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Abstract: As interest in replacing petroleum-derived aviation fuels with
resilient, alternative fuels increases, there is a great need to derive
correlations between the chemical compositions of aviation fuels and
their properties and performance. In this work, correlations between the
exact chemical structures of organic compounds and their ability to swell
the volume and decrease the tensile strength of Buna-N o-ring seals
(commonly used in airplanes) were examined. Buna-N o-ring seals are one
representative group of essential seals in the hydraulic and pneumatic
components of the aircraft fuel delivery systems. They are utilized for
preventing fuel leakage within the pumps, metering devices, and
connectors. To measure the volume swell percent of o-ring seals, a test
rig was assembled in house that suspended o-ring seals for a 48-hour
period in neat Sasol isoparaffinic kerosene (Sasol IPK) or Sasol IPK
doped individually with an organic compound at 8 % by volume. Of the
aromatic compounds tested, ethylbenzene and indane swelled o-ring seals
most effectively, with volume swell percent values of 3.08 ± 0.18 % and
2.78 ± 0.11 %, respectively. Ethylbenzene and indane swelled o-ring seals
more effectively than a 50:50 blend of Jet A and hydroprocessed esters
and fatty acids (HEFA). Alkylbenzenes with a smaller number of alkyl
groups attached to the benzene ring, less branching in the alkyl groups,
and shorter alkyl chains caused greater swelling and greater decrease in
the tensile strength for o-ring seals. Naphthene-containing aromatic
compounds (i.e., indane and tetralin) swelled o-ring seals more
effectively than alkylbenzenes with the same number of carbons (i.e., n-
propylbenzene and n-butylbenzene). Therefore, steric hindrance seems to
have an important impact on these compounds' ability to swell o-rings.
Nonaromatic unsaturated hydrocarbons, such as cyclohexene, 1-
methylcyclohexene and 1,5-hexadiene, were also found to swell o-ring
seals to some extent but substantially less than aromatic compounds. Of
these compounds, cyclohexene swelled o-ring seals with the greatest
efficiency, with a volume swell percent value of 1.67 ± 0.10 %. On the
other hand, saturated hydrocarbons, such as cyclohexane, contributed to
minimum or no swelling. Hence, the presence of benzene rings, C=C bonds
and the lack of steric hindrance appeared to influence the ability of

organic compounds to swell the o-ring seals. The ranges in volume swell percent values for aromatic and nonaromatic compounds were 0.29 - 3.08 % and 0.02 - 1.67 %, respectively. Based on above findings, previous correlations linking a decreasing molar mass and molar volume of a compound to an increasing o-ring volume swelling are not necessarily valid. Aromatic compounds that facilitated greater swelling of o-ring seals also caused greater decrease in the tensile strength of the o-rings seals. For example, ethylbenzene and sec-butylbenzene, with volume swell percent values of 3.08 ± 0.18 % and 0.86 ± 0.14 %, respectively, reduced the o-ring tensile strength down to 13.6 MPa and 14.9 MPa, respectively, from 15.4 MPa. Additional experiments demonstrated that volume swell and tensile strength of o-ring seals are not static properties but reversible. Hence, a decrease in tensile strength for o-ring seals does not imply irreversible damage. Overall, the extent of volume swelling and lowering of tensile strength for o-ring seals was found to depend on the exact chemical structure of the organic compound.

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Cover Letter

We are hereby submitting a manuscript for consideration for Fuel that focuses on the dependence of aircraft o-ring seal swelling on the exact chemical composition of the organic compounds that the o-rings are exposed to. If these o-rings do not swell adequately, the airplane fuel will leak in the fuel circulation system. The development of novel alternative aviation fuels requires a better understanding of what sort of compounds would most efficiently swell these o-ring seals.

The Capability of Different Organic Compounds to Swell Acrylonitrile Butadiene O-rings: Steric and Mechanical Properties

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Submitted to Fuel

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Abstract

As interest in replacing petroleum-derived aviation fuels with resilient, alternative fuels increases, there is a great need to derive correlations between the chemical compositions of aviation fuels and their properties and performance. In this work, correlations between the exact chemical structures of organic compounds and their ability to swell the volume and decrease the tensile strength of Buna-N o-ring seals (commonly used in airplanes) were examined. Buna-N o-ring seals are one representative group of essential seals in the hydraulic and pneumatic components of the aircraft fuel delivery systems. They are utilized for preventing fuel leakage within the pumps, metering devices, and connectors. To measure the volume swell percent of o-ring seals, a test rig was assembled in house that suspended o-ring seals for a 48-hour period in neat Sasol isoparaffinic kerosene (Sasol IPK) or Sasol IPK doped individually with an organic compound at 8 % by volume. Of the aromatic compounds tested, ethylbenzene and indane swelled o-ring seals most effectively, with volume swell percent values of 3.08 ± 0.18 % and 2.78 ± 0.11 %, respectively. Ethylbenzene and indane swelled o-ring seals more effectively than a 50:50 blend of Jet A and hydroprocessed esters and fatty acids (HEFA). Alkylbenzenes with a smaller number of alkyl groups attached to the benzene ring, less branching in the alkyl groups, and shorter alkyl chains caused greater swelling and greater decrease in the tensile strength for o-ring seals. Naphthene-containing aromatic compounds (*i.e.,* indane and tetralin) swelled o-ring seals more effectively than alkylbenzenes with the same number of carbons (*i.e., n*-propylbenzene and *n*-butylbenzene). Therefore, steric hindrance seems to have an important impact on these compounds' ability to swell o-rings. Nonaromatic unsaturated hydrocarbons, such as cyclohexene, 1-methylcyclohexene and 1,5-hexadiene, were also found to swell o-ring seals to some extent but substantially less than aromatic compounds. Of these compounds, cyclohexene swelled o-ring seals with the greatest efficiency, with a volume swell percent value of 1.67 ± 0.10 %. On the other hand, saturated hydrocarbons, such as cyclohexane, contributed to minimum or no swelling. Hence, the presence of benzene rings, C=C bonds and the lack of steric hindrance appeared to influence the ability of organic compounds to swell the o-ring seals. The ranges in volume swell percent values for aromatic and nonaromatic compounds were 0.29 – 3.08 % and 0.02 – 1.67 %, respectively. Based on above findings, previous correlations linking a decreasing molar mass and molar volume of a compound to an increasing o-ring volume swelling are not necessarily valid. Aromatic compounds that facilitated greater swelling of o-ring seals also caused greater decrease in the tensile strength of the o-rings seals. For example, ethylbenzene and *sec*-butylbenzene, with volume swell percent values of 3.08 ± 0.18 % and 0.86 ± 0.14 %, respectively, reduced the o-ring tensile strength down to 13.6 MPa and 14.9 MPa, respectively, from 15.4 MPa. Additional experiments demonstrated that volume swell and tensile strength of o-ring seals are not static properties but reversible. Hence, a decrease in tensile strength for o-ring seals does not imply irreversible damage. Overall, the extent of volume swelling and lowering of tensile strength for o-ring seals was found to depend on the exact chemical structure of the organic compound.

Introduction

Within the last decade, efforts to replace petroleum-based aviation fuels with resilient, non-petroleum-based fuels have received national attention.[1] Access to alternative fuels will enhance energy security, decrease reliance on foreign countries for crude oil and improve resiliency during periods of vulnerability to existing crude oil infrastructure.[2]

The United States Department of Defense has made significant efforts to utilize alternative fuel blending components produced via the Fischer-Tropsch (FT) catalytic process in military aircraft.[3] Feedstocks for the FT process include biomass, coal and natural gas[4,5] and the products are mixtures of linear and branched saturated hydrocarbons.[6,7] The chemical compositions of these mixtures differ considerably from petroleum-derived fuels (*i.e.,* Jet A and JP-8), which contain linear, branched and cyclic saturated hydrocarbons as well as aromatic and polyaromatic compounds. The absence of the aromatic compounds in the FT-derived hydrocarbon mixtures is a major concern because these compounds facilitate o-ring seal swelling in aircraft fuel circulation systems and fuel tanks.[3,8] The linear and branched saturated hydrocarbons in fuel blending components have been shown to swell o-ring seals less than 10 % of the swelling caused by petroleum-based aviation fuels.[9,10] If aromatic compounds are absent or have too low concentration, o-ring seals may not swell to an adequate volume, which results in fuel leaks.[11] Hence, FT-derived saturated hydrocarbon mixtures cannot currently be used as a fuel without blending with a petroleum-based fuel.[12]

The extent of o-ring swelling by a fuel is largely dependent on the polymer matrix, the degree of polymer crosslinking and the physical and chemical properties of the fuel molecules.[3,8,12,13-16] The o-ring seals found in aircraft fuel circulation systems are commonly composed of copolymer chains of nonpolar polybutadiene and polar polyacrylonitrile (commercially known as Buna-N or nitrile rubber).[12,17,18] Polybutadiene contributes to the softness and pliability of the o-rings via formation of weak intermolecular bonds through dispersion forces between polymer chains.[8] Polyacrylonitrile is fuel resistant[17] as it has strong dipole-dipole intermolecular forces between polymer chains through the polar cyano groups on opposing polymer chains.[8]

O-ring swelling is dictated by two competing processes: the free energy of mixing, ΔF_m, and elastic free energy, ΔF_{el}.[13] When in contact with fuel, o-ring seals contribute to the volume into which the fuel may spread. Hence, the compounds in fuel are provided with an opportunity to increase their entropy upon entry into the o-ring seals.[13] Upon entry, the compounds contribute to the elongation of the polymer chains and elastic retractable forces develop within the matrix. As the chains continue to elongate, the elastic free energy gradually increases until the energy is equal in magnitude, but opposite in sign, to the free energy of mixing. At this point, an equilibrium is established between the force of fuel compounds entering the o-ring and the force of the polymer matrix pushing against the fuel. Combining both terms, the free energy change of swelling can be expressed[13] as shown in Equation 1.

$$\Delta F = \Delta F_m + \Delta F_{el} \quad \text{Equation 1}$$

Recently, efforts have been undertaken to develop correlations between the structures of crude-oil related aromatic compounds and their propensity to swell Buna-N o-ring seals.[8] Generally, aromatic compounds with a low molar mass, low molar volume and a polar functionality that exhibits hydrogen bonding (*e.g.,* benzyl alcohol, ethylphenol and phenol) have been found to show the greatest propensity to swell Buna-N o-ring seals.[3,8,12,14] Further, as the length of an *n*-alkyl group attached to a benzene ring increases, the propensity of the compound to swell Buna-N o-ring seals decreases as follows: ethylbenzene > *n*-propylbenzene > *n*-pentylbenzene.[8] Different swelling properties are also displayed by different subclasses of aromatic compounds (*i.e.,* alkylbenzenes vs alkylnaphthalenes). Comparison of the volume swell percent values for o-ring seals immersed in a mixture predominantly composed of alkylnaphthalenes versus a mixture composed of only alkylbenzenes revealed that the mixture composed of alkylnaphthalenes caused three times more swelling.[19]

This study seeks to identify the specific aromatic, and possibly nonaromatic, compounds that swell o-ring seals most effectively. Another goal was to evaluate the mechanical properties of o-ring seals by determining their ultimate tensile strength after interaction with the selected compounds. Organic compounds that are highly effective in seal swelling would make beneficial dopants for alternative fuels in lieu of blending them with petroleum-based fuels, which would reduce the total aromatic content required to induce seal swelling and enhance fuel quality.

Experimental

<u>Chemicals and materials</u>

Ethylbenzene (99 % purity) was purchased from Alfa Aesar. *n*-Propylbenzene (98 % purity), isopropylbenzene (98 % purity), 1,3,5-trimethylbenzene (98 % purity), *n*-butylbenzene (≥ 99 % purity), *sec*-butylbenzene (≥ 99 % purity), *tert*-butylbenzene (99 % purity), 1,2,4,5-tetramethylbenzene (98 % purity),1,5-hexadiene (97 % purity), 1-methylcyclohexene (97 % purity), cyclohexene (99 % purity), phenol (≥ 99.0) and 2,6-di-*tert*-butyl-4-methylphenol (≥ 99 % purity) were purchased from Sigma-Aldrich. Indane (95 % purity) and cyclohexane (99 % purity) were purchased from Acros, and tetralin (≥ 97 % purity) and *n*-hexane (≥ 97 % purity) from Fluka. Sasol isoparaffinic kerosene (referred to as Sasol IPK), and Jet A mixed with hydroprocessed esters and fatty acids at a 50:50 volume ratio (referred to as Jet A/HEFA) were received from Dr. Tim Edwards of the Wright-Patterson Air Force Base, Dayton, OH. All compounds, Sasol IPK and Jet A were used as received without additional purification.

Durometer 70A Buna-N nitrile o-ring seals were purchased from USA Sealing Incorporated and used as received. Buna-N nitrile o-rings were chosen for this study

because they have a variety of fuel related applications[3,12,14] and are commonly used in aircraft fuel circulation systems.[18]

Instrumentation and methods

Volume swell percent studies

To evaluate organic compounds' propensity to swell o-ring seals, Sasol IPK was doped with different organic compounds at 8 % by volume and the o-ring seals were immersed in these solutions for 48 hours in a custom-built test rig closely replicating the conditions and guidelines[20] set by ASTM D471 (Figure S1). Briefly, an Erlenmeyer flask was fitted with a rubber stopper with a small opening to insert a condenser. During immersion studies, cold water was circulated through the condenser. The temperature of the laboratory where the o-ring seals were studied ranged from 22 up to 23 ^{o}C. Approximately 100 mL of Sasol IPK or 92 mL of Sasol IPK and 8 mL of an organic compound were added into the Erlenmeyer flask and mixed thoroughly. For 1,2,4,5-tetramethylbenzene, 6.94 grams were added into a flask containing Sasol IPK and the mixture was stirred to dissolve it completely, ending up with a final volume of 100 mL. Three o-ring seals were immersed in neat and doped Sasol IPK by using a metal suspension wire that was crafted in house. The wire was designed to accommodate three o-ring seals, ensure that the o-ring seals were completely immersed, and prevent the o-ring seals from contacting the Erlenmeyer flask or other o-ring seals during the immersion period.

To determine the volume swell percent for o-ring seals, a Nikon Profile Projector V-12 was used to measure the cross-sectional diameters of the o-ring seals before and immediately after the immersion period (Figure S2). The average cross-sectional diameter for each o-ring seal was determined from eight measurements of each o-ring seal (please see Figure S3 for an illustration). The volume swell percent for each o-ring seal was determined by using equation 2,[10]

$$ \mu_i = \left[\left(\frac{d_i}{d_o} \right)^3 - 1 \right] \times 100 \qquad \text{Equation 2} $$

where μ_i is the average volume swell percent, and d_i and d_o are the average diameters of the o-ring seals before and after the immersion period, respectively. The average volume swell percent and a standard deviation ($\mu = \pm 1\sigma$) was determined.

Ultimate tensile strength and ultimate elongation percent

The ultimate tensile strength is defined as the amount of stress (force over unit area) applied to an o-ring seal to cause it to rupture. The ultimate elongation percent is the difference between the original length of an o-ring seal (*i.e.,* not stretched) and the length of the o-ring seal at rupture. An MTS Insight Electromechanical Testing Instrument was used to determine the   ultimate tensile strength and ultimate elongation

percent of intact o-ring seals after immersion according to the guidelines set by ASTM D1414-15.[21] For each mixture (*i.e.,* Sasol IPK or Sasol IPK doped with an organic compound at 8 % by volume), five o-ring seals were immersed for a 48-hour period. The two spool grips of the MTS instrument used to measure the ultimate tensile strength and ultimate elongation percent of o-ring seals consisted of two ball-bearing spools with a diameter of 11 mm. Each o-ring seal was placed around both spools and pulled apart by the grips at a rate of 500 mm/min. The frictional stresses between the o-ring and the spool were minimized by rotating one spool at 3.3 revolutions/min. The force and elongation at the time of o-ring rupture were recorded by using an MTS load cell with a resolution of 1 mN. The ultimate tensile strength was calculated by using equation 3,[22] which takes into consideration that non-cut o-ring seals have twice the cross-sectional area compared to a cut o-ring:

$$\text{Ultimate tensile strength} = \frac{F}{1.57W^2} \qquad \text{Equation 3}$$

where F is the force registered by the load cell and W is the average diameter of an o-ring seal after the immersion period. Similarly, the ultimate elongation percent of the o-ring seals was calculated by using equation 4,[22]

$$\text{Ultimate elongation, \%} = \left[\frac{2D+G-C}{C}\right] \times 100 \qquad \text{Equation 4}$$

where D is the distance between the spool grips at the time of o-ring rupture, G is the circumference of the ball-bearing spools and C is the internal circumference of the o-ring seals. The ultimate tensile strength and ultimate elongation percent values given for o-ring seals immersed in Sasol IPK doped with an organic compound were the average of five measurements.

Quantitation of ethylbenzene by using GCxGC/FID

An Agilent GCxGC 7890B dual-stage gas chromatograph equipped with a flame ionization detector (FID) was used to determine the concentration of ethylbenzene diffusing out of o-ring seals in the experiments described below. Standards of ethylbenzene were prepared at concentrations of 10, 20, 30, 50 and 125 µM in *n*-hexane. Ethylbenzene was chosen for the quantitation studies as it swells o-ring seals with the greatest propensity compared to the other organic compounds tested. An auto injector (Agilent 7683B) was used to inject 0.5 µL of each standard solution into a split/splitless injector with a split ratio of 1:20. The injector inlet temperature was held constant at 280 °C. A flow of ultrapure helium carrier gas at a flow rate of 1.25 mL/min was used. The columns were arranged in reversed-phase mode, consisting of a 30 m primary polar column (DB-17MS, Agilent, Santa Clara) and a 0.8 m secondary nonpolar column (DB-1MS, Agilent, Santa Clara). The GCxGC system was equipped

with quad-jet dual stage modulator, which unites the primary column to the secondary column. The modulator collects the eluate from the first column and then transmits the eluate into the secondary column via hot and cold pulses of nitrogen gas. The GCxGC method used for the quantitation of ethylbenzene has been previously described.[23] Briefly, the total modulation time between the two columns was set to 6.5 s. This time was split into two stages, 3.25 s each, of which 1.06 s corresponded to the hot pulse time and 2.19 s corresponded to the cold pulse time. The primary oven was set to 40 ^{o}C and the heat was ramped up 1 ^{o}C/min until the final temperature of 280 ^{o}C was reached. The secondary oven and the modulator hot jet temperature had + 55 ^{o}C and + 15 ^{o}C offsets, respectively, from that of the primary oven. An acquisition delay of 175 s was applied to prevent the detection of solvent n-hexane. The frequency of the FID was set to 200 Hz and it was maintained at a constant temperature of 300 ^{o}C. The integrated peak areas measured for the standards were plotted as a function of their known concentrations to obtain a calibration plot.

To test whether the volume swell and decrease in tensile strength for o-ring seals are dynamic or static properties, o-ring seals were immersed in Sasol IPK doped with ethylbenzene at 8 % by volume for 48 hours. The o-ring seals were removed, dried with a flow of nitrogen gas and re-submerged in neat Sasol IPK. Approximately 20 µL aliquots were taken from Sasol IPK containing the immersed o-ring seals at 0 hour, 4 hours, 8 hours, 24 hours, 48 hours, 72 hours and 96 hours. Each aliquot was diluted with 2.0 mL of n-hexane and doped with 30 µM of ethylbenzene to ensure that the unknown concentration of ethylbenzene diffusing out of o-ring seals was within the calibration plot. An auto injector was used to inject 0.5 µL of each diluted aliquot into the GCxGC/FID system. The calibration plot produced by the standards (see above) was used to quantify the unknown concentration of ethylbenzene diffusing out of the o-ring seals as a function of time. Further, the volume swell percent and ultimate tensile strength values were determined as described above.
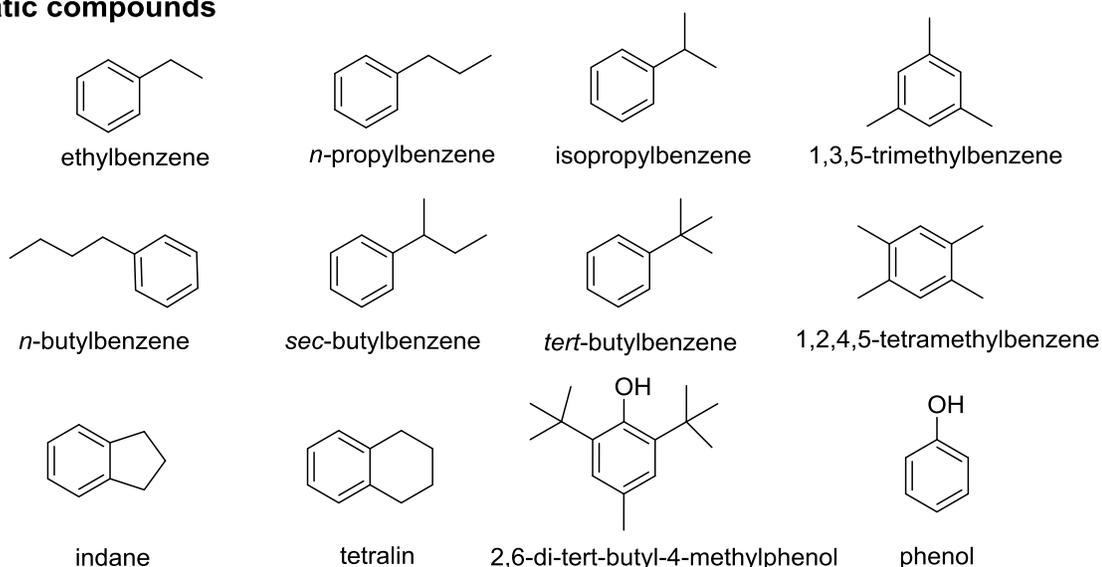
Computer program

All graphs were plotted by using OriginPro 2017 software.

Results and Discussion

Fuel blending component Sasol IPK was chosen for this study as it is composed primarily of linear and branched saturated hydrocarbons and contains approximately 0.4 % of aromatic content by volume (Figure S4 and Tables S1and S2). Hence, additional aromatic compounds must be doped into Sasol IPK for it to be considered an alternative fuel. According to Defense Standard 91-91, the minimum aromatic content by volume in an alternative fuel is 8 %.[24] Therefore, Sasol IPK was doped with different aromatic and nonaromatic compounds at 8 % by volume to systematically evaluate the dopant's effectiveness to swell seals at the mandatory minimum volume (Figure 1). In addition, the ultimate tensile strength and ultimate elongation percent of o-ring seals after

immersion in above solutions were examined. Finally, the reversibility of the volume swelling and decrease in tensile strength of o-rings seals was evaluated.

Aromatic compounds

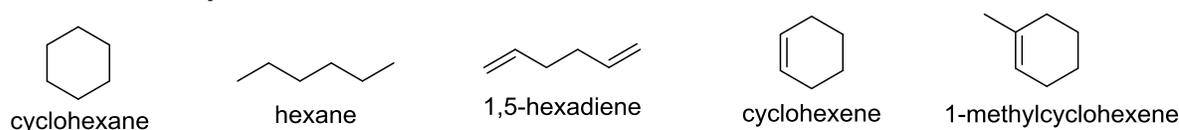ethylbenzene   n-propylbenzene   isopropylbenzene   1,3,5-trimethylbenzene

n-butylbenzene   sec-butylbenzene   tert-butylbenzene   1,2,4,5-tetramethylbenzene

indane   tetralin   2,6-di-tert-butyl-4-methylphenol   phenol

Nonaromatic compounds

cyclohexane   hexane   1,5-hexadiene   cyclohexene   1-methylcyclohexene

Figure 1. Structures of the compounds studied.

Swelling of o-ring seals by nonaromatic compounds

Evaluation of the ability of nonaromatic compounds at swelling o-ring seals was performed because aromatic compounds form more soot and cause more particulate emissions upon combustion than nonaromatic compounds.[25-28] Hence, discovering nonaromatic compounds capable of swelling these seals could enhance overall fuel quality and lower the environmentally harmful effects of the fuel. O-ring seals were immersed in neat Sasol IPK and Sasol IPK doped with nonaromatic organic compounds at 8 % by volume for 48 hours. The volume swell percent values measured for the o-ring seals are presented in Table 1 and Figure 2.

O-ring seals immersed in neat Sasol IPK and Sasol IPK doped with n-hexane did not swell to any significant extent (volume swell percent values 0.05 ± 0.04 and 0.02 ± 0.03, respectively). These results are consistent with previous findings demonstrating that linear and branched saturated hydrocarbons are not major contributors to o-ring swelling.[9,10] The volume swell percent for o-ring seals immersed in Sasol IPK doped

with cyclohexane was greater than that observed for *n*-hexane, 0.43 ± 0.10 %. This finding is

Table 1. Volume swell percent values for o-ring seals immersed in neat Sasol IPK or Sasol IPK doped with different organic compounds at 8 % by volume.

Organic mixture used to swell o-ring seals	Volume swell percent[a]	Molar mass of dopant (g/mol)	Molar volume of dopant (ml/mol)
Jet A / HEFA	2.23 ± 0.17	N/A	N/A
Sasol IPK	0.05 ± 0.04	N/A	N/A
Aromatic dopants			
ethylbenzene	3.08 ± 0.18	106.168	122.45
indane	2.76 ± 0.11	118.179	122.47
tetralin	2.05 ± 0.14	132.206	135.74
n-propylbenzene	1.94 ± 0.20	120.195	139.44
isopropylbenzene	1.63 ± 0.09	120.195	139.44
n-butylbenzene	1.37 ± 0.13	134.222	156.07
1,3,5-trimethylbenzene	1.00 ± 0.12	120.195	139.12
sec-butylbenzene	0.86 ± 0.14	134.222	156.44
tert-butylbenzene	0.68 ± 0.10	134.222	154.81
1,2,4,5-tetramethylbenzene	0.29 ± 0.02	134.222	151.15
Nonaromatic dopants			
cyclohexene	1.67 ± 0.10	82.143	101.29
1,5-hexadiene	1.48 ± 0.16	82.143	118.70
1-methylcyclohexene	0.64 ± 0.10	96.173	118.59
cyclohexane	0.43 ± 0.10	84.162	108.04
hexane	0.02 ± 0.03	86.178	130.77
Heteroatomic dopants			
Phenol[b]	1.47 ± 0.20	94.113	87.96
2,6-di-*tert*-butyl-4-methylphenol[b]	0.04 ± 0.07	220.351	209.86

[a] Values are reported as an average of three o-rings. The standard deviation ($\mu = \pm 1\sigma$) was also determined. [b] Approximately 24 mg of phenol and the 2,6-di-*tert*-butyl-4-methylphenol were dissolved individually in 100 mL of Sasol IPK.

in agreement with literature correlating the volume swell percent of a compound to its inverse of molar volume as cyclohexane has a smaller molar volume than *n*-hexane, which is expected to facilitate diffusion and partitioning into the polymer matrix.[8,14,29] However, examination of additional organic compounds (see below) proved that this correlation is not always valid.

The nonaromatic, unsaturated hydrocarbons cyclohexene, 1-methylcyclohexene and 1,5-hexadiene were found to be more effective at swelling o-ring seals than the saturated hydrocarbons. For example, cyclohexene swells o-ring seals four times more effectively than cyclohexane (Table 1). 1,5-Hexadiene swell seals 74 times more effectively than *n*-hexane and 3.5 times more than cyclohexane. Cyclohexene also swells seals 13 % more effectively than acyclic 1,5-hexadiene.

Swelling of o-ring seals by aromatic compounds

Compositional analysis performed on petroleum-derived aviation fuel Jet A 1 has shown that alkylbenzenes are the most abundant aromatic subclass in this aviation fuel[30] and that it contains many isomeric alkylbenzenes.[31,32] Hence, isomeric alkylbenzenes are a key focus in this study. The results presented in Table 1 show that as the *n*-alkyl group attached to a benzene ring becomes longer, the propensity of the compound to swell o-ring seals decreases. For example, ethylbenzene swells o-ring seals approximately 1.5 and 2.2 times more effectively than *n*-propylbenzene and *n*-butylbenzene, respectively (Table 1 and Figure 2). This result is in agreement with the experimental findings of a previous study that related the observations to the molar mass and molar volume of the compound.[8] Further, the presence of a naphthene ring fused to a benzene ring also improves the effectiveness of the compound to swell the seals. Indane (for the structure, see Figure 1) swells o-ring seals 42 % more effectively than *n*-propylbenzene with the same number of carbons. Tetralin (for the structure, see Figure 1) swells o-ring seals equally to *n*-propylbenzene, but 50 % more effectively than *n*-butylbenzene with the same number of carbons as in tetralin.

The steric effects of an alkyl group attached to a benzene ring correlates with the ability of the compound to swell o-ring seals. For example, as the number of alkyl groups attached to the main alkyl chain increases, the extent of swelling of o-ring seals decreases: *n*-propylbenzene swells o-ring seals 16 % more effectively than isopropylbenzene. When the extent of volume swell of o-rings attributed to $C_{10}H_{14}$ isomers is compared, the order for o-ring swelling increases as follows: *tert*-butylbenzene < *sec*-butylbenzene < *n*-butylbenzene, correlating a decrease in the steric effects for the main alkyl chain to the extent of swelling. Despite having the smallest molar volume, *tert*-butylbenzene swells o-rings less efficiently than *sec*- and *n*-butylbenzenes. The steric effects attributed to the number of alkyl groups attached to the benzene ring also influence the effectiveness of the compound to swell seals. 1,3,5-Trimethylbenzene and 1,2,4,5-tetramethylbenzene have the smallest molar volume among their isomers but contribute the least to o-ring swelling. In order to systematically explore the dependence of the volume swell percent values measured for o-ring seals of the molar mass and molar volume of the dopant organic compounds, plots were prepared for each set of data. No correlation was found in these plots (Figures 2A and 2B). This finding is in disagreement with previous literature.[8]
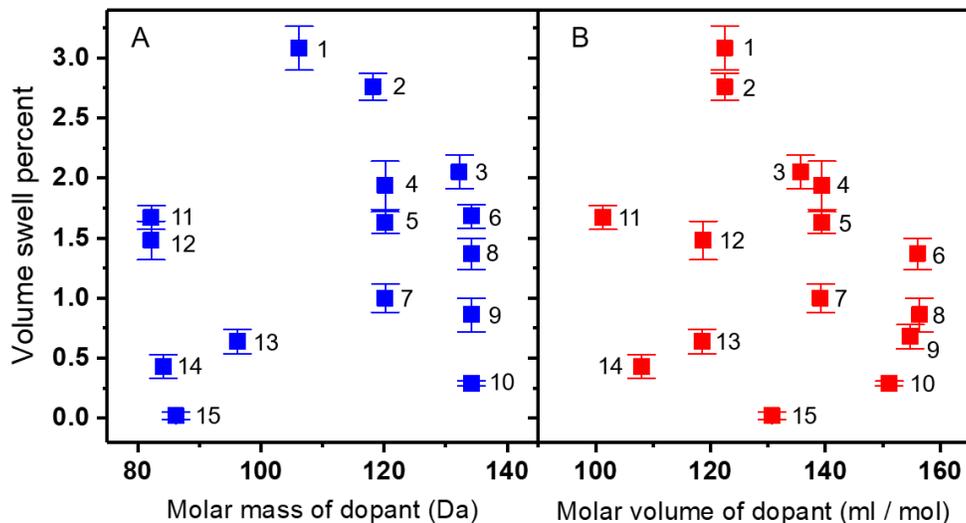
Figure 2. Volume swell percent values for o-ring seals immersed in Sasol IPK doped with different organic compounds at 8 % by volume vs the dopant molar mass (A) and molar volume (B). The identity of the compounds is as follows: ethylbenzene **1**, indane **2**, tetralin **3**, *n*-propylbenzene **4**, isopropylbenzene **5**, *n*-butylbenzene **6**, 1,3,5-trimethyl-benzene **7**, *sec*-butylbenzene **8**, *tert*-butylbenzene **9**, 1,2,4,5-tetramethylbenzene **10**, cyclohexene **11**, 1,5-hexadiene **12**, 1-methylcyclohexene **13**, cyclohexane **14** and *n*-hexane **15**.

An alternative explanation for the structural trends observed for dopant organic compounds and their ability to swell o-ring seals may be related to the diffusivity of the compounds and their partition coefficients into the seals. The diffusivity for some aromatic compounds in Buna-N o-rings decreases as follows: benzene > toluene > xylene isomers.[15,29] The partition coefficients for these and some additional aromatic compounds into Buna-N o-ring seals decrease as follows: benzene > toluene > xylene isomers > ethylbenzene > *n*-propylbenzene > *n*-pentylbenzene. Hence, a greater steric hindrance, *e.g.*, a larger number of alkyl substituents or longer alkyl chains in the aromatic compounds, appears to attenuate the diffusivity and increase the partition coefficients of the compounds into the polymers in o-ring seals. The steric hindrance likely prevents favorable interactions of the compounds with the polymer material. Steric hindrance may also explain the observation that cyclohexene swells seals 3.5 times more effectively than 1-methylcyclohexene. Additionally, stronger intermolecular interactions via van der Waal forces of the long *n*-alkyl groups of dopants with the hydrocarbons in fuel may attenuate the partitioning coefficients of the dopants into the seals. However, none of the above considerations can be used to rationalize why ethylbenzene causes greater volume swelling than any of the other compounds studied.

Previously, the effectiveness of organic compounds at swelling of o-ring seals has been correlated to Hansen solubility parameters that are used to determine the solubility of a solute into a specific solvent.[8] Compounds with greater hydrogen-bonding and polar solubility parameters were found to swell the seals more effectively, likely because of

favorable interactions with the polar polyacrylonitrile chains, and specifically, the polar cyano groups.[8] Plots of the volume swell percent as a function of the Hansen solubility parameters for the dispersive, polar and hydrogen-bonding abilities of several organic compounds studied here are shown in Figure 3. With the exception of ethylbenzene (data point 1) and cyclohexene (data point 3; only for the plot for hydrogen bonding parameter), a correlation is observed for all three parameters plotted, although the correlations for the solubility and hydrogen bonding parameters are nonlinear. Therefore, solubility definitely plays a role in determining the volume swell percent of o-ring seals although it is not the only important parameter.
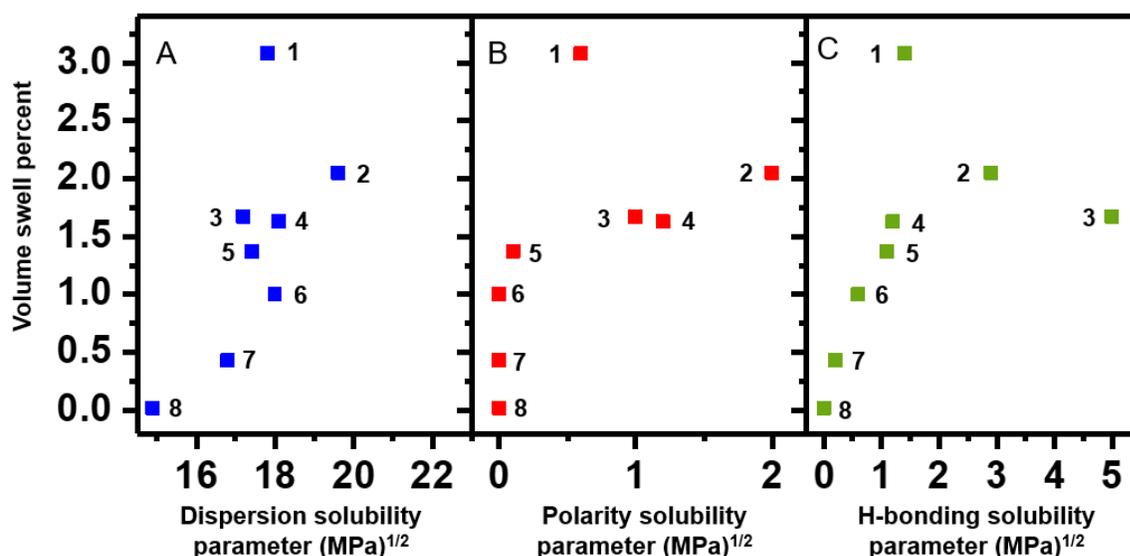
Figure 3. Volume swell percent versus (A) dispersion solubility parameter, (B) polarity solubility parameter and (C) H-bonding solubility parameter. The identity of the organic compounds is as follows: ethylbenzene **1**, tetralin **2**, cyclohexene **3**, isopropylbenzene **4**, n-butylbenzene **5**, 1,3,5-trimethylbenzene **6**, cyclohexane **7**, and n-hexane **8**. The parameter values were taken from reference 34.

Finally, to test the effectiveness of compounds with a polar functionality to swell o-ring seals, phenol and a hindered phenol, the 2,6-di-*tert*-butyl-4-methylphenol, were evaluated. Phenol and 2,6-di-*tert*-butyl-4-methylphenol were doped in Sasol IPK to achieve a concentration of 24 mg / 100 mL (0.02 % in volume). This concentration is ten times the maximum amount specified by ASTM for phenols in aviation turbine fuels (24 mg / 1,000 mL or 0.002 % in volume).[33] Despite this great concentration, the highly sterically hindered phenol did not swell the o-ring seals to any significant extent and the volume swell percent value was approximately equal to that of neat Sasol IPK. On the other hand, phenol swells o-rings more effectively than several alkylbenzenes, despite the low volume percent studied (0.02 %) compared to the volume percent used for alkylbenzenes (8 %). Previously, polar organic compounds (*e.g.*, 2-*tert*-butylphenol and 2-ethylphenol) were reported to swell o-ring seals effectively, which was rationalized by favorable interactions of the polar dopant with the polar polyacrylonitrile chains,

specifically, the polar cyano groups.[8,14] However, the concentrations of these dopants were approximately 400 times the maximum amount specified by ASTM D1655.[14,33]

Swelling of o-ring seals by alternative aviation fuel Jet/HEFA

Approved alternative aviation fuel Jet/HEFA is composed of at least 50% of Jet A and up to 50 % (by volume) of linear, branched and cyclic saturated hydrocarbons obtained from hydroprocessed esters and fatty acids (HEFA) (Figure S5).[35] The mass percent of aromatic compounds in this alternative fuel is approximately 11.2 % as determined here by GCxGC/FID measurements. The volume swell percent for o-ring seals immersed in Jet A/HEFA was measured to be 2.23 ± 0.17. This volume swell percent is smaller than the value measured for o-ring seals immersed in Sasol IPK doped with ethylbenzene and indane (3.08 and 2.76%, respectively; the corresponding mass percent values in Sasol IPK were 10.0 % and 11.1 %, respectively). Hence, doping HEFA with about 11 wt% by either ethylbenzene or indane would cause more o-ring swelling than mixing HEFA with Jet A.

Reduction of ultimate tensile strength of o-ring seals by aromatic compounds

Aromatic compounds have been shown to be able to extract polymer material from o-ring seals, consequently damaging o-rings.[8] Hence, it is imperative not only to identify specific aromatic compounds that swell o-ring seals effectively but also make sure that they do not degrade the polymer and weaken the structural integrity of the o-rings. Previously, tensile strength measurements for o-ring seals immersed in premium or regular gasoline or alternative fuel (derived from sugarcane) were shown to be a reliable indicator for the mechanical properties of the seals after interaction with organic compounds.[35] However, correlations between the extent of swelling and decrease in tensile strength for o-ring seals exposed to different aromatic compounds have not been explored.

The measured ultimate tensile strength and ultimate elongation percent as a function of volume swell for o-ring seals immersed in neat Sasol IPK and Sasol IPK doped with different aromatic compounds are shown in Figure 3. Generally, as the volume of o-ring seals increases, their ultimate tensile strength and ultimate elongation percent decreases. For example, compared to neat Sasol IPK, Sasol IPK doped with ethylbenzene at 8 % by volume decreases the ultimate tensile strength and ultimate elongation percent of seals by 11.7 % and 12.9 %, respectively. O-ring seals immersed in Sasol IPK doped with aromatic compounds that exhibit less swelling retained greater mechanical loads than seals immersed with aromatic compounds with greater propensities to induce volume swelling. For example, seals immersed in Sasol IPK doped with *tert*-butylbenzene or 1,2,4,5-tetramethylbenzeneg, the aromatic compounds that caused the least amount of swelling, had the largest ultimate tensile strength and ultimate elongation percent after immersion.

The decrease in ultimate tensile strength and ultimate elongation percent for o-ring seals immersed in Sasol IPK doped with different aromatic compounds was

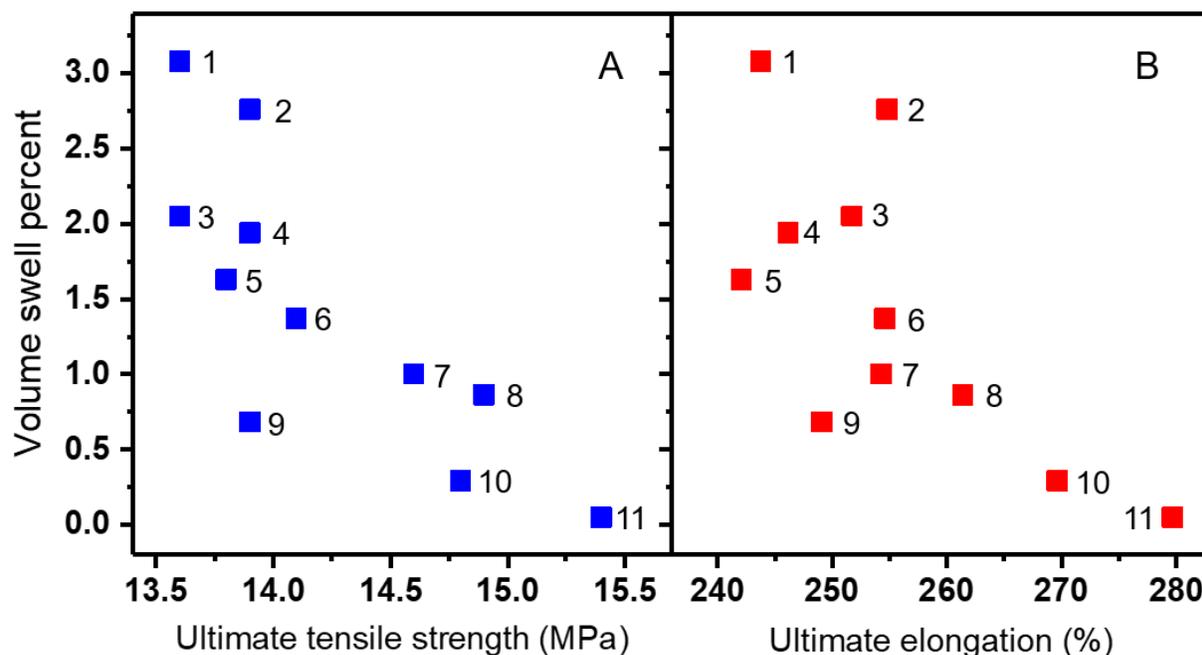demonstrated above to correlate with the percent swelling caused by the compounds, and therefore, be

Figure 3. Volume swell percent vs ultimate tensile strength (A) and ultimate elongation percent (B). The identity of each model compound is as follows: ethylbenzene **1**, indane **2**, tetralin **3**, *n*-propylbenzene **4**, isopropylbenzene **5**, *n*-butylbenzene **6**, 1,3,5-trimethylbenzene **7**, *sec*-butylbenzene **8**, *tert*-butylbenzene **9**, 1,2,4,5-tetramethylbenzene **10**, and neat Sasol IPK **11**.

influenced by the exact structure of the aromatic compound. However, the decrease in the strength of the seals may not necessarily mean that the aromatic compounds are extracting polymer from the seals, a process that is likely to be irreversible. Instead, as aromatic compounds permeate into the o-ring seals, the intermolecular forces of polymer chains may be disrupted, which may weaken the material toward tension, resulting in premature rupture. This process may be reversible, *i.e.*, if the aromatic compounds diffuse out of the o-ring seals, intermolecular bonds of the polymer chains may re-form, allowing the seals to regain their strength and withstand greater mechanical loads.

Volume swell percent and ultimate tensile strength of o-ring seals after change of solvent

To test above hypothesis, o-ring seals were immersed in a consecutive manner in two different solutions, first in Sasol IPK doped with ethylbenzene for 48 hours and then in

neat Sasol IPK. While the seals were immersed in the latter solution, their volume swell percent and ultimate tensile strength were measured and the concentration of ethylbenzene in the solution was determined by using GCxGC/FID as a function of time (at the beginning and after 4 hours, 8 hours, 24 hours, 48 hours, 72 hours and 96 hours of immersion) (Figure 4A). The volume swell percent of o-ring seals was found to decrease for the first 48 hours and then to gradually level off after about 50 hours. The volume swell percent after 96 hours was 0.76 ± 0.17 compared to 0.05 ± 0.04 % for o-ring seals immersed only in neat Sasol IPK and to 3.08 ± 0.18 % for o-rings immersed in Sasol IPK doped with ethylbenzene for 48 hours (Table 1). Therefore, the volume swelling of o-ring seals is reversible.

Further, the concentration of ethylbenzene in the neat Sasol IPK was found to increase for the first 48 hours of o-ring immersion and gradually level off after about 50 hours (Figure 5A). This finding suggests that since neat Sasol IPK has only low aromatic content, ethylbenzene diffuses out of the o-ring seals into Sasol IPK until a new equilibrium is established. Therefore, the volume swelling decrease observed in above experiments was caused by ethylbenzene diffusing out of the o-ring seals.

In addition to the measurement on the o-ring swelling, the tensile strength was also studied in above experiments. The tensile strength was found to increase as a function of time for the first 48 hours and to level off after about 50 hours (Figure 4B). After 96 hours of immersion in neat Sasol IPK, the ultimate tensile strength of the o-rings had increased by 8.5 % compared to the tensile strength of the seals at the beginning of the immersion. This finding suggests that intermolecular forces between the polymer chains in the o-ring seals can reestablish themselves upon diffusion of ethylbenzene out of the
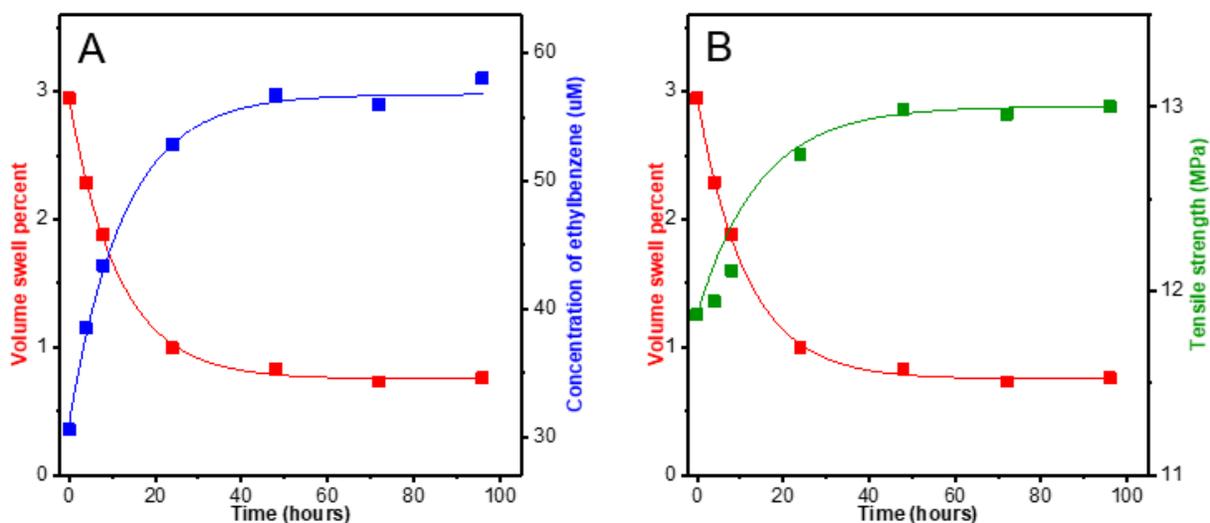

Figure 4. (A) Volume swell percent of o-ring seals (red) and concentration of the ethylbenzene (blue) (quantified by using GCxGC FID) in Sasol IPK after diffusion out of

o-ring seals vs time and (B) the volume swell percent of o-rings (red) and tensile strength of o-ring seals (green) vs time.

o-ring seals. Hence, the seals withstand greater mechanical forces. These findings suggest that no permanent damage occurred to the o-ring seals upon interactions with the aromatic dopants in Sasol IPK as the changes to the o-ring seals are reversible. This finding also suggests that the aromatic dopants did not extract polymer from the o-ring seals.

Conclusions

The volume swell percent of Buna-N o-ring seals was shown to be influenced by the exact structure of the aromatic and nonaromatic dopants in Sasol IPK. Steric effects (*e.g.,* the number of alkyl groups attached to the main alkyl chain, the length of the alkyl groups, and the number of alkyl groups attached to a benzene ring) affect the propensity of the compounds to swell o-ring seals. Further, cyclic saturated compounds swell the seals more effectively than acyclic compounds of the same carbon number (*e.g.,* cyclohexane swells o-ring seals more effectively than *n*-hexane and cyclohexene swells the seals more effectively than 1,5-hexadiene). Based on the results presented here, literature correlations linking a decreasing molar mass and molar volume of a compound to increasing o-ring volume are not valid. While steric hindrance and solubility of the compounds into the o-ring polymers definitely play a role in determining the volume swell percent of o-ring seals, these are not the only important parameters as they cannot be used to rationalize why ethylbenzene swells the o-rings more efficiently than any other compound studied.

The ultimate tensile strengths of o-ring seals were shown to decrease as the volume swell percent of o-ring seals increased. The ultimate tensile strength and volume swell percent for o-ring seals are dynamic properties whose extent depends on the composition of the fuel or doped fuel that the o-rings are immersed in. Hence, the decrease in tensile strength of o-ring seals upon exposure to organic compounds does not appear to be indicative of irreversible damage to the structure of the o-rings. The intermolecular bonds of polymer chains that were disrupted by the dopants can re-form upon diffusion of the dopants out of the o-ring seals.

The results presented here demonstrate that ethylbenzene is a highly effective seal swelling dopant (the best in this study) but also that it does not permanently damage the o-ring seals. Addition of this compound into alternative fuel blending components may result in drop-in alternative fuels with equal swelling abilities but fewer harmful effects than petroleum-derived aviation fuels. By comparison, ethylbenzene doped in Sasol IPK fuel blending component swells o-ring seals more effectively than an alternative aviation fuel Jet A/HEFA.

Acknowledgements

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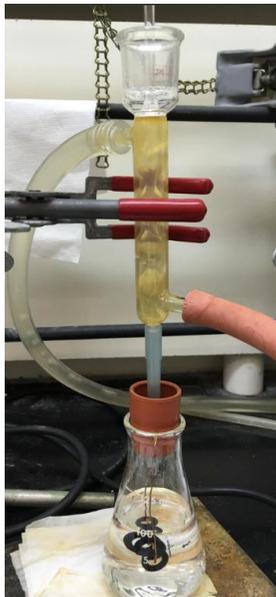
Supplementary Information

Figure S1. Test rig used to immerse o-ring seals for the volume swell percent studies.

Figure S2. Nikon Profile Projector V-12 used to measure the diameters of o-ring seals before and after immersion in neat and doped Sasol IPK.
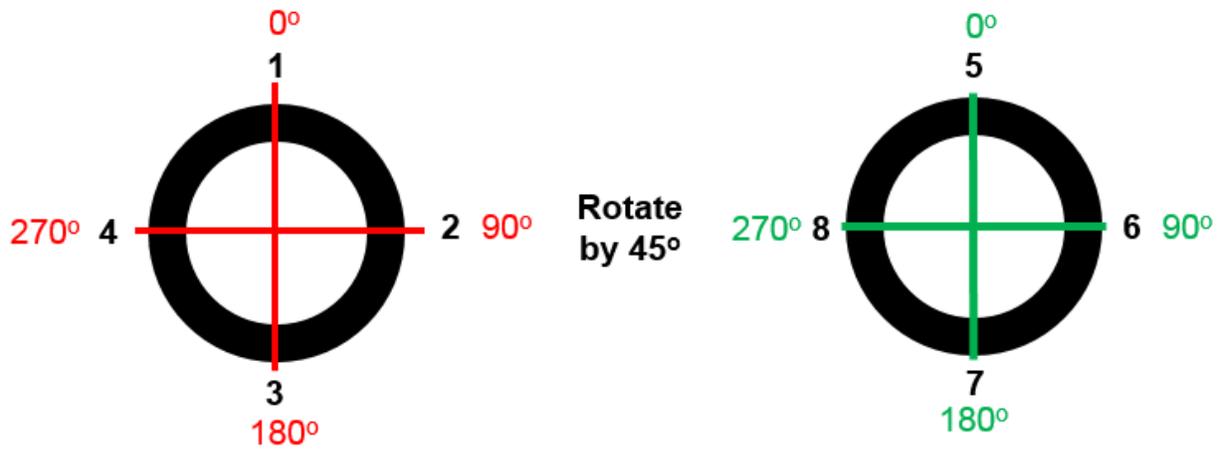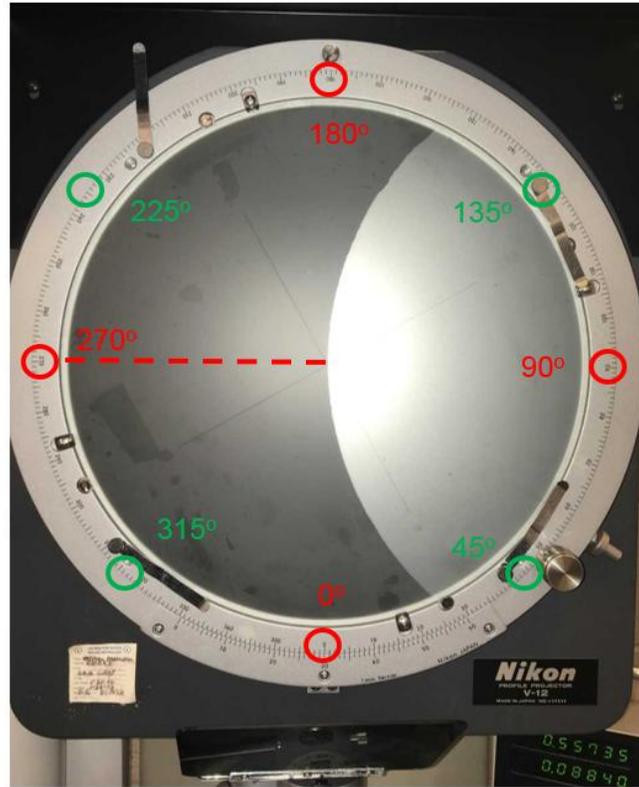
Figure S3. The Nikon projector has markings from 0 to 359 degrees (top picture). The o-ring seals were positioned in the center of the Nikon projector. The cross-sectional diameter for each o-ring seal was measured at 0°, 90°, 180° and 270° (red lines in the bottom picture). Each o-ring seal was rotated by 45° and the diameters were measured again at 0°, 90°, 180° and 270° (green lines in the bottom picture). Hence, the o-ring seal was measured eight times at 45° degree intervals.
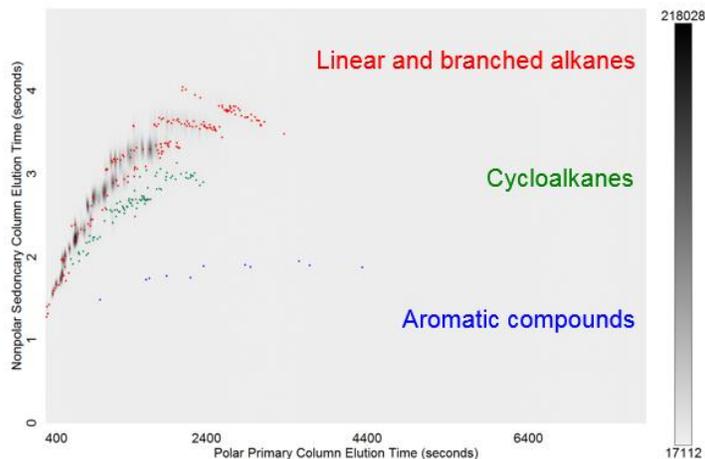
Figure S4. Total ion current chromatogram of Sasol IPK measured by using a Leco Pegasus GC-HRT high resolution GCxGC/(EI)TOF MS in the reversed phase column configuration. Based on these data, Sasol IPK is predominantly composed of linear and branched saturated hydrocarbons.
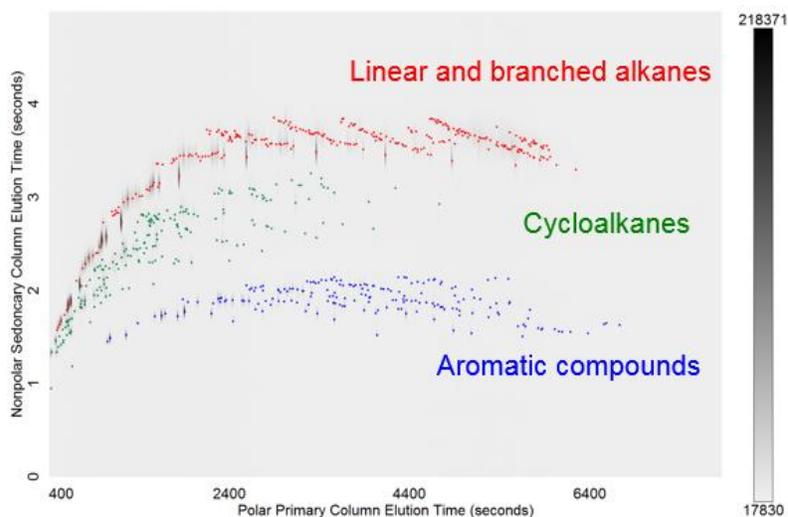

Figure S5. Total ion current chromatogram of Jet A measured by using a Leco Pegasus GC-HRT high resolution GCxGC/(EI)TOF MS in the reversed phase column configuration. Based on these data, Jet A/HEFA is composed of linear, branched and cyclic saturated hydrocarbons and aromatic hydrocarbons.

Table S1. The mass percent values for the linear, branched and cyclic alkane classes and the aromatic compound class in Sasol IPK quantified by using GCxGC/FID.

Compound class	Trial 1	Trial 2	Trial 3	Average
Linear alkane class	0.35	0.42	0.39	0.39 ± 0.04
Branched alkane class	96.98	96.91	96.94	96.94 ± 0.04
Cycloalkane class	2.37	2.38	2.37	2.37 ± 0.01
Aromatic compound class	0.30	0.29	0.30	0.30 ± 0.01

Table S2. The volume percent for aromatic compounds in Sasol IPK was determined by multiplying the average mass percent of the compound class measured by GCxGC/FID by the density of a compound representative of that class.

Compound class	Representative compound	Density of representative compound	Average mass percent	Volume	Volume percent
Linear alkane class	n-decane	0.730 g / mL	0.39	0.28 mL	0.38 %
Branched alkane class	2-methyldecane	0.726 g / mL	96.94	70.38 mL	96.59 %
Cycloalkane class	n-butylcyclohexane	0.818 g / mL	2.37	1.94 mL	2.67 %
Aromatic compound class	n-butylbenzene	0.86 g / mL	0.30	0.26 mL	0.36 %