Chemical Engineering Journal 221 (2013) 238–246

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Journal

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

Evaluation of mass and energy balances in the integrated microalgae growth-anaerobic digestion process

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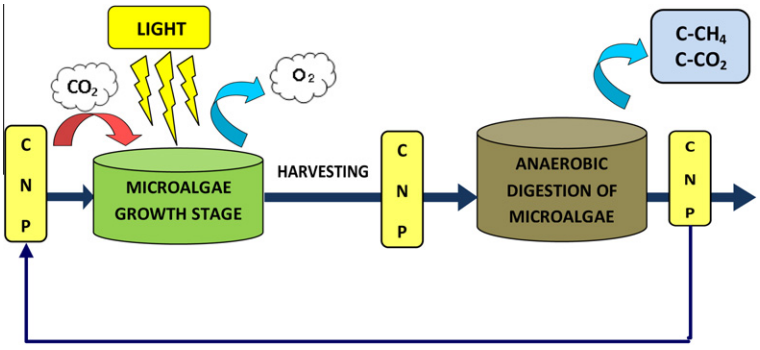
HIGHLIGHTS

- The C source did not significantly modify the *Chlorella sorokiniana* composition.
- During anaerobic digestion ≈50% of the initial C in the biomass was hydrolyzed.
- CO_2 and CH_4 accounted for 14% and 35% of the initial microalgae C, respectively.
- The recoveries of $N\text{-}NH_4^+$ and $P\text{-}PO_4^{-3}$ from anaerobic digestion were 65% and 83%.
- The total energy recovered as CH_4 in the growth-digestion process was ≈3.6%.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 13 November 2012
Received in revised form 28 January 2013
Accepted 30 January 2013
Available online 9 February 2013

Keywords:
Biomethanization
Mass and energy balances
Microalgae anaerobic digestion
Nutrient recovery
Photosynthetic efficiency

ABSTRACT

The production of biofuels based on microalgae as feedstock is associated with a high demand of nutrients, mostly nitrogen and phosphorus. The integration of microalgae growth with anaerobic digestion can significantly improve the economic and energy balance of such a promising platform technology. However, the lack of information about the fundamental mass and energy balances of this integrated process restricts its full scale implementation. This study quantified both the mass (carbon, nitrogen and phosphorus) and energy balances in the integrated process of *Chlorella sorokiniana* cultivation (under photoautotrophic and mixotrophic conditions) coupled with anaerobic digestion in batch mode in order to properly design the microalgae growth-anaerobic digestion process and minimize the overall microalgae cultivation costs. Under fully photoautotrophic growth, the productivity during the microalgae exponential growth phase was 147 g/m^3 d, with an overall photosynthetic efficiency of 7.4%. The productivity of the mixotrophically-grown microalgae was 165 g/m^3 d. However, the photosynthetic activity of *C. sorokiniana* decreased at increasing glucose concentrations in the tested range (180–440 g/m^3). During the anaerobic digestion of photoautotrophically-grown microalgae 55 ± 1% of the initial carbon present in the biomass was hydrolyzed (15 ± 1% to $C\text{-}CO_2$ and 33 ± 1% to $C\text{-}CH_4$). The potential recovery of the N and P present in the biomass accounted for 59 ± 2% as $N\text{-}NH_4^+$ and 89 ± 2% as $P\text{-}PO_4^{-3}$, respectively. During the anaerobic digestion of mixotrophically-grown microalgae, 46 ± 1% of the initial carbon as biomass was hydrolyzed (14 ± 1% to $C\text{-}CO_2$ and 36 ± 1% to $C\text{-}CH_4$) with a nutrient recovery of 70 ± 3% as $N\text{-}NH_4^+$ and 77 ± 2% as $P\text{-}PO_4^{-3}$. The energy recovery from the chemical energy fixed as biomass under photoautotrophic and mixotrophic conditions was 48% and 61%, respectively, and decreased to ≈3.5% when referred to the total energy available during the growth stage.

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http://dx.doi.org/10.1016/j.cej.2013.01.100

Fig. 1. Experimental set-up of microalgae cultivation under autotrophic and mixotrophic conditions.

1. Introduction

The current scenario of exhaustion of fossil fuel resources, increasing oil prices and global warming as a result of the accumulation of greenhouse gases in the atmosphere are strongly motivating research on biofuel production from renewable biomass [1,2]. Nowadays, conventional biodiesel is mainly produced from plant oils (palm, canola and soybean), and despite its lower CO_2 footprint compared to fossil fuels the production of biodiesel from crops entails severe negative environmental impacts [3]. Hence, land overexploitation due the uncontrolled use of pesticides and fertilizers, and competition for cropland (which might result in a global food crisis if expected to satisfy the current world's fuel demand) rank among the main drawbacks of conventional biodiesel [4].

In this context, microalgae have emerged as a promising feedstock for biofuel production based on their high photosynthetic yields, year-round production and ability to grow in both marine, fresh and wastewaters. Besides the above mentioned advantages, microalgae have the ability to mitigate greenhouse emissions by photosynthetically fixing the CO_2 released in industrial processes and do not compete with cropland [5,6]. Despite most research carried out in the past 5 years has mainly focused on microalgal biodiesel, the high cost (4–20 €/kg) and technical limitations of axenic microalgae biomass cultivation nowadays have limited its industrial application [7–11].

Anaerobic digestion appears as a promising alternative for biofuel production based on the possibility of using residual algal biomass as a substrate for biomethane production and its potential for recovering an important part of the nutrients (N and P) provided in the growth stage, which can offset a significant fraction of the process operating costs [12]. In this regard, recent sustainability studies have shown that the indirect energy input associated to nutrients supply constitutes a major energy cost and environmental burden during microalgae cultivation [13–15]. However, despite the potential of microalgae anaerobic digestion, there are still significant technical–economic limitations in the cultivation and biomethanization of microalgae that restrict its full-scale implementation [16]. Of them, the lack of empirical studies evaluating the fundamental mass and energy balances of the integrated microalgae growth-anaerobic digestion process [17,18]. This information is crucial to quantify the potential for nutrient and energy recovery in the overall biofuel production process [19,20].

The main objective of this work was the quantification of the C, N, P and energy balances in the integrated process of microalgae growth (under autotrophic and mixotrophic conditions) coupled with anaerobic digestion. On the one hand, the photosynthetic efficiency, nutrient and carbon requirements, and biomass productivities of *Chlorella sorokiniana* were determined under photoautotrophic and mixotrophic conditions. On the other hand, the biomethane production yield and the potential for nutrient and energy recovery during the anaerobic digestion of the microalgae produced were also quantified.

2. Materials and methods

2.1. Microorganisms and inoculum growth conditions

The microalgae *C. sorokiniana 211/8k* was obtained from the Culture Collection of Algae and Protozoa of the SAMS Research Services (Argyl, Scotland) and was cultivated in SK MSM (Sorokin–Krauss mineral salt medium). This medium was composed of (per cubic decimeter of distilled water): 1.25 g KNO_3, 0.625 g $MgSO_4{\cdot}7H_2O$, 0.1105 g $CaCl_2{\cdot}2H_2O$, 0.1142 g H_3BO_3, 0.0498 g $FeSO_4{\cdot}7H_2O$, 0.0882 g $ZnSO_4{\cdot}7H_2O$, 0.0144 g $MnCl_2{\cdot}4H_2O$, 0.0071 g MoO_3, 0.0157 g $CuSO_4{\cdot}5H_2O$, 0.0049 g $Co(NO_3)_2{\cdot}6H_2O$, 0.5 g EDTA, 0.6247 g KH_2PO_4, 1.3251 g K_2HPO_4. pH was adjusted at 6.8 with KOH and the medium was autoclaved before use ($MgSO_4{\cdot}7H_2O$ was autoclaved separately and added to complete the culture medium afterwards to avoid salt precipitation). Prior to inoculation, the MSM was enriched with a sterile solution of glucose, peptone and yeast extract to give 3.125, 0.0625 and 0.0625 g/dm^3, respectively. The inoculum was incubated at 30 °C under continuous magnetic agitation at 300 rpm and continuously illuminated for 4 days. The alga was subcultivated every 4 weeks on agar plates (enriched MSM plus 1% w/v agar) at room temperature (23 °C) under light for 10 days and stored at 4 °C afterwards.

2.2. Microalgae growth under photoautotrophic and mixotrophic conditions

The cultivations of microalgae under photoautotrophic and mixotrophic conditions were carried out separately but in the same experimental set-up (see Fig. 1). Once the first cultivation test was finished all the glass bottles were rigorously cleaned and sterilize to start the second cultivation test.

2.2.1. Test 1: Microalgae grown photoautotrophically

Photoautotrophically-grown microalgae were cultivated for 9.5 days in ten 1.25 dm^3 sterile glass bottles containing 0.5 dm^3 of a sterile minimum mineral salt medium (MSM) composed of (per cubic meter of distilled water): 6805 g $NaHCO_3$, 2015 g Na_2CO_3, 78.6 g K_2HPO_4, 355.7 g NH_4Cl, 500 g K_2SO_4, 500 g NaCl, 100 g $MgSO_4{\cdot}7H_2O$, 20 g $CaCl_2{\cdot}2H_2O$, 6.8 g $FeSO_4{\cdot}7H_2O$, 42 g EDTA (Ethylenediaminetetraacetic acid), 0.00025 g $ZnSO_4{\cdot}7H_2O$, 0.0005 g $MnSO_4{\cdot}H_2O$, 0.0025 g H_3BO_3, 0.00025 g $Co(NO_3)_2{\cdot}6H_2O$, 0.00025 g $Na_2MoO_4{\cdot}2H_2O$, 1.25×10^{-6} g $CuSO_4{\cdot}5H_2O$. The concentrations of carbonate and bicarbonate in the MSM corresponded with an initial equilibrium concentration (at pH of 7.6) of CO_2 at the flask's head-space of 18 ± 0.7% (82.7 ± 3.4 g/m^3) (Table 1), which represents a typical concentration of combustion process off-gases [21–23]. Prior to sterilization, the bottles were flushed with Helium in order to establish an O_2 free atmosphere, closed with butyl septa and sealed with plastic caps. Following sterilization, the pH of the cultivation medium was decreased to 7.6 by injecting 1.6 ml of HCl (37%) and the systems were allowed to equilibrate under magnetic agitation for 2 h at 25 °C prior to inoculation.

2.2.2. Test 2: Microalgae grown mixotrophically

Mixotrophically-grown microalgae were cultivated for 11.5 days in twelve 1.25 dm^3 glass bottles containing 0.5 dm^3 of