Applied Energy 212 (2018) 509–515

Contents lists available at ScienceDirect

Applied Energy

journal homepage: www.elsevier.com/locate/apenergy

Microbial electrolysis treatment of post-hydrothermal liquefaction wastewater with hydrogen generation

Ruixia Shen[a,b], Yong Jiang[b], Zheng Ge[b], Jianwen Lu[a], Yuanhui Zhang[a,c], Zhidan Liu[a,*], Zhiyong Jason Ren[b,*]

[a] Laboratory of Environment-Enhancing Energy (E2E) and Key Laboratory of Agricultural Engineering in Structure and Environment, Ministry of Agriculture, College of Water Resources and Civil Engineering, China Agricultural University, Beijing 100083, China

[b] Department of Civil, Environmental, and Architectural Engineering, University of Colorado Boulder, Boulder, CO 80309, USA

[c] Department of Agricultural and Biological Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA

HIGHLIGHTS

- Microbial electrolysis effectively removed both organics and nitrogen from post-HTL wastewater.
- It also generated high rate H_2 that can be used for biocrude upgrading.
- Operating conditions can be optimized by varying loading rate, applied voltages and others.

ARTICLE INFO

Keywords:
Organic wet waste
Hydrothermal liquefaction
Hydrogen production
Microbial electrolysis cell
Wastewater treatment

ABSTRACT

Hydrothermal liquefaction (HTL) directly converts wet organic waste into biocrude oil, but it also generates post-HTL wastewater (PHWW) with concentrated nutrients that require further treatment before discharge or reuse. While traditional technologies showed limited success, this study demonstrates that microbial electrolysis cell (MEC) can be an effective approach to treat the swine manure PHWW and recover H_2 for onsite HTL biocrude upgrading. The onsite H_2 production and utilization makes MEC an ideal wastewater treatment process for HTL operations. Using actual swine manure PHWW, the MEC reactors showed excellent removals of organics (90–98%) and nitrogen (57–93%) under various organic loadings, applied voltages, and flow rates. Increasing organic loadings and applied voltages showed positive influences on system performance, while changes of flow rates showed limited impacts. The highest H_2 production rate was 168.01 ± 7.01 mL/L/d with a H_2 yield of 5.14 ± 0.22 mmol/kg COD (3000 mg COD/L, 1.0 V), and the highest cathodic H_2 recovery and energy efficiency were 74.24 ± 0.11% and 120.56 ± 17.45%, respectively. System configuration and operation can be further optimized to improve system performance.

1. Introduction

Hydrothermal liquefaction (HTL) is a promising process to convert wet organic waste into biocrude oil and value-added biochemicals [1–3]. It has shown great advantages in waste valorization compared to traditional processes such as anaerobic digestion (AD), because it has high carbon efficiency, short conversion time, small footprint, and high-value end product than biogas and biosolids [4]. In addition to biocrude oil, the HTL process also generates byproducts such as hydrochar solids, CO_2-rich gas, and high concentration wastewater [5,6]. While most researches to date have focused on improving biocrude oil production and quality, very few studies investigated the management of the post-HTL wastewater (PHWW), which contains up to 40% of the carbon and 80% of the nutrients from the feedstock [7]. Such concentrated wastewater brings a major challenge in wastewater treatment and an opportunity for energy recovery.

The properties of the wastewater generated during HTL vary substantially depending on the feedstock and operational conditions [8,9]. For example, to convert 1000 kg feedstock with 20 wt% total solid content into biocrude oil, an estimated 800 liter PHWW will be generated [10,11], which has very high chemical oxygen demand. The PHWW not only contains sugars, carboxylic acids, and ammonia, but also it contains toxic compounds such as phenols and nitrogenous organic compounds [12]. The wastewater is acidic (pH = 4.2), thus it has

* Corresponding authors.
E-mail addresses: zdliu@cau.edu.cn (Z. Liu), zhiyong.ren@colorado.edu (Z.J. Ren).

https://doi.org/10.1016/j.apenergy.2017.12.065
Received 5 September 2017; Received in revised form 6 December 2017; Accepted 10 December 2017

to be neutralized before discharge [13]. Some studies used catalytic hydrothermal gasification to designate the aqueous solution at high temperature (~370°C) and pressure (~3000 psia) and convert it into CO_2, H_2, and CH_4 [14], but this process is energy intensive [15]. Biological processes such as AD and microalgae cultivation have been investigated in treating PHWW, but the water was found significantly inhibiting to algal growth or biogas production [16]. To reduce the toxicity, the PHWW had to be diluted tens of times for algae growth, or pretreated by zeolite adsorption, granular activated carbon adsorption, or petroleum ether extraction to remove recalcitrant compounds before AD [5,13,16,17]. Even with such combinations, the COD removal (40–60%) was still not satisfactory.

In this study, we hypothesized microbial electrolysis cell (MEC) can be an effective treatment method for swine manure PHWW with additional benefits of H_2 generation for onsite use. The MEC is a microbial electrochemical technology which employs consortia of anaerobic bacteria to convert biodegradable waste into electrical current [18–20]. The electrons are then transferred to the cathode to reduce the protons for H_2 production under the assistance of a low external voltage (0.2–0.8 V) to overcome the thermodynamic barrier of water electrolysis. The external voltage can be supplied by a small solar panel, low-grade heat, or microbial fuel cells (MFCs) [21]. MECs have been used to treat a variety of wastewater streams, including those with high strength or recalcitrant compounds such as industrial wastewater, municipal wastewater, sludge, landfill leachate, and agricultural wastewater [22–29], but no study made the connection on how H_2 can be used in system operation. Even though H_2 is an excellent renewable energy source, the utilization of H_2 has been a barrier because its requires expensive infrastructure and operation. In this context, producing and utilizing H_2 during swine manure PHWW treatment becomes a unique advantage and niche application, because H_2 is needed for HTL biocrude oil upgrading [31]. Biocrude oil upgrading relies on H_2 as a reducing agent to remove oxygen in biocrude oil and reduce molecular weight through hydrotreating and hydrocracking methods [32,33]. However, currently H_2 is provided by steam reforming or purchased natural gas, which is expensive and not sustainable.

There has been limited information in taking advantage of the synergy between H_2 generation and its onsite utilization. We demonstrated MEC can be used in cornstalks PHWW treatment, with more than 80% COD removal and 79–95% removal in recalcitrant organic matters such as dimethyl phthalate and diethyl phthalate [30]. However, H_2 production rate (3.92 mL/L/d) and the Coulombic efficiency (C_E, 7.00%) were very low. Therefore, here we demonstrated for the first time that the MEC potential can be fully realized by using advanced operation and nickel foam electrode materials in MECs for swine manure PHWW treatment. The study showed excellent MEC performance in organic and nitrogen removals from swine manure PHWW, and it systematically characterized contaminants removal and H_2 production under different operational conditions including organic loading, applied voltage, and flow rate. These results indicate that MEC systems can be a high-efficiency pathway for PHWW treatment as well as H_2 recovery and utilization.

2. Materials and methods

2.1. Characteristics of the wastewater generated from swine manure HTL process

The PHWW generated from swine manure HTL was collected from the Environment-Enhancing Energy (E2-Energy) laboratory in the Department of Agricultural and Biological Engineering at University of Illinois at Urbana-Champaign. After HTL process, the wastewater was separated from mixed HTL products using vacuum-filtration method. Table 1 shows the characteristics of the PHWW, which had high concentrations of organics (TCOD = 37366.7 ± 351.2 mg/L). The wastewater has a low pH (4.2) and relatively high conductivity (5.1 ms/cm), and it contains significant amount of ions (Table 1).

Table 1
Main characteristics of the PHWW from swine manure.

Indexes	Values
Conductivity	5.1 ms/cm
pH	4.2
TSS	98.0 ± 10.5 mg/L
TCOD	37366.7 ± 351.2 mg/L
SCOD	35700.0 ± 655.7 mg/L
TOC	13500.0 mg/L
DOC	13400.0 mg/L
TKN	956.0 ± 2.8 mg/L
NO_3-N	54.9 ± 0.1 mg/L
NO_2-N	14.7 ± 0.1 mg/L
NH_3-N	376.5 ± 0.7 mg/L
PO_4^{3-}	0.7 ± 0.4 mg/L
SO_4^{2-}	89.4 ± 0.4 mg/L
Si	44.6 ± 9.8 mg/L
Zn	4.4 ± 0.2 mg/L
Mn	8.6 ± 0.3 mg/L
Fe	303.9 ± 28.4 mg/L
Mg	49.4 ± 2.3 mg/L
Ca	28.5 ± 1.0 mg/L
Na	318.0 ± 19.9 mg/L
K	1185.5 ± 59.6 mg/L
Cl	586.0 ± 14.8 mg/L
Br	29.8 ± 1.7 mg/L

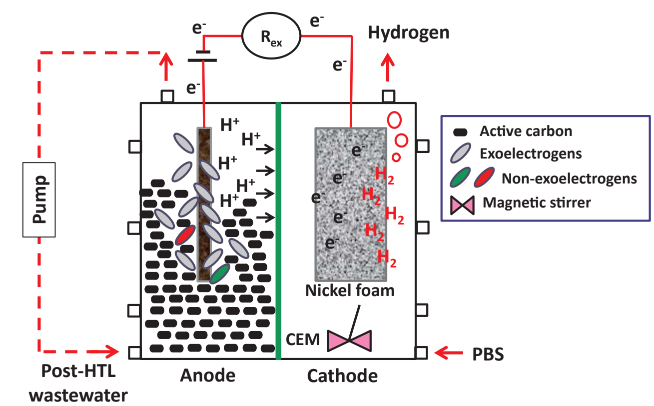

Fig. 1. Schematic diagram of the MEC system used in this study.

2.2. MEC reactor setup and operation

Two-chamber fixed-bed MEC reactors were made of acrylic glass and operated in batch mode (Fig. 1). For each reactor, the working volume of the anode and cathode chamber was 500 mL and 1000 mL, respectively. Each anode consisted a piece of carbon felt (6 cm × 14 cm) embedded in activated carbon granules with a titanium nanowire as a current collector. The cathode was a "W" shape nickel foam (24 cm × 14 cm), which has been reported with excellent catalytic activities for hydrogen evolution [34]. A cation exchange membrane (CEM) was used to separate the two chambers, and a 10 Ω resistor was added between the anode and cathode for current measurement.

The MEC reactors started with 1 g/L CH_3COONa in 50 mM PBS buffer with the inoculum from the effluent of a working MFC [35]. A 0.7 V external voltage was applied to enable hydrogen evaluation in the cathode. The anolyte was recirculated between the anode chamber and an external reservoir (500 mL) for improved mass transfer, while the catholyte (50 mM PBS) was mixed by a magnetic stirrer [36]. After a month operation when the current output was stable, the substrate was changed to 1:1 mixture of 1.64 g/L CH_3COONa and actual PHWW from the HTL of swine manure. After another 30 days, only actual swine