

Swell Behavior Of Elastomers With A Hydrothermal Liquefaction Bio-Crude And A Fast Pyrolysis Bio-Oil

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ABSTRACT

The compatibility of seventeen elastomer materials with two heavy biofuels (fast pyrolysis bio-oil and hydrothermal liquefaction (HTL) bio-crude) and diesel was assessed through volume change measurements. The elastomers included two fluorocarbons, six acrylonitrile rubbers (NBRs), and one each of fluorosilicone, neoprene, polyurethane, silicone, epichlorohydrin rubber (ECO), a blend of polyvinyl chloride and NBR (OZO), styrene butadiene rubber (SBR), hydrogenated NBR (HNBR) and ethylene propylene diene monomer (EPDM). The specimens were immersed in each test fuel for four weeks at 50°C and then measured for volume change. Afterwards, the specimens were dried, and the volume was remeasured. In general, the bio-oil produced unacceptable swelling in the fluoroelastomers, ECO, OZO, neoprene, polyurethane, SBR, HNBR, EPDM, silicone and five of the NBRs. In most cases, the HTL bio-crude produced lower (though still unacceptable) swelling than the bio-oil. Materials that showed good compatibility with the HTL biocrude were the fluoroelastomers, OZO, and silicone.

Key words: elastomer, bio-oil, bio-crude, compatibility, volume change

DISCLAIMER

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INTRODUCTION

Fast pyrolysis-derived bio-oils and hydrothermal liquefaction bio-crudes are being explored as renewable fuels for use in home heating, transportation (especially as marine fuels) and electrical power generation.¹⁻³ These fuels are attractive in that the processes used to develop these fuels can utilize a wide range of feedstocks. The fast pyrolysis process is defined by rapidly heating (around 1000°C/sec) of biomass feedstock in the absence of oxygen. Liquid yields may reach 75% depending on feedstock type, reactor design and other processing variables.⁴⁻⁹ The resulting oils have high viscosity and water content relative to petroleum distillates and are considered corrosive. The bio-oil derived from fast-pyrolysis contains high levels of water, acids, ketones and other oxygenates.

Hydrothermal liquefaction (HTL) uses a combination of high pressures and high temperatures to break apart (depolymerize) long chains of feedstock molecules to form a crude-like oil. Oxygen is removed through dehydration (of water) and by forming CO₂. In contrast to pyrolysis oils, the feedstock does not need to be dried beforehand to remove moisture to improve process efficiency. The resulting bio-crude contains much lower quantities of acid or water content. Because of this feature and the reduced oxygen content, the energy density of HTL bio-crudes is generally higher than bio-oils. Like pyrolysis oils, bio-crudes may contain appreciable levels of ketones, which may impact polymer compatibility. Bio-crudes also typically contain high concentrations of phenolics and alkanes.²

These oils (bio-oils and bio-crudes) are often referred to a bio-precursors or bio-intermediates since they are almost always upgraded to improve energy density and remove water and oxygenates. Upgrading via hydrotreating is also needed to improve the miscibility with distillates fuels (such as diesel) and improve combustion properties. In the raw state (prior to upgrading) the properties of these oils do not allow them to be used as transportation fuels, with the possible exception of marine engines designed to operate on heavy fuel oils. They are used as fuel in some boiler applications.

In order for these fuels to become acceptable and common, it is necessary that they are compatible with existing fuel systems and the associated infrastructure materials, which includes metals and polymers. The corrosion behavior of bio-oils derived via fast pyrolysis have been studied extensively.¹⁰ Bio-oil (due to its acid content) is highly corrosive to mild carbon steels, but stainless steels are more corrosion resistant.¹⁰ HTL bio-crudes have been shown to have less acidity than bio-oils, and as a result they are less corrosive to mild carbon steels.

Since 2012, the U. S. Department of Energy Bioenergy Technologies Office has been evaluating the compatibility of bio-oil with infrastructure materials. These efforts are primarily focused on the corrosion behavior of bio-oil with metals since many of the infrastructure components are composed of steels. However, many of the seals are composed of elastomers. As such, they are critical components that must exhibit compatibility with the contained fuel to prevent leaks and/or fugitive emissions. Many o-ring manufacturers provide compatibility tables rating the compatibility of their polymer materials with various chemicals. These compatibility tables include ratings that are based almost solely on volume

swell. In most instances the rating value is determined for exposure of the polymer with a neat chemical, and ratings for chemical or fuel blends are not common. It is extremely difficult to predict the actual performance in a given application based solely on the measured swell, since factors such as temperature, tear strength, compression set, friction, and softening also play a role. For o-rings the general rule of thumb is that volume expansions below 30% are acceptable for most static applications, while values less than 15% are tolerated for most dynamic applications.¹¹ However, it is important to note that swelling in excess of 50% is not considered beyond the limits of acceptability for some applications. Because elastomers are ubiquitous in fueling infrastructure systems, it is important to understand their performance with potential fuel types, including HTL bio-crudes.

Bio-oils have been shown to be incompatible with many elastomers.¹²⁻¹⁷ Studies have shown excessive swelling in fluorocarbons and acrylonitrile rubbers which are ubiquitous in fuel storage and delivery systems. This swelling is attributed to the appreciable levels of ketones and phenolic compounds present in bio-oil. Compatibility studies on HTL liquids have not been studied as extensively as bio-oils. In this study, we measured the volume change behavior of 17 elastomer materials with bio-crude derived from algal feedstock. The results are compared to bio-oil derived via fast pyrolysis bio-oil and No. 2 diesel.

EXPERIMENTAL PROCEDURE

Materials and Test Fuels

Test Fuels

In this study the bio-crude was produced in a hydrothermal liquefaction process with chlorella algae as the biomass feedstock using the Pacific Northwest National Laboratory (PNNL) Modular Hydrothermal Liquefaction System (MHTLS). The elemental composition and several key properties of the bio-crude are shown in Table 1. The flash point of the bio-crude was determined to be greater than 110°C. As seen in the table the total acid number and the water content are relatively low, especially when compared to bio-oils. The high sulfur content measured in the bio-crude was likely introduced by the catalyst (which contained sulfur) used in the HTL process.

Table 1. Composition and Key Properties of the Bio-crude

Composition/Property	Basis	Unit	Value
Component			
Carbon	Dry basis	wt%	77.8
Hydrogen	Dry basis	wt%	10.1
H:C ratio	Dry basis	mol ratio	1.54
Oxygen	Dry basis	wt%	5.9
Nitrogen	Dry basis	wt%	5.3
Sulfur	Dry basis	wt%	0.59
Moisture	Wet basis	wt%	6.8
Ash	Wet basis	wt%	0.30
Viscosity	Wet basis	cSt@40C	180
Filterable Solids	Wet basis	wt%	0.07
Property			
High Heating Value	Dry basis	MJ/kg	36
Total Acid Number (TAN)	Wet basis	mgKOH/goil	49.42
Density	Wet basis	g/ml@40C	0.970

The bio-oil used in this study was produced by the National Renewable Energy Laboratory (NREL). It was produced via fast pyrolysis at 500°C and consisted of a blended feedstock composition of 60% air-classified forest residues, 30% clean pine, and 10% hybrid poplar. The residues (which are pine) were air-classified to remove the fines and with them the ash they carry, making it closer to a clean pine composition. The pyrolysis oil produced during these runs appeared as a single phase. The water concentration in the bio-oil was determined to be 24 mass%. Acid content of the bio-oil was determined using aqueous modified total acid number (AMTAN) measurement, which was determined to be 112 mg KOH per g oil. A compositional analysis was conducted on the bio-oil using gas chromatography-mass spectrometry (GC-MS) and the resulting profile is shown in Figure 1. As shown in the figure, the pine-derived bio-oil contained a complex mix of carboxylic acids, phenols, dodecane, and other oxygenates. It is important to note that although the method used for this analysis did not capture the ketone peaks, appreciable ketone concentrations are expected with this bio-oil.

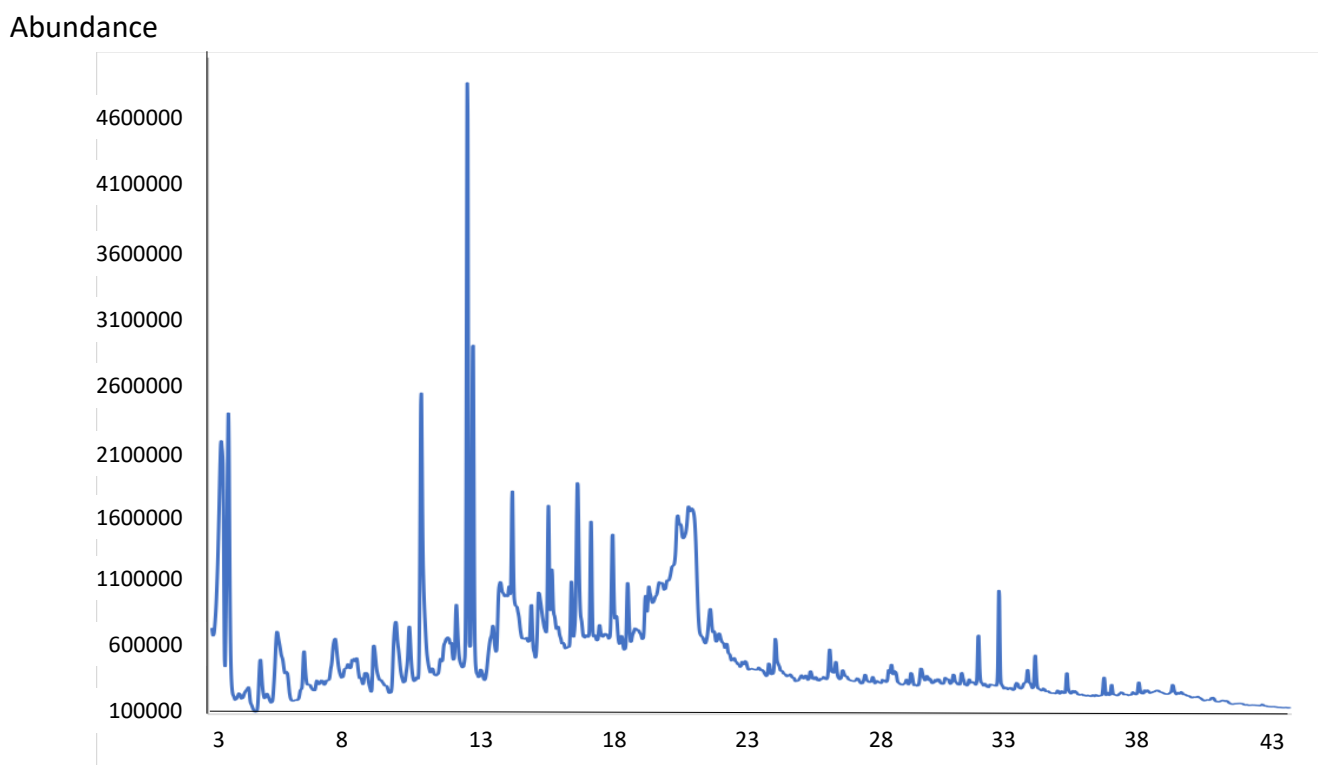


Figure 1. GC-MS results of the bio-oil used in this study

Because different approaches were used to assess the composition of the bio-crude and bio-oil, it is difficult to make direct comparisons. The water content and acid numbers were substantially higher for the bio-oil and would be expected to lead to higher corrosion rates on steels. It is more difficult to determine relative polymer compatibility since the relative levels of ketones and phenols are not known. A GC-MS analysis was performed on the HTL bio-crude and the bio-oil. These results are shown in Figure 2. The top curve is the HTL bio-crude and the bottom curves is for the bio-oil. These results show that the composition was very different for the two fuel types. The HTL bio-crude components have significantly longer retention times than the bio-oil, indicating that its molecular components have much longer chain lengths. Many of the lighter molecules in bio-oil are polar, such as ketones and phenols, and one general conclusion that can be drawn is that the HTL bio-crude is likely to be less polar than the bio-oil for this reason. Both the HTL and fast pyrolysis processes break down the lignin and cellular structure into smaller molecules.