BETO 2015 Project Peer Review

Algal Biomass Conversion
WBS 1.3.4.201

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Goal Statement

Reduce algal biofuel production cost by developing advanced process options for the conversion of algal biomass into biofuels and bioproducts based on the three major biomass components: lipids, carbohydrates, and proteins.

Quad Chart Overview

Timeline

- **Project start date: 1/30/13**
- **Project end date: 9/30/17**
- **Percent complete: 46%**
- **Existing Project**

Barriers

Barriers addressed

- AFt-H. Overall Integration and Scale-Up
- AFt-I. Algal Feedstock Preprocessing
- Aft-J. Resource Recapture and Recycle

Budget

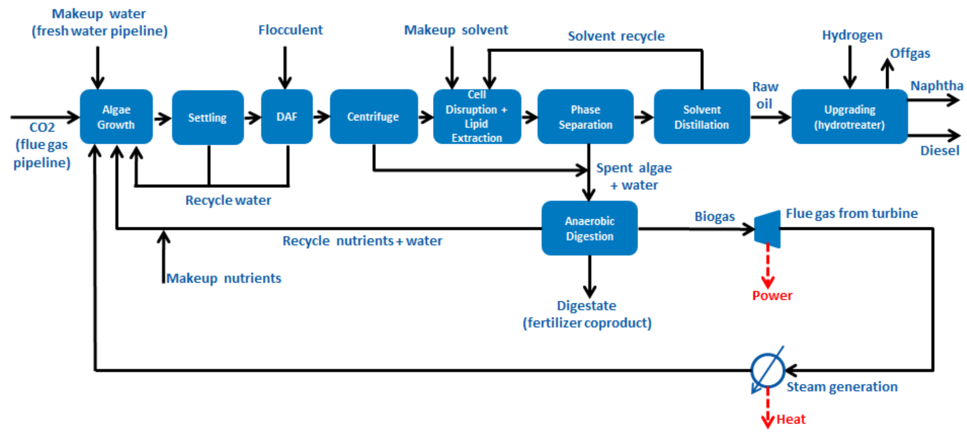
	Total Costs FY10 –FY12	FY 13 Costs	FY 14 Costs	Total Planned Funding (FY 15-Project End Date
DOE Funded	$0	$17,597	$626,735	$2,454,891

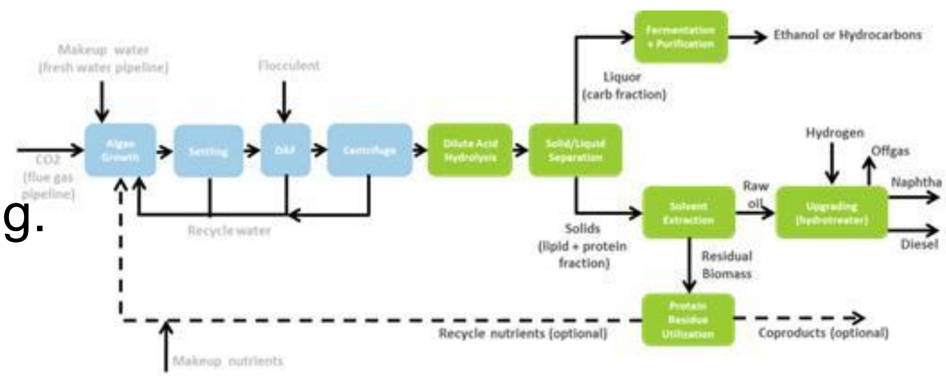
Partners

- Partners
  - ASU for biomass supply
  - SNL for fermentation of protein
- Other interactions/collaborations
  - NREL Algal Biomass Valorization and Techno-Economic Analysis projects
  - ANL for LCA modeling
  - Algix for evaluation of protein
- Non-technical project management partners
  - None

1 - Project Overview

- Work began in FY13 to reduce biofuel production cost through biomass fractionation and component valorization.
- Process evaluated for biomass produced in outdoor cultivation systems at ASU
  - *Scenedesmus acutus* (LRB-AP 0401)
  - *Chlorella vulgaris* (LRB-AZ 1201)
  - *Nannochloropsis granulata* (CMP535 aka LRB-MP-0209)
- Additional cost savings can be achieved by replacing parallel processing with sequential processing.
- Biomass conversion process has become the framework for the Algal Lipid Upgrading (ALU) Design Case and State of Technology.





2 – Approach (Technical)

- **Project plan has four components**
  - Development of pretreatment process for hydrolysis of algal carbohydrates and release of monomeric sugars
  - Development of extraction process for efficient recovery of fuel-grade lipids
  - Demonstration of fermentation processes for valorization of algal sugars
  - Development of lipid upgrading process for evaluation of feedstock quality and feedback with upstream processes
- **Scale processes from 10 gram to 100 kg.**
- **Interact with TEA project for guidance on technical plan and to provide data for modeling**
- **Interact with Algal Biomass Valorization project for identification of novel coproduct strategies**

2 – Approach (Management)

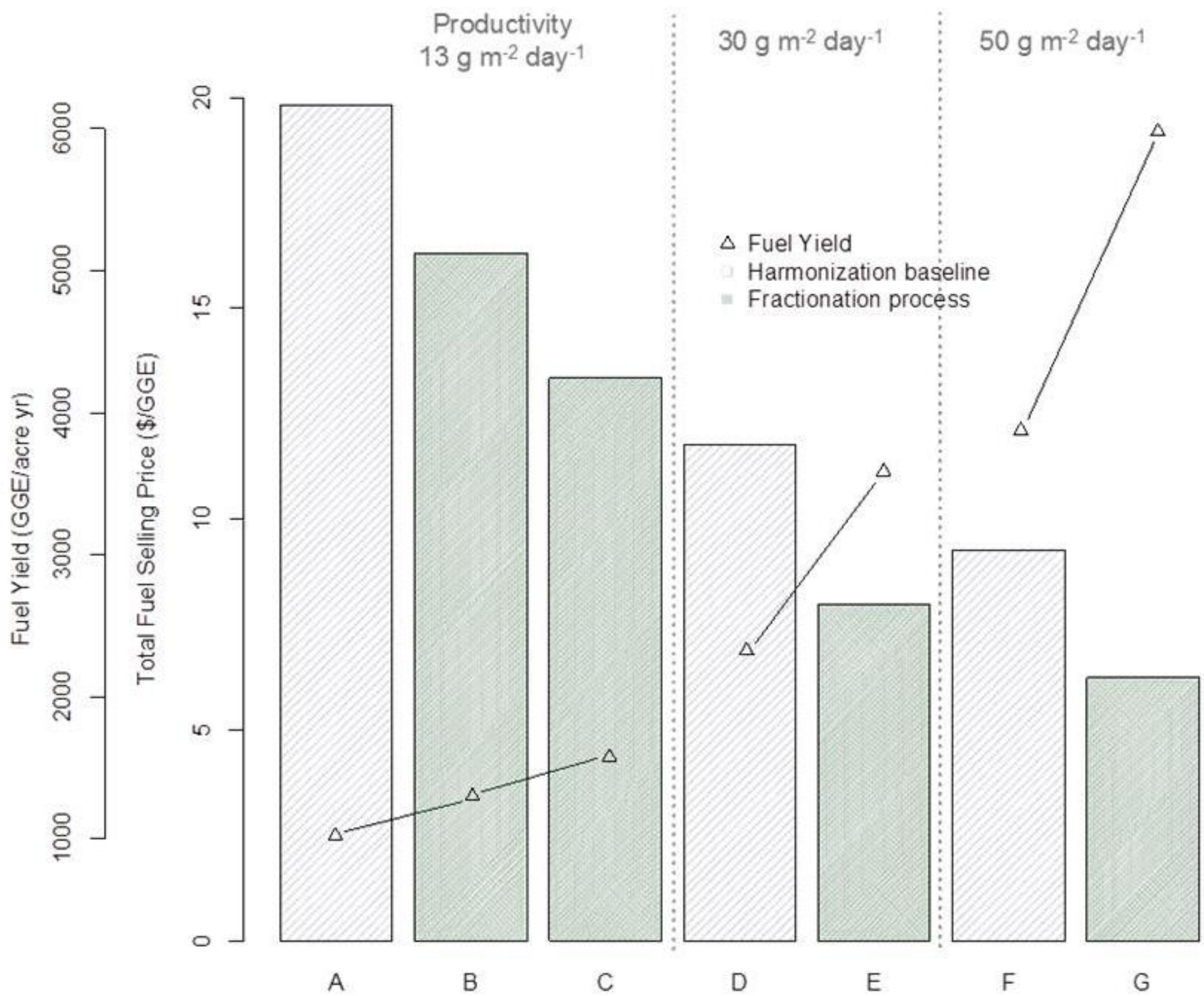
- **Critical Success Factors**
  - Extraction lipid yield
  - Extraction CAPEX
  - Hydrotreating CAPEX
  - Solids content in slurry
  - Pretreatment glucose yields
- **Top potential challenges**
  - Low cost scalable extraction process
  - High sugar yields with minimal degradation products
  - Lipid upgrading to achieve product specifications (diesel vs diesel blendstock)
- **Management Structure**
  - Pretreatment and extraction (Nick Nagle)
  - Lipid upgrading (Bob McCormick)
  - Weekly progress update meetings
  - Quarterly milestones to track progress

3 – Technical Accomplishments/ Progress/Results:

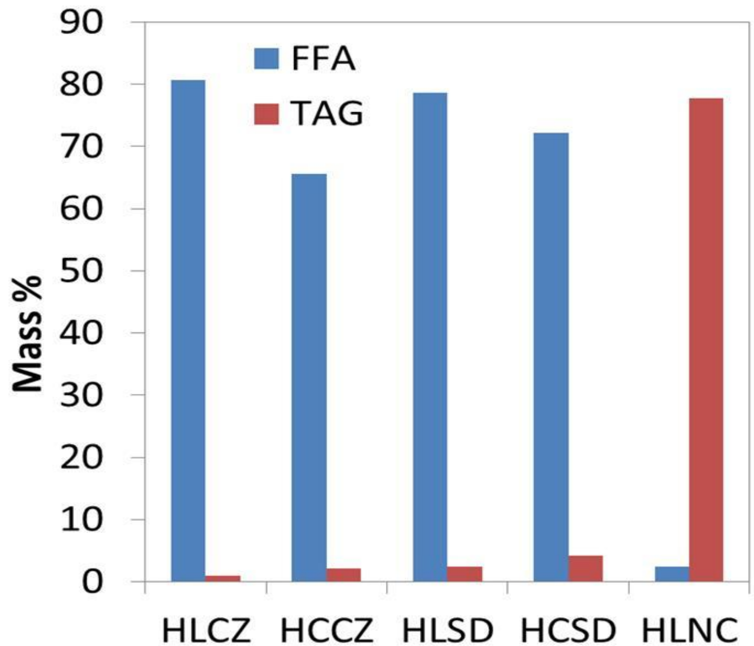
Potential Fuel Yields From Algal Biomass

	Scenedesmus acutus			*Chlorella vulagaris*			*Nannochloropsis granulata*		
	early	mid	late	early	mid	late	early	mid	late
Fermentable Sugars (% DW)	14	48	38	5	29	33	6	9	9
Ethanol (gallon/ton)	22	74	59	7	45	50	9	14	14
Gasoline equivalent (gal/ton)	14.	49	39	5	29	33	6	9	9
Fatty Acids (FAME) (% DW)	9	17	39	12	15	23	12	26	57
Diesel equivalent (gal/ton)	22	41	93	29	36	56	30	62	138
Total Theoretical Fuel Value (GGE/ ton)	38	92	138	36	68	92	38	74	156
Total Observed Fuel Value (GGE/ton)		73	116			76			125

Potential Cost Savings from Fractionation Process



Algal Lipids and Carbohydrates

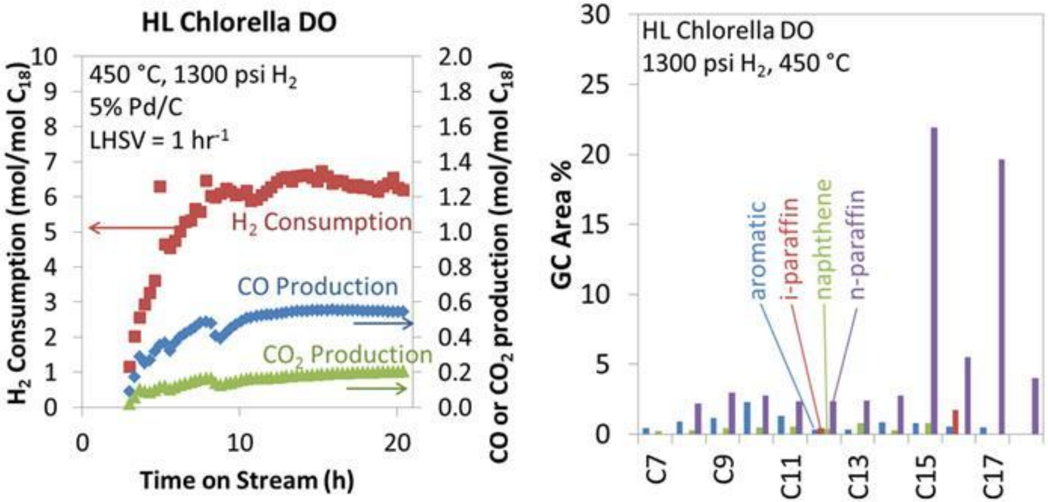


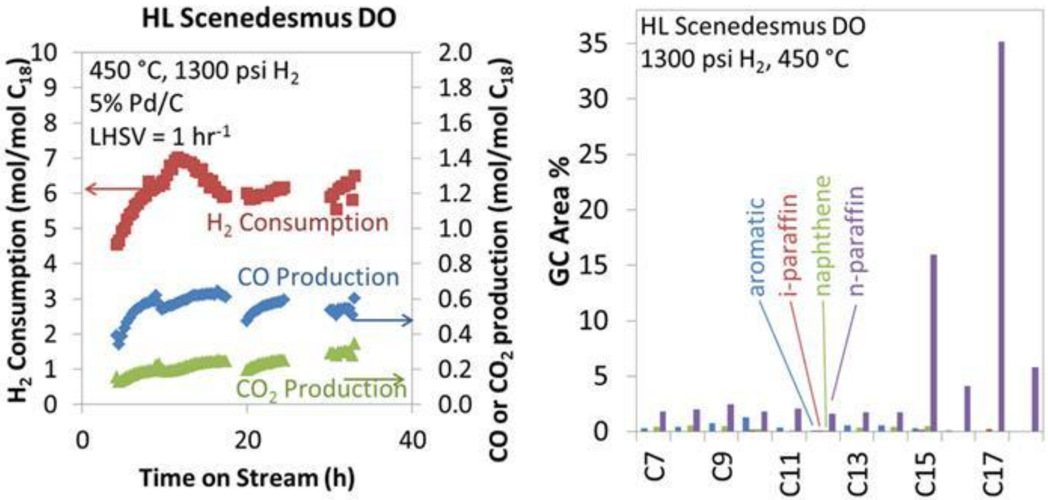
Microalgae	Glucose	Galactose/ Rhamnose	Mannose
	% (based on total carb)		
HCNC	69.6	21.4	8.9
HLNC	72.5	18.3	9.2
HCCZ	80.1	17.0	2.9
HLCZ	84.9	12.1	3.0
HCSD	81.7	3.8	14.5
HLSD	75.9	3.3	20.8

Element	HL CZ	HC CZ	HL SD	HC SD	HL NC
Carbon	76.83	77.42	77.53	76.61	76.87
Hydrogen	11.74	11.54	12.00	11.91	11.77
Nitrogen	0.04	0.05	0.03	0.10	0.09
Oxygen	11.86	11.37	11.04	11.93	11.96
Sulfur	0.004	0.006	0.005	0.026	0.036
Phosphorus	**<0.001**	**<0.001**	**<0.001**	**0.001**	**0.039**

NC: Laminarin
CZ: Starch
SD: Glucomannan

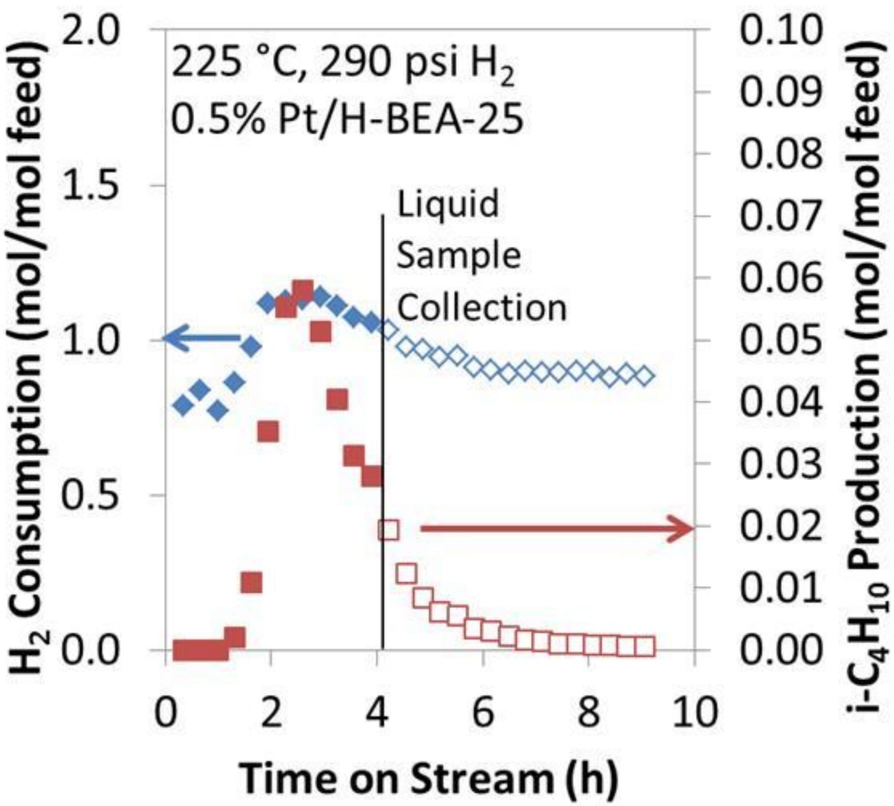
Hydrodeoxygenation





- **Algal oil diluted to 25% in hexane**
- **Liquid product is primarily n-paraffin**
- **Oxygen removal is primarily through decarbon/xylation**

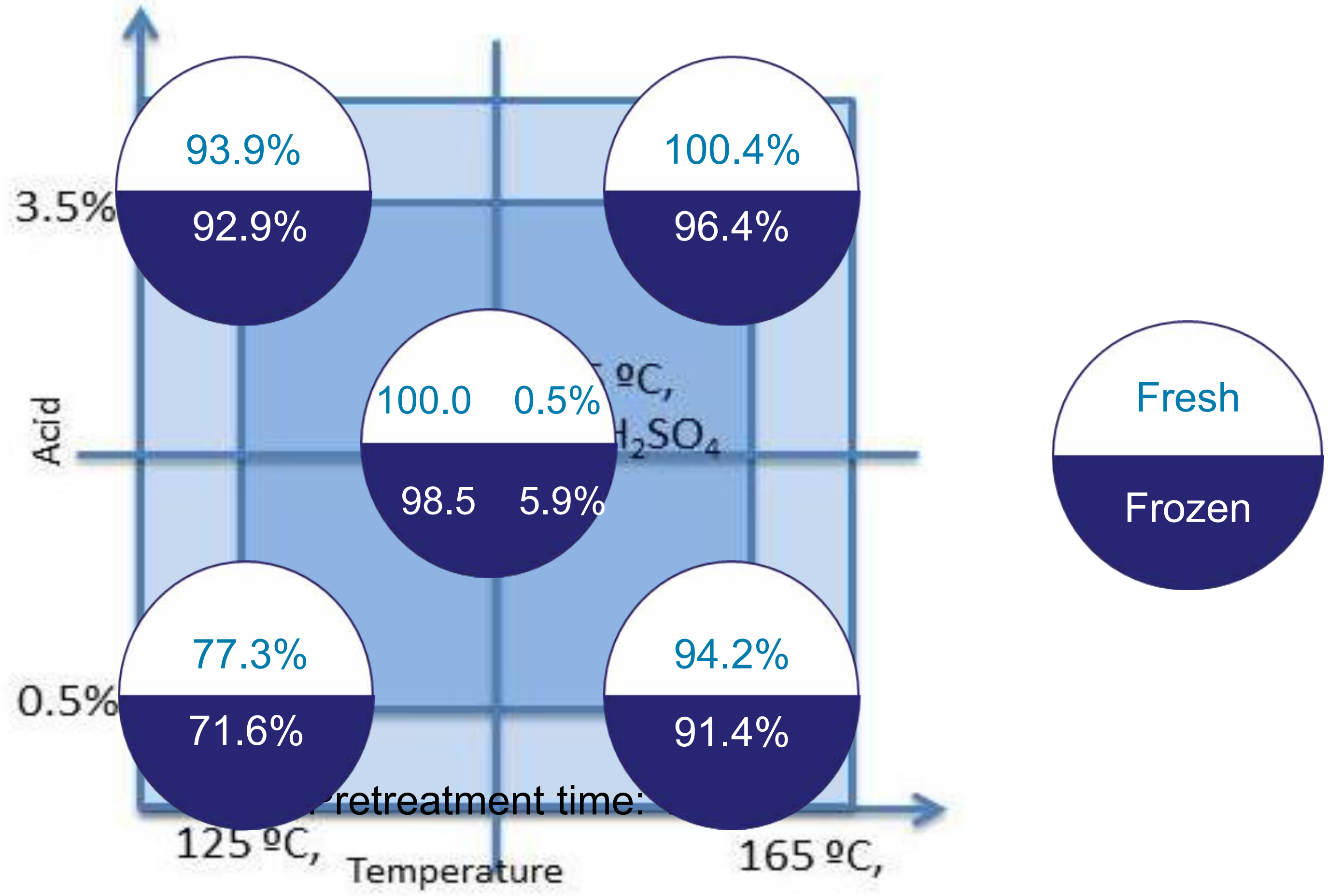
Hydroisomerization of *S. acutus* HDO Oil



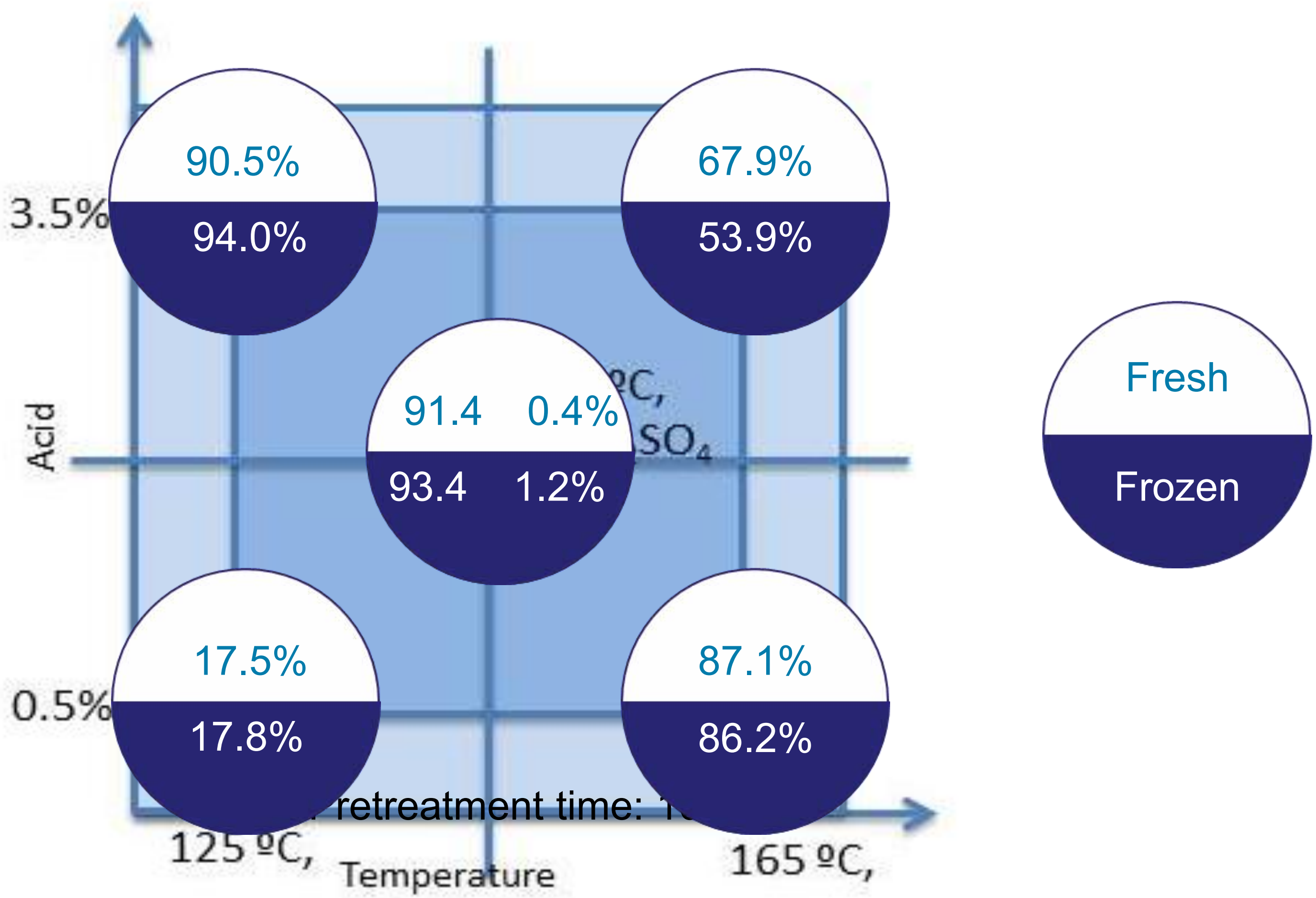
Sample	Nitrogen Content (ppm)
Soy HDO	<1.0 ppm
HLCZ oil	309 ppm
HLCZ HDO	134 ppm
HLSD oil	326 ppm
HLSD HDO	40 ppm

- **Rapid deactivation of HI catalyst**

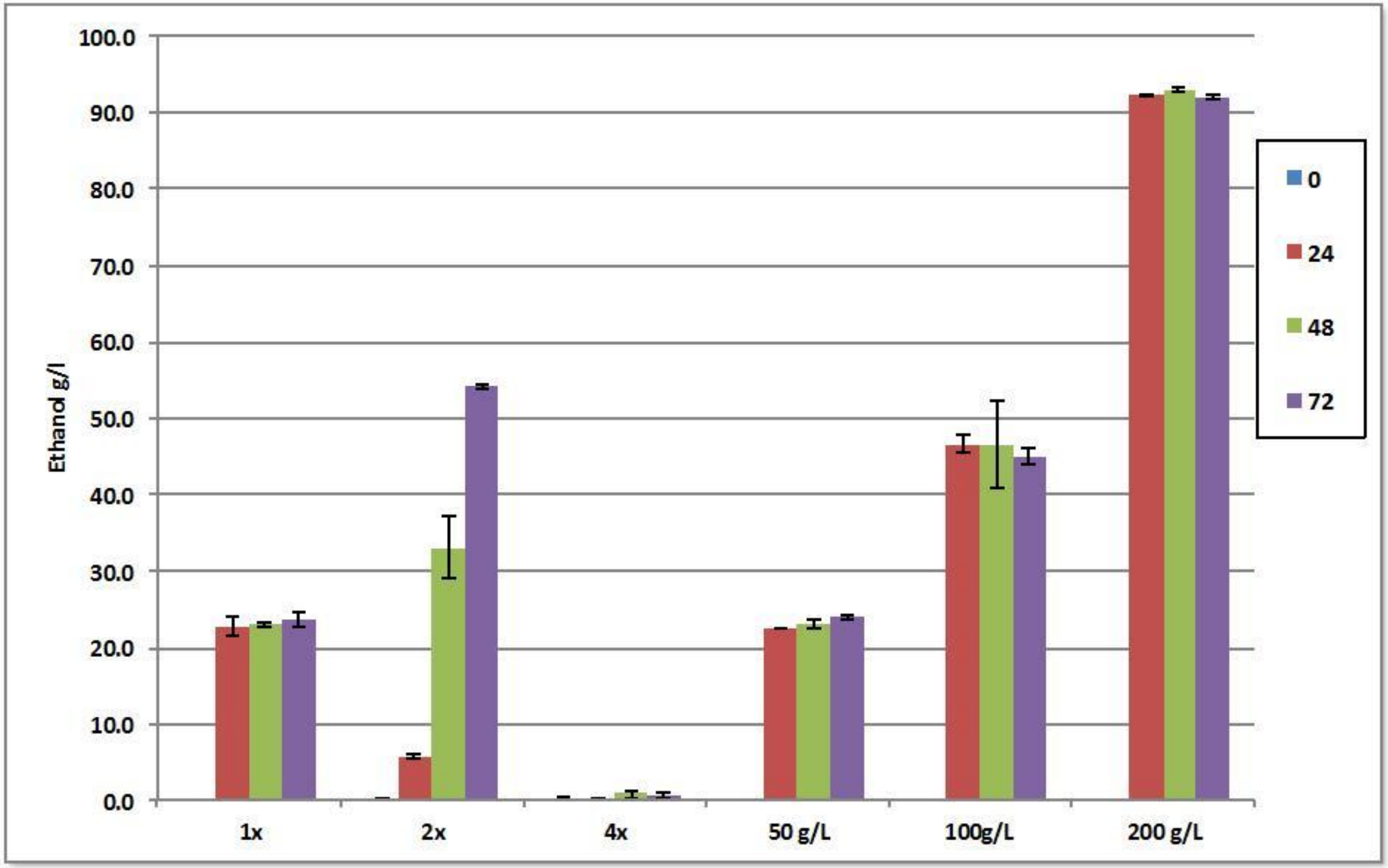
Lipid Recovery in Fresh vs. Frozen *S. acutus* Biomass



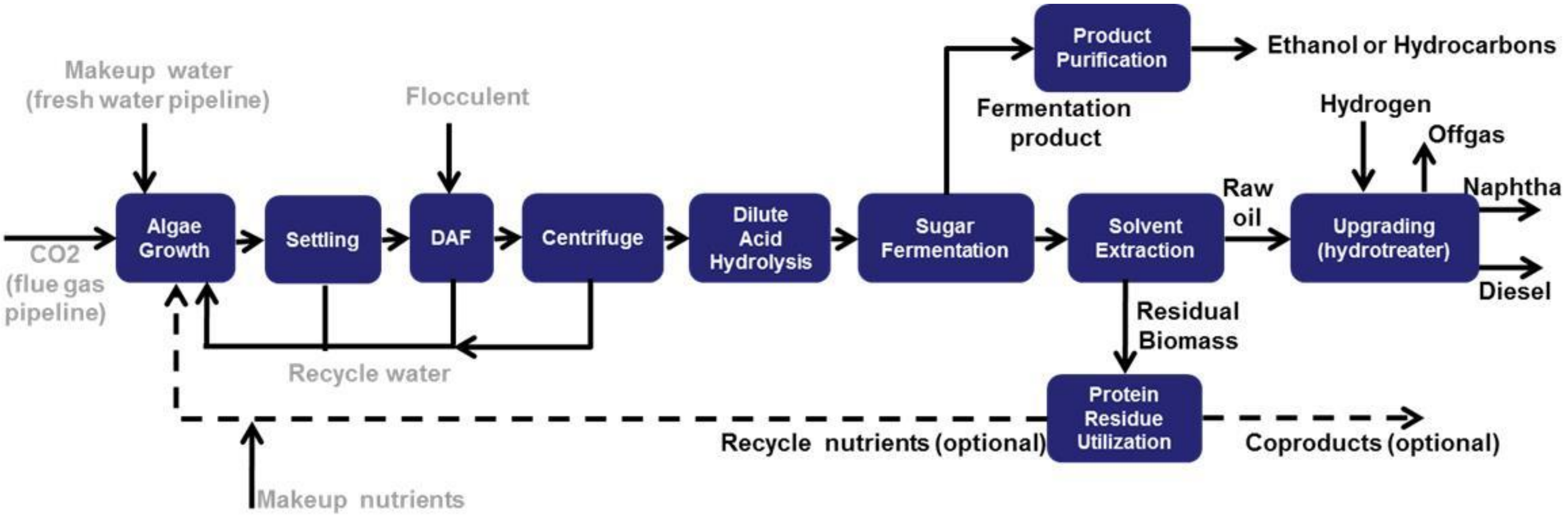
Sugar Recovery in Fresh vs. Frozen *S. acutus* Biomass

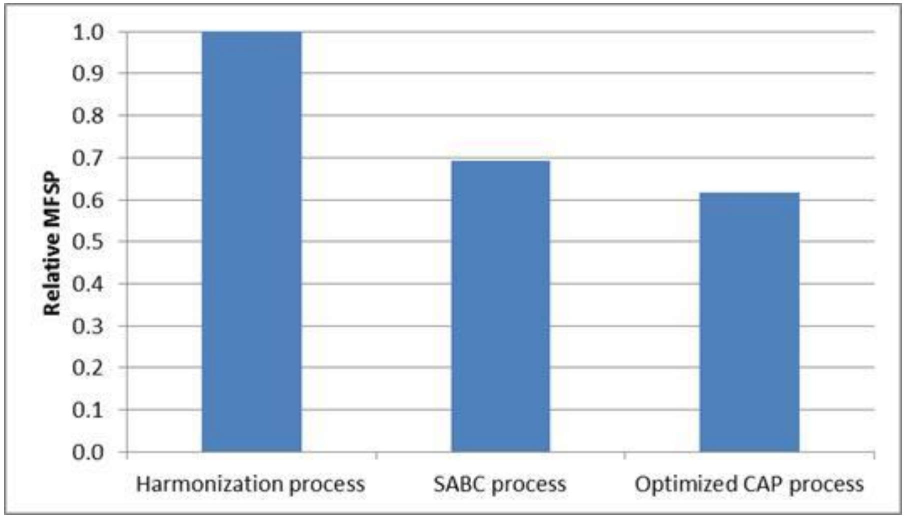


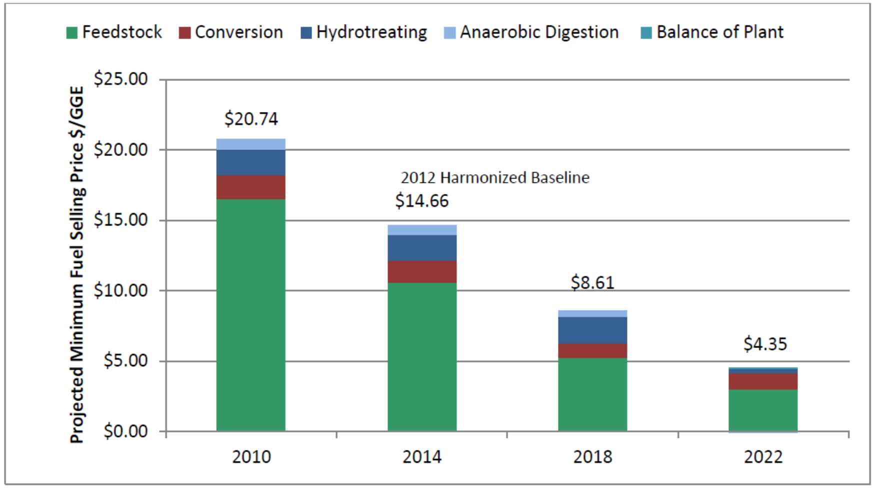
Fermentation of Concentrated Sugars from *S. acutus*



Combined Algal Processing



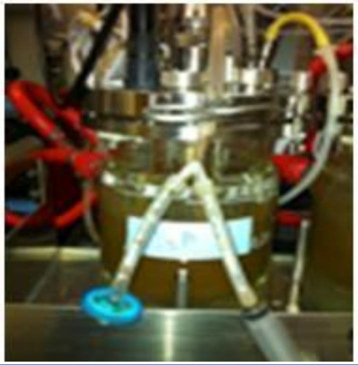


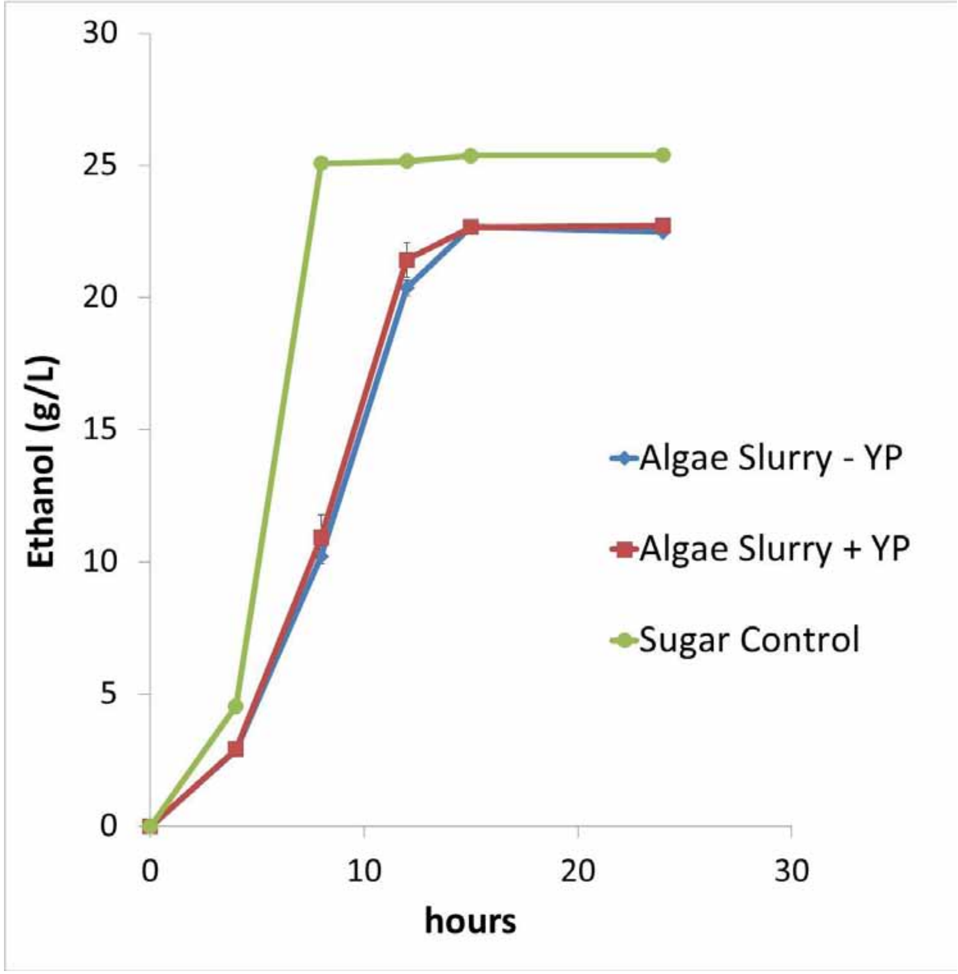


*Note: Information from the 2012 Harmonized Baseline 2010 State of Technology; 2014–2022 Projection.

Figure 2-16: Cost contribution by process area (per GGE total fuel) for ALU Pathway

Bench Scale CAP Results

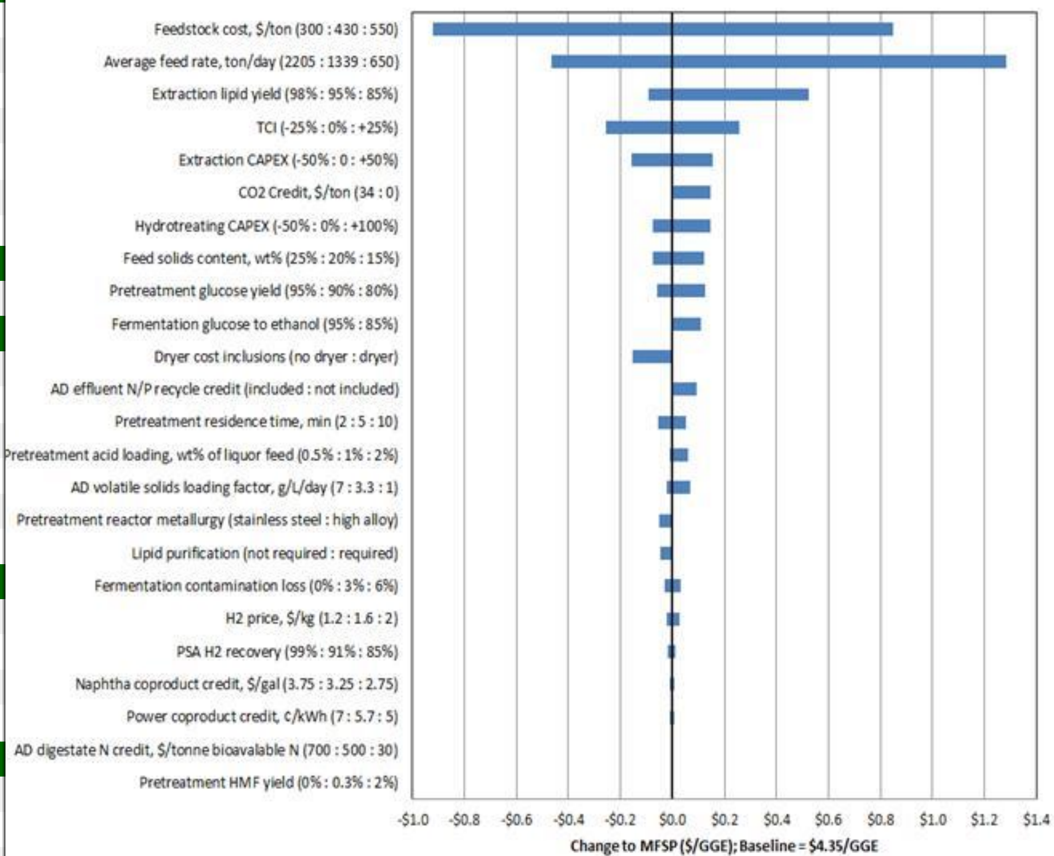




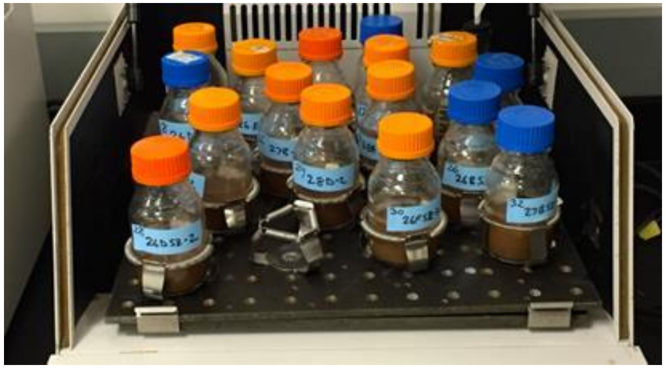
Final Yields		
Sample	**Ethanol Process Yield**	**FAMEs Extraction Yield**
Slurry + YP	82%	87%
Slurry – YP	85%	86%
Sugar Control	90%	nd

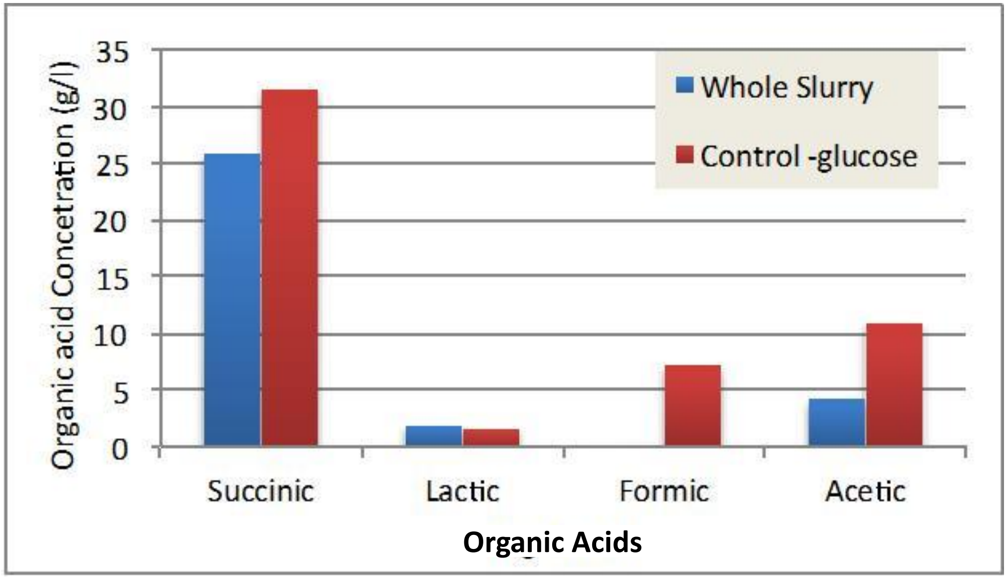
TEA for CAP Process

Metric	Target
Minimum Fuel Selling Price ($/GGE, 2011$)	**$4.35**
Feedstock Contribution ($/GGE, 2011$)	$3.05
Conversion Contribution ($/GGE, 2011$)	$1.30
Yield (GGE/ton afdw)	141
RDB Yield (GGE/ton afdw)	105
Ethanol Yield (GGE/ton afdw)	36
C Efficiency to Fuels from Biomass	64%
Feedstock	
Feedstock Cost ($/ton afdw)	$430
Pretreatment + Conditioning*	
Solids Loading (wt%)	20% *[15-25%]*
Acid Loading (wt% versus feed water rate)	1% *[2%]*
Fermentable Sugar Release ("glucose yield")	90% *[74%]*
Glucan to Degradation Products	0.3% *[1.5%]*
Hydrolysate solid-liquid separation	No *[No]*
Sugar Loss	*NA (CAP process)*
Fermentation*	
Total Feed Solids Loading (wt%)	20% *[~6% sugars]*
Fermentation Batch Time (hr)	36 *[18]*
Sugar diversion to organism seed growth	4% *[ND]*
Fermentable Sugar to Product	95% *[84%]*
Lipid Extraction + Upgrading*	
Solvent Loading (solvent/dry biomass ratio, wt basis)	5.0 *[5.9]*
Total convertible Lipid Extraction Yield	95% *[87%]*
Polar Lipid Impurity Partition to Extract	33% *[<11.5%]*
Hydrotreating RDB Yield (wt% of oil feed)	80% *[ND]*
Hydrotreating H_2 Consumption (wt% of oil feed)	1.7% *[ND]*



CAP Process with Succinic Acid Coproduct





Sample	Total Sugar (g/l)	Succinate (g/l)	Succinate Yield (g/g sugar)	FAME Recovery (%)
Control	40	31.2	0.78	-
Slurry	61.6	25.8	0.42	71

4 – Relevance

- ***We have demonstrated all steps for conversion of algal biomass to upgraded products from lipids and sugars.***
- ***Valorization of non-lipid components provides more flexibility in cultivation process and resulting biomass quality.***
- ***Potential 30% reduction in MFSP from fractionation process and 40% reduction from CAP.***
- ***Cost reductions are independent of improvements in biomass production costs anticipated by MYPP.***
- ***CAP process with value added coproducts from algal sugars could reduce MFSP still further. Proof of concept with succinate has been demonstrated, leveraging BETO-funded work in terrestrial biomass.***
- ***CAP process with value added products from algal protein could reduce MFSP still further (with negative LCA implications). Initial evaluation of algal protein fraction by Algix indicate good properties for plastic applications.***
- ***Fractionation and CAP processes fit with business plans of a number of algae companies***

5 – Future Work

- ***FY15 Q2: Carry out small-scale fractionation parametric studies on at least four biomass samples to estimate potential fuel yields.***
- ***FY15Q3: Determine process benefits to HDO and HI for each of the standard refining steps: degumming, neutralizing, bleaching, and deodorization.***
- ***FY15Q4: Improved process yields from CAP process to 90% ethanol yield on input fermentable sugars and 60% extraction yield of FAME lipids from fermenter.***
- ***FY15Q4: Provide data for updated SOT for alternative biomass samples, improved CAP process yields, and cost benefit analysis of cleanup steps for HD and HI processes***
- ***FY16 Go/No Go: Conduct pretreatment at 10-100 L scale to demonstrate conversion of fermentable sugars to ethanol at 90% yield), recovery of FAME lipids (at 85% yield) and conversion to hydrocarbon (at 60% yield).***
- ***Reach out to refineries to determine minimum standards for diesel blendstock***

Summary

- Milestones have been met or exceeded for
  - Algal biomass pretreatment
  - Sugar fermentation to ethanol
  - Lipid extraction
  - Hydrodeoxygenation to hydrocarbons
- Fractionation and CAP processes can reduce MFSP by 30% and 40% respectively.
- Proof of concept for production of higher value coproducts from algal sugars via CAP process has been accomplished.
- Future work guided by sensitivity analysis for Design Case

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- David Robichaud

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Additional Slides

Responses to Previous Reviewers' Comments (SABC)

- *The very dilute nature of the sugar and amino acid hydrolysates make fermentation and fuel recovery uneconomical and energetically unfavorable. This is a "killer issue" that needs to be presented and addressed.* Our TEA model indicates that ethanol fermentation is economically favorable even at low sugar concentrations. Nonetheless we evaluated concentrating the sugars and fermenting to higher value products.
- *The project might have benefited from investigating other potential co-product uses for the amino acids. Fermentation of amino acids to mixed alcohols appears to have very significant issues of with the alcohols affecting membranes in the fermentation organism, likely limiting titer to uneconomically low values.* Amino acid fermentations have been dropped by NREL. Algal protein from fractionation process has been evaluated by Algix as a plastic feedstock with encouraging results.
- *The effects of freezing and thawing algae may have significantly affected experimental results.* Preliminary data indicates that performance of fresh biomass is equivalent to or even superior than that of frozen biomass.
- *Although success at fuel conversion is nice to have, the ability to convert crude algae oil to fuel does not appear to be a killer issue for algal fuel viability.* Agreed but as changes are made to upstream processes, fuel conversion data increases relevance of project
- *Investigation of possible higher value coproduct development from the hydrolysates might be a better option than fermentation.* Agreed. Ethanol is a proxy for any fermentation product and, as a fuel, fit in well with BETO position of 2013. Demonstration of succinate fermentation provides indication that algal sugars can be a versatile feedstock for higher value products which aligns with BETO's new position on coproducts.

Publications and Patents

- M. Bazilian et al. The energy-water-food nexus through the lens of algal systems. Industrial Biotechnology. 9:158-162. 2013.
- A. Miara et al. An Optimization Framework for Algal Systems in the Energy-Water-Food Nexus" Industrial Biotechnology 10:202-211 2014.
- L. Laurens et al. Strain, Biochemistry and Cultivation-Dependent Measurement Accuracy of Algal Biomass Biochemical Composition. Anal. Biochem. 452:86-95. 2014.
- L. Laurens et al. Acid-catalyzed algal biomass pretreatment for integrated lipid and carbohydrate-based biofuels production. Green Chem. http://pubs.rsc.org/en/content/articl0epdf/2015/gc/c4gc01612b 2014.
- R. Davis et al. Process design and economics for the conversion of algal biomass to biofuels: Algal biomass fractionation to lipid- and carbohydrate-derived fuel products. NREL Technical Report NREL/TP-5100-62368, September 2014. http://www.nrel.gov/docs/fy14osti/62368.pdf
- G. Huiya et al. Recycling Nitrogen from Fuel-Extracted Algal Biomass: Residuals as the Sole Nitrogen Input for Culturing Scenedesmus acutus Bioresource Technology in press 2014.

- Tao Dong et al. Integrated bio-refinery process to produce fine chemicals using microbial-derived fermentable sugars and recover lipids from post-fermented microbial biomass. Record of Invention. 2014.

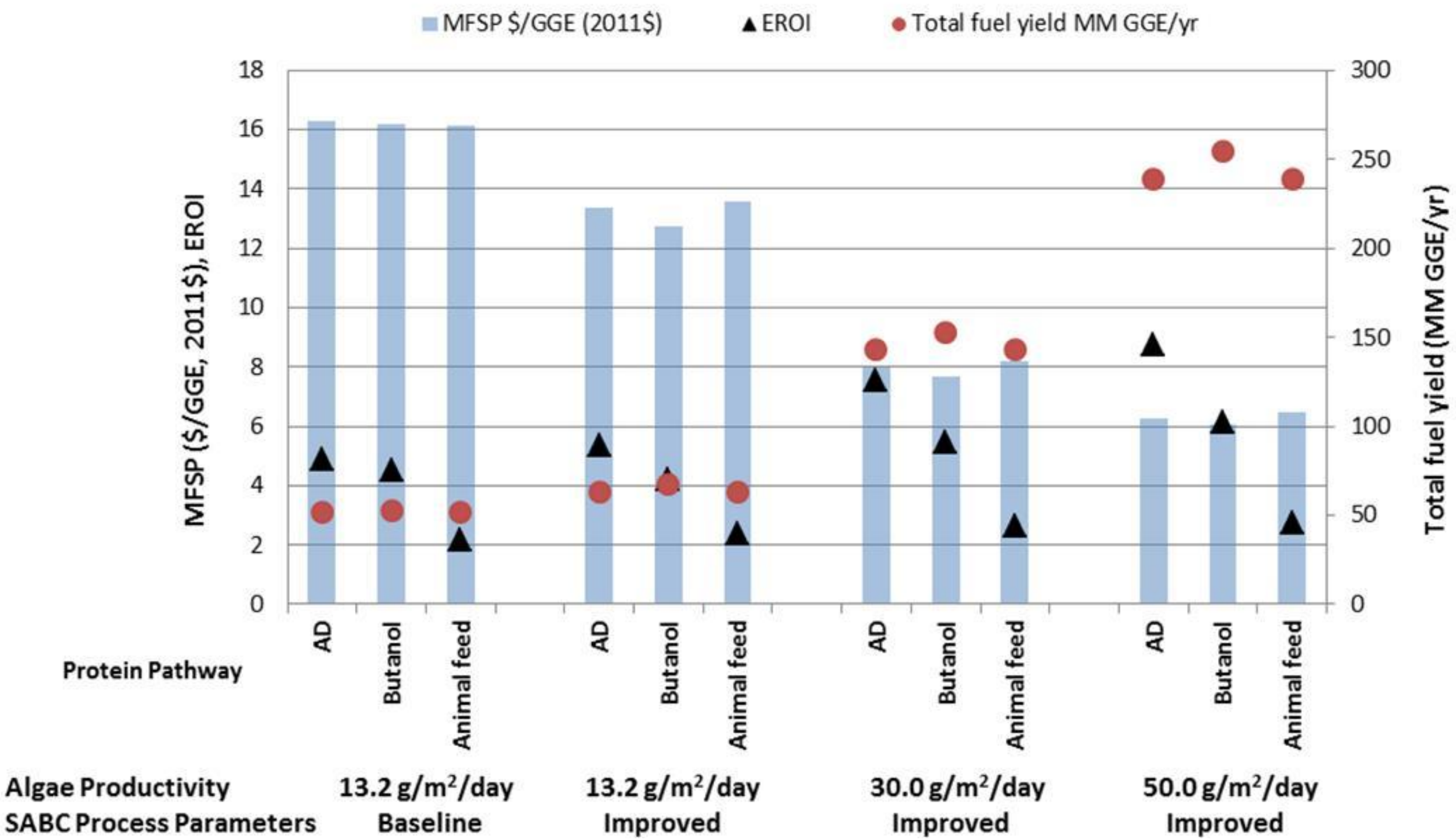
Presentations

- Algae: The Third Way for Biofuels. Philip T. Pienkos. JAIIC Symposium 2013.
- A place for algal biofuels within the energy-water-food nexus. Morgan Bazilian, Ryan Davis, Philip T. Pienkos, and Douglas Arent. Algae Biomass Summit 2013
- Novel Process to Fractionate Algal Biomass into Fuels and Value Added Chemicals Using the Flexible Biorefinery Model. Nick Nagle Lieve Laurens, Ryan Davis, Philip Pienkos and John McGowen. BIO PacRim 2014
- Dilute acid pretreatment for an integrated microalgae bio-refinery to produce lipid- and carbohydrate-based biofuels Tao Dong, Lieve Laurens, Nick Nagle, Stefanie Van Wychen, Nicholas Sweeney, Philip Pienkos. Algae Biomass Summit 2014
- Integrated Processing of Algal Biomass: Pathway Towards Biorefinery Production of Fuels and Chemicals" Nick Nagle, Lieve Laurens, Ryan Davis, Stefanie Van Wychen and Phil Pienkos. Presented at the 36th Symposium on Biotechnology for Fuels and Chemicals. April 30th 2014
- Utilization of Algal Carbohydrates for the Production of Fuels and Value Added chemicals. Nick Nagle,Lieve Laurens, Holly Smith, Nate Crawford , Phil Pienkos and John McGowen. Algae Biomass Summit San Diego CA 9/28-10/2/2014
- Increasing bioconversion of algal biomass through high-value fractionation and recovery: A novel process. Nick Nagle, Lieve Laurens, Ryan Davis, Phil Pienkos, Jake Kruger and John McGowen (ASU). Presented at the 4th International Conference on Algal Biomass, Biofuel & Bioproducts. June 19th, 2014

Commercialization

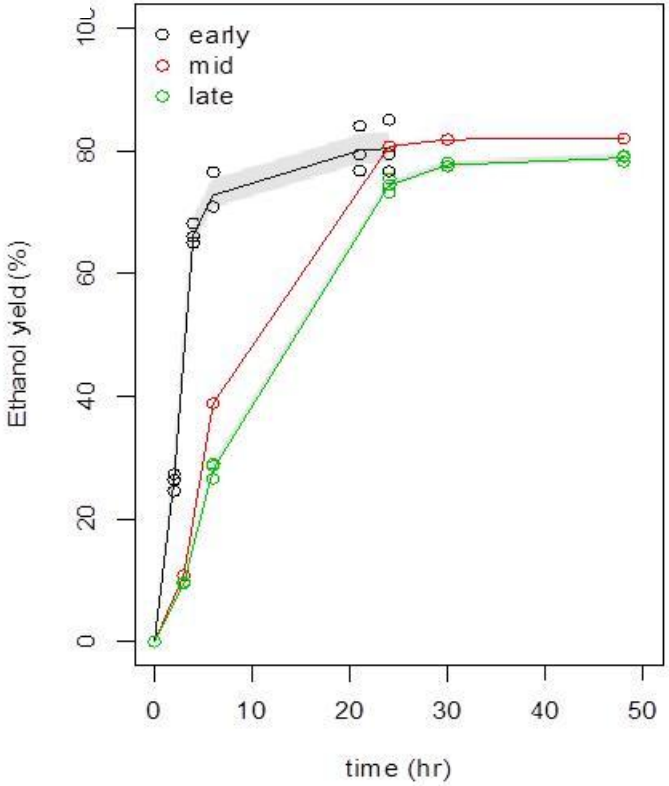
- In negotiations with Johnson Matthey for CRADA on development of catalysts for upgrading of algal oils
- In discussions with algae companies for evaluation of CAP process based on their business models
- Evaluation of algal protein with Algix
- MTA in place with National Research Council for transfer of still bottoms for evaluation in anaerobic digestion

Coproducts from Protein

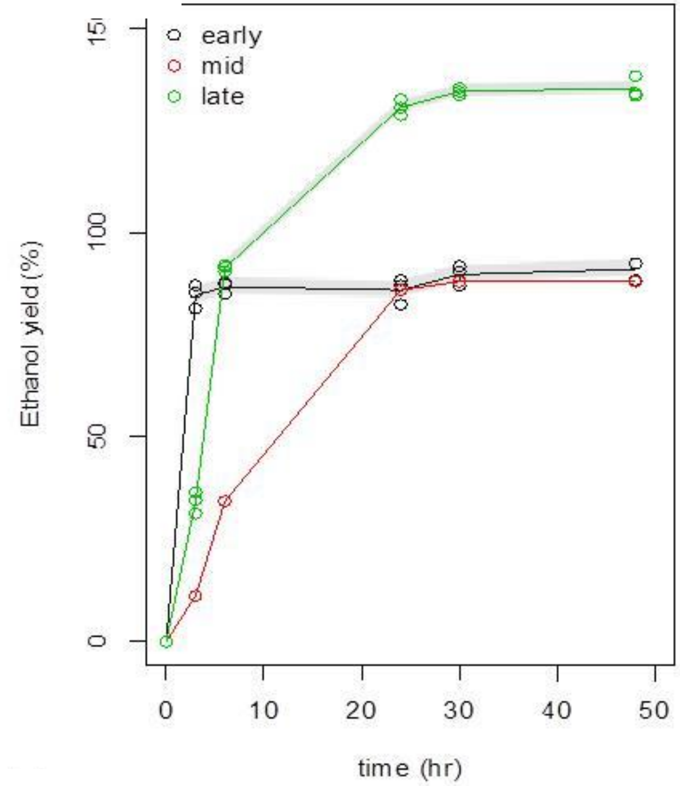


Fermentation of Algal Sugars by Yeast

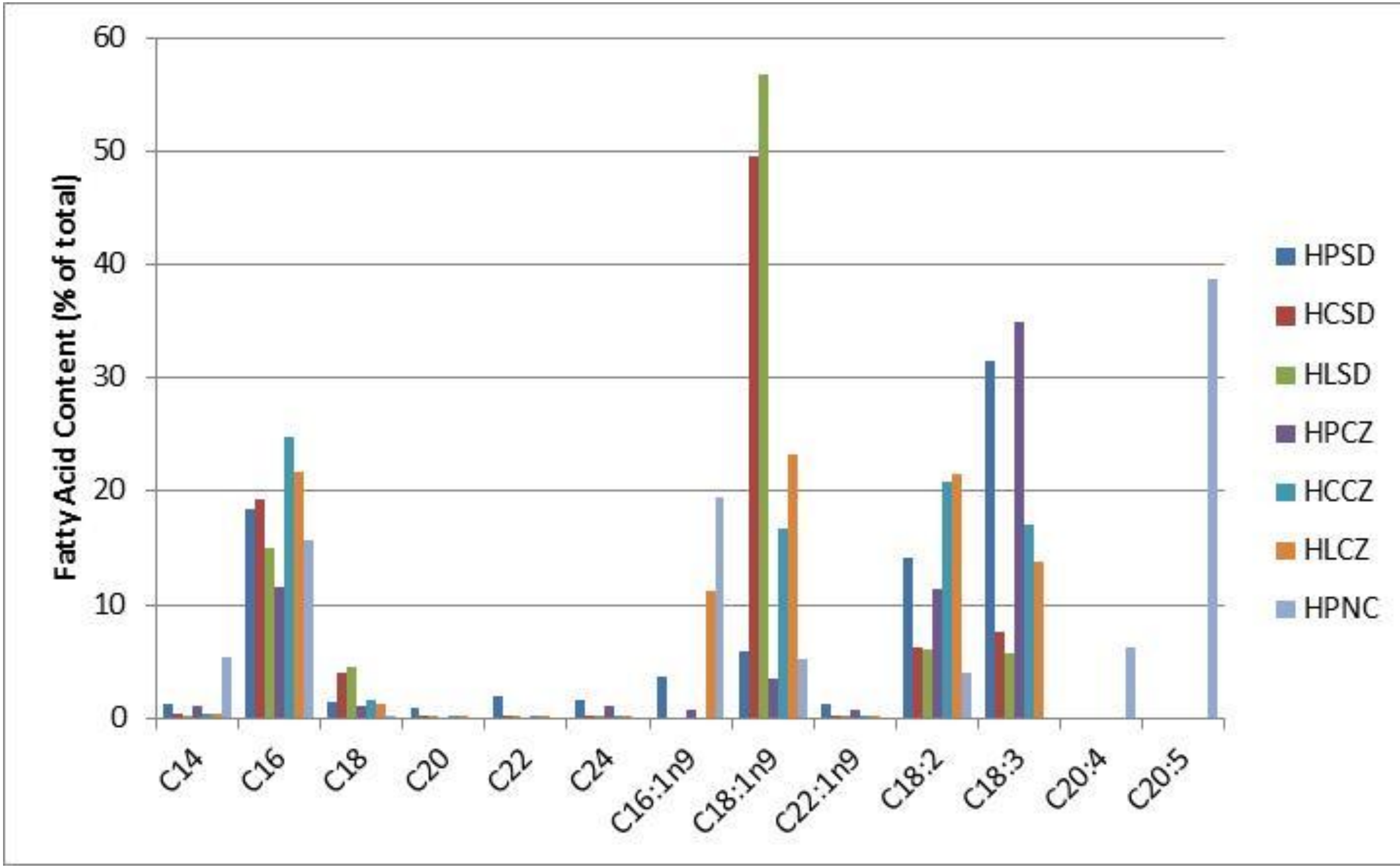
HC SD



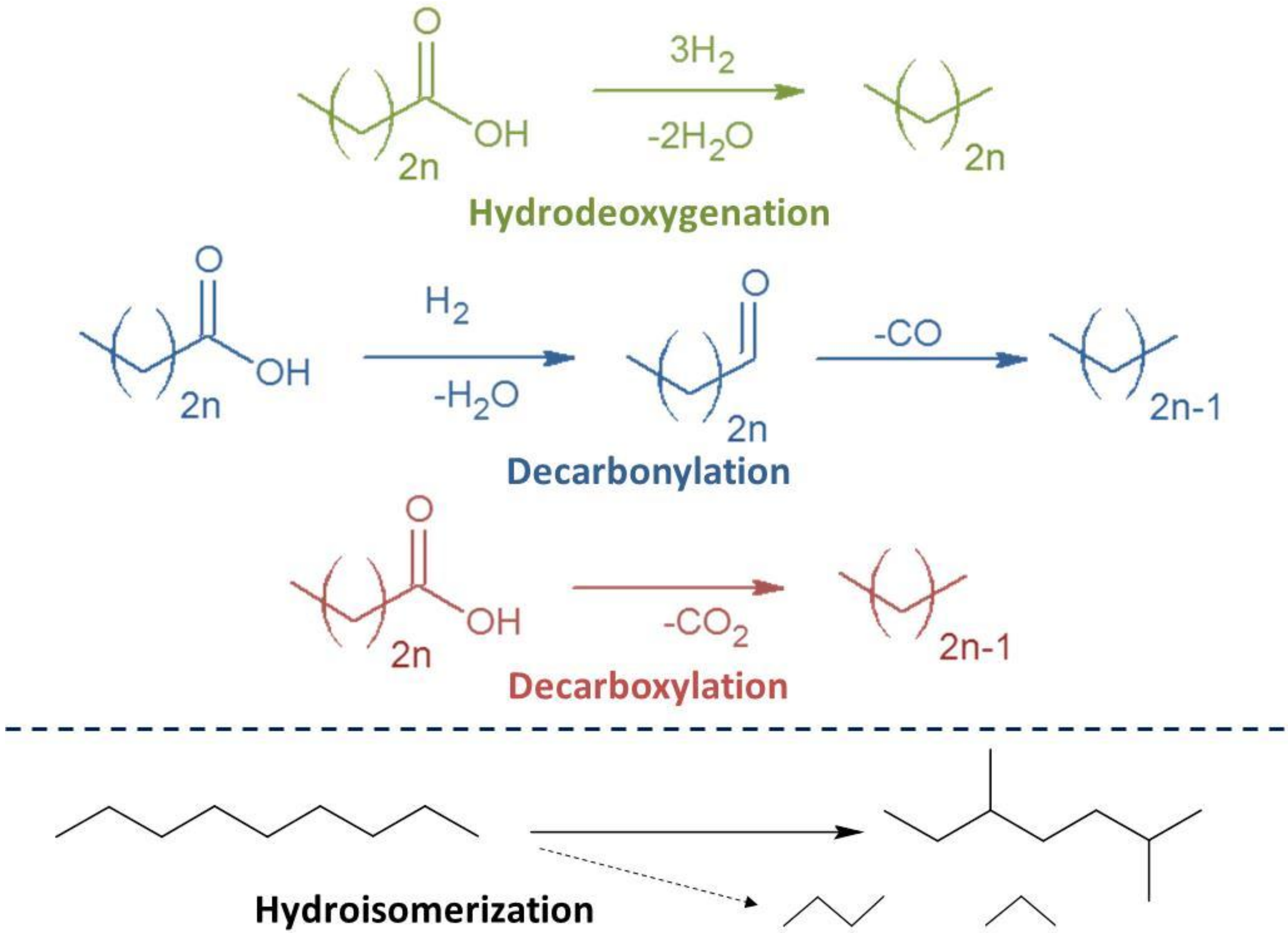
HC CZ



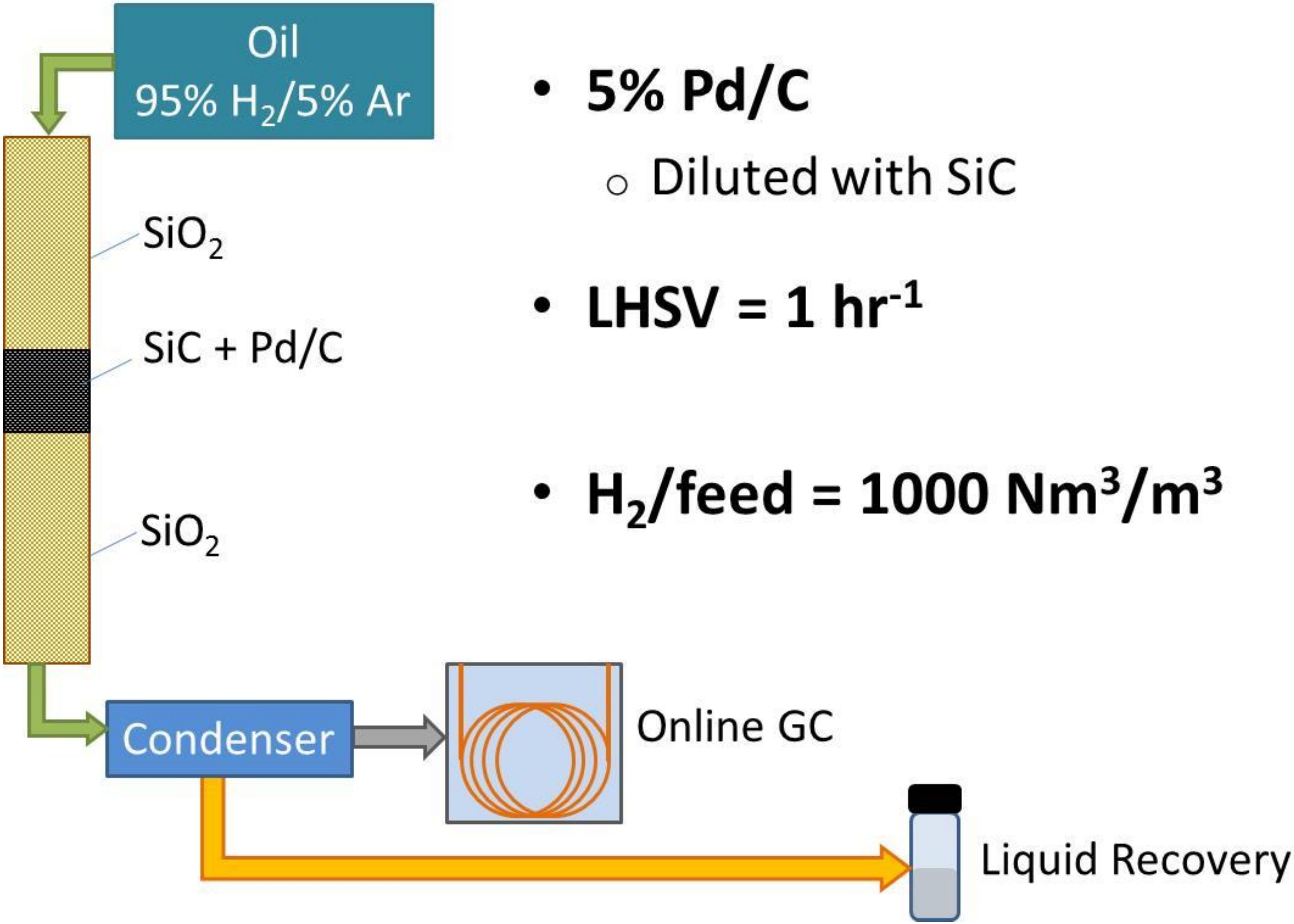
Fatty Acid Profiles in Algae Oils



DO and HI of Lipids

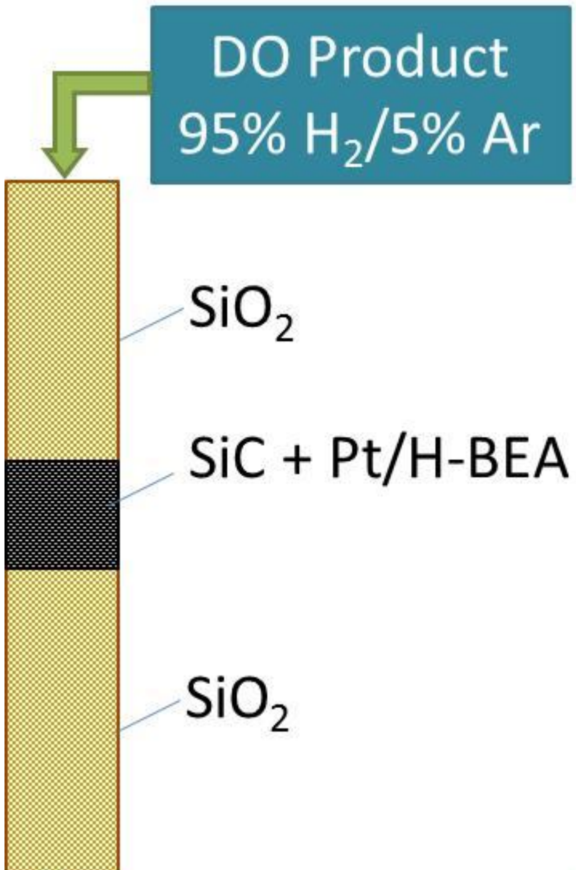


Reactor Setup: DO



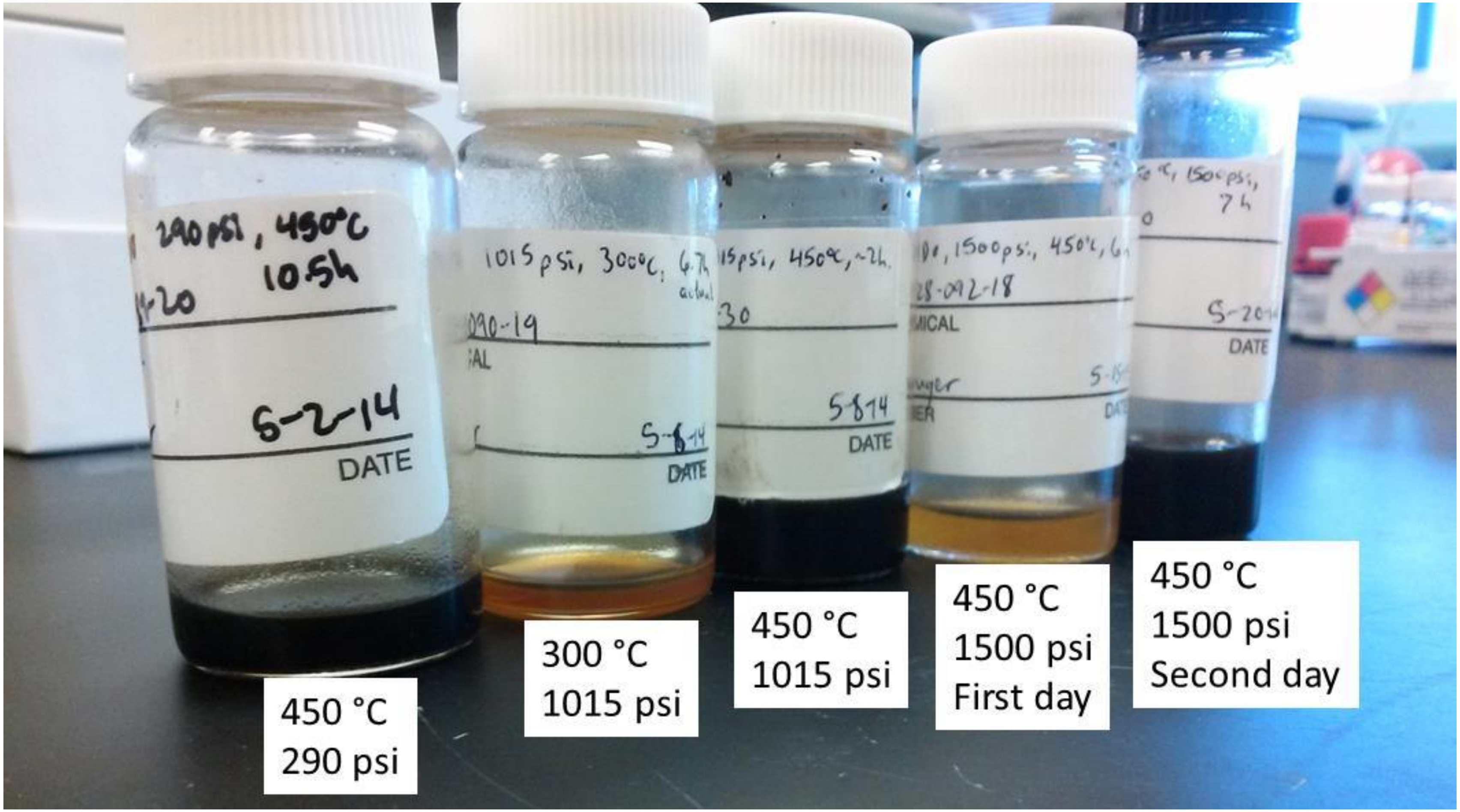
- **5% Pd/C**
  - Diluted with SiC
- **LHSV = 1 hr^{-1}**
- **H_2/feed = 1000 Nm^3/m^3**

Reactor Setup: HI



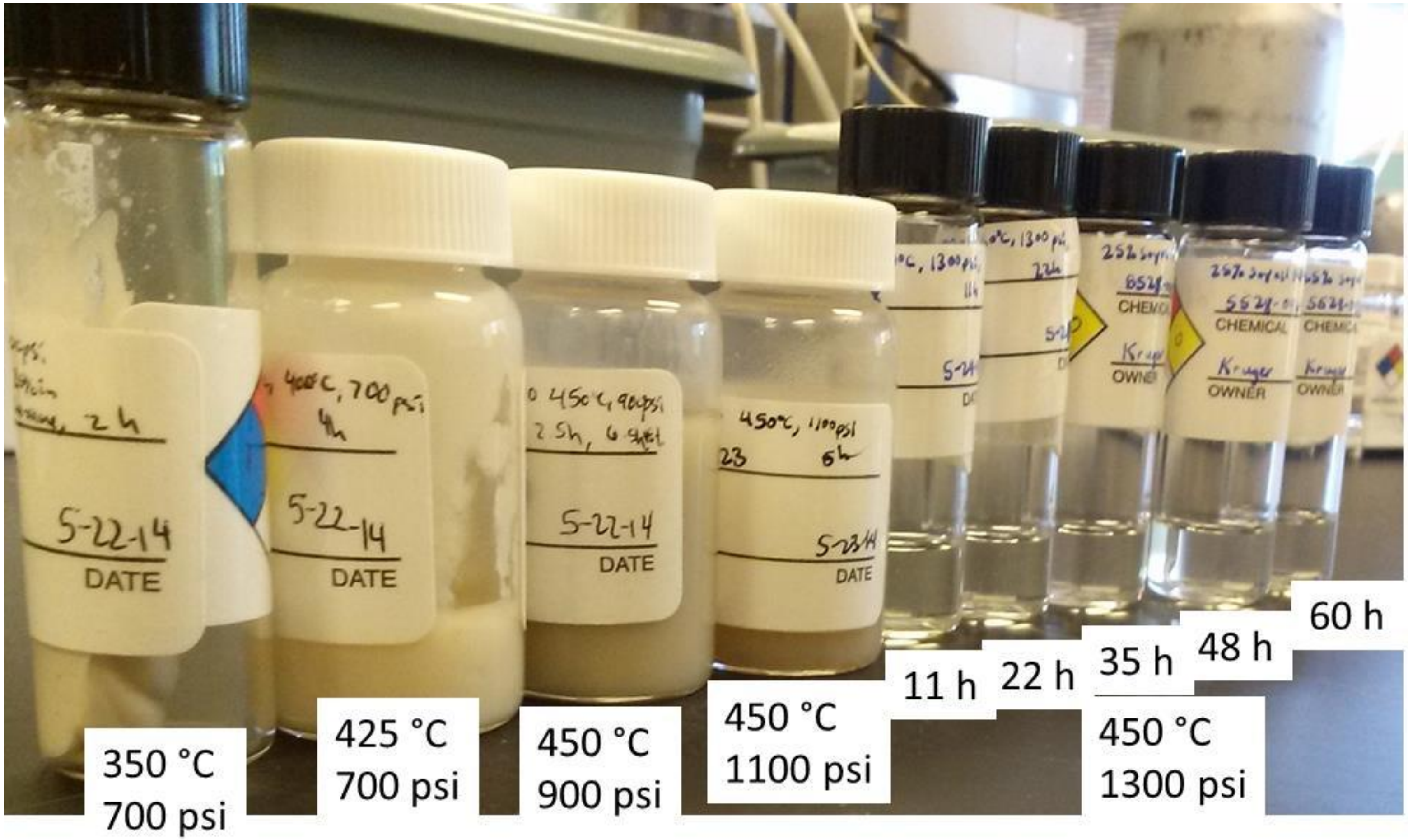
- **0.5% Pt/H-BEA-25**
  - Diluted with SiC
- **LHSV = 3 hr^{-1}**
- **H_2/feed = 1000 Nm^3/m^3**

Neat Soybean Oil DO



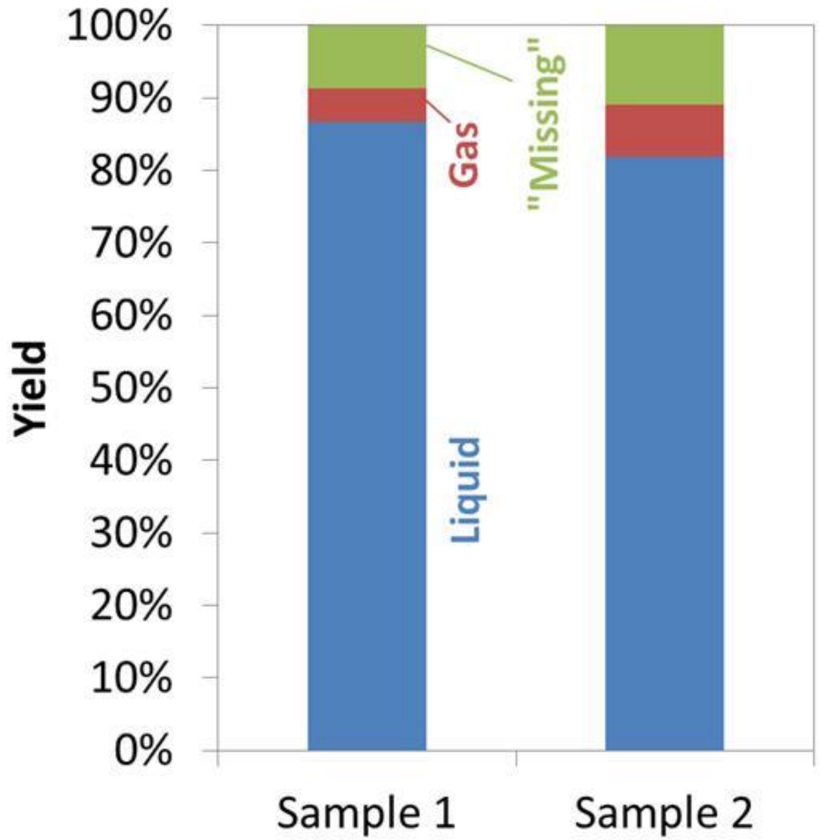
- **No conditions give satisfactory conversion with neat soybean oil**

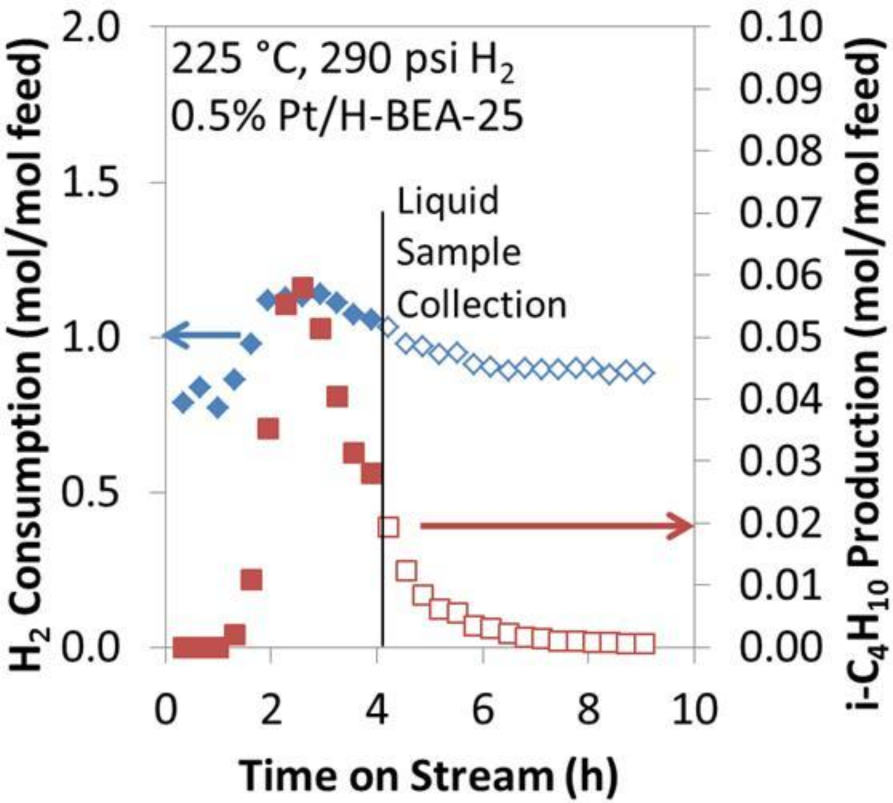
25% Soybean Oil in Hexane DO



- **Diluting oil in hexane gives free-flowing, transparent product at 450 °C and 1300 psi H_2**

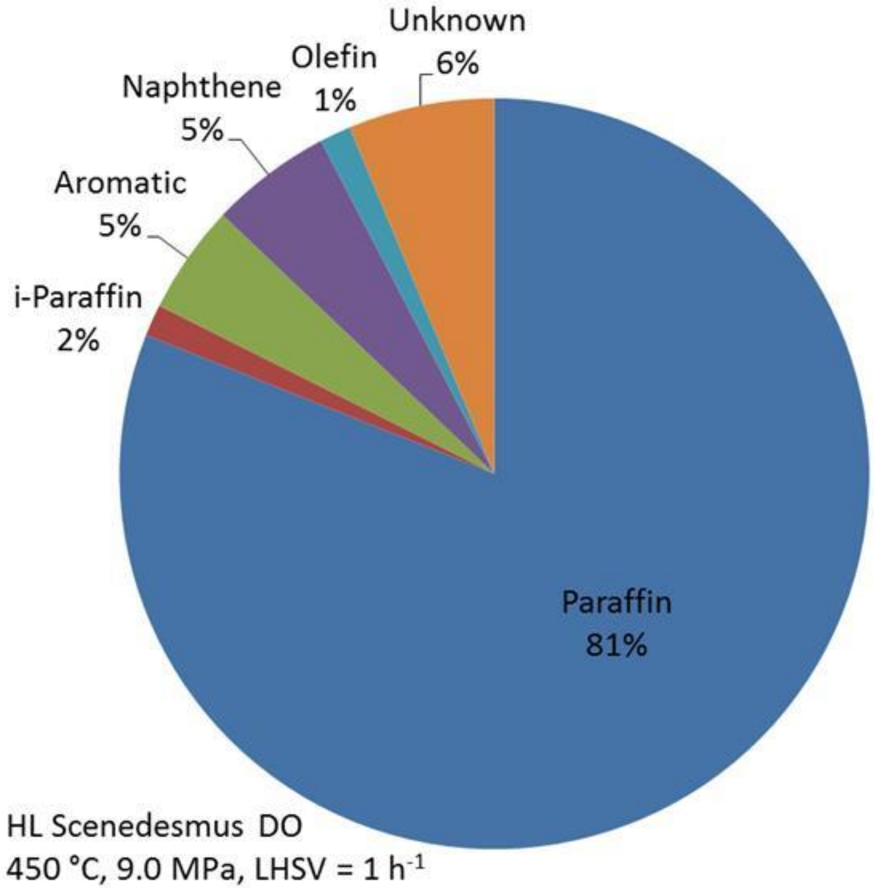
HL Scenedesmus HI

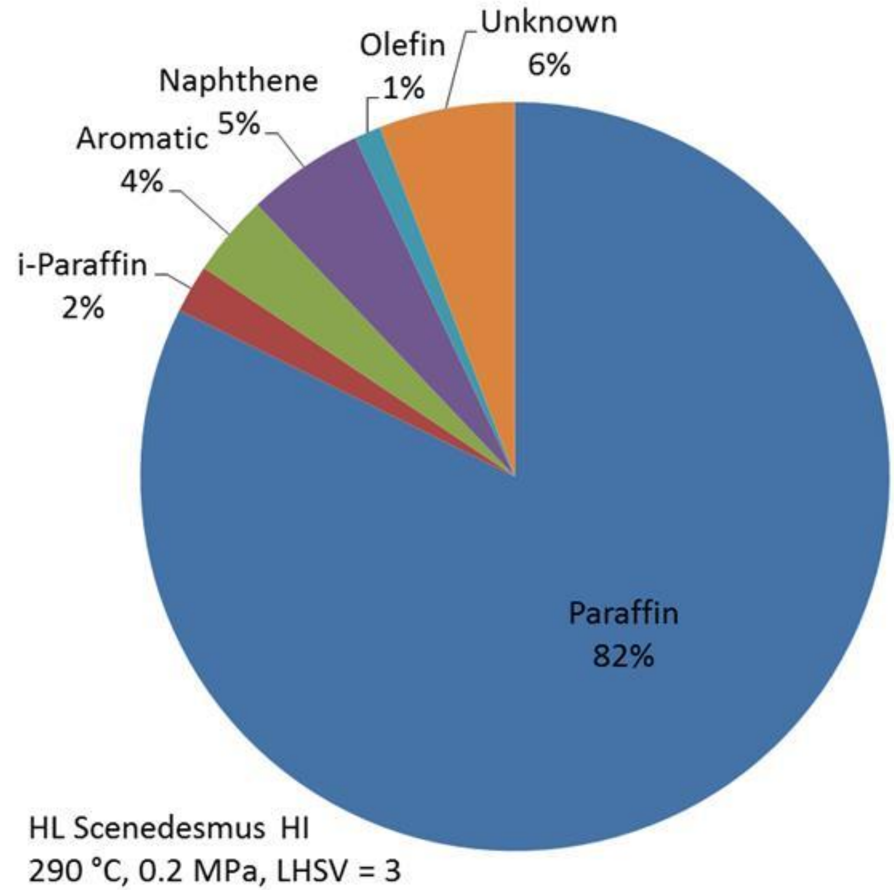




- **Good liquid yields**
- **Rapid deactivation of HI catalyst**

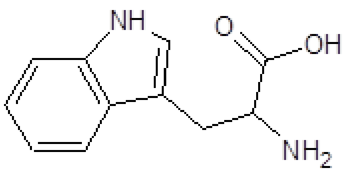
HL Scenedesmus HI



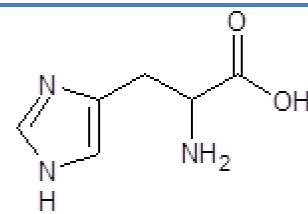


- **Liquid phase has same composition before and after isomerization step**

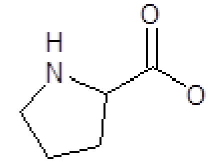
(Potential) Source of Deactivation



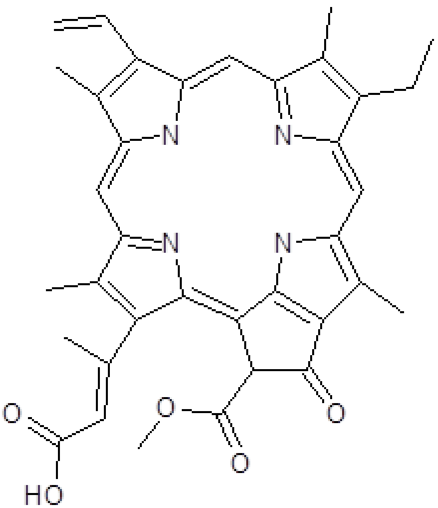
Tryptophan



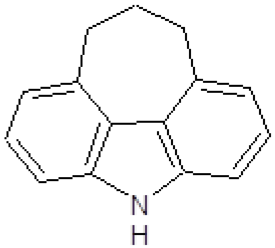
Histidine



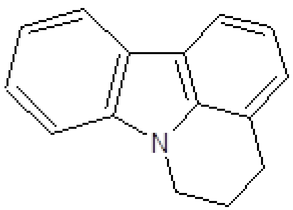
Proline



Chlorophyll *c1*



4,8,9,10-tetrahydro-cyclohepta[def]carbazole



5,6-dihydro-4H-pyrido[3,2,1-jk]carbazole

- **Condensed, cyclic N compounds stable under DO conditions[1]**
- **May form from pigments, proteins co-extracted with lipids**

[1]Wiwel et al., *Ind Eng Chem Res*, **2010**, 49, 3184-3193

Inorganic Analysis of CAP Oil

Elements	HLSD	CAP (+YP)	CAP (-YP)
TX*--------µg/g	<10	<10	12
Calcium----µg/g	2	<2	<2
Iron-------µg/g	<2	5	3
Magnesium--µg/g	<1	<1	<1
Phosphorus-µg/g	<20	<20	<20
Potassium--µg/g	<50	<50	<50
Sodium-----µg/g	<50	<50	<50
Sulfur-----µg/g	30	55	58
Nitrogen-----µg/g	317	296	286