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March 2014

Idaho National Laboratory

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Foster Agblevor[1]
Lucia Petkovic
Edward Bennion[1]
Jason Quinn[1]
John Moses[2]
Deborah Newby
Daniel Ginosar

[1]Utah State University
[2]CF Technologies LLC

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Idaho National Laboratory
Idaho Falls, Idaho 83415

http://www.inl.gov

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# Bio-Oil Separation and Stabilization by Supercritical Fluid Fractionation – 2014 Final Report

## Summary

The objective of this project is to use supercritical fluids to separate and fractionate algal-based bio-oils into stable products that can be subsequently upgraded to produce drop-in renewable fuels. To accomplish this objective, algae was grown and thermochemically converted to bio-oils using hydrothermal liquefaction (HTL), pyrolysis, and catalytic pyrolysis. The bio-oils were separated into an extract and a raffinate using near-critical propane or carbon dioxide. The fractions were then subjected to thermal aging studies to determine if the extraction process had stabilized the products.

In addition to the experimental effort, a life cycle assessment (LCA) of microalgae to biofuel was conducted and a technoeconomic analysis (TEA) was performed. The LCA examined thermochemical processing through hydrothermal liquefaction and catalytic pyrolysis. The TEA was based on a preliminary process design of the near-critical extraction process to estimate the economics of bio-oil stabilization.

During the course of the project, five different algae strains were grown. From the five species, *Scenedesmus dimorphus*, was found to have superior characteristics in terms of biomass cell density and productivity under the given growth and harvesting conditions. This species was therefore selected for scale-up production to supply biomass for larger scale testing of conversion and fraction studies.

The catalytic pyrolysis, non-catalytic pyrolysis, and HTL studies clearly showed that there were significant differences between the bio-oils from each of these processes. The qualities of the

bio-oils were different and their oxygen contents were considerably different. The non-catalytic pyrolysis and the HTL oils were both highly viscous, nearly solid tar-like substances, whereas the catalytic pyrolysis bio-oils were free flowing liquids with relatively low viscosity. Further, the extraction of catalytic pyrolysis oil was superior. Thus, the catalytic pyrolysis process was used for scale-up and further studies.

Based on energy analysis, extraction efficiency and chemical changes among the fractions, near-critical propane was chosen as the most appropriate solvent for the extraction process. It was found that the propane extract fraction was twice as stable as the parent catalytic pyrolysis bio-oils produced from *Scenedesmus dimorphus* as measured by the change in viscosity after two weeks of accelerated aging at 80°C. Further, in-situ NMR aging studies found that the propane extract was chemically more stable than the parent bio-oil. Thus the milestone of stabilizing the product was met.

A preliminary process design of the near-critical propane extraction plant was prepared by CF Technologies, Inc. Boston, Massachusetts. The design was based on a depot scale plant processing 20,000,000 gallons per year of bio-oil. It was estimated that the capital costs for such a plant would be approximately $8,700,000 with an operating cost of $3,500,000 per year. On a per gallon of product cost and a 10% annual rate of return, capital costs would represent $0.06 per gallon and operating costs would amount to $0.20 per gallon. Assuming a $3.00 per gallon of gasoline equivalent (gge), the critical fluid process would represent less than 9% of the product value. Further, it was found that the energy required to run the process represented 6.2% of the energy available in the bio-oil, meeting the milestone of less than 20%.

Life cycle analysis and greenhouse gas (GHG) emission analysis found that the energy for running the critical fluid separation process and the GHG emissions were minor compared to all the inputs to the overall well to pump system. Process energetics are presented on the metric of net energy ratio (NER) defined as the energy inputs divided by the energy in the biofuel with a NER of less than 1 being desirable. For the well to pump (WTP) system boundary, energetics in biofuel conversion are typically dominated by energy demands in the growth, dewater, and thermochemical process. Bio-oil stabilization by near critical propane extraction had minimal impact in the overall energetics of the process with NER contributions of 0.03 for both conversion technologies.

Based on the LCA, the overall conversion pathways were found to be energy intensive with a NER of about 2.3 and 1.2 for catalytic pyrolysis and HTL, respectively. GHG emissions for the catalytic pyrolysis process were greater than that of petroleum diesel at 210 g $CO_{2\ eq}$ compared to 18.9 g $CO_{2\ eq}$. Microalgae bio-oil based diesel with thermochemical conversion through HTL meets renewable fuel standards with favorable emission reductions of -10.8 g $CO_{2\ eq}$.

The importance of the outcomes of this work is that the critical fluid extraction and stabilization process improved product stability and did so with minimal energy inputs and processing costs. The LCA and GHG emission calculations point toward the HTL pathway as the more favorable thermochemical route towards upgrading algae to bio-fuels. Since the quality of the HTL oil was significantly lower than that of the catalytic pyrolysis bio-oil, the next steps point toward improving the quality of the HTL oils from algae biomass and focusing the critical fluid stabilization on that bio-oil product. Further, our oil refining partner, Big West Oil LLC, has indicated that a larger sample of stabilized oil is needed to determine the insertion point into their refinery and to reach a preliminary feedstock acceptance decision. This larger quantity is approximately 1 liter of bio-oil. If an improved quality of HTL bio-oil can be produced and if the critical fluid stabilization process proves favorable, then the critical fluid stabilization experimental system would need to be scaled up from the current level of tens of grams of sample to 1 liter of sample. The majority of equipment to perform this scale-up currently exists at INL.

## Extraction Using Near-Critical Propane

Catalytic pyrolysis oils were produced from *Scenedesmus dimorphus* algae using a fluid catalytic cracking (FCC) catalyst. The catalytic pyrolysis studies were conducted in the 4 kg/h pilot scale fluidized bed pyrolysis reactor at USTAR Bioenergy Center. The catalyst used was proprietary material supplied by BASF Inc (FCC 6705). About 1000 g of catalyst was used per run and the dried *S. dimorphus* algae biomass ground to pass 2-mm mesh was used for the studies. The pyrolysis unit consisted of Brabender hopper and screw feeder, fluidized bed reactor, hot gas filter, two condensers (whose temperatures are maintained using water and ethylene glycol mixture), Venturi scrubber, electrostatic precipitator (ESP), coalescing filter, and gas compressor to recirculate the pyrolysis gases. The reactor was externally heated through a three-zone electric furnace. Catalytic pyrolysis was carried out at 400 °C. FCC catalyst was used as both heat transfer medium and catalyst.

Preliminary extraction experiments demonstrated that propane was the most appropriate solvent for the extraction of bio-oils produced from algae feedstocks. Near-critical propane extraction was performed at 65 °C at a fluid reduced pressure of 2.0 (85 bar) using an eight to one solvent to feed ratio by weight. About 83 % of the bio-oil was extracted using propane, leaving about 17 % as raffinate. Sequential use of carbon dioxide after propane showed that only a minimum additional amount (about 3 %) was extracted. Using carbon dioxide alone did not seem to separate fractions of different composition as per infrared analyses. In contrast, propane extracts were different from the parent raw oil. For example, elemental analyses showed that the content of nitrogen in the fraction extracted with propane was about half of the original nitrogen present in the parent raw oil (see Table 1.) The propane extract had a lower viscosity than the parent oil as shown in Table 2.

Table 1. Extraction using propane at 65 °C.

| Sample | H/C mol ratio | N/C mol ratio |
|---|---|---|
| Raw Oil | 1.700 | 0.013 |
| Propane extract | 1.791 | 0.007 |

Table 2. Viscosity (cp) of parent oil and propane extract. Extraction was performed at 65 °C. Viscosity was measured at different temperatures.

|  | 30 °C | 40 °C | 60 °C | 80 °C |
|---|---|---|---|---|
| Parent oil | 8.07 | 4.66 | 1.80 | <1 |
| Propane extracts | 6.76 | 4.28 | 1.79 | <1 |

Infrared analyses (Figure 1) showed that aliphatic chains (peaks within the 2600-3100 $cm^{-1}$) and low-polarity carbonyl-containing species, such as ketones and/or esters (1700 $cm^{-1}$) were preferentially extracted with propane while hydrogen bonded OH species (broad band around 3000 $cm^{-1}$) were preferentially left in the raffinate. In addition, higher-polarity carbonyl-containing species such as acids, amides, and alcohols, were also left in the raffinate.

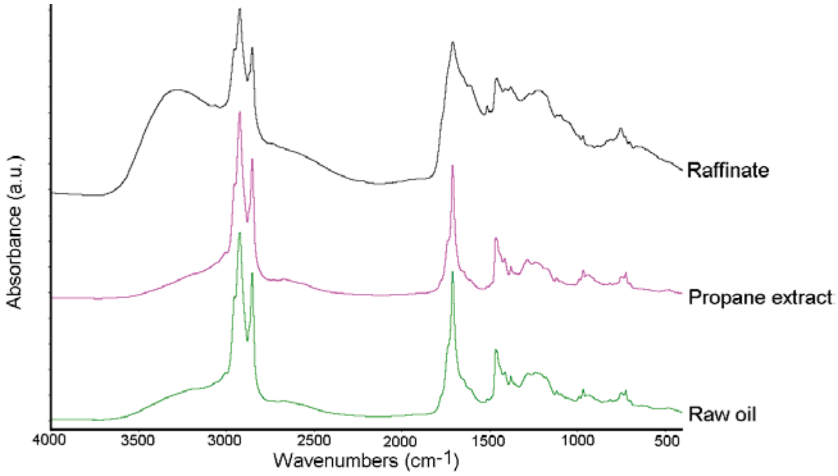

Figure 1. Extraction using propane at 65 °C.

Infrared findings were confirmed by NMR analyses. $^{13}$C NMR analyses are shown in Figure 2 and Table 3. Carbonyl and C–O contributions are higher in the raffinate. C–C–C contribution is higher in the extract. $^{1}$H NMR analyses are shown in Figure 3 and Table 4. Exchangeable OHs are reduced in the propane extracted fraction. These exchangeable OH include water, carboxylic acids, and many alcohols.

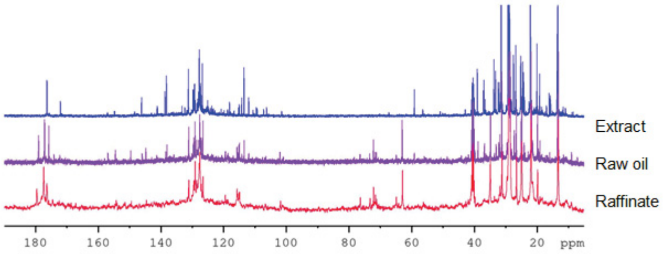

Figure 2. $^{13}$C NMR analyses. Extraction using propane at 65 °C.

Table 3. Percent contribution of different species estimated from $^{13}$C NMR analyses areas in Figure 2. Extraction using propane at 65 °C. .

| | $^{13}$C NMR Range | Propane extract | Raw oil | Raffinate |
|---|---|---|---|---|
| C=O | 215-166.5 ppm | 2.1% | 8.0% | 8.3% |
| aromatic | 166.5-95.8 ppm | 33.4% | 33.0% | 35.9% |
| C-O | 95.8-55.2 ppm | 1.8% | 4.5% | 8.1% |
| C-C-C | 55.2-0 ppm | 62.7% | 54.4% | 47.7% |

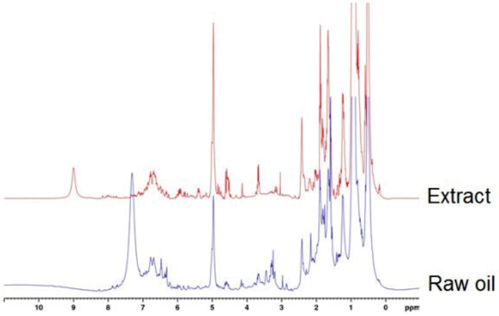

Figure 3. $^{1}$H NMR analyses. Extraction using propane at 65 °C.

Table 4. Extraction using propane at 65 °C (Exps. 27-29). Percent contribution of different species estimated from areas corresponding to Figure 3.

| | Raw oil | Propane extract |
|---|---|---|

| | | |
|---|---|---|
| Exchangeable OH | 8.0% | 1.8% |
| All other protons | 92.0% | 98.2% |

MALDI-TOF analyses (Figure 4) showed that the propane extract had a lower average molecular weight than the parent oil. The raffinate had a higher average molecular weight. The propane extract was also more volatile as measured by temperature programmed volatilization under flowing helium (Figure 5.) About 80 % of the raw oil and propane extracts volatilized below 250 °C. The last 20 % of the original oil mass required higher temperatures for the parent oil than for the extract. The raffinate seemed to be much more active when heated and sudden bursts of volatiles did not allow for a steady profile even at the low heating rate of 1 K/min that was applied. This is the reason of the incomplete curve in Figure 5. The raffinate required temperatures above 500 °C for the last 20 % to volatilize.

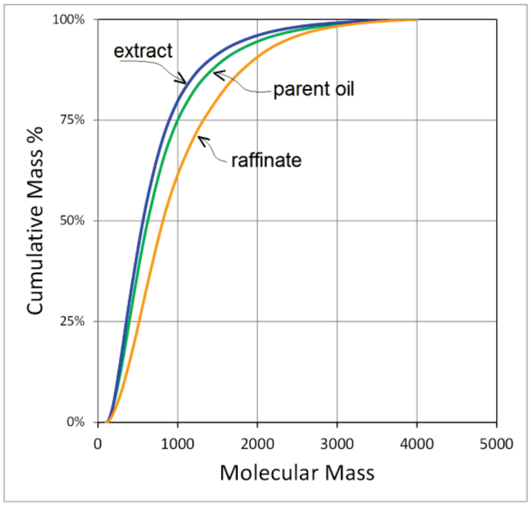

Figure 4. Cumulative molecular weight distribution by MALDI-TOF. Extraction using propane at 65 °C.

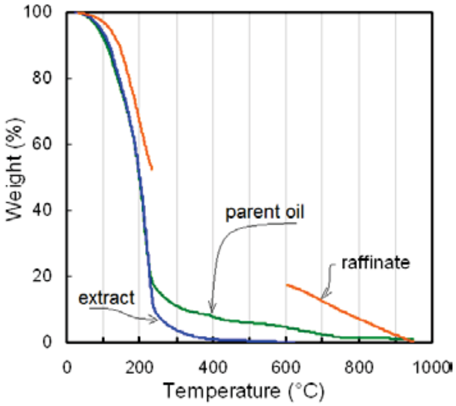

Figure 5. Thermogravimetric analyses under flowing helium. Extraction using propane at 65 °C.

### Aging of parent oil, propane extract, and propane raffinate

Samples of the parent oil, propane extract, and propane raffinate were submitted to accelerated aging which consisted in keeping bio-oil aliquots in closed vials for 24 hours and 2 weeks at 80 °C. Next, the aged samples were analyzed to determine the effects of aging on sample physicochemical properties.

Table 5 shows the results of viscosity measurements at different temperatures. For example, the viscosity at 30 °C of the parent oil, which was 8.07 cP when fresh, became 68.1 cP after 2 weeks. In contrast, the propane extract, which had a viscosity of 6.76 cP when fresh, showed a viscosity of 29.6 cP after 2 weeks. In other words, the parent oil viscosity increased about 8 times with aging and the propane extract viscosity increased only 4 times. The amount of raffinate collected was insufficient for viscosity analyses.

<u>This result was useful in meeting the milestone because it showed that the oil fraction obtained by propane extractions was twice as stable as the parent bio-oil.</u> This milestone is important because it confirmed the hypothesis that bio-oil extraction with an appropriate near critical or supercritical fluid improves oil stability.

Table 5. Viscosity (cp) of parent oil and propane extract. Extraction was performed at 65 °C. Viscosity was measured at different temperatures. Aging was for 24 h and 2 weeks at 80 °C.

| Sample | 30 °C | | | 40 °C | | | 60 °C | | | 80 °C | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 0 h | 24 h | 2 weeks | 0 h | 24 h | 2 weeks | 0 h | 24 h | 2 weeks | 0 h | 24 h | 2 weeks |
| Parent oil | 8.07 | 8.60 | 68.1 | 4.66 | 4.89 | 41.6 | 1.80 | 1.79 | 18.5 | <1 | <1 | 8.02 |
| Propane extracts | 6.76 | 5.24 | 29.6 | 4.28 | 3.26 | 18.5 | 1.79 | 1.43 | 8.02 | <1 | <1 | 4.81 |
| Raffinate | (N/A) | | | | | | | | | | | |

To understand the processes that may be affecting the stability of these oils, additional analyses were performed.

Infrared analyses (Figure 6) performed on fresh and aged samples did not show significant differences. This is an indication that the species that produced such important changes in viscosity may be present in low quantities. The molecular mass distribution shifted to higher molecular masses with aging in all samples (Figure 7.) In general, volatility also decreased with aging (Figure 8.)

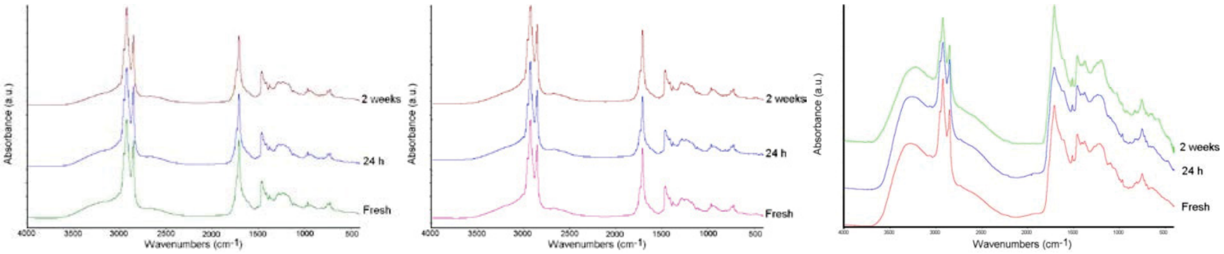

Figure 6. Infrared spectra of parent oil (left), propane extract (center), and raffinate (right) when fresh (bottom curves), aged for 24 h (center curves), and aged for 2 weeks (top curves.)

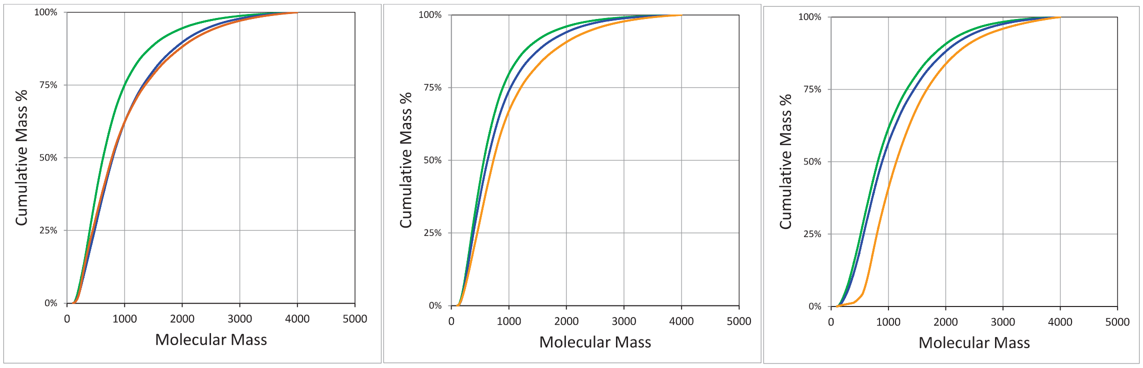

Figure 7. Cumulative mass % by MALDI-TOF. Samples are raw oil (left), propane extract (center), and raffinate (right). Curves are: fresh (green); aged 24 h (blue); aged 2 weeks (orange.)

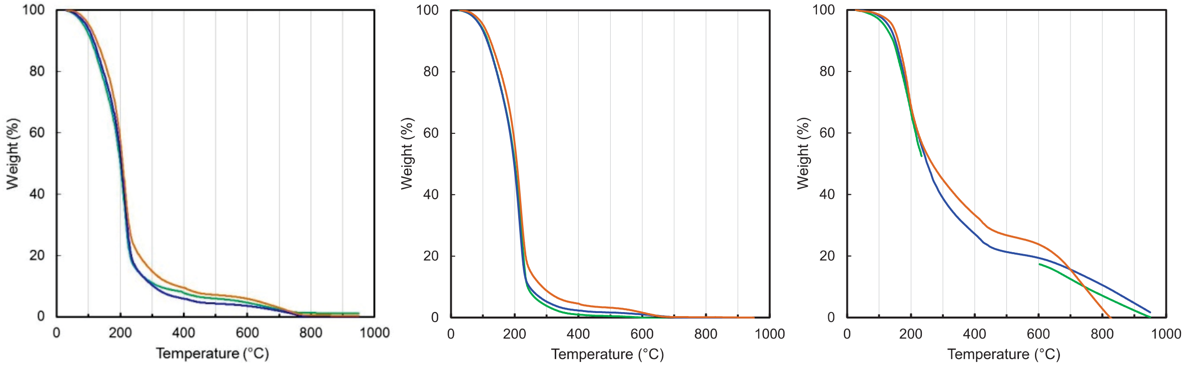

Figure 8. Thermogravimetric analyses. Raw oil (left), propane extract (center), propane raffinate (right). Curves are fresh (green); aged for 24 h (blue); aged for 2 weeks (orange.).

Parent oil and propane extract were submitted to an in-situ NMR aging study for 2 weeks at 80 °C in the NMR instrument. The results are shown in Figures 9-11 and in Tables 6 and 7. The shift of the peaks was more significant in the parent oil than in the propane extract. For example, the peak at 176-177 ppm shifted -0.45 ppm in the parent oil and -0.15 in the propane extract. This shows that the propane extract was chemically more stable than the parent oil. In addition, the parent oil started with more exchangeable protons which declined more rapidly with aging than the propane fraction. The exchangeable protons in the propane fraction displayed a downfield shift compared to the parent oil suggesting a larger fraction of acid in the exchangeable protons. A general shift of the spectrum upfield with aging suggested the consumption of acid over time in both samples. This suggests that aging was likely due to polymerization of esters with alcohols in presence of acid and base that are present within the oil.

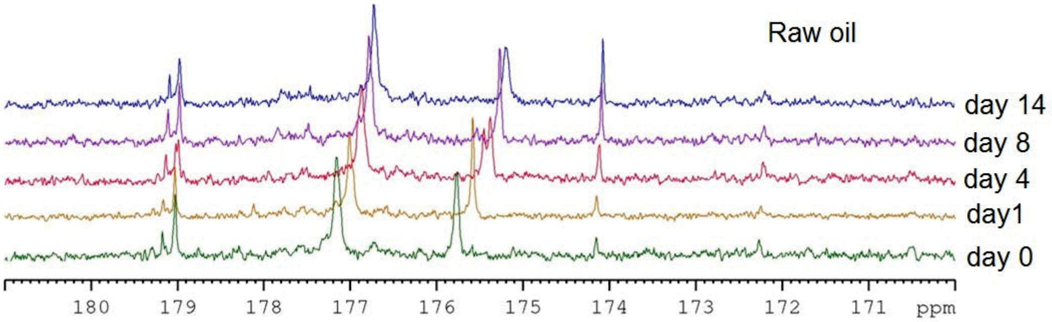

Figure 9. In situ $^{13}$C NMR aging analyses of parent oil.

Table 6. Changes in $^{13}$C NMR peak position between the initial position and position at 14 days corresponding to parent oil shown in Figure 9.

| $^{13}$C NMR (Initial ppm) | Δ ppm | Integration (%) |
|---|---|---|
| 177.2 | -0.45 | 1.1% |
| 175.8 | -0.57 | 0.6% |
| 34.8 | -0.28 | 1.5% |
| 24.7 | -0.12 | 1.2% |
| 21.7 | -0.33 | 0.8% |

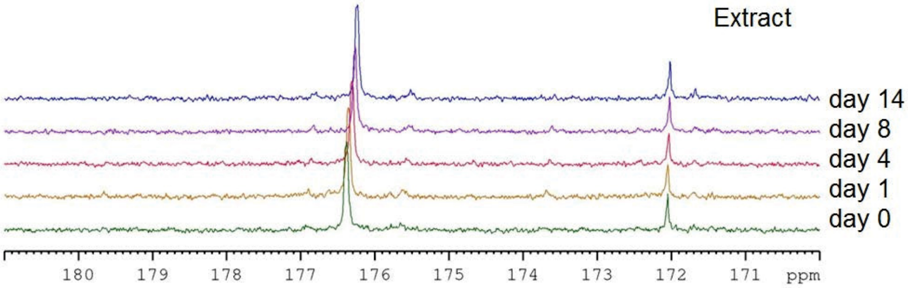

Figure 10. In situ $^{13}$C NMR aging analyses of propane extract.

Table 7. Changes in $^{13}$C NMR peak position between the initial position and position at 14 days corresponding to propane extract shown in Figure 10.

| $^{13}$C NMR (Initial ppm) | Δ ppm | Integration (%) |
|---|---|---|
| 176.4 | -0.15 | 0.8% |

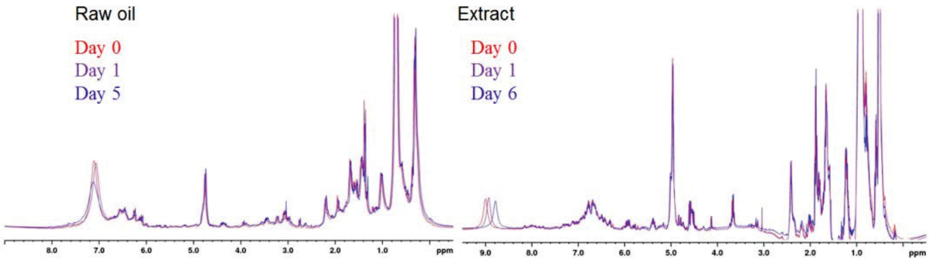

Figure 11. In situ $^1$H NMR aging analyses of parent oil (left) and propane extract (right).

In conclusion, propane extraction is a promising method to decrease the nitrogen content of bio-oils and to improve the stability of bio-oils obtained by the catalytic pyrolysis of algae based biomass.

**Preliminary Process Design Summary**

The Preliminary Process Design Package (Design) was prepared by CF Technologies, Inc. Boston, Massachusetts. This design is based on experimental results obtained in this project based on catalytic fast pyrolysis, however, the design is generic and would be appropriate to be used with other thermochemically produced oil including a suitable HTL bio-oil. Initial comparison of designs indicated the most energy efficient process for the Propane Critical Fluid Solvent Separation, Purification, and Recovery from the Extracted Oil, is a multistage vapor recompression distillation. That solvent recovery process is the basis for the design submitted.

This propane extraction process is one segment of a bio-oil from algae production facility. This plant is designed to extract bio-oil from the product of an algae based bio-oil process to remove unwanted components and to stabilize the product. The Process Flow Diagram (PFD) for the commercial-scale system is shown in Figure 12. The process is divided into two primary sections, extraction and solvent recovery. The extraction is carried out in a counter-current liquid-liquid extraction column. The solvent recovery is a three stage vapor recompression process designed to minimize energy consumption while recovering and recirculating propane. The bio-oil feedstock is the product of a thermochemical conversion process and contains organic compounds with varying degrees of oxygenation, water, triglycerides, organic acids, alcohols, etc. Using liquid propane as the solvent, the process yields bio-oil, a low viscosity oil suitable as a refinery feedstock; and a by-product raffinate containing water, inorganic materials, and highly polar organic chemical compounds. The nominal annual feed capacity of the plant is 20,000,000 gallons, 70,000 tons, or 500,000 bbls (40 gallons per minute).

The extraction process section of the plant is presented first, followed by a description of the solvent recovery system. The extraction process operates on a continuous basis, using a continuous countercurrent multistage column. The solvent recovery system also operates continuously with three vapor recompression distillation columns in series.

The feedstock, consisting of about 85% bio-oil, 10% highly oxygenated polar organic compounds, and 5% water enters the process in the feedstock tank, T-1. The feedstock is heated to 65°C, the extraction temperature, then pumped by the feed pump, P-1, to 35 bar, the extraction pressure, and fed into the top of the extractor.

In the extractor, E-1, the feedstock is contacted with liquid propane, which flows from propane storage, D-1, into the bottom of E-1 and extracts the bio-oil from the water and other polar compounds. The solvent (liquid propane) flow rate is five times the volumetric flow rate of the feed. This propane insoluble residue, the raffinate, flows out the bottom of the extractor and into the raffinate receiver, D-2. The extract with solvent flows from the top of E-1 to the first propane – bio-oil separator, S-1. The propane vapor from the top of S-1, a high pressure distillation column, is compressed, and the hot compressed vapor is used to heat the reboiler, H-2 at the bottom of S-1. The bio-oil extract from the bottom of S-1, is reduced in pressure as it flows to S-2, the second vapor recompression distillation column. Likewise, the oil from the bottom of S-2 is flashed (a further reduction in pressure as the extract and propane flow through the control valve where the liquid propane is converted to a vapor form) to S-3, the third vapor recompression distillation column, where the remaining propane is recovered from the oil. The bio-oil product flows from S-3 to the Extract Receiver, D-3, completing the extraction process.

In D-2 the raffinate pressure is reduced to allow the propane to vaporize and be recovered. The raffinate leaves the process, and is piped to an appropriate storage tank if there is chemical value or burned on site for fuel value. Detail description of major equipment is provided in the Design report.

The cost of the 20,000,000 gallon per year extraction facility is estimated at $8,685,000. Details of the cost estimate are provided in the CF Technologies Design report with major items summarized in Table 8.

Table 8. Capital Cost Estimate

| | |
|---|---|
| Major Equipment Total | $2,800,000 |
| Materials (controls, instruments, structural, etc.) | $1,905,000 |
| Engineering & Design | $1,400,000 |
| Fabrication, Construction, Assembly, Installation, Test and Start-up | $2,580,000 |
| Estimated Total Capital Cost | $8,685,000 |

Operating cost estimate is provided in Table 9. The costs can be summarized as follows: Materials $236 per hour, Labor $135 per hour, Utilities $65 per hour. The summed operating costs result in an estimated cost of $0.20 per gallon of extracted bio-oil product.

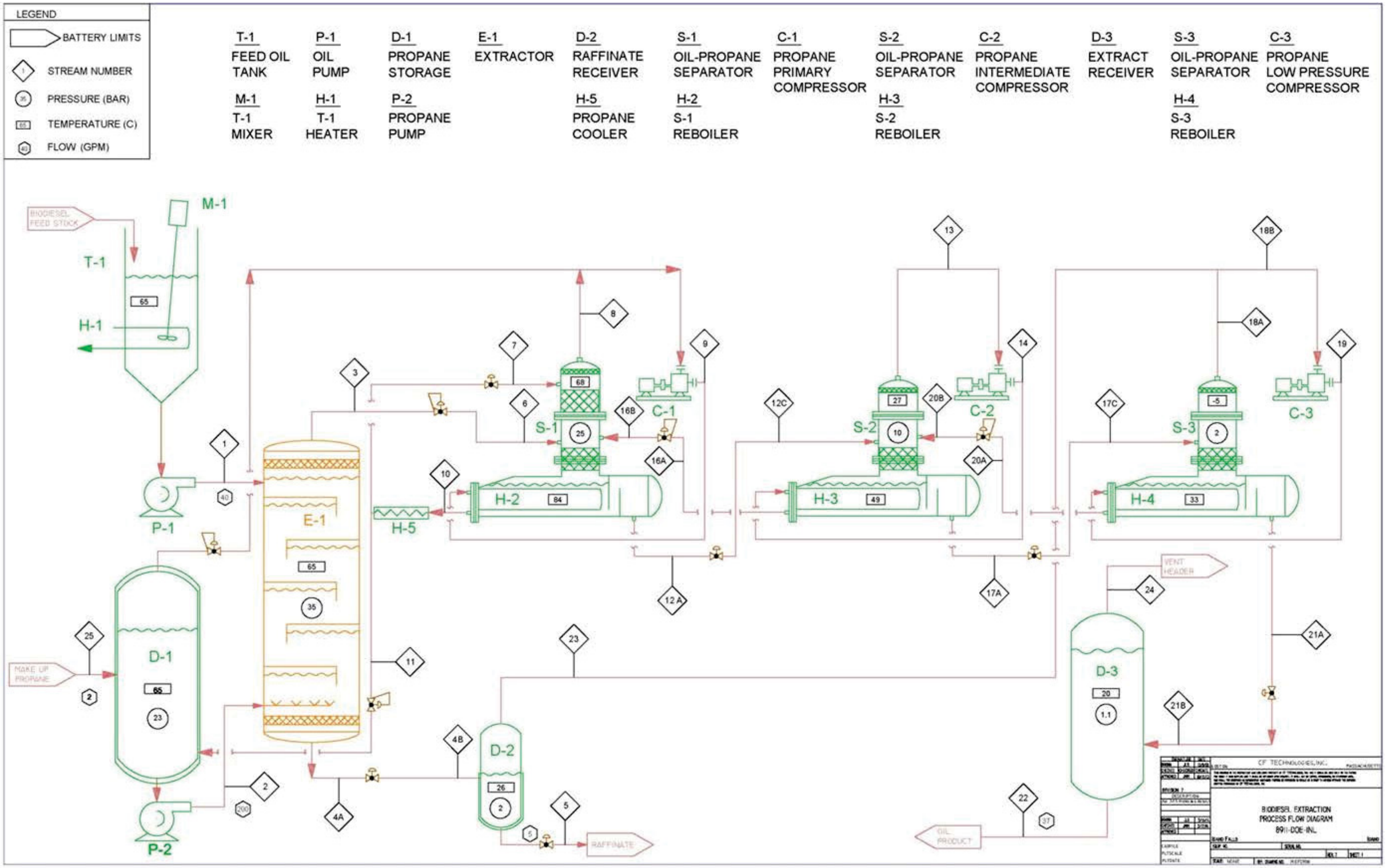

Figure 12. Near critical propane extraction process flow diagram.

Table 9. Operating Cost Estimate

| Expense Type | Items | Units | Quantity | Dollars/Unit | Dollars/Hour | Total |
|---|---|---|---|---|---|---|
| Material | Propane | Gpm | 1.6 | 1.5 | 148 | |
| | Supplies | $/shift | | 100 | 12.50 | |
| | Maintenance | % of capital annually | 7% | 607950 | 76 | |
| Total | | $/hr | | | | $236.00 |
| Labor* | Control Room | Hr | .5 | 30 | 15 | |
| | Plant | Hr | 1 | 25 | 25 | |
| | Maintenance | Hr | 0.125 | 25 | 3 | |
| | Shift Supervisor | Hr | 1 | 30 | 30 | |
| | Plant Engineer | Hr | 0.125 | 50 | 6 | |
| | Overhead | % | | | 56 | |
| Total | | $/hr | 0.7 | | | $135.00 |
| Utilities | Electricity | Kw | 1060 | 0.046333 | 49 | |
| | Heat | Btu/hr | 667549 | 0.000015 | 10 | |
| | Cooling Water | % | 90 | 0.001 | 5 | |
| Total | | $/hr | | | | $65.00 |
| Total Processing Cost* | | $/hr | | | | $436.00 |
| Total Processing Cost* | | $/yr | | | | $3,487,506 |
| Price per Feedstock* | Based on Feedstock | $/gal | | | | $0.17 |
| Price per Product* | Based on Final Product | $/gal | | | | $0.20 |

*Basis for Calculations:
Labor:
Control Room: Central Control Operator, 1/2 time on extraction, 1/2 time on other processes.
Plant: 1 Full Time Operator on the plant floor, monitoring equipment, communicating with control room regarding filling/draining tanks, cleaning filters, etc.
Maintenance: Day Shift Only, 1/2 time on extraction, 1/2 time on other processes.
Plant Engineer: Day Shift Only, 1/2 time on extraction, 1/2 time on other processes.
Other:

| | |
|---|---|
| Operating: | 8,000 hrs/year |
| Feed: | 20,000,000 gal/year |
| Product: | 17,641,765 gal/year |

Based on the capital cost listed previously, a 15 year straight line depreciation and a 10% return on investment, the capital costs can be calculated at $0.06 per gallon product, for a total capital and operating cost of $0.26 per gallon. Assuming a fuel value of $3.00 per gallon of gasoline equivalent (gge), the supercritical fluid stabilization process would amount to a cost of slightly less than 9% of the total product cost.

The process energy consumption is presented as a fraction of the energy produced. Since the design basis is gallons of oil per year, this energy analysis is done on the same basis.

From 20,000,000 gallons per year of a bio-oil feedstock, 17,600,000 gallons per year of Bio-Oil are extracted. This oil has a heating value of 13,300 btu/lb, and a density of 6.2 lb/gal for 83,000 btu/gallon. Therefore the annualized energy content of the product is 1,460x10^9 btu.

The total electrical energy consumed is 8,500 MWhr/yr, or 29x10^9 btu/yr. When taken at 35% efficiency converting bio-oil to electricity, 84x10^9 btu/yr are consumed, or 5.8% of the energy available in the bio-oil.

The total process heat requirement is 5.3x10^9 btu/yr, at 90% conversion efficiency, 5.9x10^9 btu/yr of bio-oil would be burned to produce process heat, or 0.4% of the energy available in the bio-oil. Thus, the total energy consumed to produce the process power requirements and the process heat are 6.2% of the energy available in the bio-oil.

Also to be considered is the makeup propane fed to the process, estimated at 790,000 gallons per year. At 92,500 btu/gallon of propane, 73x10^9 btu/yr or 5.0% of the bio-oil energy are not recovered. However, as most of that propane not recovered ends up in either the product or the raffinate, it is likely that its energy content will be recovered.

The Design includes a narrative description of the process and equipment, a process flow diagram, material balance, equipment list, and estimated capital and operating costs. The HAZOP analysis is included as an appendix to the Design.

## Life Cycle Assessment of Microalgae to Biofuel: Thermochemical Processing through Hydrothermal Liquefaction or Catalytic Fast Pyrolysis

A modular systems engineering model was constructed with a system boundary that included growth, dewatering, bio-oil production through hydrothermal liquefaction (HTL) or catalytic fast pyrolysis, bio-oil stabilization through supercritical fluid processing, bio-oil conversion to renewable diesel, and transportation and distribution to the pump. Two system models were developed: 1) a pathway integrating catalytic pyrolysis conversion and 2) a pathway that integrates HTL as the conversion technology. The industrial-scale model was validated through experimental and literature data, to assess facility function at commercial scale. The latter was limited to promising growth and dewatering techniques in the industrial-scale system. Environmental impact results are presented on the metrics of net energy ratio (NER) and GHG emissions with sub-processing resolution. Discussion focuses on the impact of modeling at industrial-scale, sensitivity to process parameters, and a comparison of results to other conversion technologies.

Process energetics are presented on the metric of NER defined here as the energy inputs divided by the energy in the biofuel with a NER of less than 1 being desirable. For the well to pump (WTP) system boundary, energetics in biofuel conversion are typically dominated by energy demands in the growth, dewater, and thermochemical process. Any additional processing requirements such as stabilization must not be a significant energy sink for the process to be favorable. Results for the two pathways modeled based on conversion through catalytic pyrolysis or HTL show system energetics are dominated by energy requirements in the reactor, and heating requirements. Bio-oil stabilization by near critical propane extraction had minimal impact in the overall energetics of the process with NER contributions of 0.03 for both conversion technologies. This is well within the desired range of less than 20% of the energy in the bio-oil with both processes at 3% for bio-oil stabilization processing with the near-critical propane solvent. Figure 13 illustrates the energy breakdown of the well to pump systems with the respective conversion method. Bio-oil stabilization is shown in purple and can be seen to have very little impact on the overall process energetics.

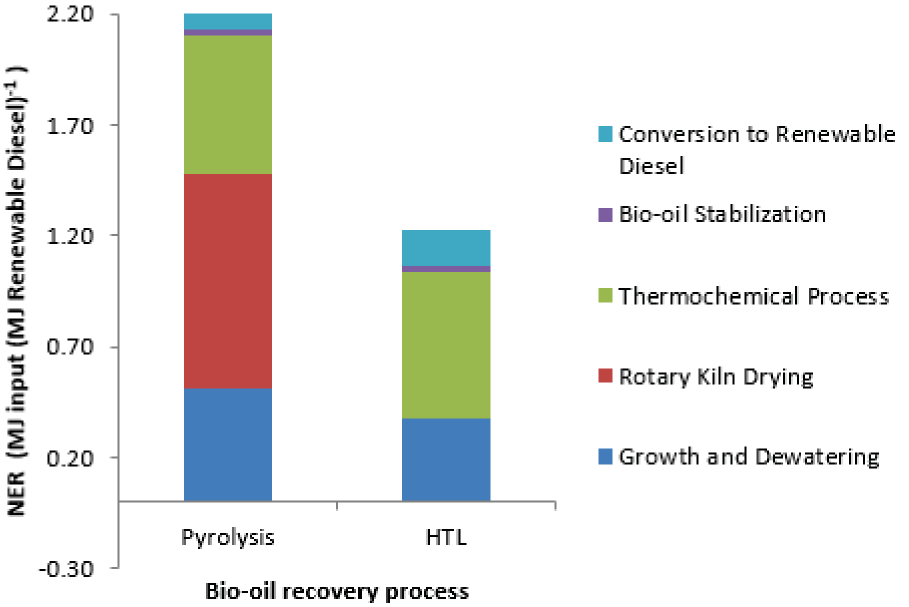

Figure 13. Net Energy Ratio (NER) for a well to pump boundary for converting microalgae to biofuel through catalytic pyrolysis or HTL

It should be noted that although bio-oil stabilization results in very little direct energy consumption it is followed by further processing through hydrocracking of the stabilized bio-oil. Due to limited experimental data, it is assumed the raffinate from the supercritical processing can be further processed into biofuel with the stabilized bio-oil through hydrogen treating.

The information collected has been used to complete a life cycle assessment comparing two different thermochemical conversion processes on the metric global warming potential (GWP) through carbon dioxide emissions. Greenhouse gas (GHG) emissions are detailed for the WTP system boundary of the industrial-scale systems for the two thermochemical conversion technologies modeled and compared to conventional diesel, and soybean based biodiesel (Figure 14). The emissions are broken down into process emissions for electrical, heating, and product consumption. Emissions from product consumption are a result of nutrient demands, material losses, and burning of process byproducts, such as char from catalytic pyrolysis or HTL gasses.

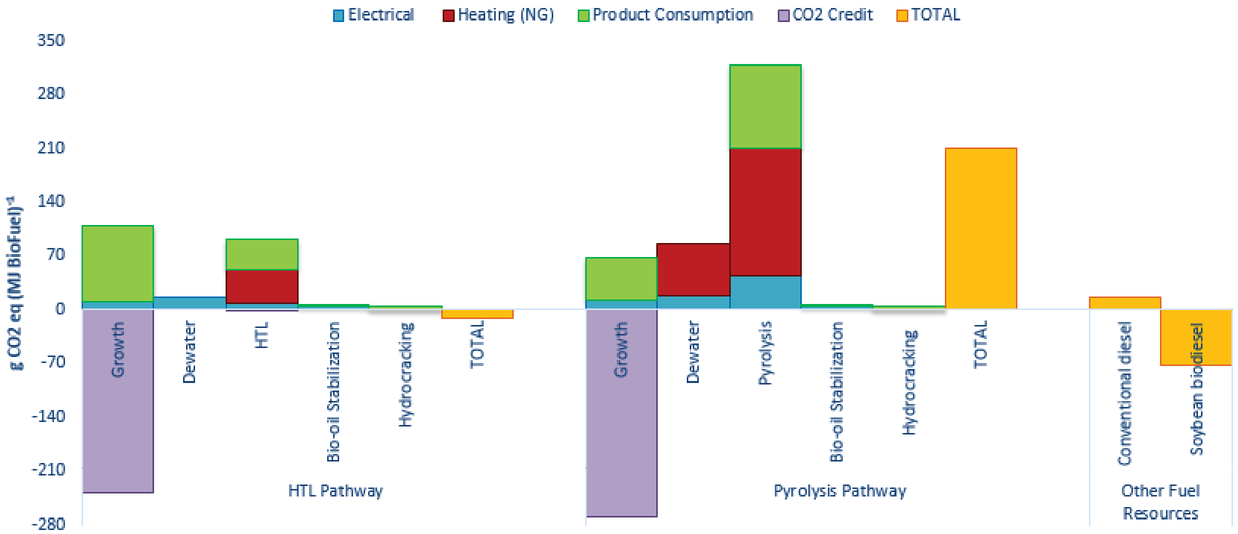

Figure 14: Well to pump GWP for industrial-scale system models. The respective WTP systems are broken out into sub-processes for the HTL and catalytic pyrolysis pathways. The pathway totals are displayed at the right of the pathway. A comparison of the WTP emissions associated with conventional diesel and soybean biodiesel are shown at the far right.

Microalgae based biofuels benefit from a carbon credit associated with the uptake of carbon dioxide in the growth phase. The emissions for a WTP systems boundary with HTL, result in an environmentally favorable carbon dioxide reduction of -10.81 g $CO_{2\ eq}$. The aqueous phase from the HTL unit contains ammonium and phosphite, which represent a co-product credit and are recycled to supplement the nutrient requirements for microalgae growth. In terms of GWP, a benefit of bio-oil recovery through HTL results from the processing of a wet microalgae slurry, eliminating the energy and GHG emissions associated with drying. In addition, HTL processing produces a small quantity of combustible gases which produce fewer GHG emissions than natural gas. This improves the HTL pathway energetics and environmental impact. Bio-oil stabilization and hydrocracking have minimal impact on overall process GHG emission.

Microalgae conversion through the catalytic pyrolysis pathway has two energy intensive processes, drying and the pyrolysis rector, which result in a high environmental impact. The reactor energy is supplemented through burning of catalytic pyrolysis byproducts, gas and char, which improves process energetics but are detrimental to GHG emissions. If burning of catalytic pyrolysis byproducts is replaced with natural gas the GHGs for the production of biofuel are reduced from 210.3 g $CO_{2\ eq}$ to 158.44 g $CO_{2\ eq}$, but the NER increases from 2.28 to 2.92. Using catalytic pyrolysis char and gasses for alternative purposes would decrease the environmental impact of the catalytic pyrolysis pathway, but GHG emissions are still significantly higher than those of conventional diesel and soy biodiesel (Figure 14), and results in a more unfavorable NER.

The need of a dry feedstock and energy demands in the reactor for the catalytic pyrolysis unit make it difficult to produce an energetically and environmentally favorable renewable fuel. Emissions from microalgae diesel with catalytic pyrolysis do not meet renewable fuel standards, and are high in comparison with conventional diesel and soybean biodiesel. Microalgae bio-oil based diesel with thermochemical conversion through HTL in the WTP system laid out meets renewable fuel standards with favorable emissions.

The importance of the outcomes of this work is that the critical fluid extraction and stabilization process improved product stability and did so with minimal energy inputs and processing costs. The LCA and GHG emission calculations point toward the HTL pathway as the more favorable thermochemical route towards upgrading algae to bio-fuels. Since the quality of the HTL oil was significantly lower than that of the catalytic fast pyrolysis bio-oil, the next steps point toward improving the quality of the HTL oils from algae biomass and focusing the critical fluid stabilization on that bio-oil product. Further, our oil refining partner, Big West Oil LLC, has indicated that a larger sample of stabilized oil is needed to determine the insertion point into their refinery and to reach a preliminary feedstock acceptance decision. This larger quantity is approximately 1 liter of bio-oil. If an improved quality of HTL bio-oil can be produced and if the critical fluid stabilization process proves favorable, then the critical fluid stabilization experimental system would need to be scaled up from the current level of tens of grams of sample to 1 liter of sample. The majority of equipment to perform this scale-up currently exists at INL.

## Conclusion

Near-critical propane was used to extract bio-oil produced from algae based biomass. It was found that the propane extract fraction was twice as stable as the parent catalytic pyrolysis bio-oils produced from *Scenedesmus dimorphus* as measured by the change in viscosity after two weeks of accelerated aging at 80°C. Further, in-situ NMR aging studies found that the propane extract was chemically more stable than the parent bio-oil. Thus the milestone of stabilizing the product was met.

A preliminary process design of the near-critical propane extraction plant was prepared assuming a depot scale plant processing 20,000,000 gallons per year of bio-oil. On a per gallon of product cost capital costs would represent $0.06 per gallon and operating costs would amount to $0.20

per gallon. Further, it was found that the energy required to run the process represented 6.2% of the energy available in the bio-oil, meeting the milestone of less than 20%.

Life cycle analysis and greenhouse gas (GHG) emission analysis found that the energy for running the critical fluid separation process and the GHG emissions were minor compared to all the inputs to the overall well to pump system. For the well to pump system boundary, energetics in biofuel conversion are typically dominated by energy demands in the growth, dewater, and thermochemical process. Bio-oil stabilization by near critical propane extraction had minimal impact in the overall energetics of the process with NER contributions of 0.03 for both conversion technologies.

Based on the LCA, the overall conversion pathways were found to be energy intensive with a NER of about 2.3 and 1.2 for catalytic fast pyrolysis and HTL, respectively. GHG emissions for the catalytic fast pyrolysis process were greater than that of petroleum diesel. Microalgae bio-oil based diesel with thermochemical conversion through HTL meets renewable fuel standards with favorable emission reductions.

The importance of this work is that the critical fluid extraction and stabilization process improved product stability and did so with minimal energy inputs and processing costs. The LCA and GHG emission calculations point toward the HTL pathway as the more favorable thermochemical route towards upgrading algae to bio-fuels. Next steps point toward improving the quality of the HTL oils from algae biomass, focusing the critical fluid stabilization on that bio-oil product, and scaling-up the critical fluid stabilization process so larger quantities of oil products can be examined by our refining partner, Big West Oil LLC.