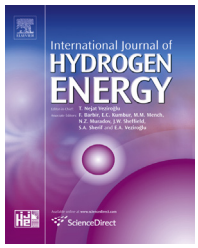
Available online at www.sciencedirect.com

ScienceDirect

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



Feasibility study of SCFAs production from microalgae during hydrogen fermentation

Yeo-Myeong Yun [a], Hang-Sik Shin [b], Dong-Hoon Kim [c,*]

[a] College of Agriculture, Forestry and Natural Resource Management, University of Hawaii at Hilo, 200 W. Kawili Street, Hilo, HI, 96720, USA

[b] Department of Civil and Environmental Engineering, KAIST, 373-1 Guseong-dong, Yuseong-gu, Daejeon 305-701, Republic of Korea

[c] Department of Civil Engineering, Inha University, 100 Inha-ro, Nam-gu, Incheon, Republic of Korea

ARTICLE INFO

Article history:
Received 31 May 2015
Received in revised form
9 September 2015
Accepted 31 October 2015
Available online 21 November 2015

Keywords:
Short-chain fatty acids
Hydrogen
Microalgae
Substrate concentration
Lactate

ABSTRACT

In the present work, the feasibility of short-chain fatty acids (SCFAs) production from microalgae was investigated during hydrogen (H_2) fermentation. The fermentation was conducted at various substrate concentrations ranging 2.5–100 g dry cell weight (dcw)/L by using anaerobic mixed cultures under mesophilic condition. It was found that H_2 yield increased to 36 mL H_2/g dcw as substrate concentration increased to 40 g dcw/L. However, a significant decrease in H_2 yield was observed at substrate concentration of ≥60 g dcw/L. As substrate concentration increased, SCFAs concentration gradually increased, reaching 12,410 mg COD/L at 100 g dcw/L. However, in terms of SCFAs conversion efficiency, it increased from 17 to 34% (on chemical oxygen demand basis) with substrate concentration increase up to 10 g dcw/L. Acetate was the major product at 2.5 g dcw/L, but butyrate became dominant at substrate concentration of 5–60 g dcw/L. At 80 and 100 g dcw/L, lactate became the major product. H_2 and SCFAs production rate were successfully described by kinetic models of Andrew's Eq. and Monod Eq., respectively. From the fermentation performance obtained, it can be concluded that microalgae could substitute the current attempt that acidifying sewage sludge to use as an external carbon source in denitrifier.

Introduction

The concerns on environmental pollution, climate change, and energy security have brought about a lot of research efforts on developing alternative production chains in transport and chemical sectors [1]. Biorefinery concept is considered the alternative and sustainable way to create value-added biofuels and products through a biomass-based industry [2]. Biomass is defined as the contemporary plant matter formed by photosynthetic capture of solar energy, splitting into terrestrial and aquatic one depending on its growth environment. Compared to terrestrial biomass, microalgae, one of the representing aquatic biomass, has a number of potential advantages: faster growth rate with higher biodegradability, lower need for land use, and no

* Corresponding author. Tel.: +82 32 860 7562; fax: +82 32 873 7560.
E-mail address: dhkim77@inha.ac.kr (D.-H. Kim).

http://dx.doi.org/10.1016/j.ijhydene.2015.10.135

competition with edible agricultural crops [3]. In addition, microalgae can be converted into a wide range of metabolites and chemicals including proteins, carbohydrates and lipids, which can subsequently be transformed into biofuels and value-added products via thermochemical and fermentation processes [4].

Hydrogen (H_2) has garnered huge interest as a promising alternative energy carrier in last years since it has high energy content and its combustion only produces water as byproduct [5]. From biomass by fermentation routes, H_2 can be produced in two ways depending on the light dependency. The photo-driven process has an advantage of high H_2 yield, but there is a limitation that requires big-sized fermenter caused by low H_2 production rate (HPR) [6]. Meanwhile, dark fermentative H_2 production, in short, H_2 fermentation, proceeded in a fast manner and can directly use solid materials as feedstock [7]. In addition, short-chain fatty acids (SCFAs, C2–C5) can be obtained as byproducts, during H_2 fermentation [8]. The produced SCFAs can be used as external carbon sources in biological nutrient removal process in wastewater treatment, and are highly suitable substrates for polyhydroxyalkanoate (PHA) production [9,10].

There have been a few studies on SCFAs production by using pure culture, but a relevant literature on fermentation using mixed culture is scarce. The use of mixed cultures can offer several advantages compared to that of pure cultures in engineering point of view, such as simpler operation, better substrate utilization, and diverse metabolic capabilities [11,12]. There are lots of factors that affect fermentation from microalgae using mixed cultures such as substrate concentration, pH, temperature, solids retention time (SRT), etc. Among these factors, substrate concentration has a significant effect on product distribution and yield, and it is a basic parameter judging the feasibility of invented process [13,14].

This study aimed to investigate the feasibility of SCFAs production from microalgae during H_2 fermentation. The batch tests at various substrate concentrations of microalgae (2.5–100 g dcw/L) were conducted by using anaerobic mixed cultures under mesophilic condition. The results obtained here might helpful to understand the mechanisms for SCFAs and H_2 production from microalgae and beneficial for the sustainability of microalgae-based biorefinery.

Materials and methods

Preparation of feedstock and inoculum

Chlorella vulgaris (carbohydrate 12.5%, protein 66.9%, lipid 13%, ash 6%, and others 1.6%) was utilized as a feedstock. The chemical oxygen demand (COD) concentration of *C. vulgaris* was 1.3 g COD/g dry cell weight (dcw). The inoculum used in this study was obtained from an anaerobic digester at a local wastewater treatment plant. The pH, alkalinity, and volatile suspended solid (VSS) concentration of the sludge were 7.2, 2.6 g $CaCO_3$/L, and 42 g VSS/L, respectively. In order to inactivate the H_2-cosuming activity of sludge, heat-shock (90 °C for 20 min) was applied prior to fermentation [15].

Experiment

The fermentation was carried out using 250 mL serum bottles with a working volume of 100 mL, and the bottles were seeded with heat-treated sludge up to 30% of the working volume. Substrate concentrations were set at 2.5, 5, 10, 20, 40, 60, 80, and 100 g dcw/L. The rest of the working volume was filled with distilled water, and no external nutrients were added. After adding all substances, initial pH was adjusted at 7.4 ± 0.2 by adding 5 N HCl solution and the bottles were purged with N_2 gas for 5 min to provide an anaerobic condition. Fermentation including a blank (adding only inoculum) was carried out in a shaking incubator (100 rpm) held at a temperature of 35 °C. Sampling was conducted at 4, 8, 12, 18, 24, 30, 36, 42, 54, and 66 h. The experiment was conducted triplicate, and the results were averaged.

Analytical methods

The concentrations of SCFAs and lactate were measured by a high-performance liquid chromatograph (HPLC) (Finnigan Spectra SYSTEM LC, Thermo Electron Co.) using an ultraviolet (210 nm) detector (UV1000, Thermo Electron) and an 100 × 7.8 mm Fast Acid Analysis column (Bio-Rad Lab.) with 0.005 M H_2SO_4 as a mobile phase at a flow rate of 0.6 mL/min. The amounts of H_2 and carbon dioxide in the biogas were analyzed by a gas chromatograph (GC, Gow Mac series 580, Gow-Mac Instrument Co., USA) equipped with a thermal

Table 1 – The performance of SCFAs production and H_2 productivities in batch fermentation of microalgae at various substrate concentrations.

Substrate concentration (g dcw/L)	SCFAs productivity				H_2 productivity			
	SCFAs concentration (mg COD/L)	SCFAs yield (mg COD/g dcw)	SCFAs yield (mg COD/g COD)	SCFAs production rate (mg COD/L/h)	Cumulative H_2 production (mL)	H_2 yield (mL/g dcw)	H_2 yield (mL/g COD)	HPR (L/L/h)
2.5	550 ± 50	220 ± 20	170 ± 15	25 ± 6	7 ± 0	26 ± 1	20 ± 1	0.003 ± 0.000
5	1340 ± 90	267 ± 17	206 ± 13	68 ± 5	11 ± 1	22 ± 2	17 ± 2	0.005 ± 0.001
10	4390 ± 130	439 ± 13	338 ± 10	99 ± 10	27 ± 2	27 ± 2	21 ± 2	0.013 ± 0.000
20	6210 ± 520	310 ± 26	239 ± 20	196 ± 16	68 ± 3	34 ± 2	26 ± 1	0.047 ± 0.004
40	10,400 ± 1400	260 ± 35	200 ± 27	280 ± 12	177 ± 3	36 ± 1	28 ± 1	0.078 ± 0.000
60	10,820 ± 1200	180 ± 20	139 ± 15	296 ± 5	132 ± 14	22 ± 2	17 ± 2	0.124 ± 0.001
80	10,650 ± 1040	133 ± 13	102 ± 10	299 ± 13	128 ± 2	16 ± 0	12 ± 0	0.125 ± 0.003
100	12,410 ± 1500	124 ± 15	95 ± 12	297 ± 16	102 ± 9	10 ± 1	8 ± 1	0.095 ± 0.004