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Microalgae Growth in Qatar for CO2 Capture and Biodiesel Feedstock Production

By Rebecca J. Wilson, Ghada Salama & Ihab H. Farag
University of New Hampshire, Durham

Abstract - Demands for and prices of liquid petroleum fuels are increasing. This challenge is motivating the development of alternative fuels, like biodiesel from non-food sources. Microalgae are a promising source of oil feedstock for biodiesel. Growing microalgae indoors uses water, chemical nutrients, artificial lights, and energy for harvesting, drying and oil extraction. The economics would be greatly improved if microalgae are grown outdoors in a hot sunny climate where the light energy is free and the temperature is adequate for growth. Using non-potable water (such as available and free salt-water) would reduce the water footprint. Open pond systems have low capital and operating costs and are wellsuited for growing microalgae in salty water. The ideal location for growing microalgae outdoors is a non-arable land that cannot be used for agriculture (such as Qatar desert). The purpose of this research is to study the growth of salt-water microalgae outdoors in Qatar's hot sunny environment and compare it to indoor growth. Three Dunaliella microalgae (Bardawil, Parva and Salina) were grown in Persian Gulf saltwater medium.

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Keywords : biodiesel, microalgae harvesting, Qatar, lipid production, hot climate.

I. Introduction

a) Biodiesel

Biodiesel is a plant-derived biofuel intended to replace petroleum diesel. It is biodegradable, essentially CO_2 neutral, and much less toxic than petro diesel. It is made in a processor (Wilson and Farag, 2012) by the transesterification of a triacylglycerides (TAGs)-containing oil feedstock (e.g., oils of soybean, rapeseed, maize and Jatropha, Tewfik et al., 2012) and an alcohol (e.g., methanol or ethanol). One of the very promising oil feedstocks for biodiesel is microalgae oil (Nkongolo, 2010, Nkongolo and Farag, 2012, Chaput et al. 2012, Zuka et al., 2012).

Author α : Chemical Engineering Dept, University of New Hampshire, Durham, NH 03824, USA. E-mail : rjd26@wildcats.unh.edu
Author σ : Chemical Engineering Dept, Texas A&M University at Qatar, Doha, Qatar. E-mail : ghada.salama@qatar.tamu.edu
Author ρ : Chemical Engineering Dept, University of New Hampshire, Durham, NH 03824-3591, USA. E-mail : ihab.farag@unh.edu

b) Microalgae

Microalgae are plant-like cells. They require a nutrient medium (water + nitrogen + phosphorous + other nutrients), CO_2 and light energy to do photosynthesis and grow. The simplest technique to grow microalgae in hot sunny areas like Qatar is in open ponds. During photosynthesis the algae capture the light energy and use it for carbon fixation, i.e., convert CO_2 (absorbed from air or water) to glucose and release oxygen. Up to 50% is converted into TAG-containing lipids (oil) that can be used as a biodiesel feedstock in the transesterification reaction (Scott, 2010). Table 1 shows that microalgae, e.g., Nannochloropsis or Chlorella, have the potential to produce more oil feedstock for biodiesel than other crops. This is due to the simple cell structure and surface water interface. Algae cells have efficient and easy access to dissolved CO_2 and other nutrients while growing suspended in water. Hence algae are considered excellent CO_2 capture and use (CCU) systems. Estimates are that 2.5 tonnes of CO_2 are needed to produce 1 tonne of microalgae and one tonne of oxygen. Assuming 50% oil content in the dry algae the 1 tonne algae can produce roughly 3.5 barrels of biodiesel (Kanes, 2009). CO_2 produced in the cement industry or in coal fired power plants can be used to fertilize the microalgae production (Chaput et al., 2012). The consumption/fixation of CO_2 takes place during daylight when exposed to the sun, hence it depends on light exposure. It has been reported that over a seven day growth period the microalgae removed 82% of CO_2 on sunny days (such as Qatar sunny weather), and 50% on rainy days. Microalgae can consume nitrogen sources 24 h/day. Testing over a seven day period showed that microalgae removed 86% of NOx with or without light. Microalgae as a feedstock for biodiesel will not compete with food crops because they can be grown on non-arable land (such as Qatar desert).

Table 1: Estimation of oil productivity from various crops (Scott 2010, Mulumba, 2010 and 2012)

Crop	Oil content per ton of biomass (wt% dry mass)	Oil production (Mton/ha-y)
Rapeseed oil (UK)	40-44% (of seed)	1.4
Soyabean	20% (of seed)	0.48
Jatropha	30% (of seed)	2.4
Chlorella vulgaris	Up to 46%	7.2*
Nannochloropsis	Up to 50%	20-30*

*Assumed productivity

c) Photosynthetic Solar Constant

The photosynthetic solar constant, which is the yearly mean solar irradiance on the surface of the earth oriented towards the sun above the atmosphere, is 1340 W/m^2. The photosynthetic active region range is 40-750 nm (Agrawal, 2010). This provides 26% of the standard solar constant or 350 W/m^2 of input power to the photosynthetic process. The theoretical maximum photosynthetic efficiency is 20% (Bonner, 1962). Thus, the photosynthetic solar constant, or the maximum output power that can be achieved under ideal conditions would be 70 W/m^2. The solar biomass constant or theoretical upper limit on the equivalent biomass harvested would be 4.5 mg/m^2-s.

d) Cost Estimates of Algae Production

There are three main factors that affect the production cost of algae: (1) cost of land used for the algae production facility, (2) the value of the by-products of algae growth and oil extraction, and (3) the algae oil production rate (g oil/L-day) and hence the importance of this investigation. For open pond algae production systems the capital costs estimates range is $50,000 to $250,000 per hectare, and the operating costs are about $15,000 to $20,000 per hectare per year. The almost free desert land in Qatar will lower the capital costs estimates. The results of this investigation of using Qatar's hot sunny climate to grow and dry the algae should lower the annual production costs.

II. Goals and Specific Objectives

The goal of this research is to investigate the feasibility of producing microalgae oil in Qatar to be used as biodiesel feedstock. To accomplish this goal, the specific objectives were to:

- Study algae oil production in an open pond system in Qatar's hot sunny desert climate.
- Identify if nutrients should be added to the Gulf (off Qatar) seawater to favor algae oil production.
- Compare different algae strains to determine the most favorable for algae oil biodiesel feedstock production.

a) Open Pond System

The design of the photobioreactor (PBR) is very important in scaling up the growth of microalgae in Qatar's hot sunny desert climate. Open ponds are inexpensive PBRs and easily maintained, but may suffer from contamination. This is less likely in Qatar due to the high salinity of the Gulf seawater. Open ponds have to be shallow to allow for sunlight penetration. Hence a large surface area is needed, which makes harvesting more difficult (Scott, 2010). Fish tanks with sides blacked out simulate a shallow open pond with a large surface area.

b) Qatar

Microalgae were grown outdoors in Doha, Qatar during the summer of 2011. This climate provides constant daylight, averaging 95,000 lux (139 W/m^2) (Hoki, 1999) whereas the average outdoor daylight in the USA is 50,000 lux or 73 W/m^2. Qatar is an excellent candidate for growing microalgae because of its high light intensity, desert land, location and CO_2 emissions. Qatar's sunlight intensity will enhance algae photosynthesis. Only 6% of Qatar is agricultural land, so there is plenty of desert land that could be used to grow algae. Qatar is located in the Gulf, which provides easy access to salt water and is a source of microalgae. Qatar has the highest per capita CO_2 emissions in the world (55.4 tonnes vs. 20 in the US in 2007) due to the petroleum and cement industries. Algae growth is an excellent method of CCU, so Qatar is an ideal candidate for algae growth.

c) Microalgae Strains

Microalgae growth in batch cultures occurs in the following phases: lag, exponential, stationary and death. Ideally, the microalgae should be harvested in the stationary phase because they have reached maximum growth, and the nutrients will have been used up so the microalgae start to accumulate lipids. There are four classes of microalgae; diatoms, green algae, blue-green algae and golden algae (Kanes, 2009). Green algae, e.g., Dunaliella, were used in the present study because they can grow in fresh water and in salt water (such as Gulf seawater). Also, Dunaliella microalgae are the most halotolerant species known and are more tolerant of fuel oil contamination than other species (Tafreshi. 2009). Three specific strains of Dunaliella microalgae were used in the present work: Salina, Bardawil and Parva. These strains were chosen for their ability to thrive under hot temperatures in saline water, and their high lipid content (Table 2) ((Abd El-Baky (2004), Peeler (1989), Tafreshi (2009), Scott (2010), Fried (1982), Ben-Amotz (1990), Evans (1982)). The selected strains were all grown in an open pond system in Doha, Qatar to select the species that exhibits growth, biomass production and oil content.

Table 2 : Optimal growth conditions and lipid content

Duna-liella Species	Temp (°C)	Salinity (M NaCl)	Lipid(% dry algae mass)	Found in Gulf salt water?
Salina	22-35	0.9-4.3	50	Yes
Bardawil	25	3.0-4.0	30	Yes
Parva	32	1.5-2.0	21-25	Unknown

III. Approach & Metrics

a) Experiment Layout

The experimental work, summarized in Table 3, was done in two phases. The first was to provide enough algae for outdoor testing and establish baseline data on the performance of microalgae in Gulf seawater. These experiments were done indoors using fluorescent lights (4 bulbs illuminating seven 500 mL PBRs) and artificial (contaminants-free) salt water. The second phase aimed at more realistic tests of growing the microalgae in Gulf seawater exposed to Qatar's sunlight and hot climate. This was done outdoors on the roof of a building. The algae growth period for each run was about 14 days. All runs were done in batch mode, i.e., the medium (Gulf seawater with or without nutrients) was placed in the PBR, algae inoculum was added and the air flow was started. Air use had the dual purpose of supplying the CO_2 required for algae growth and oil formation, and providing algae and nutrient medium mixing. Once the algae growth reached the stationary phase they were harvested and dried, then the algae oil was extracted.

Table 3 : Experimental Steps

Step	Medium	Lighting	Explanation
Phase 1			
1- Inoculum Growth for future runs.	Artificial sea water	Fluorescent 24 h/d	Grow inoculum indoors.
2- Indoors Algae Growth	Gulf salt water	Fluorescent 24 h/d	without and with nutrients.
3- Indoors non-algae Growth (with and without nutrients)	Gulf salt water - no algae	Fluorescent 24 h/d	Monitor Gulf sea water without algae to check for competing species.
Phase 2			
4- Growth outdoors in a fish tank PBR with added nutrients.	Artificial sea water and Gulf salt water	Sunlight (9 hours/day)	Measure solution absorbance daily.
5- Algae harvesting			Stationary phase
6- Algae dewatering and outdoor drying using sunlight		Sunlight (9 hours/day)	Centrifuge algae to a slurry. Dry outdoors to get dry algae.
7- Hexane extract oil then evaporate hexane			Solvent extract the lipids/oil from algae produced.

b) Analytical Procedures and Metrics

Nitrate and pH measurements are important to maintain a consistent growth environment. This was done by collecting 5 mL of algae solution daily and using Mardel test strips. Algae growth was monitored daily by measuring the algae solution absorptivity at 680 nm. This was done by placing the same 5 mL solution in a DR2800 Spectrophotometer. Table 4 lists the measured variables and the metrics calculated.

Table 4 : Measured Variables and Metrics

Measurement	Purpose/ Metrics
Algae solution absorbance, DR2800 Spectrophotometer	Algae growth, from absorbance/ turbidity
Acidity of solution (pH), nitrite and nitrate levels with Mardel test strips.	Nutrient content, depletion or starvation
Algae mass after harvesting and drying (using a balance)	Algae production rate (g dry algae/L-day)
Mass of algae oil after extraction	Algae oil yield (g oil/100 g dry algae)
Air flow rate, liters/min (using a rotameter)	Carbon sequestration/capture efficiency
Incident light intensity with a light meter, Lux.	Photosynthetic efficiency

c) Data Analysis/Calculated Indicators

The performance of the PBRs was established by calculating the indicators explained in Table 5.

Table 5 : Performance Parameters and Definitions

Parameter	Definition/How Calculated
Photosynthetic Efficiency or Light Capture Efficiency is the light energy transferred through PBR and converted to biomass	Ratio of the energy produced by the combustion of the algae to the incident light energy produced by the artificial lights used.
Carbon Sequestration/Capture Efficiency is the mass of C sequestered by the algae relative to the C supplied to the microalgae.	C in dry algae formed/ Total C from the air into the PBR during growth, assuming: -Constant air flow rate - Air CO2 (394 ppmv) is the only C source for algae. -Dry algae are 60.4% C, based on literature.

IV. Methodology

a) Algae Growth and Monitoring

i. *Algae Inoculum Growth*

The algae inoculum was grown indoors in distilled water using 1.5 M NaCl, macro and micronutrients- this growth media is called "artificial seawater". The measured light intensity of 86,400 lux= 362.9 W/m^2 = photosynthetic photon flux density (PPFD) or light intensity of 1451.5 µmol/m^2s^{-1}. The carbon source was an air feed from a fish tank air pump.

ii. *In Lab/Indoor Microalgae Growth*

Once algae inoculum had grown, the in lab salt water trials were set up (Table 6).

Table 6 : Algae species/ nutrients for different in-lab trials.

Trial Name	Algae Species	Nutrients
Bardawil-SWN	Dunaliella Bardawil	Yes
Bardawil-SW	Dunaliella Bardawil	No
Parva-SWN	Dunaliella Parva	Yes
Parva-SW	Dunaliella Parva	No
None-SWN	None	Yes
None-SW	None	No

Algae were grown in either just Gulf seawater, or Gulf seawater with added nutrients. The purpose was to determine how the algae would grow in the Gulf seawater, if nutrients are needed, and the species that grew best. Trials without microalgae were included to measure the growth rate of other species in the Gulf seawater. Each trial was exposed to a continuous (24 hour/day) air feed and fluorescent lights.

iii. *Outdoor Algae Growth*

Algae were grown outdoors in fish tanks with the sides blacked out so only sunlight would enter from the top. The growth medium had the same salinity as the Gulf seawater (40 g salt/L water), same airflow rate and natural sunlight. Nutrients were added in the same proportions as the algae inoculum growth. Two trials were set up: 20 L Dunaliella Bardawil and 20 L Dunaliella Salina (the results from the indoor lab tests indicated that the Dunaliella Parva does not grow well in the Gulf seawater, so it was not grown outdoors).

Algae were also grown using the Gulf seawater with the same nutrients, airflow and natural sunlight. Two trials were set up:10 L Dunaliella Bardawil and10 L Dunaliella Salina.

b) Algae Harvesting

Algae were dewatered by centrifuging the solution at 5000 RPM for 6 minutes. The saltwater was then removed and DI water was added to clean the algae of salt and the algae were centrifuged again (5000 RPM, 6 minutes). During centrifugation, the algae were completely removed from the water, but the salt remained dissolved in the DI water. This cleaned the algae, and the discarded water did not contain any algae. The algae were dried using natural sun heat by placing the dense algae slurry outdoors (2 hours). The dry algae were massed, then mixed with hexane, heated, and the evaporated hexane was condensed and reused. Over a period of time (2 hours) the hexane extracts the oil in the algae. The algae biomass is removed by vacuum filtration. The filtration was repeated at least four times, or until the filter paper no longer retained algae. Oil is recovered by evaporating the hexane using a hot water bath.

V. Results/Accomplishments

a) Indoor Algae Growth and Monitoring Results

Figure 1 shows the growth measurements of the six different tests of Table 4. The standard trials show very little growth, indicating there was not a strong presence of competing species. During the lag phase there was similar growth in all the microalgae species, but when they reached the exponential phase, the

Dunaliella Bardawil grown with nutrients in Gulf seawater clearly grew the best. The Bardawil without nutrients showed little growth, and both Parva samples had little growth as well. Due to the poor growth of the Parva, they were excluded from further testing. Instead, it was determined that the Bardawil should be grown outdoors in both artificial seawater and Gulf seawater solutions containing nutrients. Table 2 indicates that Dunaliella Salina is promising, so though no indoor testing was performed, Salina was grown outdoors using the same conditions as Bardawil.

b) Outdoor Algae Growth and Monitoring Results

Figure 2 shows the four outdoor growth runs. It is evident that the trials in artificial seawater had a much longer lag phase than the trials in the Gulf seawater. This could be because the Gulf seawater has its own additional nutrients that expedite the growth of the microalgae. The Dunaliella Bardawil appears to exhibit consistently better growth than the Dunaliella Salina, shown by the higher final absorbance.

c) Algae Harvesting

After harvesting, the algae are massed to determine the production rate, the carbon sequestration and photosynthetic efficiencies. Lipids are extracted to get the algae oil content and the oil production rate.

The algae production rate was calculated for the four outdoor trials done in artificial seawater or Gulf seawater with nutrients. The results in Figure 3 indicate that the Dunaliella Bardawil shows the highest production, both in artificial seawater (using DI water and nutrients) and in the Gulf seawater off the coast of Qatar. The Dunaliella Salina grew well in the artificial seawater, but there was very little algae production in the Gulf seawater. This indicates that among the algae strains investigated, Bardawil has the highest growth rate in the Gulf seawater with nutrients. The algae production of Bardawil in artificial seawater is 0.02 g/L-day. This is equivalent to about 1.67 g/m^2-day or 0.0192 mg/m^2-s. This is less than 1% of Agrawal theoretical upper limit of biomass harvested of 4.5 mg/m^2-s. The daily algae production rate of 1.67 g/m^2-day is lower than the 12 g/m^2-day reported for Dunaliella Salina in Oilgae.com indicating the possibility of further improvement in the algae production.

Figure 4 shows the algae oil content results. Dunaliella Salina grown in the artificial seawater with nutrients had the highest oil content. The Dunaliella Bardawil grown in both the artificial seawater and the Gulf seawater had similar oil content. This is indicative that the Gulf seawater provides an environment similar to the artificial seawater, and the microalgae are able to produce oil as usual.

The oil production rate of the microalgae is the final oil mass per liter of initial solution per day of growth.

Figure 5 shows that all three trials were within the same range of oil produced. This further confirms that algae oil as a biodiesel feedstock, can be produced by growing Dunaliella Bardawil in the Gulf seawater.

The carbon sequestration efficiency and the photosynthetic efficiency of the microalgae were calculated for the outdoor trials of Dunaliella Salina and Dunaliella Bardawil. Table 7 shows that the carbon sequestration efficiency of the microalgae was between 3-6.5%. The photosynthetic efficiency of the microalgae ranged from 0.053-1.11%.

Table 7 : Carbon sequestration and photosynthetic efficiencies

Dunaliella Algae grown outdoors with Nutrient	Carbon Sequestration Efficiency* (%)	Photosynthetic Efficiency (%) **	Photosynthetic Efficiency relative to the photosynthetic solar constant (%) ***
Salina- DI water	6	0.6	1.1
Bardawil- DI water	6.5	1.11	2.1
Bardawil- Gulf saltwater	3.1	0.053	0.1

*Based on 60.3% carbon by mass in the microalgae, and 394 ppmv CO2 in the air
**Based on microalgae heating value of 5000 cal/g and incident light of 89,000 lux, or 130 W/m^2
*** Based on Agrawal constant of 70 W/m^2

These efficiencies are lower than the typical range of photosynthetic efficiency of microalgae. A possible explanation is that the only mixing of the algae was from the air supply bubbling through the solution. This prevents the algae at the bottom of the tank from receiving light as the solution becomes more concentrated with algae, and this will decrease the photosynthetic efficiency. It is evident that the Dunaliella Bardawil grown in DI water with nutrients had the highest photosynthetic efficiency (1.11%) and carbon sequestration efficiency (6.5%). Table 8 compares the present work results and literature values. The results confirm the feasibility of producing microalgae oil biodiesel feedstock in Qatar and that the process may be further improved.

Table 8 : Comparison of present Dunaliella results and literature (DI = DI water, GS = Gulf seawater)

Parameter	Present work: algae /medium	Literature Value
Photosyn-thetic efficiency	Bardawil/ DI1.1% Bardawil/GS 0.053% Salina/DI 0.6%	3.78% (Zemke, 2008)
Carbon Seques-tration Efficiency	Bardawil/DI 6.5% Bardawil/GS 3.1% Salina/DI 6.0%	12%
Biomass concentra-tion g Dry algae/L	Bardawil/DI 0.48 Bardawil/DI 0.17 Salina/DI 0.2	0.5 (Chisti, 2007)
Final Lipid production mg oil/L	Bardawil/DI 28 Bardawil/GS 9 Salina/DI 20	1420 (Li, 2011)

VI. Conclusions

Dunaliella Bardawil showed better algae production and slightly higher carbon sequestration and photosynthetic efficiencies than Dunaliella Salina and Parva. But Salina accumulated higher oil content per algae biomass. The present work demonstrates that Dunaliella Bardawil and Salina have potential for larger scale microalgae oil production in the hot sunny climate of Qatar using the Gulf seawater off Qatar

VII. Acknowledgements

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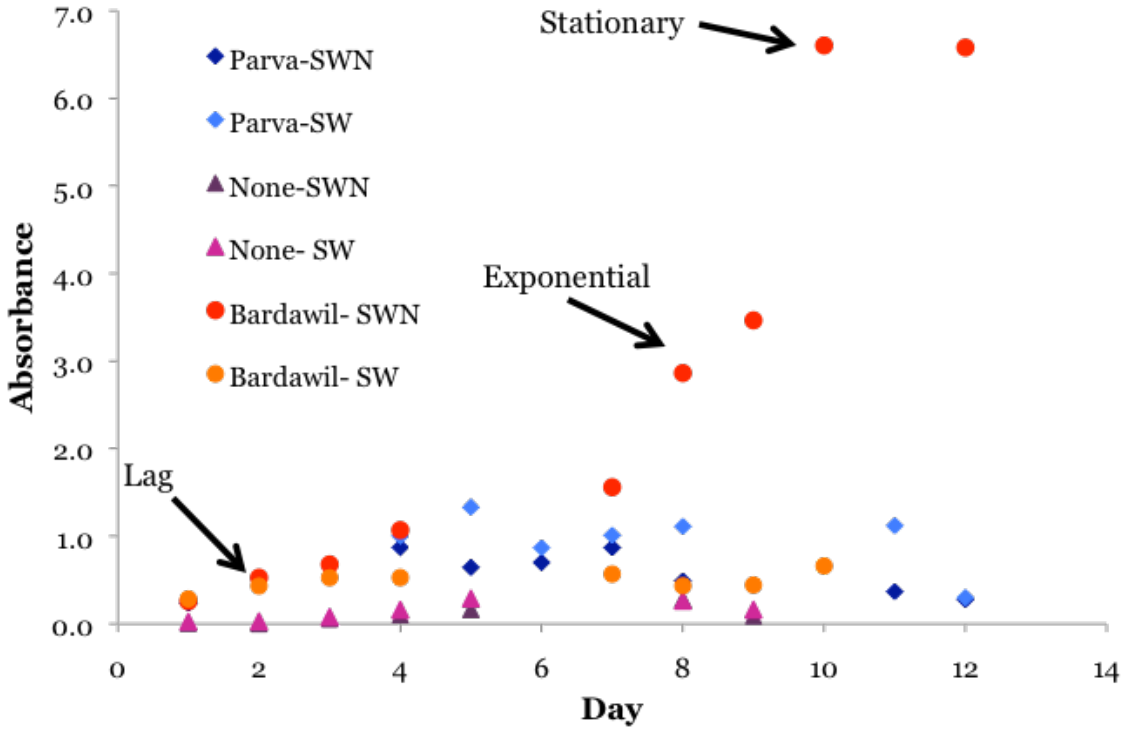

Figure 1 : Indoor salt water trials absorbance measurements (absorbance vs. time in days).

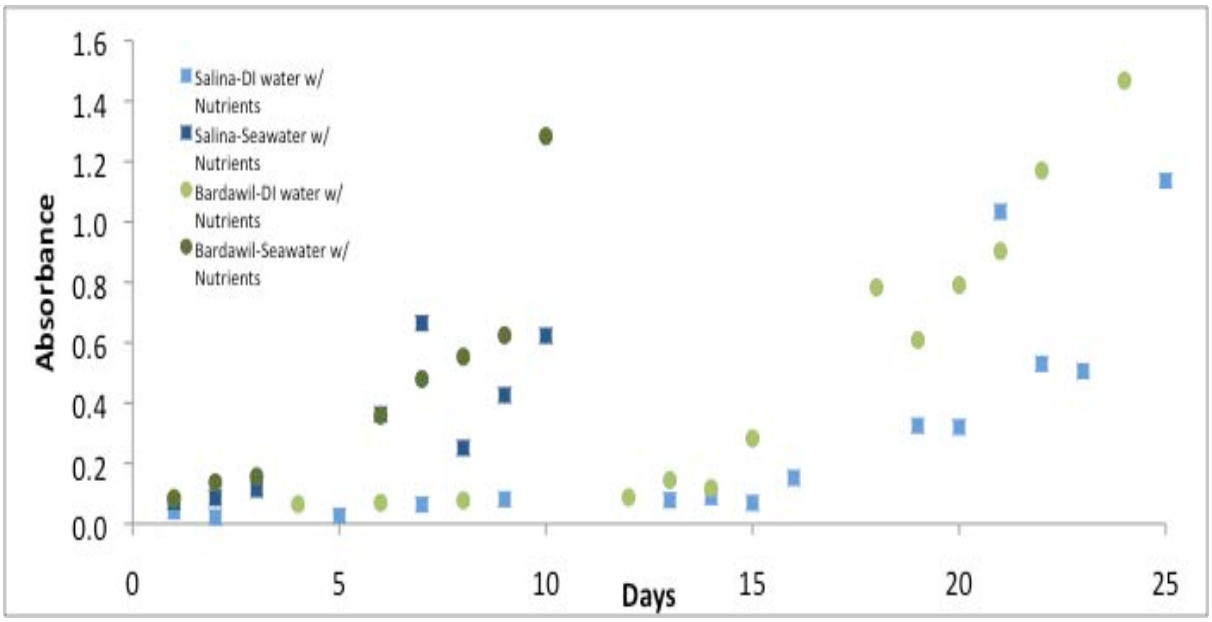

Figure 2 : Outdoor salt water trials absorbance measurements.

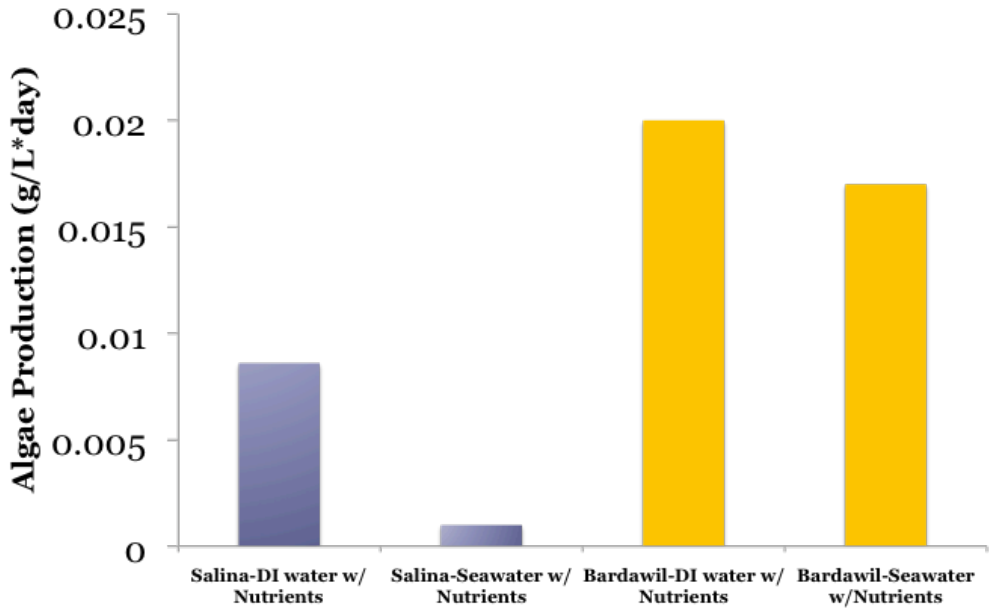

Figure 3 : Algae production (grams per liter per day, or simply g/L-day) of Dunaliella Salina and Dunaliella Bardawil grown outdoors.

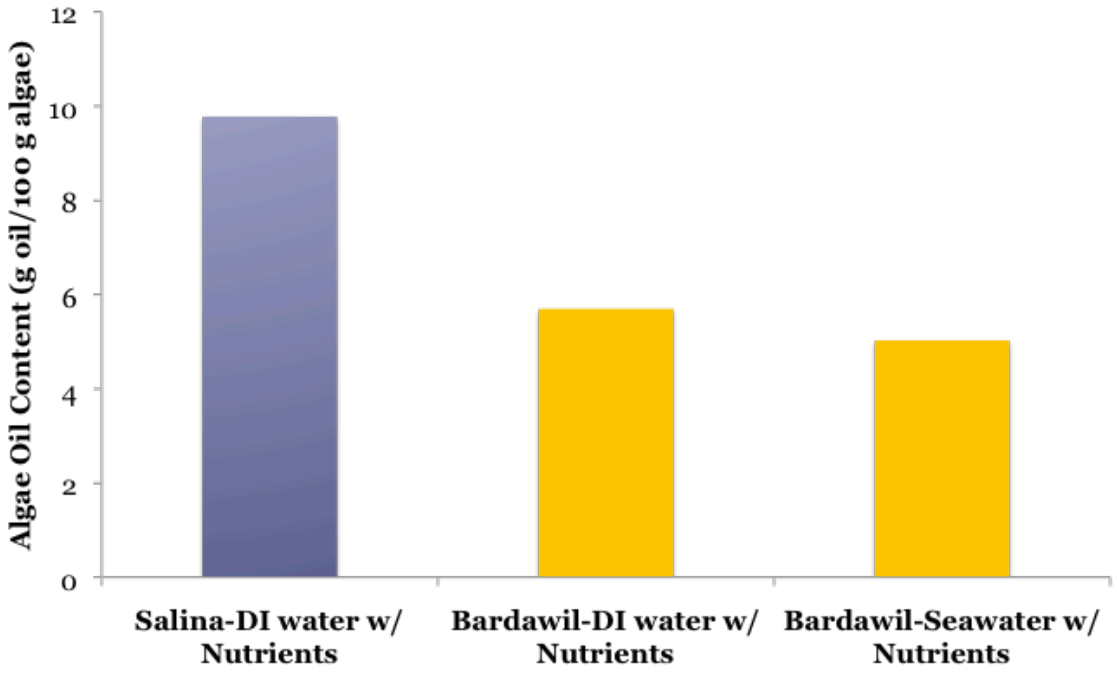

Figure 4 : Algae oil content (g oil/100 g algae) of Dunaliella Salina and Dunaliella Bardawil grown outdoors.

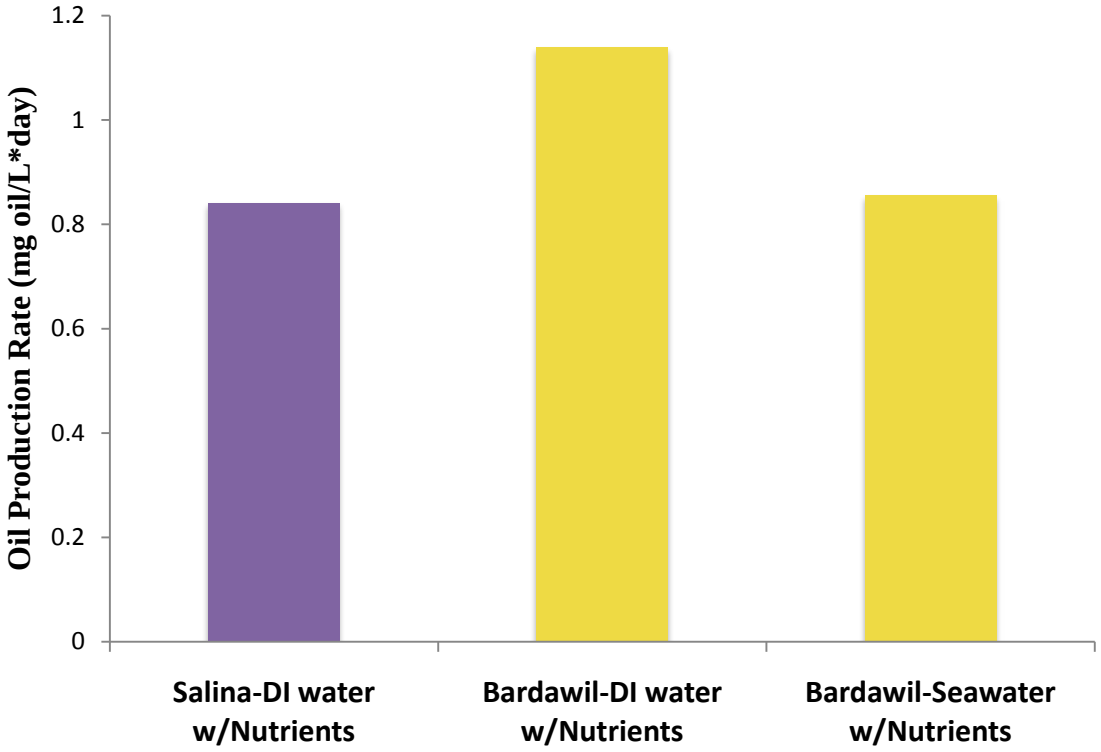

Figure 5 : Oil production rate of algae (mg oil/L solution -day) in Dunaliella Salina and Dunaliella Bardawil grown outdoors.

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