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Experimental analysis and model-based optimization of microalgae growth in photo-bioreactors using flue gas

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ABSTRACT

This study tested the growth of three algal species (*Chlorella* sp., *Synechocystis* sp. PCC 6803, and *Tetraselmis suecica*) using flue gas (generated by natural gas combustion). All the cultures showed poor biomass growth if they were exposed to continuous flue gas. To optimize the flue gas utilization in algal photo-bioreactors, we performed both model simulations and experimental analysis. First, we employed an un-segregated Monod-based model to describe the microalgal growth in response to CO₂ in the photo-bioreactor. Via the dynamic optimization approach (DOA), the model profiled time-dependent CO₂ concentrations (volume fraction ranging from 0.1 to 0.6%) to support maximal biomass growth. Second, we designed an on–off flue gas pulse mode to reduce CO₂ inhibition (a volume fraction up to 15% CO₂) to the algal cells. Based on the reported algal kinetic parameters, our model predicted that gas-on (~10 s CO₂ pulse) and gas-off (5–9 min) could achieve over 90% of the maximum theoretical algal growth rate predicted by the DOA. Third, we used mass flow controllers to apply on–off flue gas pulses in photo-bioreactors, and the experimental results verified that the flue gas pulses could reduce flue gas inhibition and improve *Chlorella* growth compared to cultures exposed to atmospheric CO₂.

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1. Introduction

CO₂ sequestration from flue gas receives intensive studies due to global warming issues. Typical flue gas discharged from fossil fuel power plants contains 4–14% CO₂, and up to 0.022% NO_x and SO_x [1]. Besides physical and chemical methods for sequestration of CO₂ from flue gas [2], microalgae culture holds great potential for converting flue gas to biomass. Microalgae can capture solar energy more efficiently than plants [3], and are also able to synthesize biofuels (such as biodiesel and bio-hydrogen) [4–6]. To facilitate the utilization of flue gas, microalgae species, such as *Chlorella* sp. and *Tetraselmis* sp., have been tested for their tolerance to CO₂ as well as SO_x and NO_x [7]. In addition, several microalgae, including *Dunaliella tertiolecta* [8,9] and *Nannochloris* sp. [10], have the capacity to use NO as their nitrogen source and thus remove it

from the flue gas. Different reactor configurations [1,6] and cultivation strategies [11,12] have been studied to improve biomass growth with flue gas, including pH control via addition of alkaline solution, high inoculum size, proper flue gas rate, and optimal nutrition level. Furthermore, kinetic models were applied to analyze influential factors on algal growth using flue gas, including hydraulic residence time, reactor geometry, light intensity, culture temperature, flow rate, and partial pressures of CO₂, NO_x and CO [13–15]. For example, an experimental study in combination with mass balance calculations indicated that *Chlorella* growth attained ~50% decarbonization of flue gas in an optimal photo-bioreactor (4.4 kg CO₂ produced 1 kg dry weight biomass) [13].

This study focused on model-based optimization for algal growth using flue gases. In general, atmospheric CO₂ (0.039% by volume fraction) is insufficient to support optimal algal

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growth [7], while the high concentration of CO₂ in industrial exhaust gases has adverse effects on algal physiology. Therefore, the control of flue gas flow into photo-bioreactors is of practical importance for effective algal CO₂ utilization. To design the optimal strategies for operation of flue gas inflow, we built Monod-based models using MATLAB/Simulink®. The model simulation linked the control of flue gas flow to microalgae growth kinetics, and thus provided guidelines in the bioprocess for maximizing algal growth with flue gases.

2. Methods and materials

2.1. Algal cultivation medium and biomass measurement

Chlorella sp., *Synechocystis* PCC 6803, and *Tetraselmis suecica* were obtained from the Pakrasi Lab at Washington University in St. Louis. The culture medium to grow *Chlorella* contained 0.55 g L⁻¹ urea, 0.1185 g L⁻¹ KH₂PO₄, 0.102 g L⁻¹ MgSO₄·7H₂O, 0.015 g L⁻¹ FeSO₄·7H₂O and 22.5 μL microelements (containing 18.5 g L⁻¹ H₃BO₃, 21.0 g L⁻¹ CuSO₄·5H₂O, 73.2 g L⁻¹ MnCl₂·4H₂O, 13.7 g L⁻¹ CoSO₄·7H₂O, 59.5 g L⁻¹ ZnSO₄·5H₂O, 3.8 g L⁻¹ (NH₄)₆Mo₇O₂₄·4H₂O, 0.31 g L⁻¹ NH₄VO₃). The pH was adjusted to 7–8 with sodium hydroxide solution. BG-11 medium [16] and ASP2 medium [17] were utilized for growing *Synechocystis* and *Tetraselmis*, respectively. Microalgae stock was maintained in shaking flasks (~100 mL culture, 2.5 Hz) at 30 °C. Algal growth was monitored by spectrophotometer (Thermal Scientific®, Texas USA) at 730 nm.

2.2. Flue gas treatment using photo-bioreactors

Fresh microalgal cultures were inoculated into 200 mL medium in glass bottles. The initial OD₇₃₀ was set to ~0.3. Microalgal growth was supported by fluorescent lamps with a photon flux of 40–50 μmol m⁻² s⁻¹ at room temperature (~25 °C). Flue gas was generated by natural gas combustion. It was pumped through a funnel to a condenser tube and then a washing bottle (0.5 L) containing water or water/limestone slurry (buffer solution), before being introduced into the microalgal cultures at an airflow rate of ~250 cm³ min⁻¹ per bottle. The volume fraction of CO₂ in the flue gas was 5–6% as measured by a CO₂ gas analyzer (LI-COR®, Biosciences, Nebraska USA). A computer control system was used to apply flue gas pulses to algal cultures (Fig. 1). The flue gas pulse included two modes (gas-on: using flue gas; gas-off: using air only). The flow rate and on–off frequency were controlled by the software coded with Visual Basic®. The actuators were two mass flow controllers (OMEGA Engineering INC, Connecticut, USA) that were connected to a data acquisition card (Measurement Computing Corporation, Massachusetts, USA). Filters (Aerocolloid LLC, Minnesota USA) were used to clean the inflow gases to the mass flow controllers (i.e., removing aerosol particles). The data acquisition card collected the real-time flow rate data that could be stored in the computer. To simulate algal culture using sun light, microalgal cultures were treated with flue gas under light for 12 h, and then stored in dark aerobically (without flue gas treatment or shaking) for 12 h (i.e., the light-dark cycle).

2.3. Kinetic model development

An un-segregated kinetic model for algal CO₂ utilization was developed with the following assumptions: (1) the culture was a well-mixed homogeneous system; (2) CO₂ concentration and light intensity were the limiting factors influencing the algal growth; (3) the complex relationship between CO₂ partial pressure and its equilibrium concentration in the liquid phase was simplified with Henry's Law (Eq. (2)).

$$\frac{dX}{dt} = \frac{S}{S + K_s + S^2/K_i} \cdot \frac{I}{I + K} \cdot \mu_{\max} \cdot X \quad (1)$$

$$\frac{dS}{dt} = K_{La}(P/H - S) - Y_{S/X} \frac{S}{S + K_s + S^2/K_i} \cdot \frac{I}{I + K} \cdot \mu_{\max} \cdot X \quad (2)$$

X was the biomass concentration, kg m⁻³; S was the dissolved CO₂ concentration, mol m⁻³; I was the average light intensity, μmol m⁻² s⁻¹; P was the CO₂ partial pressure in the gas phase, Pa; μ_{\max} was the maximum specific growth rate of microalgae, h⁻¹; K_s was the Michaelis–Menten constant of CO₂, mol m⁻³; K_i was the inhibition constant of flue gas, mol m⁻³; H was Henry's constant of CO₂, Pa m⁻³ mol⁻¹; K_{La} was the mass transfer rate, h⁻¹; K was the Michaelis–Menten constant of light intensity; and $Y_{S/X}$ was the yield coefficient, (mol CO₂)/(kg biomass). The average light intensity (I) in photo-bioreactor was calculated by the following equation [18]:

$$I = \frac{I_0}{A \cdot X} (1 - e^{-A \cdot X}) \quad (3)$$

where I_0 was the surface light intensity, μmol m⁻² s⁻¹; and A was a coefficient with units of m³ kg⁻¹. The parameters and initial conditions used for model simulation were given in Table 1 unless otherwise stated.

2.4. Dynamic optimization framework to profile optimal CO₂ concentrations

We applied the dynamic optimization approach to find the time-dependent inflow CO₂ concentration profile (P_{opt}) that could generate the maximum biomass production [19]. Because of the stiff nature of the model equations (i.e., successive sudden changes of the inlet CO₂ concentrations during algal growth), CVP (control vector parameterization method) was used in this study [20]. Specifically, the entire timespan was divided into n discrete time intervals with constant $P_{\text{opt}}(i)$ within each time interval ($i = 1, 2, \dots, n$). Eqs. (1) and (2) were simulated to find the biomass growth in each time interval using the MATLAB function “ode23s”. MATLAB function “fmincon” was employed to search the optimal $P_{\text{opt}}(i)$ ($i = 1, 2, \dots, n$) to maximize the final biomass concentration $X_{\text{end}}(n)$. Once $P_{\text{opt}}(i)$ was determined, n was updated to $2n$ (each time interval divided by half) and the same optimization procedure yielded new $P_{\text{opt}}(i)$ ($i = 1, 2, \dots, 2n$) and $X_{\text{end}}(2n)$. The procedure for searching the new set of P_{opt} was repeated until $(X_{\text{end}}(2n) - X_{\text{end}}(n))/X_{\text{end}}(n) < 0.01\%$. The flowchart of the dynamic optimization procedure was shown in Fig. S1 in the supplementary file. MATLAB and Simulink (Mathworks, Massachusetts USA) were used for model calculations. The Simulink configuration and MATLAB programs were also provided in Fig. S2 and supplementary MATLAB files.

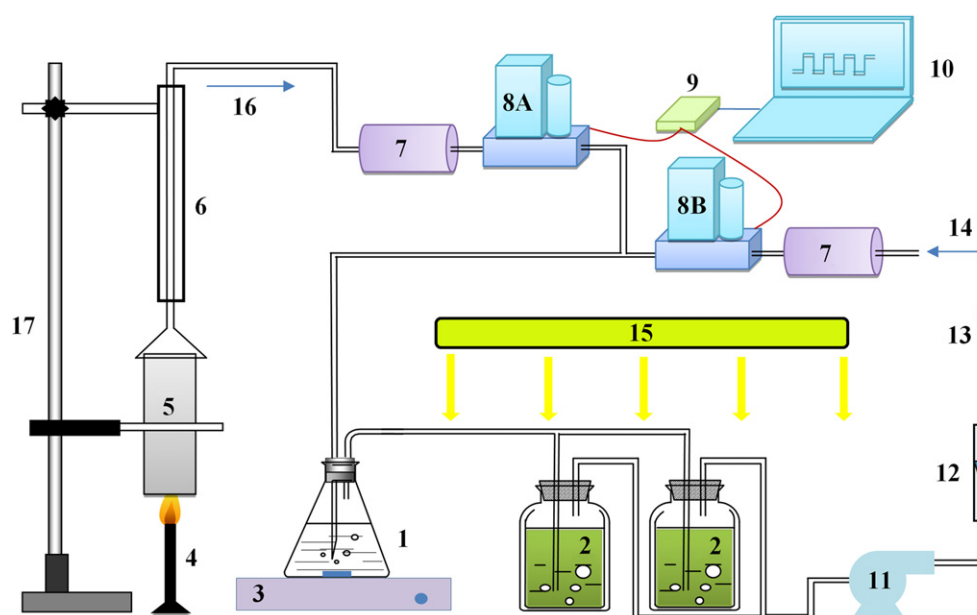


Fig. 1 – Diagram of the experiment setup. 1: Pure water or limestone buffer solution (12.5 kg m^{-3}); 2: microalgae cultures; 3: magnetic stirrer; 4: burner; 5: funnel; 6: condenser tube; 7: filter; 8: mass flow controller (A: flue gas flow; B: airflow); 9: data acquisition card; 10: computer; 11: air pump; 12: flow rate meter; 13: exhaust gas; 14: air; 15: fluorescent lamp; 16: flue gas; 17: iron support.

3. Results and discussion

3.1. Experimental analysis of microalgae growth on flue gas

Three different strains were cultivated with flue gas (Table 2). The results showed that continuous exposure (12 h) to flue gas acidified the medium ($\text{pH} \approx 5$) and highly inhibited microalgae growth. Decreasing CO_2 exposure time (<6 h-per-day) and

pre-washing of the flue gas using buffer solution (limestone slurries) only slightly alleviated flue gas stresses on microalgal cells. Comparing algal growth among the three model algal species, *Chlorella* showed the best growth under flue gas stresses. To overcome flue gas inhibition, we investigated an on–off flue gas input mode in which the flue gas was pulsed into bioreactors at a specific on/off frequency (Fig. 2). The frequency of 1 min gas-on and 29 min gas-off was first applied to support all *Chlorella* cultures. Such a gas pulse mode reduced the actual exposure time of high concentration CO_2 to

Table 1 – Parameter values used in the model.

Parameter	Description	Value range	Unit	Reference/Note
μ_{\max}	Maximum specific growth rate	0.041–0.070	h^{-1}	[21]
K_s	Michaelis–Menten constant of CO_2	0.00021–0.00036	mol m^{-3}	[21]
K_i	Inhibition constant of CO_2	10^a	mol m^{-3}	[22]
K	Michaelis–Menten constant of light intensity	14^b	$\mu\text{mol m}^{-2} \text{s}^{-1}$	[18]
K_{La}	Mass transfer rate of CO_2	6–17	h^{-1}	[23]
H	Henry's constant of CO_2	3202^c	$\text{Pa m}^3 \text{mol}^{-1}$	[24]
$Y_{\text{S/X}}$	Yield coefficient	100^d	$(\text{mol CO}_2)/(\text{kg biomass})$	[13]
A	Constant	14.7	$\text{m}^3 \text{kg}^{-1}$	[18]
I_0	Surface light intensity	45^e	$\mu\text{mol photons m}^{-2} \text{s}^{-1}$	Measured
Atmospheric CO_2	Atmospheric CO_2 concentration	0.04%	volume fraction	Assumed in model
CO_2 in flue gas	CO_2 concentration in the flue gas	15%	volume fraction	Assumed in model
$X(0)$	Initial biomass concentration	0.1	kg m^{-3}	Assumed in model
$S(0)$	Initial dissolved CO_2 concentration	0.013	mol m^{-3}	Assumed in model

Note: Model simulation used $\mu_{\max} = 0.041 \text{ h}^{-1}$, $K_s = 0.00021 \text{ mol m}^{-3}$ and $K_{\text{La}} = 17 \text{ h}^{-1}$ unless otherwise stated.

a In the reference, $K_i = 10 \text{ mM}$, and the test range in this study is $0.5\text{--}10 \text{ mol m}^{-3}$.

b In the reference, $K = 1011 \text{ lux}$, which is close to $14 \mu\text{mol m}^{-2} \text{s}^{-1}$ [25].

c In the reference, $H = 31.6 \text{ atm M}^{-1}$.

d The experimental results showed that 1 kg CO_2 was needed for production of 1 kg (dry weight) of biomass.

e The measured light intensity was $40\text{--}50 \mu\text{mol m}^{-2} \text{s}^{-1}$.

Table 2 – Maximum OD₇₃₀ increase rate observed (d⁻¹) within four days.

Strains	12-h continuous flue gas aeration per day		5–6 h flue gas aeration followed by 5–6 h air aeration per day	
	With buffer	Without buffer	With buffer	Without buffer
<i>Chlorella</i>			0.121 ± 0.001	0.058 ± 0.012
<i>Tetraselmis</i>	Very poor growth under continuous flue gas treatment		0.040 ± 0.003	0.012 ± 0.002
<i>Synechocystis</i>			0.088 ± 0.007	0.034 ± 0.024

Note: The increase rate was calculated by the equation $k = \ln(OD_f/OD_i)/\Delta t$, where OD_f and OD_i are the final and initial optic density at 730 nm, respectively, and Δt is the timespan; the standard deviation was based on two observed rates. After treatment, all the cultures were stored in the dark without gas treatment.

the microalgae, and thus minimized the inhibitory effect of flue gas-on microalgal physiologies. For example, 12-h-per-day on-off flue gas pluses allowed *Chlorella* to generate 20–50% more biomass than shaking flask conditions using atmospheric CO₂ during the exponential growth phase.

3.2. Model simulation of algal growth under different flue gas treatments

To improve our understanding of the optimal control of flue gas inflow for microalgal growth and reduce experimental efforts, we developed an empirical model to simulate biomass growth with flue gas treatment. Fig. 3 unveiled the effects of CO₂ volume fraction and inhibition constant (K_i) on the biomass production. The simulation showed that CO₂ with a volume fraction ranging from 0.1 to 1% favored microalgal

biomass production. The inhibition coefficient K_i exerted a dramatic influence on algal biomass production. For example, decreasing K_i from 10 mol m⁻³ to 0.5 mol m⁻³ reduced the overall biomass production by 60% (7-day culture) when CO₂ volume fraction was ~10%.

The Monod-model also simulated algal growth in the on-off CO₂ pulse modes (Fig. 4) in which the cultures were exposed to different CO₂ volume fractions of 15% (gas-on) and 0.04% (gas-off, with atmospheric CO₂) alternately. Fig. 4 showed the simulated biomass growth, the decrease of average light intensity in the photo-bioreactor due to biomass growth, and variation of dissolved CO₂ in the culture medium. Comparing to microalgal growth with atmospheric CO₂, the model indicated that the biomass production (in a 7-day culture) could be improved by 35% with 1 min gas-on/29 min gas-off CO₂ treatment when microalgal growth rate was $\mu_{\max} = 0.041 \text{ h}^{-1}$. If microalgal specific growth rate μ_{\max} was raised to 0.070 h^{-1} , the biomass production was increased by 77% compared to the air treatment in the same CO₂ pulse mode. These model results suggested that CO₂ pulses more effectively supported biomass growth when μ_{\max} was high.

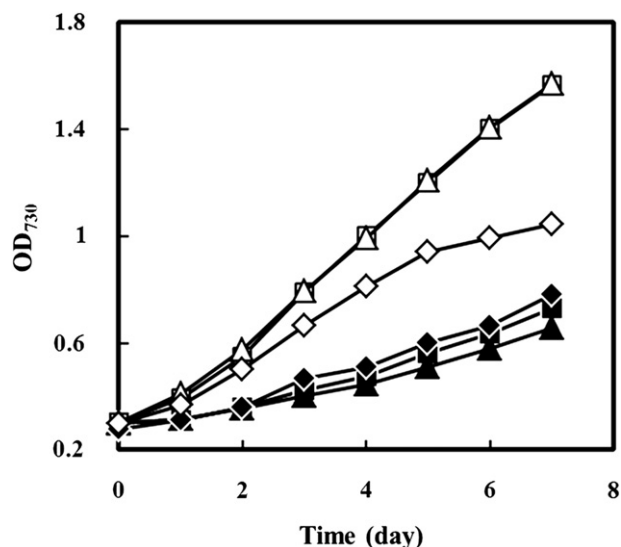


Fig. 2 – *Chlorella* growth curves. The flue gas pulses were only in the light period and the frequency was 1 min gas-on/29 min gas-off. □: Flue gas pulses without buffer pretreatment (12–12 h light-dark cycle); △: flue gas pulses with buffer pretreatment (12–12 h light-dark cycle); ◇: cultivation in shaking flasks (12–12 h light-dark cycle, with atmospheric CO₂); ■: flue gas pulses without buffer pretreatment (5–19 h light-dark cycle); ▲: flue gas pulses with buffer pretreatment (5–19 h light-dark cycle); ◆: cultivation in shaking flasks (5–19 h light-dark cycle, with atmospheric CO₂).

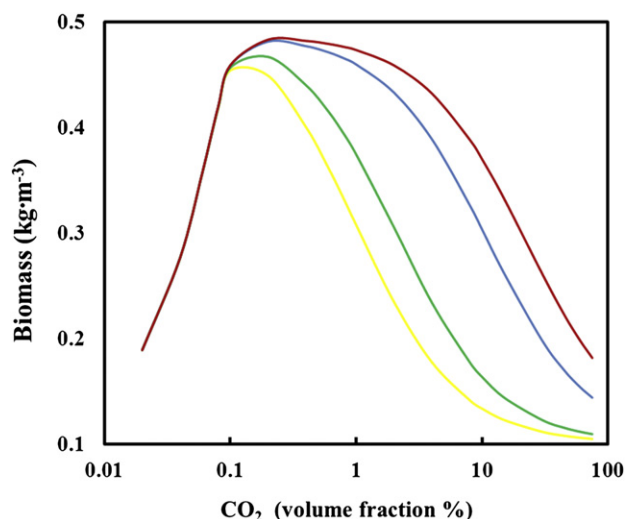


Fig. 3 – Simulated effects of CO₂ volume fraction and inhibition constant (K_i) on the biomass production. The model assumed that microalgae grew in a 12–12 h light-dark cycle for 7 days. Red Line: $K_i = 10 \text{ mol m}^{-3}$; Blue Line: $K_i = 5 \text{ mol m}^{-3}$; Green Line: $K_i = 1 \text{ mol m}^{-3}$; Yellow Line: $K_i = 0.5 \text{ mol m}^{-3}$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

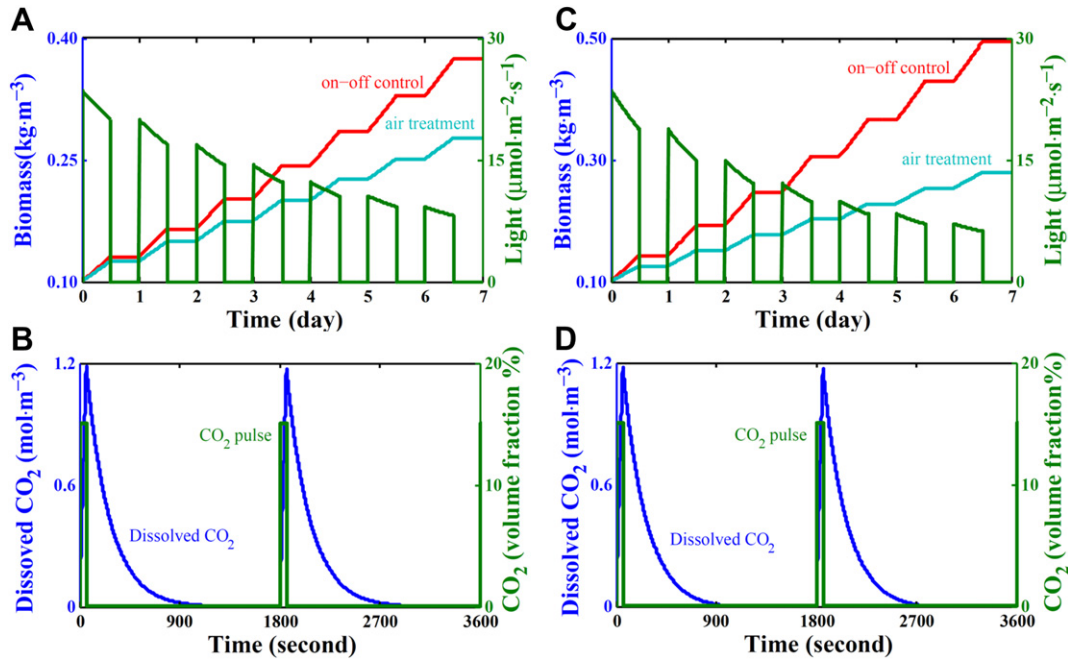


Fig. 4 – Simulation of microalgae growth (red lines) under CO₂ (15%) pulses at a frequency of 1 min gas-on/29 min gas-off in a 12–12 h light-dark cycle. CO₂ pulses were only in the light period. Microalgal growth with atmospheric CO₂ was also simulated (cyan lines). (A): Biomass growth (red and cyan lines) and average light intensity (green line), $\mu_{\max} = 0.041 \text{ h}^{-1}$. (B): CO₂ concentrations in the culture (blue line) and in the gas phase (green line), $\mu_{\max} = 0.041 \text{ h}^{-1}$. (C): Biomass growth (red and cyan lines) and average light intensity (green line), $\mu_{\max} = 0.070 \text{ h}^{-1}$. (D): CO₂ concentration in the culture (blue line) and in the gas phase (green line), $\mu_{\max} = 0.070 \text{ h}^{-1}$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

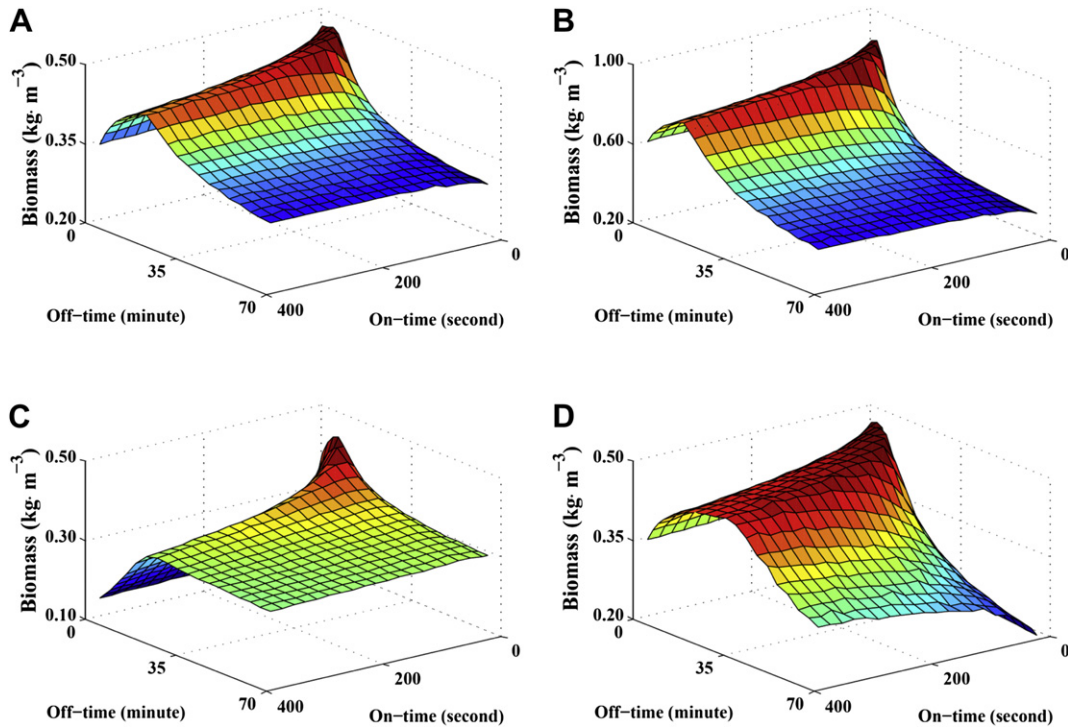


Fig. 5 – Effect of pulse function on biomass production. The model assumed that microalgae grew under 12–12 h light-dark cycle for 7 days. The tested model parameters included (A): $\mu_{\max} = 0.041 \text{ h}^{-1}$, $K_I = 10 \text{ mol m}^{-3}$, $K_{La} = 17 \text{ h}^{-1}$; (B): $\mu_{\max} = 0.070 \text{ h}^{-1}$, $K_I = 10 \text{ mol m}^{-3}$, $K_{La} = 17 \text{ h}^{-1}$; (C): $\mu_{\max} = 0.041 \text{ h}^{-1}$, $K_I = 1 \text{ mol m}^{-3}$, $K_{La} = 17 \text{ h}^{-1}$; (D): $\mu_{\max} = 0.041 \text{ h}^{-1}$, $K_I = 10 \text{ mol m}^{-3}$, $K_{La} = 6 \text{ h}^{-1}$.

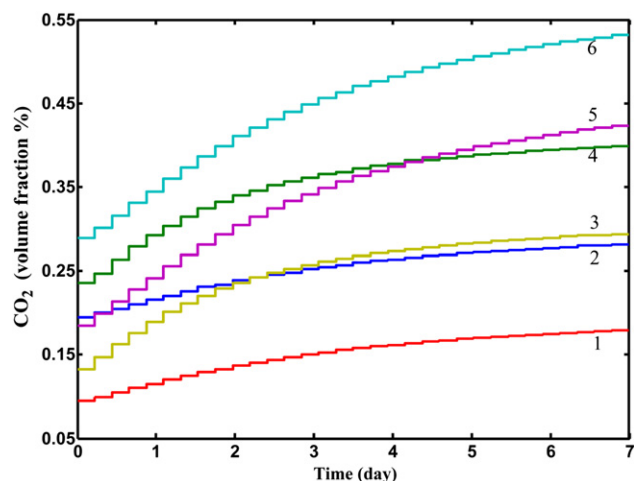


Fig. 6 – The optimal CO₂ concentration profiles. The model assumed that the cultures were grown under continuous light illumination for 7 days. The tested model parameters included (1): $\mu_{\max} = 0.041 \text{ h}^{-1}$, $K_I = 1 \text{ mol m}^{-3}$, $K_{La} = 17 \text{ h}^{-1}$; (2): $\mu_{\max} = 0.041 \text{ h}^{-1}$, $K_I = 10 \text{ mol m}^{-3}$, $K_{La} = 17 \text{ h}^{-1}$; (3): $\mu_{\max} = 0.070 \text{ h}^{-1}$, $K_I = 1 \text{ mol m}^{-3}$, $K_{La} = 17 \text{ h}^{-1}$; (4): $\mu_{\max} = 0.070 \text{ h}^{-1}$, $K_I = 10 \text{ mol m}^{-3}$, $K_{La} = 17 \text{ h}^{-1}$; (5): $\mu_{\max} = 0.041 \text{ h}^{-1}$, $K_I = 1 \text{ mol m}^{-3}$, $K_{La} = 6 \text{ h}^{-1}$; (6): $\mu_{\max} = 0.041 \text{ h}^{-1}$, $K_I = 10 \text{ mol m}^{-3}$, $K_{La} = 6 \text{ h}^{-1}$.

To find the optimal CO₂ pulse operation (i.e., the width and the frequency of rectangular pulse), we examined the influence of pulse function on algal growth (Fig. 5). It was clear that a frequent on–off control of flue gas inflow generally promoted microalgal growth. When $\mu_{\max} = 0.041 \text{ h}^{-1}$, the final biomass achieved a maximum of 0.481 kg m^{-3} at the frequency of 10 s gas-on/7 min gas-off, whereas biomass production dropped to 0.326 kg m^{-3} at the frequency of 380 s gas-on/67 min gas-off (Fig. 5A). We also tested the effects of μ_{\max} , K_I and K_{La} on biomass production with different CO₂ pulse functions. First, if μ_{\max} was raised from 0.041 h^{-1} to 0.070 h^{-1} (Fig. 5B), the gas-off duration should be shortened (i.e., a frequency of 10 s gas-on/5 min gas-off for supporting optimal biomass growth). Second, when the inhibition constant K_I dropped from 10 mol m^{-3} to 1 mol m^{-3} , an optimal on–off control was achieved at a frequency of 10 s/9 min (i.e., increase gas-off period, Fig. 5C). Third, reduction of mass transfer coefficient K_{La} from 17 h^{-1} to 6 h^{-1} lowered the rate of CO₂ transfer from gas phase to liquid phase and abated CO₂ inhibition to the microalgal physiology. Accordingly, the gas-off period was reduced to 5 min to promote biomass growth (Fig. 5D). In summary, the maximal biomass production required a short period of on-time (a few seconds) and a comparatively longer off-time (5–10 min) depending on the severity of CO₂ inhibition and values of μ_{\max} . The off-period could be elongated when flue gas showed strong inhibition.

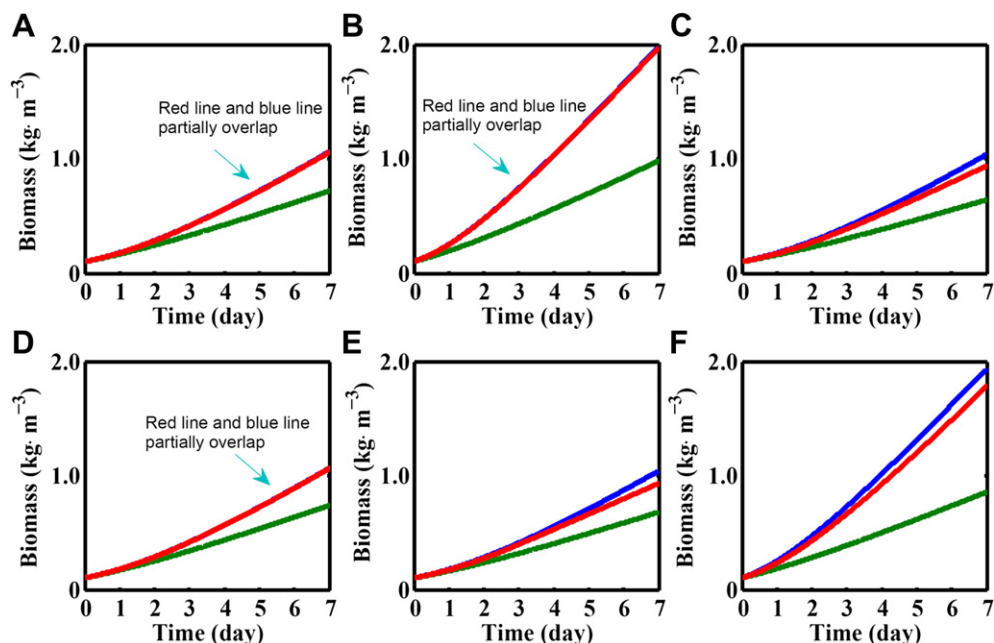


Fig. 7 – Simulation of microalgal growth under three CO₂ treatment modes in continuous illumination condition. Blue line: growth with optimal inflow CO₂ concentration (i.e., theoretical maximal biomass growth); Green line: growth with flue gas pulses at a frequency of 1 min/29 min; Red line: growth with frequent flue gas pulses (A: 10 s/7 min; B: 10 s/5 min; C: 10 s/9 min; D: 10 s/5 min; E: 10 s/7 min; F: 10 s/5 min). Parameters used were: (A): $\mu_{\max} = 0.041 \text{ h}^{-1}$, $K_I = 10 \text{ mol m}^{-3}$, $K_{La} = 17 \text{ h}^{-1}$; (B): $\mu_{\max} = 0.070 \text{ h}^{-1}$, $K_I = 10 \text{ mol m}^{-3}$, $K_{La} = 17 \text{ h}^{-1}$; (C): $\mu_{\max} = 0.041 \text{ h}^{-1}$, $K_I = 1 \text{ mol m}^{-3}$, $K_{La} = 17 \text{ h}^{-1}$; (D): $\mu_{\max} = 0.041 \text{ h}^{-1}$, $K_I = 10 \text{ mol m}^{-3}$, $K_{La} = 6 \text{ h}^{-1}$; (E): $\mu_{\max} = 0.041 \text{ h}^{-1}$, $K_I = 1 \text{ mol m}^{-3}$, $K_{La} = 6 \text{ h}^{-1}$; (F): $\mu_{\max} = 0.070 \text{ h}^{-1}$, $K_I = 1 \text{ mol m}^{-3}$, $K_{La} = 17 \text{ h}^{-1}$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.3. Optimal CO₂ conditions for microalgal growth

The dynamic optimization of inlet CO₂ partial pressure was established by control vector parameterization. The results showed that the objective function (maximization of the final biomass production) converged (within 0.01% difference) after dividing the microalgal growth period into 64 time intervals. The simulated optimal CO₂ profiles from dynamic optimization were displayed in Fig. S3. The optimal CO₂ concentration was not constant during microalgal growth, instead, it should gradually increase to support algal growth during the cultivation. Fig. 6 tested the effect of different model parameters on optimal dynamics of inflow CO₂ partial pressure. In general, increasing μ_{\max} and decreasing K_{La} demanded high CO₂ concentration to compensate for fast biomass growth and inefficient CO₂ transport. On the other hand, decreasing K_i enhanced CO₂ inhibition and thus low CO₂ concentration should be employed for biomass growth. With the optimal inflow CO₂, the biomass production was most influenced by μ_{\max} (increasing μ_{\max} from 0.041 h⁻¹ to 0.070 h⁻¹ resulted in ~80% more biomass growth), while biomass production was insensitive to parameters K_i and K_{La} . Moreover, the model simulation indicated that the high frequency on–off flue-gas pulses (15% CO₂) could support biomass growth almost as well as optimal CO₂ conditions (Fig. 7). CO₂ pulses could yield over 90% of theoretical biomass growth achieved under optimal CO₂ conditions.

Although the dynamic control of inflow CO₂ concentration served theoretically as the best way for biomass production, the on–off gas pulse mode still holds many advantages in the scaled-up bioprocess. For instance, constant flue gas treatment is much easier to operate than the dynamic increase of the inflow concentration. From the energy conservation point of view, the flue gas pulses reduce electricity consumption by avoiding continuously pumping flue gases into the photobioreactors or algal ponds. Furthermore, the common photobioreactor design often utilizes feedback control based on

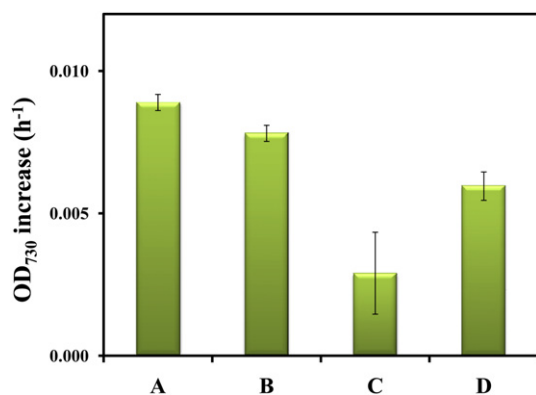


Fig. 8 – Effect of flue gas pulse modes on *Chlorella* growth (without buffer pretreatment). The figure showed the *Chlorella* growth within the first 12 h under light condition unless otherwise stated $n = 4$. The increase OD₇₃₀ per hour was calculated by $(OD_f - OD_i)/\Delta t$, where OD_f and OD_i were the final and initial optic density at 730 nm, respectively. Δt was the timespan. A: 10 s gas-on/7 min gas-off; B: 30 min gas-on/30 min gas-off; C: 5-h continuous flue gas treatment; D: cultivation in shaking flasks.

algal biomass and CO₂ concentrations to adjust inflow CO₂. However, such strategy is limited by the time delay of the actuators, unreliable online sensors to measure biomass and CO₂ concentrations, and sophisticated design of PID (proportional-integral-derivative) control loop. In this study, we have demonstrated that the high frequency on–off flue gas pulses could serve as a cost-effective operation for algal cultivation.

3.4. Experimental verification and model limitations

To experimentally verify the effectiveness of on–off control of flue gases for algal culture, we conducted the flue gas treatment with *Chlorella* using two on–off frequencies (10 s gas-on/7 min gas-off and 30 min gas-on/30 min gas-off). Fig. 8 showed that higher on–off frequency yielded better algal growth than the lower one, and it was also better than the shaking flasks condition (atmospheric CO₂). Therefore, the results qualitatively verified our model, and confirmed that the on–off control of flue gases was able to alleviate flue gas inhibition and promote *Chlorella* growth.

The model was subject to several limitations. First, the model did not directly account for the influence of toxic compounds SO_x and NO_x on algal growth. Second, it oversimplified the chemical reactions and equilibriums in the culture medium including CO₂, H⁺, OH⁻, NH₃, etc. Third, the model did not include CO₂ fluid dynamics, while the actual gaseous mass transfer was not instantaneous and homogeneous in the culture medium. Despite these limitations, all kinetic models always represent a compromise between complexity and practical simplicity. In this study, our model simulation still provided useful insights into optimal strategies for algal growth and avoided costly experimental efforts.

4. Conclusions

Exposure to continuous flue gas severely inhibited the algal growth. To overcome this problem, we tested an on–off flue-gas treatment to enhance algal growth. The model simulation showed that the frequency of ~10 s on-time and 5–9 min off-time was an ideal strategy for sustaining optimal algal production, close to theoretical maximum biomass growth. The effectiveness of flue gas control was also experimentally validated. Compared to continuously pumping diluted flue gas or chemical pretreatment of flue gas, the simple on–off pulse mode can effectively reduce energy and material expenses.

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Appendix. Supplementary material

Supplementary data related to this article can be found online at [doi:10.1016/j.biombioe.2012.02.025](https://doi.org/10.1016/j.biombioe.2012.02.025).

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