Electrochemical Hythane Production for Renewable Energy Storage and Biogas Upgrading

Zhe Huang^{1,2}, Lu Lu^{1,2}, Daqian Jiang³, Defeng Xing^{1*}, Zhiyong Jason Ren^{2*}

1. State Key Laboratory of Urban Water Resource and Environment, School of Municipal and Environmental Engineering, Harbin Institute of Technology, Harbin 150090, China
2. Department of Civil, Environmental, and Architectural Engineering, University of Colorado Boulder, Boulder, CO, 80309
3. School of Forestry and Environmental Studies, Yale University, New Haven, CT, 06511

*Corresponding author

Ren E-mail: zhiyong.ren@colorado.edu; phone: (303) 492-4137; fax: (303) 492-7217

Xing E-mail: dxing@hit.edu.cn; Phone: 86-186-86864920

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 CO₂ present in biogas. The H₂ 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 CO₂ 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.

Keywords: Electricity storage; Hythane; CO₂ capture; Biogas upgrade; Electrochemistry

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% to 65% CH_4 and 30% to 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

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

Each two-chamber electrolysis reactor consisted of two cylindrical glass chambers (Figure 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 Na₂SO₄ (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. 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 CaSiO₃ (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 N₂ (99.999%) to remove CO₂ in the headspace. A voltage was then applied through the DC power supply for direct electrolysis for 2 hours. A control experiment followed the same procedure but without any external voltage supply. At the end of 2 hr 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% CH₄, 40% CO₂) was slowly flushed into the remaining catholyte at the rate of 10 ml/min and recirculated 5 times for quality upgrade via CO₂ 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 CO₂ 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 H₂, CH₄ and CO₂ 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 calculated by multiplying the concentrations of each gas with the total volume in the gasbag and headspace:

$$V_{gas} = (V_{gas\ bag} + V_{head\ space}) \times \alpha,$$

Where α is the percentage of each gas.

2.3 Energy analysis

Two types of energy benefits, namely with and without accounting for the energy costs of CO₂ capture, were calculated:

$$Net\ energy\ without\ CO_2\ benefit = W_H - W_E$$

$$Net\ energy\ with\ CO_2\ benefit = W_H + W_C - W_E$$

The enthalpy of final gas mixtures combustion (W_H) was calculated using the high heating value (HHV) of related gases, which were 285.8 KJ/mol and 890.8 KJ/mol for H₂ and CH₄ respectively.

The corrected electrical energy consumption (W_E) by electrolysis was calculated by $W_E = \int_0^t (IE_{ap} - I^2 R) dt$, where E_{ap} was the voltage applied by the power source, R was the resistor, I was the current across the resistor, and t was the time. The current I was calculated based on the voltage (V) across the resistor (R), as $I = V/R$.

The energy costs for CO₂ capture was calculated by

$$W_C = V_{CO_2\ absorbed}(ml) \times \frac{426\ KJ}{mol\ CO_2} \div 24500 \frac{ml}{mol}$$

where 426 KJ/mol CO₂ was the typical energy consumption of atmospheric CO₂ capture [29].

2.4 Economic analysis

The economic analysis was calculated as follows:

$$Net\ Value = Value\ of\ hythane - capital\ cost - O\&M\ cost$$

A widely accepted market value of hythane was unavailable. But it was estimated that the production cost of hythane was ~5% more than that of natural gas, and the sale price of hythane was ~10% more than natural gas [34]. Therefore, the price of hythane was estimated to be \$3.0 per thousand cubic feet, since natural gas was approximately \$2.80 per thousand cubic feet in 2015. It should be clarified that this is a conservative estimate of the economic benefits because the price of natural gas ranged from \$2.80 to \$8.86 between 2005-2015 [35].

With the increasing natural gas consumption to replace coal, the price is expected to increase.

The cost of this system included the capital cost and the operation and maintenance costs. The capital cost of electrochemical H_2 production was reported to be \$600/t (about \$1.38/thousand cubic feet) of H_2 produced [36, 37]. The high cost of H_2 storage and transportation is excluded, but is a cost that can be avoided in this system. The O&M costs included electricity, materials (silicate and water), and nonelectrical and non-mineral O&M charges, which were \$60/MWh for electricity [38], \$20/t for silicate delivered [39, 40], \$0.05/t for water consumed, and 3% of capital expenditure [36] respectively. The cost of biogas was assumed to be free.

3. Results and discussion

3.1 pH variation and current generation

Figure 2 shows the pH and current profile under different applied voltages. pH is a key indicator in the electrochemical systems, as it influences CO_2 capture efficiency and conversion product (carbonate or bicarbonate). Compared to the control experiment, dramatic increases in catholyte pH were observed when a voltage was applied (Figure 2A). After 60 min of electrolysis, the catholyte pH increased from 9.21 to 10.9 when the applied voltage was increased from 2.5 V to 4.5 V (Figure 2A). However, after 120 min of electrolysis, the highest catholyte pH was achieved under 3.5 V. The final pH was 11.15 under 3.5 V, which represented a 3.5 mM increase in $[OH^-]$ compared to the control solution. The catholyte pH after 120 min electrolysis were 10.97 and 11.05 under 4.0 V and 4.5 V, respectively, which was a result of decreased current density after 60 min of electrolysis. This is likely due to the mass transfer limitation of cations from the anode to the cathode, which was insufficient to sustain a high electron flow. The smaller pH increases observed under 2.5 V and 3.0 V were likely due to the smaller current during electrolysis. After the biogas injection at 120 min, the catholyte pH decreased in all conditions, indicating that CO_2 was effectively absorbed (Figure 2A). The biggest drop was the catholyte generated by the 3.5 V electrolysis, which decreased from 11.15 to 9.56. Smaller pH changes were observed for 4.5 V and 2.5 V applications, in which the electrolyte pH dropped from 11.05 to 9.54 and from 9.82 to 9.14, respectively (Figure 2A).

The responding current increased in correspondence with the applied voltage (Figure 2B). For example, the initial current was 16.05 mA under 4.5 V but only 1.51 mA under 2.5 V (Figure 2B). The current decreased gradually over time during electrolysis, possibly as a result of the changes in electrolyte characteristics over time due to chemical reactions. Similar results were also reported in Rau et al. [29]. Sharper current decreases were observed under higher voltages of 4.5 V (from 16.02 mA to 4.44 mA) and 4.0 V (from 11.27 mA to 3.16 mA) (Figure 2B). These decreases may be caused by the rapid increase of pH in the first hour, which led to the lack of protons in the catholyte. In addition, the H_2SO_4 produced at the

anode could react with the silicate minerals to form a metal sulfate and hydrated silica, which was reported to reduce the conductivity and depress the current flow within the cell over time [29, 41].

Figure 2. pH change (A) and current generation (B) of the catholyte under different applied voltages. The arrow indicates biogas injection.

3.2 Hythane production and biogas upgrade

Figure 3 depicts how did different applied voltages affect gas composition during electrochemical reactions. It can be seen that when voltages were applied, the CO_2 content in the biogas dropped while the percentages of CH_4 and H_2 increased, which led to the increase of biogas quality and heat values. When the applied voltage was increased to 3.5 V or higher, significant increases in CO_2 capture and H_2 production were observed, leading to the production of higher quality hythane gas (Figure 3). The highest CO_2 removal (15.73 ml) was achieved at 3.5 V, in which case the CO_2 content dropped from 40% to 11.79% and the CH_4 percentage increased from 60% to 73.66%. In the meantime, 5.84 mL H_2 was produced, which comprised 14.55% of the hythane volume (Figure 3). The maximum production rate was 10.22 ml H_2 /liter catholyte/hour. Higher voltages of 4.0-4.5 V achieved a similar level of CO_2 removal (12.92 -13.84 ml CO_2), which resulted in similar hythane content mix (71.47-72.25% CH_4 , 11.34-14.58% H_2 , and 15.02-17.19% CO_2). Much smaller CO_2 was

captured in lower voltages due to insufficient alkalinity generation in electrolysis. The CO₂ removal was correlated with the final catholyte pH changes as well, as higher CO₂ capture resulted in greater pH changes (Figure 2).

The hythane gas product under 3.5 V (73.66% CH₄, 11.79% CO₂, 14.55% H₂) had the highest heat value of 698 KJ/mole, which was 30% more than the original synthetic biogas (60% CH₄, 40% CO₂, 0% H₂). Slightly lower heat values (669- 672 KJ/Mole) were achieved under 4.0 V and 4.5 V (Figure 3). The ideal volumetric content of H₂ in hythane should be 10% to 25% in order to be applied as a gas fuel for internal combustion engine. Therefore, voltages higher than 3.5 V should be applied for electrochemical hythane production and biogas upgrading, which can be easily provided by excess renewable energy (Figure 3). The methane content in the hythane gas was in the range of 98.1 - 99.2% of the amount in the original biogas fed into the system. This demonstrates that the loss of methane gas in the electrochemical process was minimal compared with other biogas upgrading methods [24, 27]. This can be attributed to short hydraulic retention time of the operation, which was 25 minutes from biogas injection to flow through quantification.

Figure 3. The variation of CH₄, CO₂, and H₂ contents in the hythane gas and their heat values under different voltages applied for electrolysis.

3.3 Ion transfers under 3.5 V applied voltage

Since the reactor under 3.5 V showed the best performance in hythane generation, more detailed ion transfer analysis was conducted for this condition. Results showed significant increases in Ca²⁺ (from 0.33 to 107.12 mg/L) and Si (0.66 to 44.99 mg/L) in the anolyte compared with the control experiment (Table1). This indicates successful silicate dissolution and cations liberation, a mechanism essential for electrochemical H₂ evolution and CO₂ capture[28-30]. Meanwhile, the catholyte Ca²⁺ concentration increased by ~0.12 mM while the Na⁺ concentration increased by ~16.26 mM (Table 1). This suggests that Ca²⁺ only accounted for ~16% of the CO₂ captured, while the majority of the CO₂ captured was associated with the primary electrolyte cation Na⁺. This is consistent with previous experiments [29]. It also suggests that although the addition of silicate minerals and the migration of Ca²⁺ successfully achieved CO₂ capture and hythane production, further

improvements can be realized if higher mass transfer can be achieved through measures such as enlarged membrane surface and optimized reactor configuration.

Table1. Changes in ion concentration (ppm), conductivity (ms/cm), DIC (mM) and TIC (mM) of the electrolytes under 3.5 V electrolysis.

	Conductivity	DIC	TIC	SO ₄ ²⁻	Cl ⁻	Na ⁺	Ca ²⁺	Si
Cathode Initial	32.3	ND	ND	23274	ND	11177	0.35	0.65
Cathode Final	32.5	0.6	0.75	23178	3.12	11551	5.01	0.62
Cathode Control	32.3	ND	ND	23286	ND	11165	0.76	0.68
Anode Initial	32.3	ND	ND	23274	ND	11205	0.33	0.66
Anode Final	32.0	ND	0.1	22757	3.59	10656	107.12	44.99
Anode Control	32.3	ND	ND	23157	ND	11192	8.92	3.14

Based on the experimental results and ion analysis, we reasoned that the cations transported from the anode to the cathode chamber to capture CO₂ in the biogas. A series of reactions took place to achieve CO₂ absorption and hythane production. In the anode chamber, Ca²⁺ was liberated from CaSiO₃ during electrolysis, which was accompanied by the SiO₂ formation. The cations (Na⁺, Ca²⁺) then migrated to the cathode chamber to react with the OH⁻ generated during H₂ evolution, which generated alkalinity for CO₂ capture and hythane production.

As a result, the overall reaction was inferred as follows:

Where V_{dc} was the applied voltage. The exact format of salts produced in the solution depends on the cation availabilities and solution alkalinity.

3.4 Energy and economic analysis

Table 2 summarizes the findings of preliminary energy and economic benefits of electrochemical hythane production and biogas upgrading. The highest heat value and net energy gain (with CO₂ benefit) were both achieved at 3.5 V on a per mole basis, which were

697.76 KJ/mol and 208.60 KJ/mol, respectively (Table 2). The heat value and net energy gain decreased with increased external voltage due to a higher fraction of H₂ in the produced hythane gas, which has a lower heat value than methane on per mole basis.

The highest economic benefits were achieved at 4.0 V (Table 2), which was estimated to be \$ 0.20/ 1000 cubic feet hythane. Decreasing the voltage to 3.5 V or increasing the voltage to 4.5 V lowered the economic benefits, to \$0.095 and \$-0.64 per thousand cubic feet of hythane gas respectively (Table 2). This indicates the need to balance CO₂ capture and hydrogen gas production to achieve the highest energy and economic benefits, because excessive hydrogen gas increases the costs and lowers the heat value of produced hythane, while insufficient hydrogen gas limits the usability of the hythane produced.

The economic benefit of the production process was based on the capital costs, electricity costs and material costs. For example, at 3.5 V, the final hythane gas was 73.66% CH₄, 14.55% H₂ and 11.79% CO₂. Therefore, 1000 ft³ of hythane gas was 1156 moles under room temperature, which included 168 moles of H₂. The capital cost of electrochemical hydrogen production was reported as \$600/t H₂, which equaled \$0.0012/mole H₂, and translated to \$0.0012*168=\$0.2 /1000 ft³ of hythane gas in the studied process. The electricity cost was based on the total electric energy consumed in this process, which was 116.88 KJ/mol hythane gas and \$2.22/1000 ft³ hythane gas when the applied voltage was 3.5 V. Based on the stoichiometry, 0.02 tons of silicate and 0.003 ton of water were needed for 1000 ft³ of hythane produced, which would cost \$0.4 and \$0.00015.

$$Net\ value = \$3 - (\$0.2 + \$2.22 + \$0.4 + \$0.00015) \times 103\% = \$0.095/1000\ ft^3\ of\ hythane\ gas$$

In the current calculations, standard price of electricity was applied, which made it a major contributor to the total cost. If excess renewable electricity could be used in off-peak hours for this process, the cost could be significantly lower, making the process economically more appealing. It is estimated that if excess renewable electricity is used, the economic benefits can be approximately 25 times higher than using current grid electricity at 3.5 V (Table 2).

Table2. Energy Expenditure, Energy Production (as hythane gas) and CO₂ Benefits of the System

Gas Product		Initial Biogas	Final Hythane gas		
Voltage applied/V		ND	3.5 V	4.0 V	4.5 V
Enthalpy of combustion/ KJ mol ⁻¹		534.48	697.76	669.04	672.05
Net energy	With CO ₂ Benefit	ND	208.60	163.56	136.31

gain /KJ mol⁻¹	Without CO ₂ Benefit	ND	46.48	29.91	-13.92
Economic benefits/\$ 1000 ft³⁻¹	Without Electricity Cost	ND	2.38	2.28	2.37
	With Electricity Cost	ND	0.095	0.20	-0.64

4. Conclusion

This study represents the first electrochemical approach for biogas upgrading to hythane using excess renewable electricity. It is a new way of converting renewable electricity to storable and transportable fuels. The system performance was affected by the applied voltage, and the optimal range was 3.5-4.0 V, which could be easily supplied by excess solar power. Additional benefits can be realized in carbon capture and utilization as well as biogas upgrading, but more studies are needed to improve mass transfer, reduce cost, and facilitate process integration. This process shows promise of scale-up and is optimal for regions with excess supply of solar, wind and other renewable energy sources yet facing storage and transportation problems. It is also ideal for coastal regions which can take advantage of the abundant seawater containing minerals and alkalinity.

5. Acknowledgement

This work was partially supported by the US National Science Foundation under Award CEBT-1510682 and the open project of State Key Laboratory of Urban Water Resource and Environment in China under award QAK201603.

6. Reference

- [1] Panwar N, Kaushik S, Kothari S. Role of renewable energy sources in environmental protection: a review. *Renewable and Sustainable Energy Reviews*. 2011;15:1513-24.
- [2] Mitigation CC. IPCC special report on renewable energy sources and climate change mitigation. 2011.
- [3] Turner JA. A realizable renewable energy future. *Science*. 1999;285:687-9.
- [4] Sims RE, Rogner H-H, Gregory K. Carbon emission and mitigation cost comparisons between fossil fuel, nuclear and renewable energy resources for electricity generation. *Energy policy*. 2003;31:1315-26.
- [5] Sommer L. Accessed May 24, 2016 <http://ww2.kqed.org/science/2016/04/04/what-will-california-do-with-too-much-solar/>. 2016.
- [6] Andersen AN, Lund H. New CHP partnerships offering balancing of fluctuating renewable electricity productions. *Journal of Cleaner Production*. 2007;15:288-93.
- [7] Dresselhaus M, Thomas I. Alternative energy technologies. *Nature*. 2001;414:332-7.
- [8] Fulton J, Marmaro RW, Egan GJ. System for producing a hydrogen enriched fuel. Google Patents; 2010.
- [9] Hraiech I, Sautet J-C, Yon S, Mhimid A. Combustion of hythane diluted with CO₂. *Thermal Science*. 2015;19:1-10.
- [10] Pasupuleti SB, Mohan SV. Single-stage fermentation process for high-value biohythane production with the treatment of distillery spent-wash. *Bioresource technology*. 2015;189:177-85.
- [11] Gattrell M, Gupta N, Co A. Electrochemical reduction of CO₂ to hydrocarbons to store renewable electrical energy and upgrade biogas. *Energy conversion and Management*. 2007;48:1255-65.
- [12] Agarwal J, Alam M, Jaiswal A, Yadav K, Kumar N. Comparative Study of Emissions and Performance of Hythane Boosted SI Engine Powered by Gasoline-Methanol Blend and Gasoline-Ethanol Blend. *SAE Technical Paper*; 2016.
- [13] Liu Z, Zhang C, Lu Y, Wu X, Wang L, Wang L, et al. States and challenges for high-value biohythane production from waste biomass by dark fermentation technology. *Bioresource technology*. 2013;135:292-303.
- [14] Abatzoglou N, Boivin S. A review of biogas purification processes. *Biofuels, Bioproducts and Biorefining*. 2009;3: -71.
- [15] Harasimowicz M, Orluk P, Zakrzewska-Trznadel G, Chmielewski A. Application of polyimide membranes for biogas purification and enrichment. *Journal of Hazardous Materials*. 2007;144:698-702.
- [16] Osorio F, Torres J. Biogas purification from anaerobic digestion in a wastewater treatment plant for biofuel production. *Renewable energy*. 2009;34:2164-71.
- [17] Lastella G, Testa C, Cornacchia G, Notornicola M, Voltasio F, Sharma VK. Anaerobic digestion of semi-solid organic waste: biogas production and its purification. *Energy conversion and management*. 2002;43:63-75.

- [18] Cavinato C, Giuliano A, Bolzonella D, Pavan P, Cecchi F. Bio-hythane production from food waste by dark fermentation coupled with anaerobic digestion process: a long-term pilot scale experience. *international journal of hydrogen energy*. 2012;37:11549-55.
- [19] Micolucci F, Gottardo M, Bolzonella D, Pavan P. Automatic process control for stable bio-hythane production in two-phase thermophilic anaerobic digestion of food waste. *International Journal of Hydrogen Energy*. 2014;39:17563-72.
- [20] Giuliano A, Zanetti L, Micolucci F, Cavinato C. Thermophilic two-phase anaerobic digestion of source-sorted organic fraction of municipal solid waste for bio-hythane production: effect of recirculation sludge on process stability and microbiology over a long-term pilot-scale experience. *Water Science and Technology*. 2014;69:2200-9.
- [21] Show K-Y, Lee D-J, Chang J-S. Bioreactor and process design for biohydrogen production. *Bioresource technology*. 2011;102:8524-33.
- [22] Chinellato G, Cavinato C, Bolzonella D, Heaven S, Banks C. Biohydrogen production from food waste in batch and semi-continuous conditions: evaluation of a two-phase approach with digestate recirculation for pH control. *International Journal of Hydrogen Energy*. 2013;38:4351-60.
- [23] Liu Q, Ren ZJ, Huang C, Liu B, Ren N, Xing D. Multiple syntrophic interactions drive biohythane production from waste sludge in microbial electrolysis cells. *Biotechnology for Biofuels*. 2016;9:162.
- [24] Petersson A, WeLLInGer A. Biogas upgrading technologies–developments and innovations. *IEA Bioenergy*. 2009;20.
- [25] Hullu Jd, Waassen J, Van Meel P, Shazad S, Vaessen J. Comparing different biogas upgrading techniques. *Eindhoven University of Technology*. 2008:56.
- [26] Cavenati S, Grande CA, Rodrigues ArE, Kiener C, Müller U. Metal organic framework adsorbent for biogas upgrading. *Industrial & Engineering Chemistry Research*. 2008;47:6333-5.
- [27] Deng L, Hägg M-B. Techno-economic evaluation of biogas upgrading process using CO₂ facilitated transport membrane. *International Journal of Greenhouse Gas Control*. 2010;4:638-46.
- [28] Lu L, Huang Z, Rau GH, Ren ZJ. Microbial Electrolytic Carbon Capture for Carbon Negative and Energy Positive Wastewater Treatment. *Environmental science & technology*. 2015;49:8193-201.
- [29] Rau GH, Carroll SA, Bourcier WL, Singleton MJ, Smith MM, Aines RD. Direct electrolytic dissolution of silicate minerals for air CO₂ mitigation and carbon-negative H₂ production. *Proceedings of the National Academy of Sciences*. 2013;110:10095-100.
- [30] Huang Z, Jiang D, Lu L, Ren ZJ. Ambient CO₂ capture and storage in bioelectrochemically mediated wastewater treatment. *Bioresource technology*. 2016;215:380-5.
- [31] Wiedmann T, Minx J. A definition of ‘carbon footprint’. *Ecological economics research trends*. 2008;1:1-11.
- [32] Lu L, Fang Y, Huang Z, Huang Y, Ren ZJ. Self-sustaining carbon capture and mineralization via electrolytic carbonation of coal fly ash. *Chemical Engineering Journal*.

2016;306:330-5.

[33] Chookaew T, Prasertsan P, Ren ZJ. Two-stage conversion of crude glycerol to energy using dark fermentation linked with microbial fuel cell or microbial electrolysis cell. *New biotechnology*. 2014;31:179-84.

[34] Solomon G. AGM Presentation. Accessed April 8th, 2016 <http://www.sx.com.au/asxpdf/20131129/pdf/42l89p0y9y3wxppdf>. 2013.

[35] US Energy Information Administration. International Energy Statistics. Accessed May 25, 2015 from <http://www.eia.gov/cfapps/ipdbproject/iedindex3.cfm?tid=90&pid=44&aid=8>

[36] Energy Bo, Council ESNR, Engineering Do, Council PSNR, Engineering WNAo. The hydrogen economy: Opportunities, costs, barriers, and R&D needs: National Academies Press; 2004.

[37] Bourgeois R, Sanborn S, Assimakopoulos E. Alkaline electrolysis final technical report. General Electric Global Research Center, Niskayuna NY; 2006.

[38] Schmidt TS, Born R, Schneider M. Assessing the costs of photovoltaic and wind power in six developing countries. *Nature Climate Change*. 2012;2:548-53.

[39] Metz B, Davidson O, De Coninck H, Loos M, Meyer L. Carbon dioxide capture and storage. 2005.

[40] Steen B, Borg G. An estimation of the cost of sustainable production of metal concentrates from the earth's crust. *Ecological Economics*. 2002;42:401-13.

[41] Wang W, Jenkins PE, Ren Z. Electrochemical corrosion of carbon steel exposed to biodiesel/simulated seawater mixture. *Corrosion Science*. 2012;57:215-9.