

Compatibility Assessment of Elastomeric Infrastructure Materials with Neat Diesel and a Diesel Blend Containing 20 Percent Fast Pyrolysis Bio-oil

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ABSTRACT

The compatibility of elastomer 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. (This fuel blend is not to be confused with B20, which is a blend of diesel fuel with 20% biodiesel.) The elastomer types evaluated in this study included fluorocarbon, fluorosilicone, acrylonitrile rubber (NBR), styrene butadiene rubber (SBR), polyurethane, neoprene, and silicone. All of these elastomer types are used in sealing applications, but some, like the nitrile rubbers are also common hose materials. The elastomer specimens were exposed to the two fuel types for 4 weeks at 60°C. After measuring the wetted volume and hardness, the specimens were dried for 65 hours at 60°C and then remeasured. 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 elastomers exhibited higher solubility (volume swell) with the Bio20 fuel blend consistent with a solubility assessment. However, many of the elastomers (except neoprene, SBR, and silicone) exhibited very little swelling with exposure to the baseline diesel which was not predicted in the solubility study. When dried, those elastomer specimens that swelled when immersed in the test fuel, remained swollen (albeit to a lesser degree) when dried. All of the elastomers showed the highest extent of swelling with Bio20 (even when compared to specimens exposed to ethanol-blended gasoline test fuels). The lone exception was silicone which exhibited lowered volume expansion in diesel and Bio20 than in ethanol-blended gasoline. Even fluorocarbon, which is rated as highly compatible in most fuel types, swelled over 60% when exposed to Bio20. The bio-oil used in this study, like most bio-oils contained appreciable levels of ketones and phenols. The compounds are notorious solvents for many elastomers and likely contributed to the observed volume expansions.

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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 a transportation 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 markedly 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 show in Table 1 [2].

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

Property	Pyrolysis Oil	Diesel
Density, g/cc	1.2	0.85
Viscosity, 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,	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]. The acidity of these oils is expected to impact the infrastructure used to process, store and deliver fast pyrolysis bio-oil.

Currently, in the United States, bio-oil has not yet been established as a fuel for direct energy conversion (via boiler or turbine generator) or as a transportation fuel. The primary research focus (at this time) is to improve the economics associated with fuel production. In order to be economically viable the production costs will need to be comparable with those for petroleum production. Large-scale production facilities do not yet exist in the United States; however, a number of small-scale research centers are producing bio-oil in large enough quantities to support limited compatibility testing.

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 resistant 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 elastomers. In fact, ketonization of existing carboxylic acids is gaining interest as an additional upgrading step to mitigate acid components in bio-oil [10]. Unfortunately ketones are known solvents for many polymers, especially fluorocarbons which are now used in many systems for their improved compatibility with alcohol-based biofuels.

The compatibility of elastomeric materials with new fuel chemistries need to be considered since they are used extensively in fuel lines as hoses and as seals. Their performance, when exposed to a particular solvent, is critical to ensure leak-tight joining of structural components and proper operation of valves, meters and sensors. Failure of a seal 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 elastomers, when they are exposed so fuels mixed with bio-oils, in order to provide guidance on proper seal material selection, and identify potential leak sites in fuelling hardware.

In 2013 ORNL performed a study to evaluate the compatibility of fuel storage and delivery infrastructure materials to test fuels representing off-highway diesel fuel (used in home heating) and a blend containing 20% bio-oil. Another objective was to perform a solubility analysis for each material type and bio-oil blended diesel fuel. The materials included in this study included advanced fluorocarbons, fluorosilicone, acrylonitrile butadiene rubber (NBR), styrene butadiene rubber (SBR), silicone, neoprene and polyurethane. It is important to note that many

of these materials are also used in vehicle fueling systems. Data obtained from prior ethanol compatibility studies on these materials are included for additional interpretation.

SOLUBILITY AND ITS IMPACT ON OTHER PLASTIC MATERIALS PROPERTIES

For polymers, fuel compatibility is predominantly determined by the mutual solubility between the polymer and fuel. In practice, the degree, or extent, of solubility, is assessed by measuring the resulting volume expansion of the polymer following exposure to the test fluid. In lieu of direct measurement, the solubility potential between an elastomer 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 elastomers) having similar solubility parameters will have a higher affinity for permeation and dissolution than those with dissimilar values. There are several different approaches of assigning solubility parameters. The Hildebrand approach 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. To better facilitate discussion, the total solubility parameter is used in this section.

The relationship between the total solubility parameters for mixtures of gasoline blended with ethanol and diesel blended with bio-oil are shown in Figure 1. 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 plastic and elastomer materials. The chart shows that gasoline containing 10 to 50% ethanol is within the shaded polymer solubility range. In contrast, are much larger compositional range of diesel fuel and bio-oil (0 to 90%) 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 polymer swell, which is not desirable in most plastic applications since it can lead to buckling and damage.

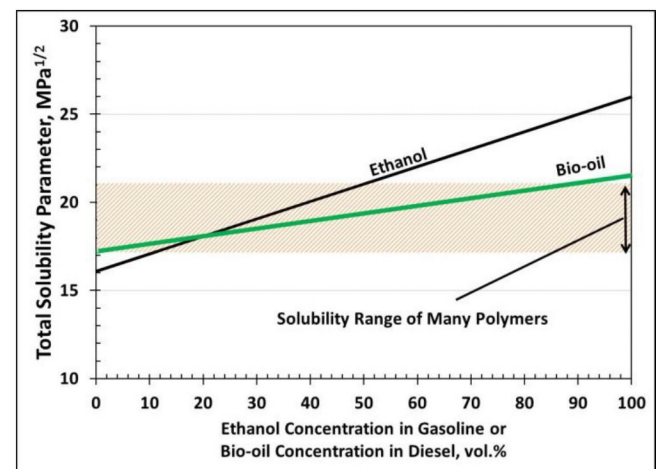


Figure 1. Total solubility parameter curves for gasoline blended with ethanol diesel fuel blended with bio-oil.

Another consideration is that many polymer materials used in fueling systems are complex compositions of one or more polymers (or copolymers) and low molecular weight 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.

Additionally, shrinkage of the elastomer upon drying is also an important parameter since contraction (and mass loss) of a seal may promote leaking. Shrinkage is also indicative of the removal of one or more components of the elastomers (by the solvent). This extraction of additives can negatively change the properties of the elastomer, leading to reduced performance and durability. For most seal applications, some level of volume swell is acceptable, since the expansion will serve to maintain the seal. The actual acceptable level of swell is dependent on the particular application. However, excessive swell can lead to extrusion of the elastomer beyond the sealed interface where it becomes susceptible to physical damage. Also, since high swell is indicative of high solubility, there is a heightened potential for fluid to permeate through the seal material and into the environment. The absorption of fluid into the elastomer is typically accompanied by a reduction in its hardness, since the added fluid lowers its resistance to penetration.

The change in hardness following drying is another key property used to assess whether structural or compositional changes have taken place in the elastomer from the exposure to the test fuels. An elastomer, which was not compounded with plasticizers, would not typically be accompanied by a change in hardness (unless the polymer chemically reacted with the test fuel). Plasticizers, such as phthalates, are often added to impart pliability (or softness) to an otherwise brittle material. If a solvent was able to extract the plasticizer component, then seal shrinkage will be accompanied by a hardness increase (embrittlement) which may reduce the durability of the seal. On the other hand, shrinkage accompanied by a loss in hardness (softening) is indicative of chemical degradation of the polymer.

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 as home heating oil. The baseline fuel was supplied by Connell Oil, Inc. and had a sulfur concentration up to 500ppm. Off-highway diesel fuel is used as the base fuel since many of the elastomers in this study are used for both off-highway transport and home heating oil systems.

The bio-oil used in this study was produced by a proprietary fast-pyrolysis method and partially upgraded via hydrotreatment to remove carboxylic acids and other oxygenates. 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 test fuels containing 20% bio-oil was prepared by splash blending. The bio-oil was found to be fully miscible with the baseline diesel fuel.

Description of Elastomers

The elastomer materials evaluated in this study included two fluorocarbons (Viton A401C and Viton B601), six NBRs and one type of fluorosilicone, polyurethane, neoprene, SBR, and silicone. Fluorocarbon and fluorosilicone are both classified as fluoroelastomers. Fluorosilicone is actually a composite of fluorocarbon and silicone rubbers, and as such can be expected to display properties ranging between that of fluorocarbon and silicone. The six NBR grades include those developed for use as fuel lines or hoses. NBR#3 is a marine grade and is designed to have improved compatibility with a wider range of solvents than the other NBRs. The other elastomers were selected as generic representatives, and therefore may not reflect the actual grades used in fueling systems. Three specimens were evaluated for each elastomer type, 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.

Experimental Protocol

Much of the experimental protocol was determined from an earlier study which found that full saturation of the elastomers was achieved following a 4-week exposure period [4]. A test temperature of 60°C was selected to be consistent with the dispenser test protocol used by Underwriters Laboratories [12,13]. 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. A schematic drawing of the test chamber is shown in [Figure 2](#). For each test fuel, the specimen array included the elastomer materials, along with plastic and metal samples. 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, but their performance was similar to those measured for the liquid exposures.

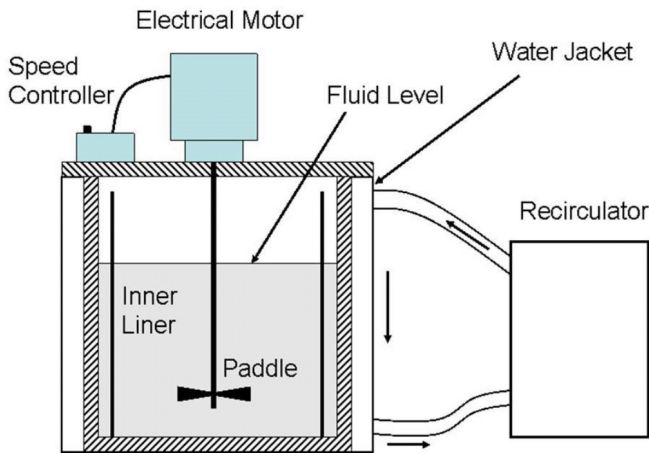


Figure 2. Schematic drawing of the test chamber assembly.

A flow chart highlighting the treatments and measurements for each material type is shown in Figure 3. The specimens were exposed to the test fuels for a period of 4 weeks (after which they were fully saturated), then they were removed and measured for volume, mass, and Shore A hardness while in the wetted (or saturated) state. The volume change for each specimen was determined using the protocol in ASTM D471-06, while the hardness measurements were performed according to ASTM D2240 [14,15]. The hardness was measured at five locations on each specimen and they were found to match the hardness values provided by the suppliers. (The specimens were not doubled up to achieve the desired Shore A test thickness of 0.635 cm.) Once the wetted properties were measured, the elastomers were oven heated at 60°C (in air) for 20 hours. After drying, 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.

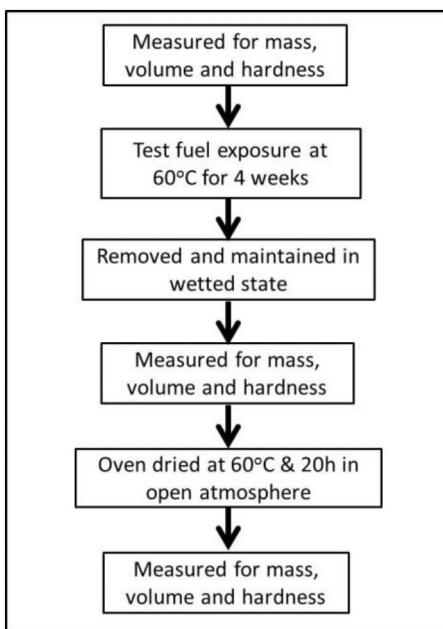


Figure 3. Flow chart showing the exposure protocol and test methods.

RESULTS

Chemical Analysis of Bio-Oil and Derivation of Solubility Parameters

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

The chemical composition of the bio-oil was assessed using gas chromatography-mass spectroscopy (GC-MS) analysis. The results in Figure 4 show that the bio-oil used in this study contained significant levels of ketone, phenols, and aromatics, which are 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 these oil types. The relative concentrations of these primary components were not determined, but an estimate of these parameters was established by assuming equal concentrations (20 percent by volume) of the aromatics, phenols, ketones, ethyl acetate, and naphthalenes. Most bio-oils contain concentrations ranging from 10 to 20 percent for phenols, acetones, aromatics, acids. For many bio-oils the phenol concentration is around 1.5 times higher than the other primary components.

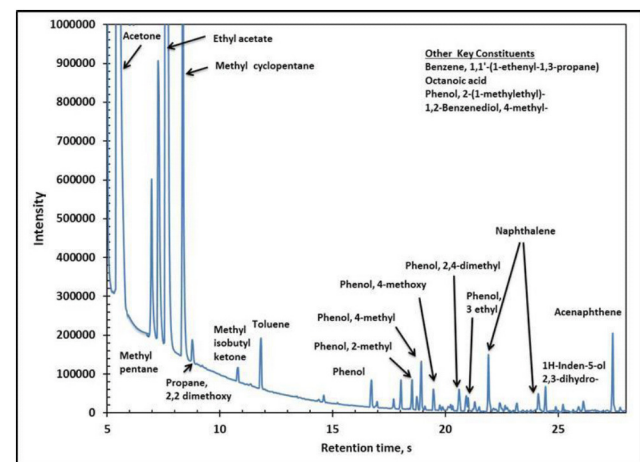


Figure 4. GC-MS results for the bio-oil.

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. The Hansen solubility parameters are listed in Table 2 for each primary component of the bio-oil. (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 its hydrogen bonding parameter is significantly higher.

Because many of these component parameters are similar to each other, the effect of their relative concentrations is not expected to significantly impact the resulting solubility curves for each plastic type. To support this supposition, the authors of this report performed a preliminary analysis whereby the concentration of each individual component was exaggerated relative to the others. The results 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 bio-oil Hansen solubility parameters was made using equivalent concentrations of ketone, phenol, aromatic, ethyl acetate, and toluene. The resulting parameters are also included in Table 2.

Table 2. 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

Solubility Analysis

A solubility analysis was performed for each of the elastomer materials to better understand their solubility (compatibility) with fuel blends composed of diesel fuel and bio-oil. 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 solubility curves for the six elastomer materials are shown in Figure 5 and the IR- d_s results are plotted in Figure 6 for each material and test fuel. For fluorocarbon, the solubility distance was not observed to change dramatically with bio-oil content, though it did decrease slightly when the bio-oil content was raised from 0 to 50%. Higher levels produced a slight increase. The results in Figure 6 also suggest that low-to-moderate solubility (or volume swell) can be expected for the fluorocarbon materials in either test fuel. The solubility distance for NBR decreased with increasing bio-oil content to reach a minimum at 20%. Concentrations higher than 20% caused an increase in d_s , such that the solubility distance for 100% bio-oil was higher than for 100% diesel. The implication is that NBR can be expected to be more compatible in neat bio-oil than diesel fuel. The IR- d_s results in Figure 6 show that high solubility can be expected for NBR in either test fuel, but that swelling can be expected to be higher with the Bio20 test fuel.

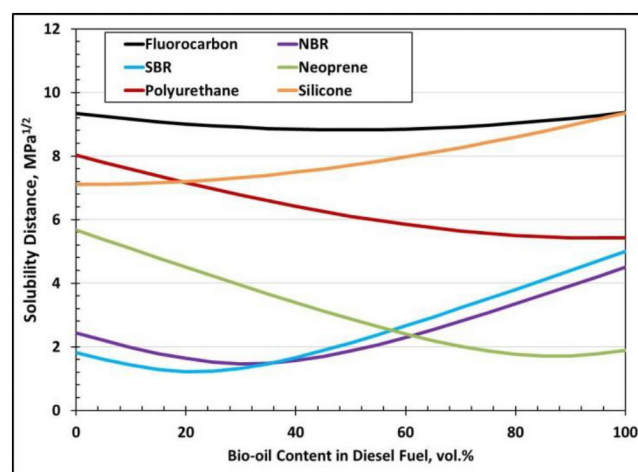


Figure 5. Solubility curves for the elastomer materials with diesel blended with bio-oil.

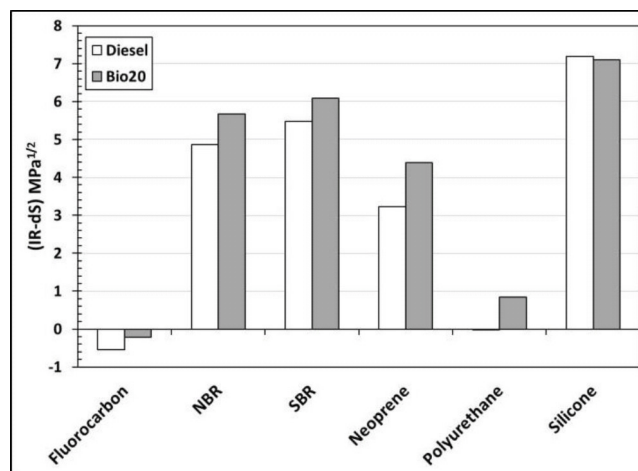


Figure 6. Chart showing IR- d_s results for the elastomer materials with neat diesel fuel and a blend composed of 20% bio-oil.

The solubility results for SBR were similar to those of NBR. For this material the minimum solubility distance is expected to be around 35% bio-oil content. The analysis indicates that neoprene is expected to be highly soluble in either test fuel and have increased solubility up to 90% bio-oil. The figures also suggest that polyurethane will

exhibit similar behavior to neoprene but the extent of solubility (or volume swell) will be low-to-moderate in the test fuels. In contrast to the other elastomers, the solubility curves for silicon increase with increasing bio-oil content up to 100% bio-oil. However, the differential between diesel fuel and Bio20 is slight and high volume swell is expected for silicone exposed to either fuel type.

Elastomer Exposures to Diesel and Bio20

To facilitate discussion and interpretation of the results, data from earlier studies with ethanol-blended gasoline was included with the results obtained with the baseline Diesel and Bio20 test fuels. Specifically, the results for a standard gasoline test fuel (Fuel C) and a blend of Fuel C with 17% ethanol were included for comparison [12, 13, 16]. Fuel C is representative of highly aromatic gasoline and is composed of equal parts toluene and isooctane [16]. Because these earlier investigations did not include an ethanol concentration equivalent to 20%, CE17a was chosen since it had the ethanol concentration closest to bio-oil concentration evaluated in this study [12,13]. Prior studies with ethanol-blended gasoline had showed that the property changes for elastomers exposed to CE17a and CE25a were similar, so a composition between these two concentrations should produce similar results.

Fluoroelastomers

The fluoroelastomers included two fluorocarbons (Viton A401C and Viton B601) and one fluorosilicone material. The volume change results for the wetted and dried specimens are shown in Figures 7 and 8, respectively. Diesel was observed to have no visible effect on the volume of the two fluorocarbons; though the fluorosilicone showed a small 4% increase, which is attributed to its silicone component. In marked contrast, exceptionally high volume swell (60-80%) occurred when 20% bio-oil was added to the baseline diesel fuel. This high swell result was not predicted by the solubility analysis, which indicated low-to-moderate swell with both fuels. The reason for this discrepancy is unclear, but fluorocarbon is known to be highly soluble with ketones. It is possible that the ketone level in the bio-oil is higher than estimated, but another explanation is that the ketone (or more specifically acetone which was present in the sample) may have been preferentially adsorbed by two fluorocarbons. Acetone has a smaller molecular size than most of the other bio-oil components, which would facilitate permeation into the fluorocarbon structure. A key limitation of solubility theory is the inability to take into account molecular size and diffusivity. It is for that reason that small molecules such as water and methanol cannot be accurately studied using this approach. Interestingly, the authors of this study also performed a solubility analysis with fluorocarbon using only acetone in the model and while the predicted solubility was higher it still did not approach (IR- d_s) values consistent with high solubility or volume swell. This result further confirms that standard solubility analysis is not an accurate predictor for fluorocarbons and bio-oil fuel blends.

The results for fluorosilicone were similar to the fluorocarbons, but it did not swell as high following exposure to Bio20. The high swell values obtained when bio-oil was present are strong indicators that the bio-oil was predominantly responsible for the observed high swell values in these fluoroelastomer materials. Also shown in Figure 7 are

the corresponding volume change results for exposures to test fuels representing gasoline and a blend containing 17%. For these two fuels, more moderate swelling (10-20%) is observed for the three fluoroelastomers exposed to the gasoline test fuel (Fuel C) and the ethanol-blended test fuel (CE17a). In contrast to the Bio20 fuel, the addition of 17% ethanol contributed only around 5% additional swell in the fluorocarbons and a slight increase in the fluorosilicone volume. The implications are that fluorocarbons are more sensitive to bio-oil than ethanol and that some elastomer seals designed for ethanol use may not be applicable for use with bio-oils, even at moderate blend levels.

The dried results are shown in Figure 8 and small, but significant volume expansion was maintained in the dried state for the two fluorocarbons exposed to Bio20, Fuel C, and CE17a. This expansion is consistent with fuel retention and has also been observed in other investigations. Following dryout, the fluorosilicone specimens returned to values close their original volume.

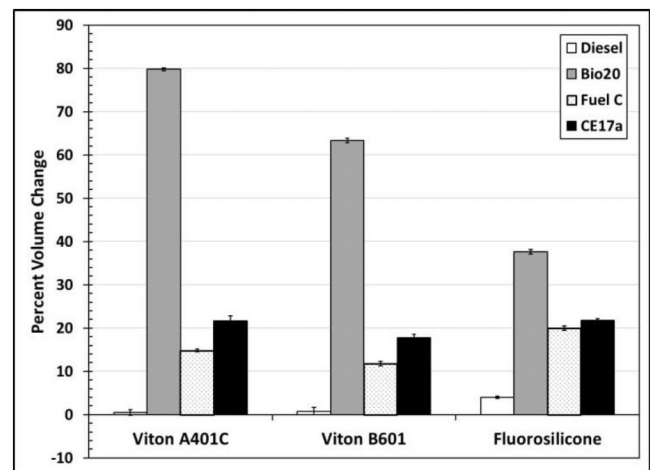


Figure 7. Wet volume swell results for two fluorocarbons and one fluorosilicone material. Specimens were submerged in the test fuels for 4 weeks at 60°C.

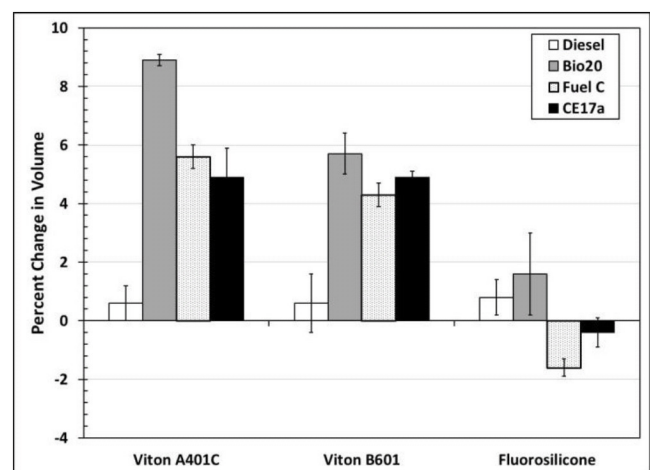


Figure 8. Volume change results for two fluorocarbons and one fluorosilicone material after drying at 60°C for 20 hours.

The point change in hardness results the wetted and dried fluor elastomer specimens are shown in Figures 9 and 10, respectively. The wetted specimens (except for fluorosilicone exposed to the diesel base fuel) exhibited a hardness decrease that was proportional to the volume swell. Swell is almost always accompanied by a drop in hardness since the absorbed fluid provides no resistance to penetration and the expanded polymer structure is weaker because there is less material (reduced density) to resist penetration by the indenter. This drop in hardness carried over into the dried states (albeit at a reduced level) due to the retained fuel. The fluorosilicone specimens differed from the two fluorocarbons in that a slight hardness increase occurred for the specimens exposed to the baseline diesel test fuel. This increase is not considered significant but does suggest possible plasticizer extraction.

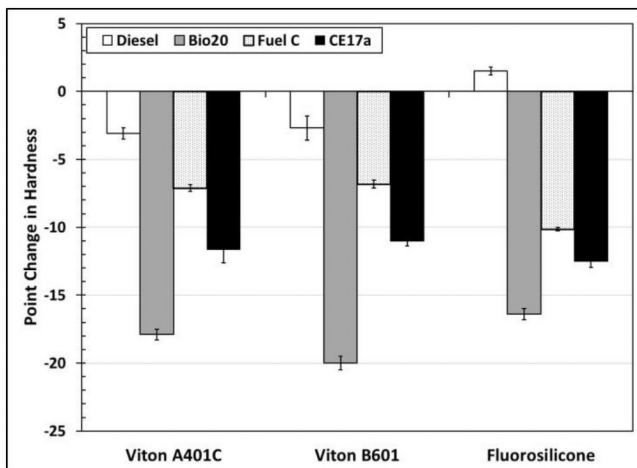


Figure 9. Point change in wet hardness results for two fluorocarbons and one fluorosilicone material. Specimens were submerged in the test fuels for 4 weeks at 60°C.

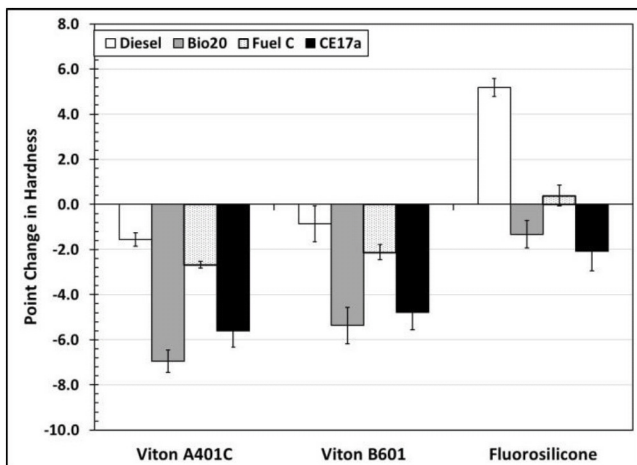


Figure 10. Point change in hardness results for two fluorocarbons and one fluorosilicone material after drying at 60°C for 20 hours.

NBR

The wet and dried volume changes for the six NBR grades are shown in Figures 11 and 12, respectively. The NBRs all performed similar to each other. Their wet volumes were essentially unchanged from their original state when exposed to the baseline diesel fuel. However, the

addition of 20% bio-oil produced swelling in excess of 50%, which is 2 to 3 times higher than the swell associated with Fuel C and CE17a. The volumes for these specimens exposed to Bio20 remained expanded 10 to 20 % from the original value, which indicates fuel retention. Interestingly, all of the specimens (except for the marine grade, NBR#3) exposed to the baseline diesel fuel contracted significantly after being dried. In most cases the level of shrinkage was between 5 and 10%, which is significant, but less than the values obtained for the specimens exposed to Fuel C and CE17a.

The solubility analysis results corresponded well with the observed volume expansion for the NBRs, except high swell was also anticipated for the specimens exposed to the baseline diesel fuel. The actual wet volumes were essentially unchanged from the starting condition; however, the shrinkage that occurred after drying is evidence that dissolution, and subsequent extraction, had taken place. Therefore, even though the bulk wetted volumes were not affected, high solubility had, in fact, taken place. The most probable reason that volume expansion was not observed (with diesel) is that the absorbed fuel effectively displaced the dissolved polymer component(s).

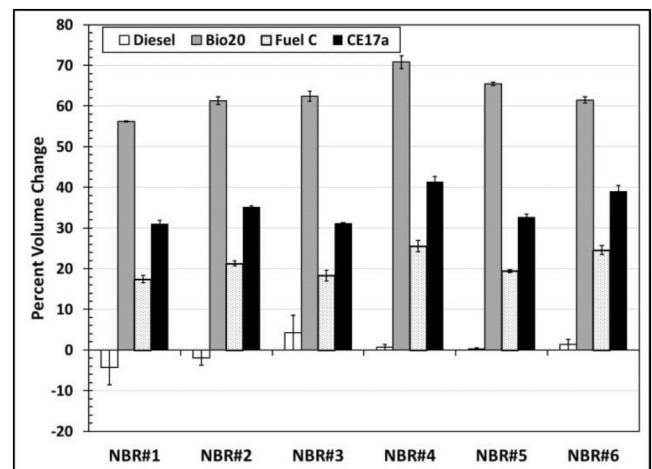


Figure 11. Wet volume change results for six NBR materials. Specimens were submerged in the test fuels for 4 weeks at 60°C.

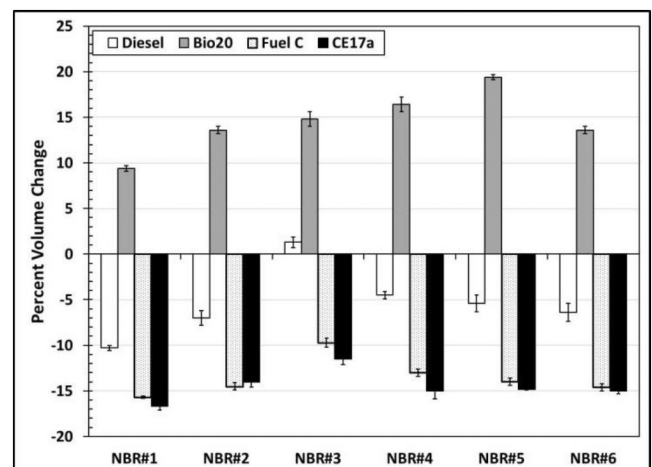


Figure 12. Volume change results for six NBR materials after drying at 60°C for 20 hours.

The changes in hardness (from the original value) for each NBR grade are shown in Figures 13 and 14 before and after drying, respectively. Each material softened appreciable in the wetted state when exposed to Bio20, Fuel C, and CE17a. Softening (while wetted) was also observed for several of the NBRs exposed to the diesel test fuel, even though their volumes were unchanged from their original values. This result further confirms that dissolved components may have been replaced with the fuel. The dried hardness results were observed to vary according to NBR type as shown in Figure 13, but embrittlement was observed in most cases. The NBRs (excluding NBR#4) experienced higher hardening with the Fuel C and CE17a exposures than they did with diesel and Bio20. The extent of embrittlement corresponded with the level of shrinkage following dryout, which indicates that Fuel C and CE17a were more effective than diesel and Bio20 at dissolution and extraction of plasticizers. In fact, Fuel C appears to be primarily responsible for this effect, as the added ethanol did not provide any additional contribution.

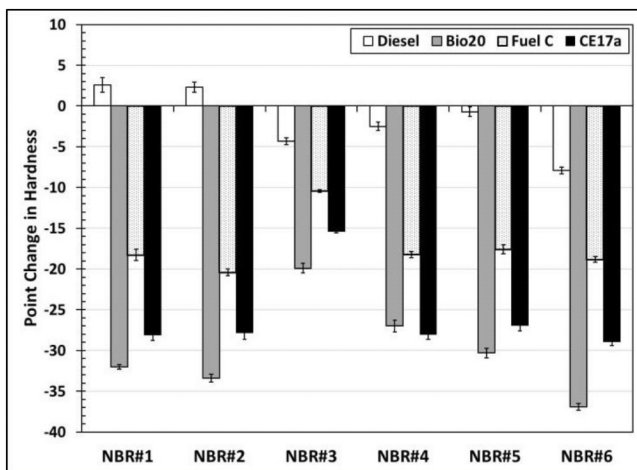


Figure 13. Point change in wet hardness results for the NBR specimens.

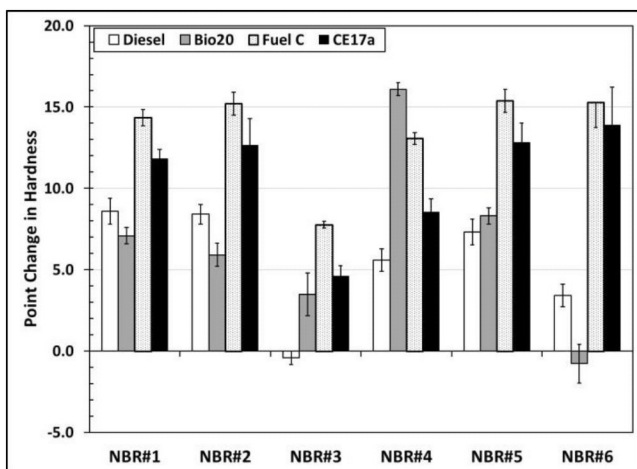


Figure 14. Point change in hardness results for six NBRs materials after drying at 60°C for 20 hours.

A key observation is that although several of the NBR grades were highly swollen after drying, they exhibited significant embrittlement. One would expect these exposures to be softened due to the high levels of retained fuel. This combination of property changes (high swell accompanied by significant hardness increase) has not been observed before and it is not obvious what the cause is. More detailed structural analyses, such as Dynamic Mechanical Analysis (DMA) or pyrolysis GC-MS, are needed to better understand the causes for these property changes.

Polyurethane, Neoprene, SBR, and Silicone

The volume change results for polyurethane, neoprene, SBR, and silicone are shown in Figures 15 and 16 for the wetted and dried conditions, respectively. These elastomers were observed to be highly sensitive to added bio-oil and ethanol. The solubility analysis did not accurately predict performance of polyurethane. The data in Figures 5 and 6 predicted low-to-moderate volume swell, yet the polyurethane was not affected by the baseline diesel fuel. However, the addition of 20% bio-oil caused the volume to swell over 80% (much higher than for Fuel C and CE17a). When dried, a significant amount of Bio20 remained in the polymer structure as evidenced by 20% volume expansion in the dried state. The other two test fuels either caused the specimens to return to their starting values or shrinkage (in the case of CE17a).

For neoprene, exposure to either diesel or Fuel C produced a 20% expansion, while Bio20 and CE17a increased this amount to 90% and 75%, respectively. When dried Fuel C and CE17a both produced significant shrinkage, but specimens exposed to Bio20 remained almost 30% swollen from their original condition. In contrast the specimens exposed to the diesel baseline were only slightly swollen from their original condition following dryout. SBR performance was somewhat similar to that observed for neoprene but degree of swelling (when wet) and shrinkage following dryout was lower. (The high volume expansions and relative performance for both neoprene and SBR were accurately predicted by the solubility study.) For SBR, baseline diesel and Fuel C test fuels increased the volume by around 62%; the addition of 20% bio-oil (to diesel) and 17% ethanol (to Fuel C) doubled this value to 120%. When dried, the specimens exposed to diesel and B20 remained swollen at 34 and 60%, respectively.

The solubility study had indicated that silicone would be highly soluble with both diesel and Bio20 and that the resulting volume expansions would be similar in extent. Silicone swelled roughly 60% in diesel and 80% in Bio20. These relative volume expansions were closer in value than for the other elastomers, indicating that correspondence with the solubility analysis for this material was good. Silicone (exposed to diesel and Bio20) also remained in a swelled state following dryout, whereas the dried volumes of the specimens exposed to Fuel C and CE17a both returned to values approaching the original volumes.

Silicone was unique among the elastomers in that it exhibited higher swelling with Fuel C and CE17a than with either diesel or Bio20. Diesel produced a 60% expansion, and the added bio-oil raised this value to around 82%

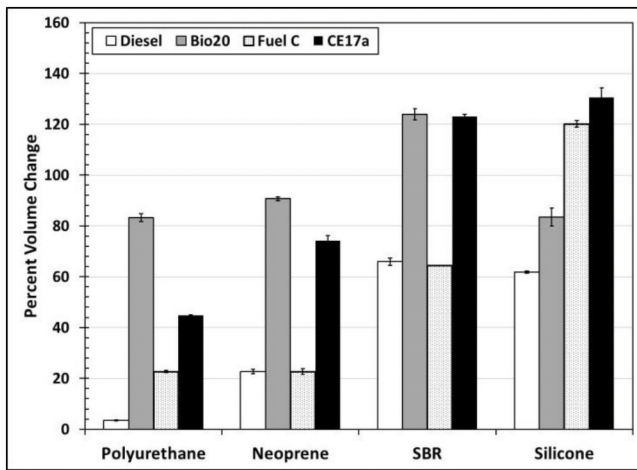


Figure 15. Wet volume change results for polyurethane, neoprene, SBR, and silicone.

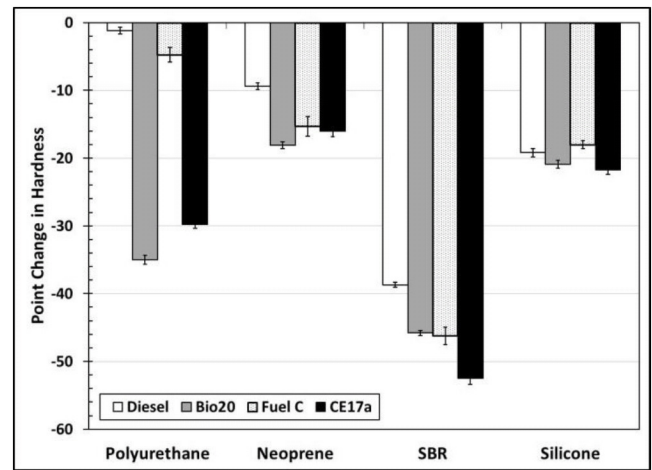


Figure 17. Point change in wet hardness results for the polyurethane, neoprene, SBR and silicone specimens.

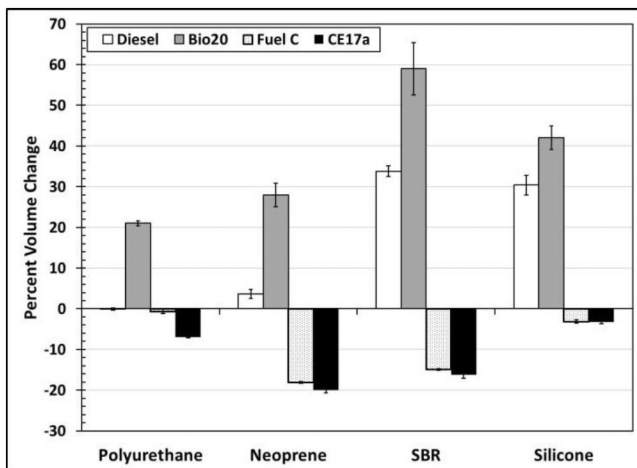


Figure 16. Volume change results for polyurethane, neoprene, SBR, and silicone after drying at 60°C for 20 hours.

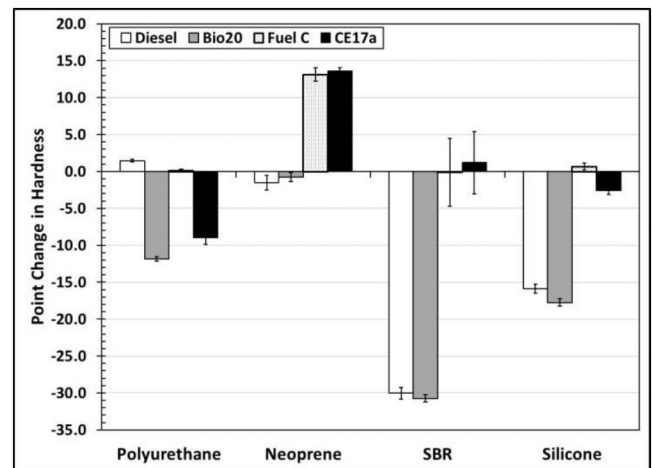


Figure 18. Point change in hardness results for the polyurethane, neoprene, SBR and silicone specimens after drying at 60°C for 20 hours.

The resulting changes in hardness from the original conditions are shown in Figure 17 and 18 for the wetted and dried specimens, respectively. The results show that in general the heavier test fuels (diesel and Bio20) produced significant fuel retention following dryout as evidenced by the positive volume values in the dried state. The lighter test fuels (Fuel C and CE17a) caused shrinkage and hardening during dryout.

The drop in hardness (softening) for polyurethane corresponded well with the relative wet and dry volume expansions. Neoprene exhibited a lower hardness reduction than the other elastomers in the group. When dried, neoprene specimens exposed to diesel and Bio20 returned to their starting values, but (given the dry volume increase from the original value) it is possible that plasticizer was extracted and replaced with test fuel. (In fact neoprene showed pronounced embrittlement when exposed to Fuel C and CE17a and dried.) SBR exhibited pronounced softening in both the wetted and dried states following exposure to diesel and Bio20, due to fuel retention. Silicone exhibited wet and dry softening proportion to the observed volume expansion. The silicone specimens exposed to Fuel C and CE17a were returned to their original volume and hardness values after drying.

DISCUSSION

In general the elastomers showed more swelling with Bio20 than they did with the ethanol-blended gasoline test fuel. The implication is that although many of these elastomers are used in fuel systems with ethanol blended gasoline, they may be not suitable for fuels containing bio-oil (especially those with similar upgrading levels and processing). More studies need to be performed characterizing bio-oils and their potential solubility with polymers to better understand the impact of these fuel types on existing infrastructure. Many of these materials are also used on vehicle fueling systems and the results from this study are expected to have utility to automakers.

It is important to note that the specimens were kept at 60°C during the exposure runs. The effect of elevated temperature and time with bio-oil has not been well studied, but it is possible that some of the bio-oil components degraded or had reacted with other components. No measurement was made of the test fuel chemistry at the end of the exposure run. However, it is recommended in any future evaluations.

SUMMARY/CONCLUSIONS

For these particular elastomeric materials, the Hansen solubility analysis generally provided good agreement to the observed volume swell. The notable exceptions were for the fluorocarbons. These materials showed very low levels of swell with diesel fuel, but when 20% bio-oil was added they expanded over 60%. The most likely explanation is the small molecular size of acetone component in the bio-oil was highly diffusive to the fluorocarbon structure. The NBRs also exhibited similar behavior, except that dissolution and extraction had taken place to mask the volume swell normally accompanying high solubility. (It's important to also note that NBRs usually have a much higher porosities and lower densities than fluorocarbons.) Their more open structure will tend to facilitate permeation and will be less sensitive to small molecule kinetics than the attractive forces governing solubility.

All of the elastomers exhibited increased volume swell when 20% bio-oil was added to the baseline diesel fuel. In fact, the highest level of swelling occurred with Bio20 for the fluorocarbons, fluorosilicone, NBRs, polyurethane, and neoprene. For SBR, the Bio20 performance matched that of CE17a. Silicone was unique in that both Fuel C and CE17a produced higher degrees of swelling than did Bio20.

When dried, the NBR materials exposed to Bio20 remained expanded when compared to their original volumes (albeit to a lesser extent than when wetted). Exposure to the other three test fuels produced significant shrinkages, which were accompanied by increases in hardness, indicating plasticizer extraction. What is remarkable is that even though specimens immersed in Bio20 remained swollen (retained fuel) after drying, they had become harder (not softer). Normally, fuel retention during dryout produces a hardness decrease, but for the specimens exposed to Bio20, the softening due to retained fuel was not able offset the hardness increase brought about by the loss in plasticizers.

Polyurethane, neoprene and SBR showed heightened sensitivity to the added bio-oil as evidenced by the high levels of swelling that occurred with the Bio20 fuel. Interestingly, the extent of swelling incurred by Bio20 for these three materials was nearly identical to that measured for CE17a. Silicone was unique among the elastomers in that it showed better compatibility with the bio-oil than it did with gasoline containing 17% ethanol.

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DEFINITIONS/ABBREVIATIONS

ASTM - American Society for Testing and Materials

B20 - diesel fuel blended with 20% biodiesel

Bio20 - test fuel composed of 80% off-highway diesel fuel and 20% bio-oil

CE17a - test fuel composed of 83% Fuel C and 17% aggressive ethanol

d_s - solubility distance

DMA - dynamic mechanical analysis

DOE - US Department of Energy

E10 - gasoline containing 10% ethanol

E15 - gasoline containing 15% ethanol

E17 - gasoline containing 17% ethanol

EPA - US Environmental Protection Agency

Fuel C - test fuel composed of 50% toluene and 50% isooctane

GC-MS - gas chromatography-mass spectroscopy

HDPE - high density polyethylene

HSP - Hansen solubility parameter

IR - interaction radius

NBR - acrylonitrile butadiene rubber

ORNL - Oak Ridge National Laboratory

SAE - Society of Automotive Engineers

SBR - styrene butadiene rubber

APPENDIX**SUMMARY TABLE FOR MATERIAL PERFORMANCE AND IMPACT WITH BIO20**

Material type	Application	Observed Impact of Bio20 Fuel	Possible Significance and Impact
Fluorocarbon	Seals (o-rings, gaskets, etc.)	Excessive (>60%) swelling	Not compatible with Bio20 fuel for many existing applications.* Potential leak risk.
Fluorosilicone	Seals (o-rings, gaskets, etc.)	High (~40%) volume expansion	Probably not compatible with Bio20 for many dynamic sealing applications.* Potential leak risk.
NBR	Seals (o-rings, gaskets, etc.) Fuel hoses	Excessive (>50%) swelling	Not compatible with Bio20 fuel for many applications.* Potential leak risk.
Polyurethane	Coatings	Excessive (>80%) swelling	Not compatible with Bio20*. As a coating material, the high volume swell translates to high permeation and likely delamination, which can lead to corrosion and decreased durability of coated components.
Neoprene	Seals (o-rings, gaskets, etc.) Fuel hoses	Excessive (>90%) swelling	Not compatible with Bio20*. Potential leak risk.
SBR	Fuel hose cover	Excessive (>120%) swelling	SBR is not normally used in fuel systems. As a fuel hose cover it will reduce the overall durability if placed in direct contact with Bio20*
Silicone	Seals (o-rings, gaskets, etc.)	Marginal volume increase with Bio20	Performance is similar to fluorocarbon. Not compatible with Bio20 fuel for many existing applications.* Potential leak risk.

*While the results show that the Bio-oil type evaluated in this study was not compatible, it is quite possible that some bio-oils do have acceptable compatibility performance.