Steel plant CO2 sequestration using high efficiency micro-algal bioreactor

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Abstract

CO₂ is concentrated in steel plant exhaust gases, providing the opportunity for biochemical fixing by photosynthetic plants such as algae. Yet with the technologies currently available, algal farming would require a large surface area (100s of hectares), to process a commercially significant volume of CO₂ from a typical steel plant. The limitations in the processing are the dissolution rate of CO₂ in water, which requires a substantial height (3-4m) for a partial transfer, the slow growth rate of algae with inhibition by the O₂ by-product, and the low density of biomass produced. In this work the feasibility of using steel plant stack gases, rich in CO₂, as a feedstock for sequestrating CO₂ and growing algal biomass, using an intensified bioreactor design was demonstrated. The novel bioreactor equipped with air lift loop exploited a recently invented micro-bubble generation technique which achieved a high transfer rate across the gas-liquid interface and therefore accelerated CO₂ dispersal, but also stripped O₂ that the algae produced during photosynthesis. The former enhanced growth rates and the later removed the toxic / growth inhibition, thus permitting much higher algal densities in production. In total, two trials were designed and took place at the Tata Steel Long Products Europe integrated steel plant at Scunthorpe. Assessing the performance of the design with industrial stack gases, including its ability to scrub the gas, determined the feasibility of treating stack gases on a large scale plant with a realistic footprint and high throughput rates. This paper therefore addressed technology which will significantly reduce CO₂ emissions from large single point source process industries.
Introduction
Micro-algae have been identified as a possible solution to several globally relevant problems associated with both the environment and climate change. If algae can be grown in large volumes, with a low energy requirement and low financial cost, then they can:

- Be converted to bio-fuels, thereby replacing hydro-carbons
- Generate biomass that can be used as animal feed or a fuel source
- Remove CO₂ from waste gas, generating O₂ in return

However, the systems currently available to grow algae are both relatively energy intensive and require large areas of land. It is also important, for example, that algae-farming does not compete for land and water resources with the agricultural sector.

Tata Steel, the University of Sheffield and Suprafilt Ltd have therefore teamed up to investigate the feasibility of intensively farming algae on a brown-field site, maximising the use of by-products from steel production as a feedstock, and testing a new ‘Micro-bubble’ bio-reactor that offers the potential to reduce the required land area ten-fold and to minimise the quantity of fresh-water usage.

Trials
In total, two trials were designed and took place at the Tata Steel Long Products Europe integrated steel plant at Scunthorpe. A small slipstream was taken from gas leaving the power station and fed into the bio-reactor equipped with micro-bubble technology developed in the University of Sheffield (Figure 1).

There are many variables in conducting a complex experimental programme such as this, and control of all of the variables was not possible, so as to test for the individual response to each. The objective however, was to assess whether microbubble mediation of the gas transfer process had the desired effect. The observations from the operation are:

- In the regime of volumetric flow rates tested (10-80 liters/min) with a single fluidic oscillator, all of the algae were suspended. No algae attached to the walls of the bioreactor or the internal baffles. Also no algae were trapped in stagnant zones. The “suspension power” was visually sufficient in this range that the bioreactor could have been an estimated 10-fold taller without any difficulty – implying there was more than sufficient mixing and stirring within the bioreactor.

- In all our lab scale ALB (Air Lift Bioreactor) studies and in both of the field trials, there was high survival rate. It was expected that some algae would die in stagnant zones. One member of the investigatory team was assigned for the purpose of broad spectrum biochemical analysis so that we could learn what might have caused the demise of an expected large fraction of the bioculture – which never occurred. There was no observation of infection either, but that may be a consequence of the salinity – D. salina thrives in 1M salt solution, where other species that could grow in this environment are not harmful to the algae or a human biohazard.

- Given that during the weekends in both trials, no dosing was done, it was remarkable that the bioculture simply waited for the arrival of fresh CO₂ nutrient. The ambient temperature during the first trial dropped below the desired temperature and due to lack of any heating
device in the bioreactor, bioreactor temperature also dropped below the optimum temperature for algae culture (see Table 1). However, temperature drop only lengthened the lag phase of growth.

• Towards the end of the second trial, the density of wet biomass was so great that the tank was visibly dark green, yet there was no appreciable impact on growth rates from the optical density potentially blocking the sunlight from the internal algae. This suggests that the suspension as well as the “parading” effect of the airlift loop of algae transported by bubble flocculation resulted in uniform exposure of the algae to the lighted surface (Figure 1).

The results of the analytical chemistry of the samples and the gas monitoring and analysis are presented in the following sections.
**Wet chemistry analysis**

200ml of algal samples were taken per working day after thorough mixing aeration. The quantity of algae presented in culture was evaluated by determination of the chlorophyll content, dry biomass weight and the lipid content.

<table>
<thead>
<tr>
<th>Trial</th>
<th>Inoculants status</th>
<th>Chlorophyll content</th>
<th>Biomass content</th>
<th>Aeration time and flow rate</th>
<th>Flow rate</th>
<th>Culture days</th>
<th>Culture temp</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Steady phase</td>
<td>Lower</td>
<td>Higher</td>
<td>3 hrs/day</td>
<td>30 L/min</td>
<td>10</td>
<td>12 to 18°C</td>
</tr>
<tr>
<td>2</td>
<td>Log growth phase</td>
<td>Higher</td>
<td>Lower</td>
<td>10 to 12 hrs/day</td>
<td>40 L/min</td>
<td>17</td>
<td>23°C</td>
</tr>
</tbody>
</table>

**Chlorophyll content**

Figure 2 gives the trend of chlorophyll content increase for field trial 1 and trial 2. Over the weekend the bioreactor was disconnected from the plant and isolated. No samples were taken over the weekends, which resulted in gaps in the data for those days.

For both trials, Dunaliella salina survived after being dosed with steel plant flue gas. The chlorophyll content increased from initially 0.45 mg/L to finally 2.44 mg/L for trial 1, and for trial 2, increased from 0.73 mg/L to 5.14 mg/L.

The chlorophyll content was higher during the second trial compared to the first trial. During trial 1, the chlorophyll content did not grow substantially until the last day of the trial. The lag phase, caused by physiological adjustment of algae, took about 7 days which was relatively long compared to trial 2. Long lag phase could have three possible causes. Firstly, for most algae, the optimal culture temperature usually ranges from 20 to 27°C. The culture temperature in the first trial was 12 to 18°C, which was too low and inhibited the algal growth.
to some extent. Second, the inoculants for trial 1 were approaching the dead phase, the low activities of these inoculants could be another factor delaying the lag phase for a new culture. Third, during the weekend (day5 - day7), the whole operation system was suspended, which means there was no CO₂ supplied to the bioreactor. The micro-bubble generation system not only transfers CO₂ into culture but also strips out O₂ from it, but without bubbling, O₂ can accumulate in the culture medium, inhibiting the algal growth. Therefore, the lack of CO₂ and the accumulation of O₂ limited the growth of algae during these days. After the lag phase, the amount of chlorophyll content doubled within 3 days, rising from 1.20 mg/L to 2.44 mg/L, and a further growth was expected to be observed if culture continued.

During the second trial bioreactor temperature was controlled and kept constant, more active inoculants were present at the start, which lead to a shorter lag phase (1 to 2 days) and higher chlorophyll content. During the second trial, the chlorophyll content increased significantly, rising from 0.73 mg/L to 5.14 mg/L within 17 days.

**Dry biomass and total lipid content**

Figures 3 and 4 show the algal dry weight for both trials in grams per litre and percentage increase. Dry biomass weight of algae increased in both trials with increasing chlorophyll content. Algal dry weight was generally higher in the first trial compared to the second trial as the dry biomass of inoculants for trial 1 was much higher than trial 2. However, in terms of dry biomass growth rate, the story was different (Figure 4). The algae had a higher biomass growth rate throughout trial 2.

During trial 1, the algal dry biomass rose from 0.125 g/L to 0.35 g/L within 10 days (a three-fold increase). A slow growth phase was also observed in the first 8 days, followed by a logarithmic growth phase. In the second trial, initially the algal dry biomass was only 0.0067 g/L, but after 17 days’ culture it increased to 0.24 g/L, a rise of more than 35 fold.

![Figure 3: The increase in concentrations of algal dry weight for trial 1 and trial 2.](image-url)
The total lipid content was extracted from the dry biomass by methanol/chloroform and analysed. The results are shown in Figure 5. The concentration of total lipid (total lipid content per dry weight, g/g) for trial 2, varied from 31% to 75% (9 to 30% for the first trial). For both trials, the concentration of total lipid content had declined by the end of the trials indicating that during culture growth the increase in biomass content exceed the increase in total lipid content of the algal cells.

The results indicate that during the first trial, a higher concentration of biomass was achieved with lower concentrations of total lipid. Inversely, in the second trial, a lower biomass concentration was achieved with higher total lipid concentration of algal cells. Initially it appears difficult to conclude which trial was more successful. However, in terms of bio-energy production potential (e.g. biodiesel), either biomass enhancement or total lipid growth are important values as the total lipid content depends on both. Therefore, in order to understand the performance of the bioreactor in both trials and to determine its performance, the concentration of total lipid content in the entire bioreactor (g/L) was determined by multiplying the total lipid content per cell weight (g/g) and the concentration of dry biomass (g/L), shown in Figure 6.
As it can be observed in Figure 6, for trial 1, the total lipid content per culture volume presented a slight fluctuation, but generally maintained at 0.03 g/L. For trial 2, the amount of total lipid increased from 0.005 g/L to 0.07 g/L. In terms of biodiesel production, trial 2 seems more favourable, and in this 2200L-culture, the total amount of total lipid content achieved was 154 g.

**Gas monitoring and analysis**

For both trials, a portable Gasmet FTIR was used for monitoring flue gases entering and leaving the bioreactor. The Gasmet FTIR Gas analyser is the most advanced measurement technology available for continuous gas analysis. Real time data were recorded directly onto the analysis laptop. FTIR analysers are able to measure in excess of 50 gases simultaneously. The samples were taken from the inlet and the outlet of the bioreactor through a heated line and heated pump. Concentrations of CO₂ and O₂ in the inlet and outlet of the bioreactor were monitored 24 hr a day over the period of both trials. Figure 7 shows an example of the daily results. In addition the bioreactor temperature and ambient temperature were monitored during the trials. There are clearly three periods; (i) before the compressor is turned on, with practically no difference between inlet and outlet, as they are both measuring the conditions in the bioreactor from opposite sides; (ii) during operation of the compressor, when the difference between O₂ inlet and outlet shows the O₂ stripping rate, and between CO₂ inlet and outlet show the CO₂ uptake rate. The outlet CO₂ and O₂ concentration profiles are anti-correlated, again demonstrating that the bioreactor is not mass transfer limited, (iii) post-compressor operation, when the bioreactor O₂ content returns to the ambient and CO₂ is dissipated to the atmosphere and taken up by the culture.
Table 2 shows summary of the results for both trials. In the first trial, the average temperature of the bioreactor was 16 °C with an overall efficiency (CO₂ uptake) of 7%. In the second trial, bioreactor temperature was controlled with average temperature of 22 °C with the overall efficiency (CO₂ uptake) of the bioreactor reaching 14%. The maximum CO₂ uptake rate in the second trial reached 226.4 g/hr compared to 92.7 g/hr in the first trial. The efficiency of the second trial improved due to better control of the bioreactor temperature and increasing mass transfer rate due to improving bubbling regime.

In this project, the CO₂ sequestration rate improved compared to work done previously by others and the overall efficiency of the micro-bubble bioreactor is in good agreement with the literature. Yun et al. [1] successfully sequestrated 0.624 g CO₂ per litre per day (0.026 g/l/hr); compared to this work (0.1 g/l/hr). Doucha [2] also reported 10 to 50 % reduction in CO₂ using Chlorella. The highest fixation rate has been reported by Morais and Costa [3] using Spirulina (53.29% for 6% v/v CO₂). However, most of the past work has shown that the efficiency decreased with increasing CO₂ concentration [4]. With typical steelplant CO₂ concentrations entering the bioreactor during the trials, 14% efficiency is a substantial reduction in CO₂ content.

Table 2: Integrated CO₂ uptake (only during compressor operation) and average bioreactor temperature throughout each trial.

<table>
<thead>
<tr>
<th>Trial No.</th>
<th>Microalga</th>
<th>T(°C)</th>
<th>Max CO₂ uptake, (g/hr)</th>
<th>Overall efficiency, (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Dunaliella salina</td>
<td>16</td>
<td>92.7</td>
<td>7</td>
</tr>
<tr>
<td>2</td>
<td>Dunaliella salina</td>
<td>22</td>
<td>226.4</td>
<td>14</td>
</tr>
</tbody>
</table>

Figure 7: FTIR gas analysis of bioreactor inlet and outlet CO₂ and O₂ concentrations on 13 September 2010 during Trial 2.
Conclusions
In this project the feasibility of using steel plant stack gases, rich in CO₂, as a feedstock for sequestrating CO₂ and growing algal biomass, using an intensified bioreactor design has been demonstrated successfully. The novel bioreactor exploited a recently invented micro-bubble generation technique which achieved high transfer rates across the gas-liquid interface and therefore accelerated CO₂ dispersal, but also stripped O₂ that the algae produced during photosynthesis. The former enhanced growth rates and the later removed the toxic / growth inhibition, thus permitting much higher algal densities in production. Assessing the performance of the design with real industrial stack gases, including its ability to scrub the gas, determined the feasibility of treating stack gases on a large scale plant with a realistic land footprint and high throughput rates. This project therefore addressed technology that will significantly reduce CO₂ emissions from large single point source process industries.

Reference

