Helios-NRG, LLC

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Project Title	**: Efficient Capture of CO_2 from Fossil Fuel Power Plants using Algae and Conversion to Value Added Products**
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Team Members	**:** ISTC
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Public Summary

The United States, the world's largest energy user and second largest CO_2 emitter, is heavily dependent on fossil energy. In 2014, CO_2 emissions from US coal burning power plants was ~ 1562 MM tons/yr, accounting for 76% of the total US power sector emission[1]. Hence, reducing the CO_2 emission footprint from coal plants is widely viewed as a key element in mitigating global warming. Despite significant interest, implementation of CO_2 capture technologies have been hamstrung by high capture costs which significantly increases the cost of electricity.

In this project, Helios-NRG in collaboration with Illinois Sustainable Technology Center (ISTC) aims to develop a novel, algae based technology to capture CO_2 from coal based power plants and convert it to renewable fuels and other value added products thus enabling substantial reductions in the net cost of carbon capture. The use of algae to capture CO_2 to produce bio-fuels has the promise to offset the key limitations of traditional bio-fuels approach including low productivity, high cost and competition with food supply.

Phase1, aimed at demonstrating technical feasibility, is complete and all Phase1 objectives were met or exceeded. The contaminants in flue gas streams both post-FGD and post-amine were quantified. The CO_2 levels in these two streams are ~12% and ~1% respectively which is much hgher than the ambient concentrations that all algae have evolved on. In addition these streams contain SOX and NOX as significant contaminants. During Phase 1, two preferred algae strains were selected based on their suitability for the flue gas enviroment and potential for high carbon capture. These species were then used in carbon capture tests using existing photo bireactors to simulate a new process. The target CO_2 capture efficiency of 70% was exceeded in these tests and stable operation demonstrated. The algae grown in the project were used in HTL tests. These tests demonstrated that the algae could be converted to biocrude at a high yield of and that the biocrude possessed good heating value (~39 MJ/kg). The other streams from HTL include a CO_2 rich gas stream, an aqueous stream which contains most of the residual nutrients and a bio-char stream. Tests were performed to investigate the feasibility of recycling the HTL waste water to the algae culture. These tests successfully demonstrated the potential for recyling to reduce water and nutrient requirements.

Data obtained in the tests were used to upgrade the model parameters and used to simulate operation of the new process at high carbon capture efficiency. A reasonable set of design and operating conditions were identified that can achieve 90% CO_2 capture from the post FGD flue gas stream. Preliminary economic analysis was performed for CO_2 capture from a 550MW power plant burning sub-bituminous coal. The results showed the potential of the proposed technology to significantly reduce the cost of CO_2 capture compared to current options. The results showed that the utilization of the CO_2 captured to generate high value products can make a step change in the cost of carbon capture.

Plans to advance the technology in Phase2 were developed and potential partners identified.

1. Executive Summary:

The United States, the world's largest energy user and second largest CO_2 emitter, is heavily dependent on fossil energy. In 2014, CO_2 emissions from US coal burning power plants was ~ 1562 MM tons/yr, accounting for 76% of the total US power sector emission[1]. Hence, reducing the CO_2 emission footprint from coal plants is widely viewed as a key element in mitigating global warming. Despite significant interest, implementation of CO_2 capture technologies have been hamstrung by high capture costs which significantly increases the cost of electricity.

In this project, supported by a SBIR grant from the US DOE, Helios-NRG in collaboration with Illinois Sustainable Technology Center (ISTC) aims to develop a novel, algae based technology to capture CO_2 from coal based power plants and convert it to renewable fuels and other value added products thus enabling substantial reductions in the net cost of carbon capture. The use of algae to capture CO_2 to produce bio-fuels has the promise to offset the key limitations of traditional bio-fuels approach including low productivity, high cost and competition with food supply.

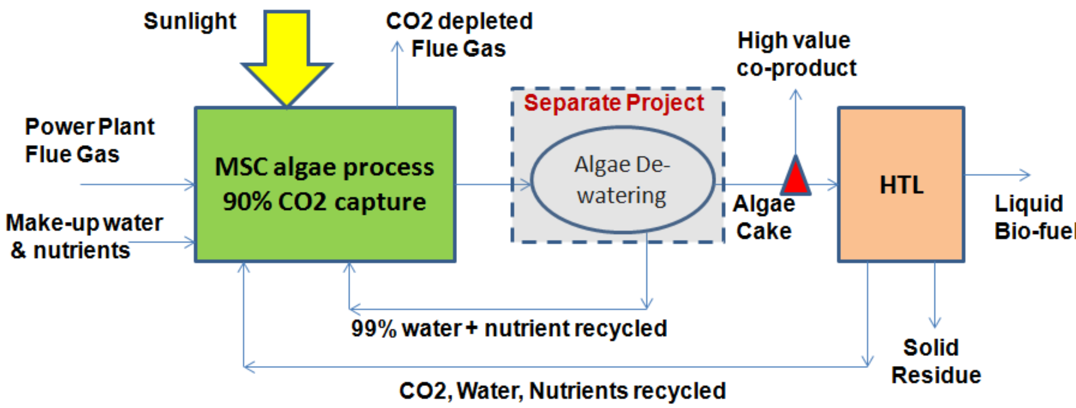

Figure 1: Schematic of Carbon Capture and Utilization Process

A schematic of the overall scheme is shown in Fig 1. Flue gas, after de-sulfurization, enters a multi-stage, continuous flow (MSC) photo-bioreactor (PBR) process where 90% of the incoming CO_2 is captured and used beneficially to accelerate the growth of algae. The algae culture leaving this process is de-watered using a new technology, being developed at Helios-NRG in a separate project, to produce an algae slurry with a solids loading ~25% wt at much lower cost than state of the art. Over 99% of the culture media is separated out in this step and recycled back to the PBR thus greatly reducing the fresh water and nutrient requirements.

Most of the algae leaving this stage is utilized in the Hydro Thermal Liquefaction (HTL) process to produce bio-crude oil. The CO_2, water and nutrients from this step are recycled to the PBR to reduce water and nutrient requirements. In addition, high value co-products are extracted from a small slip stream of the dewatered algae. Helios-NRG has confirmed the production of Astaxanthin and β-Carotene, high value nutraceuticals, by some of our preferred algae strains.

Unique features of the proposed technology which will enable a step change in carbon capture costs are as follows:

- The MSC process enables high CO_2 capture efficiency (~90%) at high algae productivity which, to our knowledge, has not been simultaneously achieved

- The continuous flow MSC process permits steady state operation wherein the productivity, concentration and capture efficiency are invariant with time - a feature not achieved in traditional operation.
- The algae is de-watered using a low cost technology and the resulting slurry fed directly into the HTL thus eliminating the cost and energy requirements for drying.
- The bio-crude produced can be used in existing refineries and significantly lowers carbon capture costs.
- Co-production of nutraceuticals can reduce carbon capture costs further.

The Phase 1 project was aimed at demonstrating technical feasibility of the proposed concept. The project is now complete and all the project objectives were met or exceeded. The contaminants in flue gas streams both post-FGD and post-amine were quantified. The CO_2 levels in these two streams are 25x and 300x of the ambient concentrations that all algae have evolved on - a significant challenge. During Phase 1 we demonstrated the ability of two preferred strains of algae to survive and grow in these high CO_2 environments. Next their ability to survive and grow in simulated flue was with included SOX and NOX in addition to the CO_2 was demonstrated.

Next species H-1903, which appeared to be slightly advantaged in our species selection task, was used in tests to mimic the operation of a 3-stage MSC process in carbon capture. Since the design and operation of the MSC is well beyond the scope of Phase1, three single stage, batch PBR's were used to replicate the conditions in the different stages of the MSC to achieve 70% capture efficiency. The test conditions corresponding to CO_2 capture were established using a Helios-NRG proprietary model developed prior to the project. The results were highly encouraging and >80% CO_2 capture efficiency was measured for both post-FGD (12% CO_2) and post-amine (1% CO_2) tests campaigns which exceeded our goal of 70% capture. In addition, both the algae concentrations and the CO_2 capture efficiency in each stage was shown to be stable over time - critical features of the new MSC process.

The algae grown in the tests were supplied to ISTC for HTL tests. The test campaign at ISTC demonstrated that the algae could be converted to biocrude at a high yield of ~40% and that the biocrude possessed good heating value (~39 MJ/kg) with somewhat better yields obtained at higher temperatures and longer residence times. The other streams from HTL include a CO_2 rich gas stream, an aqueous stream which contains most of the residual nutrients and a small bio-char stream. Tests at Helios-NRG investigated the impact of recycling the HTL waste water on the survival of the algae culture. The results were highly successful and showed that virtually all the HTL waste water could potentially be recycled without compromising algae survival or growth. A substantial number of added tests, beyond original scope, were conducted to see if the HTL water could replace a portion of the nutrients. These tests were also successful and demonstrated potential for reducing the purchase of nutrients for algae culture.

Data obtained in the tests were used to upgrade the model parameters used to simulate MSC operation at high carbon capture efficiency. This model was used to identify a reasonable design and set of operating conditions for the MSC process that can achieve 90% CO_2 capture from the post FGD flue gas stream and subsequently use this for preliminary economic analysis. Preliminary economic analysis was next performed for 90% CO_2 capture from a 550MW power plant burning sub-bituminous coal. Since photosynthesis is driven by sunlight, the analysis assumes the carbon capture occurs during 12 hours/day of natural sunlight. Details of the economic analysis are provided below under Task 4.

While this is not an optimal design, the results show that CO_2 capture with MSC with HTL for bio-crude production can lower t***he net cost of capture to ~$27/ton CO_2.*** Addition of nutraceutical production can potentially lower the cost of CO_2 capture further. For a conservative case investigated ***the cost of capture was further reduced to ~ $6-7/ton CO₂***. While the numbers shown here are preliminary, they clearly show that the utilization of the CO_2 captured to generate high value products is the key to making a step change in the cost of carbon capture.

Table 1 summarizes the actual accomplishments against the original goals for each of the primary objectives.

Objective	Original Goal	Actually Achieved
1	Identify at least one algae species that can tolerate the composition of coal derived flue gas.	Two suitable algae species identified
		Ability to survive in 12% CO2 demonstrated
		Ability to grow in 75ppm each SOX & NOX demonstrated
		High growth rate demonstrated in 12% CO2
2	Demonstrate 1-stg PBR performance consistent with 70% CO2 capture from simulated flue gas using MSC process	Demonstrated concentration stability in each stage with time
		Achieved total CO2 capture >80% in simulated MSC tests
3	Validate HTL operation using algae cake	Algae converted to bio-crude with high yield (~40%)
		Good heating value for bio-crude produced (~39 MJ/kg)
		Ability to utilize HTL waste water in algae demonstrated
4	Conduct preliminary process and economic analysis	MSC Process simulation for 90% CO2 capture complete
		Bio-crude production projected to reduce capture cost to $27/ton
		Nutraceutical co-production projected to reduce capture cost to <$10/ton

Table 1: Actual accomplishments vs Initial Goals

2. Detailed discussion of work and accomplishments by task:

Task 1: Select preferred algae species that can best tolerate the contaminants in flue gas

Subtask 1.1: Define flue gas contaminants & select critical ones

The objective of this task is to determine contaminants present in the gas stream from a coal power plant which might be detrimental to algae. Flue gas varies in its gas composition based on the source of bituminous pulverized coal (PC) and the treatment process implemented at the power plants. The flue gas streams of interest represent post flue gas desulfurization (FGD) and post CO_2 amine capture with ~12% and ~1% CO_2 respectively (300x and 25x of ambient).

Based on the studies conducted by DOE-NETL Office of Fossil Energy, SOx and NOx are identified as major contaminants present in flue gas while heavy metals and organics are identified as minor contaminants. In the Phase I project, emphasis was placed on the major contaminants (SOx, NOx and CO_2) for their impact on algae cultivation. Table 2 summarizes typical flue gas compositions for subcritical PC and supercritical PC power plants with and without amine CO_2 capture.

Case	Subcritical PC (Case B11A)		Supercritical PC (Case B12A)	
V-L Mole Fraction	Post FGD	Post Amine	Post FGD	Post Amine
Ar	0.82%	1.03%	0.82%	1.03%
CO2	12.88%	1.63%	12.88%	1.63%
H2	0.00%	0.00%	0.00%	0.00%
H2O	14.51%	6.71%	14.51%	6.71%
N2	68.54%	86.52%	68.54%	86.52%
O2	3.25%	4.10%	3.25%	4.10%
SO2	76.5 ppm	0.0 ppm	76.5 ppm	0.0 ppm
Nox	76.5 ppm	88.5 ppm	79.7 ppm	91.7 ppm

Table 2: Typical flue gas compositions for coal-fired power plant[1]

Subtask 1.2: Study impact of SOx and NOx

The objective of this task is to systematically investigate the algae survival and growth in SOx and NOx, both of which are present as major contaminants in addition to CO_2. Due to inaccessibility of coal-fired flue gas streams for this Phase I project, the selected major flue gas contaminants (CO_2, SOx, and NOx) were blended into air to produce simulated flue gas streams. High pressured cylinders of pre-mixed SOx-NOx and NOx in air and industrial grade CO_2 were procured from Linde and Praxair respectively. A new test facility with timed light chambers to mimic day/night setting, gas distribution panel and photobioreactors (PBRs) was built for experimental purposes. Two microalgae species (H-1903 and H-0322) were chosen for the contaminant studies. Table 3 outlines the test matrix for the SOx-NOx and NOx contaminants impact on algae survival.

The test matrix was designed based on two flue gas streams of interest - post CO_2 amine capture (1% CO_2) and post FGD (12% CO_2). One of the main challenge for completing this task is the algae survival in the presence of high CO_2 concentration (25 to 300x the ambient CO_2 level). Previous Helios-NRG research demonstrated algae survival at CO_2 levels of ~0.5-5%.

However, the high CO_2 concentration is expected to further decrease the pH of the algae culture, essentially inducing an acidic environment for the algae. Investigations for the impact of CO_2 concentration on algae survival are required due to the step change increase in CO_2 concentration from 5% to 12%. This investigation is discussed in Subtask 1.3.

Test Series	Objective	SOX ppm	NOX ppm	CO2 Level	Flue Gas Stream	Algae Species
1	Increasing NOX Level	0	0	1.0%	Post CO2 amine capture	H-1903
		0	25			
		0	75			
2	Increasing NOX Level	0	0	1.0%	Post CO2 amine capture	H-0322
		0	25			
		0	75			
3	Increasing NOX & SOX Level	0	0	12.0%	Post FGD	H-1903
		25	25			
		75	75			
4	Increasing NOX & SOX Level	0	0	12.0%	Post FGD	H-0322
		25	25			
		75	75			

Table 3: Impact of NOx and SOx-NOx contaminant on algae cultivation test matrix

Algae cultivation with the presence of SOx and NOx gas has not been well documented with the proposed algae strains, and therefore require detailed investigations on their impact on algae growth. Pre-mixed high pressured cylinders with concentrations of SOx+NOx (1000ppm each) and 1000 ppm NOx in air were used for blending to mimic template flue gas compositions. The NOx and SOx/NOx contaminants were increased in steps to determine their impact on algae growth, the cutoff concentration at which growth is inhibited and to determine if additional pretreatment is required to lower the concentrations in flue gas before delivery into algae cultures.

The addition of NOx and SOx/NOx into the algae cultures was carefully monitored as these cultures were used as preconditioned seed cultures for the setup of later experiments. It is essential to maintain healthy cultures free of infection with microorganisms as these accumulate in batch cultures and reduce the overall algae growth efficiency due to competition for nutrients and growing space. Precautionary methods such as utilizing in-line air filters, pasteurization of incoming culture medium, autoclaving of measuring devices, and ensuring good seals on the PBR were employed to minimize infections. Alternative methods such as utilization of UV sterilization of feed culture media, which are more cost effective for large scale operations, will be explored in Phase 2.

Growth rates of control (only CO_2) and experimental cultures (with SOx and NOx) were monitored daily via cell density measurements using a spectrophotometer. Due to the acidic nature of the SOx and NOx gases, the pH of algae cultures was measured to determine its change over time and check impact on algae cultivation. Figure 2(a) and 2(b) shows the H-0322 and H-1903 algae growth over time with 1% CO_2 and 1% CO_2 + 25ppm NOx respectively. The pH of the algae cultures decreased from 8.2 (alkaline) in ambient air to 7.8, indicating slight acidification of the media. Despite this, the presence of NOx did not adversely impact the growth rate, which is encouraging.

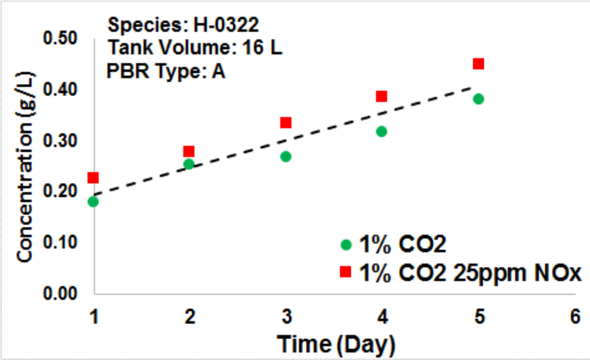

Figure 2(a): Impact of 1% CO_2 and 1% CO_2 with 25ppm NOx on H-0322 algae growth

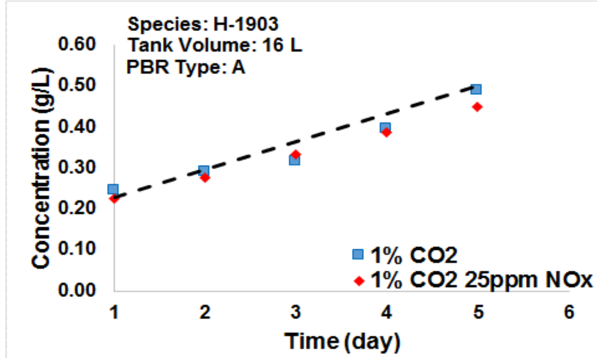

Figure 2(b): Impact of 1% CO_2 and 1% CO_2 with 25ppm NOx on H-1903 algae growth

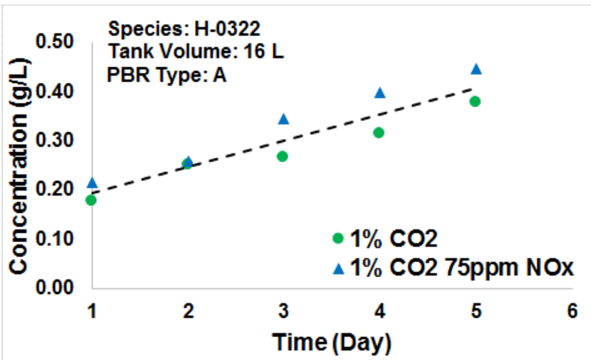

Figure 3(a): Impact of 1% CO_2 and 1%5 CO_2 with 75ppm NOx on H-0322 algae growth

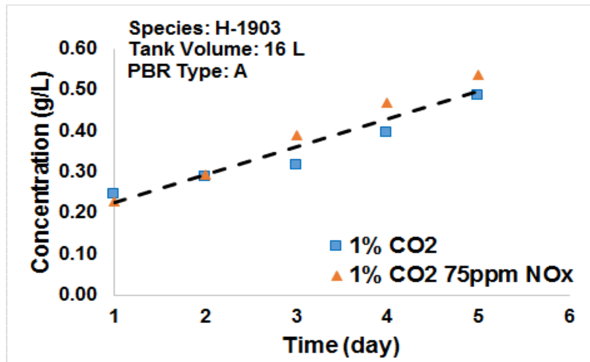

Figure 3(b): Impact of 1% CO_2 and 1%5 CO_2 with 75ppm NOx on H-1903 algae growth

The concentration of NOX was next increased to 75ppm with 1% CO_2, representative of post CO_2 amine capture flue gas, for both H-0322 and H-1903 algae cultures. The presence of 75ppm NOx decreased the pH of the culture further to 7.5. The growth results is highly encouraging, demonstrating the potential for algae survival with the NOx levels expected in post amine capture flue gas.

The next set of tests were aimed at determining algae survival in the much more demanding post FGD flue gas with 12% CO_2 (~300x ambient) and various levels of SOx and NOx. At this stage, in a parallel task (Subtask 1.3), Helios-NRG had demonstrated the survivability of both H-0322 and H-1903 algae at 12% CO_2. Figure 4(a) and 4(b) shows the H-0322 and H-1903 algae growth over time in 12% CO_2 and 12% CO_2 with 25ppm each of SOx and NOx added. The addition of SOx further decreased the pH in the two cultures from 8.2 in ambient air operation to 6.5 and 6.3 respectively, indicating significant acidification of the media. Thus the culture changed from the alkaline media preferred by the algae species to an acidic one. The results are highly encouraging since, despite this, both algae species did not exhibit any growth inhibition as was initially expected. We believe that this is due to natural evolution and conditioning of the chosen algae strains.

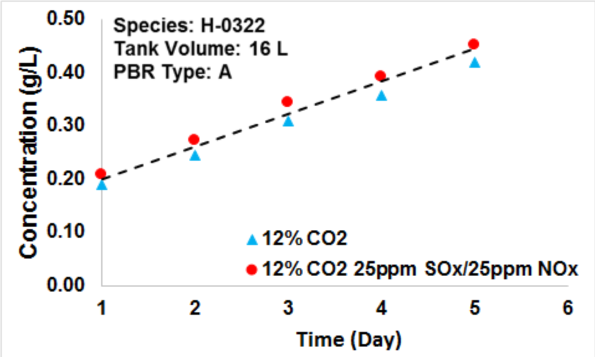

Figure 4(a): Impact of 12% CO_2 and 12% CO_2 with 25ppm SOx and 25ppm NOx on H-0322 algae growth

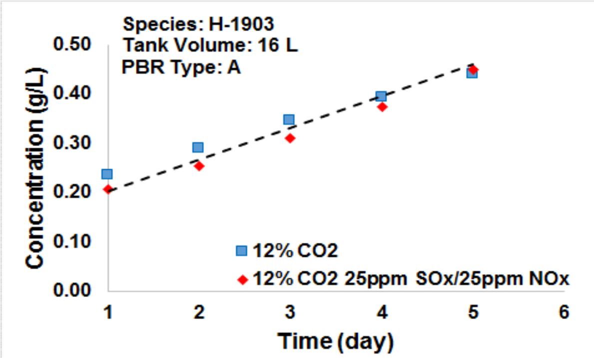

Figure 4(b): Impact of 12% CO_2 and 12% CO_2 with 25ppm SOx and 25ppm NOx on H-1903 algae growth

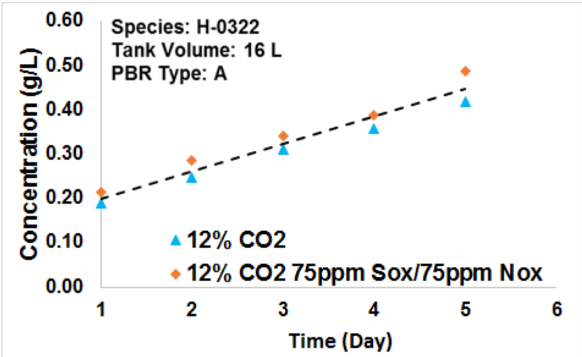

Figure 5(a): Impact of 12% CO_2 and 12% CO_2 with 75ppm SOx and 75ppm NOx on H-0322 algae growth

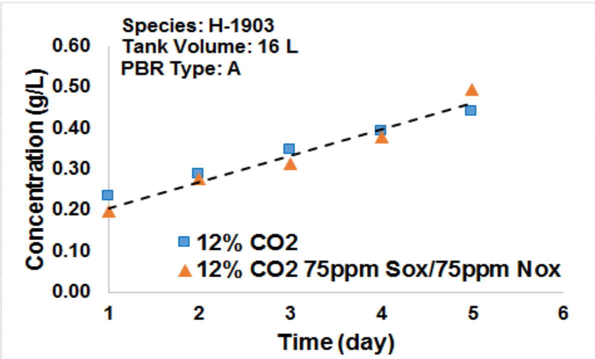

Figure 5(b): Impact of 12% CO_2 and 12% CO_2 with 75ppm SOx and 75ppm NOx on H-1903 algae growth

The final set of tests in these series increased the SOx and NOx concentrations to 75ppm in the presence on 12% CO_2 which is representative of post FGD flue gas. This resulted in the pH of the algae culture decreasing significantly from an original basic solution (pH = 8.2) to a significantly acidic one (pH = 6.1). The results from these tests are highly encouraging and depicted in Figures 5(a) and 5(b). Despite the acidic nature of the solution due to added contaminants, both H-0322 and H-1903 strains demonstrated their ability to survive and grow in the post FGD flue gas stream with no significant inhibition observed. In Phase 2 we plan to extend this work up to 200ppm each of SOx and NOx.

Subtask 1.3: Test different algae species

The objective of this task is to identify various strains of microalgae species capable of being employed in the proposed MSC system based on several primary criteria. The microalgae must be able to tolerate high CO_2 concentration (up to 12% CO_2 which is ~300x ambient), exhibit high growth rate, possess high lipid/carbohydrate content, capable of exhibiting high CO_2 fixation (capture) and have been well characterized. Additional consideration in strain selection is the ability to co-produce high value nutraceutical compounds (astaxanthin and β-carotene), although that is not part of the Phase1 project. We have intentionally focused on naturally occurring microalgae species which do not have the environmental concerns of GMO strains and permit natural evolution for handling various flue gas contaminants. H-0322 and H-1903 were identified as the two most promising species from our portfolio for this project. Table 4 illustrates the test matrix for investigating the impact of CO_2 levels on algae survival and growth.

Test Series	Algae Species	Initial Algae Conc (g/L)	CO2 Level in air
1	H-0322	0.2	1.00%
	H-1903		
2	H-0322		3.00%
	H-1903		
3	H-0322		6.00%
	H-1903		
4	H-0322		9.00%
	H-1903		
5	H-0322		12.00%
	H-1903		

Table 4: Test matrix to study Impact of feed CO_2 concentration on algae

In the experiments, both algae cultures were allowed to grow initially at lower CO_2 feed concentrations, allowing for preconditioning and natural evolution of the parent cells which act as seed cultures for the latter test series. For both H-0322 and H-1903 algae, the high CO_2 concentration was matched with cultures of moderate algae concentrations (0.1g/L and above). This was found to be crucial since additional stress occurred in the algae strains at lower algae concentrations. Hence in the MSC systems the gas flow and liquid flow are counter-current whereby the highest CO_2 concentration gas is fed into Stage 3 which has the highest algae concentration.

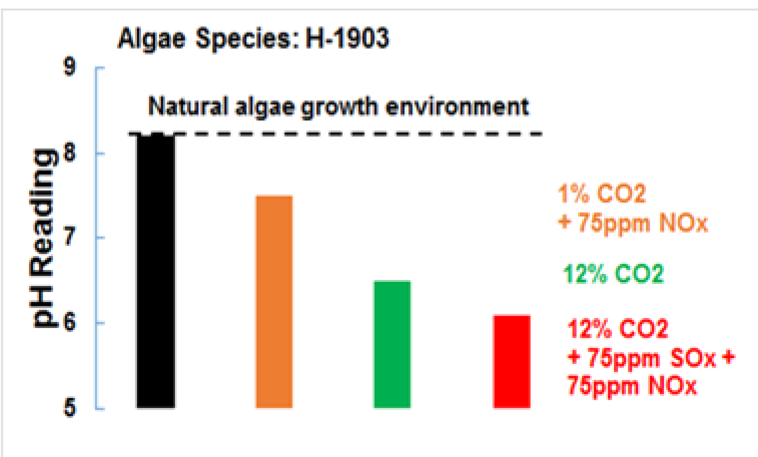

Figure 6: Impact of flue gas contaminants on H-1903 algae culture pH

A key challenge is that many algae species of interest, including the ones selected, prefer an alkaline environment. However as the CO_2 concentrations increase, the culture solution becomes increasingly acidic which can result in growth inhibition[2] or cell death. Acidification of media is significantly greater in the presence of NOx and SOx (Figure 6). In the experiments, the pH for the H-1903 algae culture decreased significantly from 8.2 in ambient air to 6.5 at 12% CO_2. The presence of additional 75ppm SOx and 75ppm NOx further reduced the pH value to 6.1. One of the implications of the acidification of the algae cultures is such that this weakens the CO_2 bio-fixation of the cells and eventually reduces CO_2 capture efficiency due to the inhibition of carbonic anhydrase (CA)[2]. The results are very encouraging as both selected algae species were successfully adapted to the acidic media. An unexpected benefit found during the current work was that the high CO_2 values helped maintain culture's health by asphyxiating aerobic organism, thus inhibiting bacteria and other pathogen growth in the culture.

Figure 7(a) and 7(b) illustrates both H-0322 and H-1903 algae growth over time with 1% and 12% CO_2 feed gas streams representative of post amine capture and post FGD flue gas CO_2 levels. These results are highly encouraging as both species successfully tolerated the high CO_2 levels and still maintained healthy growth rates. Note that in Figure 7(b) a hypothetical inhibited growth curve is included depicting what might have been expected if 12% CO_2 prevented normal growth. Fortunately, this was not the case.

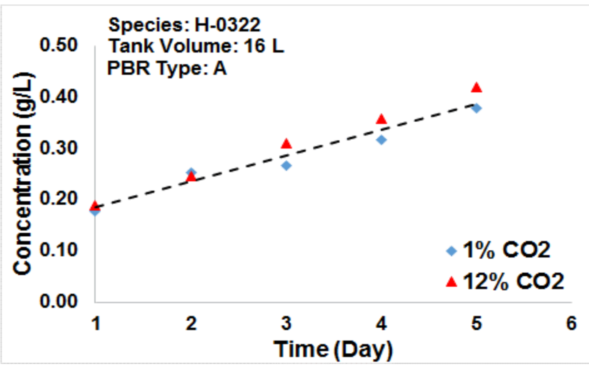

Figure 7(a): H-0322 algae growth at 1% and 12% CO_2 feed gas stream

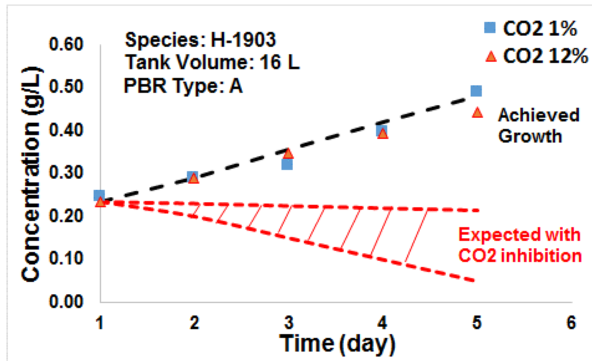

Figure 7(b): H-1903 algae growth at 1% and 12% CO_2 feed gas stream

Between the species tested, H-1903 is believed to show greater potential for scale-up due to its higher growth rates, easier cultivation and slower settling rate. As discussed later under Task 3, this species also performed somewhat better in the HTL tests. High algae growth rates are highly dependent on the intensity of light available for effective photosynthesis. Helios-NRG utilized a specially designed PBR capable to accurately measuring various intrinsic algae parameters used in Helios-NRG's proprietary algae model for predictions. Figure 8 illustrates the very high growth rates measured under ideal conditions in the lab using fluorescent lighting. It is seen that the % algae weight gain per day increases with increasing light intensity and finally plateaus, indicating the maximum algae growth rate achievable. For reference, it should be noted that unobstructed sunlight has a mid-day intensity of ~ 10,000 FC and the range of light intensities reported for green-houses range from a low of 1000 FC to a high of 5000 FC. Hence the light intensities used in the lab were conservative compared to natural sunlight.

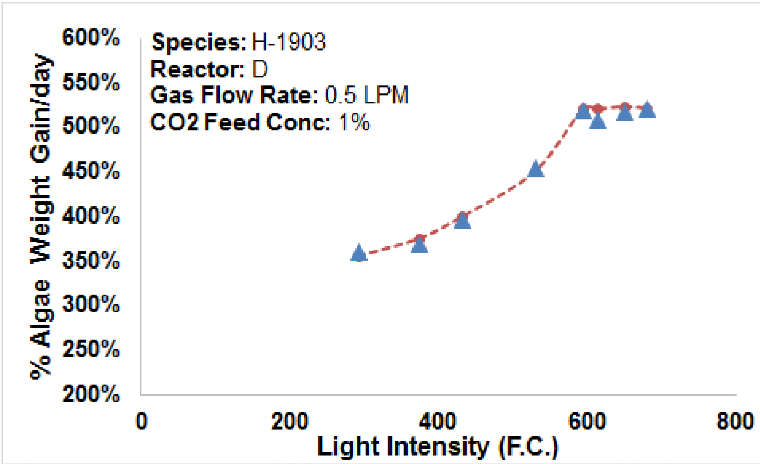

Figure 8: Impact of light intensity on H-1903 %algae weight gain per day

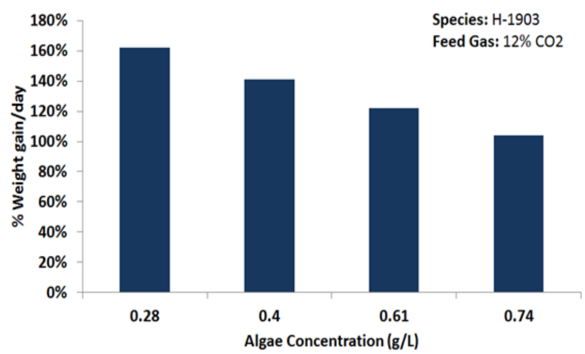

Figure 9(a): Impact of H-1903 concentration on rate of %weight gain

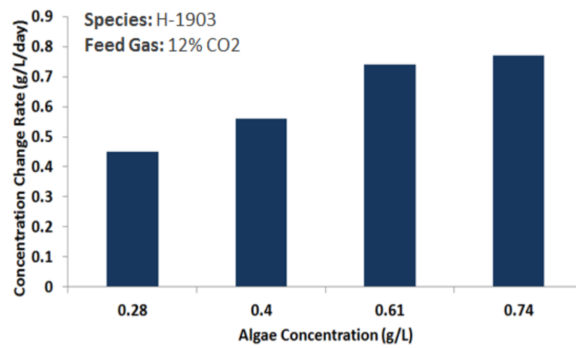

Figure 9(b): Impact of H-1903 concentration of rate of concentration change

Figure 9(a) and 9(b) illustrates the impact of various algae concentrations on growth rates at a feed gas concentration of 12% CO_2. Figure 9(a) shows that the rate of weight gain decreases as algae concentration increases. This is as expected due to the increase in light attenuation occurring across the algae culture, decreasing the growth efficiency over time. Hence, in batch reactors, the high algae growth rates diminish over time with increasing algae concentration. This reduction in growth rate is overcome in the MSC process where the algae concentration in each stage is invariant with time.

Figure 9(b) shows the increase in the rate of algae concentration change as the concentration increases. It is observed that the rate of concentration increase tends to asymptotically level off at higher concentrations. These results indicate that a traditional batch PBR design which is optimal on Day-1 will not be optimal in later days. This deficiency is addressed in the MSC process which features continuous culture flow system and multiple stages wherein the algae concentration in each stage is invariant with time and is designed to enhance growth based on the CO_2 concentration and light penetration of each stage of algae concentration.

Table 5 summarizes the results for the two species of algae. While both species are feasible for the proposed technology, H-1903 is potentially a better choice.

Features Related to Project Preference	H-1903	H-0322
Grows well in 12% CO2, and 75 ppm SOX and NOX	Yes	Yes
Highest level of HTL generated oil content (uninduced)	Yes	Slightly Lower
Algae to contain lipids to about 50% cell mass (induced)	Yes	Yes
Contains β-Carotene	Yes	Yes
Contains Astanxnthin	Yes	Not detectable
Contains desirable DHA oil	Yes	N/A
Settling rate	Moderate	Faster
Cells stay in suspension more easily	Yes	More difficult
Commonly grown algae commercially	No	Yes
Used in EPA bio-toxicity tests	Yes	N/A

Table 5: Comparison of the selected species

Task 2: Demonstrate CO_2 capture

Subtask 2.1: Model simulations of MSC process

The objective of this task is to utilize the proprietary Helios-NRG PBR model for the MSC process to simulate a process capable of 70% CO_2 capture. In the model of the MSC process the feed gas flow and culture flow are countercurrent for the reasons explained in Subtask 1.3. A key attribute, predicted by the model, is that as a consequence of the continuous flow process, the algae concentration in each stage will achieve a steady-state value over time.

The model inputs include species dependent algae parameters including intrinsic growth rates, light attenuation, stage depths, feed gas flow rate and feed CO_2 concentration. Output from the simulation includes the resultant stage algae concentration and CO_2 concentration, culture transfer rate and overall CO_2 capture efficiency based on the given operating parameters.

Figure 10 shows results of the simulation for a typical lab test with 1% CO_2 in the flue gas and equal volume distribution among the stages. It shows that the CO2 capture efficiency increases from stage 1 to 2 to 3. This is the result of higher algae concentration in the higher stages coupled with good light utilization. Further the CO_2 capture efficiency in each stage increases as the gas flow rate is reduced. While this trend is expected, it is not possible to predict the actual value without the use of a model such as the one used. The results show that the target 90% overall CO_2 capture is achievable at a lower gas flow rate.

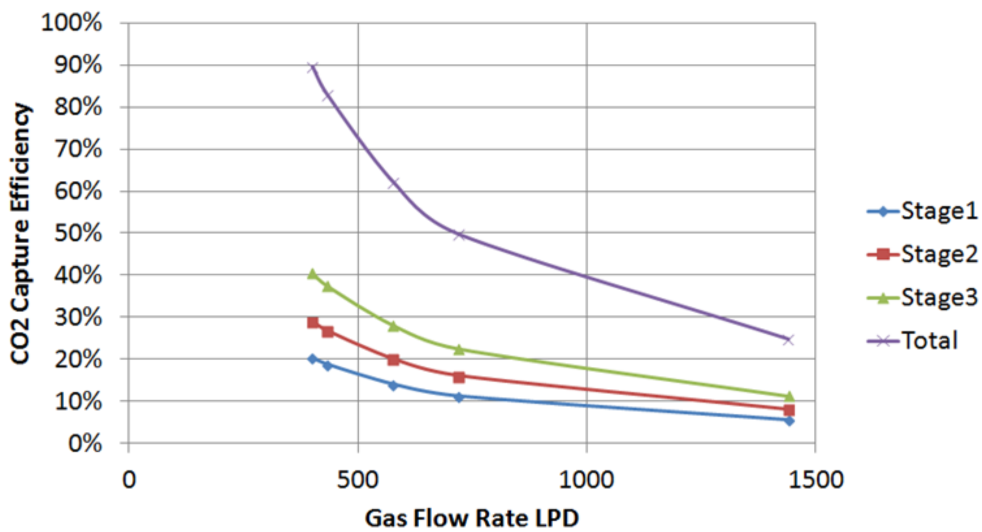

Figure 10: Impact of gas residence time on CO_2 capture efficiency for post amine flue gas Species: H-1903; Feed Gas = 1%

Figure 11 shows MSC simulation results corresponding to 12% CO_2 in the flue gas. It shows that if the above design is used on this feed stream, the CO_2 capture efficiency will fall below 10%. However, by increasing the PBR volume to 144L and the water flow to 8LPD a 90% CO_2 capture efficiency can be achieved. These two cases highlight the importance of MSC design and operation on the CO_2 capture efficiency and the reason why high capture efficiency and good productivity are difficult to achieve empirically by trial and error.

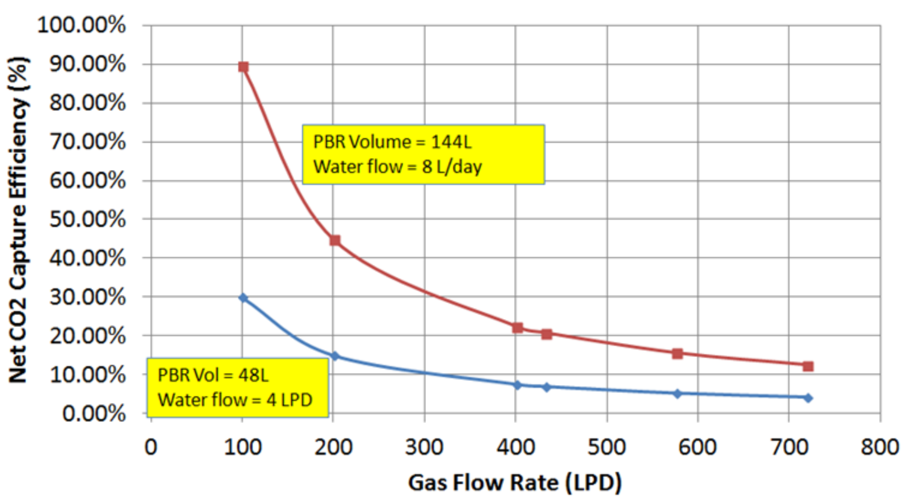

Figure 11: Importance of MSC design and operating variables on CO_2 capture efficiency for post FGD flue gas. Species: H-1903; Feed Gas = 12% CO_2

Subtask 2.2: Set up single stage tests to mimic MSC process

Single stage batch reactors were set up based on the results from the simulation in Subtask 2.1 and placed in a time-controlled light chamber to mimic natural light/dark cycle. Extensive efforts were allocated to maintain the health of the algae cultures free of any bacteria or pathogen. The culture media were pasteurized up to 80°C before the introduction of algae seeds to eliminate any possible bacteria present. A submersible pump was utilized to ensure uniform mixing in the PBR tank. The algae concentration for each stage was independently established using culture from other algae PBR's. The PBRs were sealed to avoid introduction of airborne contaminants into the culture and to capture the exiting gas for measurement. Feed CO_2 concentration to each stage was individually established by metering CO_2 into the feed air stream and the inlet and outlet stream concentrations were measured using an IR analyzer. The PBRs were operated in batch mode with periodic liquid transfers based on simulations from Subtask 2.1 to mimic the MSC process and algae concentration monitored daily through a spectrophotometer. Algae cells from each of the stages were examined periodically under a microscope for presence of contaminants to verify culture health.

Subtask 2.3: Validate CO_2 capture efficiency

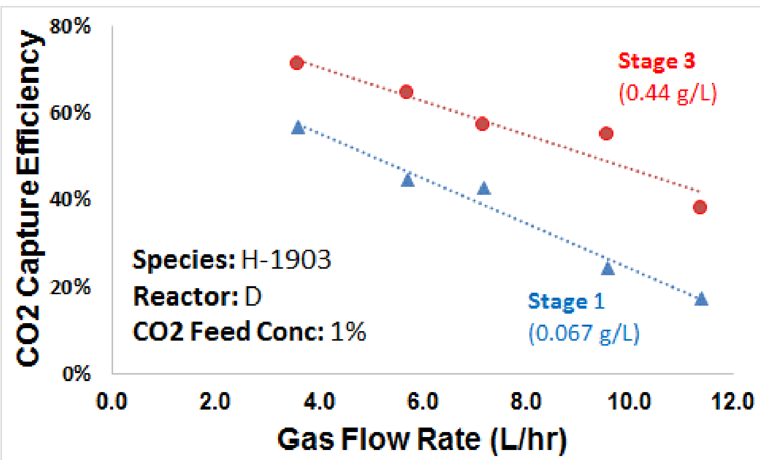

Figure 12: Impact of feed gas flowrate on CO_2 capture efficiency

Model simulations from Subtask 2.2 were utilized to set up experiments to validate the CO_2 capture efficiency of the MSC process. The impact of the feed gas flowrate on the CO2 capture efficiency is illustrated in Figure 12. As expected, the CO_2 capture efficiency in each stage increases with gas residence time. A feed gas flowrate was chosen for validating the CO_2 capture based on predicted post CO_2 amine capture in the MSC process. In this experiment, each of the MSC stages were fed with a gas stream of only 1% CO_2, and the exiting CO_2 concentration measured with an IR-CO_2 analyzer.

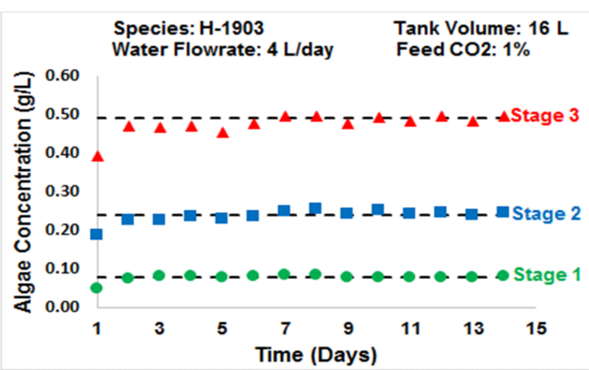

Figure 13(a): H-1903 algae concentration for post CO_2 amine capture (1% CO_2 only) MSC process

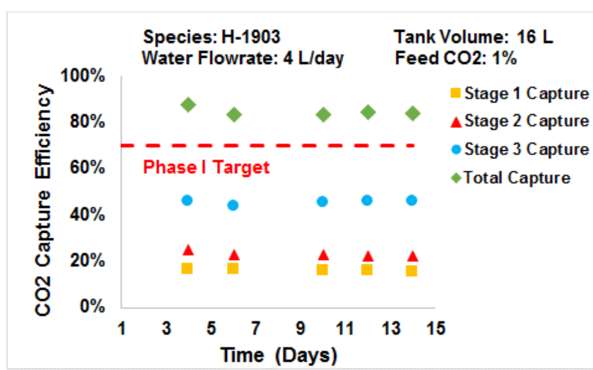

Figure 13(b): H-1903 algae CO_2 capture efficiency for post CO_2 amine capture (1% CO_2 only) MSC process

Figure 13(a) and 13(b) show results from the single-stage batch PBR test results using H-1903 algae mimicking the CO_2 capture from a feed stream with 1% CO_2 (post amine), without the presence of SOx and NOx contaminants. Figure 13(a) shows that stable algae concentration is maintained in each stage over a period of time - a key aspect of the MSC process to maintain high productivity and high CO_2 capture efficiency. The H-1903 algae culture was observed to remain healthy over this time and accumulation of pathogens were prevented - this is one of the benefits of the liquid transfer in the process. Figure 13(b) illustrates the high CO_2 capture efficiencies achieved in each stage over time. The CO_2 capture efficiency based on post CO_2 amine capture (1% CO_2 only) stream in the MSC process is estimated to be ~84%, exceeding the Phase I target of 70%. In addition, it is noted that the CO_2 capture efficiency in each stage is stable with time, thus demonstrating a key feature of the MSC process.

Model simulation work from Subtask 2.2 was utilized to predict the algae concentrations for the CO_2 capture based on post FGD stream with 12% CO_2. This experiment was significantly more challenging due to the high CO_2 concentration present in the feed gas. The CO2 capture efficiency decreases as the feed CO_2 concentration increases due to the inhibition of carbonic anhydrase (CA) mentioned earlier. However, based on results in Figures 11 and 12, the gas flow rate and PBR volume were adjusted to increase capture efficiency.

In this experiment, the CO_2 concentration into each stage was individually established such that the feed to Stage 3 was ~12% CO_2, the feed gas into Stages 2 and 1 were based on the CO_2 levels in the streams exiting Stage 3 and Stage 2 respectively, thus mimicking the MSC process. Figure 14(a) and 14(b) illustrate the results.

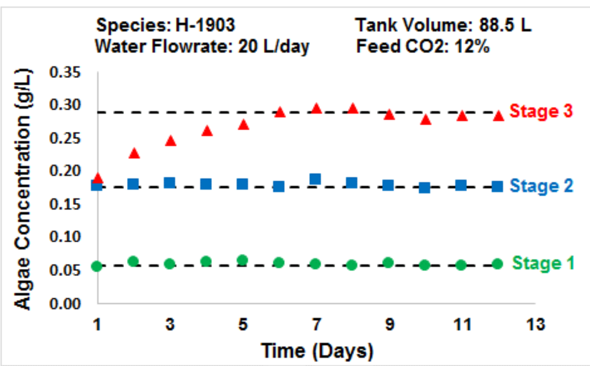

Figure 14(a): Stage algae concentration vs time in post FGD MSC process tests

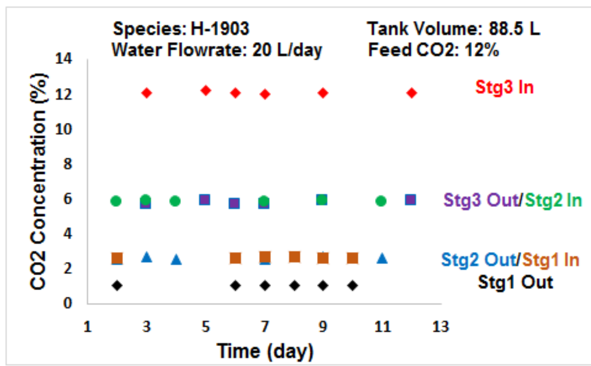

Figure 14(b): Stage and overall CO_2 capture efficiency in post FGD MSC process tests

Figure 14(a) shows that the algae concentration in each stage is stable over time - this validates one of the key assumptions underlying the MSC process. For stage 3, we intentionally started the algae concentration at a lower value and the results show that the concentration increases to the steady state value over time. Figure 14(b) illustrates the inlet and exit CO_2 concentration to/from each stage is stable over time. The overall MSC CO_2 capture efficiency based on these single stage tests is estimated to be ~90%, substantially exceeding the Phase I target of 70%.

Figure 15 illustrates the physical representation of the proposed MSC process representing this test. As explained under Task 4, this does not represent the optimal design - but one that achieves a high capture efficiency.

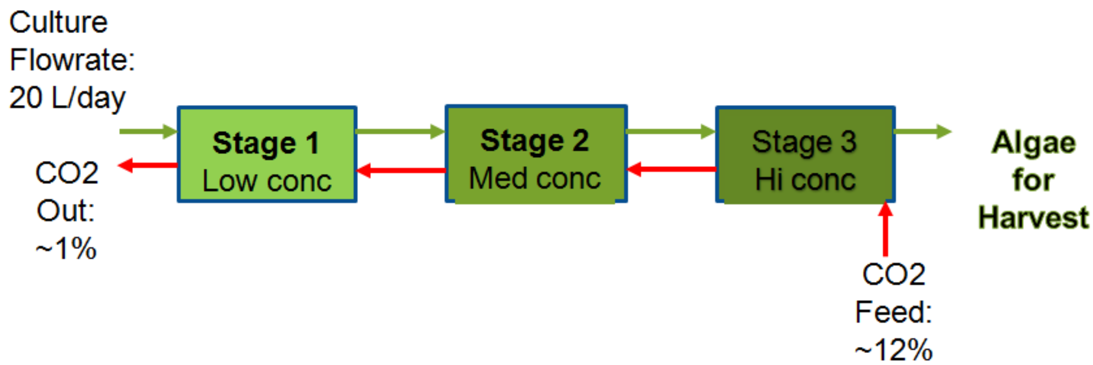

Figure 15: Physical representation of the MSC process tested using 1-stage PBR's

Although the proposed MSC process has not been fully optimized, the experiments conducted demonstrates the potential for the MSC process to achieve high and stable CO_2 capture efficiency, comparable to currently commercial technologies, using an algae based approach. To our knowledge, this has not been done before.

Task 3: Preliminary assessment of HTL performance using algae feedstock

This task evaluated hydrothermal liquefaction (HTL) as a means of making biofuel intermediate products (bio-crude) from the algal biomass grown in the CO_2 capture processes described earlier. This task was comprised of three main sub-tasks:

- **Subtask 3.1: Assess the effect of HTL operating conditions on process performance**
- **Subtask 3.2: Assess effect of feedstock characteristics on HTL process performance**
- **Subtask 3.3: Characterization of HTL aqueous product**

The materials, methods, results and conclusions for the work done in completing these three sub-tasks are detailed below.

Materials and Methods:

Two 500 gram dry samples for each of two algae species (H-0322 and H-1903) were obtained from Helios NRG, and stored at 4^{o}C prior to their use in HTL testing. The HTL tests were conducted with a stainless steel, high temperature and pressure batch reactor with an integrated magnetic drive stirrer (Figure 16). Each of the algal biomass samples was subjected to HTL under a variety of temperature (240-300 ^{o}C) and reaction time (15-60 min) conditions, with each test done at least in duplicate. A mixture of 20 g algal biomass and 80 g deionized water was used in each HTL test. After the feedstock mixture was loaded, the reactor was sealed the headspace was purged 3 times with nitrogen gas prior to heating to the desired reaction temperature.

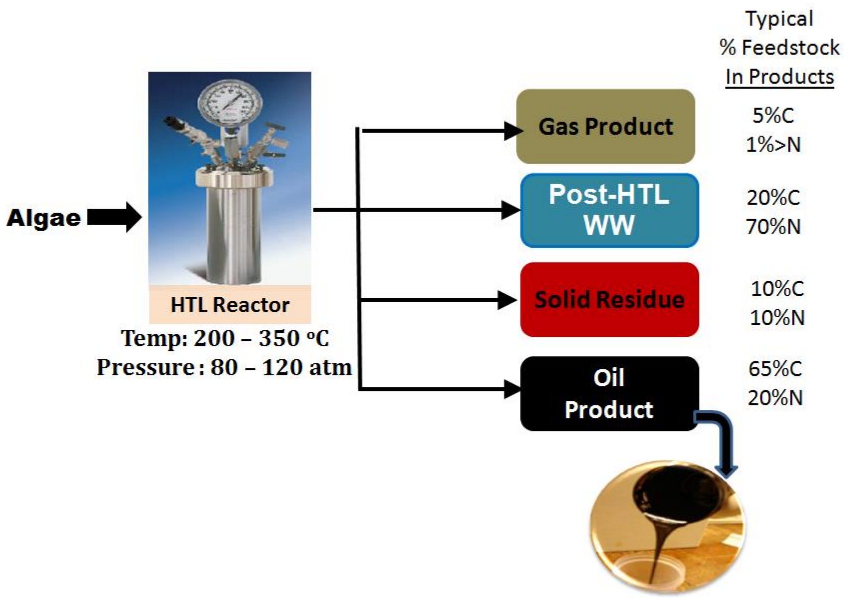

Figure 16: HTL reactor, operating conditions and typical products

After each HTL reaction, the solid, aqueous, and oil products were collected by physico-chemical separation techniques. First, a Whatman glass-fiber filter was used to separate the aqueous product, which was defined by the ability to pass the filter. The fraction that did not pass the filter was subjected to soxhlet extraction according to ASTM Standards D473-02 and D4072-98 to determine the biochar solids and bio-crude oil fractions. The HTL product yields were calculated on the basis of the mass of dry volatile solids (VS) in the algal feedstock. The higher heating value (HHV) of the bio-crude oils, feedstock, and biochar solid residues were estimated using the *Dulong* formula:

$$HHV = .3383 * C + 1.422 * \left(H - \frac{O}{8}\right)$$

, where C, H, and N are the mass percentages found in the elemental composition test using a CHN analyzer (CE-440, Exeter Analytical Inc., North Chelmsford, MA). The amount of oxygen was approximated assuming that all the remaining mass not measured in CHN analysis was oxygen. Net energy recovery is defined as the bio-crude oil HHV divided by the AB HHV.

The two algal feedstocks were characterized in terms of their volatile solids content (VSS), moisture content, and primary elements (C,H,N,O) using CHN analyzer (CE-440, Exeter Analytical Inc., North Chelmsford, MA). These properties were then compared with the analytical results from the HTL tests to identify the impact of the feedstock on the HTL process performance and if one of the algal feedstocks is preferable. To measure the dry solids content and the ash content, biomass was dried in a 105°C oven for one week and subsequently put into a 550°C oven overnight, respectively. Volatile solids content was then calculated based on the mass difference between the dry solids and ash.

A composite sample of the HTL aqueous product from several advantageous HTL conditions was characterized in terms of pH, COD, and key nutrient species. All of these water quality analyses were conducted in accordance with the Standard Methods for the Examination of Water and Wastewater[5]. Subsequently, the HTL aqueous product was used to grow algae and confirm the ability to recycle nutrients.

Results and Discussion:

Effect of HTL Operating Conditions on Oil Yield

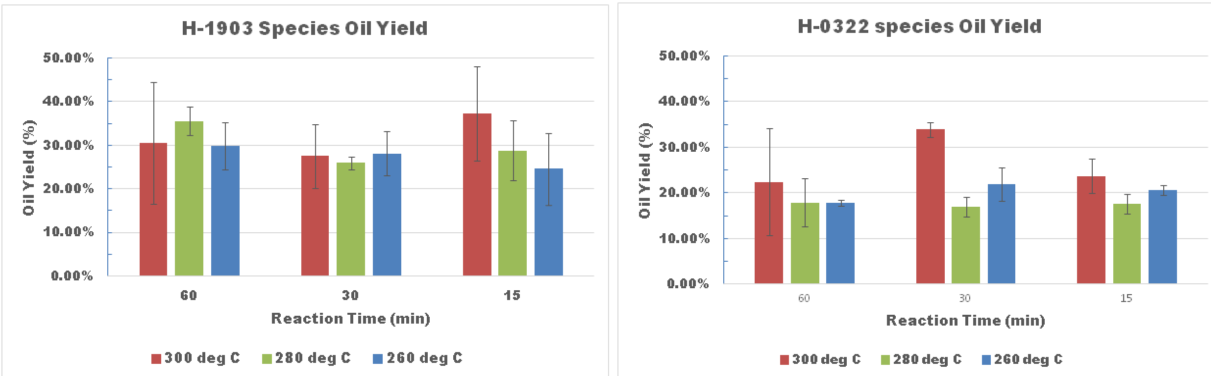

Figure 17: Bio-crude Oil Yield for Two Algae Species over the Range of HTL Operating Conditions Tested

Figure 17 presents the average and standard deviation of bio-crude oil yield data for the two algae species over a range of HTL operating conditions. The range of HTL temperature and reaction time conditions were selected based on past experience with a variety of algal biomass samples. HTL is a very complex set of chemical reactions and to date it is difficult to predict the best operating conditions for any given feedstock with precision. Thus, empirical data as provided in Figure 17 is generally needed to determine advantageous HTL operating conditions, which are specific to the feedstock. For H-1903 algae species, the best oil yield of 37% was achieved at 300^{o}C and 15 min of retention time, and a similar oil yield of 36% was achieved with HTL operations at 280^{o}C and 60 min of retention time. For H-0322 algae species, the best oil yield of 34% was achieved at 300^{o}C and 30 min of retention time, and all other operating conditions had significantly lower oil yields. The HTL results with both algae samples are promising and fall towards the middle of the range we have observed with other microalgae samples. Looking forward, it is likely that additional detailed work on optimizing the HTL process could further increase the reliable bio-crude oil yield.

Effect of Algae Feedstock Characteristics on HTL Oil Yield

Although the maximum oil yields of the two species were fairly similar, the H-1903 species generally had better oil yield over a wide range of conditions. This suggests that this species would be more robust and reliable choice from the perspective of HTL conversion processes. However, the results in Figure 17 showed an above average amount of variability between the replicates as represented by the standard deviation error bars. When analyzing the data, it became apparent that much of this variability was related to fact that we received two different samples of each type of algae, and the second set of algae samples had a lower conversion efficiency. Specifically, the second batch of algae had a lower oil yield in 17 out of 18 conditions shown in Figure 17. Thus, the variability in oil yield was most likely related to underlying variations in the feedstock, possibly moisture content. Because of the feedstock variability, the relative advantages of the H-1903 over H-0322 should be viewed as tentative, and future work should better characterize the extent and impact of feedstock variability on the HTL process.

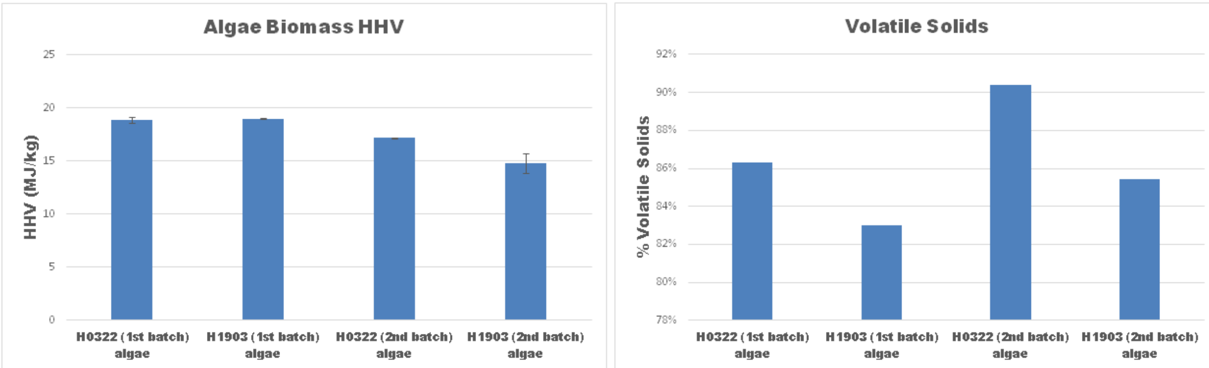

Figure 18: Algae Biomass Characteristics for the two species

To better understand the differences in the algae samples, data on the biomass characteristics of both batches of the two algae species were analyzed. Specifically, volatile solids content and the high heating value (HHV) of the various algae samples were compared to assess potential effects on the HTL process, which is provided in Figure 18. The volatile solids ranged from 83% to 90%, with the H-0322 algae samples having higher values in both batches. The H-1903 values for volatile solids did not change between the two batches and the H-0322 had a higher value in the second batch. Since higher volatile solids content is generally correlated with improved the bio-crude oil yield, these data do not explain the lower oil yields observed with the second batch of algae. In contrast, the heating value data does indicates some differences in the algae biomass batches that could explain the lower oil yield of the second batch. Specifically, the HHV of the second batch was 9% and 22% lower for the H-0322 and H-1903 algae species, respectively, and the lower heating value means there is less energy that can be harvested from the feedstock into bio-crude oil. Given that HHV was calculated based on the content of C, H and N of the feedstock, it is most likely that the second batches of algae had a higher O content.

<u>Effect of HTL Operating Conditions and Algae Feedstock on HTL Bio-crude Oil Quality</u>

Another important factor in assessing the performance of HTL processes is to analyze the quality of the bio-crude oil. One important measure of oil quality is the heating value, which is presented in Figure 19 for both algae species and all of the HTL operating conditions tested in this study. All the oil samples fell in a very narrow range of higher heating values (HHV) from 36.2 - 38.3 MJ/kg. Note that vertical axis of Figure 19 is focused in on this range, because the differences between samples would be difficult to see if the full value range was used. These HHV values represent good results for HTL bio-crude oil and are approximately 85 - 90% of the HHV for conventional petroleum. There was a general trend towards increased HHV as the HTL temperature or reaction time increased, but there were a few exceptions to this general trend. The H-1903 algae samples were on average about 3% higher than the H-0322 algae samples, and this difference was fairly consistent across all tested HTL conditions.

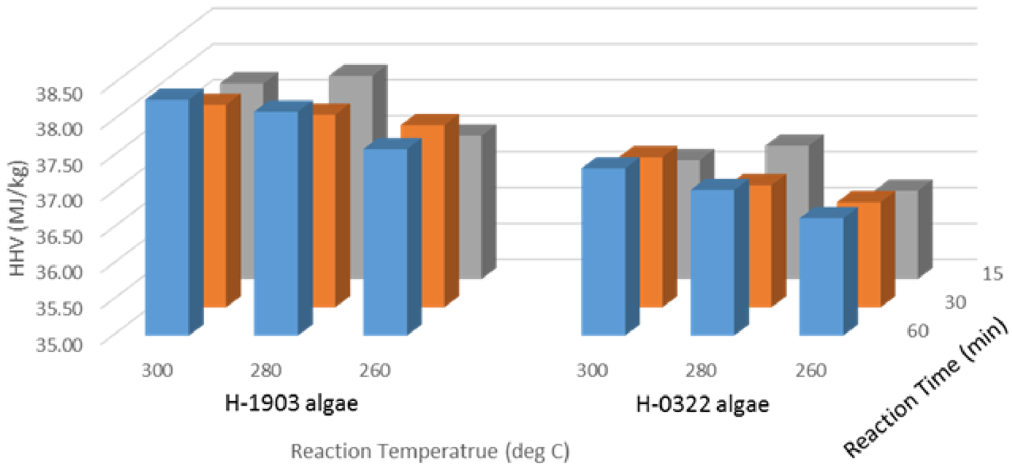

Figure 19: HTL Bio-crude Higher Heating Value (HHV) for Two Algae Species over the Range of HTL Operating Conditions Tested

Effect of HTL Operating Conditions and Algae Feedstock on HTL Biochar Solids Yield

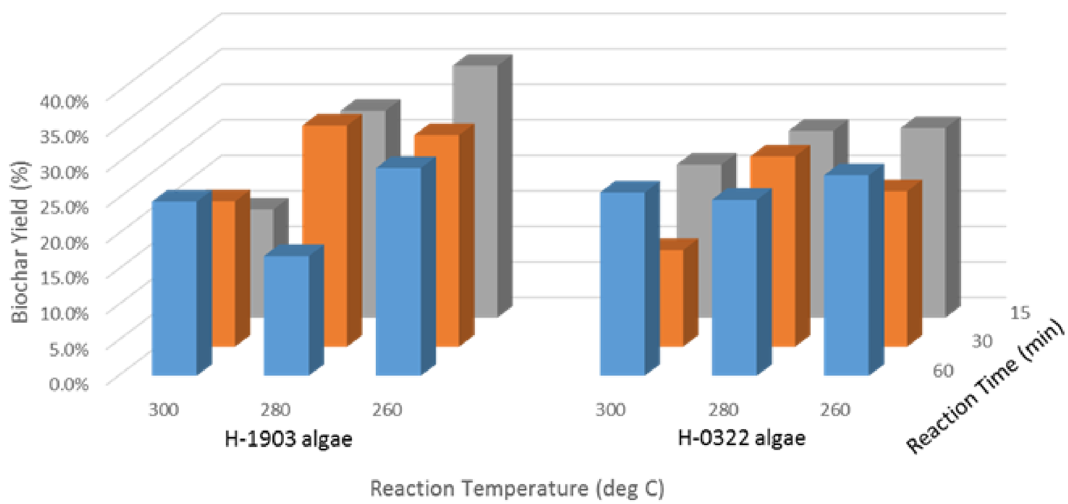

Figure 20: Bio-char Solids Yield for Two Algae Species over the Range of HTL Operating Conditions Tested

A secondary by-product of HTL is the biochar solids, which can be readily separated from the oil and aqueous products by sedimentation or filtration. The biochar product of HTL consists of some residual organics that precipitate together with inorganic salts and metals that were in the original feedstock. Figure 20 presents the average yield of biochar oil yield data for the two algae species over a range of HTL operating conditions. These data show that the range of biochar yields ranged from 14%-36%, and the lowest values of char formation were generally correlated with high yields for bio-crude oil. This is expected because the more material that partitions to the oil the less material is available for the biochar. For both algae species, there was a general trend towards more biochar when the temperature or reaction time was lower.

However, there were several exceptions to this general trend. On average the H-1903 algae species has a slightly higher biochar yield (+2%), but once again there were several exceptions to this trend. As noted earlier, the H-1903 algae had a slightly lower volatile solids content (-5%) and thus was more ash content, which likely explains the slightly higher biochar yields. The beneficial reuse of biochar from hydrothermal processes is a currently an active area of study, but there is not yet a proven and accepted commercial solution. Possible uses that have been studied include land application as a soil amendment[6] or use as an adsorbent base material[7]. Disposal in a landfill or with coal ash fines would have a higher cost and less benefit.

HTL Aqueous Product Characterization

The other major output of HTL is the aqueous product, which is the largest stream on a mass basis because of the high water content of typical feedstocks. Typically, the HTL aqueous product accounts for 90% or more of the total wet feedstock mass, and it includes significant concentrations of residual organic and inorganic compounds that are dissolved as the feedstock water moves through the HTL process. Our team's previous work has highlighted the significant advantages and potential benefits of recycling HTL aqueous product back to algae cultivation[8]. In this project, the aqueous product from several of the most promising HTL operating conditions were blended together, to make a composite sample that was used in algae cultivation experiments. The key water quality parameters for the composite HTL aqueous sample are summarized in the Table 6.

Water Quality Parameter	**Average Value**	**Standard Deviation**
Chemical Oxygen Demand (COD), g/L	**87.6**	**± 13.2**
Ammonia Nitrogen, g/L as N	**4.19**	**± 0.08**
Total Nitrogen, g/L as N	**11.5**	**± 0.86**

Table 6: Key Water Quality Parameters for the Composite HTL Aqueous Product Sample

As shown in this table, the HTL aqueous product has a high organic content (87.6 g/L of COD), which is a bulk measure reflecting the maximum amount of oxygen needed for aerobic wastewater treatment. When recycled, these organics can support heterotrophic growth of algae. The ammonia nitrogen content (4.18 g/L) is also high in comparison to typical wastewaters, and represents a readily available source of nutrients for the growth of algae. Past experience with HTL aqueous products has shown that ammonia is the only significant inorganic nitrogen compound, and thus the total the total nitrogen value (11.5 g/L) shows that there is a significant amount of organic nitrogen content present. This nitrogen is not readily available to support algae growth, but it can be broken down slowly over time to inorganic nitrogen sources that are readily used by algae.

Recycle of HTL aqueous product to algae culture

The overall objective is to determine the feasibility of recycling the waste aqueous stream from HTL to the algae culture to reduce the need for purchased nutrients and mitigate disposal costs. However, the HTL liquid also contains additional organic compounds formed during HTL operation whose impact on algae is unknown. Algae survival in the presence of nutrient rich HTL aqueous phase was investigated in a series of tests. HTL aqueous phase was provided by ISTC from their experiments and was used as received without additional pretreatment. H-1903 algae species was selected due to its inherent advantages such as high growth rate, high CO_2 capture efficiency and high oil yield content. The original plan was focused on understanding if recycling it would jeopardize the survival of algae species. However, as reported below, we were able to perform a substantial number of added tests, beyond original scope, to assess both survival as well as potential for cost savings by commercial nutrient replacement.

Table 7 outlines the test matrix designed to assess the potential for HTL aqueous phase recycle to algae. The commercial nutrients for algae cultivation were obtained from Proline F/2 Algae Food and delivered in two parts; Part A and Part B. Part A is trace elements (micronutrients) and Part B is nitrate, phosphate, and Vitamin B complex (macronutrients). In each test series in Table 7, a control culture was maintained with 2.5mL of Part A and 7.5mL of Part B, both of which are in excess to ensure sufficient availability of nutrients. Experimental cultures have a fixed volume of Part A (2.5mL) and varying volumes of Part B and HTL aqueous phase. It should be noted that the HTL results at ISTC showed that the aqueous phase produced corresponds to ~2mL per liter of the original algae culture grown. However in the following experiments, the range of HTL aqueous phase used spanned a much higher range to assess impact on algae survival and growth. All the experiments were conducted in 12% CO_2 in air.

Test Series	Algae Species	Initial Algae Conc (g/L)	Commercial Part A (mL)	Commercial Part B (mL)	HTL Liquid (mL)
1	H-1903	0.1	2.5	7.5	0
		0.1	2.5	2.5	10
2	H-1903	0.1	2.5	7.5	0
		0.1	2.5	2.5	20
		0.1	2.5	1.2	40
3	H-1903	0.1	2.5	7.5	0
		0.1	2.5	1.2	80
		0.1	2.5	0	80

Table 7: Test matrix to evaluate impact of HTL liquid on algae growth

The main potential challenge in these experiments is the presence of inhibitory components formed during HTL such as phenols which could harm the algae growth[9]. The HTL aqueous was utilized as received without further pretreatment. The 1st test series aimed at demonstrating the survival of H-1903 algae with the added HTL aqueous phase. Figure 21 illustrates the H-1903 algae growth with 10mL of HTL aqueous phase. The results are very encouraging since the growth rate with HTL liquid was similar to that obtained for the control. Hence the presence of HTL liquid did not affect algae survival or growth. Further it can be concluded that the HTL liquid is able to provide nutrient replacement for at least a portion of Part B commercial nutrient.

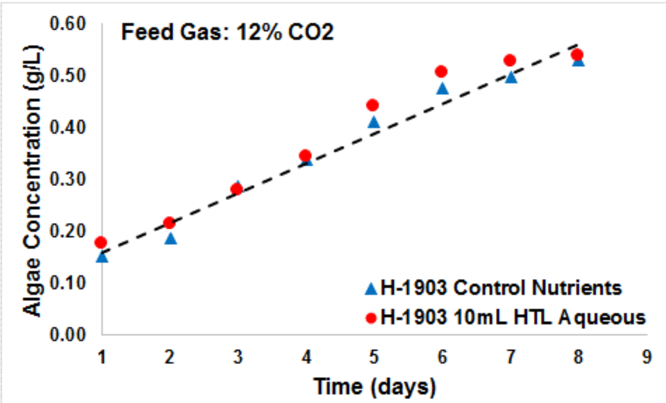

Figure 21: H-1903 algae survival with HTL aqueous;

H-1903 Control Nutrients; Part A: 2.5mL, Part B: 7.5mL

H-1903 10mL HTL Aqueous; Part A: 2.5mL, Part B: 2.5mL, HTL Aq: 10mL

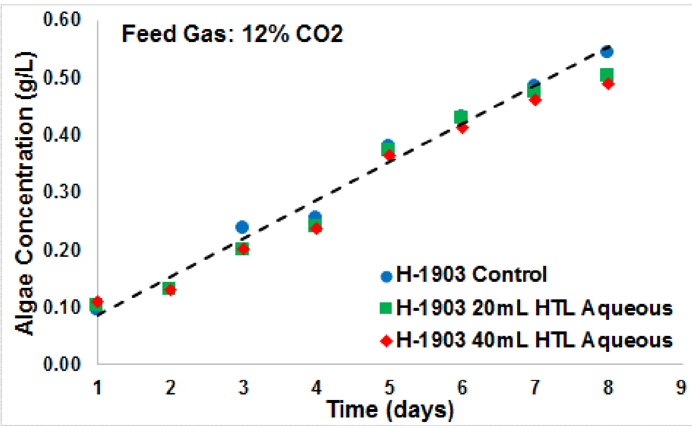

Figure 22: H-1903 algae survival with HTL aqueous;

H-1903 Control Nutrients; Part A: 2.5mL, Part B: 7.5mL

H-1903 20mL HTL Aqueous; Part A: 2.5mL, Part B: 2.5mL, HTL Aq: 20mL

H-1903 40mL HTL Aqueous; Part A: 2.5mL, Part B: 1.2mL, HTL Aq: 40mL

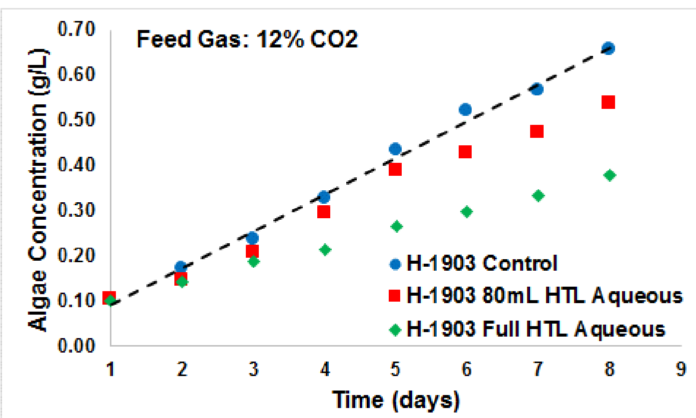

Figure 23: H-1903 algae survival with HTL aqueous;

H-1903 Control Nutrients; Part A: 2.5mL, Part B: 7.5mL

H-1903 80mL HTL Aqueous; Part A: 2.5mL, Part B: 0.6mL, HTL Aq: 80mL

H-1903 Full HTL Aqueous; Part A: 0.0mL, Part B: 0.0mL, HTL Aq: 80mL

The next the volume of HTL aqueous was systematically increased while reducing commercial Part B volume to check for inhibitory effect (Figure 22) for H-1903 algae. The results are encouraging as the HTL aqueous is indicated to provide sufficient amount of nutrients to achieve stable growth rates similar to the control despite the significant reduction of commercial nutrient. However, towards the end of these experiments, the algae growth appears to be slightly lower than the control. Based on the results a significant amount of Part B replacement appears possible by recycle (Figure 24). The next series of experiments investigated full replacement of Part B nutrient by HTL aqueous phase. Figure 23 indicates that the full nutrient replacement (no Part A or B) by HTL aqueous results in some reduction in growth rate. This is due to the lack of necessary macro- and micronutrients in the HTL aqueous phase to support efficient algae growth. When the amount of Part B nutrient was reduced to 0.6 (~90% replacement with HTL aqueous), the algae growth was comparable to control till Day-5 after which it is lower than the control. This suggests that some of the nitrogen, phosphorous and other nutrients in the HTL aqueous may not be in a form that is readily utilized by the algae. Overall the results obtained in this work demonstrate the following two key features:

- That the selected algae species can survive and grow with potentially all the HTL aqueous phase recycled.
- Recycling the HTL aqueous phase can reduce the requirement for commercial nutrients by at least 50%

It should be noted that these tests were conducted in batch PBR's similar to the other tests. However since the batch operations monotonically deplete nutrient concentration in the PBR's over time, it is not possible to replicate the continuous MSC process with recycle wherein the HTL recycle will continuously replenish nutrients in the PBR's. Note that in Figures 21-23 the growth rates with HTL recycle are virtually identical to the control in the first few days. Hence the results obtained here are preliminary and expected to be conservative with respect to MSC operation. Furthermore these tests do not include the impact of the ~99% of the culture media with nutrients that is recycled from the dewatering step which should further reduce the need for fresh nutrients. The impact of HTL and dewatering media recycle in the actual continuous MSC process will be studied in the Phase 2 project.

Conclusions from HTL work:

The HTL work on this project confirmed that the algae grown in the CO_2 capture system can be effectively converted into bio-crude oil, a biofuel intermediate feedstock that can be refined and upgraded to a wide range of fuel products. Nine different HTL conditions with two different algae species, were tested. The best biofuel conversion yield achieved was 37% for the H-1903 algae species and 34% for the H-0322 species. Hence in the following techno-economic analyses we have assumed a 35% oil yield. The best HTL operating conditions were in the range of 280-300 ^{o}C and 15 to 30 minutes of reaction time. Hence in the techno-economic analysis we assume HTL operations at 300^{o}C and 30 minutes of reaction time at this temperature. The HTL aqueous product was found to have a high content of organics and ammonia nitrogen. The recycle of this to the algae culture was investigated. It demonstrated the ability of H-1903 to survive and grow with complete recycle of the HTL aqueous phase. Potential for significant nutrient reduction was indicated.

Task 4: Process Development and Economics

Subtask 4.1: Model Refinement and Process Development

The experimental data measured in Task 2 were used to refine the Helios-NRG proprietary model used to predict MSC operation. In particular, the parameters related to intrinsic growth rate and light attenuation for both species at different conditions corresponding to high growth rates and CO_2 capture efficiencies were updated. The resulting model was used to assess strategies for 3-stage MSC design and operation to achieve 90% CO_2 capture from both 1% and 12% flue gas streams. Doing so requires tradeoff between a large number of design and operating variables such as the culture depth in the different stages, the volume distribution among the stages, the flue gas flow rate, the water flow rate and the resultant algae concentration in the stages. MSC simulation using the model has led to very valuable understanding on how the process responds to changes in key variables including some unexpected insights.

A significant new insight gained from the analysis was the critical impact of water flow rate on the CO_2 capture efficiency of the MSC process. It was found that there is an optimal water flow rate that maximizes capture efficiency. At lower flow rates the increased algae concentration in the stages increases light attenuation thus reducing growth rates and capture efficiency. At higher flow rates the algae concentration in the stages decreases which reduces overall mass productivity and hence capture efficiency. A significant finding was there is a maximum flow rate beyond which there is "wash-out" of the culture resulting in the stage concentrations being reduced to very low values over time.

Developing the global optimum design of MSC for 90% CO_2 capture from flue gas streams is well beyond the scope of the present Phase 1 project and is one of the objectives of the future Phase 2. Hence our strategy has been to use the refined MSC model to identify a reasonable design and set of operating conditions that can achieve 90% CO_2 capture from the post FGD flue gas stream and subsequently use this for preliminary economic analysis. Table 8 summarizes the MSC design and operating parameters which were used for economic assessment in this task. These conditions correspond to 90% CO_2 capture from a flue gas stream containing 12% CO_2 that is fed to Stage 3 with the gas stream exiting Stage 1 containing 1.2% CO_2.

MSC Stage	Depth (in)	Culture Conc g/L	Specific Vol ft3/cfh	Sp Liquid Flow cfh /cfh gas
1	22	0.17	8.4	3.13E-03
2	15	0.40	6.8	3.13E-03
3	10	0.70	5.4	3.13E-03

Table 8: MSC parameters for 90% CO_2 Capture from post FGD flue gas

Subtask 4.2: Economic Assessment

Parameter	Value
Power Plant Size (MW)	550
Flue gas flowrate TPY (Tons/yr)	1.98E+07
CO2 in Flue gas TPY	3.89E+06
Flue gas CO2 conc	12.9%
CO2 capture efficiency by MSC	90%
Hours of sunlight/day	12
Total CO2 Capture by Algae (TPY)	1.75E+06
Annual Algae Production (TPY)	9.29E+05

Table 9: Basis for economic analysis

Preliminary economic analysis was performed using the MSC process summarized in Table 11 for 90% CO_2 capture from a 550MW power plant burning sub-bituminous coal. The flue gas properties were obtained from DOE's baseline study[1]. Since photosynthesis is driven by sunlight, the analysis assumes that carbon capture occurs during 12 hours/day of natural sunlight. The basis for analysis are summarized in Table 9.

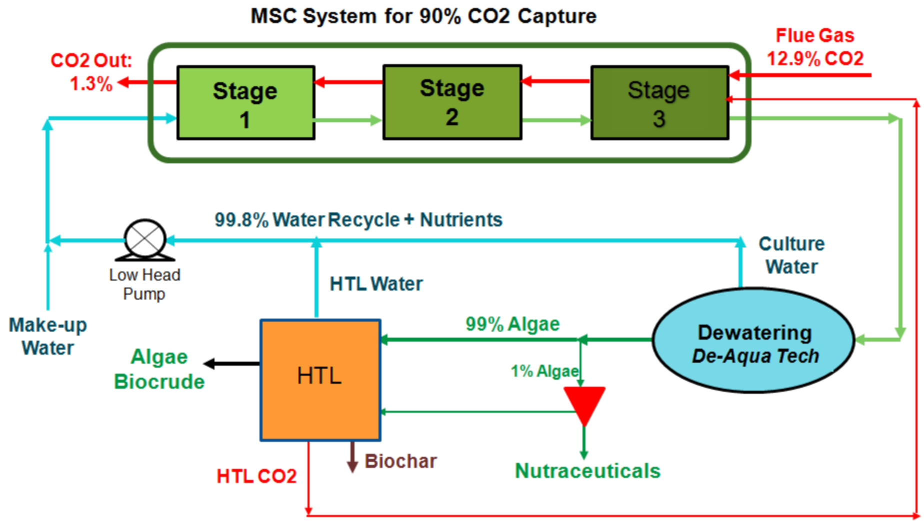

Figure 24: Schematic of overall process for Carbon Capture and Utilization

Figure 24 shows a schematic of the overall process. The algae produced by the MSC process is de-watered using the De-Aqua process - a technology for low cost algae de-watering being developed by Helios-NRG outside the present project. This technology can produce product algae with dry weight concentrations from 20-45%. The de-watered algae leaving De-Aqua is split into two streams. As shown, about 99% of the algae is fed to HTL where it is converted to a bio-crude product. The remaining 1% is used for production of two nutraceuticals (Astaxanthin and β-Carotene) which have been found to be present in our algae species in prior work. The biomass waste after nutraceuticals production is fed to the HTL process. All the water and nutrients extracted during De-Aqua and the waste water from HTL are recycled to the MSC process. The CO_2 rich gas produced by HTL is recycled.

For a preliminary life cycle analysis, the CO_2 generated from the process and also from the power consumed by the process were estimated. The CO_2 generated by HTL operations is recycled back to the algae where 90% is captured. Additional CO_2 emitted by the proposed process would arise from power requirements in the MSC process (flue gas distribution and sparging, paddle wheel operation, water and CO_2 recycle etc) and energy used in the HTL process, energy in algae dewatering and supply of make-up water and nutrients (Table 10). Note that ~90% of the CO_2 generated for the added power for the algae+HTL process will be re-captured by the algae. Our preliminary analysis indicates that this will reduce the net CO_2 capture efficiency during operation from 90% to ~86%. The total estimated energy consumption by the process of ~3.6 MJ/kg algae is only a small fraction of the energy content of the algae (~18 MJ/kg).

Component	Basis	MJ/kg-Algae
Nutrients for Algae	67% recycle	0.48
Culture pumping/mixing	Estimated	0.15
Algae Dewatering	DeAqua Technology	1.45
Water Recycle	10ft head	0.08
Flue Gas Blower	2 psig	0.18
HTL	75% heat recovery	1.23
TOTAL		**3.56**

Table 10: Energy consumption by process resulting in CO_2 emission

Capital cost for the MSC was estimated by Helios-NRG based on our proprietary design and information available in literature. Total Capex of the MSC was estimated to be $449MM and used in the present analysis. As a sanity check, the capital cost was also estimated linearly scaling the costs reported by Lundquist et al[10] for open raceway ponds assuming a 25% higher productivity (we expect this to be significantly higher) and adding costs for a top cover to capture the gas phase and other modifications. This resulted in a capital cost estimate of $387MM. Capital charges were estimated based on 10 year term with 8% annual interest. A 30 year plant life was assumed.

The operating costs included the following:

- Cost of make-up water and nutrients - based on the values reported by EISA[11] and assumed 98% recycle of water and nutrients. The expected water recycle in the process shown in Figure 24 is >99%.
- Power for a gas blower and paddle wheel operation - estimated from BETO report
- Cost estimate for de-watering with De-Aqua process - estimated by Helios-NRG based on our prior work in DeAqua
- Labor and maintenance costs - estimated based on our industrial experience

As mentioned earlier, the MSC design used here is one that appears reasonable (but not optimal) for 90% CO_2 capture. Optimization of the MSC process is expected to lead to higher productivity and lower costs, but is beyond the scope of Phase1 project.

The capital and operating costs for the HTL plant were based on the costs estimated by PNNL[12] for diesel production using HTL processing of algae. Since the output of the De-Aqua process can be directly fed into the HTL process, the costs for algae drying were excluded. Further, the output of the process envisioned is bio-crude which will be sold to a refiner. Hence only the costs for bio-crude production were included and the costs for further upgrading and processing to make diesel were eliminated. The selling price of bio-crude was assumed to be 67% of the price of petroleum in 2025[13].

Nutraceutical production is beyond the scope of Phase1 and not part of the current project. However, Helios-NRG believes that co-production of high value nutraceuticals can significantly lower the cost of carbon capture. Hence we have done additional work to include this in the present analysis. For nutraceutical production, we assume that the algae will have 0.5% by weight of Astaxanthin and β-Carotene which is significantly lower than the 1-4% typically reported. We have intentionally used conservative numbers since the level of nutraceutical production in the proposed MSC process has not been quantified. The selling price of Astaxanthin and β-Carotene produced were assumed to be 1/3rd of the current market price since the products are not purified. A net profit margin of 25% was assumed for these products - this conservative for these types of products.

Table 11 summarizes the results of the assessment. It shows that CO_2 capture with MSC alone (no products) results in a capture cost of $72/ton CO_2. The addition of HTL increases both capital and operating costs substantially but generates significant revenue from bio-crude sales. ***The net cost of capture with Bio-crude production is hence reduced to $27/ton CO_2.*** Addition of nutraceutical production can potentially lower the cost of CO_2 capture further. For the conservative case shown here, only 46 tons/year of each nutraceutical is produced. However, because of their high value, ***the cost of capture is reduced to ~$6-7/ton CO_2***. While the numbers shown here are preliminary, they clearly show that the utilization of the CO_2 captured to generate high value products is the key to making a step change in the cost of carbon capture.

System	Parameter	Value
Only MSC	Total Capex (MM$)	449
	Capital Charge (MM $/yr)	62
	Depreciation (MM $/yr)	15
	Operating Costs (MM $/yr)	48
	Total Annual cost (MM $/yr)	125
	CO2 Capture Cost w/o credits ($/ton)	**72**
MSC + HTL	Total Capex (MM$)	677
	Capital Charge (MM $/yr)	93
	Depreciation (MM $/yr)	19
	Operating Costs (MM $/yr)	63
	Total Annual cost (MM $/yr)	176
	Bio-crude production (MM Barrel/yr)	116
	Bio-crude value ($/barrel)	48
	Bio-crude reveue (MM $/yr)	(131)
	CO2 Capture Cost w/- Biocrude credits($/ton)	**27**
+ Nutraceuticals	Potential Astaxanthin production (TPY)	46
	Potential β-Carotene production (TPY)	46
	Market price Astaxanthin ($/kg)	7500
	Market price β-Carotene ($/kg)	2000
	Potential profit from nutraceuticals (MM $/yr)	(37)
	CO2 Capture Cost w/- Biocrude + Nutraceuticals credits($/ton)	**6.5**

Table 11: Summary of economic assessment of proposed technology for CO_2 capture and utilization from flue gas streams

Task 5: Project Management

This task ensured that all programmatic activities were completed in time and on budget to ensure successful completion of the overall project. Subsequent to signing of the Phase1 contract with DOE, Helios-NRG executed contracts and necessary confidentiality agreements with ISTC. Schedules for task completion, billing and reporting were established. Teleconferences were held with Dr Schideman and his team on a bi-weekly basis. Project expenditures were tracked against progress in tasks. Progress and financial reports were submitted to DOE as required. Final project cost was $149,931 vs. a budget of $149,941.

Discussions were held with GHT related to application of the technology for nutraceuticals of interest to them. Discussions were held with Jordan Walbesser of Hodgson Russ, LLP to develop an IP strategy for the technology being developed including timing and content of patent filings.

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