Available online at www.sciencedirect.com

ScienceDirect

Energy Procedia 114 (2017) 7126 – 7132

Energy Procedia

13th International Conference on Greenhouse Gas Control Technologies, GHGT-13, 14-18 November 2016, Lausanne, Switzerland

Integrated system for capturing CO_2 as feedstock for algae production

Paul Könst, Ileana Hernandez Mireles, Rob van der Stel, Peter van Os, Earl Goetheer*

Department of Process and Instrumentation Development, TNO, Leeghwaterstraat 44, 2628 CA Delft, The Netherlands

Abstract

In view of its promise as sustainable process for CO_2 capture and its potential in the production of feed, food and natural high value products such as omega-3 fatty acids and anti-oxidants such as astaxanthin, large scale algae cultivation is gaining commercial interest. Currently, most systems are based on directly contacting CO_2 containing gas, e.g. flue gas, with the algae culture. However, applicable on small scale, this approach is not applicable on a commercially relevant large scale due to mass transfer limitations. There is need for a cost effective and scalable system. TNO has developed a scalable system for efficient capture of CO_2 as feedstock for algae production. In this system, CO_2 is absorbed in an absorption liquid as bicarbonate. Subsequently, the enriched absorption liquid is fed to the algae, which convert the solubilized CO_2 into biomass and biobased products. Finally, biomass is recovered and the lean absorption liquid is recycled. TNO's integrated process concept was successfully demonstrated with continuous algae cultivation on a 2 L-scale for more than 150 days of which 40 days using flue gas as CO_2 source.

Keywords: Algae; Carbon Dioxide; CO_2 capture; CO_2 utilization; Absorption; Recycling

* Corresponding author. Tel.: +31 6 2302 7059
E-mail address: earl.goetheer@tno.nl

1876-6102 © 2017 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).
Peer-review under responsibility of the organizing committee of GHGT-13.
doi:10.1016/j.egypro.2017.03.1856

1. Introduction

1.1. The carbon capture and storage challenge

In its existence man has been responsible, mainly through the use of fossil resources and deforestation, for a significant increase in atmospheric levels of CO_2. It is generally accepted that the increase in atmospheric levels of greenhouse gasses such as CO_2 leads to global warming and eventually climatological disasters.[1] Capture and storage of CO_2 would result in a reduction of atmospheric CO_2 levels.

The classical method used for CO_2 capture involves reactive absorption followed by thermal regeneration of the absorption liquid.[2] Alternatives to this highly energy intensive method are under development involving gas membrane contactors [3], chilled ammonia processes [4], formation of carbonates [5] and the use of ionic liquids [6]. To provide a durable solution CO_2 capture must be followed by CO_2 storage, either permanently, for example by means of geological storage [7], or via its conversion into a product other than CO_2 such as methane and concrete.

An energy efficient and durable way to capture and store CO_2 would be to absorb CO_2 into an absorption liquid in such form that it could serve as carbon feedstock for algae cultivation. Subsequently, algae would be able to use solar energy to convert this feedstock into biomass and commercially relevant products such as omega-3 unsaturated fatty acids and anti-oxidants.[8], [9]

In view of its promise as sustainable process for CO_2 capture and storage and it's potential in the production of high value natural products, large scale algae cultivation is gaining commercial interest. However, there is need for cost effective and scalable technology, which is crucial for a positive business case. Currently, most systems are based on directly contacting CO_2 containing gas, e.g. flue gas, with the algae culture. Although applicable on small scale, this approach is not applicable on large scale due to mass transfer limitations.

Nomenclature

CA	Carbonic anhydrase
OD720	optical density at 720 nm, which is a measure for the biomass concentration
CSTR	continuous stirred-tank reactor

1.2. Sustainable solution for carbon capture and storage

To address the need for an energy efficient and durable carbon capture and storage technology, TNO is developing an integrated system in which CO_2 is captured and subsequently applied as feedstock for algae cultivation (Figure 1). In this system, CO_2 is captured by leading it through an absorber in which it is contacted with an absorption liquid. The CO_2 enriched absorption liquid is subsequently fed to an algae culture, which utilizes solar energy to desorb CO_2 from the absorption liquid for formation of biomass and high value products. Finally, the algae and their products are harvested, while the lean absorption liquid is reloaded with CO_2 and recycled into the system. In this way, algae cultivation is a more energy efficient alternative for classical absorption liquid regeneration technologies with the added commercial benefit of biomass and high value product formation. For TNO's integrated process two types of absorption liquids were considered: amine based and carbonate based.[10] Both have their advantages and disadvantages.

In case of an amine based absorption liquid CO_2 reacts with the amine leading to the formation of a water soluble carbamate. The main advantage of amine based absorption liquids is that they readily absorb CO_2 through reactive absorption without the need of catalysts or elevated temperatures. A challenge with the use of amine based liquids in TNO's envisioned system is their potential toxicity towards algae, which limits both the amine species that can be applied and the concentrations in which they can be applied.[11], [12] A carbonate based absorption liquid typically contains potassium or sodium carbonate, which is enriched with CO_2 in the form of bicarbonate. The advantage of the carbonate based system is that bicarbonate is a natural substrate for algae and thereby potentially enhances biomass and product formation and thereby overall productivity of the envisioned system. Disadvantage of carbonate based systems is that capture of CO_2 in the form of bicarbonate (HCO_3^-) is relatively slow and therefore requires the use of a catalyst. The most suggested catalyst for this reaction is the enzyme carbonic anhydrase (CA), which catalyzes the conversion of dissolved CO_2 into bicarbonate. CA is naturally produced and excreted by algae to enhance CO_2 uptake in the form of bicarbonate.[13] Ideally, CA production would be integrated in the envisioned system, as suggested by the patent of Bloch et al. [15].

In view of the potential toxicity of amines towards algae and the potentially enhanced productivity of algae in presence of elevated bicarbonate levels, the authors decided to investigate a carbonate based absorption system. The results of this investigation are described in this paper.

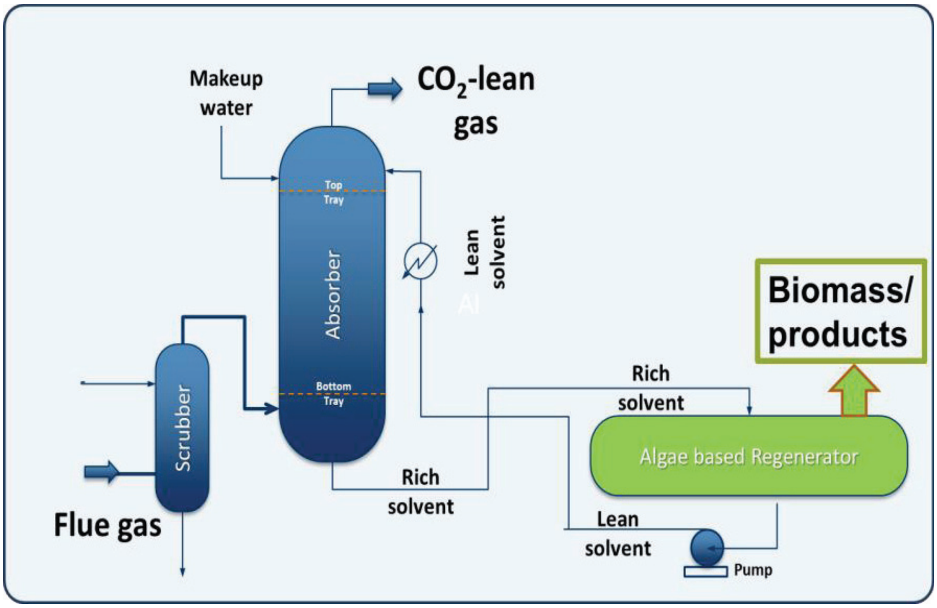


Fig. 1. Impression of TNO's integrated process concept for capturing CO_2 as feedstock for the production of algal biomass and high value natural products.

2. Proof of concept

2.1. Effect of carbonate based absorption liquid on algae growth

Algae are able to directly take up bicarbonate, which is subsequently utilized to grow and to form high value products such as anti-oxidants and poly-unsaturated fatty acids. Potentially, enrichment of the growth environment with bicarbonate, as is the case with the application of a carbonate absorption liquid (Equation 1), will lead to enhanced growth rates. To test the effect of elevated bicarbonate concentrations on the growth rate the commercially relevant algae strain *Nannochloropsis sp.* (poly-unsaturated fatty acid production) was grown at sodium bicarbonate concentrations of 0, 1, 2, and 4 $g{\cdot}L^{-1}$, in parallel in a multi-cultivator (Figure 2, Right).

$$Na_2CO_3 + CO_2 + H_2O \leftrightarrow 2NaHCO_3 \qquad (1)$$

Cultures supplemented with either 1 or 2 $g{\cdot}L^{-1}$ sodium bicarbonate showed a significantly higher biomass productivity when compared to the culture which was solely dependent on the 1% CO_2 gas feed (Figure 2, 0 $g{\cdot}L^{-1}$).

A concentration of 4 g·L^{-1} sodium bicarbonate appeared to be too high for *Nannochloropsis sp*., possibly due to the relatively high pH that comes with increased sodium bicarbonate concentrations.

These results demonstrate the additional benefit of a bicarbonate based absorption system with respect to biomass productivity.

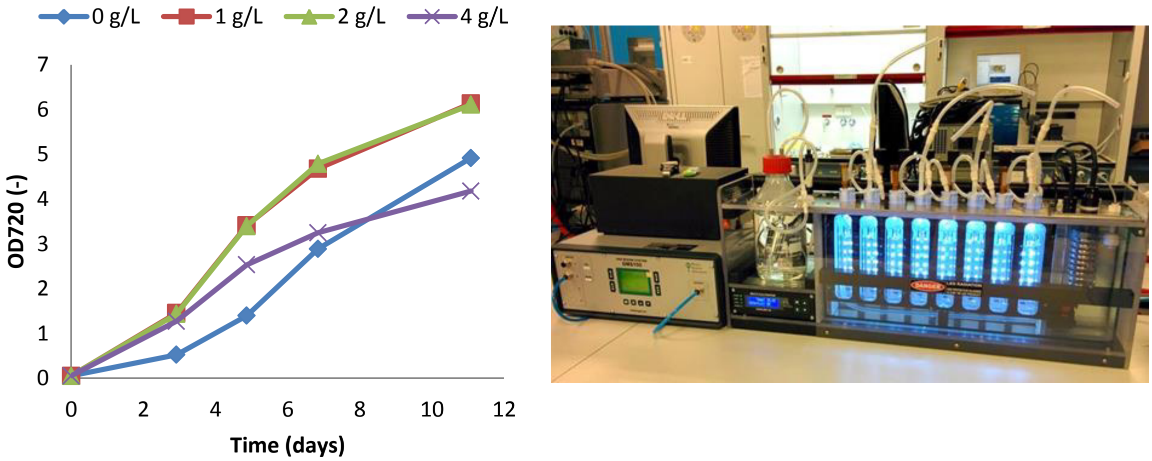


Fig. 2. Left. Growth curves of *Nannochloropsis sp.* cultures grown at different sodium bicarbonate concentrations (0, 1, 2 and 4 g L^{-1}). The biomass concentration is expressed in OD720. The cultures were grown in NO_3^- enriched F/2 medium at 25°C in 70 mL batches, supplied with 0.075 L·min^{-1} 1% CO_2 and a light intensity of 400 μE. Right. Multi-cultivator setup used for the experiments.

2.2. Absorption liquid recycling

For the envisioned integrated system for CO_2 capture and algae cultivation recycling of the carbonate based absorption liquid is crucial, both from an economical and sustainability point of view. The concept of absorption liquid recycling was tested in a 2 L-CSTR setup (Figure 3, Right).

First, *Chlorella sp.* was grown in batch modus until a dry weight biomass concentration of 0.5 g·L^{-1} was obtained (Figure 3, Left, day 0 to 7). Continuous cultivation was established by continuously feeding an absorption liquid (0.1 M potassium carbonate) that was loaded with CO_2, while continuously harvesting bioreactor content at the same rate (Figure 3, day 7 to 21).

After 14 days of successful continuous growth with freshly prepared carbonate based absorption liquid, recycling of the harvested absorption liquid was started. The harvested algae were recovered by means of filtration and the remaining, cell-free, 'lean' absorption liquid was reloaded with CO_2 (Figure 1) and recycled as continuous feed for the bioreactor (Figure 3, Left, blue diamonds). In this way a closed-loop system was established that was successfully operated for more than three weeks (Figure 3, day 21-45).

This experiment revealed that recycling of a carbonate based absorption liquid for algae cultivation is possible.

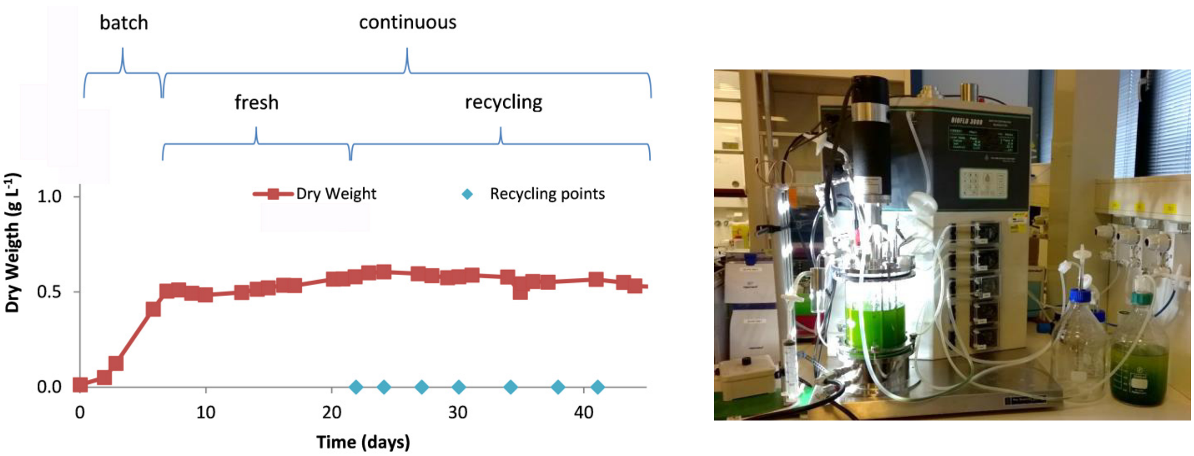


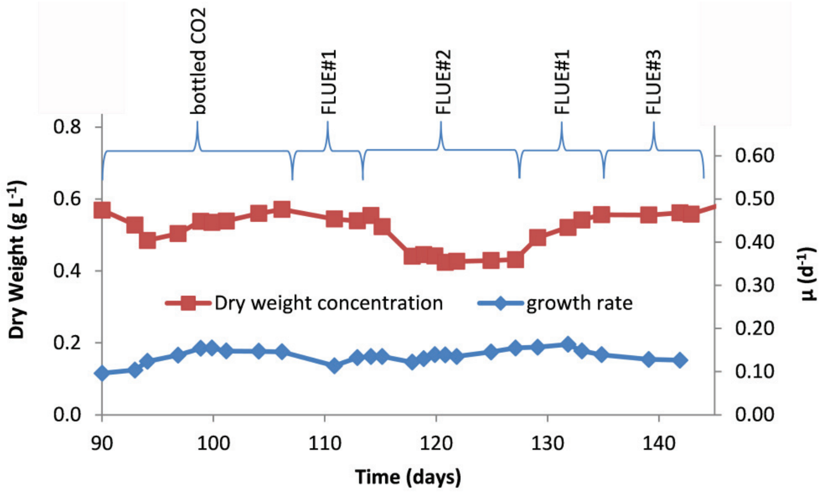
Fig. 3. Left. Graph depicting the cultivation of a *Chlorella sp.* culture in a CSTR: dry weight concentration in the CSTR (red squares); points at which the harvested absorption medium was reloaded with CO_2 and recycled into the system (blue diamonds). Right. 2 L-CSTR setup used for the experiments, including feed and harvesting bottles.

2.3. Flue gas loading

Application of the envisioned integrated system for CO_2 capture and algae cultivation would be most feasible when flue gas could be directly applied as CO_2 source. In view of this requirement, it was investigated whether the microalgae *Chlorella sp.* could be cultivated on carbonate based absorption liquid loaded with CO_2 from flue gas. This experiment was initiated by feeding the culture from the previous experiment (Figure 3) with absorption liquid loaded with bottled CO_2 and harvesting the bioreactor content with the same rate (dilution rate was 0.16 d^{-1}) (Figure 4, Top.).

Upon obtaining a dry weight concentration baseline on bottled CO_2, the content of the feed bottle was replaced by absorption liquid with an identical composition, but this time loaded with CO_2 from flue gas (FLUE#1). Loading was achieved by actively contacting flue gas from a chimney from a power plant (Uniper MPP2 plant, The Netherlands) with the absorption liquid. (Figure 4, Bottom). Subsequently, the culture was fed with four subsequent feed solutions (FLUE#1 to #4), each loaded with flue gas from the same power plant (Figure 4, Top).

Throughout the experiment, a continuous growth rate was maintained (Figure 4, blue diamonds), which revealed that flue gas from power plants is a potential source of CO_2 for the envisioned algae cultivation system.



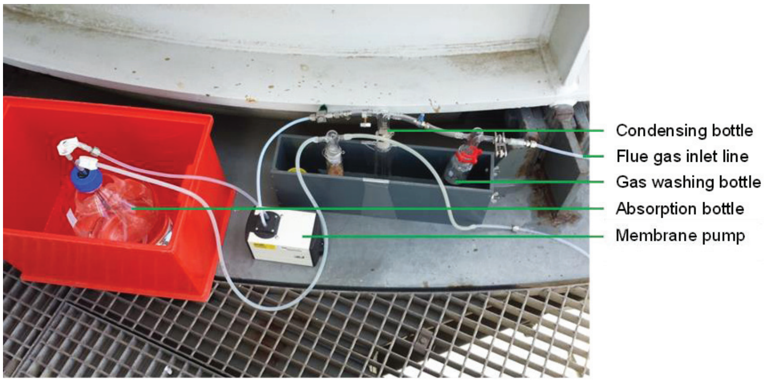


Fig. 4. Top. Graph depicting the cultivation of a *Chlorella sp.* algae culture on medium loaded with CO_2 from flue gas in a CSTR: dry weight concentration (red squares) and specific growth rate (blue diamonds). The experiment is a continuation of the culture described in Figure 3 and was started with medium loaded with bottled CO_2 after which the original feed solution was changed for medium loaded with CO_2 from flue gas that originated from the Uniper MPP2 plant at the Maasvlakte, The Netherlands (FLUE#1 to #4). Bottom. Setup that was used to actively pump flue gas from one of the chimneys of the Uniper MPP2 plant at the Maasvlakte, Netherlands, through the absorption medium. Before contacting with the absorption medium, the flue gas was base washed. The degree of CO_2 loading was determined using the hot phosphoric treatment method.

3. Conclusions

A concept of a scalable, integrated system in which CO_2 is captured and converted into algal biomass and biobased products was developed. Carbonate was selected as the basis of the absorption liquid. It is relatively cheap, has a high solubility in water and is a natural carbon feedstock for algae cultivation. *Chlorella sp.* was continuously cultivated on carbonate based absorption liquid for 150 days straight. The carbonate based absorption liquid could be harvested, reloaded and recycled up to 7 times without a decline in algae productivity. In addition, the *Chlorella sp.* culture was grown for 40 days straight on medium that was loaded with CO_2 from flue gas.

Acknowledgements

The first phase of this work is funded by the HiPerCap project. The project receives funding from the European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement no. 608555.

References

[1] G. a Meehl, W. M. Washington, W. D. Collins, J. M. Arblaster, A. Hu, L. E. Buja, W. G. Strand, and H. Teng, "How much more global warming and sea level rise?," *Science*, vol. 307, no. 5716, pp. 1769–72, Mar. 2005.

[2] J. D. Figueroa, T. Fout, S. Plasynski, H. McIlvried, and R. D. Srivastava, "Advances in CO2 capture technology-The U.S. Department of Energy's Carbon Sequestration Program," *Int. J. Greenh. Gas Control*, vol. 2, no. 1, pp. 9–20, 2008.

[3] A. Brunetti, F. Scura, G. Barbieri, and E. Drioli, "Membrane technologies for CO2 separation," *J. Memb. Sci.*, vol. 359, no. 1–2, pp. 115–125, 2010.

[4] V. Darde, K. Thomsen, W. J. M. van Well, and E. H. Stenby, "Chilled ammonia process for CO2 capture," *Int. J. Greenh. Gas Control*, vol. 4, no. 2, pp. 131–136, 2010.

[5] N. Favre, M. L. Christ, and A. C. Pierre, "Biocatalytic capture of CO2 with carbonic anhydrase and its transformation to solid carbonate," *J. Mol. Catal. B Enzym.*, vol. 60, pp. 163–170, 2009.

[6] M. Hasib-ur-Rahman, M. Siaj, and F. Larachi, "Ionic liquids for CO2 capture—Development and progress," *Chem. Eng. Process. Process Intensif.*, vol. 49, no. 4, pp. 313–322, 2010.

[7] S. M. Benson, "Carbon Dioxide Capture for Storage in Deep Geologic Formations – Results from the CO2 Capture Project Geologic," in *Volume 2: Geologic Storage of Carbon Dioxide with Monitoring and Verification*, Elsevier, 2005.

[8] A. J. Klok, P. P. Lamers, D. E. Martens, R. B. Draaisma, and R. H. Wijffels, "Edible oils from microalgae: insights in TAG accumulation," *Trends Biotechnol.*, vol. 32, no. 10, pp. 521–528, 2014.

[9] M. M. R. Shah, Y. Liang, J. J. Cheng, and M. Daroch, "Astaxanthin-Producing Green Microalga Haematococcus pluvialis: From Single Cell to High Value Commercial Products," *Front. Plant Sci.*, vol. 7, no. April, p. 531, 2016.

[10] K. Schipper, S. van der Gijp, R. van der Stel, and E. Goetheer, "New Methodologies for the Integration of Power Plants with Algae Ponds," *Energy Procedia*, vol. 37, pp. 6687–6695, 2013.

[11] I. Eide-Haugmo, O. G. Brakstad, K. A. Hoff, E. F. da Silva, and H. F. Svendsen, "Marine biodegradability and ecotoxicity of solvents for CO2-capture of natural gas," *Int. J. Greenh. Gas Control*, vol. 9, pp. 184–192, 2012.

[12] I. Hernandez-mireles, R. Van Der Stel, and E. Goetheer, "New methodologies for integrating algae with CO2 capture," *Energy Procedia*, vol. 0, 2013.

[13] H. M. Becker, M. Klier, and J. W. Deitmer, *Carbonic Anhydrase: Mechanism, Regulation, Links to Disease, and Industrial Applications*, vol. 75. Springer, 2014.

[14] E. L. V. Goetheer, P. Geerdink, I. S. Ngene, and P. Den Broeke, Leo Jacques, Van Minder, "Enzyme promoted co2 capture integrated with algae production," WO 2013022348A1, 2013.

[15] M. R. Bloch, J. Sasson, M. E. Ginzburg, Z. Goldman, B. Z. Ginzburg, N. Garti, and A. Porath, "Oil products from algae," US4341038 A, 1982.