

Compatibility Assessment of Plastic Infrastructure Materials with Off-Highway Diesel and a Diesel Blend Containing 20 Percent Fast Pyrolysis Bio-Oil

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ABSTRACT

The compatibility of plastic materials used in fuel storage and dispensing applications was determined for an off-highway diesel fuel and a blend containing 20% bio-oil (Bio20) derived from a fast pyrolysis process. Bio20 is not to be confused with B20, which is a diesel blend containing 20% biodiesel. The feedstock, processing, and chemistry of biodiesel are markedly different from bio-oil.

Plastic materials included those identified for use as seals, coatings, piping and fiberglass resins, but many are also used in vehicle fueling systems. The plastic specimens were exposed to the two fuel types for 16 weeks at 60°C. After measuring the wetted volume and hardness, the specimens were dried for 65 hours at 60°C and then remeasured to determine extent of property change. A solubility analysis was performed to better understand the performance of plastic materials in fuel blends composed of bio-oil and diesel.

All of the plastic materials evaluated in this study exhibited higher solubility (volume swell) with the Bio20 fuel blend. This result was predicted by the solubility analysis. However, there were two notable exceptions; the volume swell results for high density polyethylene (HDPE) and polypropylene (PP) did not correlate with their respective solubility curves. HDPE and PP were also unique in that they were the only two plastics that exhibited pronounced volume expansion in the baseline diesel test fuel.

The plastic materials which showed the best compatibility to the bio-oil blend were the barrier plastics polypropylene sulfide (PPS), polyethylene terephthalate (PET or Mylar™), and polytetrafluoroethylene (PTFE or Teflon™). Polyvinylidene fluoride (PVDF or Kynar™) is also used extensively as a permeation barrier material; however, it swelled over 15% when exposed to Bio20. Four grades of nylon were evaluated and the petroleum-derived nylons (Nylon 6, Nylon 6,6, and Nylon 12) showed good compatibility with the test fuels. In contrast, Nylon 11, which is derived from vegetable oil, expanded over 4% with Bio20. HDPE also swelled around 4%, but did so with both test fuels. Two acetal materials and polybutylene terephthalate (PBT) were also observed to swell to 4% with Bio20. Four fiberglass resins were included in the study and they exhibited 10-18% volume expansion. High volume swell was also noted for PP, the PET polyethylene - glycol copolymer (PETG), and polythiourea (PTU). PP also expanded over 15% following exposure to the baseline diesel test fuel.

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INTRODUCTION

Renewable fuels are becoming more widely used as a transportation fuels in the United States and in other countries. A key motivation for increasing biofuel use is to reduce petroleum consumption, thereby improving energy security and independence [1]. Oil, derived from biomass, is being evaluated as one means of offsetting foreign petroleum imports as well as utilizing a renewable energy source to meet the energy demands in the United States. Most efforts have focused on utilizing bio-oil in burners as a replacement for off-highway diesel (used in home heating applications) or in power generation. However, some efforts are considering bio-oil as possible drop-in additive to diesel fuel.

One popular means of producing bio-oil is through fast pyrolysis of biomass [2, 3, 4, 5, 6] as a substitute for crude petroleum or diesel fuel. Bio-oil differs from both biodiesel and green diesel fuels in that it does not involve conversion of vegetable oils. Biodiesel is derived via transesterification and is primarily composed of fatty acid methyl esters. Green diesel (sometimes referred to as renewable diesel) is produced by hydrocracking or hydrogenation of vegetable oil. In contrast, bio-oil is typically made via pyrolysis of hardwood tree pulp and the specific tree species does affect the resulting chemistry of the fuel. As a result, the composition of these oils varies widely, but they usually contain significant quantities of oxygenates, ketones, and phenols.

The fast pyrolysis method to produce bio-oil employs rapidly heating biomass feedstock (typically pelletized wood) at rates up to 1000°C/s (or higher) in the absence of oxygen. Liquid yields can be as high as 75% depending on the reactor configuration and process. The oil produced in this process has high viscosity and water content (relative to diesel fuel) as shown in Table 1 [2].

Table 1. List of selected properties for pyrolysis oil and diesel [2].

Property	Pyrolysis Oil	Diesel
Density at 20°C, g/cc	1.2	0.85
Viscosity at 20°C, cStoke	13	2.5
Lower heating value, MJ/kg	17.5	42.9
Ash, wt. %	0.13	<0.01
Water content, wt. %	20.5	0.1
Oxygen, wt/%	42.5	0.9

At this stage the bio-oil is immiscible with petroleum-based fuels. Additional upgrading, including hydrotreating and deoxygenation, are necessary for bio-oil to be used with conventional transport fuels such as diesel, kerosene, and gasoline [3]. Much of the oxygen exists as furanics, phenolics, and carboxylic acids, such as acetic and formic acids. These acids are difficult to remove and are corrosive to many infrastructure metals [3, 4, 5, 6, 7, 8, 9, 10].

In 2012, the U. S. Department of Energy Bioenergy Technologies Office initiated a research program to evaluate the compatibility of bio-oil with infrastructure materials. These materials include metals, which are subject to potential oxidation corrosion, and polymers. Like metals, polymer degradation can occur via direct chemical reaction, but unlike metals, polymer performance is also highly affected by its mutual solubility with contacting fluid. Many infrastructure polymers, whether elastomer or plastic, are in fact chemically unreactive to carboxylic acids, petroleum transport fuels, and bio-derived fuels. However, pyrolysis oils contain appreciable levels of phenols, ketones, and aromatics, and these compounds are highly soluble to some plastics. In fact, ketonization of existing carboxylic acids is gaining interest as an additional upgrading step to mitigate metal corrosion in bio-oil [10]. Unfortunately ketones are known solvents for many polymers. The implication is that many existing plastic materials used in fueling infrastructure and vehicle fuel delivery systems may not be compatible with bio-oils and their blends with diesel fuel or other heavy-grade fuel types.

Because plastic materials are commonly used in both rigid and flexible piping and fuel storage systems, volume expansion will impart stress on a rigidly-held plastic component. These internal stresses will reduce the durability of the part and may lead to cracking. Excessive swelling will result in buckling or leakage. Plastics used as permeation barriers need to exhibit low solubility to prevent contamination of less durable plastic materials typically used as wall structures. Failure of a structural plastic may lead to fuel leakage, which subsequently, may create a fire, explosion, or an environmental hazard. As such, it is necessary to understand the performance of plastic materials when they are exposed to new fuel chemistries, such as fast pyrolysis oils, in order to provide guidance on material selection, and identification of potential leak sites and conditions in fueling hardware.

In 2013 ORNL initiated a study to evaluate the compatibility of fueling infrastructure materials to test fuels representing off-highway diesel fuel (which is also used as home heating oil) and Bio20. Another objective was to perform a solubility analysis for each material type and bio-oil blended diesel fuel. The materials included in this study were those used as permeation barriers, flexible piping reinforcement and outer walls, fiberglass resins, coatings and other common plastics. It is important to note that many of these materials are also used in vehicle fueling systems.

SOLUBILITY AND ITS IMPACT ON OTHER PLASTIC MATERIALS

For polymers, fuel compatibility is predominantly determined by the mutual solubility between a polymer and fuel. In practice, the degree, or extent, of solubility, is routinely assessed by measuring the volume expansion of the polymer being considered. In lieu of direct measurement, the solubility potential between a polymer and solvent can be gauged by calculating the difference in the solubility parameters between the two components using the Flory-Huggins solution theory [11].

Solvents and solutes (or, in this case, fuel and plastics) having similar solubility parameters will have a higher affinity for permeation and dissolution than those with dissimilar values. There are several different solubility approaches. The Hildebrand method is one dimensional and uses a single parameter to represent the total attractive force. In contrast, the more precise (3D) Hansen method utilizes three separate parameters based on atomic dispersion, polarity, and hydrogen bonding. For the purposes of facilitating discussion, the total solubility parameter is often used since it is a single representative parameter. The total solubility parameter is square root of the sum of the squares of the three Hansen parameters. It roughly approximates the Hildebrand parameter and the two are often confused with each other.

The total solubility parameters for mixtures of gasoline blended with ethanol and diesel blended with bio-oil are shown in Figure 1 as a simplified means of displaying this effect. In this figure, the x-axis presents both ethanol-blended gasoline and bio-oil-blended diesel fuel. As shown, the total solubility of gasoline and diesel increases linearly with ethanol and bio-oil respectively. Also depicted in the figure is the typical range of solubility parameters for many plastics (and elastomers). The chart shows that gasoline containing 10 to 50% ethanol is within the shaded polymer solubility range. In contrast diesel fuel containing 0 to 90% bio-oil is within this same range. The implication is that diesel blended with bio-oil can be expected to be soluble to many polymers irrespective of bio-oil content. High solubility translates to high levels of polymer swelling, which is not desirable in many plastic applications since it can lead to buckling and damage.

Another consideration is that many polymer materials are complex compositions of one or more polymers, including low molecular weight (LMW) additives, such as oligomers, plasticizers, stabilizers,

lubricants, or other flexing agents. The extent to which these additives are solvated and extracted by fuel blends also can be assessed using solubility analysis.

The compatibility of a polymeric material typically refers to the solubility of the polymer to a particular solvent. It can also mean susceptibility to chemical attack, although the majority of the polymers and test fuels evaluated in this study were not considered to be chemically reactive with each other. Solubility is typically assessed by measuring the volume swell of the polymer exposed to the solvent of interest. Swell is almost always accompanied by a decrease in hardness (softening) that also affects performance.

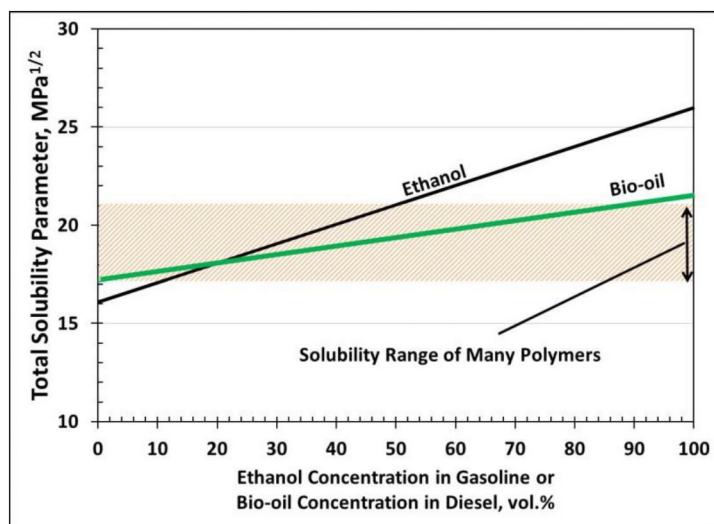


Figure 1. Total solubility parameter curves for gasoline blended with ethanol and diesel fuel blended with bio-oil.

MATERIALS, EQUIPMENT AND PROCEDURE

Test Fuels

In this study the baseline fuel was off-highway diesel fuel (also referred commercially as heating oil, #2, dyed, combustible, NA1993 Diesel Fuel 3) which is also designated at home heating oil. The baseline fuel was supplied by Connell Oil, Inc. and had a sulfur concentration up to 500ppm. It is important to note that this particular fuel is the same as that used to fuel off-highway vehicles.

The bio-oil used in this study was produced by a proprietary fast-pyrolysis method and partially upgraded to remove carboxylic acids. The oil was also hydrotreated to remove most of the water component, but it likely that some water remained afterwards (even though the bio-oil was fully miscible with the baseline diesel fuel). The chemical composition of the bio-oil was examined using gas chromatography mass spectrometry (GC-MS) analysis. The analysis showed the presence of significant levels of phenols, ketones, ethyl acetate, and the aromatics (toluene and naphthalene). This composition is similar to other bio-oils derived from fast-pyrolysis, except that acetic acid normally present in bio-oil was esterified to

ethyl acetate. Most bio-oils produced via fast pyrolysis contain levels of acetic ranging from 5 to 10%. The Bio20 test fuel was prepared by splash blending.

Description of Plastic Materials

Plastic materials are divided into two classes: thermoplastics and thermosets (or thermosetting resins). Thermoplastic polymers do not undergo a chemical change in composition when heated, though they do soften or melt. When cooled they typically return to their original composition, and consequently, they can be molded repeatedly.

Thermosets, on the other hand, can only be cured and shaped once. After forming, they remain in a highly rigid state and cannot be melted. In the thermosetting process, the chemical reaction forming the cross-linked polymer is not reversible. A complete listing of the plastic materials according to type and application is shown in Table 2. For each material type, three specimens were exposed in the test fuel liquids. Each specimen measured 2.54 cm (1 in.) wide, 7.6 cm (3 in.) long, and 0.32 cm (0.125 in.) thick.

Table 2. List of plastic materials and their respective applications.

Thermoplastics	
Application	Material type
Permeation barrier	Polyphenylene sulfide (PPS)
	polyethylene terephthalate (PET)
	polyvinylidene fluoride (PVDF)
	polytetrafluoroethylene (PTFE)
Flexible piping wall material	Nylon 11, Nylon 6, Nylon 6,6 and Nylon 12
	High density polyethylene (HDPE)
Other common plastics	Acetals: Polyoxymethylene (POM) and POM co-polymer
	Polyesters: Polybutylene Terephthalate (PBT), PETG (PET co-polymer)
	Polypropylene (PP)
	Polythiourea (PTU)
Thermosets	
Application	Material type
Fiber reinforced plastic piping and storage tanks	Isophthalic polyester resin (2 types)
	Terephthalic polyester resin
	Novolac vinyl ester resin

Thermoplastics

Thermoplastics are usually pliable, and as a result, they are used in the construction of flexible piping systems. The more chemically resistant grades are also used as high performance seals. The thermoplastic materials examined in this study are grouped according to their application and type as shown in Table 2. The first group includes those used as permeation barriers and liners in flexible piping systems. This group includes polyphenylene sulfide (PPS), polyethylene terephthalate (PET), polyvinylidene fluoride (PVDF), and polytetrafluoroethylene (PTFE). PTFE (also known as Teflon) is also used in sealing applications. PET (or Mylar) is the most commonly used barrier plastic, primarily because it has a lower cost relative to the other three materials.

The second grouping includes nylon and HDPE, which are also used in flexible piping systems. These materials typically do not have the permeation resistance (or high cost) of the four barrier materials, but they do exhibit good compatibility and are used to reinforce and support flexible piping, either as braided fiber bundles or as high strength secondary wall materials. Four grades of nylon were included. Nylons 6 and 6,6 are similar to each other and have good mechanical properties. Nylons 12 and 11 are also used in flexible piping. It is worth noting that Nylon 11 is manufactured from vegetable oil, while the other three are derived from petroleum.

The third grouping includes those plastics which are widely utilized across a range of applications. Acetals (POM and POM copolymer) are used in automotive fueling systems and PTU is a common fuel system component coating material [12]. Other common materials include polybutylene terephthalate (PBT), polyethylene terephthalate co-polymer (PETG), and polypropylene (PP).

Thermosets

Unlike thermoplastics, thermosets can only be cured and shaped once. After forming, they remain in a solid (highly rigid) state and cannot be melted. Heating will result in oxidation and thermal breakdown rather than softening. In the thermosetting process, the chemical reaction forming the cross-linked polymer is not reversible. Thermosets are used in rigid applications, especially as resins in fiber-reinforced plastics (FRPs), and as adhesives to bond flanges and pipe sections. FRPs are used extensively in fuel storage applications and rigid piping systems.

The thermosets examined in this study included two types of polyester resins (isophthalic and terephthalic polyesters). These resins represent legacy and current resins used in the construction of underground storage tanks and FRP systems. The two types of isophthalic resins differed according to the ratio of isophthalic acid to maleic anhydride. One formulation has a 1:1 ratio of isophthalic acid to maleic anhydride and is representative of resins used in FRP systems (including underground storage tanks) prior to 1990. The other isophthalic polyester resin has a 1:2 ratio of isophthalic acid to maleic anhydride, and was introduced during the 1990s. The terephthalic acid polyester resin has a 1:1 ratio of terephthalic acid to maleic anhydride and was also introduced in the 1990s for use in FRP systems. A vinyl ester resin material was also included which is representative of a newer high-performance formulation used in the construction of FRP systems.

It is important to note that the thermoset specimens consisted of pure resin only. In actuality, these resins are never used without some level of fiber reinforcement, which serves to constrain expansion and increase fracture resistance, strength, and durability. Therefore, the performance of pure resins to the test fuels does not necessarily correspond directly to the actual reinforced samples. However, should the resin become degraded, the composite itself will be less durable. It is also important to note that in addition to being used as the matrix material in FRP, these resins may also be used as adhesives to connect piping and flanges.

Experimental Protocol

Sealed stainless steel vessels having an interior volume of 175 liters were used to expose the specimens to the test fuels. The specimens were attached to mounting brackets, which were affixed to the inside surface of a cylindrical liner placed within each vessel. To achieve dynamic flow, each chamber was equipped with a paddle to impart a rotating fluid flow at a rate of 0.8 m/s past the specimens. These chambers were sealed to prevent fuel leakage and employed a heating jacket to maintain a constant temperature of 60°C during the exposure period. Each container was filled to a predetermined level with each test fuel. The majority of the specimens were completely submerged in the test fuel liquid, while a second set of specimens were positioned above the liquid fuel line in the headspace for exposure to the vapor-phase environment. The vapor exposure results are not included in this paper.

A flow chart highlighting the treatments and measurements for each material type is shown in Figure 2. The specimens were exposed to the test fuels for a period of 16 weeks, then they were removed and measured for volume, mass, and Shore D hardness while in the wetted (or saturated) state. The volume change for each specimen by the measuring the mass increase (or decrease) using the protocol described in ASTM D543-06 [13]. The hardness measurements were performed according to ASTM D2240 [14] at five locations for each specimen. Once the wetted properties were measured, the elastomers were heated in an oven at 60°C for 65 hours (in air). Afterwards, each specimen was once again measured for volume, mass, and hardness. The changes in these properties from the baseline (untreated) condition were used to assess compatibility.

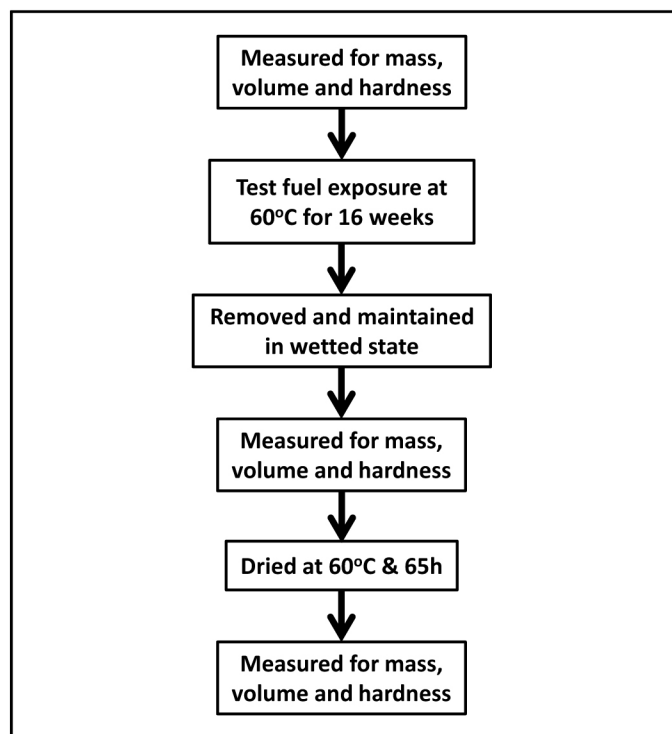


Figure 2. Flow chart showing the exposure protocol and test methods.

RESULTS

Chemical Analysis of Bio-Oil and Derivation of Solubility Parameters

The bio-oil sample used in this study was partially upgraded to remove water normally present following pyrolysis. It was found to be completely miscible with diesel fuel, further indicating low water content.

The GC-MS results are shown in Figure 3, they show that the bio-oil contained significant levels of ketone, phenols, and aromatics, which is consistent with fast-pyrolysis-derived oils.

This particular bio-oil product also showed significant levels of ethyl acetate and naphthalene. Another feature is that the acid concentration is much lower than what is typically observed for pyrolysis oils.

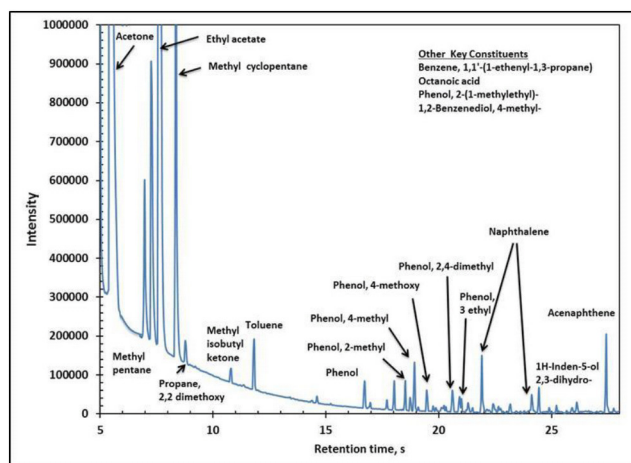


Figure 3. GC-MS results for the bio-oil.

The relative concentrations of these primary components were not determined but estimates were established by assuming equal concentrations (20 percent by volume) of the aromatics, phenols, ketones, ethyl acetate, and naphthalenes. This estimate is not unreasonable as most bio-oils contain concentrations ranging from 10 to 20 percent for phenols, acetones, aromatics, acids. In many cases the phenols are the predominant component class.

Solubility Analysis

A preliminary solubility assessment was performed by exaggerating the concentration of one or more of these five components relative to the others to examine the subsequent effect on the resulting solubility curves (i.e. the solubility distance results as a function of bio-oil content in diesel) for each plastic type. For each bio-oil component, their corresponding Hansen solubility parameters are listed in Table 3. (Also included in the table are the parameters for a bio-oil composed of equal amounts of each component.) It is important to note that the parameter values for toluene and naphthalene are similar. Ethyl acetate and ketone have similar dispersive and hydrogen-bonding parameters, though polarity parameter is much higher for ketone. Phenol has similarities to the other components, except for hydrogen bonding. Because many of these component

parameters are similar to each other, the effect of their relative concentrations was not expected to significantly impact the resulting solubility curves for each plastic type.

The preliminary study showed that the relative shapes of the solubility curves were not dramatically affected. In most cases the shape (relative change in solubility distance) was essentially the same, but the position was shifted to higher (or lower values). For a few materials, the location of minimum solubility distance was shifted to higher bio-oil concentrations, but these shifts were on the order of 10 to 20%. Given that the resulting solubility curves were not highly dependent on the component concentrations (within the 10 to 20% range), a first order approximation of a bio-oil solubility parameter was made using equivalent concentrations of ketone, phenol, aromatic, ethyl acetate, and toluene. The resulting parameters are listed in the bottom row in Table 3.

Table 3. Hansen Solubility Parameters for Key Bio-oil Components

Component	Hansen Solubility Parameters		
	Dispersive	Polarity	Hydrogen
Ethyl acetate	15.8	5.3	7.2
Phenol	18.0	5.9	14.9
Ketone	15.5	10.4	7.0
Toluene	18.0	1.4	2.0
Naphthalene	19.2	2.0	5.9
Bio-oil	17.3	5.0	7.4

A more detailed solubility analysis was performed for each of the plastic materials and is presented in this paper. The analytical approach was based on the Flory-Huggins model using the Hansen solubility parameter (HSP) methodology. This type of analysis is useful in predicting swelling behavior in polymeric materials exposed to known solvents. The solubility behavior for each material was assessed by determining the solubility distance (d_s) for each material type as a function of bio-oil content. Relative solubility for neat diesel and Bio20 was assessed by determining the solubility distance (d_s) for each material type and comparing these values to the interaction radius (IR) of the polymer. The interaction radius represents the zone of high solubility for a given polymer and is independent of solvent type. If the solubility distance falls within (or is less than) the interaction radius (positive $IR-d_s$ result), then moderate to high solubility can be expected depending on the value. Materials exhibiting distances roughly equivalent to the interaction radius would be expected to produce low to moderate solubility, while distances higher than the interaction radius (negative $IR-d_s$ result) would predict negligible to low solubility. To facilitate discussion, the differences between the interaction radius and the calculated solubility distance for the materials in both test fuels are plotted graphically along with their general solubility curves.

The graphs and charts presented in this section were derived from the analysis as stated above. The Hansen solubility parameters were taken from the tables provided in *Hansen Solubility Parameters: A User's Handbook* [11]. The use of a single set of parameters for each plastic and fuel type means that the graphs will not have any error bars to indicate variability.