2013 DOE Bioenergy Technologies Office (BETO) Project Peer Review

Development of Bio-Oil Commodity Fuel as a Refinery Feedstock from High Impact Algae Biomass

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Bio-Oil Technology Area Review

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Goal/Objective Statement

- Convert wet algae to liquid hydrocarbons
- Generate a refinery grade, low N bio-oil feedstock from algae
- Co-process algal oil with an intermediate refinery stream

Project Quad Chart Overview

Timeline

- Project start date: 1-1-2013
- Project end date: 2-1-2014
- Percent complete: 25%

Barriers

- Barriers addressed
  - Al-B. Algal Fuel Production
  - High Nitrogen Oil

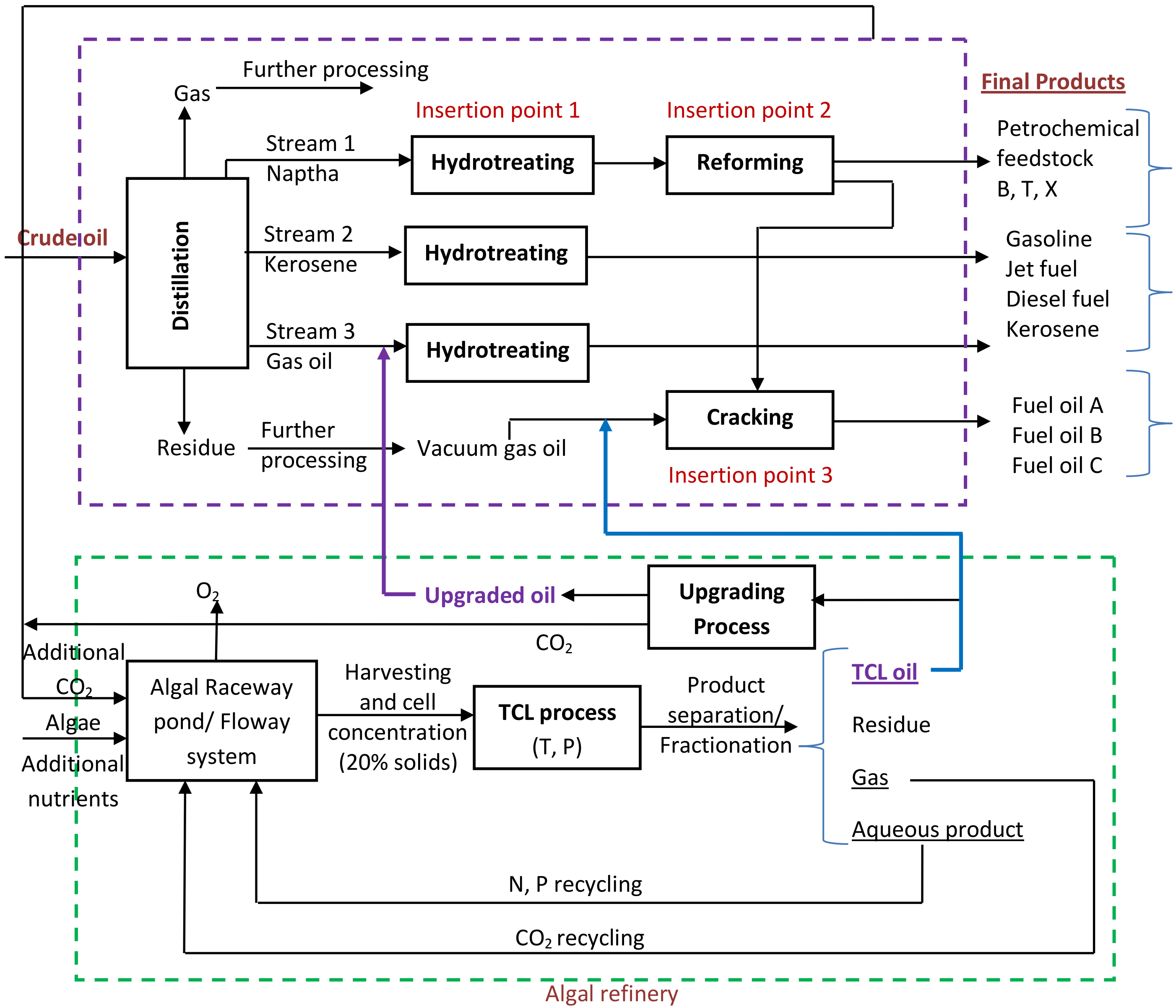
Budget

- Total project funding ($698,000)
- Funding for FY 2013 ($698,000)
- 5 months, Annual Funding Rate?

Partners & Roles

- Intertek – Microcrude Assay
- DRI – Short τ, TCL
- Refinery - TBD

Flow Diagram

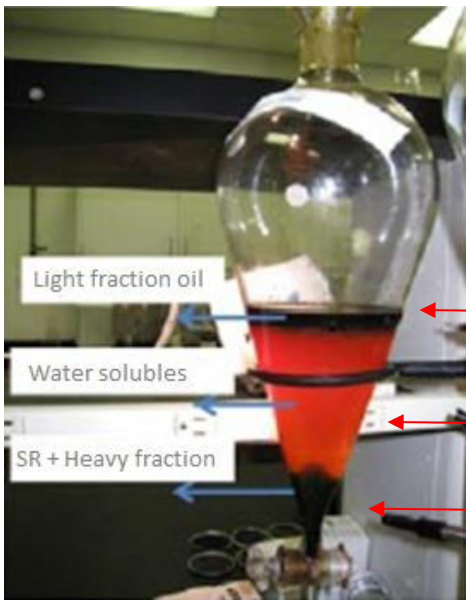


Key Unit Operations

- Open Algal Raceways – Economical
- Filtration – Increase Solids (algae biomass) to 20%
- Low Temperature Thermochemical Liquefaction
  - Cell Disruption
  - Soluble protein removal, partial protein hydrolysis
  - Recycle and reuse N in aqueous phase for algae cultivation (not a focus of this project)
- High Temperature Liquefaction (TCL)-Generate Algal Oil
  - Catalytic HTL
- Catalytic Hydrodeoxygenation of Algal Oil
- Co-Processing Upgraded Algal Oil and Refinery Intermediate

Technical Barriers

- High Levels of Nitrogenated Compounds in Algal Oil
  - 4-10% N in algal oil, increased H_2 demand in HDO/HDN, catalyst poisons

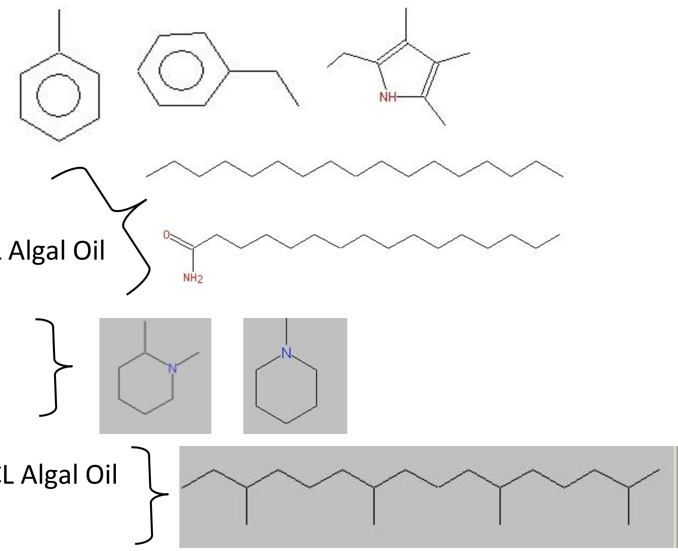


Algal Oil Generated by Typical TCL and Components Identified by GC/MS – Single Stage at 350C, 60 min

Top Layer – TCL Algal Oil

Aqueous Phase

Bottom Layer – TCL Algal Oil



BP Range Molecules > 350°C

Approach

- Grow mixed algal consortia in algal floway systems (Fig. 1)
  - *Chlorella sorokiniana*, *Chlorella minutissima,* and *Scenedesmus bijuga*)
- Use commercially available *Spirulina* for liquefaction screening studies until micro-reactors available

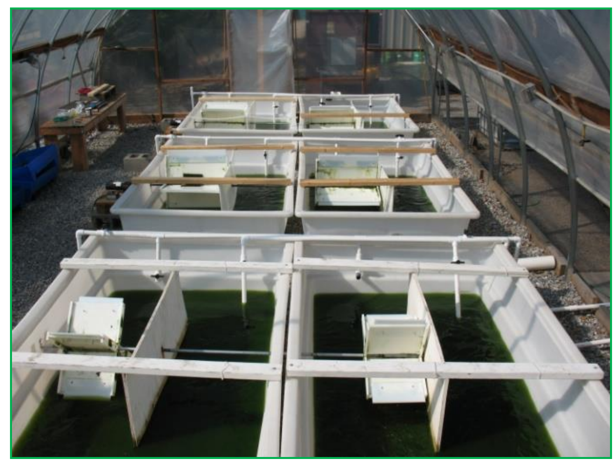
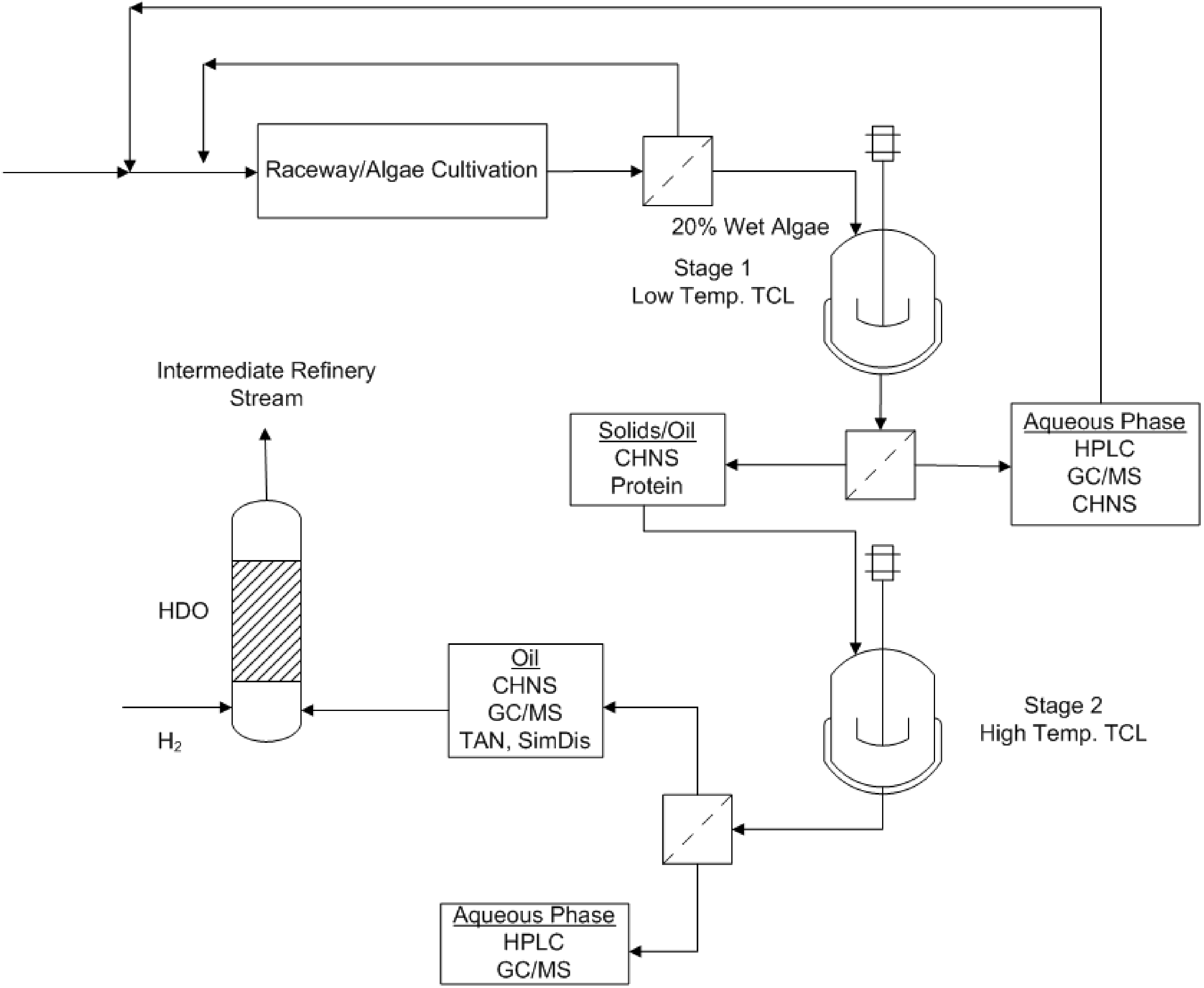



Fig. 1: Algae cultivation in 20L carboys (A) and six raceways (500L each) under green house facility (B).

Approach

- Harvest, Continuous Centrifuge, Dry, Grind, Store 4°C
- Low Temperature Thermochemical Liquefaction
  - T=175-250°C, τ=5-30 min, 50-450ml Parr batch reactors
  - Separate soluble proteins/partial protein hydrolysis
- High Temperature Thermochemical Liquefaction
  - T=350°C, τ=5-60 min, 50-450ml Parr batch reactors
  - Study catalyst effect, kinetic analysis
- Catalytic Hydrodeoxygenation/Denitrogenation
  - Study catalyst effect – Pd/Ru on carbon, 450ml Parr batch reactors
  - Measure H_2 consumption, kinetic analysis
  - Co-process with refinery intermediate
  - Measure fuel properties

Approach



Raceway/Algae Cultivation
20% Wet Algae
Stage 1
Low Temp. TCL
Intermediate Refinery Stream
Solids/Oil
CHNS
Protein
Aqueous Phase
HPLC
GC/MS
CHNS
HDO
Oil
CHNS
GC/MS
TAN, SimDis
H_2
Stage 2
High Temp. TCL
Aqueous Phase
HPLC
GC/MS

Progress

- Total of 1800 g (dry weight) of algae biomass generated in raceway
- Algae biomass has been processed and will be characterized (protein, carbohydrates, lipids)
- Satisfies biomass need for subsequent catalytic liquefaction studies using small volume batch reactors

Progress

- Initiated 2-Stage Liquefaction Studies Using *Spirulina*
  - Stage 1: T=175-250°C, τ=5-30min
  - Stage 2: T=350°C, τ=60min
  - *Spirulina* – 44% Protein, ~12% Lipids, X% Carbohydrates
  - 20% solids, 450 ml working volume, Parr Batch Reactor

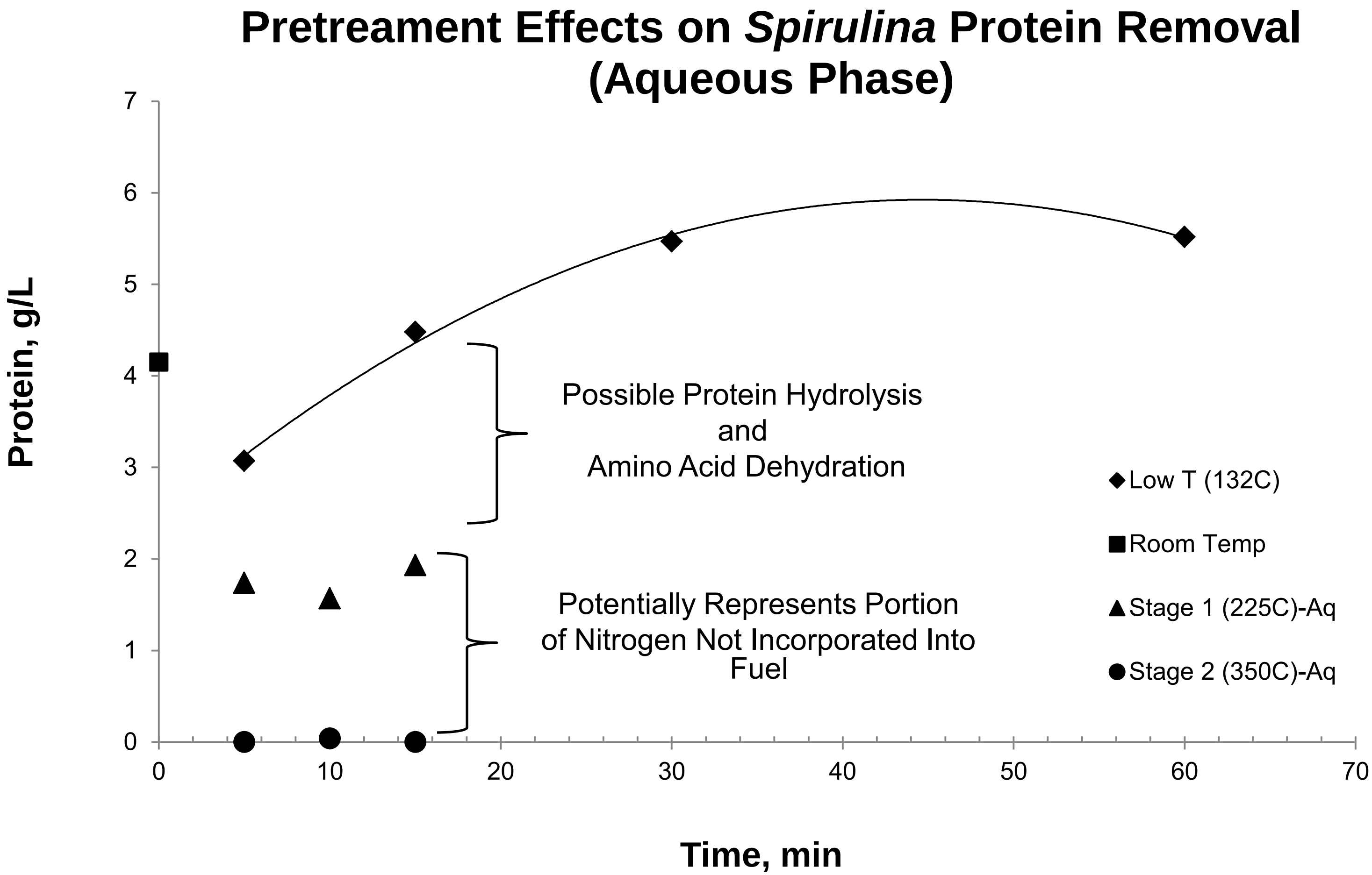
LCA Progress

- A spread sheet based techno-economic assessment of algae cultivation system was established (one acre raceway)

- Cost of producing 15-20% solid algae slurries for liquefaction developed

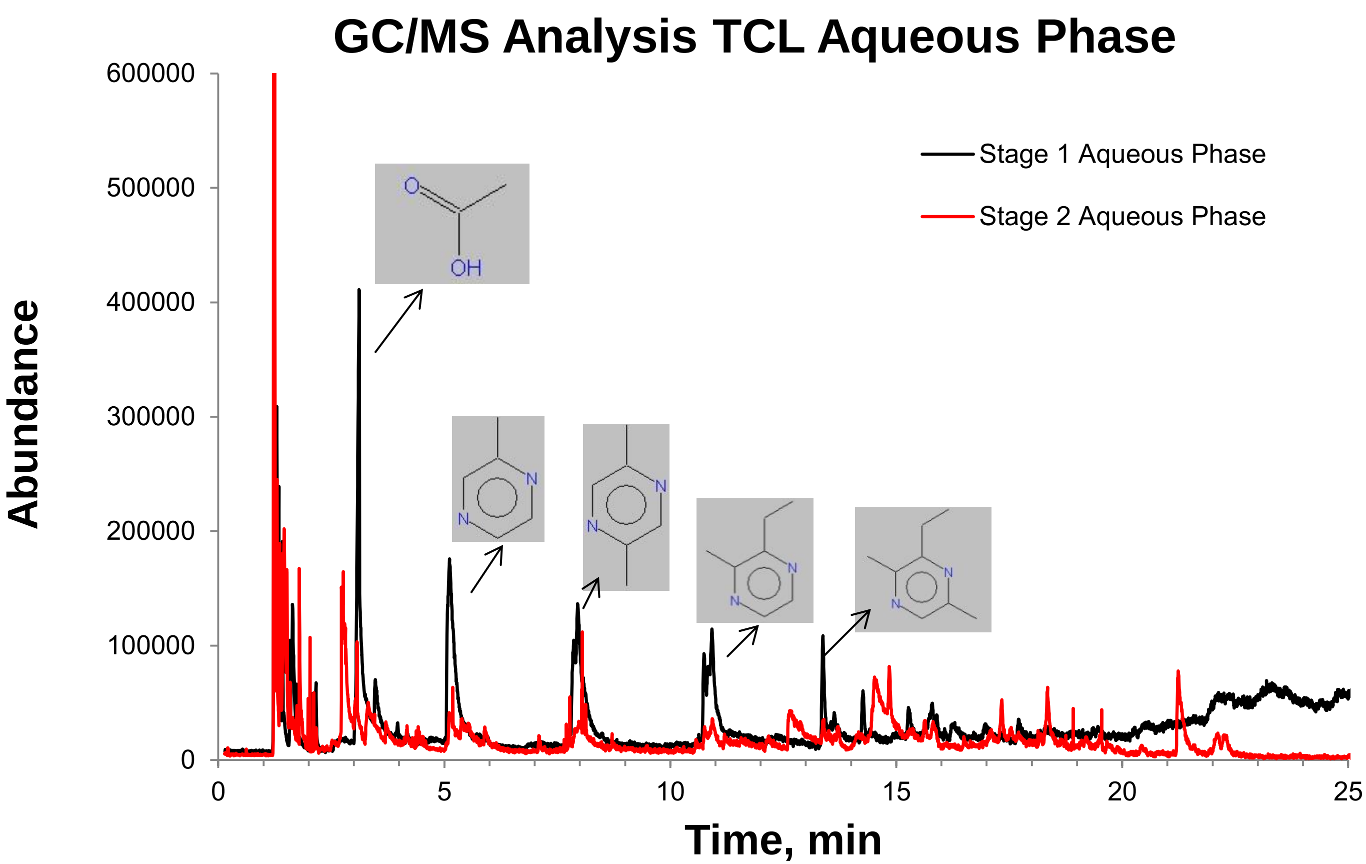
- On-going tasks:
  - Development of process simulation model from algae through liquefaction to oil intermediates
  - Plant layout and discounted cash flow analysis
  - Estimation of capital cost and operating cost

Results


Pretreament Effects on *Spirulina* Protein Removal
(Aqueous Phase)
Protein, g/L
Time, min
0
1
2
3
4
5
6
7
0
10
20
30
40
50
60
70
Possible Protein Hydrolysis
and
Amino Acid Dehydration
Potentially Represents Portion
of Nitrogen Not Incorporated Into
Fuel
Low T (132C)
Room Temp
Stage 1 (225C)-Aq
Stage 2 (350C)-Aq

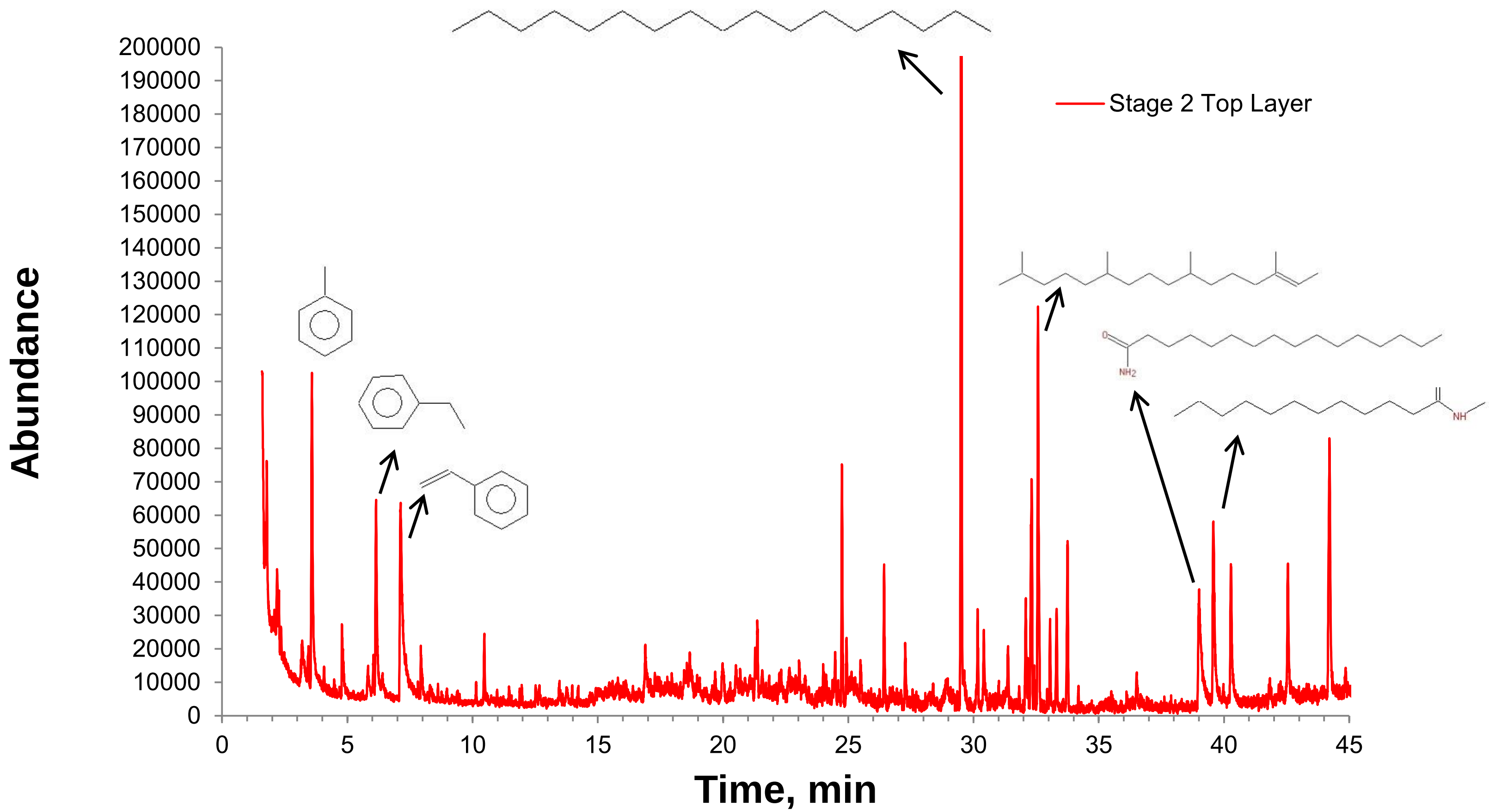
Results

- Pyrazines observed in stage 1 (S1) aqueous phase (not observed in S2)



Results

- Primary oil GC/MS analysis S1(225°C,10 min) - S2 (350°C, 60 min)
- Similar profile for heavy oil



Results

2-Stage TCL Conditions (T, °C; τ, min)				%N in Oil	Yield (HO+PO) (g oil/g algae feed)	H/C	O/C
T_1	τ_1	T_2	τ_2				
0	0	350	60	4.1 ± 1.04	1.0	TBD	TBD
225	5	350	60	1.7 ± 0.5	0.95	TBD	TBD
225	15	350	60	1.9 ± 0.7	0.66	TBD	TBD

HO – heavy oil or bottom layer

PO – primary oil or top layer

TBD – To be determined, on-going analysis

Relevance

- Strategic goal is to convert Algae into *fungible liquid fuel*
  - Utilized at one or more **insertion points** within a petroleum refinery

- TCL eliminates need for drying wet algae and lipid extraction using solvents

- Significant reduction in algal oil nitrogen required
  - Crude Oil: 0.1-1.5 %N
  - Heavy Vacuum Oil: 0.4-1.6 %N
  - Target for Algal Oil < 1.0% N

Critical Success Factors

- Generate Low N, O, Acid, and Viscosity Algal Oil
- Potential challenges
  - Low yield
  - Convert protein to platform chemicals and fuels
  - Catalyst deactivation
  - External H_2 needed (Can we use NH_3 as an internal H_2 donor?)
  - Lack of comprehensive characterization data on algal bio-oil
- Secure Refinery Partner
- Demonstrate Algal Oil Co-Processing with Refinery Intermediate

Future Work

- 2-Stage TCL analysis of raceway consortium
- SimDist analysis of algal oils (BP ranges)
- Catalyst effect on second stage TCL
- Catalytic HDO/HDN of low N, TCL algal oil
- Microcrude assay of algal oils
- Initiate refinery talks
- Co-process upgraded algal oil
- Process simulation and LCA analysis

Timeline

Tasks	May-13	Jun-13	Jul-13	Aug-13	Sep-13	Oct-13	Nov-13	Dec-13	Jan-14
Two-stage TCL Studies	■	■	■						
Algal Oil Analysis	■	■	■						
Low N Algal Oil			■						
HDO/HDN			■	■	■	■	■	■	
Large Vol Upgraded Oil								■	■
Methods for HDO/HDN									■
Intermediate Oil-Refinery			■	■	■				
Co-Processing					■	■	■	■	■
Microcrude Assay								■	■
Process Model	■	■	■	■	■	■	■	■	
LCA Analysis	■	■	■	■	■	■	■	■	
Technoeconomic Analysis								■	■

Summary

- Relevance: Algae into *fungible liquid fuel via o*ne or more **insertion points** within a petroleum refinery

- Approach: Generate low N algal oil via 2-Stage TCL

- Technical accomplishments: Protein removal reduces %N in algal by 40-50% (preliminary data)

Summary

- Future work:
  - 2-Stage TCL analysis of raceway consortium
  - Catalytic HDO/HDN of low N, TCL algal oil
  - Co-process upgraded algal oil

- Success factors and challenges
  - Target for Algal Oil < 1.0% N
  - Achieve high yields and low N algal oil

- Technology transfer
  - Secure Refinery Partner
  - Demonstrate co-processing of upgraded algal oil

Additional Slides

•Raceway

•Algae Raceway

Growth | First Harvest | Second Harvest

Pond Volume	565 cu. m
Pond area	1 acre
Height of the Pond	0.15 m
Productivity	25 g/sq.m/day
Retention time	4 days
Carbonation system	1 carbonation pit for 1 ha (3.6 m or 12 ft deep)
Harvest flow	25% pond volume
Paddle wheel speed	30 cm/sec

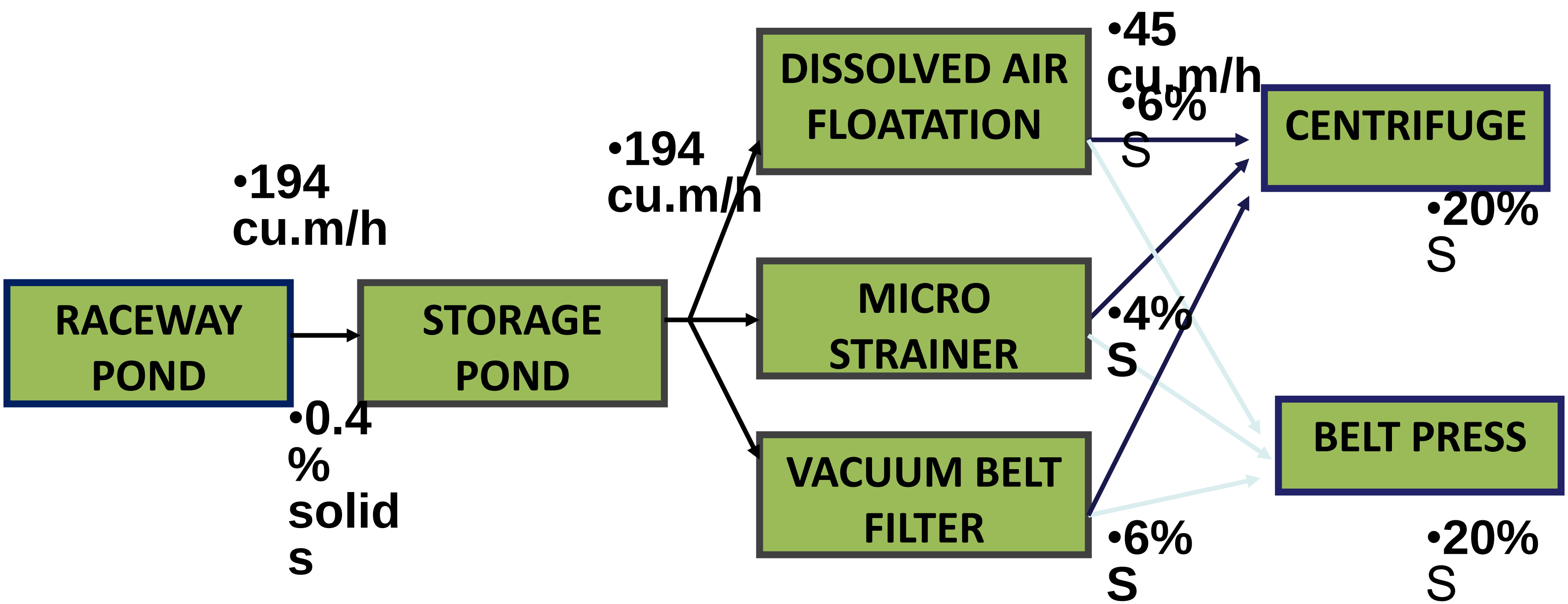
•Harvesting System

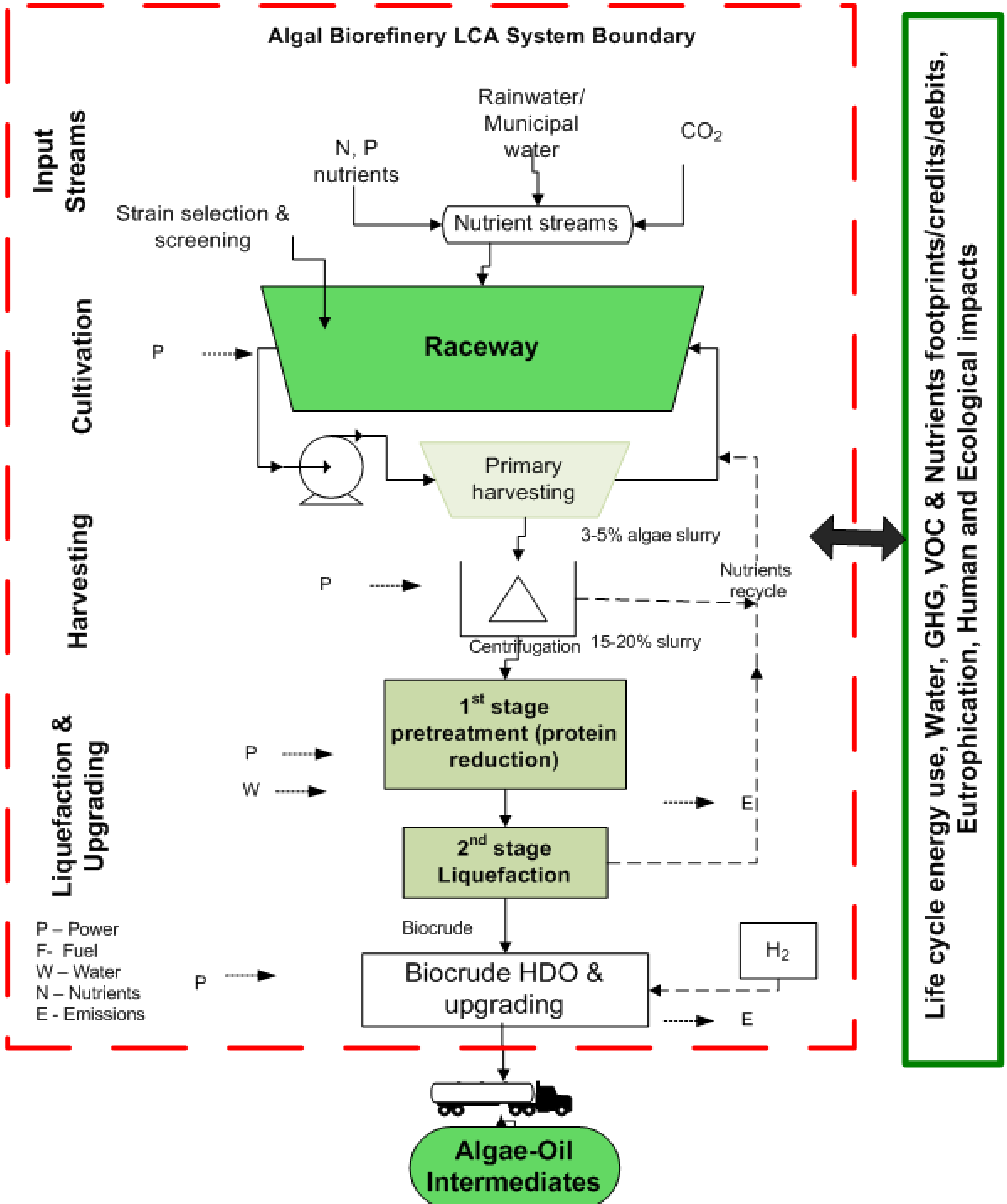
GROWTH

First harvest

Second harvest

- •Raceway pond Operation : Steady-state continuous mode, 25% vol
- •Daily Harvest Flow: 4658 cu. m @ 194 cu.m/h
- •Each harvest unit operates 24 X 7 for 300 days/year.





Life Cycle Assessment

- Established system boundary
- Functional unit - per gallon of intermediates or crude oil equivalent

On-going tasks:

(1) Mass and energy balance estimations

(2) Measurement of emissions from liquefaction & HDO studies

(3) Impact assessments

(4) Scenarios development