

## Waste to Energy from Flue Gas of Industrial Plants to Biodiesel: Effect of CO<sub>2</sub> on Microalgae Growth

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### Abstract

Microalgae are a good source of lipid and other valuable chemicals which have applications in biodiesel production and food industry. Waste management using microalgae has recently gained attention since microalgae can grow by utilizing nutrient from waste resources. Carbon is quantitatively most important nutrient for cultivation of microalgae and can be supplied from flue gas of industrial plants. In this regard, selection of a suitable species of microalgae which has capability to grow using concentrated CO<sub>2</sub> from flue gas is an important consideration. In this study, the effect supplying two concentrations of CO<sub>2</sub> (5% and 15% (v/v)) during cultivation of two microalgae strains were investigated (*Chlorella vulgaris* and *Scenedesmus obliquus*). The results showed maximum biomass concentration of 2.59 g/L under 5.0% and 1.41 g/L under 15.0% CO<sub>2</sub> concentration for *Chlorella vulgaris*. However, the maximum biomass concentrations for *Scenedesmus obliquus* turned to be 30-60% lower. Also, the results indicated 40% and 130% higher maximum biomass productivity for *Chlorella vulgaris* under 5% and 15% CO<sub>2</sub> relative to *Scenedesmus obliquus*. Similarly, the maximum carbon dioxide fixation was shown to be significantly higher for *Chlorella vulgaris* relative to *Scenedesmus obliquus*. Overall our results indicated that *Chlorella vulgaris* is the more appropriate species to be used for cultivation using flue gas of industrial plants.

**Keywords:** Microalgae; Carbon management; CO<sub>2</sub> mitigation; Biomass production; Biofuel

### Introduction

The vigorous increase in atmospheric content of greenhouse gas causes some environmental problems such as global warming and raise of ocean's water level [1]. CO<sub>2</sub> is considered as the major gaseous pollutant which is provided from burning fossil fuel. Among industries which produce high amount of carbon dioxide, power plants account for about 22% of global emission of carbon dioxide [2]. There are several methods for capturing carbon dioxide including chemical and physical methods. However these methods always impose some difficulties so that they cannot be considered as the ideal solutions. For instance, injection of carbon dioxide to the depth of ocean causes acidity of water which leads to devastation of aquatic environment. Other methods such as application of chemical catalysts for absorption of carbon dioxide require an extra location for storage of used catalysts [3]. Biofixation of carbon dioxide using microalgae is a promising alternative method for conventional sequestration techniques. 1 kg of algal dry cell weight utilizes around 1.83 kg of CO<sub>2</sub>. Annually around 67.7 tonnes of CO<sub>2</sub> can be mitigated from raceway ponds according to dry weight biomass production of 30 to 37 tonnes per hectare in open ponds [4]. Microalgae can grow using wastewater and saline water as the nutrient and water source [5]. The application of saline water for microalgae cultivation can enhance the sustainability of the cultivation can address the severe lack of fresh water worldwide [6,7]. The biomass of microalgae can be used as the source of biofuel, biopolymers and nutraceutical products [8,9]. The recent researches for production of polymer can be employed for efficient conversion of algal organic acids to high quality products [10,11]. For biofuel production hydrodeoxygenation can efficiently convert biomass to bio-oil [12]. In this regard, the application of syngas under optimum temperature is recently proposed to further enhance the conversion process [13,14]. Despite recent advance in production of biofuel from microalgae, the cost of production need to be further reduced in order to compete with fossil fuel. In this regard, the construction of cultivation systems near to industrial plants can be a promising strategy since carbon, energy, water and nutrient sources can be inexpensively supplied from flue gas

and effluent of the plants [15,16]. However, the flue gas of power plant contains high concentrated CO<sub>2</sub> and other gaseous pollutants (e.g. SO<sub>x</sub> and NO<sub>x</sub>) which can inhibit the growth of microalgae by acidifying the cultures [17]. In this regard, the selection of an appropriate species that can tolerate the flue gas condition should be evaluated in advance.

In this study, the effect of 5 and 15% CO<sub>2</sub> on growth of two species of microalgae, *Chlorella vulgaris* and *Scenedesmus obliquus*, were investigated. The results of our study suggest that *Chlorella vulgaris* has the capability to utilize the CO<sub>2</sub> from flue gas of industrial plant.

### Material and Methods

#### Microalgae cultivation

The microalgae used in this study were *Chlorella vulgaris* and *Scenedesmus obliquus*. The standard BG-11 medium [18] has been applied for cultivation of these species. The cultivation was conducted for 14 days in 250 mL Erlenmeyer flask (150 mL working volume) under 30°C temperate and continuous light irradiation. The pre-sterilized air with the rate of 20 ml/min was supplied continuously using an air compressor from the bottom of flask. The initial inoculation was 5% v/v and initial pH was 7. The pH variation during addition of flue gas of power plant is simulated by addition of a weak acid (citric acid). The inorganic carbon source is replaced by CO<sub>2</sub> [19]. Samples were daily collected to examine the cell concentration.

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Received September 01, 2017; Accepted September 08, 2017; Published September 15, 2017

Citation: Hanifzadeh MM, Nabati Z, Tavakoli O, Sarrafzadeh MH (2017) Waste to Energy from Flue Gas of Industrial Plants to Biodiesel: Effect of CO<sub>2</sub> on Microalgae Growth. Int J Waste Resour 7: 300. doi: 10.4172/2252-5211.1000300

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## Measurement of cell growth

The cell concentration was measured by measuring the optical density at 650 nm and comparison with calibration curves. For each species, the total suspended solid (TSS) of the standard solutions were measured and the calibration curve was the linear equation between TSS values and measured optical density at 650 nm [20].

To calculate the biomass productivity (Bp) (g/L/day) from change in biomass concentration during cultivation time, Equation 1 was used.

$$Bp = \frac{X_1 - X_0}{t_1 - t_0} \quad (1)$$

Where  $X_1$  is final concentration of biomass,  $X_0$  is initial concentration,  $t_1$  is final time and  $t_0$  is initial time.

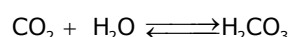
Specific growth rate  $\mu$  (1/d) was calculated according to Equation 2.

$$\mu = \frac{\ln\left(\frac{X_1}{X_0}\right)}{t_1 - t_0} \quad (2)$$

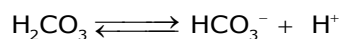
## Experiments and procedure

Flue gas of power plants usually contains 13% CO<sub>2</sub>, 60 ppm SO<sub>x</sub> and 100 ppm NO<sub>x</sub> [21]. To investigate the possibility CO<sub>2</sub> supplementation from flue gas for microalgae production, the cultivation of *Chlorella vulgaris* and *Scenedesmus obliquus* were simulated under concentrated CO<sub>2</sub> by addition of bicarbonate and decreasing the pH of the media.

If we consider the CO<sub>2</sub> reactions in water:



$$K = [\text{H}_2\text{CO}_3]/[\text{CO}_2] = 1.70 \times 10^{-3} \text{ at } 25^\circ\text{C}$$



$$K_a = 4.6 \times 10^{-7}; \text{p}K_a = 6.352 \text{ at } 25^\circ\text{C}$$

By considering CO<sub>2</sub> concentration as 5 and 15% (v/v), concentration of bicarbonate can be calculated using reactions' equilibrium equations [20]. In this regard, the accurate amount of bicarbonate was added to the culture throughout the cultivation experiment. Also, in order to evaluate the effect acidification of the cultures by addition of CO<sub>2</sub> supplementation, the pH of media were reduced according to reported data in literature throughout the experiment by using a weak acid (citric acid) [20].

In order to calculate the daily carbon dioxide fixation amount ( $R_f$ ), according to microalgal growth, Equation 3 is suggested:

$$R_f = (X_1 - X_0) \times m_{cbm} \times V \times \left(\frac{m_{\text{CO}_2}}{m_c}\right) \quad (3)$$

Where  $m_{cbm}$  is carbon content ratio of microalgal species,  $V$  is cultural volume and  $m_{\text{CO}_2}$  and  $m_c$  are the molar mass of carbon dioxide and carbon. According to proposed general structure for microalgae CO<sub>0.48</sub>H<sub>1.83</sub>N<sub>0.11</sub>P<sub>0.01</sub> by Chisti [22], Equation 3 can be simplified to Equation 4.

$$R_f = 1.88 \times Bp \quad (4)$$

Where  $R_f$  is carbon dioxide biofixation ratio (g/L/day) and  $Bp$  is biomass productivity (g/L/day).

## Results and Discussion

### Biomass production and CO<sub>2</sub> fixation

The preliminary evaluation of the scrutinized microalgae showed

the higher growth and as a result higher biomass productivity and carbon dioxide fixation for *Chlorella vulgaris* at 5% carbon dioxide concentration. Although, while CO<sub>2</sub> concentration increases, the growth of microalgae is inhibited due to reduction of pH but *Chlorella vulgaris* still is considered as the main choice for utilizing the inorganic carbon of flue gas from power plant as a result of its higher biomass productivity and energy production. The higher lipid content of *Scenedesmus obliquus* made it more suitable choice for biofuel production. Figure 1 exhibits the biomass concentration (g/L) during cultivation time (day) for CO<sub>2</sub> concentration of 5%.

The results for change in biomass concentrations were shown in Figure 1. From results of biomass concentrations and by using Equation 1 the biomass productivity were calculated. Our results indicated the maximum biomass concentration of 2.58 g/L and 0.78 g/L during 12 d cultivation under 5% CO<sub>2</sub> for *Chlorella vulgaris* and *Scenedesmus obliquus*. Also, *Chlorella vulgaris* accounts for 40% higher maximum biomass productivity (0.39 g/L/day) relative to *Scenedesmus obliquus*. (0.28 g/L/day).

While by raise in concentration of CO<sub>2</sub> from 5% to 15%, a slight decrease in amount biomass concentrations is occurred, *Chlorella vulgaris* still has higher biomass concentration relative to *Scenedesmus obliquus* (Figure 2). By using Equation 1, maximum biomass productivity for *Chlorella vulgaris* and *Scenedesmus obliquus* were calculated as 0.37 g/L/day and 0.16 g/L/day, respectively.

Varied growth parameters including maximum biomass concentration, maximum specific growth rate and maximum biomass productivity in two concentration of CO<sub>2</sub> are compared for these two species in Table 1.

The significant change in the growth and productivity of *Scenedesmus obliquus* by increasing CO<sub>2</sub> concentration is observed in Table 1. However, for *Chlorella vulgaris* the inhibitory effect of increasing CO<sub>2</sub> concentration on growth is less drastic.

The effect of high and low concentration of nutrients on microalgae growth is consistently investigated in the literature [23,24]. While studies showed that increasing carbon source concentration in the media can be advantageous for microalgae production [25,26], the high concentration of CO<sub>2</sub> can decrease pH and inhibit growth of microalgae [20]. Some studies proposed application of media with high alkalinity for enhanced dissolution of CO<sub>2</sub> in media and productivity of microalgae [27]. In addition to CO<sub>2</sub>, the modulation of other macronutrients and micronutrients can enhance the productivity of biomass and valuable products (e.g. lipid) from microalgae [28,29]. N in the media is shown to be a promising for production of carbon storage compounds which have application in biodiesel production [30]. In this regard, our results

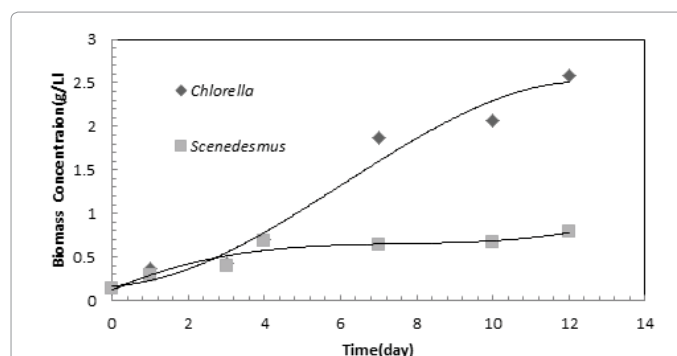


Figure 1: Change in biomass concentration during cultivation under 5% CO<sub>2</sub>.

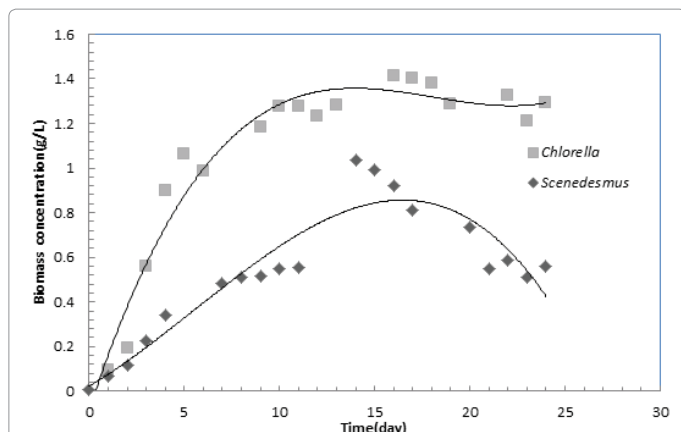


Figure 2: Change in biomass concentration during cultivation under 15% CO<sub>2</sub>.

| Microalgae species | Maximum biomass concentration(g/L) | Maximum specific growth rate, $\mu_{max}$ (1/day) | Maximum Biomass productivity, $P_{max}$ (g/L/d) | CO <sub>2</sub> concentration |
|--------------------|------------------------------------|---|---|-------------------------------|
| <i>C. vulgaris</i> | 2.587                              | 0.44  | 0.39  | 5%                            |
| <i>S. obliquus</i> | 0.78                               | 0.34  | 0.28  | 5%                            |
| <i>C. vulgaris</i> | 1.41                               | 0.46  | 0.37  | 15%                           |
| <i>S. obliquus</i> | 1.036                              | 0.28  | 0.16  | 15%                           |

Table 1: The summarized results for cultivation experiments under 5 and 15% CO<sub>2</sub>.

suggest the cultivation of *Chlorella vulgaris* with 5% CO<sub>2</sub> and low N can lead to higher productivity of biodiesel from microalgae.

The carbon dioxide fixation ratio was calculated using Equation 4 and results were illustrated in Figure 3. The results showed a reduction in CO<sub>2</sub> fixation ratio from 0.73 to 0.69 g/L/day for *Chlorella vulgaris* and from 0.53 to 0.212 g/L/day for *Scenedesmus obliquus*, respectively, as CO<sub>2</sub> concentration increase from 5% to 15% maximum. If we compare maximum CO<sub>2</sub> fixation ratio (g/L/day) for *Chlorella vulgaris* and *Scenedesmus obliquus* in two different CO<sub>2</sub> concentrations it can be easily realized that higher CO<sub>2</sub> concentration impose less carbon dioxide mitigation. However, when the CO<sub>2</sub> concentration raises from 5% to 15% this decline in amount of carbon dioxide mitigation is not significant but in pure CO<sub>2</sub> injection the sequestration efficiency can be reduced vigorously.

*Chlorella* sp. is reported to be a suitable species to grow under harsh environmental condition [31]. Application of waste for production of valuable products can create opportunities for local and global improvement of economic and environmental sustainability [32,33]. Among different methods for management of waste, microalgae is specifically significant due to possibility of nutrient utilization from waste streams, high growth rate and capability for production of valuable products (e.g. lipid, protein, pigments) [8]. In this regard, various studies were conducted for use municipal, agricultural and industrial waste for cultivation of microalgae [34]. However, the prior dilution of waste resources is necessary to enhance the productivity and nutrient utilization rate of microalgae [35]. The results of our study suggest that *Chlorella vulgaris* is more suitable species for management of CO<sub>2</sub> from flue gas and production of valuable products (e.g. biomass).

## Conclusion

In this study, two industrially important species of microalgae are

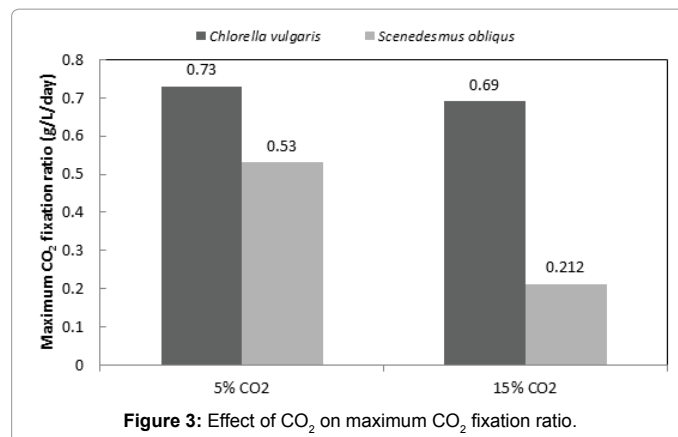


Figure 3: Effect of CO<sub>2</sub> on maximum CO<sub>2</sub> fixation ratio.

studied in two different conditions (5% and 15% CO<sub>2</sub>). These conditions are simulated through experiment by replacement of carbon dioxide gas with sodium bicarbonate and simultaneous titration. Our results show higher biomass production and CO<sub>2</sub> fixation for *Chlorella vulgaris*. Our study suggests that cultivation of *Chlorella vulgaris* is a promising technique for CO<sub>2</sub> mitigation as well as production of biomass and other valuable compounds from flue gas of industrial plants.

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