTRACT

Hythane ($H_2 + CH_4$) has attracted growing attention due to its versatile advantages as, for instance vehicle fuel. Biohythane consisting of biohydrogen and biomethane via two-stage fermentation is a potential high-value solution for the valorization of waste biomass resources and probably an alternative to the fossil based hythane. However, the significance and application potential of biohythane have not yet been fully recognized. This review focuses on the progress of biohydrogen and subsequent biomethane fermentation in terms of substrate, microbial consortium, reactor configuration, as well as the H_2/CH_4 ratio from the perspective of the feasibility of biohythane production in the past ten years. The current paper also covers how controls of the microbial consortium and bioprocess, system integration influence the biohythane productivity. Challenges and perspectives on biohythane technology will finally be addressed. This review provides a state-of-the-art technological insight into biohythane production by two-stage dark fermentation from biomass.

1. Introduction

Hydrogen and methane are the two main gaseous energy carriers and also are widely used in the chemical industry. Each has independently attracted broad commercial interest and is highly valued. Hydrogen is regarded as the cleanest fuel. The hydrogen-based economy is described as a developing trend of future society with zero carbon emissions (Turner, 2004), as it is clean and sustainable compared with the current fossil fuel-based economy. However, the development of a hydrogen-based society has been restricted mainly by its cost-intensive processes and operations. Methane is being commonly used, not only in the chemical industry but also in transport as compressed natural gas (CNG), which has been regarded as the clean energy carrier in comparison to gasoline or diesel. Based on data from NGV (Global NGV, 2011), CNG-powered vehicles have been rapidly developed throughout the past decade, particularly in China. To satisfy the huge demand in east China, several projects, for instance the west-east natural gas transmission, have been established (Xinhua, 2004).

A mixture of hydrogen and methane is called hythane, which was trademarked by Eden (2010), HCNG or methagen (Ljunggren and Zacchi, 2010). Typically, the suggested hydrogen content in hythane is 10–25% by volume (Fulton et al., 2010). By combining the advantages of hydrogen and methane, hythane is considered one of the important fuels involved in achieving the transition of technical models from a fossil fuel-based society to a terminal hydrogen-based society (Bauer and Forest, 2001; Das et al., 2000; Fulton et al., 2010). Hythane has been used commercially as vehicle fuel in the USA and India (Das et al., 2000; Eden, 2010) and has also received much attention from many individual companies such as Volvo, Fiat, Airproducts and others. Currently, the

* Corresponding author. Tel./fax: +86 10 6279 4771.
E-mail address: xhxing@tsinghua.edu.cn (X.-H. Xing).

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industrial chain of hythane is mainly limited by the production and instrumentation associated with hydrogen since methane is a kind of primary energy carrier with relatively abundant sources of diverse origins, such as natural gas, landfill gas, biogas, etc. At present, hydrogen is mainly produced by physical/chemical methods, for instance, via the reforming of methane or during the production of syngas. These approaches are mostly not sustainable due to their heavy dependence on fossil based energy. The ability of providing sustainable and environmentally benign hythane is a key factor that will allow applications of hythane to attain its potential respected market position. One method is to add clean hydrogen to natural gas. Two separate gas channels with quantitative control of the gas flow rates would be required to produce hythane with the desired H_2/CH_4 ratio.

Another approach is to biologically produce hydrogen and methane concurrently in one system, which can be realized through a two-stage dark fermentation using biomass as the substrate (Banks et al., 2010; Liu et al., 2012; Ljunggren and Zacchi, 2010; Lu et al., 2009). If the system can reach an H_2/CH_4 ratio suitable for hythane, a sustainable route for the generation of so-called biohythane can be expected. In fact, the nature of the biological method guarantees the H_2/CH_4 ratio because it can be easily regulated by adjusting the conditions of the microbial fermentations. Therefore, biohythane production from biomass via two-stage biological fermentation can be a sustainable win–win solution, as it provides an output of renewable biological hythane and the efficient utilization of waste biomass. However, the application potential of biohythane has not yet received the attention it deserves. In addition, a large body of work focused on independent biohydrogen or biomethane production from biomass. This paper firstly summarizes the status of investigations and applications of hythane, then reviews the progress in the coproduction of biohydrogen and biomethane via dark fermentation in terms of substrate, microbial consortium, reactor configuration, product yield as well as H_2/CH_4 ratio by focusing on the feasibility of biohythane generation in the past ten years. This review also covers how microbial consortium control, process control and system integration influence the performance of the two-stage system. Challenges and perspectives on the development of biohythane will finally be addressed. This review is expected to provide a state-of-the-art technological insight to the study and applications of biohythane production by two-stage dark fermentation from waste biomass.

2. Hythane and its significance

Hythane has received extensive attention as a vehicle fuel since the 1980s (Bauer and Forest, 2001; Ma, 2008; Nagalingam et al., 1983). The characteristics of hydrogen and methane are given in Table 1 (Bauer and Forest, 2001). Methane (CNG) is considered to be a clean fuel for vehicle use compared to gasoline or diesel. It is, however, limited by its narrow flammability range, slow burning speed, and high ignition temperature (Table 1), which result in poor combustion efficiency and an intensive energy requirement for ignition of CNG-powered vehicles. Interestingly, hydrogen perfectly complements the weak points of methane (CNG): (1) the H/C ratio is increased by adding hydrogen, which reduces GHG emissions; (2) the narrow range of flammability of methane can be extended by adding hydrogen, thus improving the fuel efficiency; (3) the flame speed of methane can be greatly increased by adding hydrogen, eventually reducing combustion duration and improving heat efficiency; (4) the quenching distance of methane can be reduced by the addition of hydrogen, making the engine easy to ignite with less input energy.

Thus, technically, hythane, which has been developed as high-value gas fuels for vehicles, combines the advantages of hydrogen and methane. Studies on mixtures of hydrogen and methane have been carried out since the 1980s (Nagalingam et al., 1983), although hythane was trademarked recently (Eden, 2010). The main research focus has been on combustion properties, GHG emissions and ignition performance as means of optimizing the fuel efficiency of hythane as a vehicle fuel (Bauer and Forest, 2001; Ma, 2008). In a typical industrial chain for hythane production and utilization as vehicle fuel (Fulton et al., 2010), the hythane fueling station is considered as the central role due to its importance for making hydrogen and methane into the vehicle fuel hythane. However, the independent production of hydrogen and methane from fossil-based material is unsustainable and energy intensive. Biological hydrogen and methane production from renewable biomass via fermentation possesses the unique advantage of sustainability over fossil-based processes. Furthermore, biohydrogen and biomethane can be integrated in one system to form the optimal composition of hythane (i.e. biohythane), thus making the bioprocess an alternative to fossil-based process.

3. Potential biohythane production from biomass via dark fermentation

3.1. Process description

The end use of hythane is quite straightforward with a clear business model. The production of biohythane from waste biomass can be achieved via two-stage dark fermentation if the H_2/CH_4 ratio can be feasibly controlled. The traditional anaerobic methane fermentation normally consists of four steps (Gerardi, 2003): hydrolysis, acidogenesis, acetogenesis, and methanogenesis. Microorganisms with different functions are incorporated together to establish a synthetic route for methane production from complex biomass. In particular, two kinds of bacteria take part in the methanogenesis process: one is employed for the conversion of acetic acid to methane, and the other converts carbon dioxide and hydrogen into methane. In order to harvest hydrogen from the overall process, the hydrogen-to-methane path has to be blocked. Thus a two-stage fermentation process for the respective production of biohydrogen and biomethane needs to be established via the manipulation of bioprocesses.

Compared with conventional methane fermentation, the coproduction of hydrogen and methane by the two-stage fermentation offers unique advantages. The first is improved energy recovery based on the calculations of thermodynamics (Lu et al., 2009; Siddiqui et al., 2011). The coproduction of hydrogen and methane leads to an increase in total energy recovery of 100% and 30%, respectively, higher than either single-stage hydrogen or single-stage methane production. The two-stage process also benefits the net energy balance calculated based on energy input (e.g. pretreatment, heating of substrate) and energy output (generated gas biofuels) compared to single-stage hydrogen or methane fermentation (Perera et al., 2012; Ruggeri et al., 2010). Second, the coproduction process is characterized by a significantly reduced fermentation time (Ke et al., 2005; Li and Yu, 2011; Liu et al., 2006; Ueno et al., 2007a). The retention time of hydrogenogenesis is shorter than that of methanogenesis, which allows higher organic loading rate and more stable operation in the two-stage process than the single methane fermentation (Kongjan et al., 2011; Luo et al., 2011; Ueno et al., 2007b). This will eventually benefit the practical large-scale process. Third, solubilization and saccrification of waste biomass with high solid content can be realized simultaneously during first-stage hydrogen production (Lu et al., 2009; Ueno et al., 2007a). The fermentation of complex biomass, for instance, cornstalk can be enhanced and volatile fatty acids (VFAs) beneficial for methane fermentation can be harvested from