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# New methodologies for integrating algae with CO<sub>2</sub> capture

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#### Abstract

It is generally recognized, that algae could be an interesting option for reducing  $CO_2$  emissions. Based on light and  $CO_2$ , algae can be used for the production various economically interesting products. Current algae cultivation techniques, however, still present a number of limitations. Efficient feeding of  $CO_2$ , especially on a large scale, is one of them. Current methods for  $CO_2$  feeding to algae cultures rely on the sparging pure  $CO_2$  or directly from flue gas. The limiting factor in this system is the solubility of  $CO_2$  in water, which demands a considerable amount of energy for an effective gas to liquid transfer and leads to losses to the atmosphere. Due to the current ineffective methods for  $CO_2$  introduction into algae ponds very large surface areas would be required for enough ponds to capture a considerable amount of the  $CO_2$ . At TNO, an amine-based method have been developed for algae production utilization of  $CO_2$  where algae is used as photochemical desorber of  $CO_2$  from an absorption liquid. This methods brings the advantage of higher  $CO_2$  removal efficiencies compared to current  $CO_2$  feeding systems for algae and lower operational cost compared to both conventional  $CO_2$  removal using amines and conventional autotrophic algae cultivation.

© 2014 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/3.0/). Peer-review under responsibility of the Organizing Committee of GHGT-12 *Keywords: algae, photodesorption, carbon dioxide, CO*<sub>2</sub> *capture, CO*<sub>2</sub> *utilization* 

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#### 1. Amine based CO2 capture

The current standard for post combustion capture of  $CO_2$  is based on reactive absorption [1,2]. In such a process, thermal desorption is used to liberate the removed  $CO_2$  from the amine containing aqueous solution. Due to the use of steam for the thermal desorption step, a significant powerplant efficiency will occur [3]. In Figure 1a, a typical schematic representation of the standard post combustion CO2 capture process. At this moment, significant research efforts are underway to decrease the energy consumption, for instance by improving the absorption solvent [4], by improving the process [5,6,7], by improving integration [1,2].

A novel method has been developed that mediates  $CO_2$  desorption from the absorption liquid, and subsequent regeneration thereof, through the use of algae [8]. The method is based on the use of a conventional counter current packed bed scrubber for the absorption of  $CO_2$  from the flue gas into an absorption liquid. Instead of heating the  $CO_2$  loaded absorption liquid for regeneration, the liquid is fed directly into algae ponds or bioreactors (Figure 1b). The absorbed  $CO_2$  is hereby brought into direct contact with the algae, which through photosynthesis will convert the  $CO_2$  into biomass and specific products. Once the absorption liquid has been regenerated, it is separated from the biomass through filtration and recirculated to the absorber. Suitable amines have been identified which are nontoxic, and have a low degradability by the algae species.

Besides having a number of advantages over the conventional  $CO_2$  capture system, the newly developed system is also beneficial for the algae cultivation process itself. The contact efficiency of  $CO_2$  with the liquid is higher as well, as is the concentration of  $CO_2$  in the liquid, which also has the potential to lead to increased growth rates for specific algae strains where  $CO_2$  would otherwise be limiting.

Different variant of the above mentioned concept is based on the use of carbonated systems. This methods uses an enzyme to enhance the  $CO_2$  uptake rate in absorption liquids with potassium or sodium carbonate. However, this system is not considered in this study.

#### 2. Amine characteristics

The strategy for selecting solvents for this concept is mainly based on the solvent characteristics regarding their influence on algae growth and  $CO_2$  capturing potential. Other characteristics are amongst others cost, scalability, recyclability,  $CO_2$  solubility. Nevertheless, the most relevant properties that influence algae growth are ecotoxicity and biodegradability. For instance, the solvent ecotoxicity should be as low as possible to prevent cell-death of the algae strains and enhance a faster cell growth. Furthermore, the biological degradability should also be as low as possible to prevent unwanted bacterial growth or consumption by the algae themselves which lead to a loss of solvent in the system. These two properties can also be described as the EC-50 (concentration where amines inhibited algal growth by 50%) for biodegradability and the BOD (biological oxygen demand) for ecotoxicity. An important assumption is that the measured BOC and EC-50 by traditional methods and using traditional organism can be extrapolated to the relevant algae strains.

A set of solvents was selected based on a low ecotoxicity and low biodegradability criteria. The ecotoxicity and biodegradation of amines has been previously reported [9] and are listed in Table 1. The priority of this study is to develop insights and selection methodology for identifying solvent systems suited for integrating algae cultivation with indirect  $CO_2$  removal. According to above mentioned strategy, the following initial list of solvents are selected:

BOD and EC-50 Threshold for Testing						
BOD Threshold	5%	5% 3,00E+04				
EC-50 Threshold	3,00E+0					
Molecular Name	BOD	EC-50	Test?			
Triethylamine	17%	1,50E+01	No			
Triethanolamine	16%	-	No			
Tetra-N-methyl-propanediyldiamine	31%	2,00E+03	No			
Tetrahydrothiophenedioxide	5%	1,00E+05	Yes			
Spermine	90%	1,40E+04	No			
Spermidine	100%	1,00E+05	No			
Sarcosine	75%	1,00E+05	No			
Pyrrolidine	62%	2,00E+01	No			
1.3-Propanediamine	39%	1,80E+03	No			
Piperidine	67%	1,40E+01	No			
1-(2-Hydroxyethyl)-Piperazine	1%	2,00E+03	No			
Piperazine	2%	4,00E+03	No			
N-tertbutylethanolamine	7%	4,00E+02	No			
N-methyldiethanolamine	1%	2,00E+03	No			
Neopentandiamine	8%	4,00E+03	No			
NN-dimethylethanolamine	70%	2,50E+02	No			
NN'-bis(2-hydroxyethyl)ethylenediamine	2%	4,20E+03	No			
N-(2-hydroxyethyl)-ethylenediamine	4%	9,00E+04	Yes			
Morpholine	17%	8,00E+01	No			
2-Methylaminoethanol	53%	6,00E+02	No			
Glycine	68%	2,50E+04	No			
Ethylenediamine	30%	1,00E+03	No			
2-Ethylaminoethanol	53%	2,00E+02	No			
Ethanolamine	27%	4,00E+03	No			
Dimethylpropanolamin	15%	1,40E+02	No			
Dimethylaminopropylamin	55%	4.00E+02	No			

Tabel 1. Solvent ecotoxicity and biodegradability

Dimethylamin	80%	2,00E+02	No
Diisopropanolamine	2%	5,00E+03	No
Diglycolamine	2%	4,00E+03	No
Diethylenetriamine	2%	9,00E+03	No
Diethylaminoethanol	5%	2,50E+02	No
Diethanolamine(DEA)	50%	2,00E+03	No
4-Amino-1-butanol	55%	2,40E+02	No
3-Aminopropanol	4%	1,60E+02	No
3-Amino-1-methylaminopropane	75%	1,20E+04	No
3-Amino-1-cyclohexylaminopropan	15%	1,00E+02	No
3-(2-Aminoetyl)aminopropylamine	0%	9,00E+04	Yes
2-Amino-2-methylpropanol	2%	1,00E+03	No
2-Amino-2-methyl-13-propanediol	2%	5,00E+03	No
2-Amino-2-ethyl-13-propanediol	5%	8,00E+02	No
1-Amino-2-propanol	40%	2,50E+02	No
Alanine	90%	9,00E+04	No

Based on the long list of Table 1, the following short list have been made.

 Tabel 2. Shortlist candidates screening integration capture, algae growth

 Screening solvents

 Taurine

 3-(2-aminoethylamino)propylamine

 1-(2-hydroxyethyl)-piperazine

 Piperazine

 NN'-bis(2-hydroxyethyl)ethylenediamine

 Diisopropanolamine

 Diglycolamine

Taurine [9] and diglycolamine are used as reference solvents, since they are currently being researched and used as  $CO_2$  capturing solvents. Therefore, they are a good reference to indicate the relative improvements compared to other solvents.

### 3. Amine screening methodology

The screening tests aimed to discover if the algae could survive under the presence of a solvent. Therefore, the methodology for screening the solvents considered a set of experiments varying the type of solvent under a low solvent concentration. The algae strain selected for this study is *Chlorella sp*, as one of the most common and characterized algae strains.

The screening tests are performed by preparing algae media with a low concentration of solvent. This solvent based media are loaded with  $CO_2$  by bubbling through  $CO_2$  gas. After measuring the  $CO_2$  loading, the media is inoculated with *Chlorella sp* to test the concept feasibility.

#### 4. Optimization methodology for CO<sub>2</sub> capture and amine concentration

The screening tests will provide a short list of solvents that can be further optimized for capturing  $CO_2$  and algae growth. The optimization strategy is considering the following process parameters to improve productivity. These

parameters include: solvent concentration, recyclability ratio, dilution rate for a continuous system, biomass density, and CO<sub>2</sub> loading.

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