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FINAL PROJECT REPORT

COMPATIBILITY STUDY OF ALTERNATIVE FUELS WITH EXISTING INFRASTRUCTURE

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PREFACE

The California Energy Commission Public Interest Energy Research (PIER) Program supports public interest energy research and development that will help improve the quality of life in California by bringing environmentally safe, affordable, and reliable energy services and products to the marketplace.

The PIER Program conducts public interest research, development, and demonstration (RD&D) projects to benefit California.

The PIER Program strives to conduct the most promising public interest energy research by partnering with RD&D entities, including individuals, businesses, utilities, and public or private research institutions.

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- Renewable Energy Technologies
- Transportation

Compatibility Study of Alternative Fuels With Existing Infrastructure is the final report for the RNG and Fungible Fuels Infrastructure Compatibility Program project (contract number 500-11-015) conducted by CE-CERT, University of California, Riverside. The information from this project contributes to PIER's Transportation Program.

For more information about the PIER Program, please visit the Energy Commission's website at www.energy.ca.gov/research/ or contact the Energy Commission at 916-654-4878.

ABSTRACT

Alternative fuel use in California is supported by legislation such as Assembly Bill 1900, which requires the development of standards for constituents in biogas to protect human health and to maintain pipeline integrity and safety. However, as alternative fuels expand into the marketplace, it becomes important to understand how these fuels might impact the infrastructure systems that transport, store, and distribute fuel—especially since these systems were originally built for petroleum-based fuels.

In this study, researchers investigated the compatibility of different materials found in the existing petroleum fuel infrastructure with different alternative fuels. These alternative fuels included alcohol blends and natural gas blends with varying levels of carbon dioxide, hydrogen, and water. Researchers exposed metal, plastic, and elastomer (rubber) samples to these fuels in different exposure chambers and evaluated the effects of exposure on the materials. Exposure to renewable natural gas produced relatively minor changes in the different materials. However, exposure to liquid ethanol and butanol alcohol blends caused the elastomers to undergo the most significant changes, followed by the plastics; the metals, in contrast, showed relatively minor changes.

The results of this research support California's effort to meet emission and petroleum reduction targets by providing an understanding of how the increasing availability and use of alternative fuels will affect existing fuel infrastructure. The local production and use of renewable natural gas can help California achieve its goals to improve air quality for California ratepayers as well as provide a cost-effective option for fleets of natural gas vehicles throughout the state.

Keywords: Renewable Natural Gas, Natural Gas, Ethanol, Butanol, Transportation, Alternative Fuels, Infrastructure, Materials Compatibility.

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EXECUTIVE SUMMARY

Introduction

California is currently implementing policies to promote the in-state production and distribution of renewable alternatives to non-renewable fuels. Assembly Bill (AB) 1900 is one such policy; under AB 1900, the California Public Utilities Commission is working to develop standards for constituents in biogas to protect human health and pipeline integrity and safety. Natural gas produced from renewable sources, or "renewable natural gas" (RNG), is being promoted in an effort to increase the market presence of renewable fuels. One example of an RNG is biomethane, which is produced through anaerobic digestion in landfills, lagoons, or dedicated vessels where oxygen is limited. Alternative, renewable fuels also come in liquid form. Ethanol is the most widely used alternative fuel and is expected to be the primary fuel used in meeting the Federal Renewable Fuel Standard. There is also initial interest in the use of butanol as an alternative fuel because it has higher energy content than ethanol and may be more compatible with the existing infrastructure. However, one of the most important issues to consider when bringing greater volumes of renewable fuels into the marketplace is the compatibility of these fuels with the existing fuel and vehicle infrastructure. Implementing a wider range of both gaseous and liquid fuels may be problematic considering that the fuel infrastructure, in particular, was originally designed to transport, store, and distribute petroleum-based fuels.

Project Purpose

The purpose of this project was to gather data that could be used to improve and advance California's fuel infrastructure and technologies so that they can reliably supply alternative transportation fuels throughout the state. In this project, the research team investigated the compatibility of existing petroleum transportation fuels infrastructure with gaseous and liquid alternative fuels. To do so, they exposed samples of different types of materials used to build petroleum fuel transportation and distribution systems to different types of alternative fuel for varying periods of time. The material samples included elastomers (such as Viton and rubbers), thermoplastics (plastic materials such as polyethylenes that are pliable and do not change their chemical composition when heated), and metals (such as steel and aluminum and plated metals like galvanized steel). They performed experiments using the following fuels: ten percent ethanol blends with and without added contaminants, a 55 percent butanol blend with added contaminants, and natural gas blends with carbon dioxide and varying levels of hydrogen and water saturation. The natural gas blends included a representative renewable baseline natural gas with 98 percent methane, 2 percent CO_2, saturated with water (i.e., wet), three gases using the baseline gas with the addition of 1 percent, 5 percent, and 20 percent hydrogen, respectively, a baseline gas with the water removed, and a baseline gas with the water removed and 20 percent hydrogen added. The exposure experiments were conducted in a cylindrical stir chamber for the liquid fuel exposures and in a series of tubes for the natural gas exposures. The liquid fuel exposures included both direct exposures to the fuel itself, as well as to the fuel vapors. The liquid fuel samples were also evaluated immediately after they were removed from the stir chamber and then after drying for at 140°F (60°C) for 20 to 65 hours. The material

specimens were evaluated both before and after exposure for mass loss, volume change, visual appearance/discoloration, and evidence of pitting or corrosion in the form of small holes in the material. Additionally, metals were also tested for changes in composition while elastomers and plastics were tested for tensile strength and their degree of elongation during the tensile strength test.

Project Results

A summary of the findings and conclusions of this study are as follows:

Natural Gas Exposures

The materials did not show as strong impacts for the natural gas exposures, with only minor changes seen in terms of volume and mass change. This suggests that material compatibility impacts for renewable natural gas may be less than those from the other liquid alcohol fuels tested in this study.

Elastomers

The elastomer samples showed very minor variations in volume, insignificant changes in mass, and no visual differences after being exposed to natural gas. All of the samples demonstrated a volume change of less than 3 percent, with the volume change for most samples being within 2 percent. The volume change seen in most samples was the result of size reduction post exposure; however, a few samples increased in size. The majority of the elastomer samples showed a percent weight change of 0.5 percent or less, with a few samples showing larger changes of about +2 to -3 percent. The majority of the elastomer samples had a change of tensile strength of less than ±20 percent and decreases in elongation of approximately 20 percent or less.

Plastics

All of the plastic samples demonstrated percent volume changes of less than 3.5 percent, with many samples demonstrating volume changes below 2 percent. The majority of plastic samples showed a minor increase in percent volume change, with a few samples showing a slight decrease in volume. The majority of the plastic samples showed a percent weight change of 0.2 percent or less, with the average change being 0.1 percent or less. None of the plastic samples showed a difference in visual appearance. The majority of the samples had a change in tensile strength of ±20 percent, with tensile strength increasing in most cases, while changes in elongation were ±50 percent or less.

Metals

All of the metal samples showed a percent volume change of less than 3.1 percent, with a majority of the metal samples showing a percent weight change of 0.01 percent or less. The majority of metal samples showed a minor increase in percent volume change, but a slight reduction in mass. The majority of metal samples that were exposed to natural gas did not show

a difference in appearance, although steel alloy samples exposed to the baseline wet +20 percent hydrogen gas developed rust on the surface.

Liquid Fuel Exposures

Elastomers

The elastomers showed the most significant changes of any of the materials as a result of exposure to liquid fuels. The elastomers generally increased in volume and mass immediately following the exposures, indicating that the elastomer material absorbed some of the liquid fuel. After drying, the most elastomers shrank in volume and mass compared to the original samples, indicating that some of the associated elastomer components were removed from the sample along with the liquid fuel. The samples exposed directly to the liquid fuels tended to show more significant changes than those exposed to the fuel vapors. The rubber samples (styrene butadiene rubber, nitrile butadiene rubber, and natural rubber) showed relatively significant increases in volume/mass immediately after exposure, with styrene butadiene rubber showing the largest increases. Fluorocarbons (Viton A401C, Viton B601) were the most resistant of all of the elastomers, showing smaller levels of volume swell/mass gain immediately after exposure, but retaining some of the mass gain/volume swell following drying. Most elastomers showed a reduction in tensile strength and a tendency for reduced elongation during the tensile strength test. Most materials showed changes in tensile strength of 20 percent or less, with a few samples showing reductions ranging from 36 to 100 percent and a few samples showing increases. Most materials showed changes in elongation of ±20 percent or less, with a few samples showing larger changes from 60 to 100 percent

Plastics

The plastic samples underwent fewer changes than the elastomer samples but more changes than the metal sample as a result of the liquid fuel exposures. The plastics increased in volume and mass immediately following the exposures. They also retained some of this volume swell/mass gain after drying, indicating that the liquid fuel was retained in the plastic structure. However, in general, the plastics swelled in volume less than the elastomers. Most of the plastic samples increased in size and weight by less than 10 percent when wet, with a few samples increasing by 20 to 35 percent in volume and 13 to 22 percent in mass. After drying, the majority of these plastic samples showed an increase in volume and weight of 5 percent or less from their original dimensions, with a few samples retaining between 20 to 30 percent of the volume increase and between 8 to 13 percent of the main gain upon drying. A number of plastics showed discoloration upon exposure to the fuels, with some samples showing a yellowish tint, while others showed some pinkish discoloration. Most of the plastic samples showed reductions in tensile strength ranging up to 90%, with Polyethylene terephthalate, polyethylene terephthalate G, polyethylene terephthalate, polypropylene P showing some of the largest reductions, especially for the E10 fuel. The plastics showed reductions in elongation for all samples, with most reductions on the order of 25 to 95 percent, with the exception of polyvinyl chloride, which showed increases in elongation from 130 to 180 percent.

Metals

The metal samples were the least affected by liquid fuel exposures. Metal samples had a percent volume change of less than 6 percent before drying and less than 7 percent after drying. Submerged samples did not deviate past 1/10 of a percent in weight change after fuel exposure and drying. The majority of the vapor samples also did not deviate past 0.1 percent in weight change after fuel exposure and drying, although the Zinc and S4140 samples exposed to the vapor of the E10 aggressive fuel showed reductions in weight of 0.37 percent and 0.17 percent, respectively. . The visual appearance for a number of the metal samples showed signs of rusting or a brownish tint, with the contaminated E10 and B55 fuels showing greater effects than the E10 fuel, and with the samples that were exposed to the fuel vapors showing a greater visual change compared to samples that were submerged in the fuels themselves.

Project Benefits

The results of this study provide important insights into potential material compatibility issues that might be seen as alternative fuels of different compositions become more prevalent in the fuel marketplace. Exposing the different materials to the liquid fuels revealed a clear trend in which the elastomers showed the greatest impacts and the metals showed the least. In contrast, none of the materials reacted as strongly when exposed to natural gas, with only minor changes seen in terms of volume and mass change. This information can be used to help ensure the compatibility of alternative fuels with the existing petroleum transportation fuels infrastructure and in turn help expand the use of alternative fuels in the transportation sector.

CHAPTER 1: Introduction

California and the rest of the nation are dependent upon an extensive network of fuel transportation, storage, and distribution systems that have evolved over many decades around reliability criteria associated with petroleum-based fuels. These pipelines, tank farms, and other infrastructures constitute legacy systems that cannot and will not quickly or easily be superseded. However, the state is calling for a transition to increased use of alternative fuels derived from renewable sources and produced through diverse pathways and technologies and in different blends. One concern is the notion that the new generation of alternative fuels will likely be deployed initially as blends with conventional fuels; conventional fuels are already blended with ethanol and biodiesel fuel. These new fuels could blend seamlessly with current ones or potentially present unanticipated synergistic effects. However, the American Society of Testing and Materials (ASTM) standards, which ensure that alternative fuels interact properly with existing engines, do not directly address subtle, potential infrastructure issues. The country's fuel infrastructure must be able to accommodate as many of these alternative fuels as possible to allow the greatest flexibility in adoption and use of petroleum alternatives.

Renewable natural gas (RNG), which is natural gas produced from renewable sources, is being promoted in an effort to provide additional pathways for bringing renewable fuels to the marketplace. Biomethane, which is one type of RNG, is an alternative fuel to petroleum that has been the subject of considerable study recently. Biomethane is a processed biogas that is produced via anaerobic digestion in landfills, lagoons, or dedicated vessels where oxygen is limited. Biomethane is produced from biogas by removing the carbon dioxide (CO_2) and other minor components so that the resulting gas is largely methane. Biomethane is interchangeable with natural gas in that the primary constituents of biomethane are similar to pipeline gas. No extensive studies have been conducted on how biomethane and other RNGs might impact the existing fuel infrastructure system over the long term.

California is currently implementing policies with a goal to promote the in-state production and distribution of biomethane and other RNGs. Under Assembly Bill 1900, the California Public Utilities Commission is charged with developing standards for constituents in biogas to protect human health and pipeline integrity and safety, identifying impediments that limit procurement of biomethane in California, and adopting policies and programs that promote the in-state production and distribution of biomethane. In support of these efforts, the Office of Environmental Health Hazard Assessment (OEHHA) and the California Air Resources Board (ARB), in consultation with other State agencies, conducted a joint study to evaluate potential constituents of concern in biogas and evaluate exposure scenarios related to these constituents.[1] The OEHHA compiled a list of constituents found in biogas that could pose health risks and that are at levels that significantly exceed the concentrations found in natural gas. They also determined health protective levels for these constituents. The ARB developed exposure

[1] ARB & OEHHA, 2013, "Recommendations to the California Public Utilities Commission Regarding Health Protective Standards for the Injection of Biomethane into the Common Carrier Pipeline"

scenarios, identified the associated health risk to utility workers and gas end users, determined limits on the concentrations of these constituents in biogas necessary to protect public health, and identified monitoring, testing, reporting, and recordkeeping requirements necessary to ensure that health protective standards are maintained. This study did not, however, consider pipeline integrity and safety aspects that may be associated with the use of biogas, as these issues were to be addressed by the California Public Utilities Commission during its rulemaking process.

For liquid fuels, the Energy Independence and Security Act (EISA) of 2007 and the Renewable Fuel Standard (see US EPA) have been key drivers for the expansion of renewable fuels, requiring the volume of renewable fuels used in transportation to increase to 36 billion gallons per year by 2022. Ethanol is the most widely used renewable fuel; however, there are concerns about the potential for ethanol to adversely interact with the materials used in the existing petroleum infrastructure. Ethanol is obtained from biomass sources including corn, sugar cane, sugar beet, sorghum, grain, switch grass, kenaf, cassava, molasses, and wheat, as well as many types of cellulose wastes and harvests (Ishizaki and Hasumi, 2014). Use of ethanol as a transportation fuel in the U.S. increased approximately 6-fold —from 2 to 13 billion gallons per year— from 2002 to 2012 (US Energy Information Administration, 2013). In the U.S., ethanol is currently blended into gasoline at a concentration of 10 percent by volume (E10). Ethanol is also available as E85, which after a recent change in specifications, is allowed to contain as much as 83 percent v/v and as little as 51 percent v/v ethanol. Addition of ethanol to gasoline comes with some challenges, since ethanol has rather different physical and chemical characteristics than gasoline, which could potentially affect the performance and efficiency of spark-ignition (SI) engines. Adding ethanol into gasoline potentially increases the Reid vapor pressure (RVP) of the blend and alters the distillation properties (Andersen et al., 2010a; Andersen et al., 2010b). Because key volatility properties are changed when ethanol is used, the final gasoline/ethanol blend needs to be formulated to ensure that its properties are within specification for the appropriate geographical region and season. Ethanol is highly water soluble, making it incompatible with the existing infrastructure and pipeline transportation processes due to the risk of water-induced phase separation (Anderson et al., 2012).

Butanol is another higher-chain alcohol blend that is getting attention, as it is more like gasoline and might be a better alternative than ethanol. Butanol is a four carbon alcohol compound, which exists as four different chemical isomers depending on the location of hydroxyl group (-OH) and the carbon bond structure. The carbon structure is either straight chain or branched and two isomers exist for each structure. N- or 1-butanol has as a straight chain structure with the alcohol at the terminal carbon. Sec- or 2-butanol is also a straight chain alcohol, but with the OH group at an internal carbon. Iso-butanol is a branched isomer with the OH group at the terminal carbon and tert-butanol refers to the branched isomer with the OH group at an internal carbon (Jin et al., 2011; Xue et al., 2013). Analogous to ethanol, butanol can be produced from either thermochemical pathways (such as synthesis gas to mixed alcohols) or biochemical pathways (such as fermentation). Historically, butanol has been produced by *Clostridia* via acetone-butanol-ethanol (ABE) fermentation processes. Recently, the use of genetically enhanced bacteria has increased the fermentation process productivity and it is expected that a

sustainable and cost effective process for butanol production will be realized in the near future (Ranjan and Moholkar, 2012; Swana et al., 2011; Ezeji, 2007). On a regulatory level, ASTM D7862 was announced for blends of butanol with gasoline at 1 to 12.5 percent by volume in automotive SI engines. The specification covers three butanol isomers, including 1-butanol, 2-butanol, and 2-methyl-1-propanol (iso-butanol). The specification specifically excludes 2-methyl-2-propanol (tert-butanol). Butanol offers a number of advantages over ethanol for transportation use. Butanol is less corrosive than ethanol, has a higher energy content than ethanol, and more closely resembles gasoline (Cooney et al., 2009). In comparison to ethanol, butanol has higher tolerance to water contamination, potentially allowing its use in existing distribution pipelines, whereas ethanol must be transported via rail or truck. Butanol has a lower volatility than ethanol and thus less tendency towards cavitation and vapor lock problems (Jin et al., 2011; Baustian and Wolf, 2012).

Oak Ridge National Laboratory (ORNL) has conducted a series of studies to evaluate the potential impact of different alcohol blends on infrastructure materials. The first phase of this research focused on intermediate ethanol levels (10 to 25 percent) and evaluated the impacts on elastomers, metals and sealants (Kass et al., 2011). This effort was then expanded to include plastics, which are found in fueling infrastructure systems, including piping and underground storage tanks, as well as higher ethanol blends (E50 & E85) (Kass et al., 2012a,b). More recently, ORNL has expanded this research to include butanol blends (Kass et al., 2013/ 2014a/ 2014b).

The goal of this project is to improve and advance infrastructure and fuels technologies that demonstrate the potential to reliably supply alternative transportation fuels in and for California. This study was conducted under the California Energy Commission's Public Interest Energy Research (PIER) Transportation Program. This program is designed to accelerate research, development and demonstration (RD&D) of advanced technologies and to ensure the compatibility of existing petroleum transportation fuels infrastructure with nonpetroleum alternative fuels. Specifically, this study examined materials compatibility issues in California's fuels providing system with respect to the potential RNG and ethanol and butanol blends.

This report summarizes the results of the experimental materials studies done for RNG and the alternative liquid fuels. For this program, natural gas blends with carbon dioxide (CO_2) and varying levels of hydrogen and water saturation, E10 blends with both aggressive and non-aggressive formulations, and a 55 percent butanol blend with an aggressive formulation were tested. Metal, plastic, and elastomer samples used in the infrastructure for the transport and distribution of petroleum products were exposed to these fuels for varying periods of time. These exposures were done in a cylindrical stir chamber for the liquid fuels and in a series of tubes for the natural gas exposures. The material specimens were evaluated before and after exposure for mass loss, volume change, visual appearance/discoloration, and evidence of pitting. Metals were also tested for changes in composition. Elastomers and plastics were tested for tensile strength.

CHAPTER 2: Experimental Procedures

2.1 Test Fuels

A total of 6 gaseous and three liquid fuels were used in this study. The 6 gaseous fuels all included 2 percent CO_2, along with varying levels of hydrogen (H_2) and water (H_2O), with the balance of the gas blend being methane. The gaseous blends are as follows:

- A representative RNG with 98 percent methane, 2 percent CO_2, saturated with water.
- Gas in #1 with 1 percent concentration of H_2, saturated with water.
- Gas in #1 with 5 percent concentration of H_2, saturated with water.
- Gas in #1 with 20 percent concentration of H_2, saturated with water.
- Representative RNG 98 percent methane, 2 percent CO_2, not saturated with water.
- Gas in #1 with 20 percent concentration of H_2, not saturated with water.

The liquid fuels included two blends with 10 percent ethanol, and 55 percent butanol blend. One of the two E10 blends and the 55 percent butanol blend were aggressive formulations, based on SAE J1681. For the two aggressive blends, aggressive ethanol and butanol were blended with a reference fuel C. Reference fuel C is a mixture of 50 percent isooctane and 50 percent toluene. The aggressive ethanol and butanol fuels contain contaminants that potentially could be found in the liquid fuel infrastructure system at varying levels. Aggressive ethanol contains 99 percent ethanol, 1 percent water, 5 ppm sodium chloride, 25 ppm sulfuric acid and, 75 ppm acetic acid. The aggressive ethanol composition was used as the basis for the construction of an analogous aggressive isobutanol formulation (Kas et al., 2013/2014a/ 2014b). The aggressive butanol formulation contained 99 percent ethanol, 1 percent water, 5 ppm sodium chloride, 25 ppm sulfuric acid, but with 109 ppm of isobutyric acid instead of the 75 ppm acetic acid. E10 non-aggressive fuel was a typical certification grade gasoline that contained 9.96 percent ethanol, 21.8 percent aromatics, and 5.1 percent olefins, had a specific gravity of 0.7474, and a heat of combustion of 18056 BTU/lb.

2.2 Material Samples

The test materials for the main test program consisted of metals, plastics, and elastomers. A listing of materials used for the test program is provided below for each category of material. The material lists are based on studies conducted at ORNL, a literature review conducted by ORNL, and discussions with ORNL researchers.

Metals and alloys: The metal specimens include both bare metal and plated samples. The metals selected are ones that are commonly found in the fueling infrastructure. Steel is used in underground storage tanks and piping systems. Aluminum is used in turbine pumps, valves, and nozzles. Other materials, such as bronze, brass, and nickel are used in connection, valves,

swivels, and other applications. The plated samples were tested with the full plating. A listing of the metals used in this study is provided below.

- Bare metals - 304 stainless steel (SS304), 316 stainless steel (SS316), 1100 aluminum (AL1100), 2024 aluminum (AL2024), 6061 aluminum (AL6061), nickel 200 (N200), cartridge brass (CB), phosphor bronze (PB), 4140 steel (S4140), and zinc.
- Fully plated specimens – galvanized (zinc-plated) steel (GS), chromium-plated brass (CPB), chromium-plated steel (CPS), nickel-plated aluminum (NPA), nickel-plated steel (NPS), and electroless nickel-plated aluminum (ENPA).

Elastomers: Elastomers are important components of dispenser systems and are used in sealing applications. A listing of the elastomers used in this study is provided below.

- Viton A401C (A401C), Viton B601 (B601), styrene butadiene rubber (SBR), nitrile butadiene rubber (NBR), natural rubber (NR), polyurethane (PU), neoprene (N), and a Buna-N cork blend (BN).

Plastics: Plastic materials are also widely used in fuel storage and fuel dispensing applications. The plastic materials are divided into two categories: thermoplastics and thermosets. Thermoplastics are pliable and do not change their chemical composition when heated, and are the focus of this study. Applications for thermoplastics include flexible piping systems, including as permeation barriers and liners, or as reinforcement and support for the flexible piping. A listing of the thermoplastics used in this study is provided below.

- Thermoplastics: Polyphenylene sulfide (PPS), polyvinylidene fluoride (PVDF), polytetrafluoroethylene (PTFE), polyethylene terephthalate (PET), high density polyethylene (HDPE), different nylon grades (6, 6/6), polybutylene terephthalate (PBT), polypropylene (PL), polyoxymethylene acetal copolymer (POMAC), PET co-polymers (PETG and PETP), and polyvinyl chloride (PVC).

2.3 Sample Preparation

Samples were generally cut from larger sheets into the size needed to fit the mounting fixture. Samples were all nominally cut to similar dimensions. The sizes for the samples ranged from 2.145 to 2.86 inches (5.45 to 7.26 cm) in length, 0.7325 to 0.9315 (1.86 to 2.37 cm) in width, and 0.112 to 0.2745 (0.28 to 0.70 cm) in thickness. The total sample surface area for the samples ranged from approximately 24.4 to 47.9 cm^2, with an average surface area of 36.2 cm^2. Holes were drilled into the samples in 3 locations to allow the samples to be mounted to the mounting fixture. These holes are not accounted for in the dimensions provided above. For the metal samples, the hole at the top of the sample was made larger such that and additional washer could be used to isolate the sample from the metal bolts of the mounting fixture. A picture of typical plastic samples is provided in Figure . A picture of typical metal samples is provided in Figure 2.

Samples were cleaned, sized, weighed, and photographed as part of the initial sample preparation. The size of each sample was measured with a micrometer. Plastic samples were

cleaned with an ultrasonic bath in a solution of simple green soap and water. Metal samples were cleaned with an ultrasonic bath in a solution of simple green soap and water and then with acetone. Subsequent to cleaning, samples were handled with lint-free gloves and tweezers. Samples were weighed on a Mettler Toldeo AE100 balance capable of measuring to 0.0001 g.

Figure 1: Picture of Typical Plastic Samples

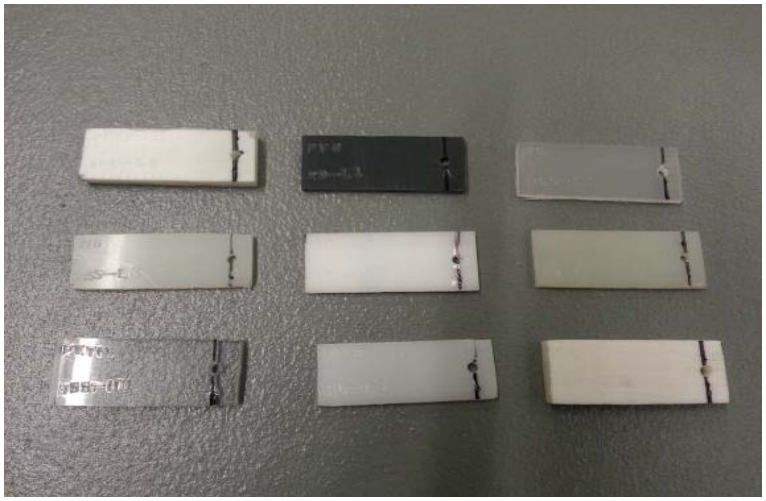


Photo Credit: Kyle Hunter, Lab Technician for CE-CERT

Figure 2: Picture of Typical Metal Samples

Photo Credit: Kyle Hunter, Lab Technician for CE-CERT

The mounting fixtures for the samples are designed to hold samples in place and isolate them from each other by Teflon spacers and washers. A Teflon crevice washer was placed between each sample to prevent sample-to-sample contact. A nut and bolt assembly was used to hold the samples onto the bracket. A picture of a mounting fixture with samples attached is provided in Figure .

Figure 3: Picture of a Mounting Fixture with Samples Attached

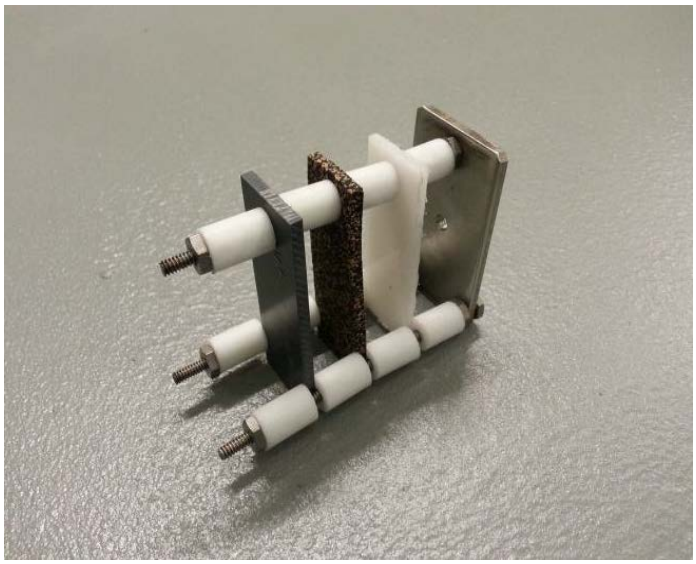


Photo Credit: Kyle Hunter, Lab Technician for CE-CERT

2.4 Exposure Vessel for RNG Fuels

A flow through exposure vessel was used to evaluate the impact of different fuels on metals, plastics, and elastomers used in the infrastructure for the transport and distribution of natural gas. The exposure vessel was designed to allow exposure of different types of materials to different types of natural gas blends over a period of several weeks/months. The exposure vessel for each fuel was a 2″ diameter pipe that was 20 feet in length. A total of 6 tubes were used to accommodate the 6 test gases. The tubes were enclosed in an insulted box to allow the tubes to all be heated to a system temperature of 105°F (40.56°C). This is an upper end temperature representing a temperature that might be found in different parts of the natural gas infrastructure system. Pictures of the exposure tubes and the exposure enclosure are provided in Figure .

Figure 4: Apparatus for the RNG Exposure Vessel

Photos Credit: Kyle Hunter, Lab Technician for CE-CERT

The gas flow through the system was taken straight from a cylinder, with a flow rate of approximately 20 cc/min. For four of the six gases, the gases were saturated with water by flowing the sample through a water bath at ambient temperature. Pictures of the water bath and inlet flow system are provided in Figure .

Figure 5: Picture of Flow System (left) and Water Bath (right)

Photo Credit: Kyle Hunter, Lab Technician for CE-CERT

The samples were placed into the chamber using a wire support, with the samples being hung from the support with a tungsten wire. A total of two of each type of plastic, elastomer, and metal samples were used in the exposure chamber for each fuel. A picture of the wire holder and the samples attached to the wire holder is provided in Figure .

Figure 6: Pictures of Sample Attached to Wire Holder

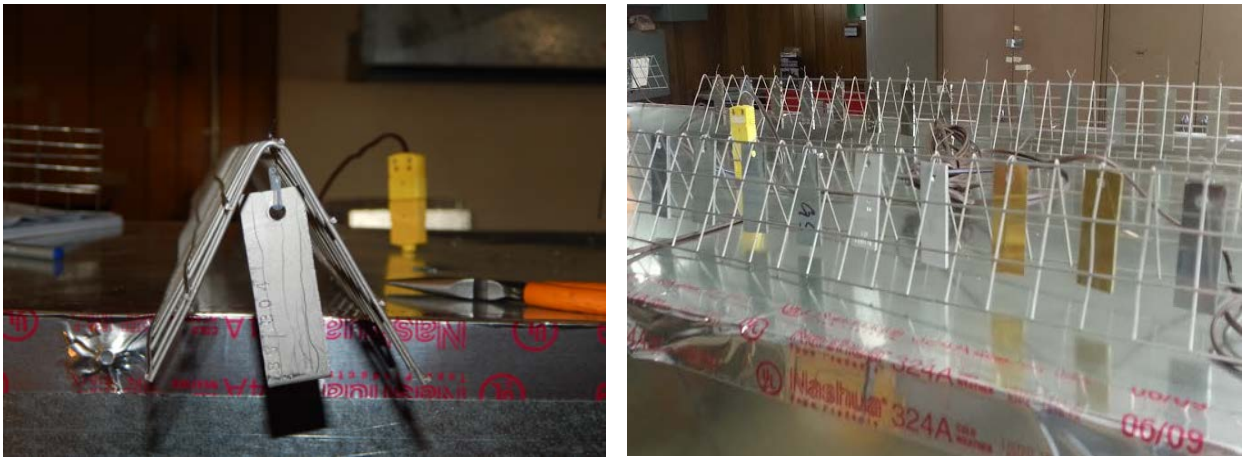


Photo Credit: Kyle Hunter, Lab Technician for CE-CERT

The RNG gas exposures were conducted for an initial period of four weeks for all of the samples. The samples were weighed, evaluated for volume, and photographed at that time. The

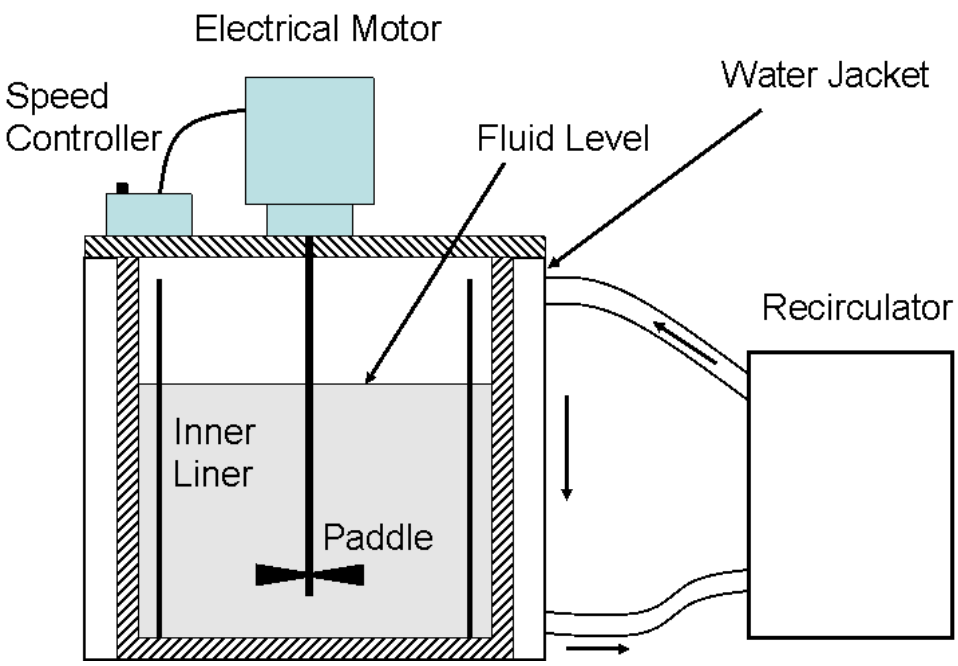
samples were then placed back into the exposure vessel and the exposures were extended another eight weeks.

2.5 Stir Chamber for Liquid Fuels

A stir chamber was used to evaluate the impact of different fuels on metals, plastics, and elastomers used in the infrastructure for the transport and distribution of petroleum products. The stir chamber was designed to allow exposure of different types of materials to different types of fuels over a period of several weeks/months.

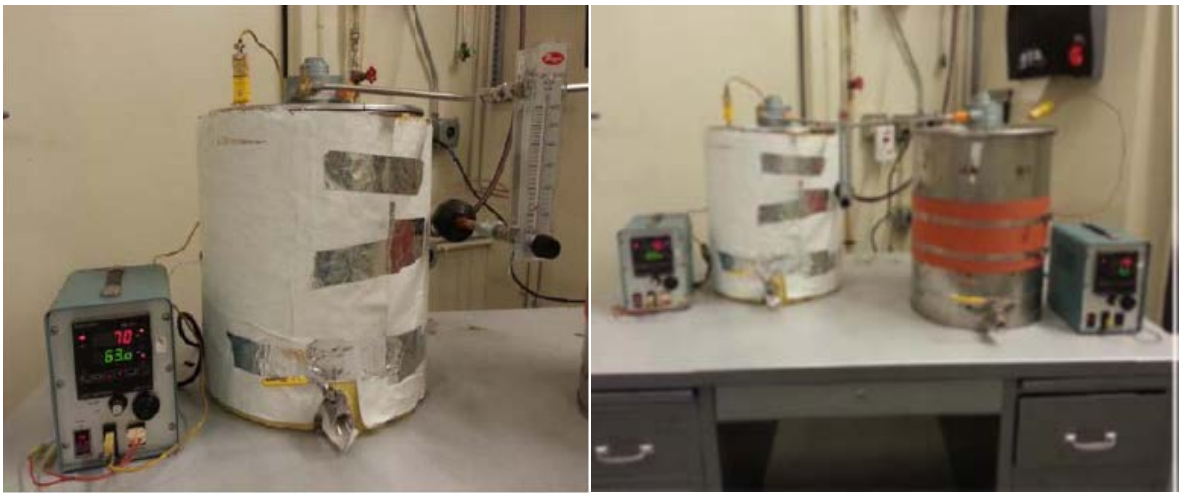
The stir chamber was a stainless steel chamber 17″ high with a circumference of 14″ that housed mounting brackets for different samples. The stir chamber had a paddle that was rotated at a constant speed to maintain a flow in the chamber. The chamber was heated to a temperature of 60°C for these experiments. Heater coils were placed on the outside of the stainless steel drum to enable the heating of the drum to the 140°F (60°C) required for the testing. The heating system has a power rating of 1200 watts and is controlled by a Love Controls series No. 2600 heater controller. A schematic representation of a typical stir chamber is provided in Figure . Figure 7 shows a picture of the stir chamber with the insulation wrapped around the outside, and two stir chambers side by side, one with and one without the insulation for comparison. The temperature controller is shown beside the stainless steel vessels. The temperature inside of the stir chamber was measured by a thermocouple that is connected through the top of the chamber.

Figure 7: Schematic Representation of a Stir Chamber



Photos Credit: Kass et al., 2011

Figure 8: Stir Chamber #1 (Left) and Stir Chambers #1 & #2 (Right)



Photos Credit: Junior Castillo, Lab Manager for CE-CERT

The samples were mounted inside of the chamber on brackets attached to the inside wall of the stir chamber. Figure shows a view of the inside of the stir chamber with the brackets for the sample holders attached. A picture with the mounting fixtures attached to the brackets inside of the chamber is provided in Figure 9. A total of four of each type of plastic and elastomer samples and three of each type of metal sample were used in the stir chamber for each fuel exposure. For the plastic and elastomer sample types, three samples of each type were immersed in the fuel while one sample was placed in the upper portion of the chamber where it was exposed to vapors. For the metal sample types, two samples of each type were immersed in the fuel while one sample was placed in the upper portion of the chamber where it was exposed to vapors.

Figure 9: Inside View of Stir Chamber

Photo Credit: Junior Castillo, Lab Manager for CE-CERT

Figure 10: Picture of the Inside of the Stir Chamber with the E10 Fuel

Inside view of stir chamber with sample mounting brackets installed

Photo Credit: Junior Castillo, Lab Manager for CE-CERT

The plastic/elastomers and the metals were exposed in separate stir chambers for each fuels. The stir chamber exposures were conducted for a period of 4 weeks for the metal and elastomer samples and 16 weeks for plastics. The stir chamber was sealed for the duration of the test, with the exception of when it is opened to remove the elastomer samples from the chambers that also included plastics. Additionally, for the E10 aggressive fuel, the samples were removed and weighed and dimensionally measured after eight weeks of the full 16 week exposure to provide information on the impact fuel effects a mid-point in the plastics exposure.

2.6 Materials Testing

2.6.1 Metals and alloys

The metal testing included measuring volume and mass change, change in visual appearance on each specimen exposed in liquid and vapor phases of test fluids. Additional tests were also conducted on a subset of samples to evaluate the chemical composition of any discoloration observed on the samples.

Samples were examined using an Optical microscope model, Hirox KH-7700 Digital Microscope with MXG-2016Z, with a 40-320x zoom lens. Optimal microscope was part of the University of California at Riverside's (UCR's) Material Sciences Engineering Department. We also evaluated the potential of using a scanning electron microscope (SEM), but the initial sample surface is too rough to get any useful data from SEM observation. Additionally, there was not really any surface corrosion removal/pitting formation, so we concluded that that optical imagines would be sufficient for the investigations being conducted.

Prior to and subsequent to the fuel exposures, the weights and dimension of the samples were measured and recorded. The sample weights were measured with a Mettler Toldeo AE100 balance and the sample dimensions were measured with a micrometer.

2.6.2 Elastomers/Plastics

The elastomer and plastic testing included measuring volume, mass, and hardness changes for both wetted and dried specimens. Measurements of tensile strength were also made.

Prior to and subsequent to the fuel exposures, the weights and dimension of the samples were measured and recorded. The sample weights were measured with a Mettler Toldeo AE100 balance and the sample dimensions were measured with a micrometer. For the post-exposure analyses, the samples were weighted and measured for volume change in a wet state (that is, immediately after removal from the stir chamber prior to drying) and in a dry state. For the dry state, the samples were dried at 140°F (60°C) for 20 hours for the elastomer samples and for 65 hours for the plastic samples.

A visual examination was performed and pictures were taken of each sample before and after exposure to determine any discoloration or degradation. Samples with and without visual degradation were examined with an optical microscope discussed above.

Ultimate tensile strength or tensile strength properties were measured using an Instron 5969 model tensile strength tester, with a 50 kN load cell, as shown in Figure 11. These properties included tensile strength as well as tensile elongation. Tensile strength was calculated by the maximum load in pounds-force at the time of failure divided by the average cross-sectional area of the material in square inches. The percent elongation was determined by measuring the change in gage length from the original specimen to the fuel affected specimen. For the liquid fuels, the tensile strength test was conducted on one sample that is not placed in the stir chamber for each of the plastic and elastomer samples, on one plastic and elastomer sample immersed in the liquid fuels, and for one plastic and elastomer sample that was exposed to vapors. For the RNG samples, tensile strength was conducted for one pre and one post sample for each of the plastic and elastomer samples. For the plastic samples, tensile strength measurements were obtained for all RNG fuel exposures, while for the elastomers, only samples after exposure in the RNG exposure chamber, for the baseline water saturated gas, for the baseline gas plus 20 percent H_2, and for the baseline gas with the 20 percent H_2 that was water saturated were tested for tensile strength. Samples were machined to the correct dimensions to fit in the tensile strength tester following drying and their final weighing, mass determination, and characterization of their visual appearance. A picture of samples machined for the tensile strength machine is provided in Figure .

Figure 11: Instron 5969 Model Tensile Strength Tester

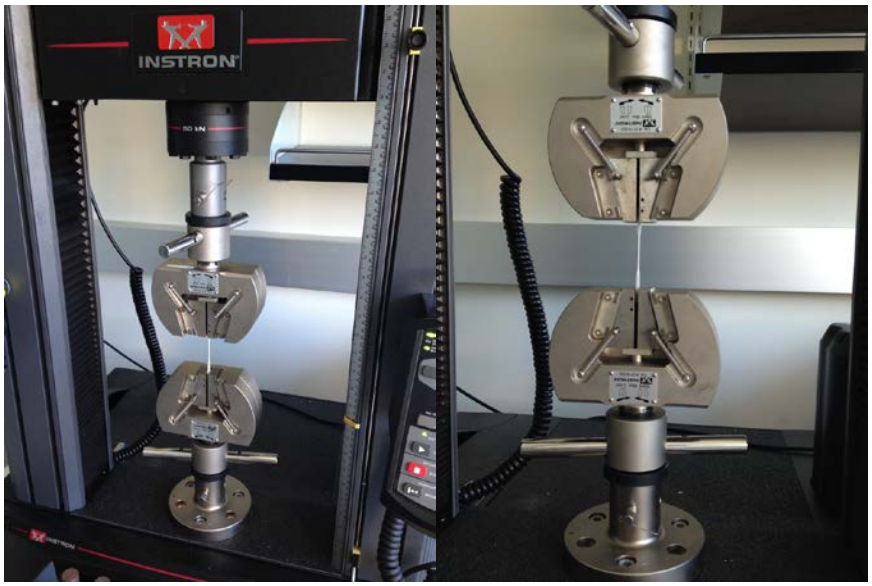


Photo Credit: Vincent Van, Lab Technician for CE-CERT

Figure 12: Picture of Sample Machined for Tensile Strength Testing

Unexposed NR samples ready for tensile strength testing

Photo Credit: Vincent Van, Lab Technician for CE-CERT

CHAPTER 3:
Material Exposure Testing Results

The material exposure results are presented in the following section. This includes the results in terms of visual appearance with the naked eye and under and optical microscope, mass change, and volume change for elastomers, plastics and metals. Tensile strength results are also included for elastomers and plastics and XPS results are presented for the metals. The different materials were exposed to natural gas blends with different levels of hydrogen and water or liquid fuels (E10, E10 aggressive, B55 aggressive) and were subsequently evaluated for changes in properties.

3.1 Visual Appearance by Naked Eye and Optical Microscope

3.1.1 Natural gas

3.1.1.1 Elastomers

Elastomer samples that were exposed to natural gas did not show a difference in appearance.

3.1.1.2 Plastics

Plastic samples that were exposed to natural gas did not show a difference in appearance.

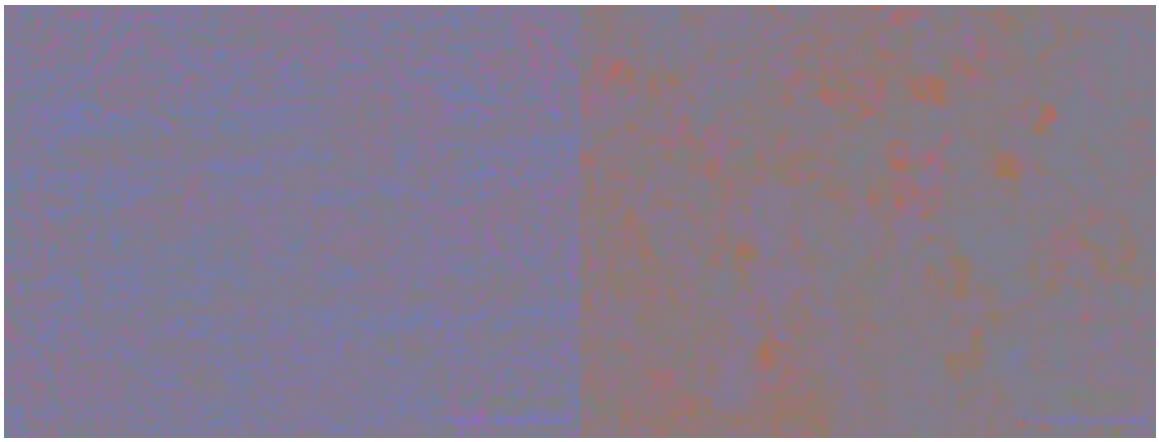
3.1.1.3 Metals

The majority of metal samples that were exposed to natural gas did not show a difference in appearance. The only changes seen were for metal samples exposed to the baseline wet +20 percent H_2 gas. S4140 samples exposed to the baseline wet +20 percent H_2 gas developed rust on the surface, as seen in Figure 13 and under higher magnification in Figure 14.

Figure 13: S4140 Samples Exposed to the Baseline Wet +20 Percent H_2 Gas.

As seen above the samples exposed to natural gas/water developed rust.

Figure 14: S4140 Samples Before (Left) and After (Right) Exposure



Microscope pictures of S4140 samples at 320 magnification after exposure to natural gas.

Photo Credit: Vincent Van, Lab Technician for CE-CERT

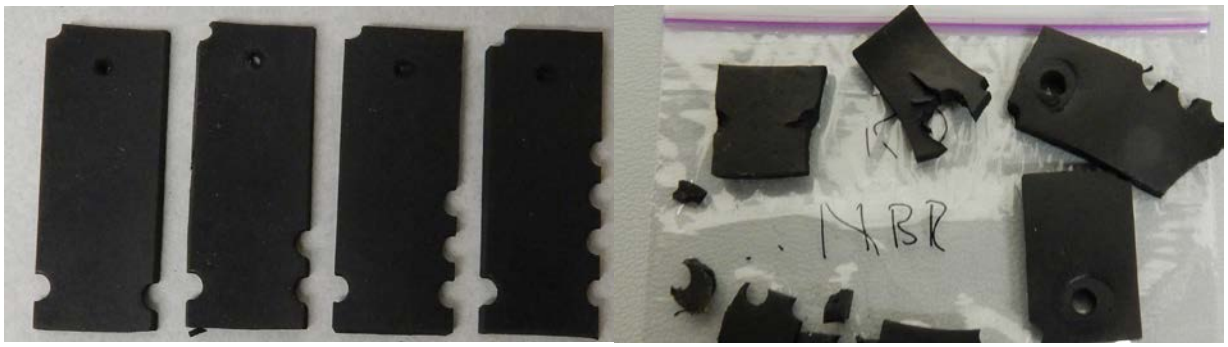
3.1.2 Liquid Fuel

3.1.2.1 Elastomers

Elastomer samples exposed to the different liquid fuels showed the most significant visual changes of any of the studied materials compared to their unexposed counterparts for the liquid fuel exposures. Each fuel (E10, E10 aggressive, and B55 aggressive) affected the samples in a similar way.

All of the elastomers besides PU and fluorocarbons/Vitons (A401C, B601) increased in size while wet and then decreased in size when dried. SBR, N, and BN, all swelled slightly upon removal from the chamber. SBR and N returned to approximately their original size after being dried, while BN shrank to dimensions slightly smaller than its original size. NR and NBR swelled the most. This caused some of the NBR samples to break apart. This can be seen in the comparison between the unexposed NBR samples and the exposed NBR samples in **Figure 15**. As a result of the swelling from the fuel exposure, some NR samples showed wrinkles after subsequent drying that can be seen under closer examination under a microscope, as seen Figure 16. After drying, the NBR samples became brittle and broke. The NR samples shrank after drying, but remained elastic. The PU and the fluorocarbons/Vitons (B601, A401C) samples showed no visual changes.

Figure 15: NBR Sample Before (Left) and After (Right) Exposure



As seen above the samples exposed to the E10 fuel became swollen and brittle.

Photo Credit: Vincent Van, Lab Technician for CE-CERT

Figure 16: NR Sample Before (Left) and After (Right) Exposure

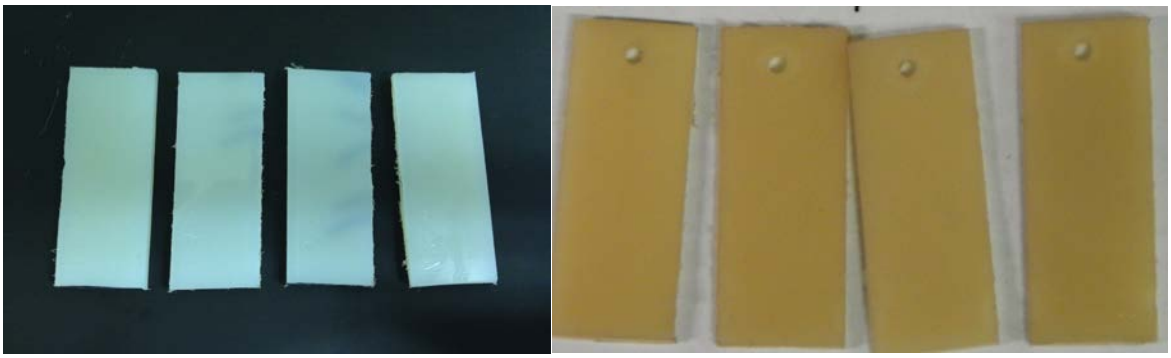
Microscope pictures of NR samples at 200 magnification after exposure to B55 aggressive fuel

Photo Credit: Vincent Van, Lab Technician for CE-CERT

3.1.2.2 Plastics

Discoloration for the plastics was common after exposure to the different fuels. Plastic samples that were discolored mainly gained a yellowish tint. PBT acquired a minor yellow tint from exposures to E10 and B55 aggressive fuels. PETG acquired a minor yellow tint and a glossy exterior from E10, E10 aggressive, and B55 aggressive fuel exposures. Nylon samples (N6, N6/6) were affected the most and changed to a yellow tint. The E10 aggressive fuel discolored nylon samples the most and produced a slightly darker color compared to the E10 and B55 aggressive fuels, which can be seen in Figure 17. Figure Figure 18 shows the color change of Nylon 6/6 under magnification. PVDF showed some pinkish discoloration for with the E10 aggressive fuel, but no changes for the E10 and B55 aggressive fuels, as seen in Figure 19. Plastics that did not show any visual color changes included PET, PTFE, PPS, HDPE, PL, POMAC, and PETP.

Figure 17: N6/6 Before (Left) and After (Right) Exposure



As seen above the samples exposed to the E10 aggressive fuel became discolored.

Photo Credit: Vincent Van, Lab Technician for CE-CERT

Figure 18: N 6/6 Sample Before (Left) and After (Right) Exposure

Microscope pictures of N 6/6 samples at 40 magnification after exposure to E10 aggressive fuel.

Photo Credit: Vincent Van, Lab Technician for CE-CERT

Figure 19: PVDF Before (Left) and After (Right) Exposure

As seen above the samples exposed to the E10 aggressive fuel became discolored.

Photo Credit: Kyle Hunter, Lab Technician for CE-CERT

Some plastics experienced visually observable swelling and shrinking after exposure to the E10, E10 aggressive, and B55 aggressive fuels. PVC and PETG swelled the most for all fuels and maintained a majority of their increased volume when dried. While wet and dry, PVC was deformed in shape, which can be seen in Figure 20. Note that Figure 20 does not show the increase in size that was observed for the PVC because the after exposure picture is somewhat zoomed out. HDPE and PL also swelled, but by a small amount, and these samples returned to near to their original size after drying. The rest of the plastics did not seem to increase in size, as visible by the naked eye.

Figure 20: PVC Sample Before (Left) and After (Right) Exposure

PVC samples exposed to E-10 aggressive fuel became swollen and disfigured during exposure

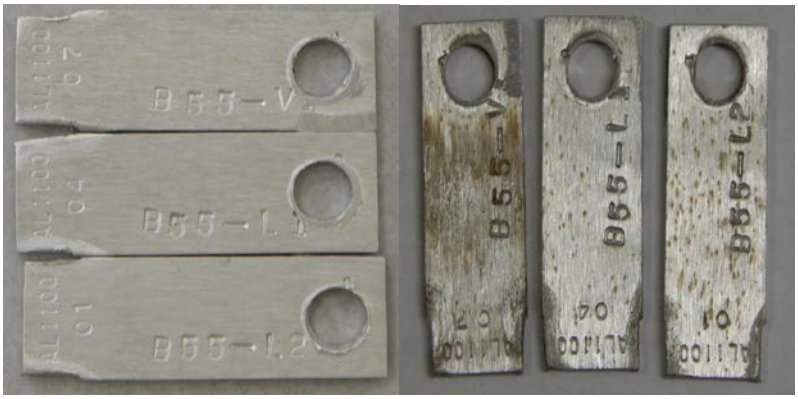
Photo Credit: Vincent Van, Lab Technician for CE-CERT

3.1.2.3 Metals

The metal samples were the least impacted of the different sample types. Visually, metal samples that were exposed to E10, E10 aggressive, and B55 aggressive fuels did not show a difference in dimensions to the naked eye. Stainless steel samples (SS304, SS316) were not affected by exposure to the E10, E10 aggressive, or B55 aggressive fuels. Chrome plated samples (CPB, CPS) acquired a surface build up after testing with the different fuels.

The main effect seen for the metals was a discoloration from corrosion. The majority of samples that were exposed to the fuel vapors appeared to show a greater visual change compared to samples that were exposed to the fuels directly. All aluminum samples were prone to mild rust for the E10 aggressive and B55 aggressive fuels, with the latter affecting the aluminum samples the most. Aluminum that was exposed to the B55 aggressive fuel can be seen in Figure 21**,** along with the original unexposed samples. Nickel-plated samples (NPS, NPA, ENPA) all acquired a brown tint after exposure to the E10, E10 aggressive, and B55 aggressive fuels. S4140 and CB were the most discolored metal samples for both E10 aggressive and B55 aggressive fuels, and showed major rust, as shown in Figure 22Figure . S4140 exposed to B55 aggressive fuel can be seen under magnification in Figure 23. PB, GS, Zinc, and N200 also had heavy dark brown stains after exposure to the E10 aggressive and B55 aggressive fuels.

Figure 21: AL1100 Samples Before (Left) and After (Right) Exposure



AL1100 began to rust from exposure to B-55 aggressive, the worst case being the vapor sample.

Photo Credit: Kyle Hunter, Lab Technician for CE-CERT

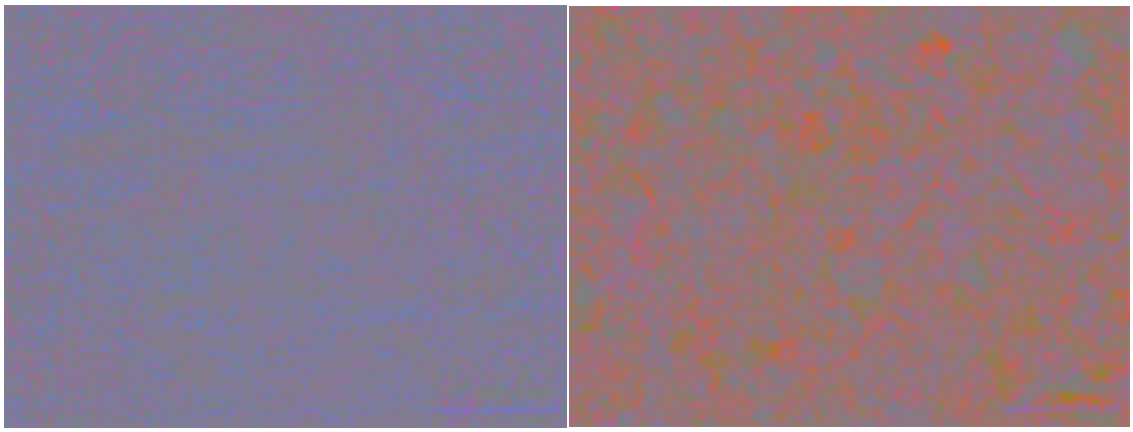
Figure 22: Pictures for S4140 (Top) and CB (Bottom) Metal Samples

Photo Credit: Vincent Van, Lab Technician for CE-CERT

Before (left) and after exposure (right)

Photo Credit: Vincent Van, Lab Technician for CE-CERT

Figure 23: S4140 Samples Before (Left) and After (Right) Exposure



Microscope pictures of S4140 samples at 200 magnification after exposure to B55 aggressive fuel.

Photo Credit: Vincent Van, Lab Technician for CE-CERT

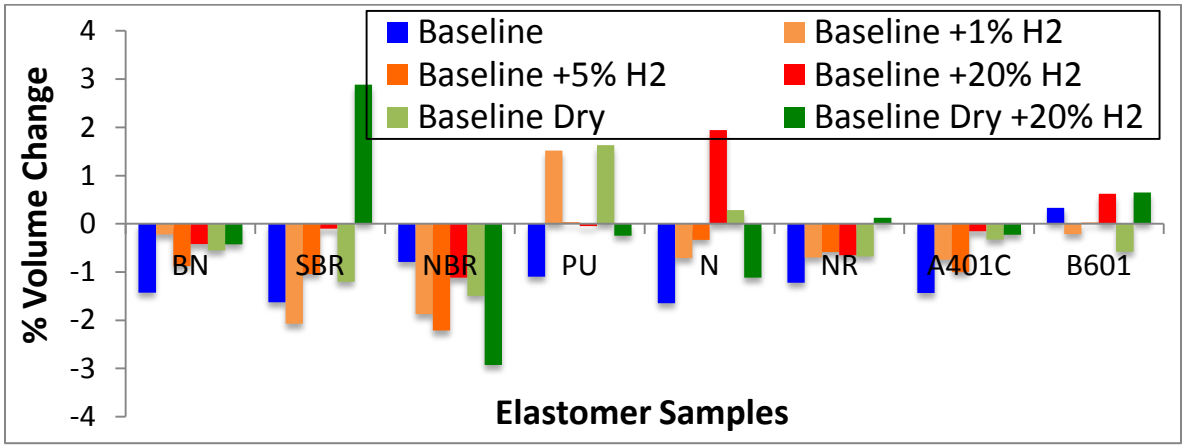
3.2 Volume Change

3.2.1 Natural gas

3.2.1.1 Elastomers

Figure 24 represents the percent volume change of elastomer samples that were exposed to natural gas. Elastomer samples showed very minor variations in volume between the unexposed and exposed samples. The elastomer samples had a volume change of less than 3 percent for all samples, with the volume change for most samples being within 2 percent. The volume change was a reduction in size for most samples, although a few samples did show increases in size.

Figure 24: Percent Volume Change of Elastomer Samples

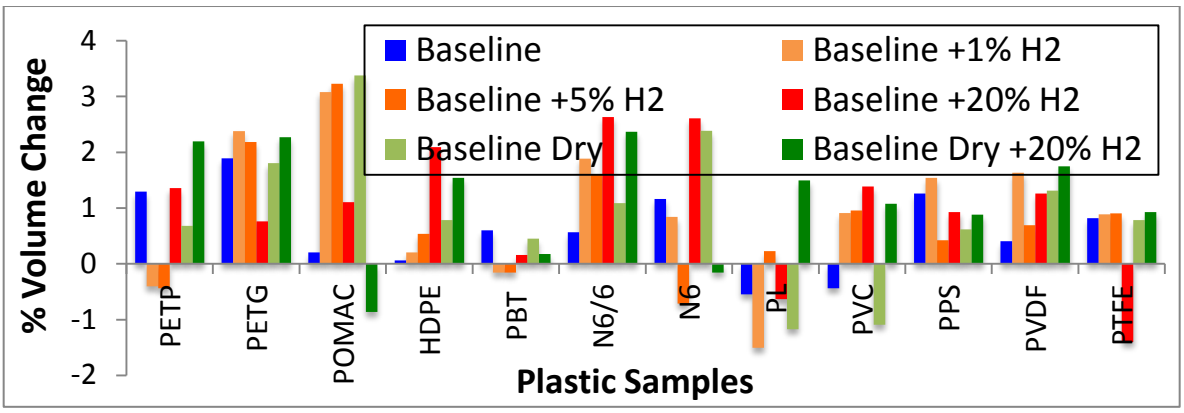


Source: CE-CERT

3.2.1.2 Plastics

Figure 25 represents the percent volume change of plastic samples that were exposed to natural gas. All plastic samples had percent volume changes of less than 3.5 percent, with many samples have volume changes below 2 percent. The majority of plastic samples show a minor increase in percent volume change, with a few samples showing a slight decrease in volume.

Figure 25: Percent Volume Change of Plastic Samples

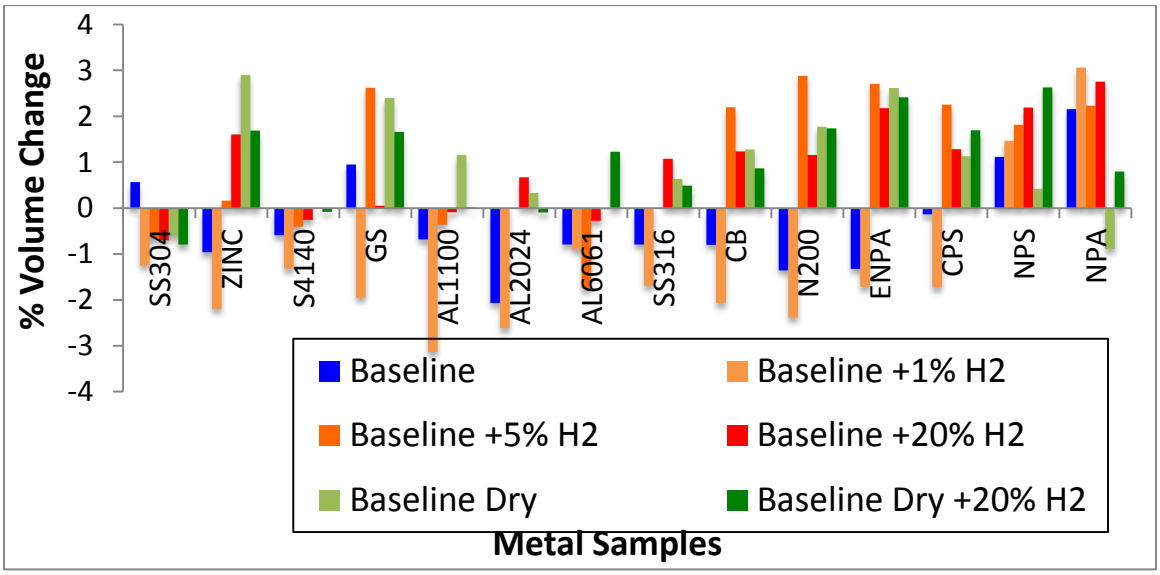


Source: CE-CERT

3.2.1.3 Metals

Figure 26 represents the percent volume change of metal samples that were exposed to natural gas. Metal samples have a percent volume change of less than 3.1 percent. The majority of metal samples show a minor increase in percent volume change. For the baseline wet and baseline + 1 percent H_2 wet exposures, the majority of samples lost a slight amount of volume.

Figure 26: Percent Volume Change of Metal Samples



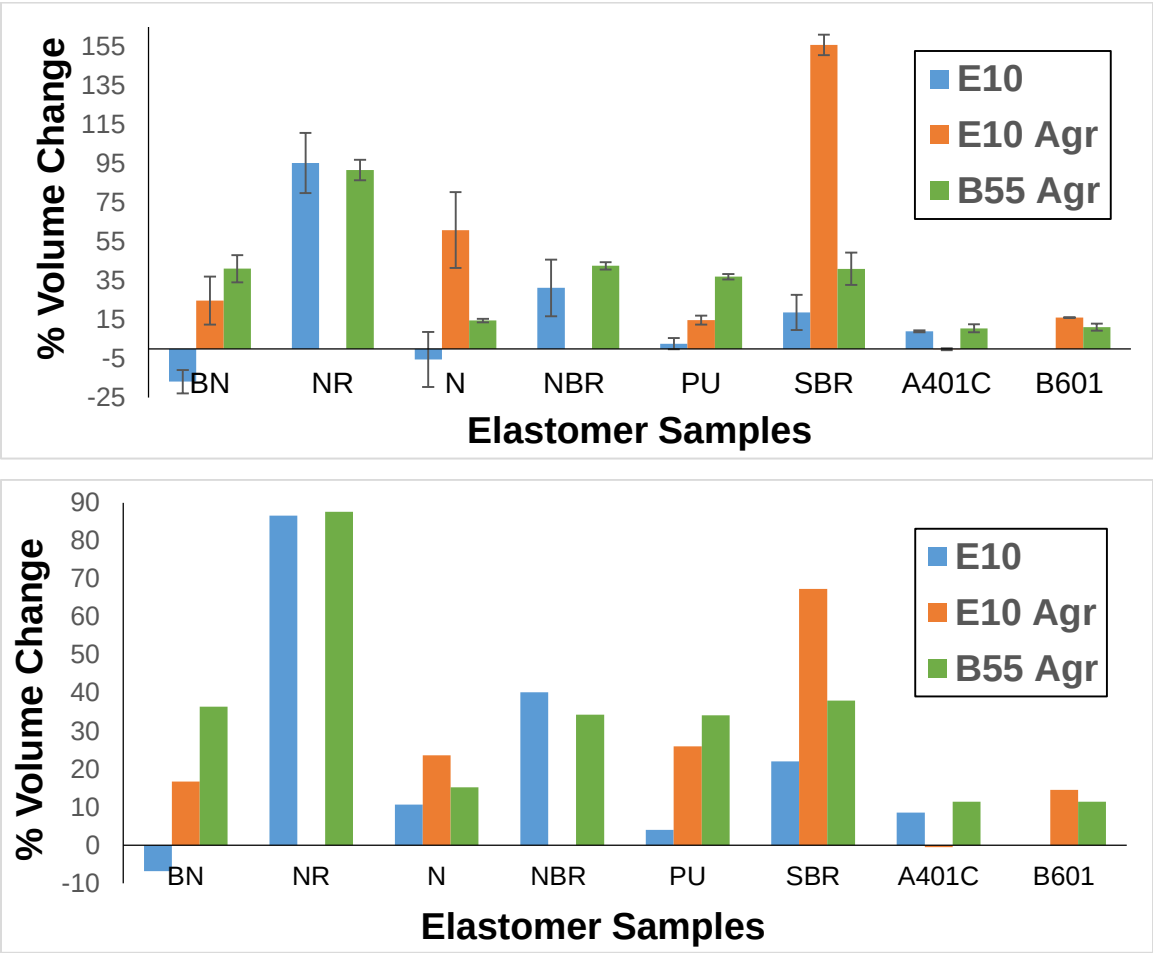
Source: CE-CERT

3.2.2 Liquid Fuel

3.2.2.1 Elastomers

The majority of the elastomer samples increased in volume when wet and then decreased in volume when dried. Elastomers generally showed greater volume changes compared to the plastics or metals. Comparisons between wet and dried samples that were exposed to the fuel directly and to fuel vapors can be seen in Figure 27 and Figure 28, respectively, for the before and after drying exposures. Liquid samples usually had a higher volume percent change compared to vapor samples. NR and NBR samples are missing information for E10 aggressive fuel exposure due to damage, while B601 was not available for E10 fuel exposures.

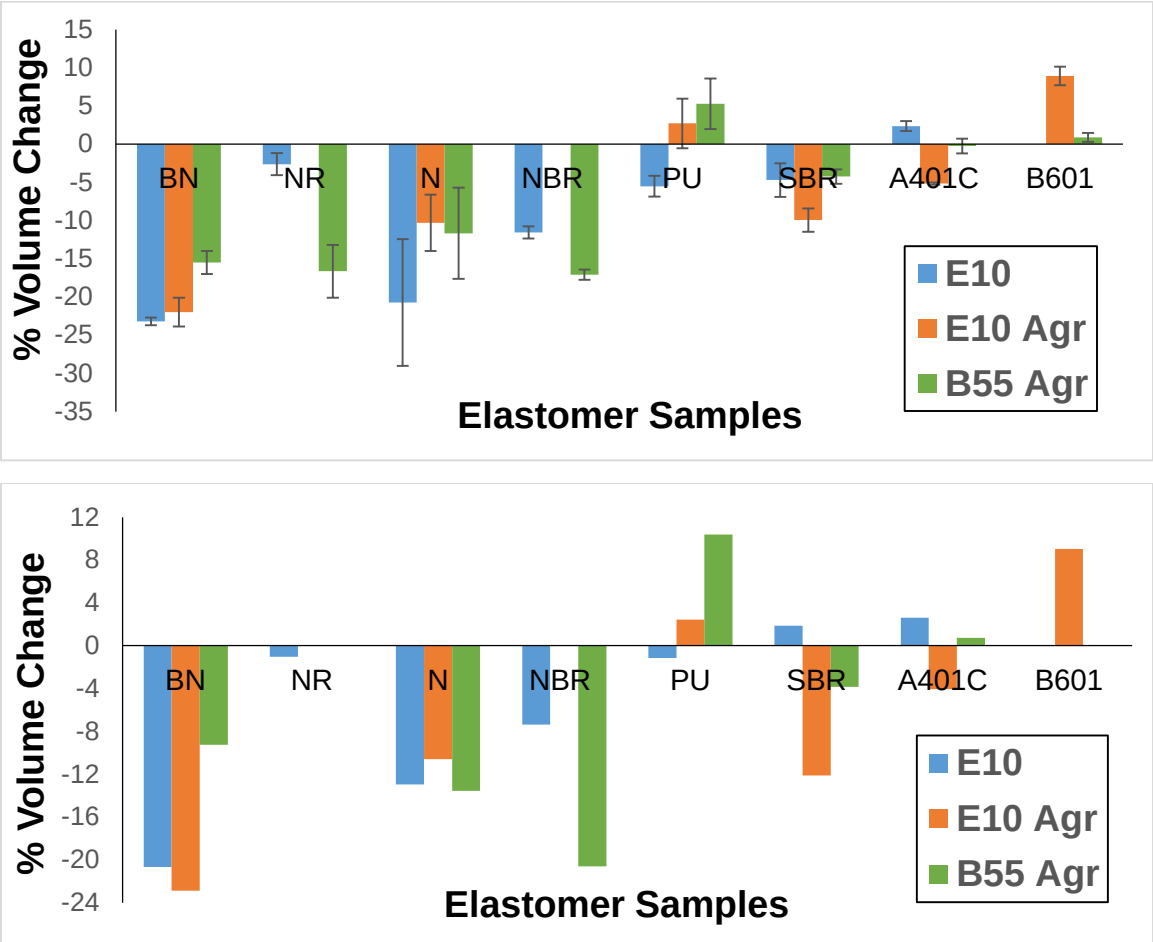
Figure 27: Percent Volume Change of Elastomer Samples Before Drying



Volume change of liquid (top) and vapor (bottom) samples, Errors Bars Represent ± One Standard Deviation

Photo Credit: Vincent Van, Lab Technician for CE-CERT

Figure 28: Percent Volume Change of Elastomer Samples After Drying



Volume change of liquid (top) and vapor (bottom) samples

Photo Credit: Vincent Van, Lab Technician for CE-CERT

Fluorocarbons (A401C, B601) generally showed the smallest volume change after exposure to the different fuels, with less than a 16 percent volume increase. These volume increases are in a similar range to those found by ORNL in their studies, which ranged from about 10 to 25% for a broader range of fluorocarbons (Kass et al., 2011/ 2012a,b) and from about 15 to 22% for A401C and B601 specifically for alcohol fuel exposures (Kass et al., 2013/ 2014a). The fluorocarbons showed a slight peak in volume swell at about the E20 level and a slight tailing off of swell about E50, but generally did not show strong differences as a function of oxygen content (Kass et al., 2012a,b) or between ethanol and butanol content (Kass et al., 2013/ 2014a). After drying the B601 retained about a 10 percent increase in volume for the E10 fuel, while the A401C showed mixed results some samples showing volume reductions and others showing volume increases compared to their original volume. For the fluoroelastomers, the ORNL results showed a more consistent retention of about 7 percent or less after drying (Kass et al., 2011 2012a,/; 2013/ 2014a), whereas our results were more mixed.

E10 aggressive fuel caused SBR to have the largest change at about 155 , respectively, for submerged samples. A change of 87 percent was seen for SBR samples that were submerged in E10 before drying. The vapor exposure SBR samples showed smaller increases in volume, ranging from 67 percent for the E10 aggressive to 22 percent for the E10. The relatively high volume change seen for the SBR exposures to the E10 aggressive fuel were similar to, but slightly greater than, those reported by ORNL (Kass et al., 2011; 2012; 2013; 2014a). ORNL also showed a strong drop off of volume swell for higher oxygen contents, with volume swell dropping off to about 70% at E35 (the approximately oxygen equivalent of B55), about 35% for E55, and to about 5% for E85 (Kass et al., 2012), as a well as a drop for a B24 fuel (Kass et al., 2013; 2014a), consistent with the smaller volume increases seen for the B55 aggressive fuel in our study. After drying the liquid exposed SBR samples shrank to 90 to 96 percent of their original volume. The vapor exposure SBR samples shrank to 88 to 96 percent of their original volume for the E10 aggressive and B55 aggressive samples, respectively, but retained some of the volume increase for the E10 fuel. SBR samples for the ORNL study showed volume reductions on the order of 15 to 18 percent (Kass et al., 2011; 2012; 2013; 2014a), slightly greater reductions in volume than what was found in this study.

NR and NBR were only available for the E10 and B55 aggressive fuels, which had an average percent volume change of about 90 to 95 and 30 to 45 percent, respectively, before drying. The volume changes for the NBR samples are similar to those seen in the ORNL work, although the E10 aggressive samples are missing from our data set. Kass et al. found a strong dependence in volume swell as a function of alcohol content (Kass et al., 2012), with decreasing swell for higher oxygen contents, but not strong differences between ethanol and butanol (Kass et al., 2013; 2014a). After drying, NBR showed decreases of 17 to 21 percent below the original sample volume for the B55 aggressive exposures and 7 to 12 percent below the original sample volume for the E10 exposures. The reductions for the NBR samples were similar to those seen by ORNL in their studies, which ranged from 10 to 18 percent less than the original volume (Kass et al., 2011; 2012; 2013; 2014a).

N showed volume changes from a 60 percent increase to a slight decrease in volume for the liquid and vapor exposures, with again the E10 aggressive fuel showing the greatest increases and the E10 fuel showing the smallest volume changes. The volume increases for the N were comparable to those seen by ORNL, which reported approximately 60 to 80 percent increases for lower level ethanol/butanol exposures (Kass et al., 2011; 2012, 2013; 2014a). They also showed a drop in volume swell with increasing ethanol content, with the volume swell down to about 40 percent for a E50 blend and down to zero for a E85 blend (Kass et al., 2012). The N samples showed volumes between 10 to 20 percent lower than their original volume following drying. The N samples for the ORNL studies showed volume reductions on the order of 17-20, in the range of, but generally slightly higher than, the values found in this study (Kass et al., 2011; 2012; 2013; 2014a).

3.2.2.2 Repetitive

PU showed volume increases ranging from 15 to 36 percent for the liquid and vapor exposures for the E10 aggressive and B55 aggressive blend exposures. The E10 fuel, on the other hand,

showed volume changes of less than 5 percent after drying. For the PU samples, ORNL showed more consistent increases of approximately 40% for the different aggressive alcohol blends, which is comparable to values reported in this study for the B55 aggressive exposures (Kass et al., 2011; 2012; 2013; 2014a), but greater than the volume increases found here for the E10 and E10 aggressive exposures. The BN samples also show a wider range in volume change from -17 to 41 percent for the liquid and vapor exposures, with again the B55 aggressive fuel showing the greatest increases and the E10 fuel showing the volume decreases. BN samples after drying lost volume compared to PU samples. BN lost about 15 to 25 of their original volume, while PU retained close to 5 to 10 percent of the increased volume for the B55 aggressive fuel, but decreased up to 6 percent below its original weight for the E10 exposures. For the ORNL studies, PU samples showed more consistent reductions ranging from -1 to -12, whereas this study showed some reductions and some increases (Kass et al., 2011; 2012; 2013; 2014a).

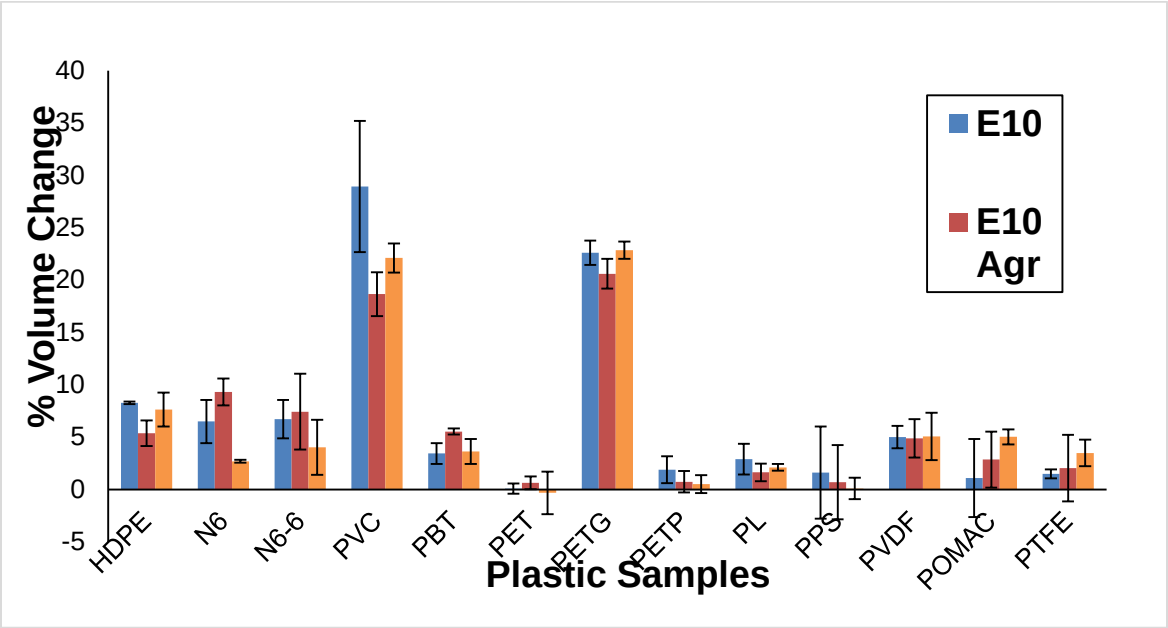
For elastomers and other materials, volume expansion is a function of the mutual solubility between the material and the fluid or fuel. Solvents (test fuels) and solutes (elastomers) having similar solubility parameters will have a greater affinity for permeation and dissolution than those with dissimilar values. ORNL has evaluated the compatibility of fuels and sample materials using the Flory-Huggins model using the Hansen solubility parameter methodology (Kass et al., 2012a,b/ 2013/ 2014a). This type of analysis can help predict the potential for swelling for elastomers for in a given solvent or fuel. Specifically, the relative potential for volume swell can be assessed by comparing the solubility distance for each elastomer as a function of the fuel it is being exposed to compared to interaction radius of the polymer, where the interaction radius represents the zone of high solubility for a given elastomer independent of the solvent/fuel. The solubility between the fuel and elastomer is expected to be moderate to high, low to moderate, or negligible to low, respectively, depending on whether the solubility distance is less than, roughly equal to, or higher than the interaction radius. For the materials evaluated by ORNL via this analysis, moderate to high swelling was predicted for SBR, NBR, and N, whereas low to moderate swelling was predicted for fluoroelastomers and PU. This is consistent with the results found in our study. This analysis also predicted higher swelling for fuels containing alcohols, with ethanol based fuels showing the potential for more swelling compared to butanol.

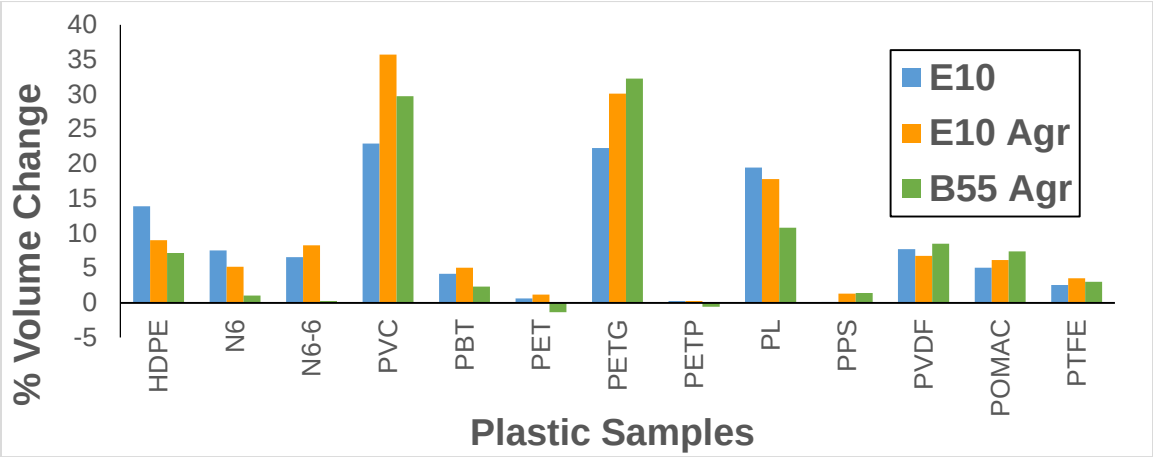
The volume reductions after drying represent different phenomena, where the test fuel is being removed from the elastomer. For samples shrinking to volumes less than their original sample volume, this indicates the dissolution and extraction of one or more of the components for the elastomer in addition to the removal of the fuel. For elastomers, these components could be plasticizers that are typically phthalate chemicals added to improve pliability. The removal of these plasticizers could lead to embrittlement or the potential to crack under compression. Previous studies of elastomers exposed to fuels by ORNL suggest that alcohol fuels showed similar levels of shrinkage to those for a reference C gasoline, suggesting the additional alcohol contents did not significantly affect the overall shrinkage of these materials. In cases such as fluorocarbons, there was even some retention of the test fuel in the microstructure, as the volumes for the samples even after drying were higher than those of the original/unexposed samples.

3.2.2.3 Plastics

Figure 29 and Figure 30 present the comparison of percent volume change of wet and dried plastic samples, respectively, that were exposed to E10, E10 aggressive, and B55 aggressive fuels and fuel vapors with error bars representing one standard deviation. The majority of the liquid and vapor plastic samples increased in volume after exposure. The samples had the largest volumes immediately after removal from the chamber, while wet. After drying the samples shrank, but still had a larger volume then their original measurements, which can be seen in Figure 30.

Figure 29: Percent Volume Change of Plastic Samples Before Drying

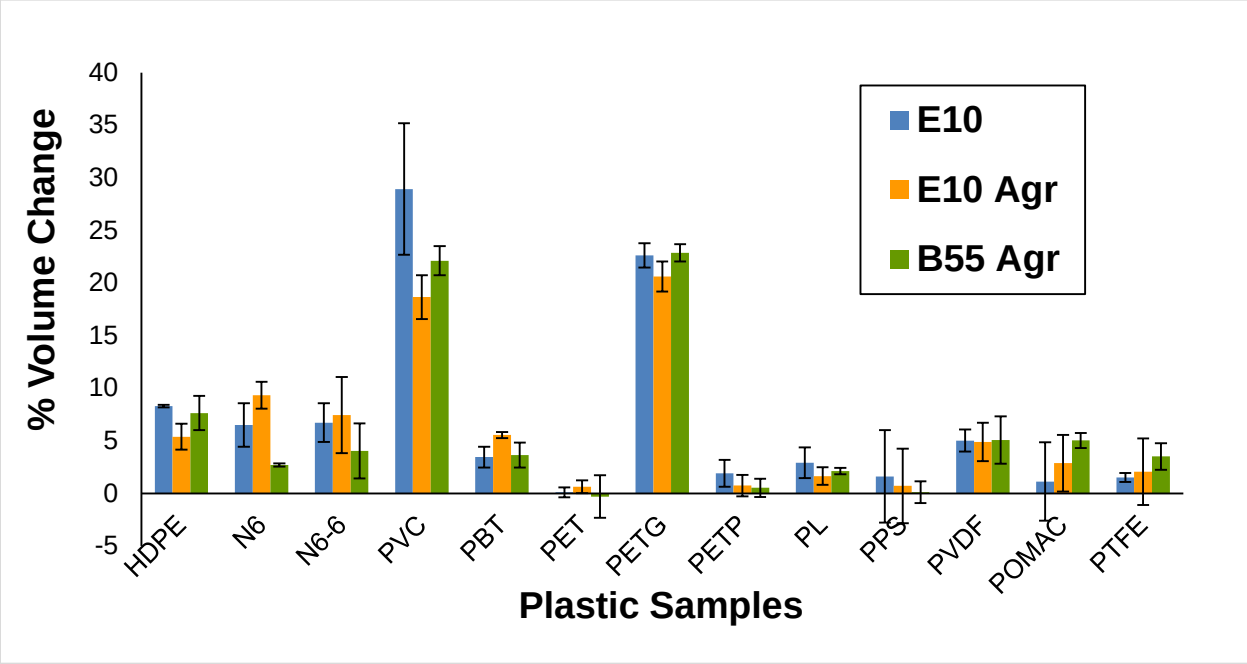


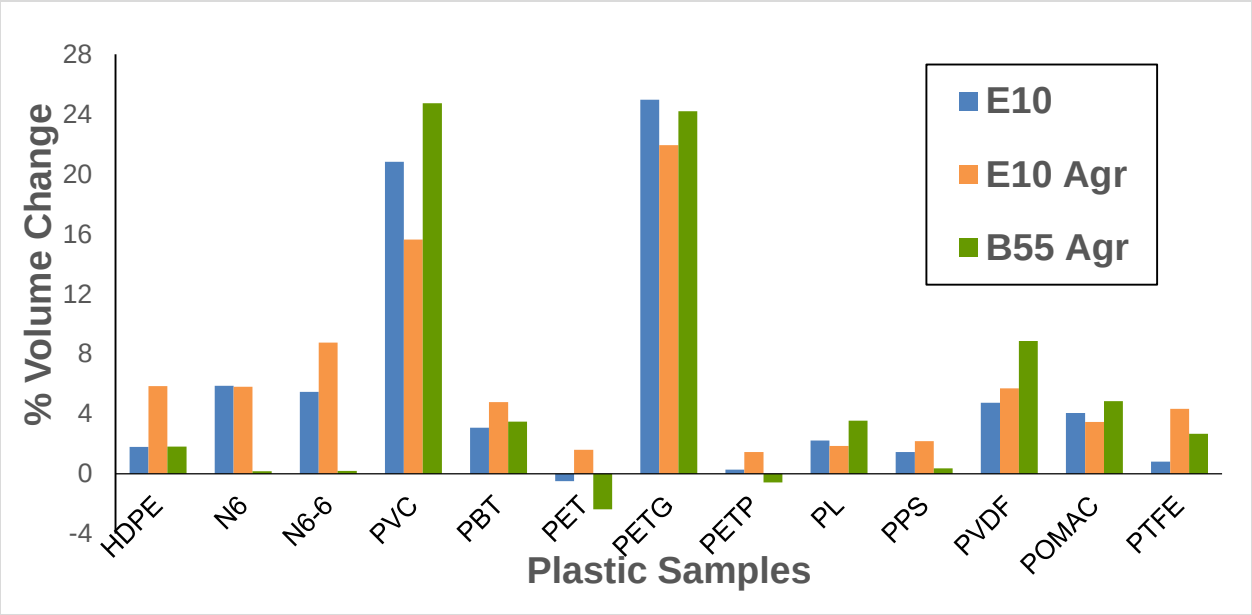


Volume change of liquid (top) and vapor (bottom) samples, Errors Bars Represent ± One Standard Deviation

Photo Credit: Vincent Van, Lab Technician for CE-CERT

Figure 30: Percent Volume Change of Plastic Samples After Drying





Volume change of liquid (top) and vapor (bottom) samples, Errors Bars Represent ± One Standard Deviation

Photo Credit: Vincent Van, Lab Technician for CE-CERT

The plastic generally showed smaller volume changes than the elastomers. N6, N6/6, PBT, PET, PETP, PPS, PVDF, POMAC, and PTFE increased less than 10 percent for all samples before drying. When dried, the majority of the plastic samples that were listed had an increase in volume of 5 percent or less from their original dimensions. The ORNL study similarly showed

increases of less than 5 percent for PPS, PET, PTFE, POMAC, and PBT after fuel exposures before drying (Kass et al., 2012a/ 2013/ 2014b). Our N6 and N6-6 samples showed volume increases comparable to ORNL's for the E25 aggressive exposure, but our volume increases were greater than those seen by ORNL for Fuel C, and for B16 aggressive and B24 aggressive formulations (Kass et al., 2013/ 2014b). For the ORNL study, the net volume increases after drying for PPS, PET, PTFE, POMAC, PBT, and PVDF were all 5 percent or less. For N6 and N6/6, the net increases after drying were generally higher than those found by ORNL, which found net increases of less than 2 percent for most fuel combinations, with the exception of some E25 exposures that gave net increases closer to 5 percent (Kass et al., 2013/2014b).

PVC and PETG showed the strongest effects for the plastic samples. PVC samples were strongly affected by all fuels with an expansion of 27 to 35 percent for all samples, with E10 aggressive showing the largest increases. PETG increased the most for E10 aggressive and B55 aggressive fuels at about 30 to 35 percent for both vapor and liquid samples. Both the ORNL and our study also showed generally greater volume increases for the PETG samples, with their results ranging from approximately 25 percent for the lower level aggressive alcohol blends to about 15 percent for the reference fuel C and the higher ethanol blends (Kass et al., 2012a/ 2013/ 2014b). When dried, PVC and PETG retained a majority of the increased volume at 18 to 31 percent. The ORNL study also found that PETG retained a good percentage of its initial volume increase after drying, with net increases of approximately 8 to 15 percent (Kass et al., 2012a/ 2013/ 2014b), compared to the 20 to 25 percent increase for our study.

The E10 fuel caused a notable volume change for HDPE and PL, at about 15 percent for both liquid and vapor samples. E10 aggressive and B55 aggressive caused smaller changes to HDPE at less than a 10 increase percent when wet. The HDPE results for the ORNL study showed increases of approximately 10 percent, which is in a similar range to those of our study (Kass et al., 2012a/2013/ 2014b). PL shrunk in volume more than HDPE after drying. PL retained almost 5 percent of the volume increase, while HDPE retained anywhere from 2 to 8 percent of the volume increase after drying. The HDPE after drying volumes are within the ranges reported by Kass et al. (2012a/ 2013/ 2014b).

The very low to moderate level of swell for the plastic samples is also consistent with calculations done by ORNL materials using the Flory-Huggins model using the Hansen solubility parameter methodology (Kass et al., 2012a/ 2013/ 2014b). These calculations indicated that the plastics most susceptibility to volume swell would be PTFE, PTEG, and PP, and that alcohols and that ethanol would provide a higher level of volume swell than the butanol fuels at lower alcohol concentrations. The higher volume swell was observed for PTEG, but not for PTFE. The solubility calculations also showed relatively low levels of solubility for PVDP, but showed higher levels of volume swell than expected. The observation of increased volumes compared to the original sample volumes indicates that the fuels are retained in the samples.

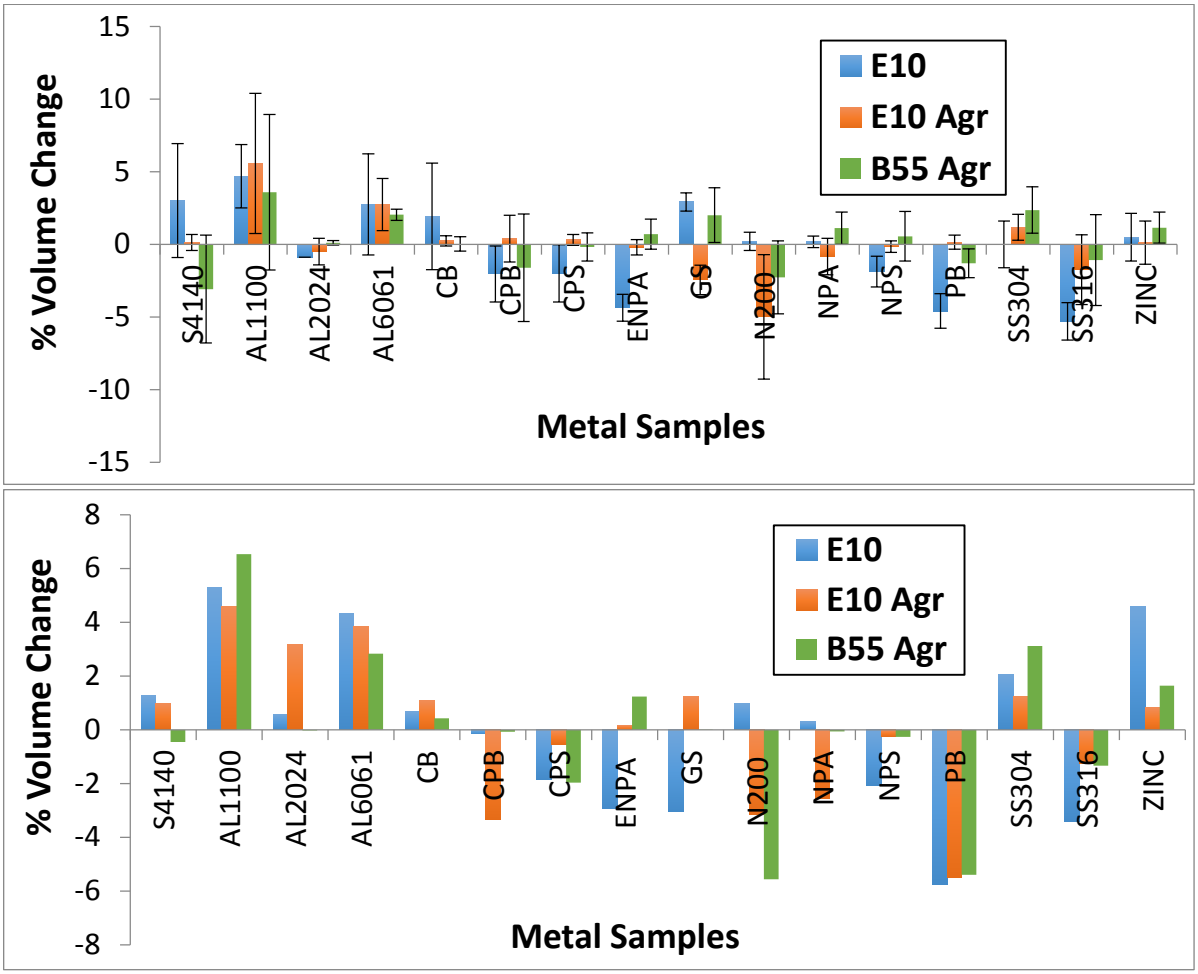
3.2.2.4 Metals

Figure 31 and Figure 32 represent the percent volume change of wet and dried metal samples, respectively, that were exposed directly to E10, E10 aggressive, and B55 aggressive fuels and vapors with error bars representing one standard deviation. Wet and dried metal samples

showed minor variation. Metal samples exposed to vapor generally have a lower volume compared to samples that were exposed to the fuel directly.

The B55 aggressive fuel produced increases in volume for nearly all of the metal samples. On the other hand, the majority of metal samples exposed to E10 aggressive fuel decreased in volume slightly. The E10 results were more mixed. The metal samples all had a minimal increase or decrease in volume of 6 percent or less before drying and 7 percent or less after drying.

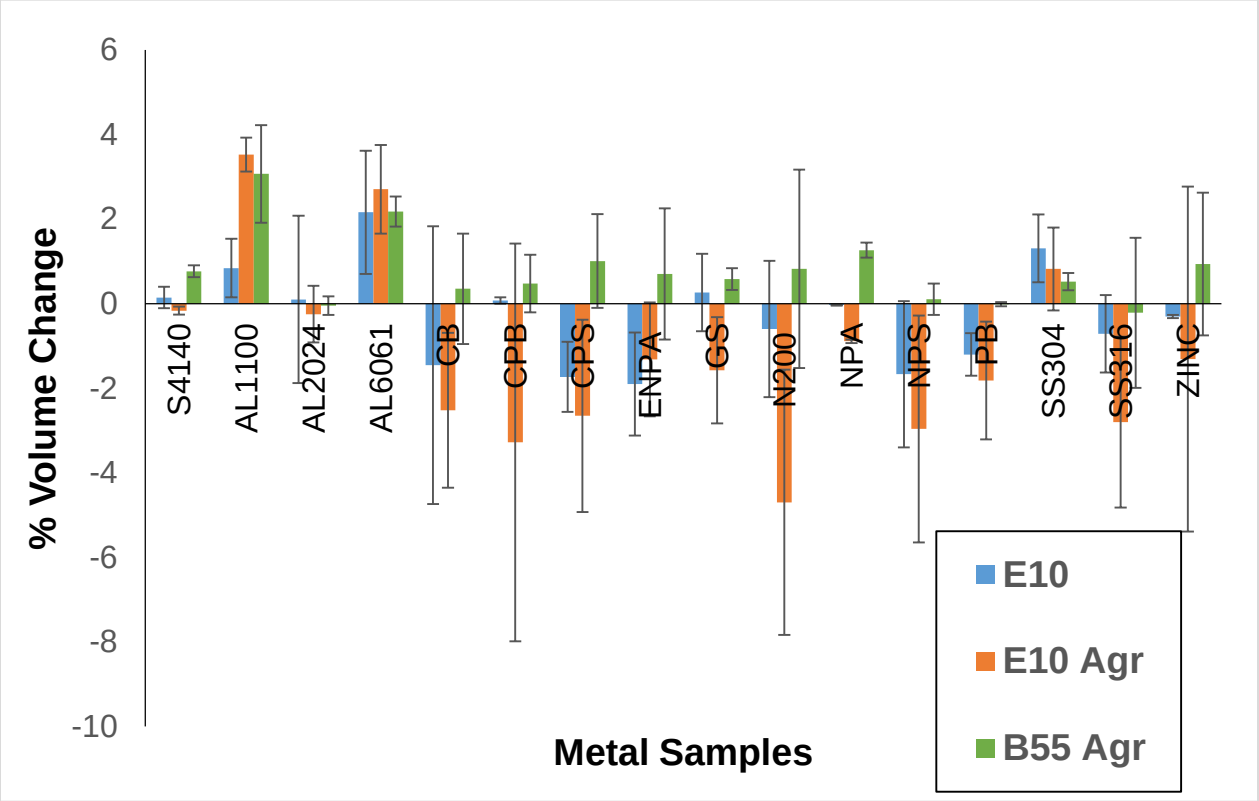
Figure 31: Percent Volume Change of Metal Samples Before Drying

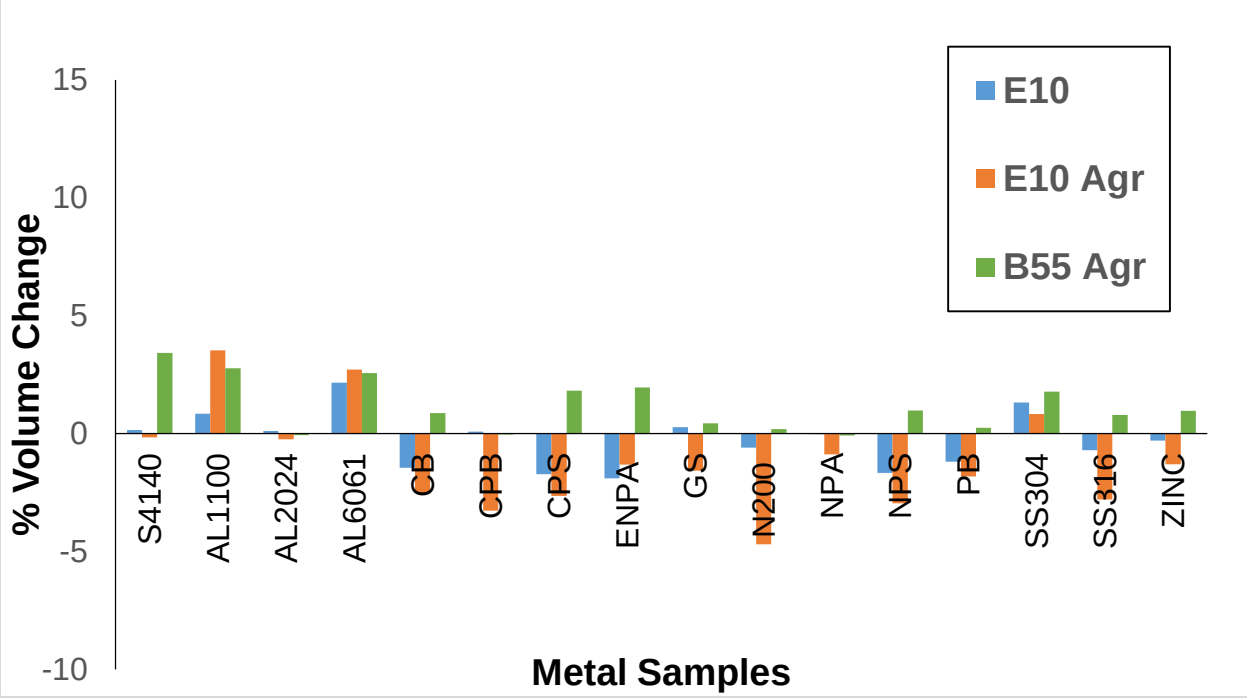


Volume change of liquid (top) and vapor (bottom) samples, Errors Bars Represent ± One Standard Deviation.

Photo Credit: Vincent Van, Lab Technician for CE-CERT

Figure 32: Percent Volume Change of Metal Samples After Drying





Volume change of liquid (top) and vapor (bottom) samples, Errors Bars Represent ± One Standard Deviation.

Photo Credit: Vincent Van, Lab Technician for CE-CERT

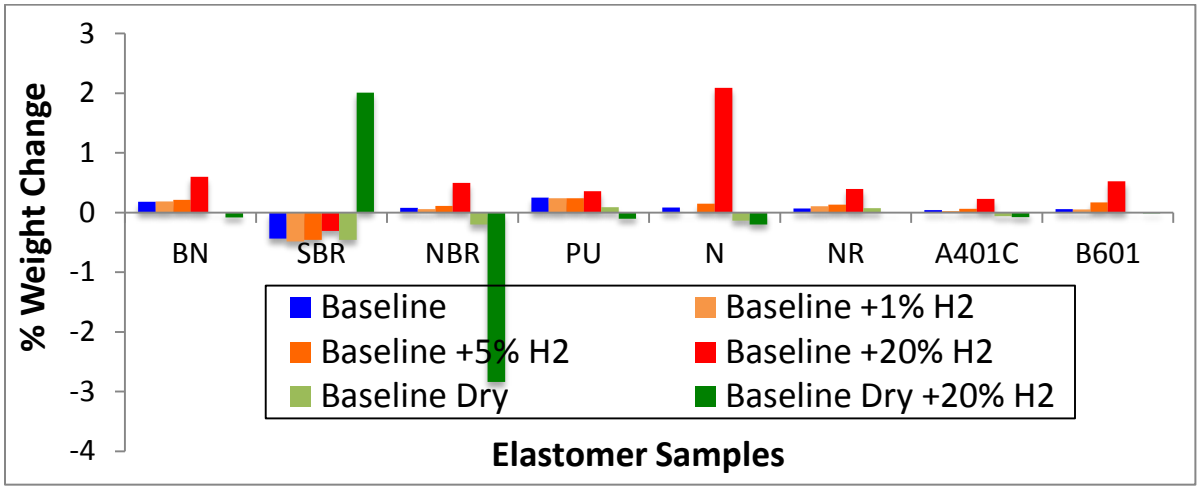
3.3 Mass Change

3.3.1 Natural Gas

3.3.1.1 Elastomers

Figure 33 represents the average percent weight change of elastomer samples exposed to natural gas. The elastomer samples show an insignificant change in mass change. The majority of the elastomer samples showed a percent weight change of 0.5 percent or less. SBR and NBR samples from the dry 20 percent H_2 Tube, and N samples from the wet 20 percent H_2 Tube were outliers at a change of about +2 to -3 percent.

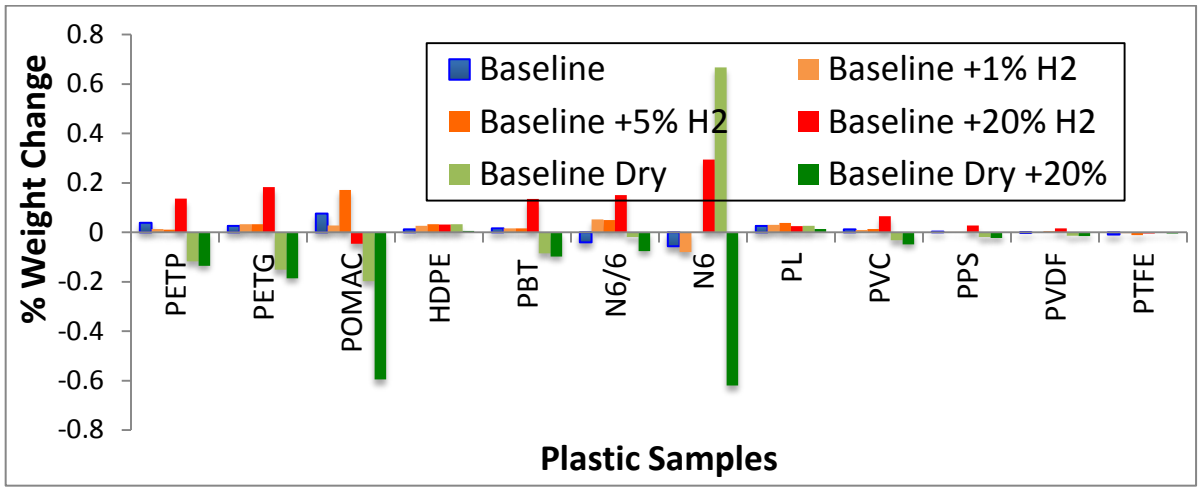
Figure 33: Percent Weight Change of Elastomer Samples



3.3.1.2 Plastics

Figure 34 represents the average percent weight change of plastic samples exposed to natural gas. The plastic samples show an insignificant change in mass change. The majority of the plastic samples showed a percent weight change of 0.2 percent or less with the average being 0.1 percent in percent weight change or less.

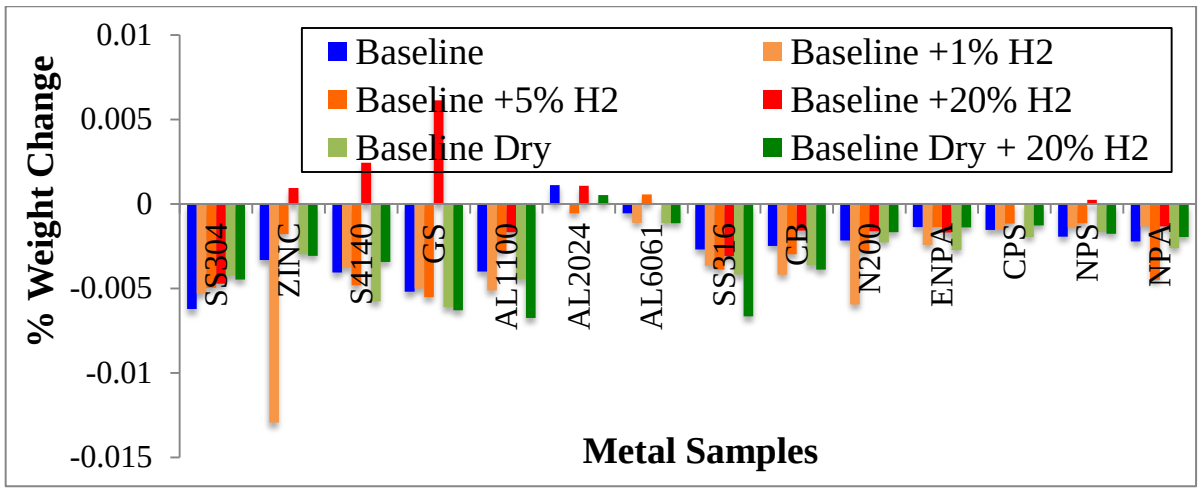
Figure 34: Percent Weight Change of Plastic Samples



3.3.1.3 Metals

Figure 35 represents the average percent weight change of the metal samples exposed to natural gas. The metal samples show an insignificant change in mass change. Nearly all of the metal samples showed a percent weight change of 0.01 percent or less, these changes predominantly being a decrease in weight.

Figure 35: Percent Weight Change of Metal Samples



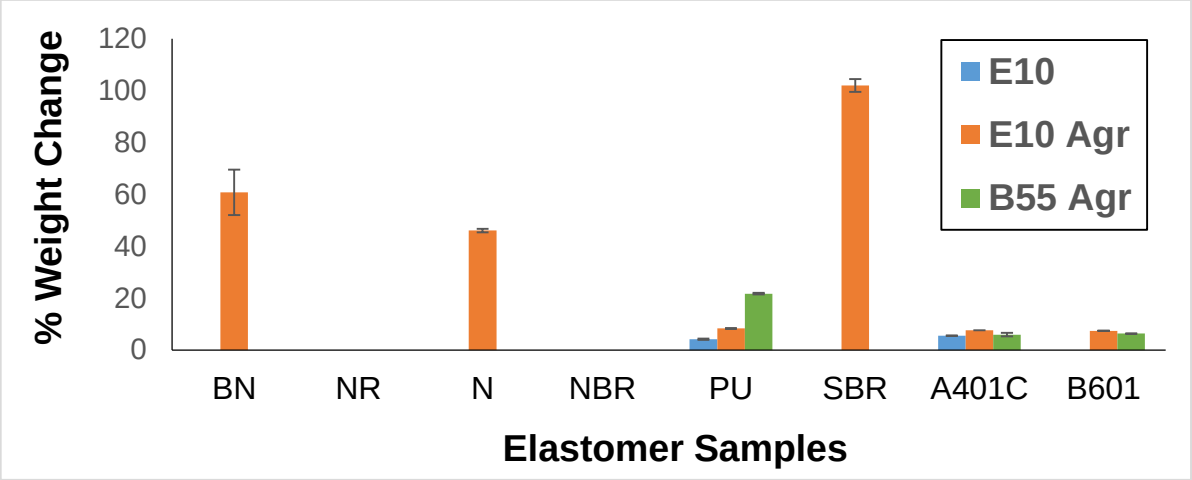
3.3.2 Liquid Fuel

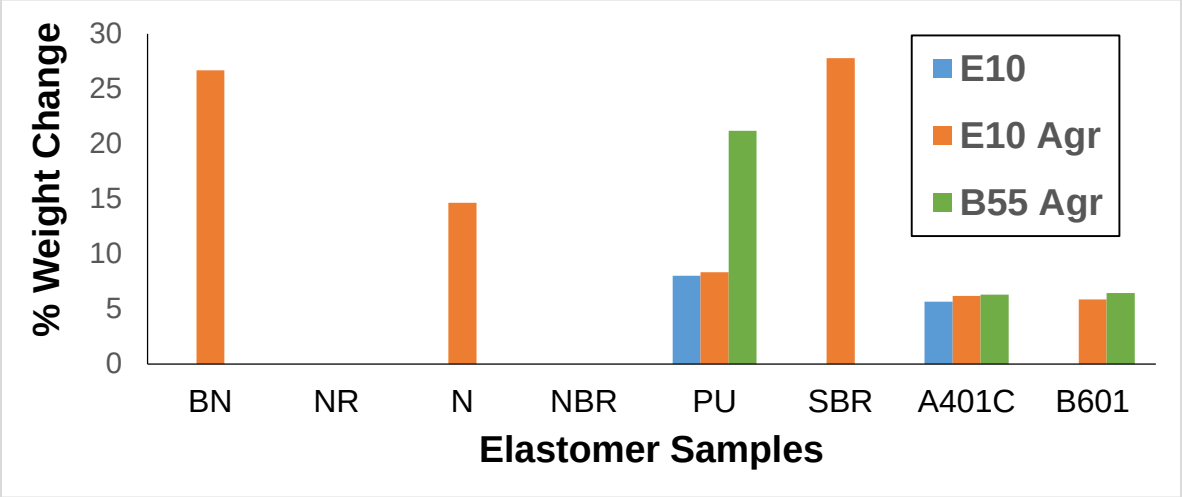
3.3.2.1 Elastomers

Figure 36 and

Figure Figure 37 show the average percent weight change of the elastomer samples exposed to E10, E10 aggressive, and B55 aggressive fuels before drying and after drying, respectively, with error bars representing one standard deviation of the measurements. BN, N, and SBR samples that were exposed to E10 and B55 aggressive are missing data for the liquid exposures due to evaporation and stabilization issues while weighing, and hence were not included in Figure . NR and NBR samples are also missing data due to stabilization issues and from being damaged after exposure. Excessive damage for NR can be seen in Figure 38. When dried, samples that were having stabilization problems when "wet" could often be weighed, so more data is available for the dried samples. Elastomers increased in weight while wet and generally decreased to below their original weight when dried. Elastomers generally had the greatest change in mass of all the material types both wet and dried conditions, which can be seen in Figure 36andFigure 37.

Figure 36: Percent Weight Change of Elastomer Samples Before Drying

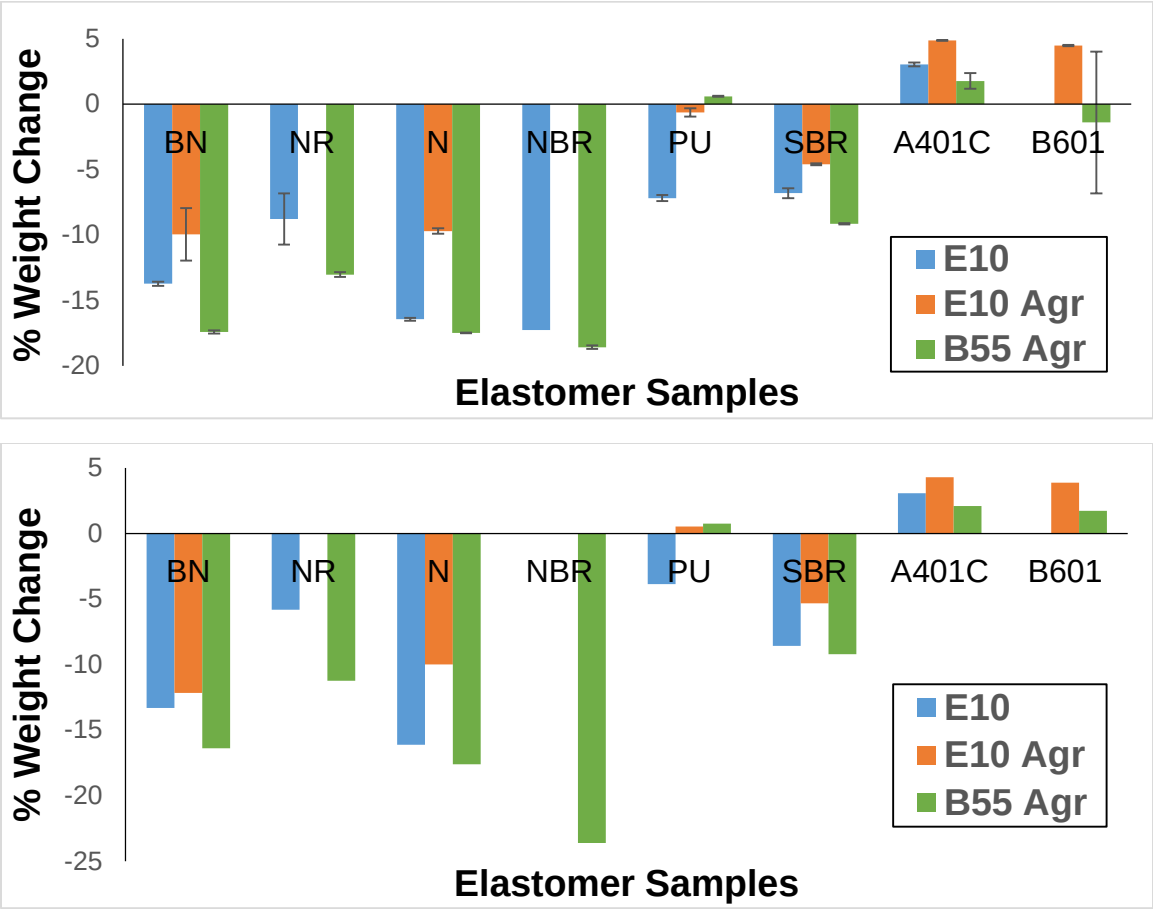




Weight change of liquid (top) and vapor (bottom) samples, Errors bars represent ± one standard deviation.

Photo Credit: Vincent Van, Lab Technician for CE-CERT

Figure 37: Percent Weight Change of Elastomer Samples After Drying



Weight change of liquid (top) and vapor (bottom) samples, Errors Bars Represent ± One Standard Deviation.

Graph Credit: Vincent Van, Lab Technician for CE-CERT

Figure 38: NR Samples Exposed to E10 Aggressive Fuel

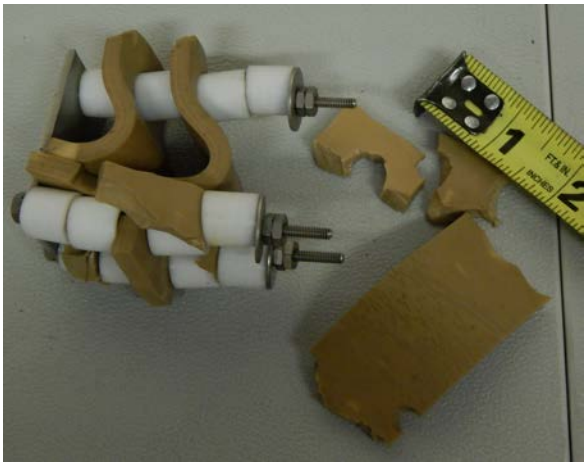


Photo Credit: Vincent Van, Lab Technician for CE-CERT

All of the samples increased in weight while wet or after vapor exposure. Elastomers generally increased more in weight with direct exposure to the fuel, as opposed to vapor exposure, as seen comparing the graphs in Figure . BN, NR, N, and SBR had the largest weight changes of all of the samples, even though many samples could not be measured accurately on the scale, due to evaporation during the weighing process or excessive damage. The percent weight change of SBR increased the most, more than doubling for direct exposure to the E10 aggressive fuel, and increasing just under 30 percent for the SBR samples exposed to vapors. BN and N increased roughly 45 to 60 percent after the direct liquid exposures, and 27 to 15 percent, respectively, for the vapor exposures. Mass increases ranged from 65 to 75 percent for SBR and from 40 to 50 percent for N in a previous ORNL study, similar to the values found in our study (Kass et al., 2013/2014b). PU showed about a 20 percent increase for exposure to the B55 aggressive fuel as either a liquid or vapors. On the other hand, PU only increased about 8 percent for the E10 and E10 aggressive fuel exposures, and only a 4 to 8 percent increase for the vapor exposures. Mass increases in previous work by ORNL were in the 20 to 30 percent for alcohol blends, which is comparable to our results for the B55 aggressive fuel, but greater than the volume increases we found for the E10 and E10 aggressive fuels (Kass et al., 2013/ 2014b). Overall, the fluorocarbons showed the smallest increases of less than 8 percent for the submerged samples and 5 to 6 percent for the vapor exposed samples. This is in a similar range of mass increases found by ORNL, which were in the range of 6 to 10 percent (Kass et al., 2013/ 2014b).

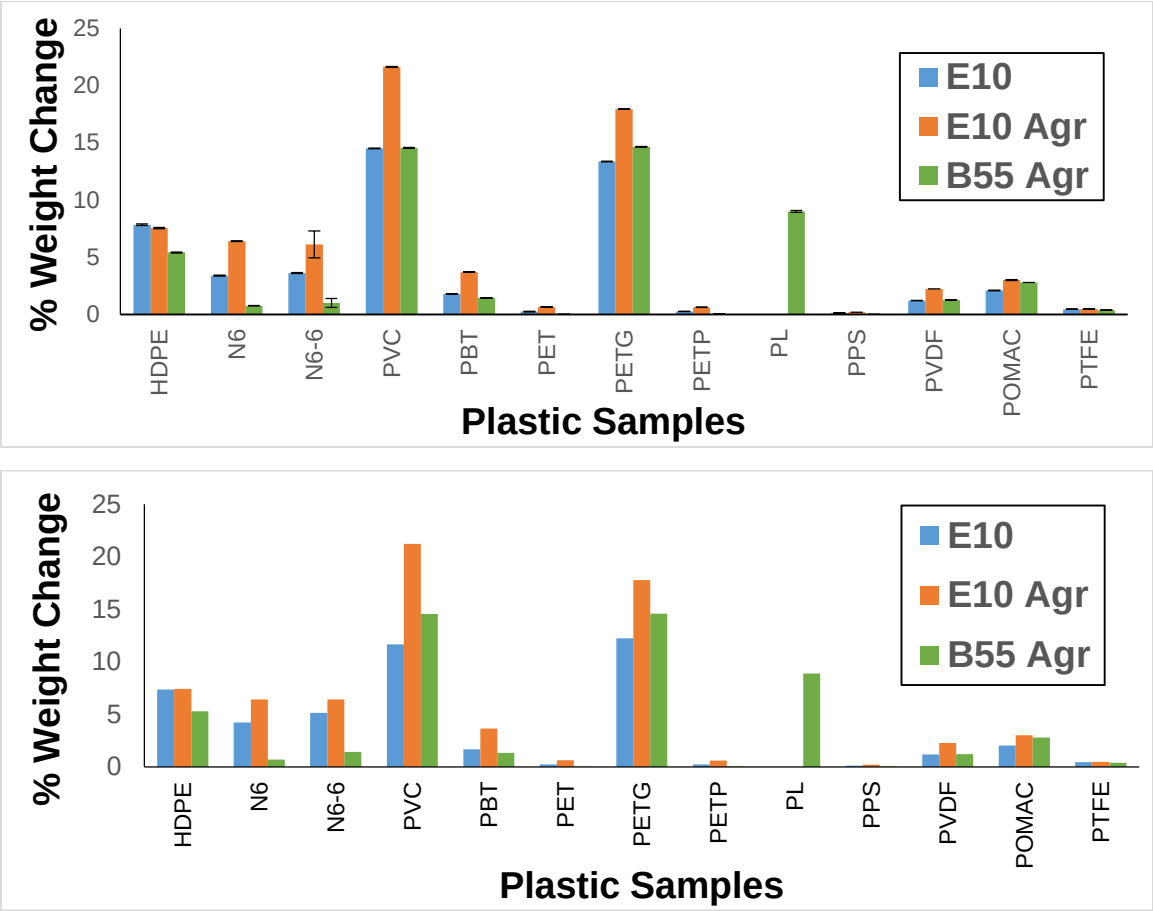
The elastomers all decreased below their original weights after drying, except the fluorocarbons (A401C and B601), which maintained about a 5 percent increase in weight even after drying, similar to the results reported by ORNL (Kass et al., 2011/ 2013/ 2014b). The BN, NR, N, and NBR samples all exhibited weights between 10 and 25 percent below their original weights after drying, with the E10 aggressive samples generally showing the smallest weight loss and the B55 aggressive samples showing the largest weight loss. The mass decreases were somewhat larger than those reported in ORNL studies after drying, which showed mass decreases of 8 to 13 percent for NBR and a mass decrease of about 14 percent for N (Kass et al., 2011/2013/2014b). SBR after drying had a percent weight change of roughly 5 to 10 percent below its original weight. The PU samples after drying had weights comparable to their original values prior to exposures for the E10 aggressive and B55 aggressive fuels, and showed decreases of 3 to 7 percent for E10 fuel exposures. These mass decreases were in the range of those reported by ORNL after drying, which were a mass decrease of about 10 percent for SBR and a mass decrease of 6 to 13 percent for PU for alcohol fuels (Kass et al., 2011/2013/2014b).

3.3.2.2 Plastics

Figure 39 shows the weight percent change of wet submerged and vapor plastic samples exposed to E10, E10 aggressive and B55 aggressive fuels before drying with error bars representing one standard deviation. Figure 40 represents the weight percent change of submerged and vapor plastics samples that were exposed to E10, E10 aggressive, and B55 aggressive fuels after drying with error bars representing one standard deviation. The different types of plastics tested either maintained most of their original weight or increased in weight after exposure to the various fuels, as seen in Figure 39. The samples generally remained heavier than their original weight after being dried, depending on the type of plastic, as seen in

Figure 40. In general, the samples had a similar change in weight whether they were exposed either directly to liquid or to the vapors.

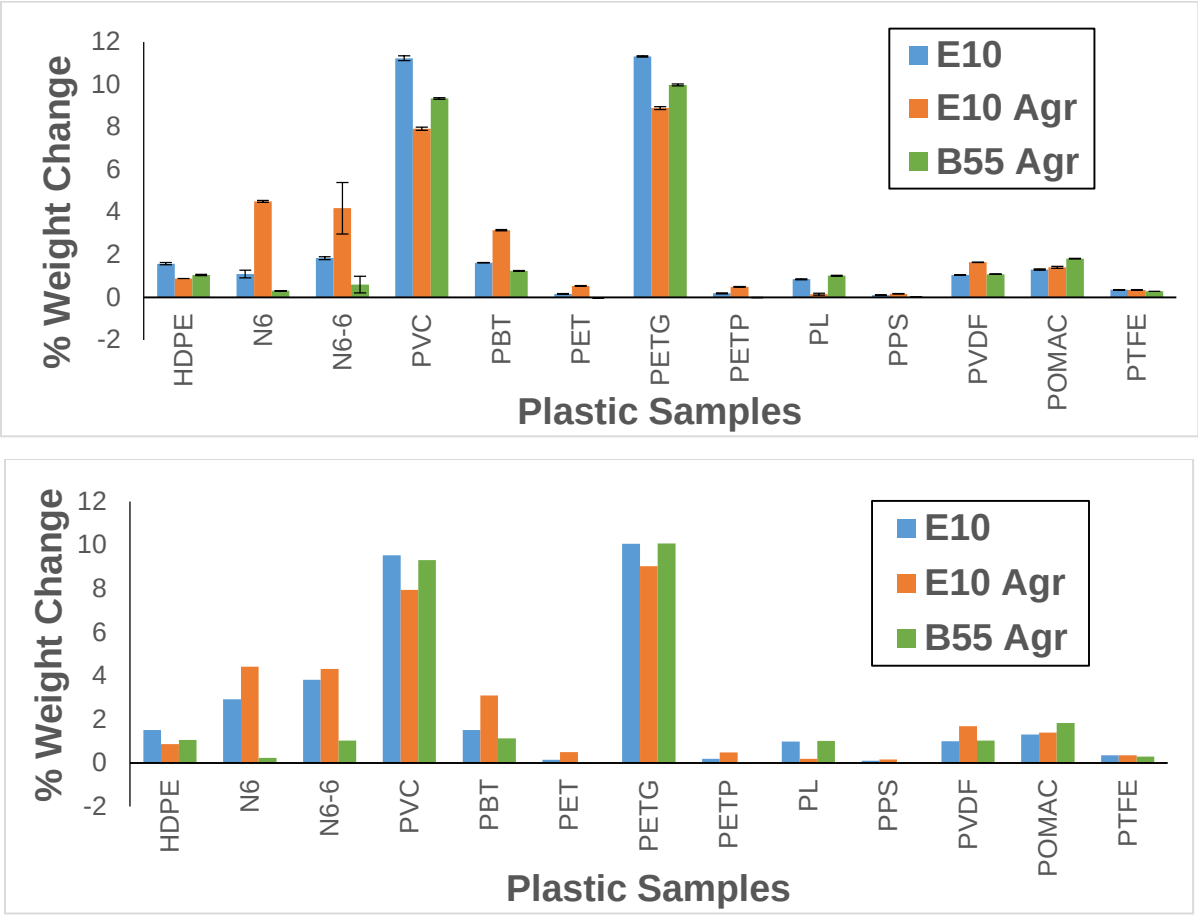
Figure 39: Percent Weight Change of Plastic Samples Before Drying



Weight change of liquid (top) and vapor (bottom) samples, Errors Bars Represent ± One Standard Deviation.

Graph Credit: Vincent Van, Lab Technician for CE-CERT

Figure 40: Percent Weight Change of Plastic Samples After Drying



Weight change of liquid (top) and vapor (bottom) samples, Errors Bars Represent ± One Standard Deviation.

Photo Credit: Vincent Van, Lab Technician for CE-CERT

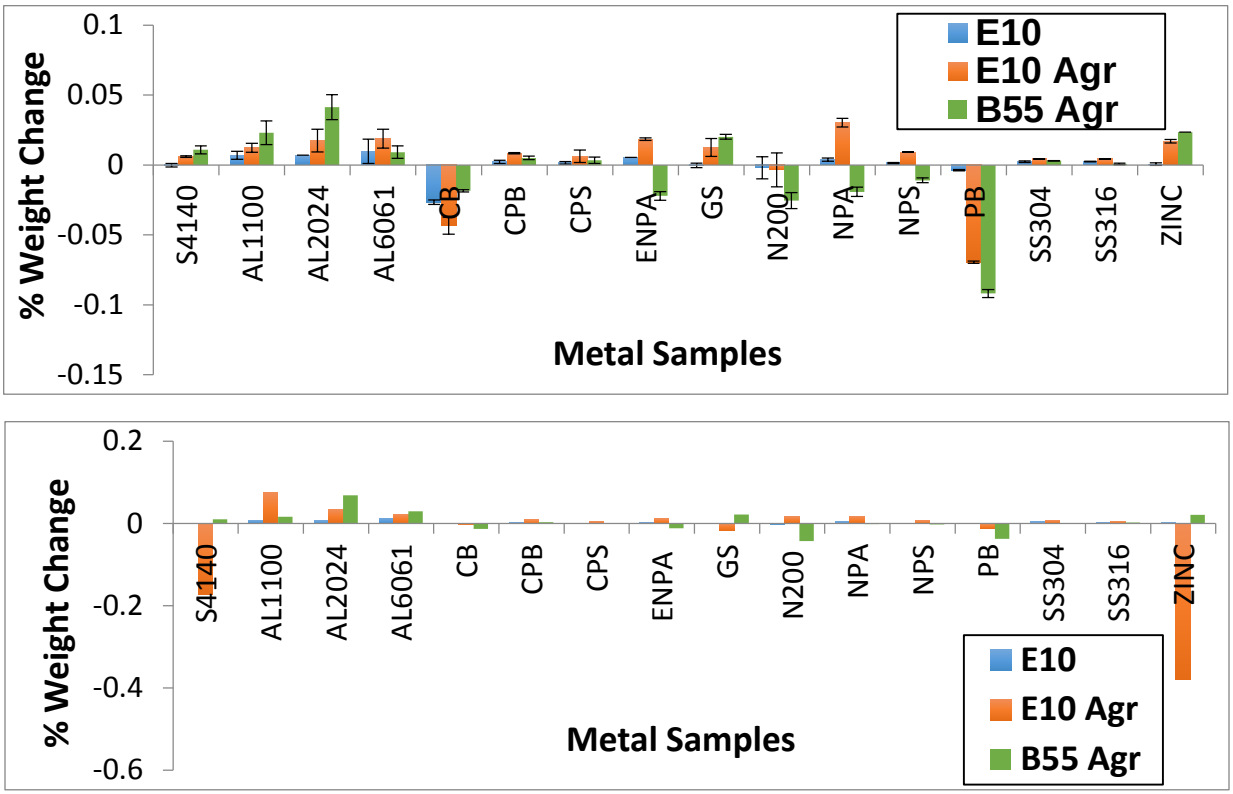
Plastics did not have major changes in weight compared to the elastomers. The majority of the plastic samples besides PVC, PETG, and PL had a weight increase of 10 percent or less, with the majority of wet samples showing an average increase of less than 5 percent in weight. When dried, all plastic samples except for PVC and PETG had an increase of less than 5 percent, as seen in the Figure 40, with the majority of the dried samples having a weight increase of 2 percent or less. PVC and PETG had the greatest percent increase in weight at 12 to 21 percent for both wet and vapor samples. The E10 aggressive fuel generally had the greatest effect on weight change for plastic samples before drying. When dried, PVC and PETG retained some of the weight at an 8 to 12 percent increase compared to their original weight. Previous studies by ORNL have shown mass increases for these materials of approximately 15 percent for wet mass and approximately 10 percent for dry mass, similar to our results (Kass et al., 2013/ 2014b). PL had a smaller average weight change of 12 percent and 9 percent, respectively, when exposed to the E10 aggressive and B55 aggressive fuels for both wet and vapor samples. When dried, however, PL lost most of the increased weight and shrunk back down to its original weight.

The most resilient plastics are PBT, PET, PETP, PPS, PVDF, POMAC and PTFE, which had a change of less than 3 percent from their original weight for all samples exposed to E10, E10 aggressive, and B55 aggressive when both wet and dried, as seen comparing Figure 39 with and Figure 40. ORNL showed similarly for most of these materials that mass increases were small for both the wet and dry mass (Kass et al., 2013/2014b). Nylon samples (N6, N6/6) had weight increases of 7 percent or less for the initial fuel and vapor exposures, and a weight increase of 4 percent or less after drying. The Nylon samples were most affected by the E10 aggressive fuel, but showed minimal impacts for exposure to the B55 aggressive fuel. ORNL observed mass increases for nylon of 6 to 7 percent wet and 2 to 3 percent dry for an E25 blend, but mass increases of less than 1 percent for other fuel exposures (Kass et al., 2013;/2014b). The HPDE samples showed increases of 8 percent or less for the fuel and vapor exposures, and increases of 2 percent or less after drying, with the E10 fuel showing slightly higher weight changes compared to the other fuels in all cases. This is similar to the ORNL results, which showed increases for HPDE of 7 percent wet and 1 percent or less dry (Kass et al., 2013/2014b).

3.3.2.3 Metals

Metal samples that were exposed to E10, E10 aggressive, and B55 aggressive fuels showed a negligible change in weight for both samples exposed directly to the fuel and to the vapors, as seen in Figure 41 and Figure 42. Figure 41 and Figure 42 show the percent weight change for all of the metal samples exposed to E10, E10 aggressive, and B55 aggressive that were wet and dried, respectively, with error bars representing one standard deviation. Submerged samples did not deviate past 1/10 of a percent in weight change after fuel exposure and drying. The majority of the vapor samples also did not deviate past 0.1 percent in weight change after fuel exposure and drying, although the Zinc and S4140 samples exposed to the vapor of the E10 aggressive fuel showed reductions in weight of 0.37 percent and 0.17 percent, respectively.

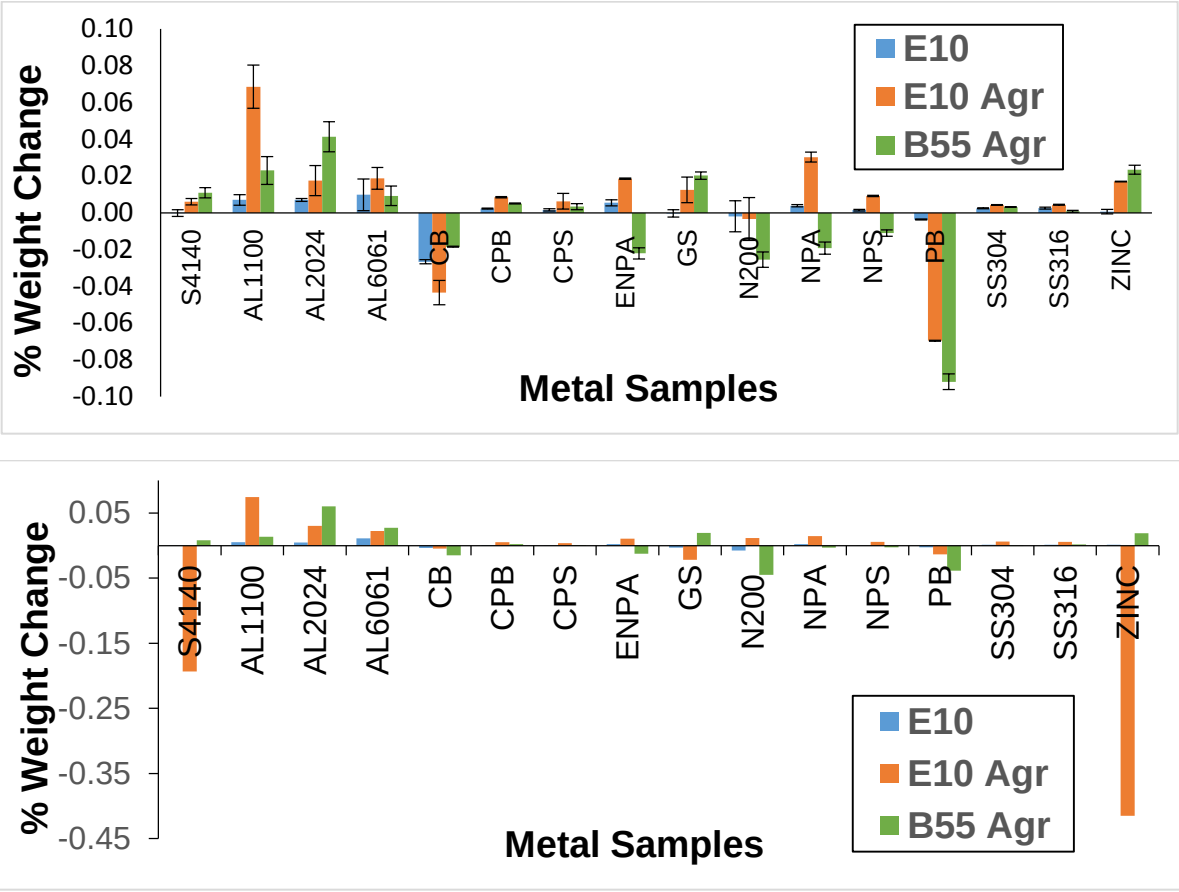
Figure 41: Percent Weight Change of Metal Samples After Drying



Weight change of liquid (top) and vapor (bottom) samples, Errors Bars Represent ± One Standard Deviation.

Photo Credit: Vincent Van, Lab Technician for CE-CERT

Figure 42 Percent Weight Change of Metal Samples After Drying



Weight change of liquid (top) and vapor (bottom) samples, Errors Bars Represent ± One Standard Deviation.

Photo Credit: Vincent Van, Lab Technician for CE-CERT

3.4 Tensile Strength

The ultimate tensile strength or tensile strength of a material is the maximum amount of tensile strength the materials can take before it breaks or fails. Tensile strength was calculated by the maximum load in pounds-force at the time of failure divided by the average cross-sectional area of the material in square inches. The percent elongation is another property measured with the tensile strength test. The percent elongation was determined by measuring the change in gauge length from the original specimen to the fuel affected specimen.

3.4.1 Natural Gas

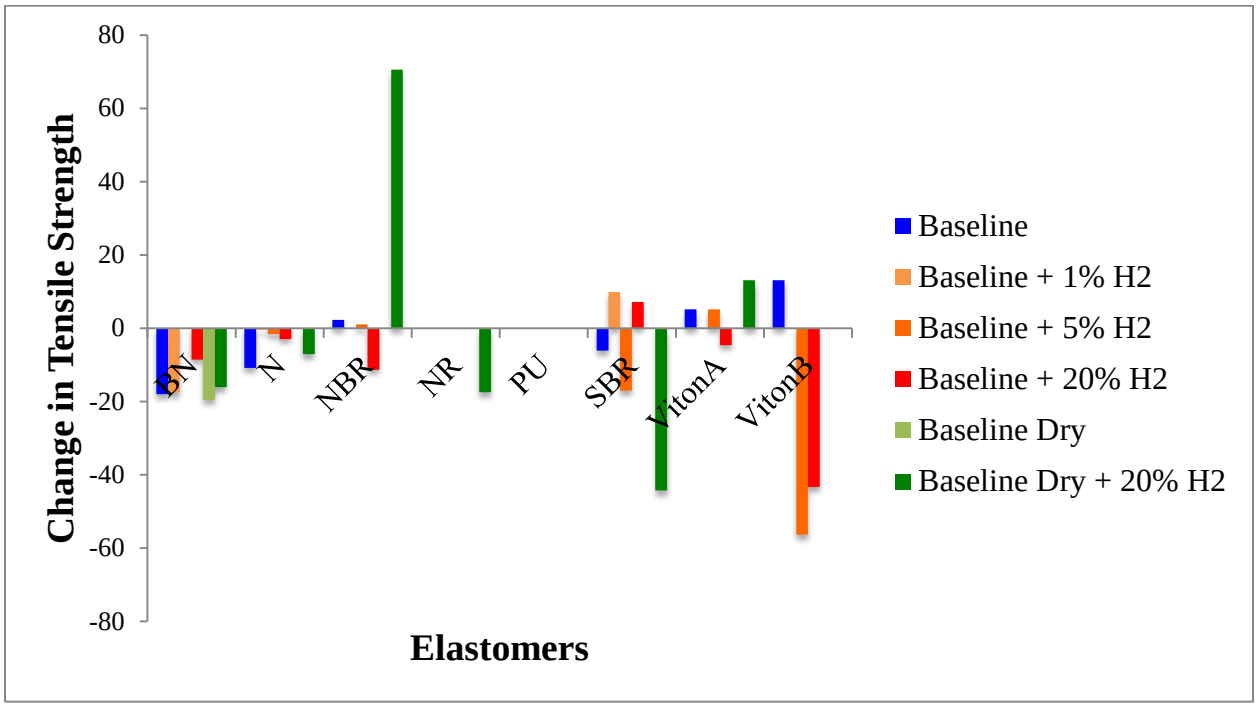
3.4.1.1 Elastomers

The changes in tensile strength and elongation for elastomer samples exposed to different natural gas blends are provided in Figure 43. These changes represent the percentage differences between the samples that were not exposed to the fuels and those that were exposed to fuels. For tensile strength, the NBR exposed to baseline dry +20 percent H_2 showed the

biggest change, with an increase of roughly 70 percent. SBR and Viton B that were exposed to baseline dry +20 percent H_2 and baseline wet +20 percent H_2, respectively, had a decent decrease in tensile strength of approximately 43 to 44 percent. Viton B exposed to baseline wet +5 percent H_2 also had a decrease of tensile strength of approximately 56 percent. The remainder of the samples had a change in tensile strength of less than ±20 percent. BN and N both showed decreases in tensile strength for all exposures, while NR showed a decrease for the baseline dry +20 percent H_2.

The majority of the samples that were exposed to natural gas showed decreased levels of elongation. NBR showed decreases in elongation of 45 to 55 percent for the baseline wet, the baseline wet +5 percent H_2 exposures, and the baseline wet +20 percent H_2 exposures, but a less than 10 percent decrease in elongation for the baseline dry +20 percent H_2. SBR showed a 57 percent decrease in elongation for the baseline dry +20 percent H_2, but decreases in elongation of 20 to 29 percent for the other exposures. Viton B also showed a decrease in elongation of 50 to 55 percent for the baseline wet +20 percent H_2 and baseline wet +5 percent H_2 exposures. BN showed a decrease of 33 percent for the baseline dry exposures, but increases for the some of the other exposures. The remainder of the samples showed decreases in tensile strength of approximately 20 percent or less.

Figure 43: Percent Change of Elastomers Tensile Strength and Elongation



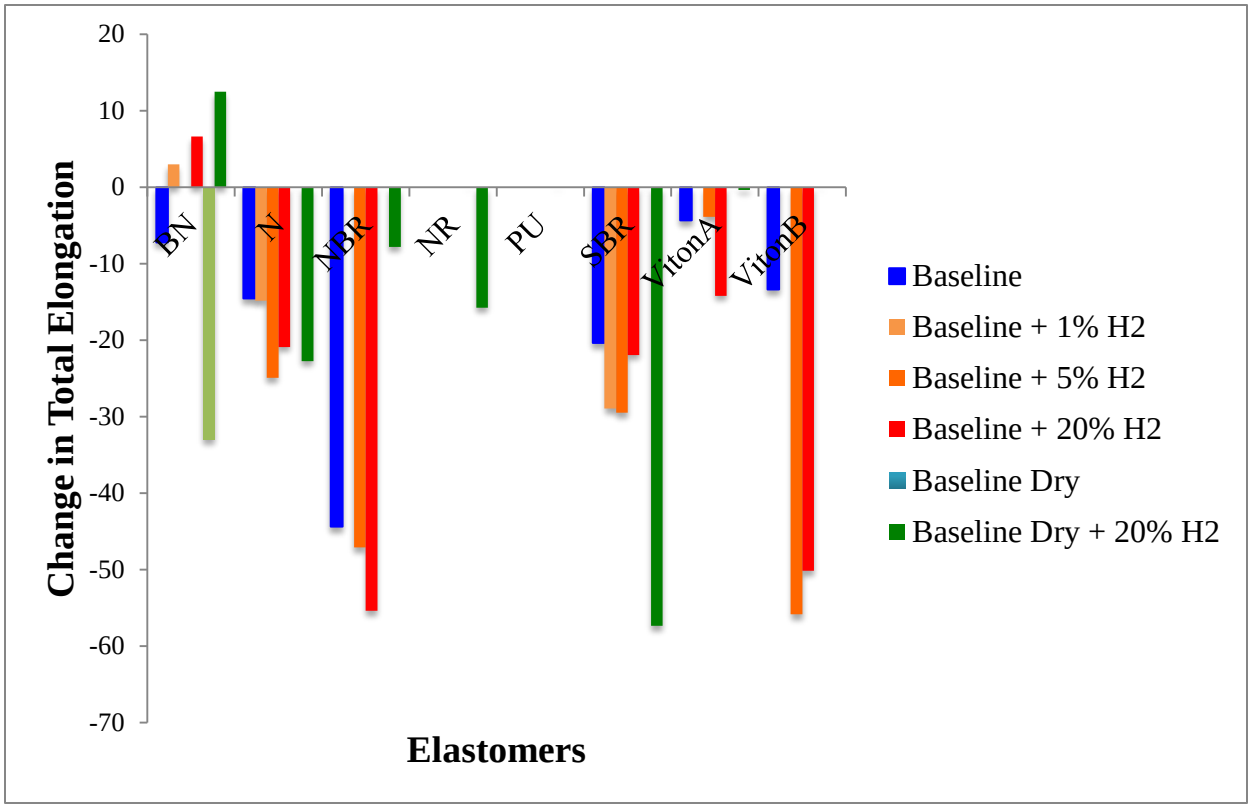


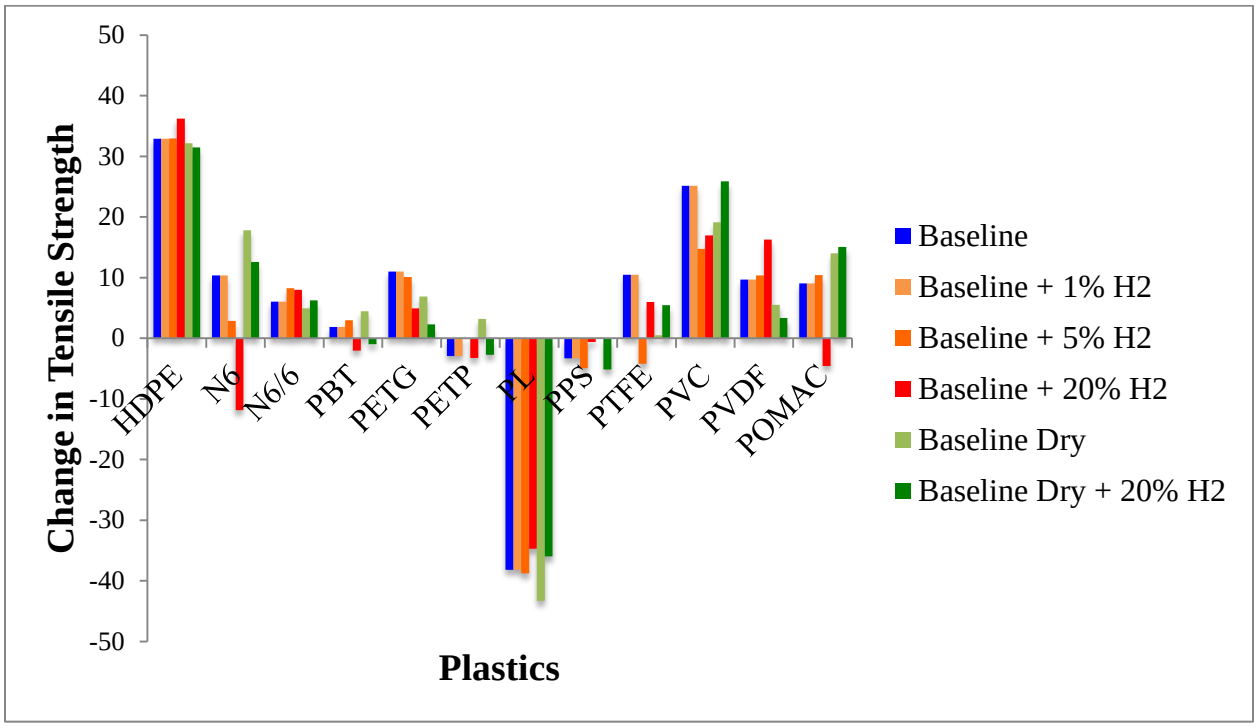
Photo Credit: Kyle Hunter, Lab Technician for CE-CERT

3.4.1.2 Plastics

Figure 44 represents the percent change of tensile strength for plastic samples exposed to a variety of natural gases. HDPE and PL when exposed to natural gas had the greatest change in tensile strength at an increase on average of slightly greater than 30 percent and decrease on average of 34 to 43 percent, respectively. There was not a significant difference between plastics that were exposed to natural gas and different levels of H_2. The majority of the samples had a change in tensile strength of ±20 percent or less, with tensile strength increasing in most cases. PBT, PETP, and PPS had the lowest deviation from their original tensile strength at an average of ±5 percent.

Some of the largest changes in elongation are were seen with the baseline dry +20 percent H_2 gas, showing elongation increases from 150 to 195 percent for the PBT, PL, and POMAC samples. Increases in elongation of 103 and 206 percent, respectively, were also seen for the POMAC samples for baseline wet +1 percent H_2 and baseline wet +5 percent H_2. The majority of the remaining samples had a change of ±50 percent or less in change in elongation. In contrast to the other samples, HDPE, N6/6, and PL all showed reductions in elongation for the different test fuels, with the exception of the baseline dry +20 percent H_2 gas for the PL. PETG, PTFE, and PVDF had the lowest change in elongation at ±20 percent or less.

Figure 44: Percent Change of Plastics Tensile Strength and Elongation



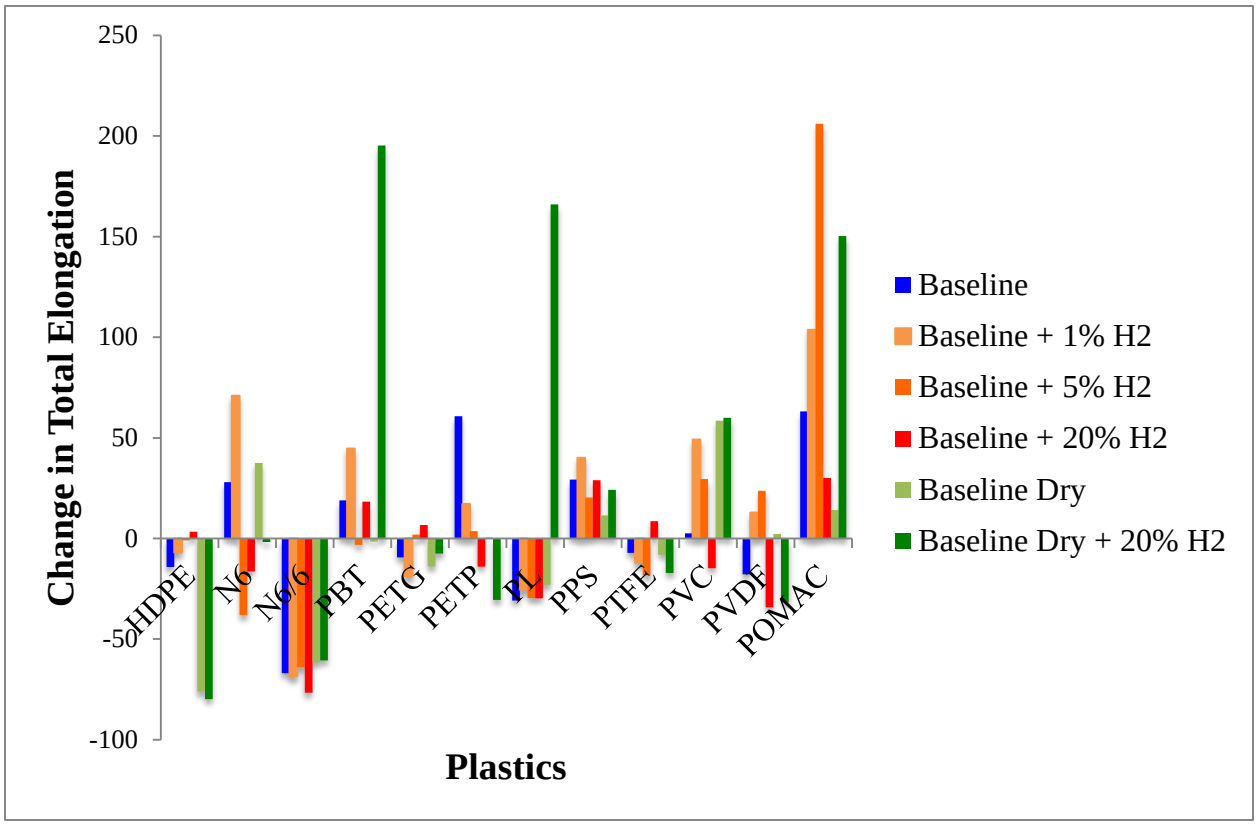


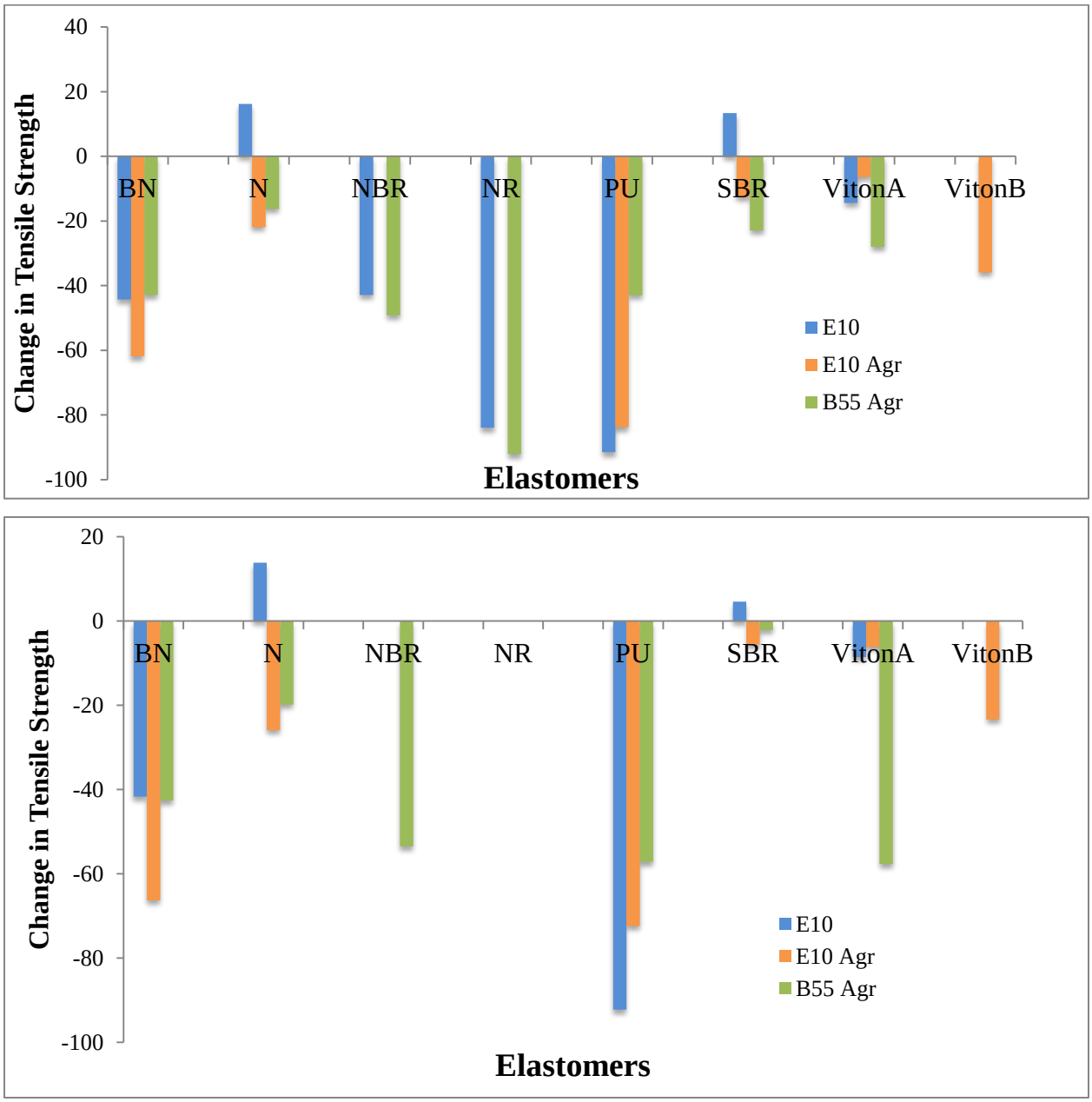
Photo Credit: Kyle Hunter, Lab Technician for CE-CERT

3.4.2 Liquid Fuel

3.4.2.1 Elastomers

Figure 45 represents the percent change of tensile strength for liquid and vapor exposed elastomer samples exposed to E10, E10 aggressive, and B55 aggressive fuel. PU, NR, NBR, and BN showed the biggest reductions in tensile strength. PU showed reductions from 43 to 92 percent, with the Bu 55 aggressive samples showing the smallest change. NR showed reductions from 84 to 92 percent in tensile strength for the liquid exposures. NBR showed reductions from 43 to 49 percent. The BN shows reductions from 43 to 62 percent, with the E10 aggressive fuel showing the largest reductions. The Viton A sample for the vapor exposure to the Bu55 aggressive fuel and the Viton B sample for the E10 aggressive liquid fuel exposure also showed reductions of 58 and 36 percent, respectively. The Viton A samples showed for largest reductions for the Bu55 aggressive fuel for both the liquid and vapor exposures. The other materials showed changes of 25 percent or less. Most samples became less resistant to stress after fuel exposure, but SBR and N showed an increase in tensile strength when exposed to the E10 fuel. The liquid and vapor exposures affected all elastomer samples the same, except for Viton A exposed to B55 aggressive fuel, which decreased 28 percent when exposed to vapor and 57 percent when exposed to liquid fuels.

Figure 45: Percent Tensile Strength Change for Elastomer Samples



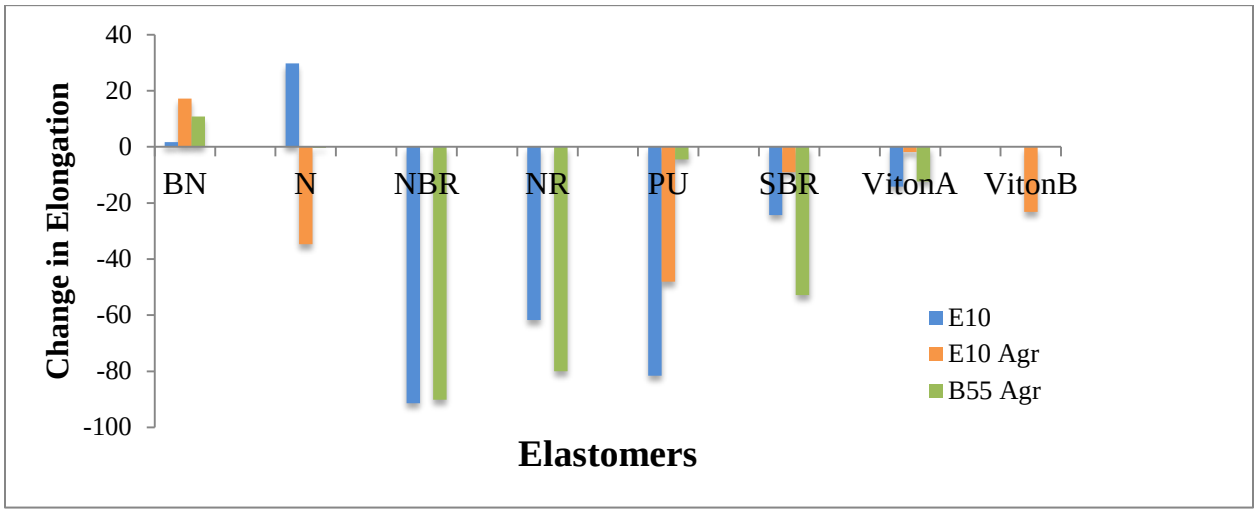
Tensile strength change of liquid (top) and vapor (bottom) samples

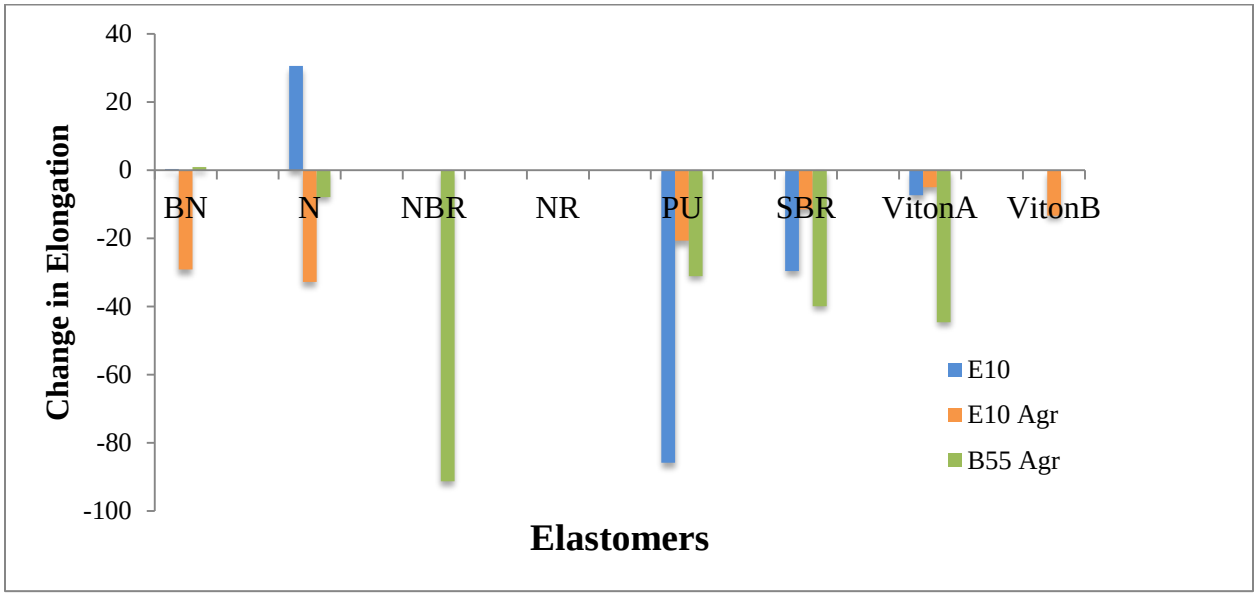
Photo Credit: Kyle Hunter, Lab Technician for CE-CERT

The percent change in elongation is shown in **Error! Not a valid bookmark self-reference.** for the elastomer samples. The NBR and NR samples lost approximately 90 percent and 62-80 percent, respectively, of their elongation. The large reduction in the elongation for the NBR samples is consistent with the visual results that showed the samples breaking apart after exposure and embrittlement when they were dried. The PU samples showed reductions in elongation of 82 percent for the E10 fuel, but smaller reductions in elongation for the two

aggressive fuel blends. SBR showed reductions in elongation ranging from 9 to 53 percent, with the smallest reductions for the E10 fuel and the largest reduction in the Bu55 aggressive fuel. The Viton A sample showed a reduction in elongation for the Bu55 aggressive vapor exposures, but less than a 20% reduction in elongation for the other fuel exposures. The other materials showed reductions of approximately 35 percent or less, with the exception of the N samples exposure to E10, which showed increases in elongation on the order of 30 percent, and the BN samples, which also showed increases for the liquid fuel exposures. Although there were some differences in the vapor and liquid exposures, generally similar trends were seen between the two different types of exposures.

Figure 46: Percent Change in Elongation of Elastomers





Elongation Percent change of liquid (top) and vapor (bottom) samples

Photo Credit: Kyle Hunter, Lab Technician for CE-CERT

These results can be compared with those of previous studies. Although the studies by ORNL researchers did not include tensile strength tests, they did include tests for hardness and elasticity via Dynamic Mechanic Analysis (DMA). The hardness tests were conducted using a durometer following the ASTM D2240 Shore A and Shore D protocols for elastomers and plastics, respectively. The ORNL studies showed reductions in hardness following liquid fuel exposure. The samples regained back some hardness following drying, although not necessarily back to the hardness of the original samples. For the wet exposures, SBR, N, NBR, fluorocarbons, and PU showed reductions in hardness of 25 to 50 points, up to 20 points, up to 30 points, about 15 to 20 points, and up to 40 points, respectively (Kass et al., 2011/ 2012a/2012b/2013/2014a). After drying, fluorocarbons continued to show slight reductions in hardness, while PU showed reductions of up to 10 points. After drying, SBR changed in hardness back to the range of the original samples, while N and NBR showed increases of up to 20 points harder than the original samples (Kass et al., 2011; 2012a,b/ 2013/ 2014a).

ORNL has also conducted dynamic material analysis (DMA) as part of its previous material compatibility studies (Kass et al., 2011; /2012a/2013/ 2014a). This analysis is useful for studying the viscoelastic behavior of polymer and provides another measure of whether the material has had any structural changes. For this analysis a sinusoidal stress is applied and the strain in the material is measured, allowing one to determine the complex modulus. The temperature of the sample or the frequency of the stress are often varied, leading to variations in the complex modulus; this approach can be used to locate the glass transition temperature (T_g) of the material, as well as to identify transitions corresponding to other molecular motions. T_g is the onset temperature associated with the change between a low temperature, where the molecular bonding creates a rigid glassy state, to the temperature where the molecular structure relaxes into a more flexible and pliable state.

In previous studies ORNL observed reductions in T_g for 52luorocarbons, increases in T_g for NBR, and no significant change in T_g for PU, N, and SBR after fuel exposures (Kass et al., 2014a). The reductions for the fluorocarbons were on the order of 50°F (10°C), while the increases for the NBR were on the order of 68°F (20°C). The reductions in T_g were attributed to test fuel being retained in the sample, resulting in a larger volume, which allows molecular relaxation to occur at lower temperatures. The increases in T_g suggest the removal of a plasticizer additive that would effectively reduce the operational temperature range of the elastomer.

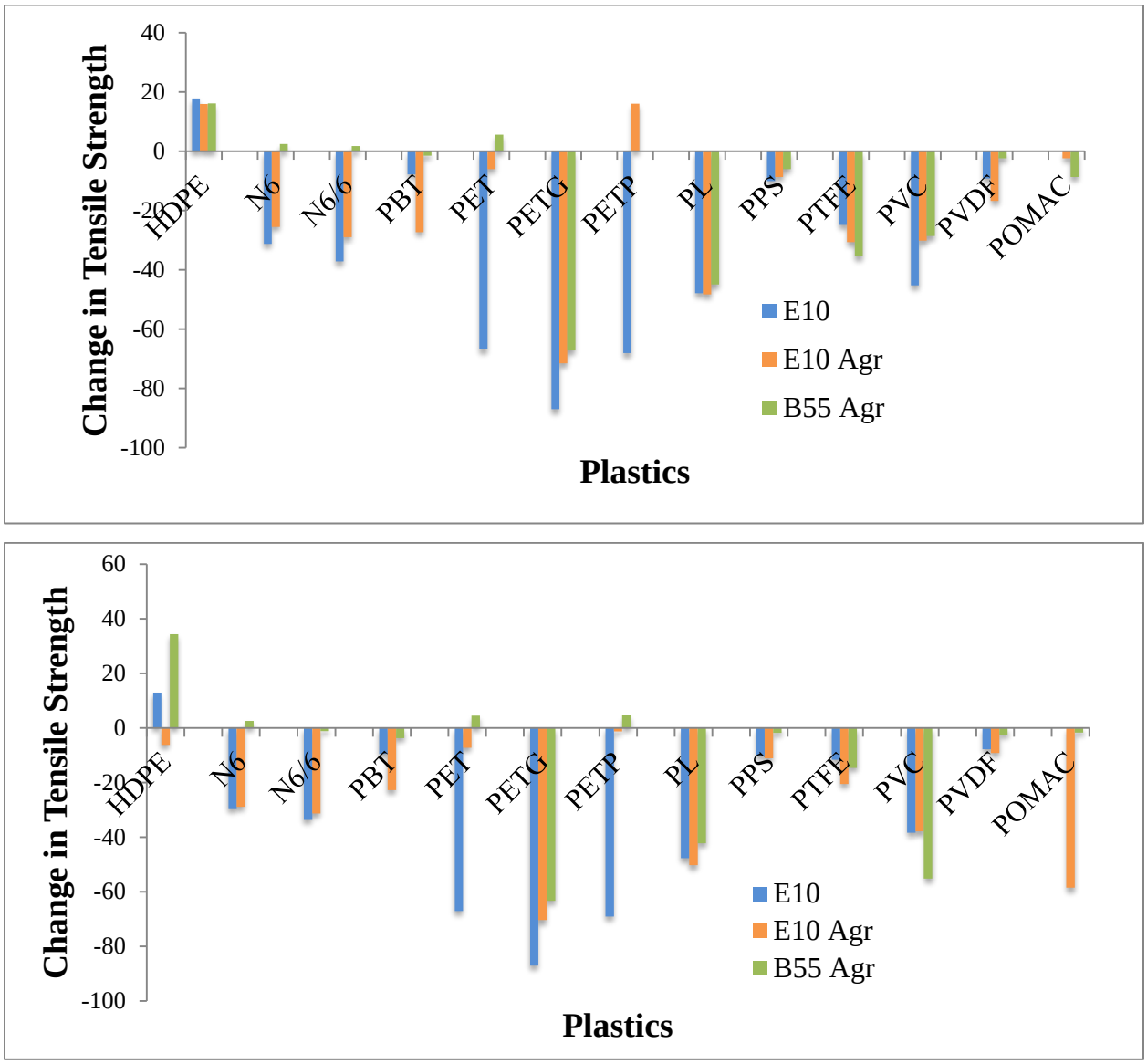
3.4.2.2 Plastics

Figure 47 represents the percent change of tensile strength for liquid and vapor plastic samples exposed to E10, E10 aggressive, and B55 aggressive fuels. Major changes can be seen in PET exposed to E10 vapor and liquid fuels, PETG exposed to E10, E10 aggressive, and B55 aggressive vapor and liquid fuels, PETP exposed to E10 vapors and liquid fuels, PL exposed to E10, E10 aggressive, and B55 aggressive vapor and liquid fuels, PVC exposed to E10, E10 aggressive, B55 aggressive vapor and liquid fuels, and POMAC exposed to E10 aggressive vapors. The majority of these samples weakened by 40 percent or more, with most fuels for the PETG and PETP showing reductions in tensile strength ranging from 60 to 90 percent.

Notable changes can be seen in N6 and N6/6 exposed to E10 and E10 aggressive vapor and liquid fuels, and PTFE and HDPE exposed to E10, E10 aggressive, and B55 aggressive vapor and liquid fuels. HDPE samples showed increases in tensile strength for all three liquid fuels and for the E10 and B55 aggressive vapors, whereas the other materials showed reductions in tensile strength.

Other samples showed smaller changes in tensile strength, on the order of 10 percent or less, including N6, N6/6, PET, PBT, and PPS for the Bu55 aggressive exposures, PET, PPS, and PVFE for both liquid and vapor exposures, PETP for the vapor exposure to the E10 aggressive fuel, and PVDF for the E10 fuel.

Figure 47: Percent Tensile Strength Change for Plastic Samples

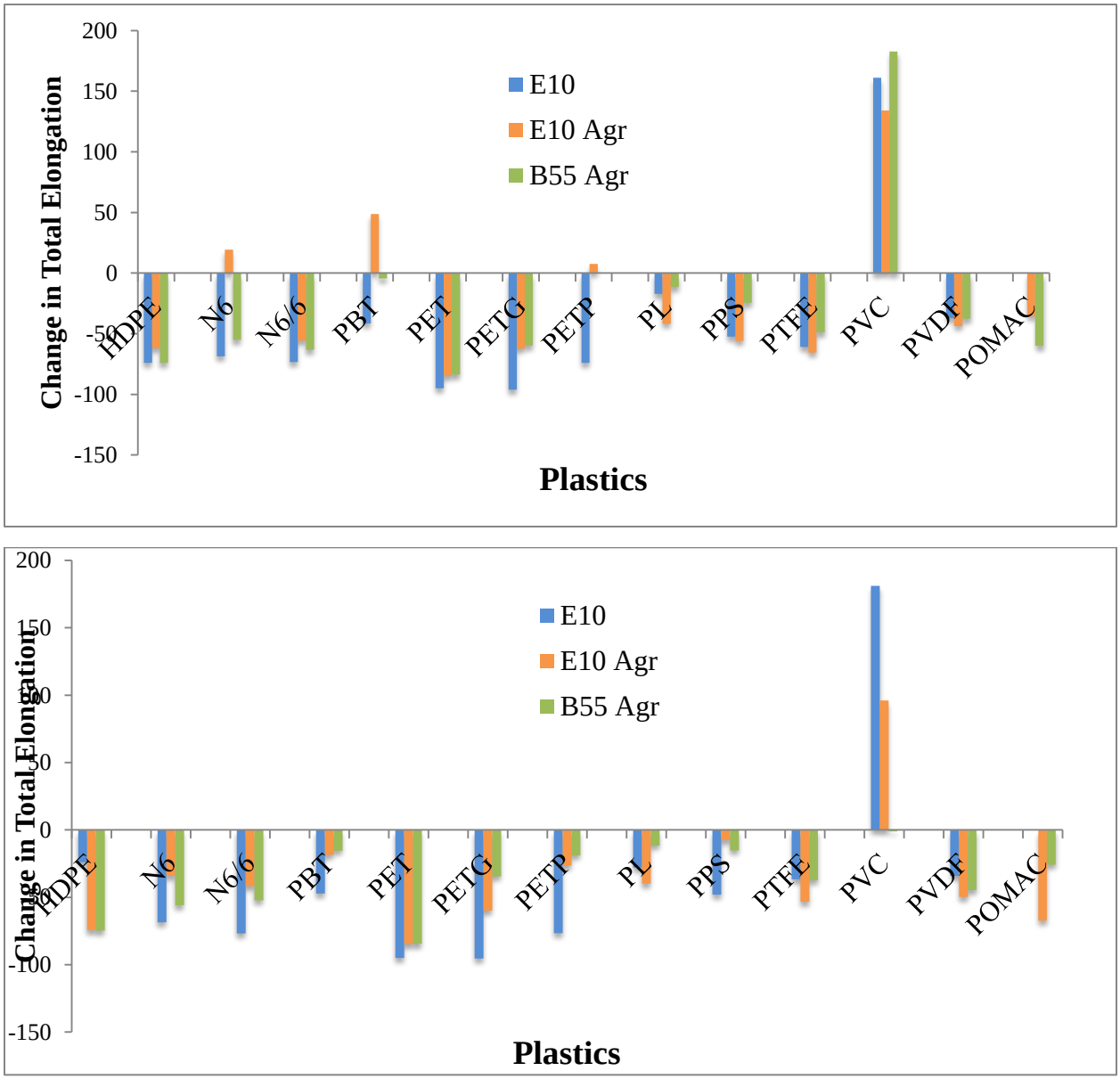


Tensile Strength change of liquid (top) and vapor (bottom) samples

Photo Credit: Kyle Hunter, Lab Technician for CE-CERT

The percent change in elongation is shown in **Error! Not a valid bookmark self-reference.** for the plastic samples. The plastics showed reductions in elongation for all samples, with the exception of the PVC and some E10 aggressive samples. The PVC showed increases in elongation from 134 to 183 percent. The majority of the reductions in elongations were on the order of 25 to 95 percent. For the samples showing a reduction in elongation, the E10 fuel showed the greatest reductions for some materials. PET, PETG, and POMAC are three materials that showed the largest losses in elongation.

Figure 48: Percent Change in Elongation of Plastics



Elongation Percent change of liquid (top) and vapor (bottom) samples

Photo Credit: Kyle Hunter, Lab Technician for CE-CERT

In previous studies, ORNL researchers found reductions in hardness for most plastics of 5 points or less (Kass et al., 2012a/ 2013/ 2014b). Larger reductions in hardness were found for PETG ranging from 10 to 25 percent after fuel exposures, with reductions for lower alcohol blends generally in the 20 to 25 point range, and reductions of hardness of about 10 percent after drying (Kass et al., 2012a/ 2013/2014b).

ORNL has also conducted previous studies of the viscoelastic properties of plastics exposed to different fuels via DMA as part of its material compatibility studies (Kass et al., 2012a/ 2013/ 2014b). In these previous studies, a number of plastic samples did not show large transitions in T_g, including PPS, PTFE, PDVF, HDPE, and POM. Other plastics showed reductions in T_g, consistent with the retention of test fuel having an impact of the molecular structure of the sample. PET showed about a 86°F (30°C) drop in T_g for exposure to a E25 aggressive blend, but not major changes for the reference C gasoline or the isobutanol fuels. N6 and N6/6 also showed reductions of 104°F (40°C) to 140°F (60°C) in T_g for the E25 aggressive fuel, but increases in T_g for the reference C gasoline, while the iosbutanol fuels did not cause major changes in T_g. PETG, PBT, and PP also showed reductions in T_g, with PETG showing the largest reduction of about 140°F (60°C) to 158°F (70°C). PBT showed a reduction of about 86°F (30°C) for the reference C fuel, and an additional 50°F (10°C) reduction in T_g for the ethanol and isobutanol blends.

CHAPTER 4:
Summary and Conclusions

California and the rest of the nation are dependent upon an extensive and pervasive network of transportation, storage, and distribution systems that have evolved over many decades around reliability criteria associated with petroleum-based fuels. There is now a need for this infrastructure to accommodate a more diverse array of fuels, as the use of alternative fuels expands in the marketplace.

The goal of this California Energy Commission's Public Interest Energy Research (PIER) Transportation program is to accelerate research, development and demonstration (RD&D) of advanced technologies and to ensure the compatibility of existing petroleum transportation fuels infrastructure with nonpetroleum alternative fuels in and for California. This study, in particular, examined materials compatibility issues for infrastructure components that would be found in the existing petroleum fueling infrastructure. For this program, E10 blends with both aggressive and non-aggressive formulations, a 55 percent butanol blend with an aggressive formulation, and natural gas blends with CO_2 and varying levels of hydrogen and water saturation were tested. Metal, plastic, and elastomer samples used in the infrastructure for the transport and distribution of petroleum products were exposed to these fuels for varying periods of time. These exposures were done in a cylindrical stir chamber for the liquid fuels and in a series of tubes for the natural gas exposures. The material specimens were evaluated before and after exposure for mass loss, volume change, visual appearance/discoloration, and evidence of pitting. Metals were also tested for changes in composition. Elastomer and plastic were tested for hardness changes, impact resistance, tensile strength, and a dynamic mechanical analysis.

A summary of the findings and conclusions of this study are as follows:

Natural Gas Exposures

Elastomers

- Elastomer samples showed very minor variations in volume between the unexposed and exposed samples. The elastomer samples had a volume change of less than 3 percent for all samples, with the volume change for most samples being within 2 percent. The volume change was a reduction in size for most samples, although a few samples did show increases in size.
- The elastomer samples show an insignificant change in mass change. The majority of the elastomer samples showed a percent weight change of 0.5 percent or less. SBR and NBR samples from the dry 20 percent H_2 Tube, and N samples from the wet 20 percent H2 Tube were outliers at a change of about +2 to -3 percent.
- Elastomer samples that were exposed to natural gas did not show a difference in visual appearance.
- The majority of the samples had a change of tensile strength of less than ±20 percent. For tensile strength, the NBR exposed to baseline dry +20 percent H_2 showed the biggest

change, with an increase of roughly 70 percent. SBR and Viton B that were exposed to baseline dry +20 percent H_2 and baseline wet +20 percent H_2, respectively, had a decent decrease in tensile strength of approximately 43 to 44 percent. Viton B exposed to baseline wet +5 percent H_2 also had a decrease of tensile strength of approximately 56 percent. BN and N both showed decreases in tensile strength for all exposures, while NR showed a decrease for the baseline dry +20 percent H_2.

- The majority of the samples that were exposed to natural gas showed decreases in elongation. The majority of the samples showed decreases in elongation of approximately 20 percent or less. A few individual samples showed larger decreases, including a decrease of 45 to 55 percent for NBR, a 57 percent decrease for SBR, and a decrease of 50 to 55 percent for Viton B. BN showed a decrease of 33 percent for the baseline dry exposures, but increases for the some of the other exposures.

Plastics

- All plastic samples had percent volume changes of less than 3.5 percent, with many samples having volume changes below 2 percent. The majority of plastic samples show a minor increase in volume, with a few samples showing a slight decrease in volume.
- The plastic samples showed an insignificant change in mass change. The majority of the plastic samples showed a percent weight change of 0.2 percent or less, with the average being 0.1 percent in percent weight change or less.
- Plastic samples that were exposed to natural gas did not show a difference in visual appearance.
- The majority of the samples had a change in tensile strength of ±20 percent, with tensile strength increasing in most cases. PBT, PETP, and PPS had the lowest deviation from their original tensile strength at an average of ±5 percent. HDPE and PL when exposed to natural gas had the greatest change in tensile strength at an increase on average of slightly greater than 30 percent and decrease on average of 34 to 43 percent, respectively. There is not a significant difference between plastics that were exposed to natural gas and different levels of H_2.
- The majority of the samples had a change of ±50 percent or less in elongation. PETG, PTFE, and PVDF had the lowest change in elongation at ±20 percent or less. PL, PETP, and POMAC all showed increases in elongation for various blends that were greater than 100 percent, ranging up to a 200 percent increase.

Metals

- The majority of metal samples show a minor increase in percent volume change, with all samples showing less than a 3.1 percent volume change. For the baseline wet and baseline + 1 percent H_2 wet exposures, the majority of samples lost a slight amount of volume.

- The metal samples show an insignificant change in mass change. The majority of the metal samples showed a percent weight change of 0.01 percent or less.
- The majority of metal samples that were exposed to natural gas did not show a difference in appearance. The only changes seen were for metal samples exposed to the baseline wet +20 percent H_2 gas. S4140 samples exposed to the baseline wet +20 percent H_2 gas developed rust on the surface.

Liquid Fuel Exposures

Elastomers

- The elastomers showed the most significant changes of any of the materials as a result of the liquid fuel exposures. The elastomers generally increased in volume and mass immediately following the exposures, indicating the absorption of the liquid fuels into the elastomer material. Following drying, the most elastomers shrank to volume/mass below that of the original sample, indicating that the liquid fuel and some of the associated elastomer components were removed from the sample. The samples exposure directly to the liquid fuels tended to show more significant changes than those exposed to the fuel vapors.
- The rubber samples (SBR, NBR, and NR) showed relatively significant increases in volume/mass immediately after exposure, with SBR showing the largest increases. The NBR and NR samples exposed to the E10 aggressive formulation were also damaged and broke apart during the fuel exposures. SBR showed differences as a function of alcohol content, but the E10 aggressive exposures leading to much higher volume swell than the Bu55 exposures. NBR has also shown a similar dependence of higher volume swell for exposures to lower alcohol content fuels in previous studies.
- Fluorocarbons (A401C, B601) were the most resistance of all of the elastomers, showing smaller levels of volume swell/mass gain immediately after exposure, but retaining some of the mass gain/volume swell following drying. The fluorocarbons also did not show significant changes in visual appearance.
- Most elastomers showed a reduction in tensile strength and a tendency for reduced elongation during the tensile strength test.
- The biggest reductions in tensile strength were seen for PU (43 to 92 percent), NR (84 to 92 percent), NBR (43 to 53 percent), and BN (40 to 60 percent). Most of the other materials showed changes of 25 percent or less. Most samples became less resistant to stress after fuel exposure, but SBR and N showed an increase in tensile strength when exposed to the E10 fuel.
- Most materials showed changes in elongation of ±20 percent or less. A few samples showed larger changes of anywhere from 60 to 100 percent for various fuel blends including NBR, NR, and Viton B. The samples exposed to vapor showed similar changes in elongation as the liquid fuel exposures.

Plastics

- The plastics showed changes that were less than those for the elastomers, but greater than those for the metals as a result of the liquid fuel exposures. The plastics increased in volume and mass immediately following the exposures, and generally retained some of this volume swell/mass gain after drying, indicating that the liquid fuel was retained in the plastic structure. The volume swell for the plastics was generally less than that found for the elastomers.
- N6, N6/6, PBT, PET, PETP, PPS, PVDF, POMAC, and PTFE increased less than 10 percent in volume and mass for all samples before drying. When dried, the majority of these samples had an increase in volume and mass of 5 percent or less from their original dimensions. The smallest changes were seen for the PET, PETP, and PPS samples.
- PVC and PETG showed the strongest effects for the plastic samples, increasing by 20 to 35 percent in volume and 13 to 22 percent in mass upon exposure and retaining between 20 to 30 percent of the volume increase and between 8 to 13 percent of the main gain upon drying.
- A number of plastics showed discoloration upon exposure to the fuels. PBT, PETG, and the nylon (N6, N6/6) samples all showed a yellowish tint after fuel exposures, while PVDF showed some pinkish discoloration for with the E10 aggressive fuel. Plastics that did not show any visual color changes included PET, PTFE, PPS, HDPE, PL, POMAC, and PETP.
- PET, PETG, PETP, PL, PVC, and POMAC all showed significant changes in tensile strength for different liquid fuel and vapor exposures, with many of these weakening by over 40 percent and with PET, PETG and PETP showing reductions ranging from 60 to 90 percent. Exposures to E10 liquid and vapor resulted in higher tensile strength changes for a number of the samples, but not all of them. Notable changes were also seen for some exposures of N6 and N6/6, PTFE and HDPE, and PVC, with most exposures showing reductions in tensile strength, with the exception of HDPE which showed increases. Other samples showed smaller changes in tensile strength, on the order of 10 percent or less, including N6, N6/6, PET, PBT, and PPS for the Bu55 aggressive exposures, PET, PPS, and PVFE for both liquid and vapor exposures, PETP for the vapor exposure to the E10 aggressive fuel, and PVDF for the E10 fuel.
- The plastics showed reductions in elongation for all samples, but the PVC. The PVC showed increases in elongation from 130 to 180 percent. The majority of the reductions in elongations were on the order of 25 to 95 percent. For the samples showing a reduction in elongation, the E10 fuel showed the greatest reductions for some materials. PET, PETG, and POMAC showed the largest losses in elongation.

Metals

- Metal samples were the least affected by the liquid fuel exposures. The metal samples all had a increase or decrease in volume of 6 percent or less before drying and 7 percent or less after drying.
- The B55 aggressive fuel produced increases in volume for nearly all of the metal samples. On the other hand, the majority of metal samples exposed to E10 aggressive fuel decreased in volume slightly. The E10 results were more mixed, although S4140 and CPB showed consistent increases for both the liquid and vapor samples. Metal samples exposed to vapor generally have a smaller volume compared to samples that were exposed to the fuel directly.
- The metal samples show an insignificant change in mass change. Submerged samples did not deviate past 1/10 of a percent in weight change after fuel exposure and drying. The majority of the vapor samples also did not deviate past 0.1 percent in weight change after fuel exposure and drying, although the Zinc and S4140 samples exposed to the vapor of the E10 aggressive fuel showed reductions in weight of 0.37 percent and 0.17 percent, respectively.
- The main effect seen for the metals was a discoloration from corrosion, particularly for the E10 aggressive and B55 aggressive fuels. The majority of samples that were exposed to the fuel vapors appeared to show a greater visual change compared to samples that were exposed to the fuels directly. All aluminum samples were prone to mild rust for the E10 aggressive and B55 aggressive fuels, with the latter affecting the aluminum samples the most. Nickel-plated samples (NPS, NPA, ENPA) all acquired a brown tint after exposure to all three fuels. S4140, CB, PB, GS, Zinc, and N200 showed major rust/heavy dark stains after exposure to the E10 aggressive and B55 aggressive fuels.

Implications and Recommendations

The results of this study provide an important comparison between materials in terms of their compatibility with different fuels. Particularly with respect to liquid fuels, there is a definitive trend in terms of elastomers showing greater fuel impacts than plastics, while metals showed much smaller impacts. The volume increases due to the fuel exposures by itself does not necessarily indicate that the material is incompatible with a particular fuel, as the swelling for elastomers, for example, can help in providing a tight seal, even in cases where the swell is greater than 50 percent (Kass et al., 2014a). Nevertheless, excessive swelling can lead to protrusion that could subject the seals to breakage or abrasion. Some of the more susceptible elastomers included SBR, NR, and NBR, in terms of either swelling or embrittlement and breakage. Plastics were not subject to as much volume swell as elastomers, and most plastics showed volume swell of less than 10 percent. PVC and PETG showed the highest swell, and as such care should probably be used in considering these materials for use with alcohol-based fuels. For both plastics and elastomers, analyses based on the mutual solubility of the material and the fuel provided a good indication of the degree of volume swell that could be expected in different cases, such as PTFE and PVDP. The metals overall did not show strong liquid fuel effects in terms of mass or volume changes, but did show some discoloration from corrosion. In comparing different fuels, the 55 percent butanol fuel had less of an impact on volume swell

than the 10 percent ethanol fuel. Previous studies have indicated that lower concentration alcohol blends can have greater impacts on material compatibility than higher blends (Kass et al., 2012a), so this could largely be due to the differences in the alcohol blend content, as previous studies of ethanol and butanol at more comparable blends levels have indicated similar material compatibility for the two fuels.

For the natural gas exposures, there were very limited impacts were seen in terms of volume and mass change over the exposure regime tested for hydrogen or water for either the elastomers, plastics, or metals. Some changes were observed in tensile strength and/or elongation, with materials including SBR, NBR, and Viton B elastomers, and HDPE, PL, PETP, and POMAC plastics. Additional testing for longer periods of time could further provide insight into the materials compatibility impacts for natural gas blends with various contaminants.

GLOSSARY

Term	Definition
A401C	Viton A401C
ABE	Acetone-Butanol-Ethanol (a fermentation process)
AL1100	Aluminum 1100
AL2024	Aluminum 2024
AL6061	Aluminum 6061
ARB	California Air Resources Board
ASTM	American Society of Testing and Materials
B601	Viton B601
BN	Buna-N Cork Blend
BTU	British Thermal Unit
CB	Cartridge Brass
CH_2	Methane
CO_2	Carbon Dioxide
CPB	Chrome Plated Brass
CPS	Chrome Plated Steel
E10	Gasoline blended with 10 percent ethanol by volume
EISA	Energy Independence and Security Act
ENPA	Electroless Nickel-Plated Aluminum
GS	Galvanized Steel
H_2	Hydrogen
H_2O	Water
HDPE	High Density Polyethylene
Lb.	Pound
N	Neoprene
N200	Nickel
N6	Nylon 6
N6/6	Nylon 6/6
NBR	Nitrile Butadiene Rubber
NPA	Nickel Plated Aluminum
NPS	Nickel Plated Steel
NR	Natural Rubber
OEHHA	Office of Environmental Health Hazard Assessment
ORNL	Oak Ridge National Laboratory
PB	Phosphor Bronze
PBT	Polybutylene Terephthalate
PET	Polyethylene Terephthalate
PETG	Polyethylene Terephthalate
PETP	Polyethylene Terephthalate
PL	Polypropylene

POMAC	POM Acetal Copolymer
PPS	Polyphenylene Sulphide
PTFE	Teflon
PU	Polyurethane
PVC	Poly Vinyl Chloride
PVDF	Polyvinylidene Difluoride
RNG	Renewable Natural Gas
S4140	Alloy Steel
SBR	Styrene Butadiene Rubber
SS304	Stainless Steel 304
SS316	Stainless Steel 316
ZINC	Zinc

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