2013 DOE Bioenergy Technologies Office (BETO) Project Peer Review

Pt-based Bi-metallic Monolith Catalysts for Partial Upgrading of Microalgae Oil

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Alexandria, Virginia
Bio-Oil Technology Area Review

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Goal

Development of cost-effective technologies for conversion of microalgae to an algal oil suitable for insertion into the hydrotreatment unit of a petroleum refinery to produce green diesel

Objectives

- ***Refine the novel Valicor microalgae fractionation technology for continuous mass scale operation and commercialization***
- ***Conduct performance and optimization studies of <u>first-stage</u> hydrodeoxygenation (HDO) of Valicor pre-refined algal oil***
- ***Develop a blueprint for the process design, economic analysis & life-cycle assessment (LCA) of the integrated process for conversion of microalgae to a partially upgraded bio-oil***

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Project Quad Chart Overview

Timeline

- **Start Date – February 01, 2013**
- **End Date – January 31, 2014**
- **Percent Complete ~ 25%**

Barrier Addressed

- **Al-B Algal Fuel Production**

Budget

- **Total Project Funding – $819,240**
  - ➢ **DOE Share – $651,194**
- **Funding for FY 2013 – $546,160**

Partners & Roles

- **Lead Institution – Stevens**

➢ **Performance & Optimization Studies of HDO of Pre-refined Algal Oil**

➢ **Initial catalyst preparation and screening**

➢ **Process Design, Economic Analysis & LCA of integrated process (in conjunction with consultants)**

- **Valicor Renewables**

➢ **Extraction, fractionation &**

➢ **purification of Algal oil**

- **Columbia University**

➢ **Monolith catalyst preparation**

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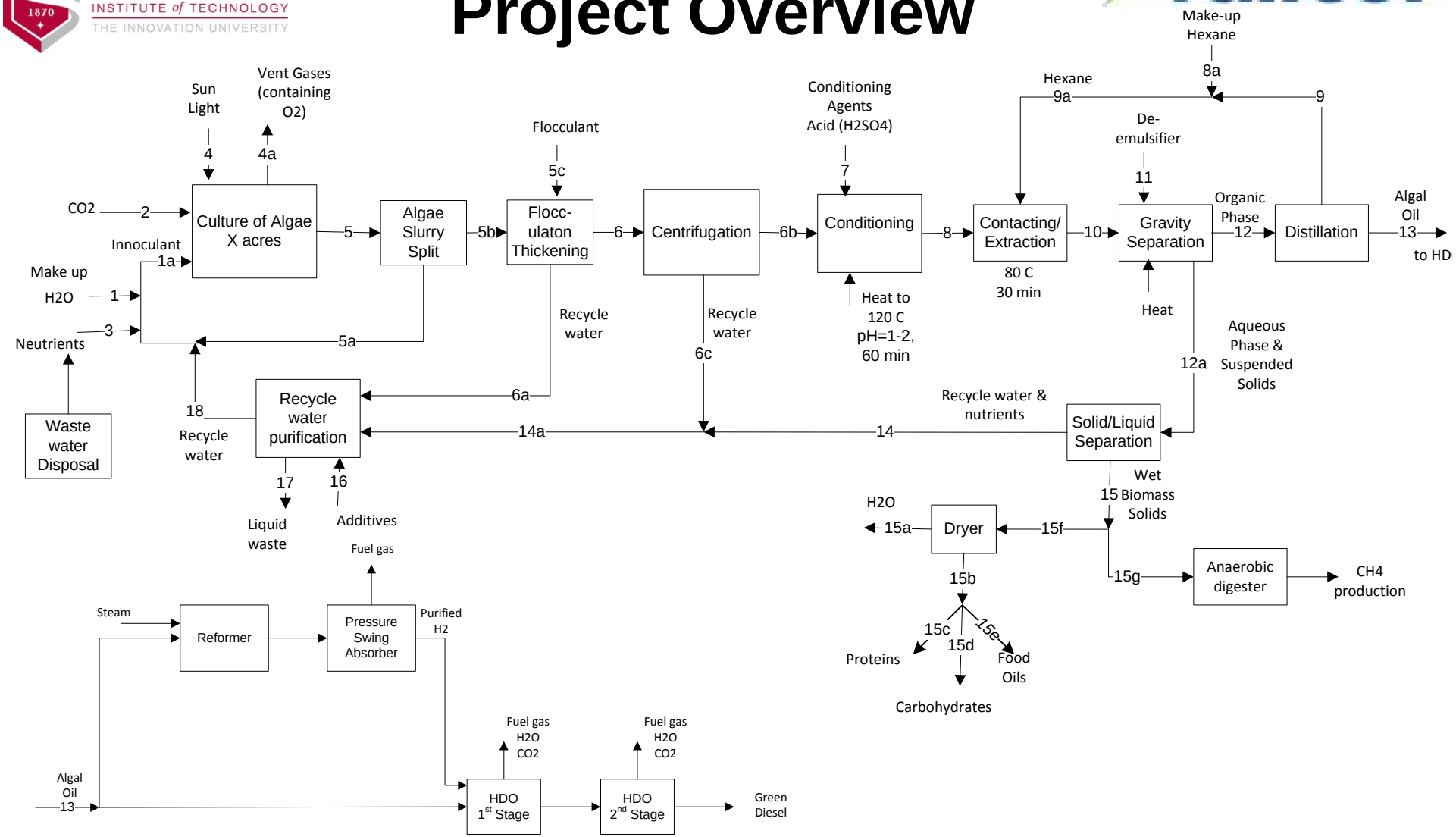
Project Overview



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Project Overview (Contd.)

Key Technical Barriers Addressed

Pre-processing of Algal Oil

- Presence of polar lipids that can poison precious metal catalysts
- Presence of catalyst deactivating metals and metalloids (especially phosphorus in the form of phospholipids)

Hydrodeoxygenation of Algal Oil

- Poor selectivity of conventional HDO (Ni/Mo, Co/Mo) catalysts
- Need for sulfided form of catalysts
- Susceptibility of Ni/Mo, Co/Mo to rapid deactivation
- Lack of experimental data on HDO of algal oils
- High hydrogen pressure requirements
- Low space-time yield and large pressure drop in conventional reactors negatively impact process economics

Approach

- ***Valicor algae oil extraction process employs heat and chemical conditioning of algae cells followed by proprietary physical extraction to unlock difficult to reach membrane bound lipids (pilot plant)***
- ***Use of mild conditions for algae oil processing to minimize energy, and use of a single non-polar solvent***
- ***Hydrolysis of polar lipids and other hydrotreating catalyst poisons (metals and inorganics).***
- ***Replacement of sulfided Ni/Mo, Co/Mo with Pt-based bi-metallic which does not require sulfur addition for HDO***
- ***Pt-based catalysts are resistant to coking and deactivation; easily regenerates when deactivated***
- ***Use of microreactor-enabled monolith reactor (lab) to enhance space-time yield, reduce pressure drop and thus render process economics favorable***

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Technical Accomplishments

Task 1: Chemical & Physical Characterization of Process Streams

Oil Compounds in Algal Oil

- Monoacylglycerides (w/w%) 4.41
- Diacylglycerides (w/w%) 4.56
- Triacylglycerides (w/w%) 29.23
- Free Fatty Acids (w/w%) 9.25

Total Fatty Acids 47.45%

- Chlorophyll a&b (w/w%) 0.78
- Carotenoids (w/w%) 0.46

Total solvent residues 0.05%

Water content (KF titration) 0.86%

Fatty Acid Profile (w/w%)

C14:	4.52
C16:	57.04
C18:	11.27
C20:	26.56
>C21:	0.61

Elemental Analysis (w/w%): C: 76.29; H: 11.22; N: 0.43; O: 12.06
Sulfur: 2033ppm; Phosphorus: 246ppm

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Technical Accomplishments

Task 2: Extraction, Fractionation & Purification of Algal Oil

- ***We have grown 20 kg algal biomass (Nannochloropsis Salina) in open raceway ponds in New Mexico and harvested the algae using flocculation and de-watered to 12% solids using centrifugation***
- ***We have extracted oil from the biomass using our wet extraction platform with hexane as the solvent. We observed extraction efficiency (relative to the lab analytical standard "Bligh Dyer" technique) of ~ 90%.***
- ***We are currently tabulating mass balance data (oil, biomass, water, etc.)***
- ***The pre-refined algal oil appears to exceed all the analytical specs we set ourselves (N, S, P)***

Performance Metrics for Task 2

	Proposed	Achieved
Extraction Efficiency	80%	90%
Nitrogen	<1 wt%	0.43 wt%
Sulfur	<< 0.1wt%	0.2wt%
Phosphorus	<0.1wt%	0.025wt%

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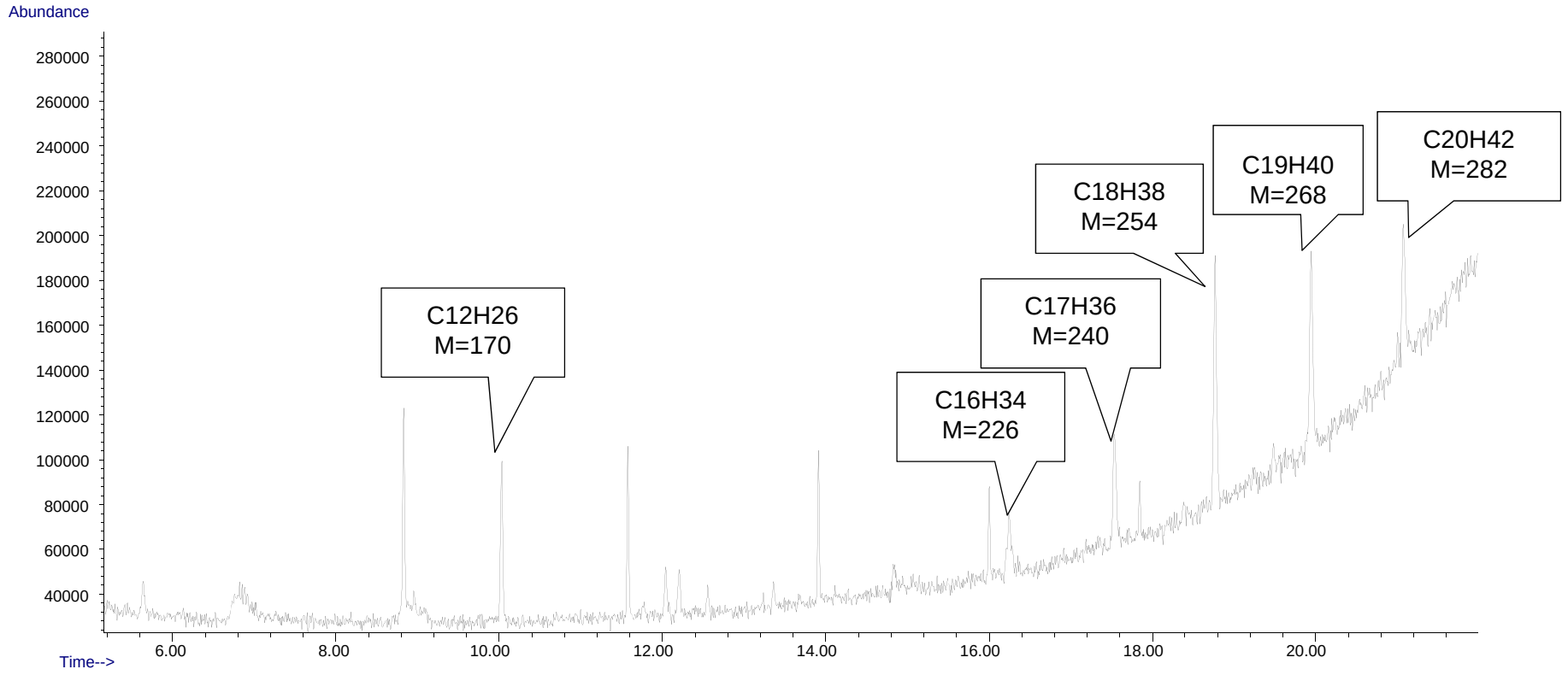
Technical Accomplishments

Task 3: Evaluation of Monolith Reactor for First Stage HDO of Algal Oil

- ***Initial catalyst screening undertaken in existing 800µm packed-bed microreactor (pressure ~ 500 psi)***
- ***Successfully performed HDO on mixture of algal oil and hexane with three different catalysts; sulfided Ni/Mo on γ-alumina, Pt A and Pt B on γ-alumina***
- ***Straight chain alkanes produced at 300°C and moderate hydrogen pressure (500psi)***
- ***Prepared Pt-Sn and Pt-Mo particulates for evaluation***
- ***Completed the design of the high pressure monolith HDO reactor system***
- ***Assembly of monolith HDO reactor system begun***

Technical Accomplishments

Platinum A on γ-alumina
800 µm packed-bed microreactor
Temperature = 300°C; 500 psi H_2



GC/MS Chromatogram of Product Stream

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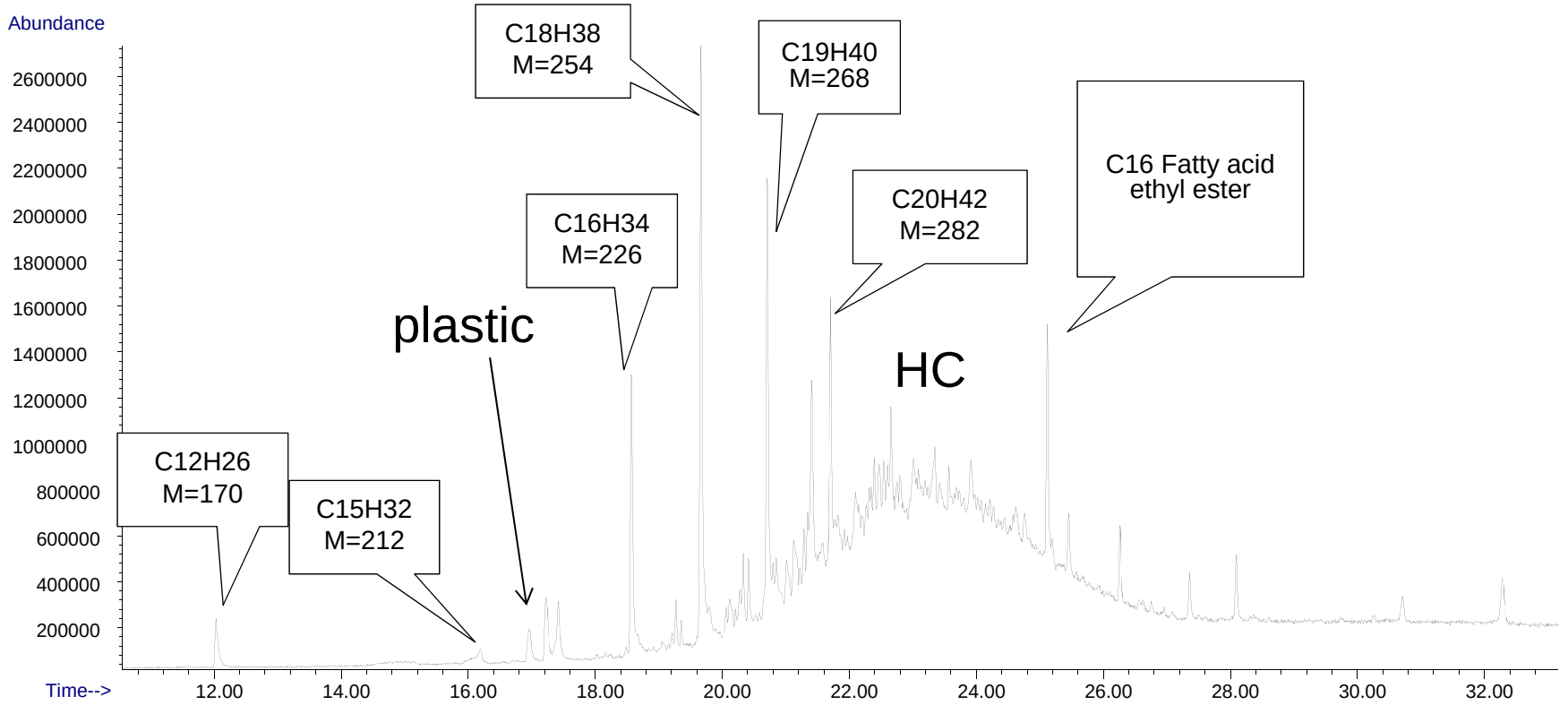
Technical Accomplishments

Sulfiided Ni/Mo on γ-alumina
800 µm packed-bed microreactor
Temperature = 300°C; 500 psi H_2



GC/MS Chromatogram of Product Stream

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Technical Accomplishments

Feed and Product Samples from Initial Catalyst Screening

Reactor Feed **Reactor Effluent**

Sulfided Ni/Mo **Pt A** **Pt B**

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Technical Accomplishments

Task 4: Process Analysis, Design & LCA of Integrated System for Production of Partially Upgraded Algal Oil

- ***Developed the detailed process flow diagram for the integrated process (see Project Overview section)***
- ***Performed preliminary material balance on the PFD***

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Relevance

Project will demonstrate:

- ***Conversion of various high-lipid content microalgae to a partially upgraded algal oil that can be inserted into the hydrotreatment unit of a petroleum refinery***
- ***Feasibility of the conversion of high quality partially-upgraded algal oil into green diesel in realization of BETO's platform goal of algal biofuel***
- ***Energy efficient and economically viable route from microalgae to transportation fuel in collaborative partnership with a petroleum refiner***

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Critical Success Factors

- *Economical and energy-efficient algal oil extraction*
- *Production of pre-refined algal oil with low concentration of catalyst poisons (phospholipids, metalloids, etc.)*
- *High reactivity HDO catalysts for algal oil*
- *Catalysts with high resistance to deactivation*
- *Process intensification leading to smaller, & more energy efficient system than conventional reactor systems*

Potential Challenges for Commercial Viability

- *Cost of production of pre-refined algal oil*
- *Catalyst life and associated cost*
- *High pressure requirements for HDO*
- *Availability of cost-effective hydrogen supply*

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Future Work

Task 2: Continued advancement of Valicor algal oil extraction technology to enable reduction of processing cost from current value of $0.50/gal to $0.40/gal

Task 3: Completion of the construction of the high pressure HDO reactor system
Preparation of catalysts with different formulations
Completion of catalysts screening
Performance & optimization studies using the best performing catalyst

Task 4: Completion of process design, economic analysis and LCA of integrated process

Summary

- *Overall goal of the project is the production of a partially upgraded algal oil suitable for insertion into the hydrotreatment unit of a petroleum refinery.*
- *Advanced stage discussion with one of the oil majors to serve as petroleum refinery partner; on-going discussions with other refiners*
- *Approach focuses on addressing the major technical challenges which include: (i) cost-effective production of algal oil with safe levels of catalyst poisons, (ii) development of high activity catalyst with extended life, and (iii) the need for a smaller, cleaner and energy-efficient HDO step*
- *Valicor has developed patent pending, energy efficient and cost-effective algal oil extraction technology*

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Summary (Contd.)

- *Using Valicor extraction technology, we have produced pre-refined algal oil with low concentration of catalyst poisons*
- *Preliminary results from HDO of pre-refined algal oil confirm the production of upgraded algal oil comprising straight chain alkanes with chain length in diesel range*
- *Preliminary results from HDO of algal oil confirm activity of sulfided Ni/Mo and Pt-based catalysts*
- *Future work will focus on improving algal oil extraction, formulating a catalyst that is capable of maintaining high activity for an extended period, performing optimization studies in microreactor-enabled monolith reactor, and completing the process design, economic analysis and LCA*
- *Major challenges to successful commercialization include cost of pre-refined algal oil, catalyst deactivation, low space-time yield, and high hydrogen pressure requirement*

Acknowledgement

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- *You may refer to them during the Q&A period if they are helpful to you in explaining certain points.*

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Responses to Previous Reviewers' Comments

- **If yours is an on-going project that was reviewed previously, address 1-3 significant questions/criticisms from the previous reviewers' comments**

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Publications and Presentations

- **List any publications and presentations that have resulted from work on this project. Use at least 12 point font.**

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Approach (Contd.)

Milestones

- Optimization of algal oil conditioning/hydrolysis
- Scale up of pre-refined algal oil
- Performance & Optimization studies of HDO of algal oil in a monolith reactor
- Plant design, process economics & LCA of integrated process.

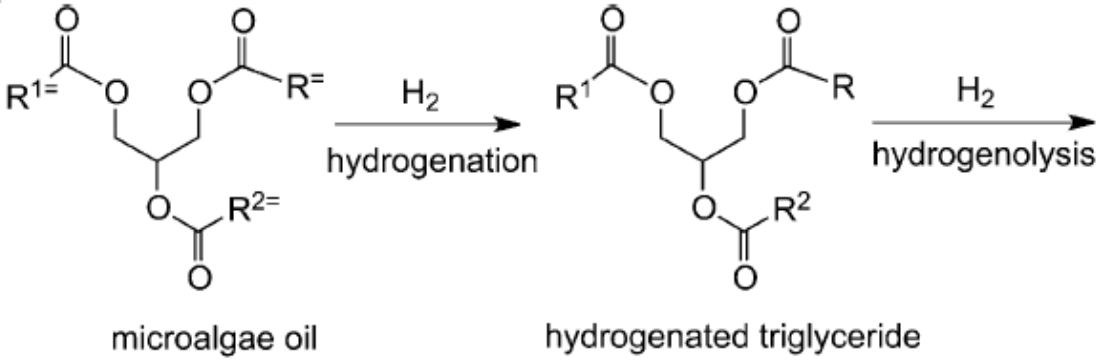
Performance Metrics

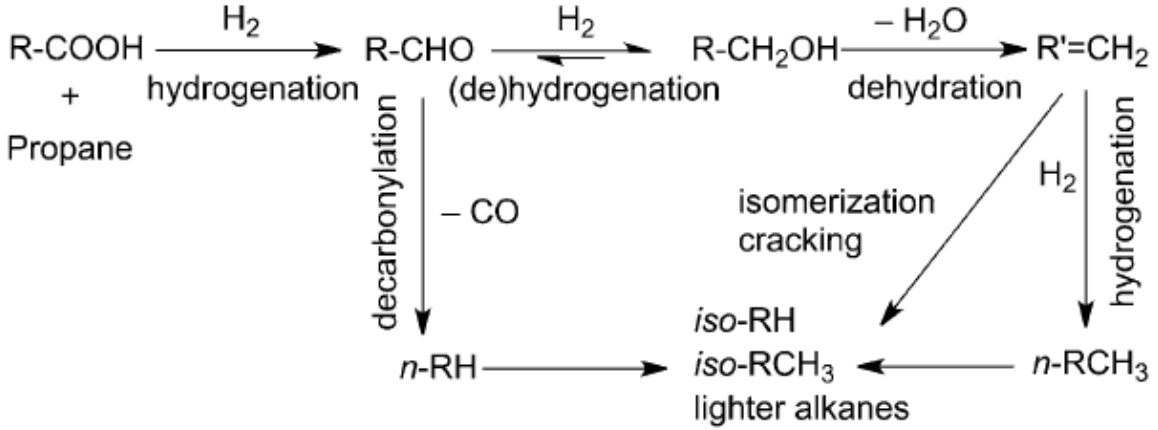
- (1) Algal Oil extraction efficiency > 80% (2) Strict zero water discharge balance (3) Production of pre-refined algal oil suitable for first stage partial hydrotreating (N < 1%, S <<0.1%, and P < 0.1%, all in wt%) in the HDO monolith reactor.

- (1) Production of a partially hydrotreated algal oil suitable for final hydrotreating (N ~0.3%, S <<0.1% , P <0.1% , O < 2%, and Metals and metalloids < 0.1%, all in wt%) in the refinery (2) Process Conditions: LHSV (h^{-1}) > 15; Reactor Pressure 300 – 500psi; H_2/Oil ratio <25 scm/m^3) (3) Catalyst on-stream time of at least 100 hours in-between regeneration (4) Development of a viable catalyst regeneration strategy capable of restoring the HDO catalyst to at least 90% of original activity (5) < 5 wt% of carbon lost as coke during the catalyst on-stream time.

- Blueprint for plant design, economic analysis, and LCA of the integrated process with a projected sales price of ~ $2.50/gal. diesel (ex. tax) for production capacity of 200,000 bpd.

Technical Accomplishments





$R^{1=}$, $R^{2=}$, $R^{=}$: unsaturated alkyl chain

Methanation: $CO + H_2 = CH_4 + H_2O$

Proposed Reaction Network for HDO of Algal Oil (Peng, B. et al., Agnew. Chem. Int. Ed. 2012, 51, 2072-2075

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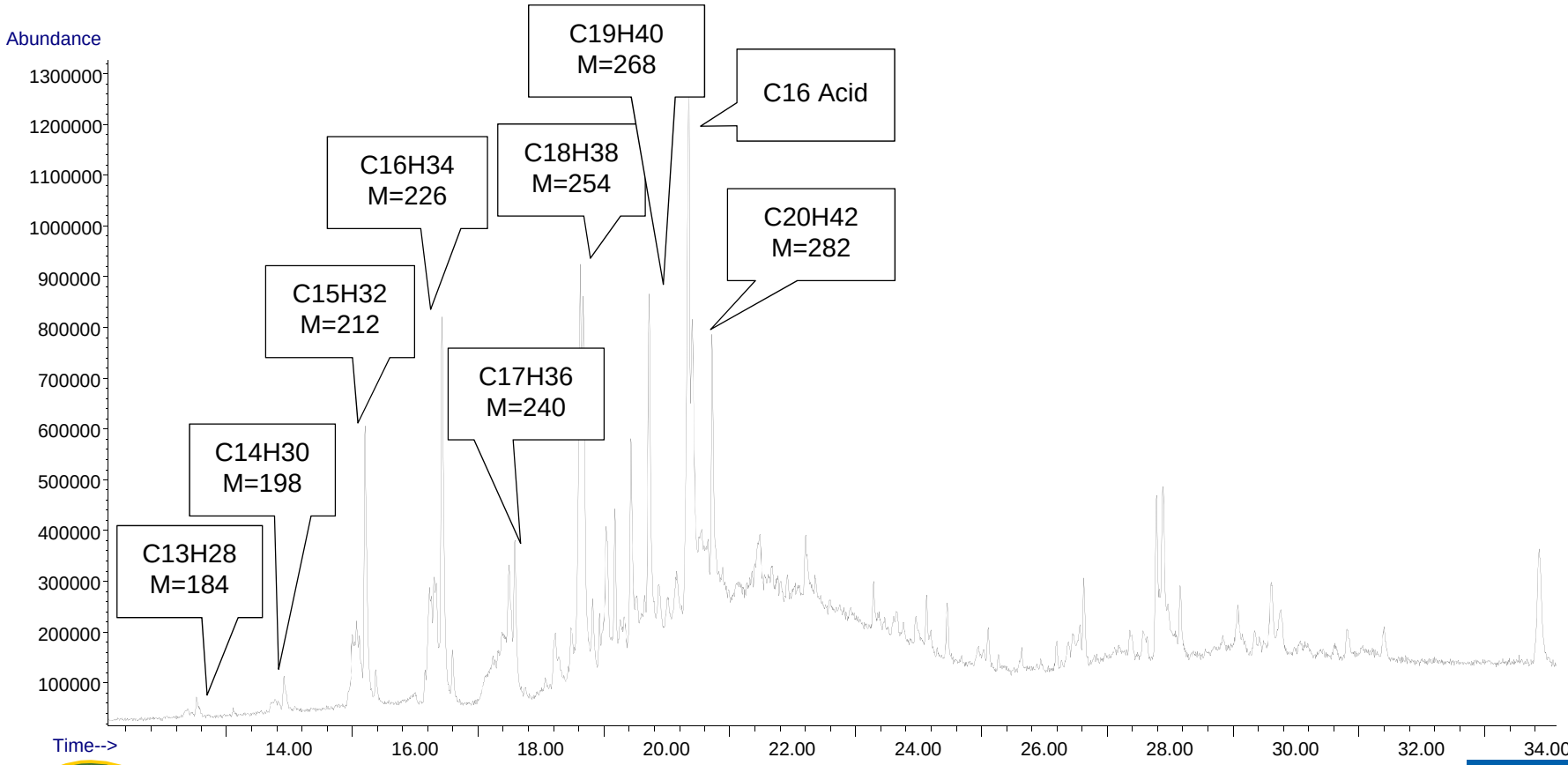
Technical Accomplishments

Sulfiided Ni/Mo on γ-alumina
Batch Reactor
Temperature = 300°C; 1000 psi H_2



GC/MS Chromatogram of Product Stream

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Technical Accomplishments

Estimates of Product Yield (C15-C20) in Microreactor

	Reaction conditions	Carbon Yields [wt%]	
		Based on Total Carbon in Microalgae Oil	Based on Total Carbon in Lipids
NiMo	250 ℃, 500psi	9.31%	18.95%
	300 ℃, 500psi	21.42%	43.57%
Pt A	250 ℃, 500psi	10.93%	22.24%
	300 ℃, 500psi	25.53%	51.94%
Pt B	300℃, 500psi	21.32%	43.38%

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Preliminary Material Balance

Production Rate, bpd	20,000					
Algae strain	Nannocholoropsis sp	Moisture content of biomass, strm 15	70			
Total flow rate thru reactor, gpm	100	Partitioning, % bdw biomass:organic phase	25.9			
Feed broth algae concentration, g (dry wt??)/L	1.46	aqueous phase	29.1			
Retention time in reactor, hr	48	insoluble phase	45	1a calc		
Algae doubling time, hr	48			72.9	Algae (dry)	
Area of reactor or pond, ac	3.9	Algal Exit conc, g/L	2.92	28,558	H2O	
Algae composition: oil, % of dry wt	26	Algal recycle ratio (stm5a/stm6)	1.00	0.0	CO2 (assume pure)	
water solubles, % of dry wt	29	Fraction of total feed flow that is recycled	0.5	0.0	O2 (assume pure)	
Insolubles, % dry wt	45	Reactor volume, gal	288,000	1.0	Neutrients	
Oil yield, %	77	Algal area productivity, g (dry wt algae)/m^2/day	50.4	0.0	Oil	
CO2 usage, lb CO2/lb algae	1.83	Algae production rate,g/h	33,113	36.3	Water solubles	
Nutrient (Guillard F/2) usage, L/lb of algae (dry wt??)	0.31	Algae production rate, lb/h	73	0.0	Insolubles	
Conc of neutrients in F/2, g/L	20	Algae production rate, lb/day	1,750	0.0	H2SO4	
Oxygen production, lb O2/lb algae	1.07	Annual production, ton algae/ac/y	82	0.0	Base	
Conc of algae in floc thickener exit (strm 6), wt %	2	Algal oil production rate, gal/yr/ac	5,107	0.0	hexane	
Conc of algae in centrifuge exit (strm 6b), wt %	12			28,668		
Conditioning H2SO4 dosage, lb 100% acid/lb slurry	0.01					
Wt ratio of hexane to algae (dry wt)	15					

"Reactor" means algal pond or photobioreactor

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