Electrochemical hythane production for renewable energy storage and biogas upgrading

Zhe Huang [a,b], Lu Lu [a,b], Daqian Jiang [c], Defeng Xing [a,*], Zhiyong Jason Ren [b,*]

[a] State Key Laboratory of Urban Water Resource and Environment, School of Municipal and Environmental Engineering, Harbin Institute of Technology, Harbin 150090, China
[b] Department of Civil, Environmental, and Architectural Engineering, University of Colorado Boulder, Boulder, CO 80309, United States
[c] School of Forestry and Environmental Studies, Yale University, New Haven, CT 06511, United States

HIGHLIGHTS

- Demonstrated effective biogas upgrading to hythane gas using electrochemical process.
- Analyzed the benefits of converting renewable electricity to hythane for energy storage and transport.
- Different voltages and conditions were investigated and performance was reported.
- Preliminary technoeconomic analysis showed the benefits of such conversion process.

ARTICLE INFO

ABSTRACT

This study investigates the feasibility of using an electrochemical process to convert excess renewable electricity and biogas into hythane gas, which has higher value than biogas and can be stored and transported using current natural gas infrastructure. The electrochemical process utilizes the protons generated in water electrolysis to liberate cations in silicate minerals, which in turn forms metal hydroxide and efficiently captures the CO_2 present in biogas. The H_2 produced in electrolysis is blended with purified biogas to generate mixed hythane product, which has a higher combustion rate in methane fueled vehicles. Results show that under a voltage of 3.5–4.0 V, the system reduced CO_2 in biogas from the original 40% to less than 15% and increased the heat value of the gas product from 534 kJ/mol to over 669 kJ/mol. Preliminary techno-economic analysis showed a net profit of $0.28 per thousand ft.cu hythane generated when standard grid electricity is used, and the profit may be increased by orders of magnitude if excess renewable electricity is used. The process offers a new route for renewable energy storage and upgrade.

1. Introduction

Renewable energy plays a critical role in reducing fossil fuel consumption and greenhouse gas (GHG) emissions [1–4]. However, many renewable energy sources such as solar, wind, and tidal energy are geographically limited and only produce electricity intermittently. The fluctuant production of renewable energy often creates a mismatch between electricity demand and supply, leading to excess renewable electricity during off-peak hours. For example, solar power is over-generated in early afternoon hours in California but it is insufficient for peak hours in late afternoons [5]. Similar challenges are faced by Denmark and Germany, as excess wind power is often produced in Jutland and Schleswig Holstein during off-peak hours [6]. Many energy storage technologies such as hydrogen storage, natural gas storage, rechargeable batteries, and high-temperature superconductivity [7] have been developed to manage the mismatch between power availability and demand.

Hythane is an emerging alternative fuel that contains a mixture of methane and hydrogen and can be transported and stored using current natural gas infrastructure [8]. By blending a small percentage of H_2 (10–25%) in methane, the hythane gas was shown to greatly enhance the combustion rate and extend the lean limit of combustion, making it a promising fuel that can improve the efficiency of methane-fueled vehicles [9–12]. Given its superior performance, hythane-fueled vehicles are being commercialized in the US and India and have attracted attention from major automobile manufacturers such as Volvo [13].

Sustainable production of hythane gas, however, remains a major challenge for low cost and large scale applications [13]. The methane used in the hythane gas is often produced via fermentation of waste organics, such as wastewater, sludge, animal manure, and landfill [14]. Such biogas product contains a large percentage of CO_2. For example, typical biogas produced in fermentation consists of 55–65% CH_4 and 30–45% CO_2 (by volume) [15]. The high CO_2 content significantly reduces the heat value of biogas and requires additional treatment when used as a source for hythane [13]. Traditional biogas upgrading methods such as water washing or alkaline treatment consume high energy or chemicals, and they do not produce value-added hythane products [14–17]. Biohythane is currently generated via a two-phase anaerobic digestion process. Hydrogen production is realized in the first fermentation stage, which is then followed by the methanogenesis stage. The two-step process faces challenges in maintaining a proper ratio between H_2 and CH_4, and the production rate is low and not stable [18–20]. Different parameters that may affect the final H_2/CH_4 ratio and process design were studied, but effective control regime faced major challenges [10,21,22]. For example, by combining thermophilic dark fermentation with anaerobic digestion, Cavinatoa et al. produced stable hythane gas from food waste with a specific H_2 rate of 66.7 L/kg of total volatile solid (TVS) in the first phase and a biogas rate of 0.72 m^3/per kgTVS fed in the second phase. The ratio among $H_2:CH_4:CO_2$ in the hythane mixture was around 6:58:36 [18]. Recently, Liu et al. reported for the first time that biohythane could be produced from sludge using microbial electrolysis cell (MEC). Compared with traditional anaerobic digestion. The alkali-pretreated sludge fed MEC showed the highest biohythane rate of 0.148 L/L/day, which was 40% and 80% higher than raw sludge fed MECs and anaerobic digestion [23].

In this study, we investigated a new electrochemical method to produce hythane gas from biogas. This electrochemical process has multiple advantages. Firstly, it achieves the dual purpose of excess renewable electricity storage [5,6] and biogas upgrading. Unlike conventional biogas upgrading processes, which only removes CO_2 to produce higher purity methane [24–27], this electrochemical process achieves the dual purpose of removing CO_2 and replacing it with H_2 [28–30]. The resulted hythane gas has a higher economic value and better performance for methane-fueled vehicles. Also, the tunable electrochemical process provides a more precise control and therefore addresses the challenge of unstable H_2/CH_4 ratios observed in traditional anaerobic fermentation process. Furthermore, this approach can be applied to capture and upgrade biogas produced from different sources especially landfills and small wastewater treatment facilities, as their biogas is largely unused due to the low quality and unstable generation [31]. The feasibility and effects of voltage on hythane gas generation and mix ratio were characterized, and energy recovery was quantified. Preliminary techno-economic analysis was conducted to assess the economic benefits and market potential of the process.

2. Materials and methods

2.1. Reactor setup and operation

Each two-chamber electrolysis reactor consisted of two cylindrical glass chambers (Fig. 1). The chambers were 320 ml each and separated by a cation exchange membrane (CEM) (CMI-7000, Membrane International [32]). Based on Rau et al. [29], 0.25 M Na_2SO_4 (conductivity 32.3 ms/cm) was added to both chambers to mimic the ion concentration in seawater for better electrolytic efficiency. A graphite rod (1 cm diameter and 10 cm length each) was vertically inserted into each chamber as the anode or cathode.
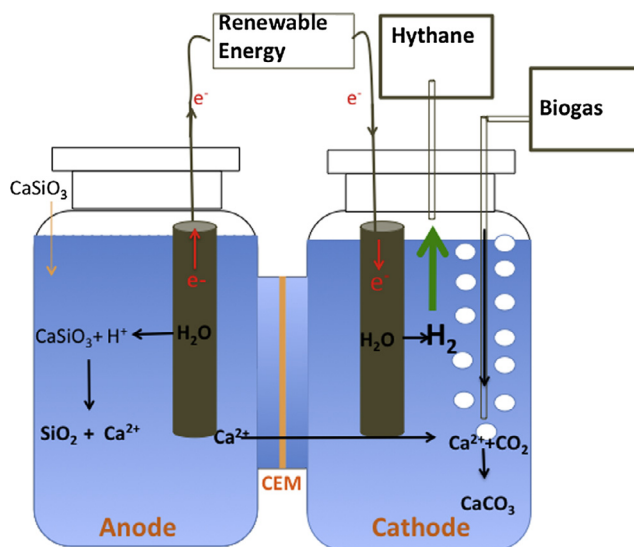

Fig. 1. The schematic of the two-chamber electrolysis reactor for tunable electrochemical hythane production.

The horizontal distance between the two electrodes was 10 cm. The electrodes were connected in series with a DC power source and a 10 Ohm resistor. The current across the resistor was monitored as different voltages were applied by the power source [33]. A gas bag (0.1 L capacity; Cali-5-Bond, Calibrated Instruments Inc.) was connected to the cathode chamber to collect the gas produced. The electrolyte in both chambers was stirred by a magnetic bar at 120 rpm.

Low cost and abundant $CaSiO_3$ (12 g wollastonite, 200 mesh, Sigma-Aldrich) was used as the cation source in the anode chamber similar to a previous study [29]. Prior to experiments, the headspace of both cells was sparged with ultra-high purity N_2 (99.999%) to remove CO_2 in the headspace. A voltage was then applied through the DC power supply for direct electrolysis for 2 h. A control experiment followed the same procedure but without any external voltage supply. At the end of 2 h electrolysis, the anolyte was filtered with 0.4-um filter to remove the precipitates. 40 mL filtered anolyte and 40 ml catholyte were then sampled for chemical analysis, including pH, conductivity and ion concentration. For biogas upgrading, 50 ml synthetic biogas (60% CH_4, 40% CO_2) was slowly flushed into the remaining catholyte at the rate of 10 ml/min and recirculated 5 times for quality upgrade via CO_2 capture. After the flushing of biogas, the final catholyte was sampled again for chemical analysis.

2.2. Analysis

The pH and conductivity were measured hourly using a benchtop multi-meter (HACH, HQ440d). The elemental compositions of the anolyte and the catholyte were analyzed by an inductively coupled plasma optical emission spectroscopy (ICP-OES) (ARL Fisons 3410+) and ion chromatography (Dionex 4500). The CO_2 absorbed was calculated based on the total inorganic carbon (TIC) in the catholyte, which was measured according to previously described methods [28]. Dissolved inorganic carbon (DIC) of catholyte was measured using the same method after removing carbonate precipitate with 0.22 μm membrane filtration.

The concentrations of H_2, CH_4 and CO_2 were analyzed using a gas chromatograph (Model 8610C, SRI Instruments) equipped with a thermal conductivity detector and nitrogen and helium as the carrier gas. The volume of each gas after flushing of biogas was