# ENITECNOLOGIE R&D PROJECT ON MICROALGAE BIOFIXATION OF $CO_2$: OUTDOOR COMPARATIVE TESTS OF BIOMASS PRODUCTIVITY USING FLUE GAS $CO_2$ FROM A NGCC POWER PLANT

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## ABSTRACT

Microalgae mass cultures could contribute to the mitigation of greenhouse gas (GHG) emissions by enabling the direct utilization of fossil $CO_2$ streams from concentrated sources and the production from the algal biomass of renewable biofuels and fossil fuel-sparing products. EniTecnologie, the R&D arm of the Italian oil & gas company Eni, is carrying out an in-house R&D project focused on demonstrating and improving on the achievable biomass productivities of outdoor microalgale mass cultures under outdoor conditions. The objective is toWe evaluated the feasibility of fixing flue gas $CO_2$ from a natural gas combined cycle (NGCC) power plant and to produce renewable methane fuel to replace a fraction of the input fossil methane of input. Initial experiments at the EniTecnologie R&D Centre in Monterotondo, central Italy, compared the productivity of thea marine microalga, *Tetraselmis suecica*, mass cultured in an outdoor experimental system consisting of a scale-down system that design simulatesing a large-scale microalgae production systems and comprisesing both open ponds and closed photobioreactors. RThe results indicated that closed and open cultivation systems have similar productivities, , and that in open ponds the areal values are close to the maximal productivities so far reported under outdoor operating conditions and significantly higher than those using flue gas $CO_2$ in similar scale-down systems. This R&D activity is being coordinated with other projects on microalgae mass cultures for biofixation of $CO_2$ througha constituent project of the International Network on Biofixation of $CO_2$ and GHG Abatement with Microalgae, an initiative that operates under the auspices of the IEA GHG R&D Programme.

## INTRODUCTION

EniTecnologie is actively involved in evaluating and developing technologies for the abatement of GHGs resulting from the use of fossil fuels, in particular methane (natural gas), to allow the continued use of these resources in an environmentally acceptable way. Biofixation of $CO_2$ by microalgae mass cultures represents an advanced, climate friendly biological process that enables the direct utilization of fossil $CO_2$ streams produced from concentrated sources, such as power plants. Mitigation of GHG emissions would result from the conversion of the algal biomass to renewable biofuels (methane, ethanol, biodiesel and hydrogen) and fossil fuel-sparing products (fertilizers, biopolymers and lubricants).

The Microalgae cultures have been investigated as a source of renewable fuels for several decades. The concept of a renewable energyn algal-methane process, proposed during the 1960s at the University of California Berkeley, was to grow algae in municipal wastewaters, harvest the biomass, and then convert it to methane to generate electricity [1]. AThe algal cultures, wereas to be grown in high rate (shallow, channelized, mixed) ponds, to produce dissolved $O_2$ required for bacterial oxidation of the wastes and the harvested algal biomass was to be thenwould be converted by the process of anaerobic digestion to methane. Over the years, several Eeconomic analyses of such processes were carried out, in particular for the production of biodiesel from microalgal biomass with a high lipid (vegetable oil) content were made [2, 3, 4]. These studies used the same basic production process of high rate ponds, mixed with paddle wheels, and were based on favorable assumptions, in particular the achievement of very high biomass productivities and low-cost harvesting, by the spontaneous flocculation of algae once removed from the ponds (bioflocculation). IThe interest in biodiesel production by microalgae was driven by the U.S. Department of Energy (DoE) [5]. These studies showed that it is possible to grow selected algal strains in large-scale raceway, paddle wheel mixed, unlined open ponds (1,000 $m^2$) at relatively high productivity (30 $g/m^2/d$ peak monthly, about half that for annual average) with efficient utilization of $CO_2$ , although microalgae oil production did not prove as efficient [6]. The potential of microalgae mass cultures to utilise actual flue gas $CO_2$, in particular from coal-fired power plantsusing different microalgal strains, in particular marine, cultivated in both laboratory and outdoor systems, both open ponds and closed photobioreactors showed that the algal growth was not affected by the $SO_x$, $NO_x$ and or other trace components [7-10]. These experiments] in the flue gases. Currently, about 5,000 tons of food- and feed-grade microalgal biomass are commercially produced per year in large open pond systems and plant gate production costs exceed U.S. $ 5,000/ton, an order of magnitude higher than what could be allowable for renewable fuel production and GHG abatement. In Hawaii, Cyanotech operates a small power plant on biodiesel, producing renewable electricity and flue gas $CO_2$ supplied to algal cultures. Microalgae ponds are also used for municipal wastewater treatment and a plant in California is using the methane fuel obtained from the harvested algal biomass, produced from some 180 hectares of oxidation ponds, to generate electricity. Engineering cost analyses project that for larger systems (>100 hectare) and assuming higher biomass productivities (>100 metric tons/hectare/year) and low-cost harvesting [11, 12] competitive renewable fuel costs could be achievable. These targets require long-term applied R&D into algal photosynthesis and physiology, mass cultivation, harvesting and conversion of the biomass to fuels. The development of multipurpose microalgae processes that combine biofuels production with wastewater treatment, in particular nutrient removal, and co-production of high-volume energy-sparing co-products, such as fertilizers and biopolymers, would provide a pathway to the longer-term development of microalgae technologies with significant GHG abatement potential.

To advance the development and applications of microalgae biofixation processes for biofuels production and GHG abatement, the U.S. DoE–NETL and EniTecnologie, organized the “International Network on Biofixation of $CO_2$ and GHG Abatement with Microalgae” [12, 13, 14]. This initiative operates under the auspices of the IEA GHG R&D Programme and includes as members, energy companies, government agencies and other organizations supporting R&D activities in this field [15]. The purpose is to provide a forum to share information and expertise and enhance understanding of R&D issues. The strategic objective of the Network is to demonstrate within five years the feasibility of microalgae $CO_2$ biofixation technologies for GHG abatement and to achieve practical applications within the decade. This is pursued through research coordination, project development and review, technical assistance, techno-economic analyses and resource assessments. As a tool for guiding future R&D activities, integrating in its broad vision the projects carried out by the Network members, a Technology Roadmap has been completed [16, 17]. Four general multipurpose biofixation processes with potential to be developed within the ten year time-frame of the Network have been identified. They combine $CO_2$ fixation and renewable biofuels production with additional GHG abatement functions or products (wastewater treatment and high-volume energy-sparing co-products) and share common R&D issues, such as the need of techniques allowing the mass culture of selected microalgae species in open ponds, the low-cost harvesting of the algal biomass and the achievement of high productivities.

## ENITECNOLOGIE R&D PROJECT

The immediate objective of the EniTecnologie R&D project on microalgae biofixation of $CO_2$ is to evaluate on pilot scale the feasibility of using fossil $CO_2$ emitted from a NGCC power plant to produce algal biomass. The biomass would be harvested and then fermented by anaerobic digestion to methane to replace a fraction of the natural gas, with the residual sludge, containing most of the N, P and other nutrients, recycled back to the cultivation ponds. In a preliminary mass balance calculation, assuming near-theoretical productivities, a 700 ha system was projected to be able to mitigate 15% of the annual $CO_2$ emissions from a 500 MWe NGCC power plant [12]. The R&D focuses on how to increase the productivities of algal mass cultures under outdoor operating conditions. The target is to double biomass productivities from the currently projected 30 gDW/m$^2$/day to 60 gDW/m$^2$/day for peak monthly productivities, corresponding to a solar energy conversion efficiency of about 5%. This would reduce land area requirements (footprint of the process) and costs of algal biomass production. As a first step towards this goal we set out to demonstrate the currently achievable algal biomass productivity under outdoor conditions using a simulated NGCC-flue gas for $CO_2$ supply and two different mass cultivation systems. These data will then be used as a baseline to design future strategies aimed at increasing biomass productivities under our operating conditions. Our first season of experimental work studied the performance of several marine microalgal strains, cultivated side-by-side in open ponds and closed photobioreactors. These comparative tests were run continuously from late April until the end of October, the favourable season for microalgae in our geographic area (Rome, Italy). Here we report on the data from one strain, *Tetraselmis suecica*, tested for constant (30% per day) and different (up to 60% per day) culture dilutions during this period in both ponds and photobioreactors. In the first set of tests, one culture was fixed at a 30% per day dilution (the control culture), while dilution in the second was increased from stepwise (each step allowed to run for two weeks in May-September and three weeks in the colder months of April and October). These culture dilutions were selected to bracket the maximal achievable productivity under our operating conditions.

## EXPERIMENTAL SYSTEM AND METHODS

### Outdoor Cultivation System

The comparative tests of productivity were carried in our facility in at Monterotondo, central Italy (latitude: 43°N8’, longitude: 10°E51’), (latitude: 43°N8’, longitude: 10°E51’), using two open ponds (ponds 1 and 2) and two closed photobioreactors (reactors 3 and 4). The two Plexiglas paddle wheel-mixed raceway ponds have a depth of 30 cm, an illuminated surface of 2.5 m$^2$ and were operated at a volume of 375 liters (culture depth of 15 cm) and at a mixing velocity of 30 cm/s. The photobioreactors have an operating volume of 35 litres and an illuminated surface of 0.96 m$^2$ [18]. Temperature in the photobioreactors during the day was controlled by water spraying. The pH was regulated by a solenoid-valve that supplied $CO_2$ on demand. An NGCC-simulating flue gas produced by a boiler (containing 8% v/v $CO_2$) was supplied and a computer-assisted data acquisition system was used.

### Analytical Parameters

The time-course of these comparative tests was monitored by measuring both climatic and biological parameters. In particular, the internal temperatures and the total incident Photosynthetic Active Radiation (PAR, integral area of total moles of photons with $\lambda$ ranging from 400 to 700 nm), were recorded on-line as well as $CO_2$ supply and pH values. The total dry weight was measured on a daily basis before culture dilution according to [19]. The content of chlorophyll *a*, *b* and *c* as well as the amount of carotenoids were determined three times per week according to [20]. Microalgal cells were also routinely checked for purity by microscope and their growth monitored by $OD_{750}$. The dilution of the cultures was carried out daily on early mornings. The algal biomass productivity was calculated as a function of the illuminated surface (areal productivity) according to the following equation: g biomass produced daily x litres of the culture daily harvested/illuminated surface/time. The amount of biomass produced daily was calculated from the difference between the total dry weigh of the current day, measured before culture dilution, minus the total dry weigh of the prior day calculated after dilution. The photosynthetic efficiency, the ratio between the biomass output energy and the solar input energy, was computed from an assumed higher heating value of the algal biomass produced (5.5 kCal/g biomass) divided by the energy content of the total moles of photons of average visible wavelength ($\lambda$ 550 nm) ?(51.8 kCal/mole photons).

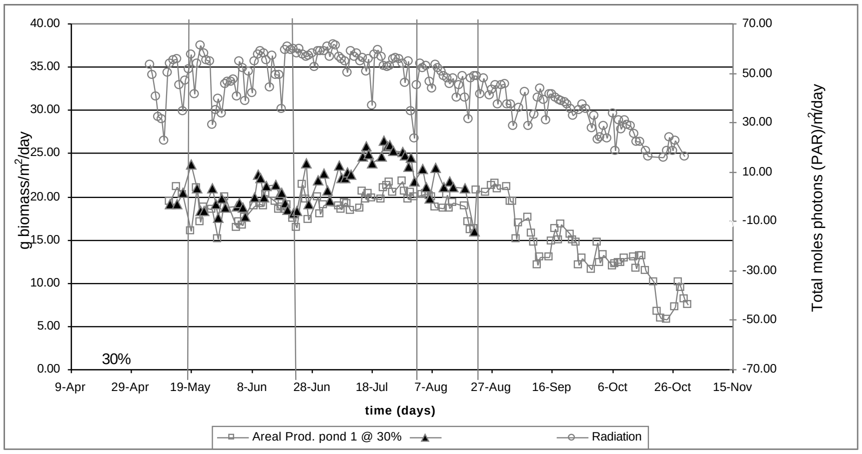
## Microalgal Strain and Growth Medium

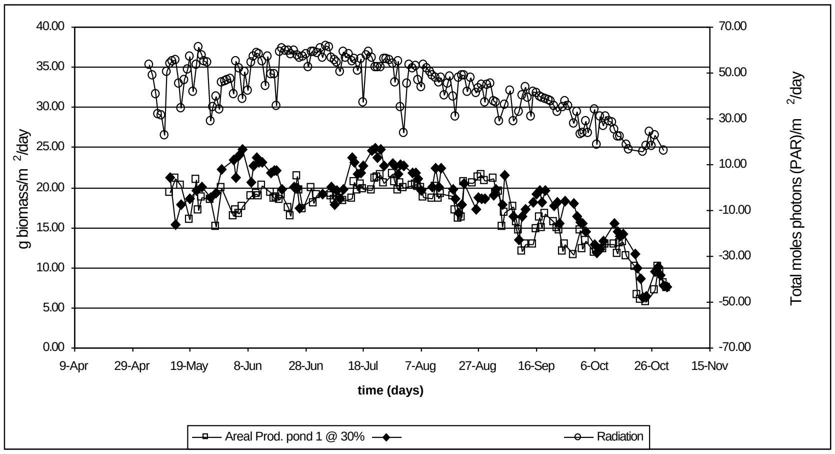
The marine strain *Tetraselmis suecica*, from the University of Florence, was selected as it was already tested for sustained cultivation outdoor in photobioreactors. A modified f/2 seawater medium [21] in which nitrogen and phosphorous were enriched twice to prevent nutrient limitation (in photobioreactors) was used in the reactors and Sea Salt Zoo Mix (Tropic Marin) was used instead of natural seawater.

## RESULTS AND DISCUSSION

The time-course of climatic parameters such as temperatures, maximal, minimal and average, and the solar radiation was recorded from late April until October. Maximal daily temperatures show the highest variation between closed photobioreactor (with spray-cooling) and open pond systems, with the latter some 5°C higher in the hottest months (at almost 35°C in June-August), but about 5°C colder in the September-October period (20–25°C). Minimal daily temperatures, about 15°C colder for the open ponds than the maximal temperatures, were rather similar between the open ponds and the closed photobioreactors, as were average temperatures. Insolation averaged about 50 mole photons PAR/m$^2$/day during the summer months, decreasing by about 40% by the September-October period. Several periods of heavy cloud cover, particularly in May-June decreased sunlight.

Figure 1 shows the time-course of the areal productivities, together with the solar radiation, of the tests designed to compare side-by-side in ponds and photobioreactors different culture dilutions using the strain *Tetraselmis suecica*. The graphs on the left hand side and on the bottom report the values measured in the pond 2 and reactor 4, operated by ramping the culture dilution to 40%, 50% and 60%, in comparison to those of the pond 1 and reactor 3, constantly operated at culture dilution of 30%. Both in ponds and photobioreactors and with all dilutions tested, *Tetraselmis suecica* was very stable as monoculture during the whole time-window. This implies that in the open systems as well a good control over environmental conditions was achieved. A daily dilution of 50% gave the best overall productivity, with areal values in July of up to 26 g/m$^2$/day, versus 21 g/m$^2$/day of 30% dilution in the same system and the same period (23% increase). A daily dilution of 40% of the culture gave the best productivity for the photobioreactors in June, with areal values up to 27 g/m$^2$/day versus 24 g/m$^2$/day of 30% dilution in the same system in July. Comparing the performance of the two cultivation systems, the pond 1 and the reactor 3 continuously





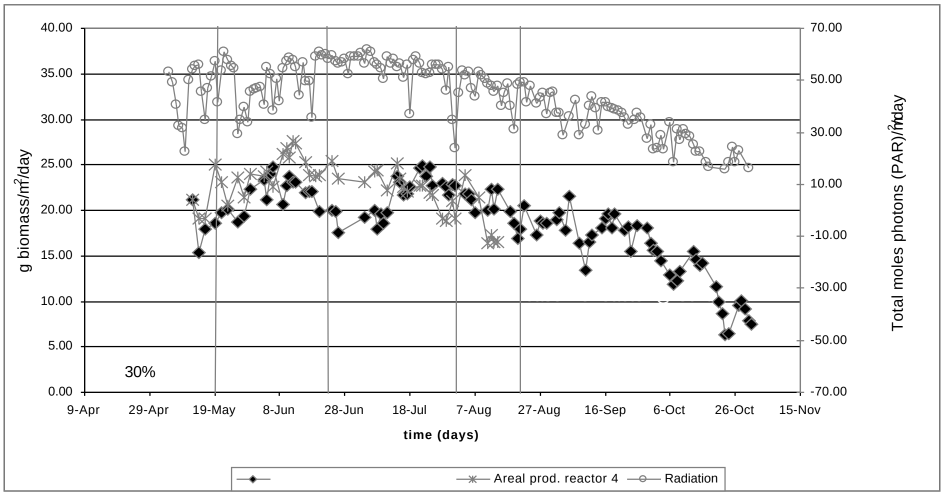


**Figure 1:2** Time-course of the areal productivities (g biomass produced x litres of the culture harvested/$m^2$/day) of the tests comparing side-by-side in ponds and photobioreactors different culture dilutions (from 30% up to 60%) using the strain *Tetraselmis suecica*. The time-course of the solar radiation (PAR) is also shown.

operated at 30% dilution, slightly higher areal productivities were obtained, overall, with the photobioreactor. However, considering the data at all dilution rates, there was no significant differences between the open ponds and closed photobioreactors.

At 30% per day dilution, the performance of the pond 1 and reactor 3 were similar in May, August and October, whereas the photobioreactor had slightly higher productivities in June, July and September (Figure 2). At 40% dilution in June, photobioreactor 4 performed better than ponds 1 and 2, at 30% and 40% daily dilutions, respectively. In July with a 50% per day dilution, pond 2 was slightly better than reactors 4 operated at the same dilution. Overall, the photobioreactors and open ponds exhibited similar productivities. This is significant, as there is a general opinion in this field that closed photobioreactors are inherently more productive than open ponds, although direct comparisons are few. As it is not practical (e.g. economically feasible) to produce microalgal biomass for GHG abatement in closed photobioreactors, the fact that there are no significant differences between open and closed systems is an important conclusion from this work. The areal productivity values in the ponds were generally similar to the best data in the literature [6, 11] and significantly higher than prior work using flue gas $CO_2$ and similar scale-down systems operated outdoors (10-15 g/m$^2$/day) [9, 10]. This research also confirms prior studies that flue gas itself is not a problem in algal cultivation.

The photosynthetic efficiencies, were on average about 4% of PAR, which would correspond to approximately a 2% total solar conversion efficiency. This is several-fold higher than obtained with higher plants, but several-fold lower than what is anticipated to be possible with algal mass cultures, and required for purposes of GHG abatement. The solar conversion efficiency more than doubled during low insolation and increased significantly when insolation decreases. This inhibition, due to light saturation, suggests an avenue for the development of more productive algal strains that exhibit less light saturation [16]. Future research will emphasize the potential for increasing productivity at full solar intensities to the level observed at reduced insolation.

## Figure Legendss

**Figure 1** Flow sheet of the outdoor cultivation system that includes two paddle wheel-mixed raceway ponds (Ponds 1-2) and two near horizontal manifold-type photobioreactors (PBRs 3-4). Also shown are the $CO_2$ and nutrient supply and the data acquisition system.

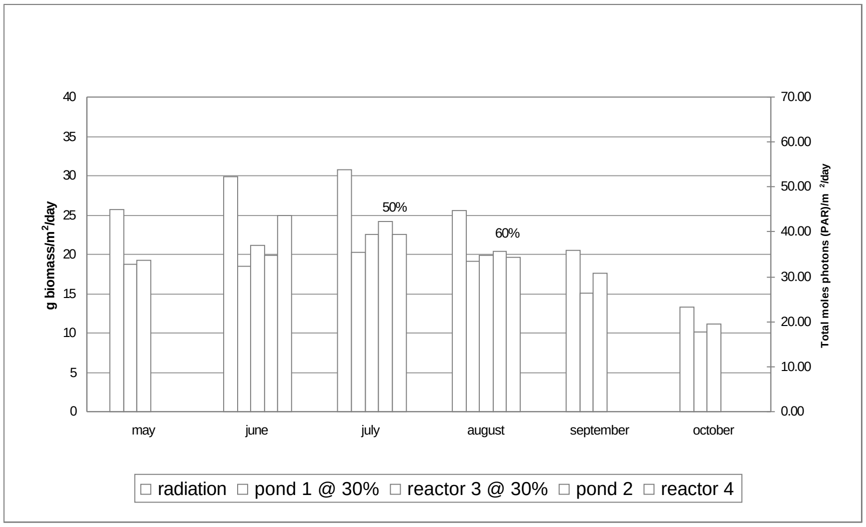


**Figure 2:** Average monthly areal productivities of the comparative tests described in Figure 1. The average monthly solar radiation (PAR) is also shown.

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