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## Introduction

Bio-oils produced by thermal process, such as fast pyrolysis, catalytic fast pyrolysis (CFP), and hydrothermolysis are promising sources of sustainable, low greenhouse gas alternative fuels. These thermal processes are also well suited to decentralized energy production due to low capital and operating costs.

Algae feedstocks for bio-oil production are of particular interest, due in part to their high-energy growth yields. Further, algae can be grown in non-arable areas in fresh, brackish, salt water, or even waste water. These feedstocks have faster growth rates and productivities than any agricultural feedstock and require much less land than terrestrial crops [1,2].

Unfortunately, bio-oils produced by thermal processes present significant stability challenges [3,4]. These oils have complex chemical compositions, are viscous, reactive, and thermally unstable [1]. Further, the components within the oils are difficult to separate by fractional distillation. By far, the most effective separation and stabilization method has been solvent extraction. However, liquid phase extraction processes pose two main obstacles to commercialization; they require a significant amount of energy to remove and recover the solvent from the product, and they have a propensity for the solvent to become contaminated with minerals from the char and ash present in the original bio-oil.

Separation and fractionation of thermally produced bio-oils using supercritical fluids (SCF) offers the advantages of liquid solvent extraction while drastically reducing energy demands and the predisposition to carry over solids into the extracted phase. SCFs are dense fluids with liquid-like solvent properties and gas-like transport properties. Further, SCF density and solvent strength can be tuned with minor adjustments in pressure, co-solvent addition, or gas anti-solvent addition.

## Experimental

Catalytic pyrolysis oils were produced from *Scenedesmus dimorphus* algae using a fluid catalytic cracking catalyst. The catalytic pyrolysis studies were conducted in the 4 kg/h pilot scale fluidized bed pyrolysis reactor. The catalyst used was proprietary material supplied by BASF Inc. About 1,000 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. Catalytic pyrolysis was carried out at 400 °C. FCC catalyst was used as both heat transfer medium and catalyst.

Bio-oil produced from catalytic fast pyrolysis (CFP) was separated using critical fluids. The system consisted of two high-pressure syringe pumps, a temperature controlled stainless steel 32 mL high-pressure extraction vessel, an automated micro-metering valve, a high-pressure sight glass collection vessel, and a back pressure regulator. The system was protected from over-pressurization with two spring loaded relief valves and back flow was prevented with one-way check valves. 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.

## Results and Discussion

About 83 % of the bio-oil was extracted using propane, leaving about 17 % as raffinate. 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. The propane extract had a lower viscosity than the parent.

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

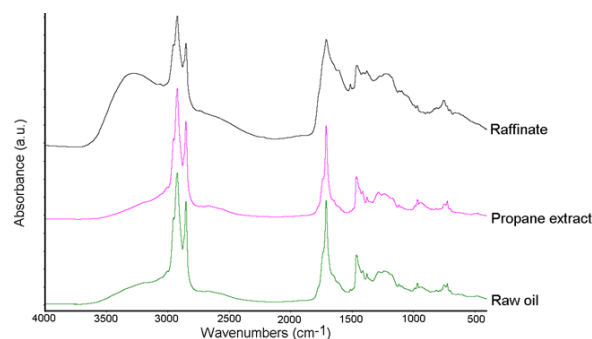


Figure 1. Extraction using propane at 65 °C.

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

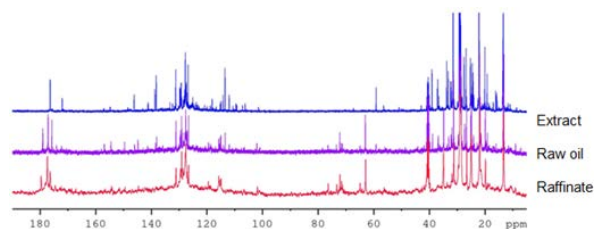


Figure 2.  $^{13}\text{C}$  NMR analyses. Extraction using propane at 65 °C.

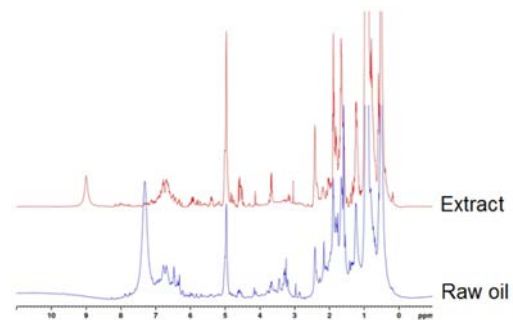


Figure 3.  $^1\text{H}$  NMR analyses. Extraction using propane at 65 °C.

MALDI-TOF analyses 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. 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. The raffinate required temperatures above 500 °C for the last 20 % to volatilize.

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

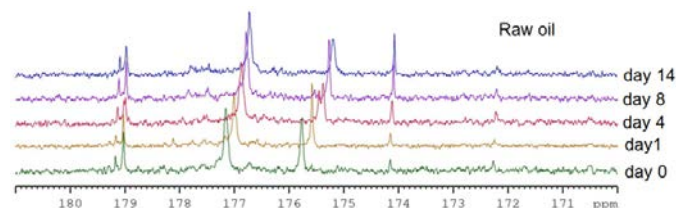
Samples of the parent oil, propane extract, and propane raffinate were submitted to accelerated aging which consisted in keeping bio-oil aliquots in closed vials for 24 hours and 2 weeks at 80 °C. Next, the aged samples were analyzed to determine the effects of aging on sample physicochemical properties.

The results of viscosity measurements at different temperatures showed that the propane extract was more stable than the raw oil. 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.

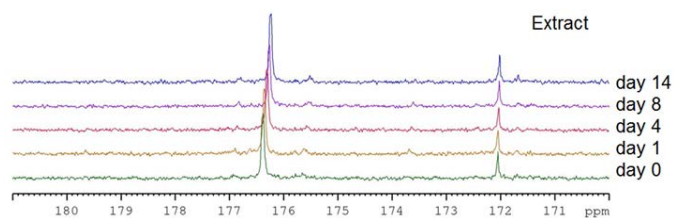
To understand the processes that may be affecting the stability of these oils, additional analyses were performed.

Infrared analyses 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. In general, volatility also decreased with aging.

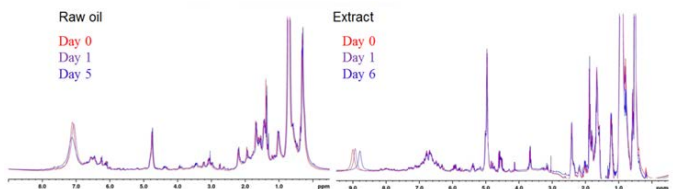
Parent oil and propane extract were submitted to an in-situ NMR aging study for 2 weeks at 80 °C in the NMR instrument. The results are shown in Figures 4-6. The shift of the peaks was more significant in the parent oil than in the propane extract. For example, the peak at 176-177 ppm shifted -0.45 ppm 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 4.** In situ  $^{13}\text{C}$  NMR aging analyses of parent oil.



**Figure 5.** In situ  $^{13}\text{C}$  NMR aging analyses of propane extract.



**Figure 6.** In situ  $^1\text{H}$  NMR aging analyses of parent oil (left) and propane extract (right).

#### Conclusions

Extraction of catalytic fast pyrolysis oil with near critical propane produced an oil extract that was physically and chemically different from and more stable than the original oil. The propane extract displayed lower viscosity and lower average molecular weight. The species present in the propane extract were likely the less polar that would be expected from using a non-polar solvent (propane). Carbonyl containing species in the extract were likely ketones and esters. The raffinate contained a higher amount of OH bonded species along with the more polar more polar acids, amides, and alcohols. The higher concentration of nitrogen in the raffinate may confirm the presence of amides.

Viscosity of the propane extract increased only half as much as that of the CFP bio-oil. Further, In situ NMR aging studies showed that the propane extract was more stable than the raw oil. 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.

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