

## **Elastomer and Plastic Compatibility with a Pyrolysis-derived Bio-oil**

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### **ABSTRACT**

The compatibility of fueling infrastructure elastomers and plastics in bio-oil and diesel fuel was determined by measuring the volume swell. The bio-oil was produced via fast pyrolysis of woody feedstocks. The elastomer materials included fluorocarbons, acrylonitrile butadiene rubbers, neoprene, polyurethane, neoprene, styrene butadiene (SBR) and silicone. The plastic materials included polyphenylene sulfide (PPS), polyethylene terephthalate (PET), polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), polyoxymethylene (POM), POM copolymer, high density polyethylene (HDPE), polybutylene terephthalate (PBT), polypropylene (PP), polyethylene terephthalate glycol (PETG), polythiourea (PTU), four nylon grades, and four thermosetting resins. The majority of the elastomer and plastic materials exhibited higher volume expansion in bio-oil than in diesel. These elastomers and plastics had high polarity values which more closely align with the polarities of the bio-oil versus the diesel fuel. Conversely, SBR, silicone, HDPE, and PP are relatively nonpolar and this matches the low polarity of the diesel fuel, which resulted in higher volume expansion in diesel, rather than the bio-oil for these four polymers.

Key words: Elastomer, Thermoplastic, Plastic, Resin, Compatibility, Bio-oil

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## INTRODUCTION

Fast pyrolysis-derived bio-oils are being evaluated as a renewable fuel for use in transportation, home heating, and energy production. Fast-pyrolysis consists of 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. The resulting oil have high viscosity and water content relative to petroleum distillates. Because the feedstock is biomass (typically pelletized wood), these fuels provide a pathway toward reducing the dependency on foreign petroleum, while utilizing a cleaner, and renewable, resource. Bio-oil derived from fast pyrolysis of woody feedstock is being investigated as an alternative fuel. 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, both metals and polymers. The chemical profile of these fuels depends on the feedstock and can vary considerably (even among tree species). As a result, the composition of these oils can vary widely, but they usually consist of significant quantities of phenols, ketones, and other oxygenates (including short-chain carboxylic acids).

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, and plastic use in fuel storage and transport has been expanding. Because plastics are ubiquitous in fueling infrastructure systems, it is important to understand their performance with bio-oils and fuels mixed with bio-oils.

Many of the constituents of bio-oils have varying degrees of solubility with key infrastructure polymers. These polymers include elastomer materials used as seals and hoses, and structural plastics. Common elastomers include fluorocarbon, acrylonitrile butadiene rubber (NBR), styrene butadiene rubber (SBR), neoprene, polyurethane, and silicone. Plastic materials include both thermoplastics and thermosetting resins. The objective of this study was to assess the compatibility of bio-oil with infrastructure polymers (elastomers and plastics). Number 2 diesel fuel was used as the baseline. The authors have previously evaluated these materials in bio-oil but, for elastomers, no attempt was made to explain the observed results [1-2]. In this paper the resulting volume swell behaviors for the elastomers were correlated with their respective weak bonding forces which govern solubility. Prior studies on plastics are also included for completeness and to facilitate discussion.

## EXPERIMENTAL PROCEDURE

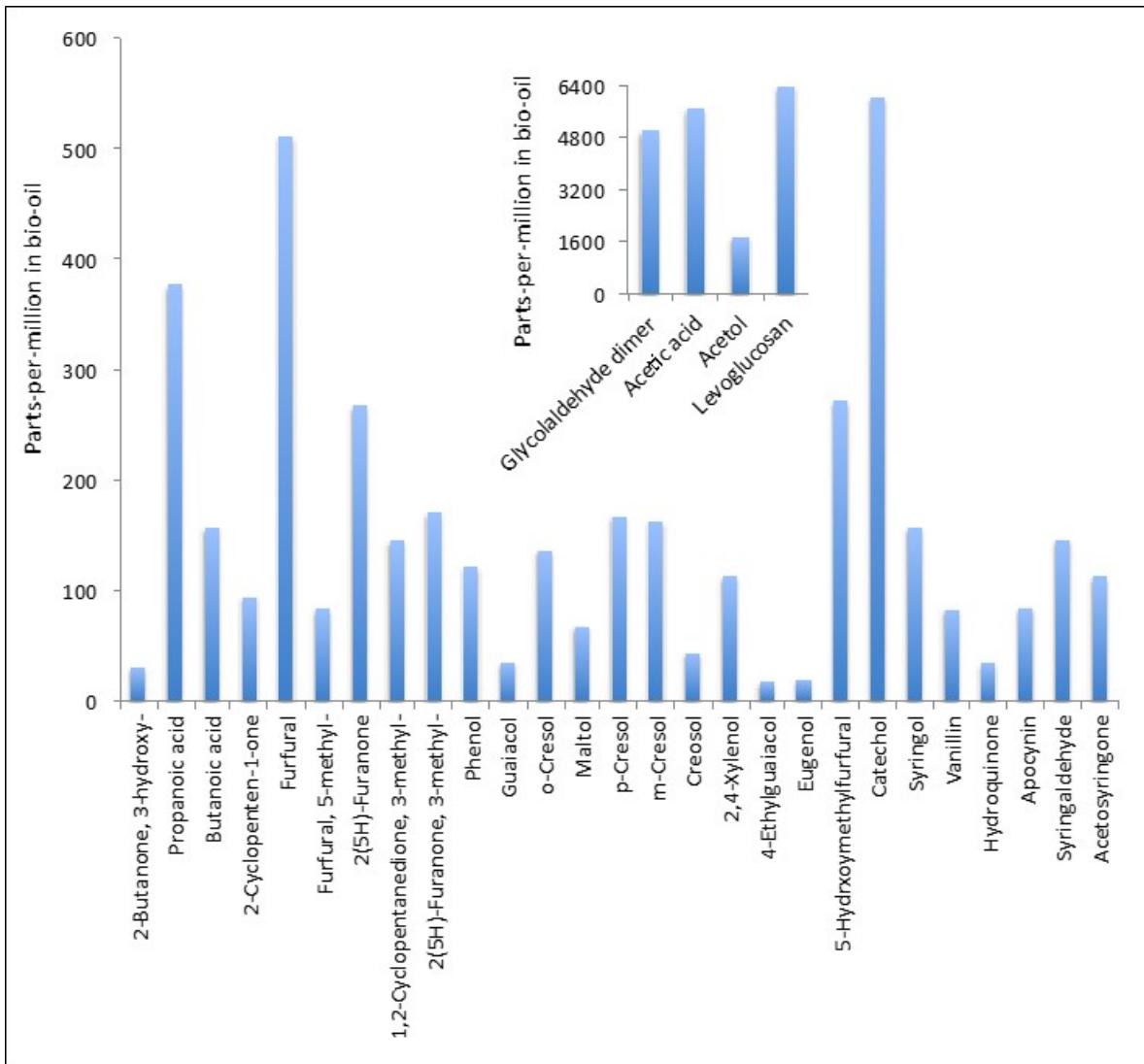
### Materials and Test Fuels

#### 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 for use as home heating oil. This fuel was supplied by Connell Oil, Inc. and had a sulfur concentration up to 500ppm. The bio-oil used in this study was produced by the National Renewable Energy Laboratory. As noted earlier, the bio-oil was produced via fast pyrolysis from commercially-available oak feedstock (Country Boy White Lightning Heating Pellets) in the Thermochemical Process Development Unit (TCPDU). The TCPDU is a half-ton-per-day, pilot-scale plant used to research thermochemical routes of processing cellulosic biomass to liquid fuels. In this process, the oak pellets are crushed to less than 2 mm, entrained in preheated nitrogen gas, and then fed into the 500°C entrained-flow pyrolysis reactor. Char and ash are removed by a cyclone separator, and the pyrolysis vapors are condensed into oil in the liquid scrubber, which uses dodecane as the scrubbing liquid. The pyrolysis oil produced during these runs appeared as a single phase. Acid content of the bio-oil was determined using aqueous modified total acid number (AMTAN) measurement, while capillary electrophoresis (CE) was used to determine acetic and formic acid content. Other oxygenates were measured using gas chromatography-mass spectrometry (GC-MS). The results in Table 1 indicate that the neat bio-oil has moderate-to-high acidity, while the GC-MS graph in Figure 1 identifies other oxygenated polar compounds representative of bio-oils produced from woody feedstock.

**Table 1. Acid speciation and concentration of bio-oil [1,2].**

AMTAN, mg KOH per g oil	94
Formic acid concentration, ppm (mass)	4174
Acetic acid concentration, ppm (mass)	5816



**Figure 1: Composition of partial polar oxygenate semi-composition of bio-oil [1,2]**

It is important to note that diesel is essentially a nonpolar liquid, while the bio-oil would be considered highly polar due to its composition as shown in Figure 1. This distinction is important because many of the plastic materials evaluated in this study are also polar in nature. Materials having similar polarity (and other weak bonding forces) with bio-oil would be expected to be more soluble due to this similarity [16]. Since solubility corresponds with volume expansion, more swelling would be expected with these plastic materials in the bio-oil test fuel.

#### Elastomer Materials

The elastomer materials evaluated in this study included two fluorocarbons (Viton A401C and Viton B601), six acrylonitrile butadiene rubber (NBR) grades and one type of fluorosilicone, polyurethane, neoprene, styrene butadiene (SBR), and silicone as shown in Table 2. The two Viton grades are similar in composition. Viton A401C is a common grade containing 66% fluorine, while Viton B601 contains 68% fluorine. Fluorine content is important since the volume expansion of the fluorocarbon typically decreases with increasing fluorine levels. Viton grades having low fluorine contents also tend to exhibit improved sealing properties at low temperatures. Six NBR grades were evaluated in this study. NBR is a copolymer of acrylonitrile and butadiene and is frequently compounded with

plasticizers, such as phthalates, to impart pliability, which is an important property for hose applications. The six NBR materials were provided by two suppliers and are predominantly used as hose materials (rather than as seals) as shown in Table 2. It is worth noting that NBR 3 is a marine grade which is designed to have improved compatibility with a wider range of solvents than other NBR grades. SBR is similar to NBR but incorporates styrene (rather than acrylonitrile) as the co-polymer with butadiene. SBR is not typically used in fuel system components, but it is sometimes employed as a fuel cover and therefore may shield system components from ultraviolet (UV) radiation.

**Table 2. Elastomer Materials and Applications**

Elastomer Type	Application
Viton A401C	Seal
Viton B601	Seal
Fluorosilicone	Seal
NBR 1	Gasoline dispenser hose
NBR 2	Gasoline dispenser hose
NBR 3	Marine fuel line hose
NBR 4	Small engine fuel line hose
NBR 5	Gasoline dispenser hose
NBR 6	Tanker truck transfer hose
Neoprene	Seal
Polyurethane	Coating
SBR	Cover
Silicone	Seal

Neoprene has limited use as a sealant and fuel line hose, and, like NBR, has plasticizers added to impart flexibility. The fluorosilicone grade that was selected for evaluation is used in sealing applications involving fuels and aromatic mineral oils, and as such is expected to provide good compatibility results relative to the other elastomer types. The silicone rubber material is considered industrial grade and is commonly used in sealing applications. For each elastomer material, three specimens were prepared, and the length, width, and thickness for each were 3.8, 1.3, and 0.2 cm (1.5, 0.5, and 0.08 in.), respectively.

### Plastic Materials

A total of eighteen plastic materials were evaluated in this study. These included fourteen thermoplastic and four thermosets (or thermosetting resins). A complete listing of these polymers, along with their trade names and applications, is shown in Table 3. The thermoplastics were further divided into three subcategories based on application, while thermosets were placed in a single grouping.

**Table 3. Plastic Materials and Applications**

Plastic Type and Grade	Trade Name	Application(s)
<b>Thermoplastics</b>		
<b>Permeation Barrier Plastics</b>		
Polyphenylene sulfide (PPS)	Techtron™	Permeation barrier liner material (plastic

		piping)
Polyethylene terephthalate (PET)	Mylar™	Permeation barrier liner material (plastic piping)
Polytetrafluoroethylene (PTFE)	Teflon™	Permeation barrier liner (plastic piping) and seal material
Polyvinylidene fluoride (PVDF)	Kynar™	Permeation barrier liner material (plastic piping)

#### ***Nylons and Acetals***

Nylon 6		Plastic piping and seal material
Nylon 6/6	Zytel™	Plastic piping and seal material
Nylon 11		Fuel tank material
Nylon 12		Automotive fuel lines and plastic piping material
Polyoxymethylene (POM) or acetal homopolymer	Delrin II™	Fuel line valves, pump, and tank components
POM co-polymer	Acetron GP™	Fuel lines valves, pump, and tank components

#### ***Other Infrastructure Thermoplastics***

Polypropylene (PP)		Fuel containment and cable insulation
High density polyethylene (HDPE)		Fuel tank material
Polyethylene terephthalate glycol (PETG)	Spectar™	Sheathing material for automotive applications
Polythiourea (PTU)		Steel coating material

#### ***Thermosetting (Fiberglass) Resins***

Novolac vinyl ester		Resin for rigid fiberglass piping and tanks
Terephthalic polyester		Resin for rigid fiberglass piping and tanks
Isophthalic polyester (1:2)		Resin for rigid fiberglass piping and tanks
Isophthalic polyester (1:1)		Resin for rigid fiberglass piping and tanks

Thermoplastics are a class of polymers that soften or melt when heated. As such, they can be shaped, molded, or extruded while softened at elevated temperature and then typically return to their solid (rigid) physical properties when cooled. Thermoplastics are inherently more pliable than thermosets and, and are the predominant material used in flexible piping. Their pliability also allows their use in sealing applications, especially PTFE, PVDF, and nylons. As shown in Table 3, the three thermoplastic subgroupings are permeation barrier plastics, nylons and acetals, and other infrastructure plastics. The first grouping includes those used as high-performance permeation barriers in flexible piping systems. These four materials, PPS, PET, PVDF and PTFE have demonstrated excellent compatibility (negligible to low volume swell) with a variety of fuel types, including biofuels. PTFE (also known as Teflon™) is a common coating material and is also used in high performance seals. Of these four, Kynar™ or PVDF is the most commonly used barrier material.

The second grouping includes nylons and acetals (also known as POM). The two acetal materials (POM homopolymer and POM co-polymer) are grouped with the nylons since they have similar properties and applications. Acetals are frequently employed as a polymer replacement for aluminum and are considered to be an upgrade to HDPE in applications requiring high strength, thermal and chemical resistance. Nylons are commonly used as seals, flexible piping, and as tank coatings. It is important to note, however, that in some legacy piping systems, Nylon 11 and Nylon 12 are used as permeation barrier materials. The remaining thermoplastic materials includes those plastics which are broadly used over a wide range of applications. HDPE is used in some fuel lines and as tank

components, while PBT, PETG, PP and PTU have limited uses as coatings, tank materials or other undefined role in fuel systems.

Unlike thermoplastics, thermosets can only be cured and shaped once. After forming, they remain in a solid state and cannot be melted. Excessive heating will eventually result in oxidation and thermal breakdown rather than softening. 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 more recent high-performance formulation used in the construction of FRP systems.

It is important to note that the thermoset specimens evaluated in this study 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 Procedure

The exposure conditions were determined from an earlier study, which found that full saturation of the elastomers was achieved following a 4-week exposure period, while the plastics were exposed for 16-weeks.<sup>25</sup> A test temperature of 60°C was selected to be consistent with the dispenser test protocol used by Underwriters Laboratories to accelerate fluid permeation and sample aging.<sup>26</sup> Three specimens for each elastomer and plastic material were placed below the fluid line for liquid exposure evaluation. The test fluid volume was approximately 75 liters. The chambers were sealed to prevent fuel leakage and employed a heating jacket to maintain a constant temperature of 60°C during the exposure period. These chambers are also equipped with paddles to stir the liquid to provide dynamic flow conditions, and this feature was used for the baseline diesel fuel. After removal from the exposure chamber, the specimens were kept wetted prior to initially measurement. Afterwards, they were dried to assess additional structural changes. The elastomers were dried at 60°C for 20 hours, while the plastics were dried at 60°C for 65 hours.

Since volume swell is dependent on the mutual solubility between the fuel and polymer, an analysis using the Hansen solubility parameters method for each polymer and fuel type was conducted to ascertain the weak bonding forces most responsible for the observed volume swell behavior. Using the Hansen solubility parameters (HSPs) approach, parameters representing the dispersive, polarity, and hydrogen bonding forces were obtained from literature sources each polymer and then matched with the corresponding parameters for each fuel type [3]. Solubility (and hence swell) will be highest for polymers having corresponding HSP values which are closer (more similar) to those of the fuel. This approach is useful for explaining observed swell and the relative impact of each weak force (dispersive, polarity, and hydrogen bonding).

## RESULTS

After the 4 weeks of exposure at 60°C was completed, it was discovered that the bio-oil had undergone significant polymerization, and removal of the polymerized bio-oil from the specimen surfaces was not possible without damaging the specimens in the process. Therefore, another set of exposures were conducted at 50°C, to minimize polymerization. At this lower temperature, bio-oil polymerization was significantly reduced, and the bio-oil could be removed from the specimen surfaces for volume, mass and hardness measurements. All of the specimens were intact after exposure from the bio-oil, except for polyurethane, which was partially dissolved and fragmented.

For each of the bio-oil key components shown in Figure 1, Hansen solubility parameters were obtained from the literature. The bio-oil constituents and their respective Hansen solubility parameters are listed in Table 4 along with those for the baseline diesel fuel. As can be seen in the table, the majority of the key bio-oil components exhibit much high polarity and hydrogen-bonding than the neat diesel. The implication is that the bio-oil, itself, is highly polar and has high hydrogen-bonding forces.

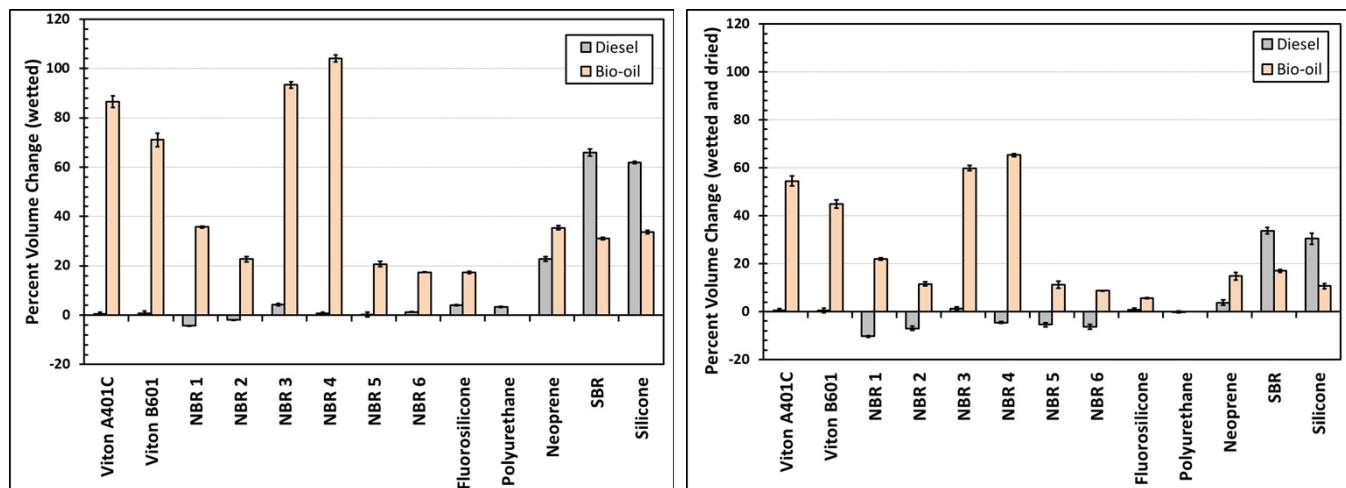
**Table 4. Hansen solubility parameters for key bio-oil components [3]**

Bio-oil Component	Hansen Solubility Parameters (MPa <sup>1/2</sup> )		
	Dispersive	Polarity	Hydrogen Bonding
Acetic acid	14.5	8.0	13.5
Glycolaldehyde dimer	18.2	11.9	18.6
Acetol	17.4	12.8	16.5
Levoglucosan	17.7	11.2	19.4
m-Cresol	18.0	5.1	12.9
Phenol	18.0	5.9	14.9
Furfural	18.6	14.9	5.1
Catechol	20.0	11.3	21.8
<b>Diesel (baseline)</b>	17.0	2.0	2.0

### Elastomer Results

The resulting changes in volume are shown in Figure 2 for the wetted and dried elastomers, respectively. The results show that the baseline diesel fuel had negligible impact on the volumes of the fluorocarbons, NBRs, fluorosilicone, and polyurethane. However, the neoprene specimens swelled around 20%, and SBR and silicone both exhibited volume expansions over 60%, which is considered excessive. In marked contrast, exposure to the bio-oil showed pronounced volume expansion for the fluorocarbon, NBRs, fluorosilicone, and neoprene. For these elastomers the volume expansion was higher for those specimens exposed to bio-oil compared to those exposed to the baseline diesel. grades. The volume expansion for the two fluorocarbons, NBR 3, and NBR 4 was excessive (>70%), while the swell noted for the remaining NBRs, neoprene and fluorosilicone was more modest (17 – 40%). Polyurethane actually underwent partial dissolution and is therefore clearly unacceptable in applications requiring contact with bio-oil. Interestingly both SBR and silicone showed higher volume expansion with the neat diesel. Analysis of the solubility parameters of the elastomers in Table 5 shows that fluorocarbon and polyurethane, which exhibiting the highest levels of swell (and therefore solubility) of the elastomer materials also have the highest polarity. (NBR 2 and NBR 3 also showed high swell, but their bonding force parameters were not known.) Their high polarities more closely match those of the majority of the bio-oil components listed in Table 4. It this similarity of the polar forces that is believed to be responsible for the high swell levels in bio-oil. Likewise, SBR and silicone, both have low polarity and hydrogen bonding values which more closely align with the diesel values. Therefore, the similarity between these forces is likely responsible for the higher swelling in SBR and silicone specimens exposed to diesel rather than bio-oil.

The dried volume swell results shown in Figure 2 show that much of the absorbed test fuels remained in the polymer structures following dry out at 60°C for 20 hours. The level of volume change (and therefore retained fluid) roughly compares to the wetted results albeit at lower levels.



**Figure 2: Volume change results for the elastomer materials exposed to the bio-oil for 4 weeks the wetted and dried conditions.**

**Table 4. Hansen solubility parameters for elastomer materials**

Elastomer Type	Hansen Solubility Parameters, MPa <sup>1/2</sup>		
	Dispersive	Polar	H-bonding
NBR (Buna N)	17.8	3.2	3.4
Acrylonitrile	16.0	12.8	6.8
Butadiene	14.8	2.8	5.6
Fluorocarbon	14.6	10.0	1.6
Polyurethane	18.1	9.3	4.5
Neoprene	18.1	4.3	6.7
Styrene butadiene	17.0	4.0	3.0
Silicone	13.8	5.0	1.2

## Plastic Results

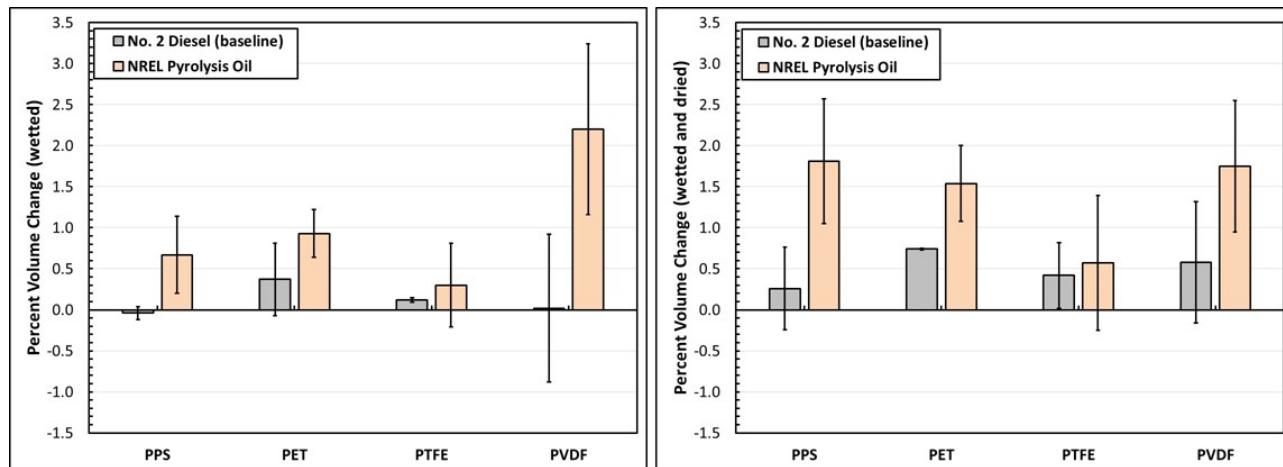
All of the plastic specimens were intact following exposure in the bio-oil for 16 weeks at 50°C. The resulting changes in volume are shown in Figures 3 through 7 for each grouping of the plastic materials evaluated in this study. In each figure, the wetted and dried results are shown in the right and left changes, respectively to facilitate comparison.

### Permeation Barrier Plastics

As shown in Figure 3, the volume was relatively unchanged for the specimens exposed to diesel. Following exposure to the bio-oil, a very small volume increase (<1%) was noted the PPS, PET, and PTFE specimens when wetted. The results for PTFE confirm those made by Haverly et al. [4] and Kirk et al. [5], that PTFE undergoes <1% volume expansion following exposure to bio-oil. Slightly higher swelling (around 2%) was observed for the PVDF specimens. Relative to the other permeation

barrier plastics, PVDF has higher polarity and hydrogen bonding forces (as shown in Table 5). These values more closely match those of the key bio-oil components (listed in Table 3) resulting in higher volume expansion for PVDF relative to the other permeation barrier plastics. However, it is important to note that a swell value of 2% is still very low and, therefore, indicative of a high compatibility with bio-oil.

Exposure to diesel did not produce any significant increase in volume when wetted; however, when dried, a small, but measurable increase in volume was observed. For PPS, PET, and PTFE, this volume increase was also noted for the bio-oil exposures as well.



**Figure 3. The volume change results (compared to the original values) for the permeation barrier plastic materials when wetted and after being dried at 60°C for 65 hours.**

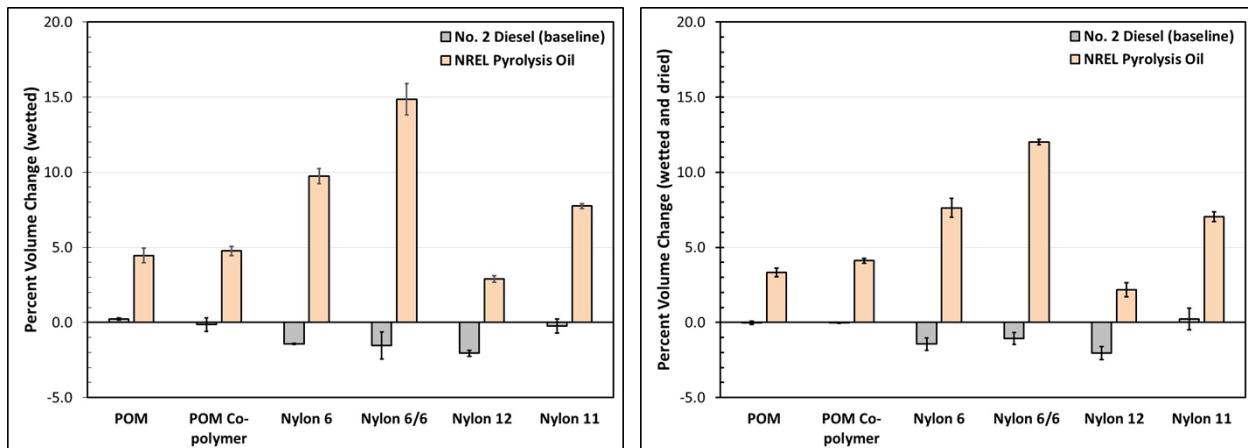
**Table 5. Hansen Solubility Parameters for Permeation Barrier Plastics [18]**

Plastic Material	Hansen Solubility Parameters (MPa <sup>1/2</sup> )		
	Dispersive	Polarity	Hydrogen Bonding
PPS	18.8	4.8	6.8
PET	18.0	6.2	6.2
PTFE	16.2	1.8	3.4
PVDF	17.0	12.1	10.2

#### Nylons and Acetals

The volume and mass change results for the four nylon grades and two acetal types (POM and POM co-polymer) are shown in Figure 4. For Nylon 6, Nylon 6/6, and Nylon 12, the baseline diesel produced a slight loss in volume, but no noticeable impact was observed for Nylon 11. When exposed to the bio-oil, the volume increased significantly (10-15%) for the Nylon 6, Nylon 6/6 and the Nylon 11 specimens. Nylon 12 exhibited a much smaller volume increase (~3%). As shown in Table 6, these plastics have high hydrogen bonding parameter values, and for POM (acetal) and Nylon 12, relatively high polarity as well. These high polarity and hydrogen bonding forces are likely responsible for the higher volume swelling observed for those specimens exposed to the bio-oil. However, it is important to note that nylons are highly susceptible to water adsorption, which would also be a contributor to volume expansion [6].

When dried, these nylon materials still retained a portion of the bio-oil fluid as evidenced by the mass and volume gain compared to the original starting value. The magnitudes of the respective increases in dried volumes were only lowered by a few percent from the wetted condition, which indicates that most of the absorbed fluid was tightly bound to the molecular structure. The exact nature of the retained fluid chemistry was not determined, but nylons are known to be hygroscopic and it's possible that water makes up a significant fraction of the retained fluid.



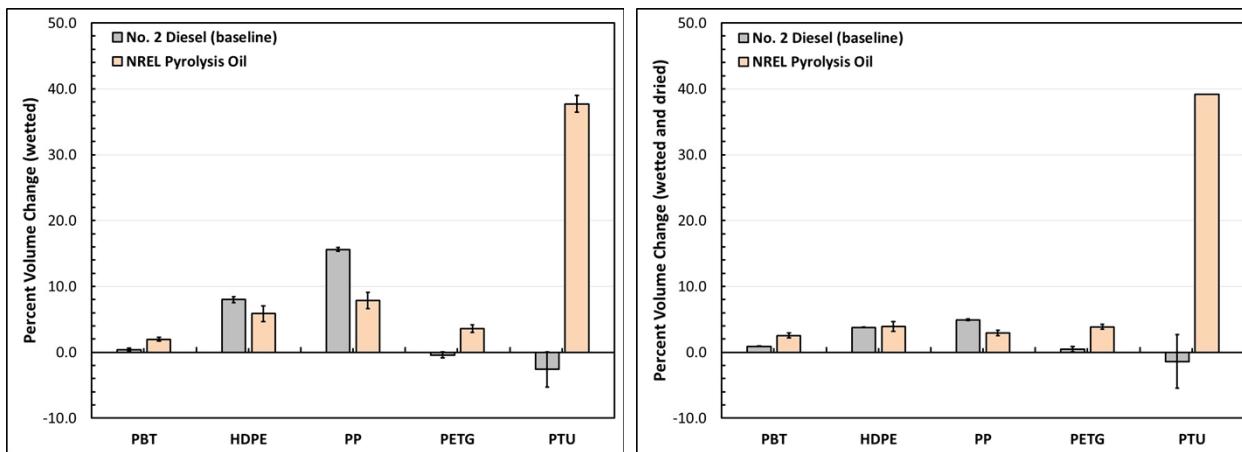
**Figure 4. The volume change results (compared to the original values) for the nylons and acetals when wetted and after being dried at 60°C for 65 hours.**

**Table 6. Hansen Solubility Parameters for Nylons and Acetal (POM) [18]**

Plastic Material	Hansen Solubility Parameters (MPa <sup>1/2</sup> )		
	Dispersive	Polarity	Hydrogen Bonding
Nylon 6 and 6/6	17.0	3.4	10.6
Nylon 11	17.0	4.4	10.6
Nylon 12	18.5	8.1	9.1
Acetal (POM)	17.2	9.2	9.8

#### Other Infrastructure Thermoplastics

As shown in Figure 5, the HDPE and PP specimens differed from the other plastic materials evaluated in this study in that they both exhibited better compatibility (significantly less swelling) in bio-oil than for diesel. The diesel fuel caused HDPE and PP to expand 8% and 15%, respectively. In contrast, the bio-oil intermediate caused significantly lower swelling (6% for HDPE and 8% for PP). (For the other infrastructure plastic materials, no change in volume was noted for diesel fuel exposures.) This behavior was also maintained after drying for the PP specimens, but the dried volumes for the HDPE specimens were similar for both test fuels. The reason for the higher volume swell measurements observed with diesel fuel is attributed to the nonpolar nature of HDPE and PP as shown in Table 7. Diesel, having significantly less polarity than the bio-oil, would be expected to have higher solubility with HDPE and PP, which leads to the observed higher levels of volume expansion.



**Figure 5. The volume change results (compared to the original values) for other infrastructure thermoplastics when wetted and after being dried at 60°C for 65 hours.**

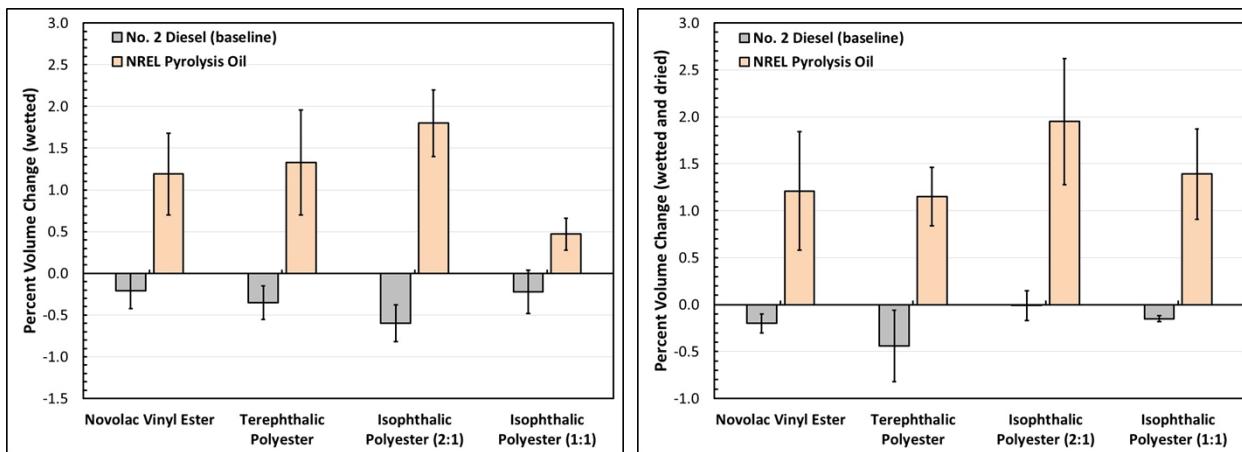
**Table 7. Hansen Solubility Parameters for Other Infrastructure Thermoplastics [18]**

Plastic Material	Hansen Solubility Parameters (MPa <sup>1/2</sup> )		
	Dispersive	Polarity	Hydrogen Bonding
HDPE	18.0	0.0	3.0
PBT	18.0	5.6	8.4
PETG	18.0	3.0	4.0
PP	18.0	0.0	1.0
PEI	17.4	4.6	9.0
PVC	18.8	9.2	6.3
Poly thiourea (PTU)	20.2	19.4	14.8

For the other materials in this grouping, bio-oil produced noticeable increases in volume and mass. For PBT and PETG, this increase was less than 5%. The plastic most affected by bio-oil was PTU. As can be seen in Figure 5, the volume of PTU was dramatically increased to around 38% and 45%, respectively in the wetted and dried states. These high values were maintained even after drying for 65 hours at 60°C. Polythiourea differed from the other plastic materials by having exceptionally high polarity and hydrogen bonding forces as seen in Table 7, and it is these forces that are responsible for the exceptionally large volume expansion observed for PTU, even after drying.

#### Thermosetting Resins

The volume change results for the four resin materials are shown in Figure 6. A slight reduction in volume and mass were noted for the diesel exposures, while the bio-oil was observed to increase the volume by a small amount (0.5 to 2%). This volume increase remained after drying. The isophthalic polyester resin (1:1) differed from the other three in that the dried volume was higher than the wetted volume. This increase did not correspond with the change in mass and indicates that added porosity (or molecular spacing) may have occurred during the dry-out process. Consistent with the small changes in volume and mass is a very low decline in hardness. The very low property changes imply that these plastics would be expected to be highly compatible with the bio-oil. It is important to note that representative solubility parameters have not been determined for these thermosetting resins, which prevents correlating their performance to predicted solubility.



**Figure 6. The volume change results (compared to the original values) for resins when wetted and after being dried at 60°C for 65 hours.**

## CONCLUSIONS

In general, common fuel storage and dispensing infrastructure elastomers and plastics showed marked difference in swell and hardness when exposed to bio-oil versus a diesel distillate baseline. In most cases exposure to bio-oil produced notable swelling, but not all. Of the elastomer materials, fluorocarbons, polyurethane, and two NBR grades showed unacceptably high levels of swelling. In contrast, SBR and silicone exhibited higher swelling with neat diesel. The mechanisms for both behaviors can be traced to their respective solubility forces. Fluorocarbon, polyurethane, and some NBRs have high polarity. This high polarity more closely matches the high polarity of the bio-oil and it is this similarity which results in excessive swell for these polymers when exposed to the bio-oil. For SBR and silicone, the low polarity of these elastomers more closely aligns with the low polarity of diesel fuel, and as a result, these elastomers swell more in the diesel fuel (than bio-oil).

A similar behavior was noted for the plastics. Higher volume swelling of many of the plastics corresponded with the higher polarity of these materials. Key exceptions were HDPE, and PP. Both of these plastics have very low polarity and, as a result, they expanded more in the baseline diesel fuel than the bio-oil.

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## REFERENCES

1. M.D. Kass, C.J. Janke, R.M. Connatser, S.A. Lewis, J. R. Keiser, K. Gaston, "Compatibility Assessment of Fuel System Infrastructure Plastics with Bio-oil and Diesel Fuel," *Energy Fuels* 32, 1 (2018): p. 542-553.
2. M.D. Kass, C.J. Janke, R.M. Connatser, S.A. Lewis, J. R. Keiser, K. Gaston, "Compatibility Assessment of Fuel System Elastomers with Bio-oil and Diesel Fuel," *Energy Fuels* 30, 8 (2016): p. 6486-6494.

3. C.M. Hansen, *Hansen Solubility Parameters: A Users Handbook*, 2<sup>nd</sup> ed. (Boca Rotan, FL: CRC Press, 2007).
4. M.R. Haverly, L.E. Whitmer, R.C. Brown, "Evaluation of Polymer Compatibility with Bio-oil Produced from Thermochemical Conversion of Biomass," *Energy Fuels* 29, 12 (2015): p. 7993-7997.
5. D.W. Kirk, Z.R. Li, D. Fuleki, P.C. Patnaik, "Materials Compatibility with Pyrolysis Biofuel," ASME Turbo Expo 2001, paper no. 2001-GT-0006 (New Orleans, LA: Proceedings of the ASME Turbo Expo 2001, 2001)
6. H.W. Starkweather, *Water in Nylon* in S. Rowland, ed. *Water in Polymers* (Washington, DC: American Chemical Society, 1980) p.433-440.