2013 DOE Bioenergy Technologies Office (BETO) Project Peer Review

Bio-Oil Separation and Stabilization by SCF Fractionation - 3.3.1.19

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Bio-Oil Technology Area Review

Daniel M. Ginosar, Ph.D,
Idaho National Laboratory

www.inl.gov

Idaho National Laboratory

Goals and Objectives

- Stabilize algae based pyrolysis and hydrothermal liquefaction oils by separating them into similar polarity groups using energy efficient supercritical fluid fractionation
- Bio-Oil Stabilization and Commoditization, DE-FOA-0000686. Accelerate the development of thermochemical liquefaction technologies to produce a bio-oil feedstock from high-impact biomass or from algal biomass. Overcome R&D barriers for making bio-oil feedstock acceptable in a petroleum refinery.
- Pathway barriers addressed: Tt-E Pyrolysis of Biomass and Bio-Oil Stabilization and Al-B. Algal Fuel Production.

Project Quad Chart Overview

Timeline

- Project start date: 11/2012
- Project end date: 12/2013
- Percent complete: 25%

Barriers

- Barriers addressed
  - Tt-E. Pyrolysis of Biomass and Bio-Oil Stabilization
  - Al-B. Algal Fuel Production

Budget

Total project funding:	$ 937,486
Federal	$750,000
Cost Share	$187,486
Funding in FY 2011:	$ 0
Funding in FY 2012:	$ 0
Funding for FY 2013:	$ 937,486
ARRA Funding:	$ 0

Years the project funded & average annual funding: 1 year, $937,486 per year

Partners & Roles

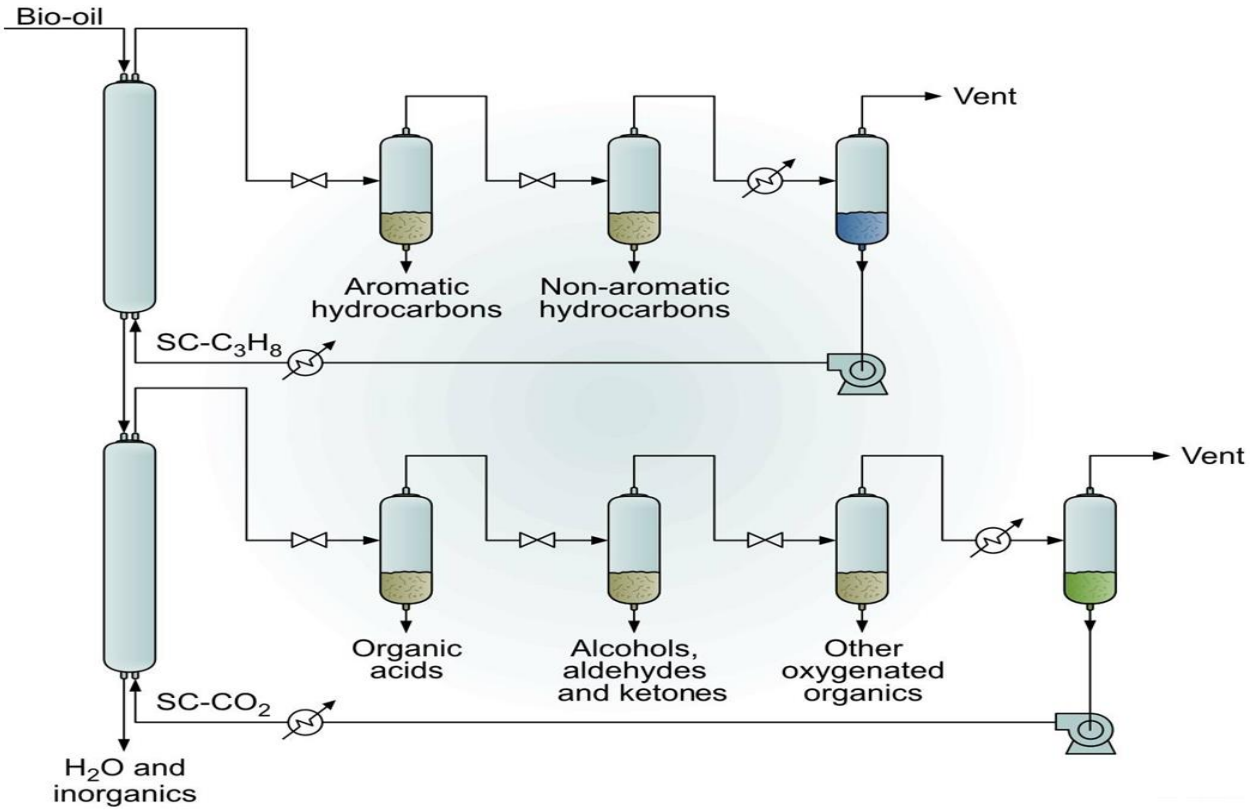
INL: Project Lead
Algae Growth
SCF Fractionation
Fraction Stability Study
LCA and TEA

USU: Algae Growth
Thermochem Conv.
LCA and TEA

CF Tech: TCA, Process Design

Project Overview

- Bio-oil is first extracted by a SC alkane
- Unextracted bio-oil is then exposed to polar solvent modified SC CO_2
- Temperature and pressure are adjusted to drop out fractions with similar polarity
- Fractions with similar chemical composition are anticipated to be more stable



1 - Approach

- Bio-oils are generated from algae biomass
  - Fast pyrolysis using catalysts and silica sand
  - Hydrothermal liquefaction
- The bio-oils are subjected to supercritical alkane and CO_2 extraction in a semi-batch system
- The extracts are examined using chemical and physical methods to determine composition and stability
- The supercritical extraction is similar to liquid extractions but anticipated to be more energy efficient
- Major decision points:
  - Choose thermochemical pathway – June 28, 2013
  - Choose alkane and CO_2 co-solvents – June 28, 2013

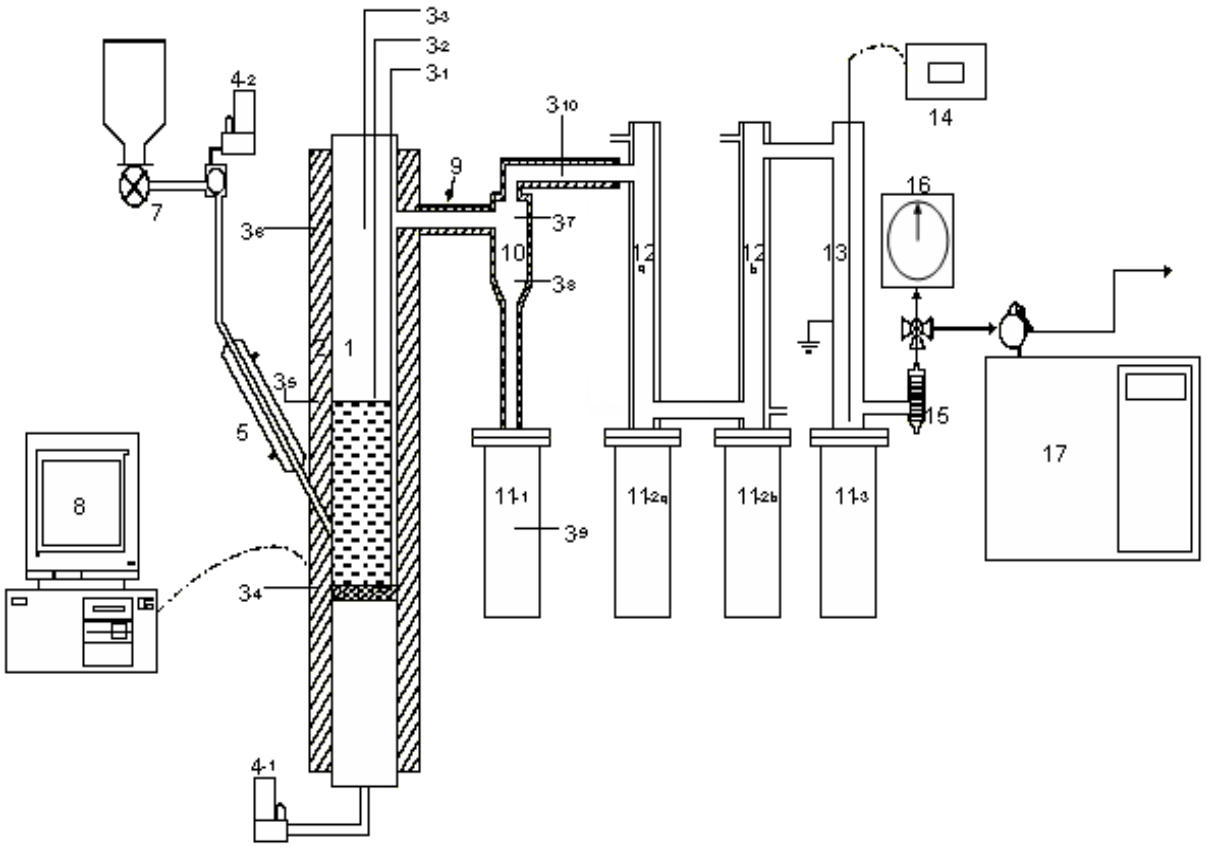
2 - Technical Accomplishments/Progress/Results

- Algae growth has been initiated
- Both pyrolysis and hydrothermal liquefaction of algae biomass have been performed
- Supercritical fluid extractions using propane and un-modified CO_2 have been carried out
- Analysis of the extracts is in progress

Scenedesmus dimorphus Properties

Property	Composition (wt%)
Moisture	4.6
Ash	5.3
Lipids	13.5
Carbon	49.5
Hydrogen	7.13
Nitrogen	7.9
Sulfur	0.85
Oxygen	34.5

Biomass Catalytic Pyrolysis Unit



1- Fluidized bed reactor,
3- Thermocouple,
4- Mass flow controller,
5- jacketed air-cooled feeder tube,
6- Hopper,
7- Screw feeder,
8- Computer,
9- Heating tape,
10-Hot gas filter,
11-Reservoir,
12-Condenser,
13-ESP,
14-AC power supply,
15-Filter,
16-Wet gas meter,
17-Gas chromatograph)

Pyrolysis conditions

- Biomass: *S. dimorphus*
- Temperatures: 350, 400, 450 C
- Feed rate: 100 g/h
- Pyrolysis medium, Silica sand and zeolite

Pyrolysis Products Distribution

Pyrolysis medium	Pyrolysis temp (°C)	Product distribution (wt %)		
		Total liquid	Char	Gas
Sand	350	51.70	29.42	18.88
Sand	400	53.81	29.28	16.91
Sand	450	50.21	22.69	27.10
HZSM5	350	55.10	31.82	13.08
HZSM5	400	53.73	31.80	14.47

Elemental Composition and HHV of Bio-oils and Whole Algae

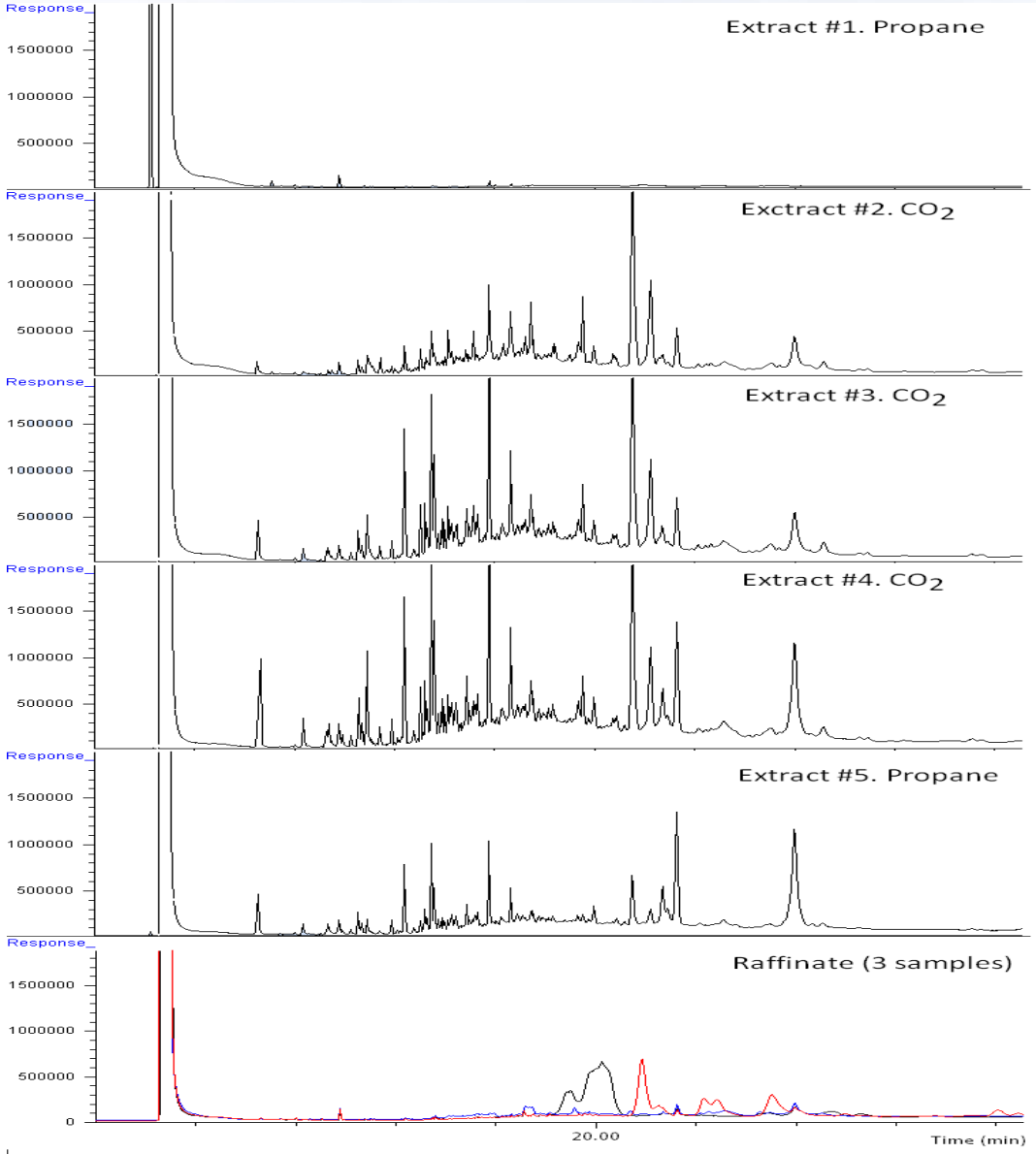
	Whole Algae	Sand Biooil (350C)	Sand Biooil 400C	Sand Biooil (450C)	HZSM5 Biooil (350C)	HZSM5 Biooil (400C)
Carbon (wt %)	49.5	63.11	62.80	63.97	65.03	66.60
Hydrogen (wt%)	7.13	8.41	8.28	8.34	8.54	8.57
Nitrogen (wt%)	7.9	9.01	9.12	9.49	9.17	9.49
Sulphur (wt%)	0.85	0	0	0.35	0	0.26
Oxygen (wt %)	34	19.48	19.80	17.85	17.26	15.08
HHV (MJ/kg)			31.83			33.2

SCF Extraction Experimental System

Sequential Extraction of 475°C Pyrolysis Oil

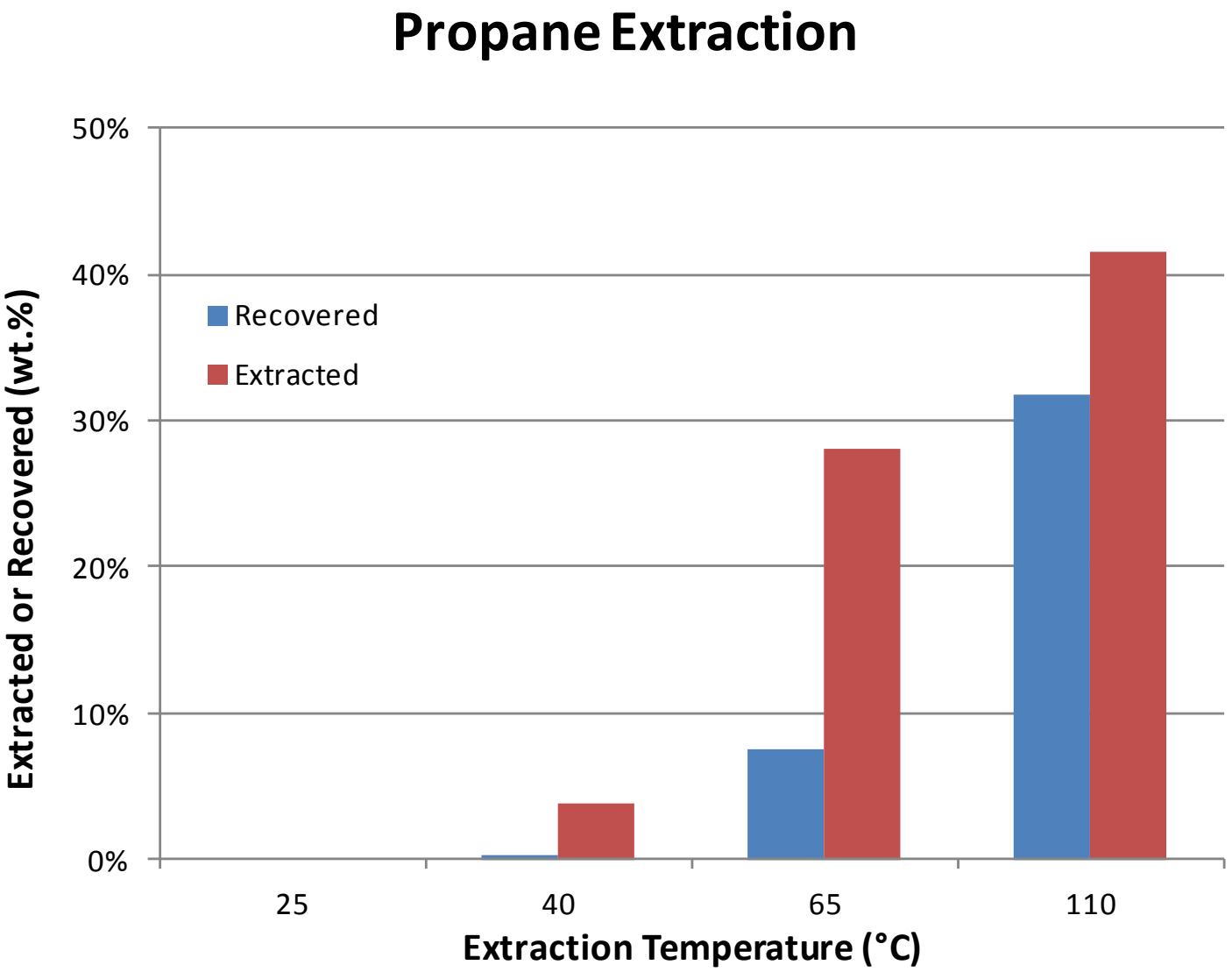
- Liquid propane at RT and 500 psi –
  - 0.2% recovered
- Supercritical CO_2 at 40°C and 1,200 psi –
  - 6.6% recovered
- Supercritical CO_2 at 40°C and 2,500 psi –
  - 1.5% recovered
- Supercritical CO_2 at 65°C and 2,500 psi –
  - 4.6% recovered
- Supercritical propane at 110°C and 2,500 psi –
  - 2.3% recovered

Extract and Raffinate GC Analysis

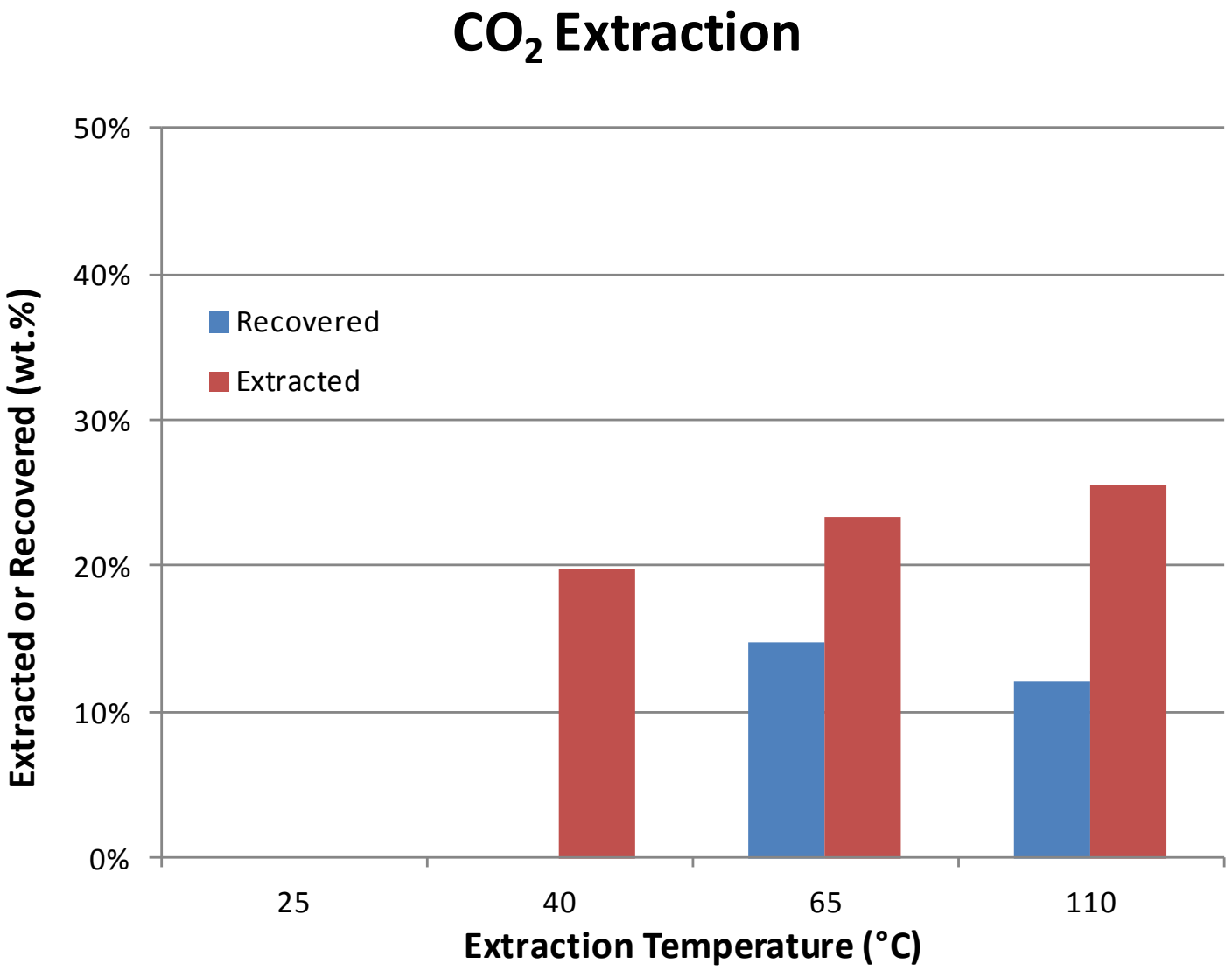


Pyrolysis Oil Raffinate

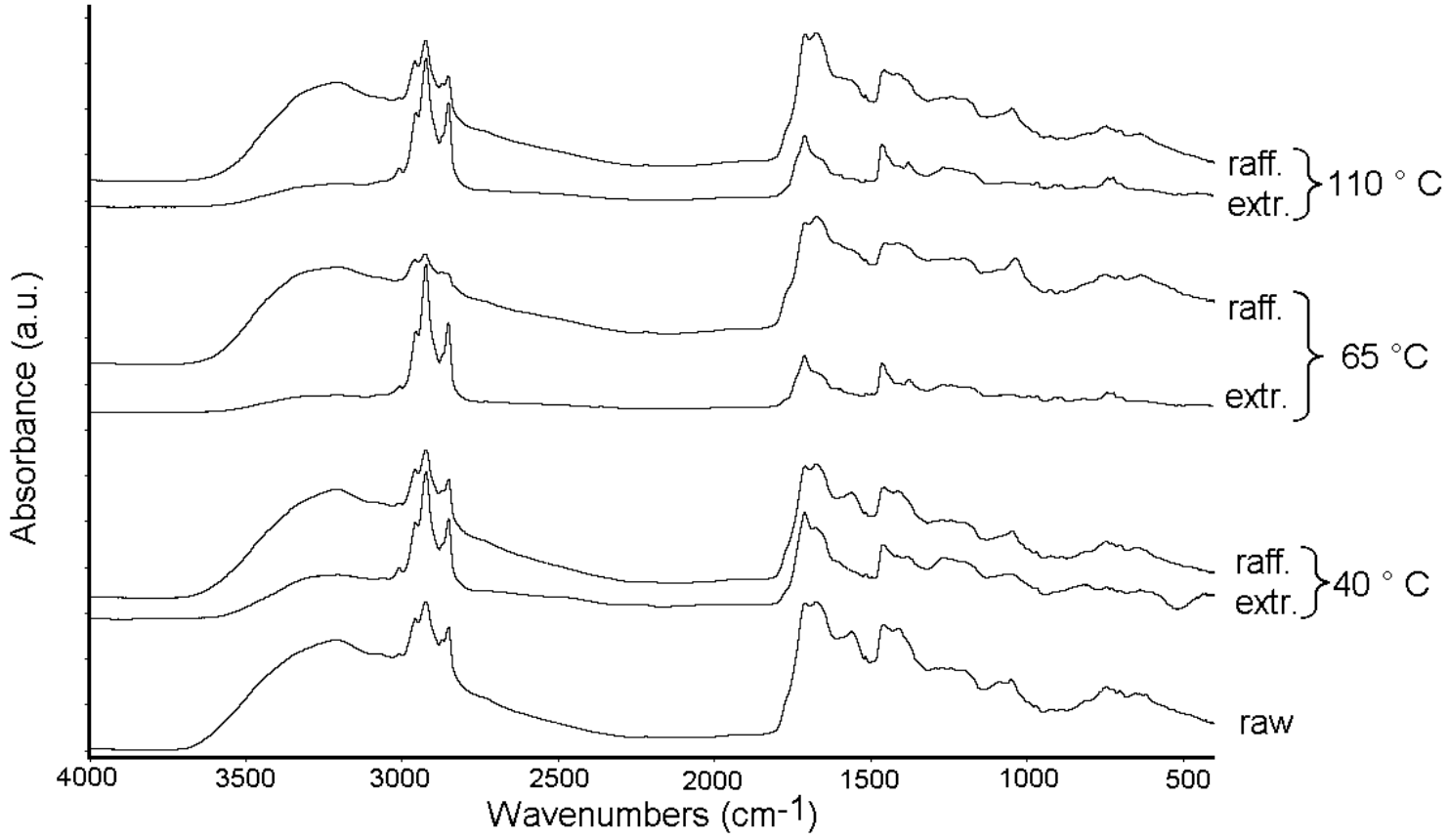
Extraction of 475°C Pyrolysis Oil



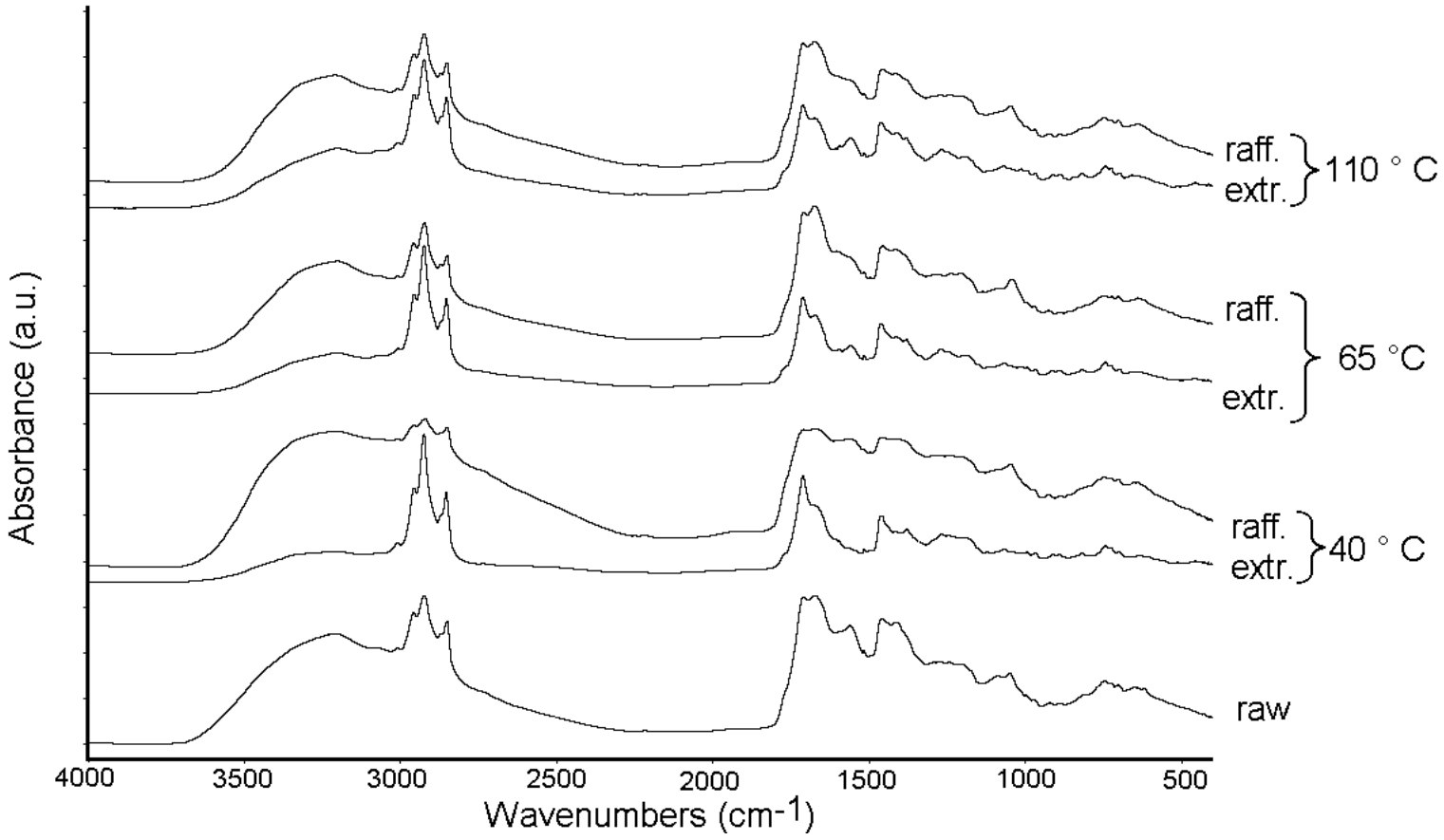
Extraction of 475°C Pyrolysis Oil



FTIR Spectra of Propane Extracts and Raffinates

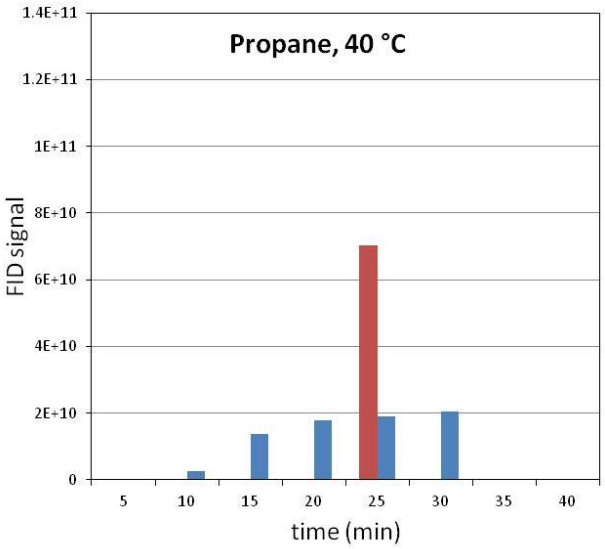


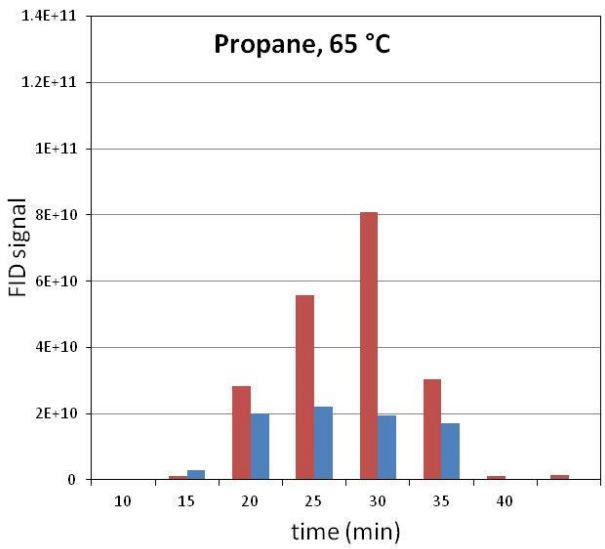
FTIR Spectra of CO_2 Extracts and Raffinates

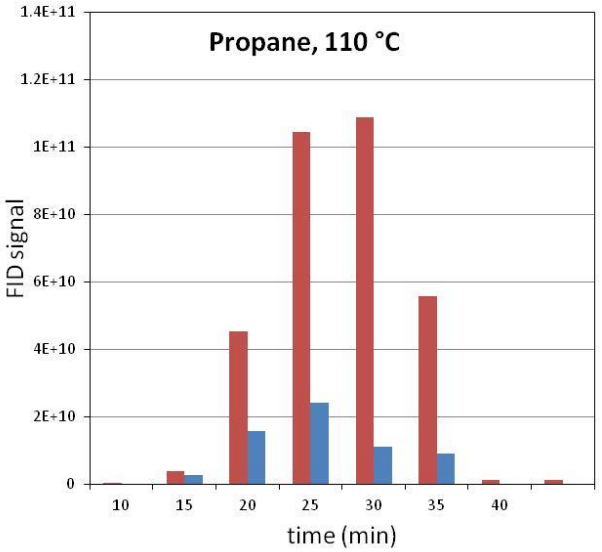


GC analyses of extracts (red) and raffinates (blue) Propane

Grouped as a function of retention time (min)

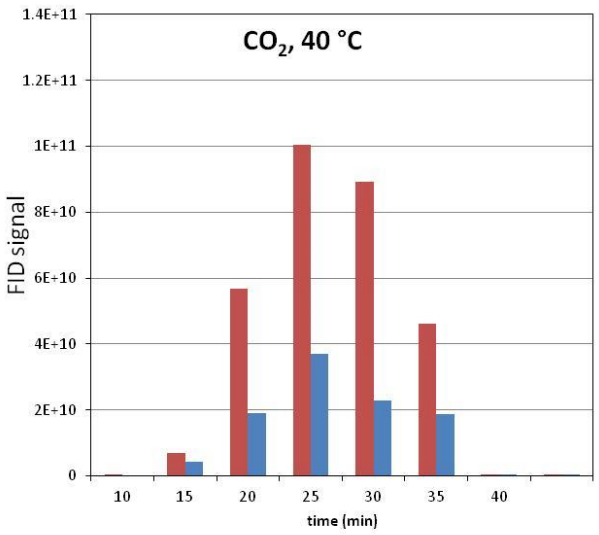


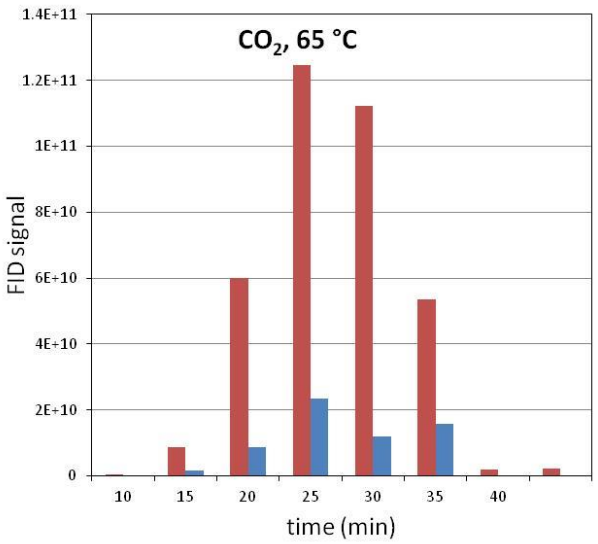


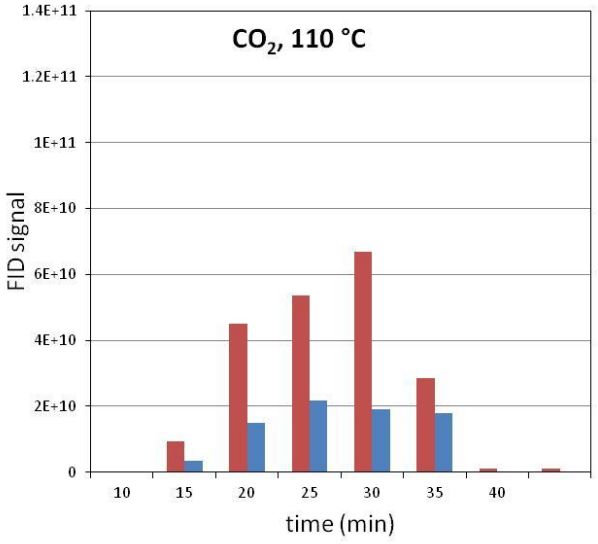


GC analyses of extracts (red) and raffinates (blue) CO_2

Grouped as a function of retention time (min)







3 - Relevance

- SCF fractionation of pyrolysis oils is expected to enable stabilization and commoditization of thermochemically processed bio-oils.
- SCF process will be designed for depot scale applications
- Project is advancing work on producing acceptable bio-oil intermediates for petroleum refineries to leverage their existing capital to produce finished fuels

4 - Critical Success Factors

- Process must be energy efficient with low operating and capital cost. Economic to implement on a small scale.
- Bio-oil needs to be stable with respect to time and temperature
- Fractions must be acceptable to upgrade in oil refinery
- Successful process technology would enable thermally processed biomass to be inserted into existing refinery infrastructure.

5. Future Work

- Complete experimental studies
- Generate process design
- Conduct TEA and LCA analysis

Task Name
3.3.1.19 Bio-Oil Separation and Stabilization by Supercritical Fluid Fractionation
3.3.1.19.A Production and characterization of biomass feedstock
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3.3.1.19.B Thermal Treatment to generate bio-oil
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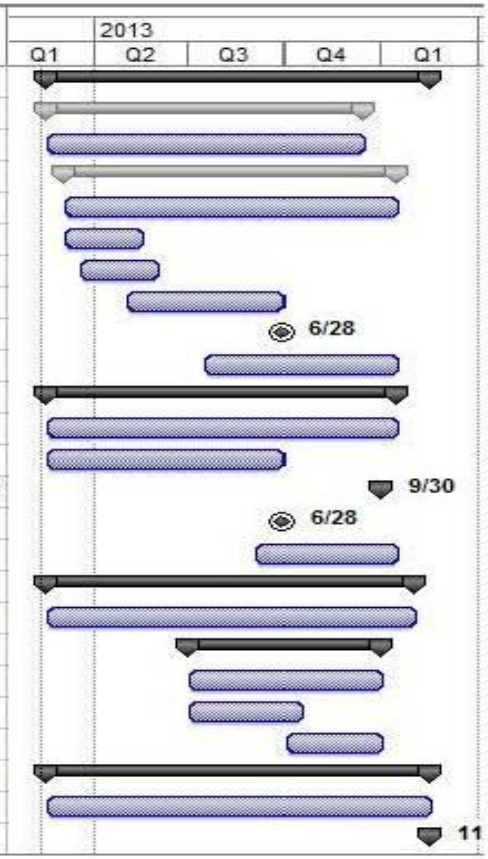
3.3.1.19.B.1 Pyroprobe analysis
3.3.1.19.B.2 Pyrolysis of algal biomass
3.3.1.19.B.3 Hydrothermolysis of algal biomass
3.3.1.19.B.3.ML.1 Choose thermochemical bio-oil production pathway
3.3.1.19.B.4 Bio-oil production
3.3.1.19.C SCF Fractionation and Separation
3.3.1.19.C SCF Fractionation and Separation
3.3.1.19.C.1 Bench scale SCF Studies
3.3.1.19.C.1.DL.1 Provide presentation at national meeting on SCF fractionation of bio-oil
3.3.1.19.C.1.ML.1 Choose thermochemical bio-oil production pathway
3.3.1.19.C.2 Liter-scale extraction/fractionation
3.3.1.19.D Fraction Stability
3.3.1.19.D Fraction Stability
3.3.1.19.E Technoeconomic Analysis
3.3.1.19.E Technoeconomic Analysis
3.3.1.19.E.1 Process design package
3.3.1.19.E.2 Life-cycle analysis
3.3.1.19.F Project Management
3.3.1.19.F Project Management
3.3.1.19.F.DL.1 Submit final report to include draft manuscript to DOE



Summary

- Project is addressing stabilization of thermally produced bio-oils for improved acceptance at oil refineries
- Algae is being produced, thermally processed, fractionated using supercritical fluids and thoroughly characterized
- Initial work demonstrates that extracts and raffinates are chemically different from each other
- Future efforts will characterize fraction stability
- Process design will consider operating and capital cost for depot scale systems, TEA and LCA analysis to be performed
- Project team consists of commercial algae producer (BKS Energy) and supercritical fluid technology company (CF Technologies)

Acknowledgements

Co-PIs:
Foster A. Agblevor - Utah State University
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Jason Quinn - Utah State University
John M. Moses - CF Technologies

Cost Share Partners:
Origin Oil
BKS Energy