



## Full Length Article

# The capability of organic compounds to swell acrylonitrile butadiene O-rings and their effects on O-ring mechanical properties



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## ABSTRACT

As interest in replacing petroleum-derived aviation fuels with resilient, alternative fuels increases, the ability to derive correlations between the chemical compositions of aviation fuels and their properties and performance becomes more important. In this work, correlations between the exact chemical structures of organic compounds and their ability to increase the volume and decrease the tensile strength of Buna-N o-ring seals were explored. Buna-N o-ring seals are a representative group of essential seals in the hydraulic and pneumatic components of aircraft fuel delivery systems. They are utilized to prevent fuel leakage within the pumps, metering devices, and connectors. To measure the volume swell percent of o-ring seals caused by various organic compounds, a test rig was assembled that suspended o-ring seals in neat Sasol IPK (isoparaffinic kerosene) or in 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  $3.1 \pm 0.2\%$  and  $2.8 \pm 0.1\%$ , respectively. In comparison, the approved aviation fuel Jet A/HEFA has volume swell percent value of  $2.2 \pm 0.2\%$ . Alkylbenzenes with a smaller number of alkyl groups, 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 the ability of these compounds to swell o-rings. Nonaromatic unsaturated hydrocarbons, such as cyclohexene, were also found to swell o-ring seals to some extent. On the other hand, saturated hydrocarbons, such as cyclohexane, contributed to minimum or no swelling. Tensile strengths of intact o-rings were measured using an MTS Insight Electromechanical Testing Instrument. Aromatic compounds that facilitated greater swelling of o-ring seals also caused greater decrease in the tensile strength. For example, ethylbenzene and *sec*-butylbenzene, with volume swell percent values of  $3.1 \pm 0.2\%$  and  $0.9 \pm 0.1\%$ , respectively, reduced the o-ring tensile strength from 15.4 MPa to 13.6 MPa and 14.9 MPa, respectively. Additional experiments demonstrated that volume swell and tensile strength of o-ring seals are reversible properties. Hence, a decrease in tensile strength for o-ring seals does not imply irreversible damage. Overall, the extent of volume swelling and the lowering of tensile strength for o-ring seals was found to depend on the exact chemical structure of the organic compound.

## 1. Introduction

Within the last decade, efforts to replace petroleum-based aviation fuels with resilient, nonpetroleum-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].

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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 in a fuel, 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 an aviation 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 and the degree of polymer crosslinking of the o-ring as well as the physical and chemical properties of the compounds in the fuel [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 weak intermolecular interactions between polymer chains through dispersion forces [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,  $\Delta F_m$ , and elastic free energy,  $\Delta F_{el}$  [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 via 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 Eq. (1).

$$\Delta F = \Delta F_m + \Delta F_{el} \quad (1)$$

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, organic 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 and ultimate elongation percent after interaction with the selected organic compounds. 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, consequently enhancing fuel quality.

## 2. Experimental

### 2.1. Chemicals and materials

Ethylbenzene (99% purity) was purchased from Alfa Aesar. *n*-Propylbenzene (98% purity), isopropylbenzene (98% purity), 1,3,5-trimethylbenzene (98% purity), *n*-butylbenzene ( $\geq 99\%$  purity), *sec*-butylbenzene ( $\geq 99\%$  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 ( $\geq 99.0\%$  purity) and 2,6-di(*tert*-butyl)-4-methylphenol ( $\geq 99\%$  purity) were purchased from Sigma-Aldrich. Indane (95% purity) and cyclohexane (99% purity) were purchased from Acros, and tetralin ( $\geq 97\%$  purity) and *n*-hexane ( $\geq 97\%$  purity) from Fluka. Naphthalene was purchased from Fisher Scientific (certified grade). Sasol isoparaffinic kerosene (referred to as Sasol IPK) and Jet A mixed with HEFA (hydroprocessed esters and fatty acids) at a 50:50 volume ratio (referred to as Jet A/HEFA) were received from Dr. James Edwards of the Wright-Patterson Air Force Base, Dayton, OH. Catalytic hydrothermal conversion jet (CHCJ) fuel (lot number LIMS 10128 10/18/16) was provided by Dr. Dianne J. Luning Prak of the United States Naval Academy, Annapolis, MD. All compounds 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].

## 3. Instrumentation and methods

### 3.1. Volume swell percent studies

To evaluate the propensity of different organic compounds to swell o-ring seals, Sasol IPK was doped with several organic compounds at 8% by volume. 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). Naphthalene was doped at 1% by volume due to its lack of solubility into Sasol IPK. Approximately 100 mL of Sasol IPK or 92 mL of Sasol IPK and 8 mL of an organic compound were added into Erlenmeyer flasks and mixed thoroughly. For 1,2,4,5-tetramethylbenzene, 6.94 g of this compound 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 each of these solutions for 48 h by using a metal suspension wire 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 each other during the immersion period. The flask was fitted with a rubber stopper with a small opening that was used to insert in a condenser. This custom-built test rig (Fig. 1) was designed to closely replicate the conditions and guidelines [20] set by ASTM D471. During immersion, 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 °C.

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 (Fig. 2). The average cross-sectional diameter for each o-ring

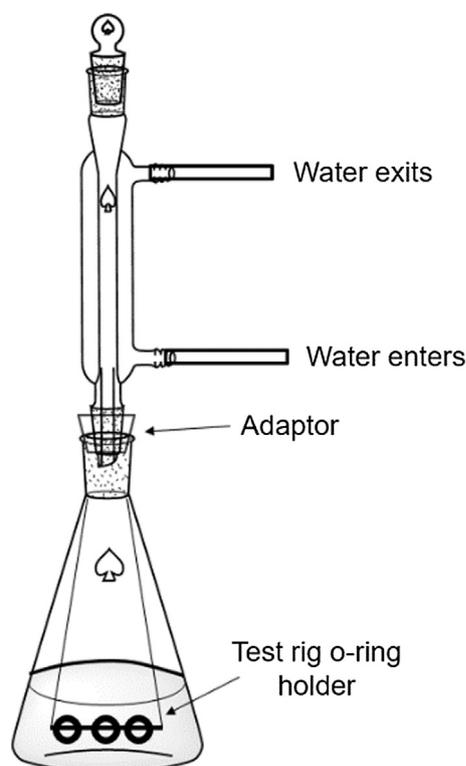


Fig. 1. Test rig used to immerse o-ring seals for the volume swell percent studies.



Fig. 2. Nikon Profile Projector V-12 used to measure the diameters of o-ring seals before and after immersion in neat and doped Sasol IPK.

seal was determined from eight measurements of each o-ring seal (Fig. 3). The volume swell percent for each o-ring seal was determined by using Eq. (2), [10]

$$\mu_i = \left[ \left( \frac{d_f}{d_o} \right)^3 - 1 \right] \times 100 \quad (2)$$

where  $\mu_i$  is the average volume swell percent and  $d_o$  and  $d_f$  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.

### 3.2. 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]. These measurements were performed for five o-ring seals that had been immersed in the test rig as discussed above. The two spool grips of the MTS instrument 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 determined by using Eq. (3), [22] which takes into consideration that non-cut o-ring seals have twice the cross-sectional area compared to a cut o-ring:

$$\text{Ultimate tensile strength} = \frac{F}{1.57W^2} \quad (3)$$

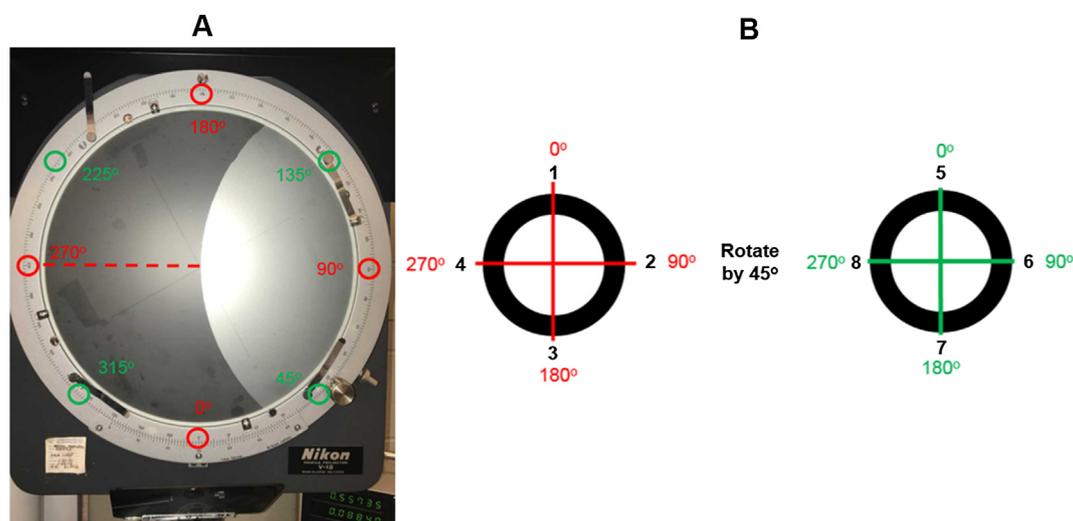
where  $F$  is the force registered by the load cell and  $W$  is the average diameter of an o-ring seal after the immersion period. Similarly, the ultimate elongation percent of the o-ring seals was determined by using Eq. (4), [22]

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

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 determined for o-ring seals after immersion are the average of five measurements.

### 3.3. Quantitation of ethylbenzene by using GC × GC/FID

An Agilent GC × GC 7890B two-dimensional 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. Ethylbenzene was chosen for this study as it swells o-ring seals more effectively than any other compound studied here. Standards of ethylbenzene were prepared at concentrations of 10, 20, 30, 50 and 125  $\mu\text{M}$  in *n*-hexane. An auto injector (Agilent 7683B) was used to inject 0.5  $\mu\text{L}$  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. The carrier gas was ultrapure helium at a flow rate of 1.25 mL/min. The columns were arranged in the 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 GC × GC 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 it into the secondary column via hot and cold pulses of nitrogen gas. The GC × GC method used for the quantitation of ethylbenzene has been previously described [23].



**Fig. 3.** (A) The Nikon projector has markings from 0 to 359°. The o-ring seals were positioned in the center of the Nikon projector. (B) The cross-sectional diameter for each o-ring seal was measured at 0°, 90°, 180° and 270° (red lines). Each o-ring seal was then rotated by 45° and the diameter was measured again at 0°, 90°, 180° and 270° (green lines). Hence, each o-ring seal was measured eight times at 45° degree intervals (for interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

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 °C and the heat was ramped up 1 °C/min until the final temperature of 280 °C was reached. The secondary oven and the modulator hot jet temperature had +55 °C and +15 °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 °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 h. The o-ring seals were then removed, dried with a flow of nitrogen gas and re-submerged in neat Sasol IPK. Approximately 20  $\mu$ L aliquots were taken from this solution at 0 h, 4 h, 8 h, 24 h, 48 h, 72 h, and 96 h. Each aliquot was diluted with 2.0 mL of *n*-hexane and doped with 30  $\mu$ M of ethylbenzene to ensure that the total concentration of ethylbenzene was within the concentration range of the calibration plot. An auto injector was used to inject 0.5  $\mu$ L of each diluted aliquot into the GC  $\times$  GC/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 for o-ring seals were determined as described above.

### 3.4. Measurements by using GC $\times$ GC/(EI)TOF MS

An Agilent 7890A GC  $\times$  GC coupled to a Pegasus-HRT 4D electron ionization (EI) time-of-flight (TOF) mass spectrometer (Leco Co., St Joseph, MI, USA) was used for the mass spectrometry measurements as described previously [24]. Approximately 9.0  $\mu$ L and 13  $\mu$ L of Sasol IPK and Jet A/HEFA, respectively, were diluted into 2.0 mL by using *n*-hexane. An auto injector (Agilent G4513 A) was used to inject 0.5  $\mu$ L of each mixture into the split/splitless injector with a split ratio of 1:20 at an inlet temperature of 260 °C. The Agilent 7890A was equipped with a quad-jet dual stage thermal modulator positioned between the primary and secondary columns. The modulator time was set to 5 s that was split between two stages, 2.5 s each. The hot pulse time was set 0.80 s and the cold pulse time was set to 1.70 s. The primary oven was set to 40 °C

and the heat was ramped up at a rate of 1 °C/min until the final temperature of 168 °C was reached. The secondary oven and the modulator hot jet temperature had +10 °C and +70 °C offsets, respectively, from that of the primary oven and the secondary oven, respectively. An acquisition delay of 400 s was employed to prevent the detection of the solvent, *n*-hexane.

All graphs were plotted by using OriginPro 2017 software.

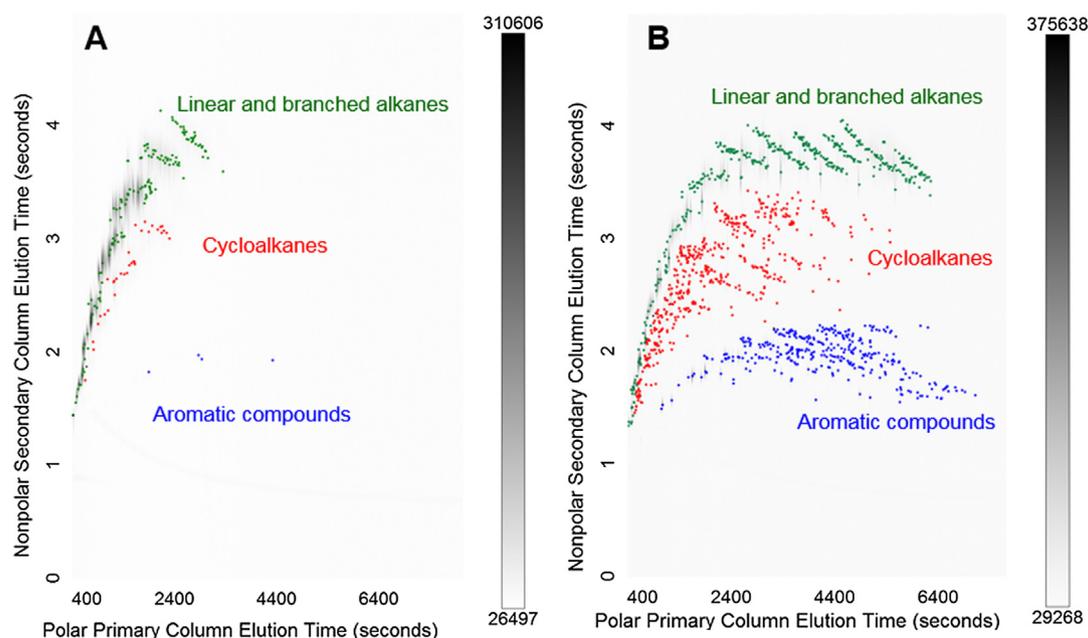
## 4. Results and discussion

Fuel blending component Sasol IPK was chosen for this study as it was determined to contain primarily branched saturated hydrocarbons and only approximately 0.4% of aromatic compounds by volume (Fig. 4 and Tables 1 and 2). Hence, additional aromatic compounds must be doped into Sasol IPK for it to be used as an aviation fuel. According to Defense Standard 91-91, the minimum aromatic content by volume in an alternative fuel is 8% [25]. Therefore, Sasol IPK was doped with different aromatic (and nonaromatic) compounds (Fig. 5) at 8% by volume to systematically evaluate the dopant's effectiveness to swell seals at the mandatory minimum volume. 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 tensile strength of o-rings seals was evaluated.

### 4.1. Swelling of o-ring seals by nonaromatic compounds

Evaluation of the ability of nonaromatic compounds to swell o-ring seals was performed because aromatic compounds form more soot and cause more particulate emissions upon combustion than nonaromatic compounds [26–29]. Hence, discovering nonaromatic compounds capable of swelling these seals could enhance the overall fuel quality and lower the environmentally harmful effects of the fuel. The volume swell percent values measured for nonaromatic compounds are presented in Table 3 and Fig. 6.

O-ring seals immersed in neat Sasol IPK and Sasol IPK doped with *n*-hexane did not swell the seals to any significant extent (volume swell percent values  $0.05 \pm 0.04\%$  and  $0.02 \pm 0.03\%$ , 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]. Although o-ring seals absorb linear and branched saturated hydrocarbons, the overall net volume swell percent is near



**Fig. 4.** Total ion current chromatograms for (A) fuel blending component Sasol IPK and (B) an approved alternative aviation fuel Jet/HEFA (50:50 blend of Jet A and hydroprocessed esters and fatty acids) measured by using GC  $\times$  GC/(EI)TOF MS. Based on these data, Sasol IPK is predominantly composed of linear and branched saturated hydrocarbons while Jet/HEFA is composed of linear, branched and cyclic saturated hydrocarbons and aromatic hydrocarbons.

**Table 1**

The mass percent values for the linear, branched and cyclic saturated hydrocarbon classes and the aromatic compound class in Sasol IPK as quantified by using GC  $\times$  GC/FID.

Compound class	Trial 1	Trial 2	Trial 3	Average
Linear saturated hydrocarbons	0.35%	0.42%	0.39%	0.39 $\pm$ 0.04%
Branched saturated hydrocarbons	96.98%	96.91%	96.94%	96.94 $\pm$ 0.04%
Cyclic saturated hydrocarbons	2.37%	2.38%	2.37%	2.37 $\pm$ 0.01%
Aromatic compounds	0.30%	0.29%	0.30%	0.30 $\pm$ 0.01%

zero due to the offset of volume loss contributed to extraction of plasticizers and processing aides [30]. The volume swell percent for o-ring seals immersed in Sasol IPK doped with cyclohexane was greater than that observed for *n*-hexane, 0.4  $\pm$  0.1%. This finding is in agreement with literature correlating the volume swell percent of a compound to the inverse of its molar volume as cyclohexane has a smaller molar volume than *n*-hexane, which is expected to facilitate diffusion and partitioning into the polymer matrix [8,14,31].

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 4 times more effectively than cyclohexane (Table 3). 1,5-Hexadiene swell seals 75 times more effectively than *n*-hexane and 3.5 times more effectively than cyclohexane. On the other hand, the cyclic cyclohexene swells seals 13% more effectively than the acyclic 1,5-hexadiene containing two C=C bonds. This may be attributed to the greater molar volume of 1,5-hexadiene compared to

**Table 2**

The volume percent of different compound classes in Sasol IPK as determined by multiplying the average mass percent of the compound class measured by GC  $\times$  GC/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 saturated hydrocarbons	<i>n</i> -Decane	0.730 g/mL	0.39	0.28 mL	0.38%
Branched saturated hydrocarbons	2-Methyldecane	0.726 g/mL	96.94	70.38 mL	96.59%
Cyclic saturated hydrocarbons	<i>n</i> -Butylcyclohexane	0.818 g/mL	2.37	1.94 mL	2.67%
Aromatic compounds	<i>n</i> -Butylbenzene	0.86 g/mL	0.30	0.26 mL	0.36%

cyclohexene.

#### 4.2. 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 [32] and that it contains many isomeric alkylbenzenes [33,34]. Hence, several isomeric alkylbenzenes were doped into Sasol IPK. The results presented in Table 3 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 1.6 and 2.2 times more effectively than *n*-propylbenzene and *n*-butylbenzene, respectively (Table 3 and Fig. 6). This result is in agreement with the findings of a previous study that related above observations to the molar mass and molar volume of the compounds [8]. 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 Fig. 5) swells o-ring seals 47% more effectively than *n*-propylbenzene with the same number of carbons. Tetralin (for the structure, see Fig. 5) swells o-ring seals equally to *n*-propylbenzene but 50% more effectively than *n*-butylbenzene with the same number of carbons. The molar volume of indane and tetralin are smaller than those of *n*-propylbenzene and *n*-butylbenzene. This result supports the hypothesis that the molar volume can play a role in o-ring swelling.

Steric effects of alkyl groups attached to a benzene ring correlate 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,

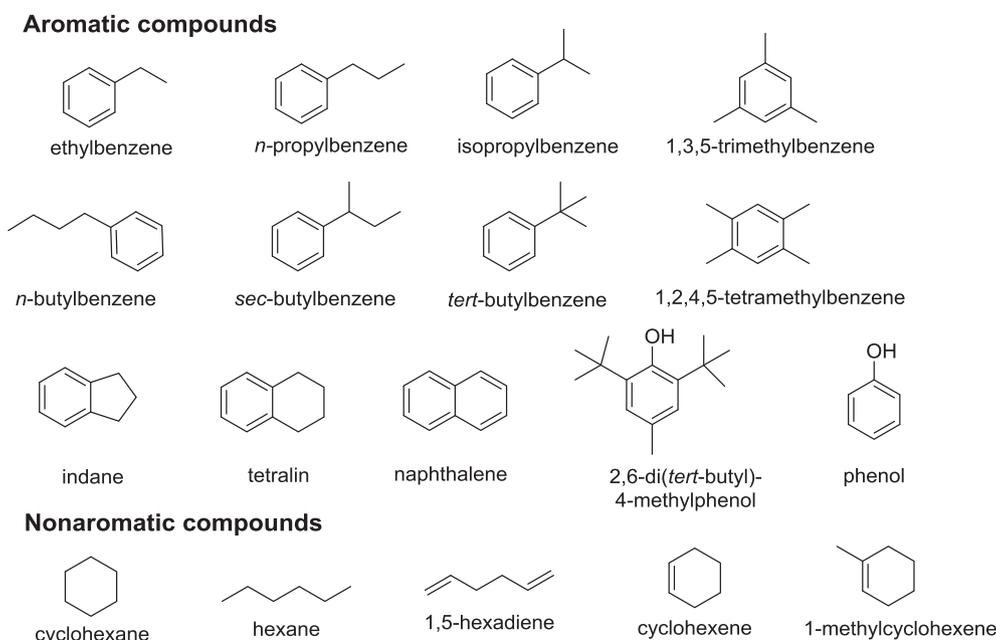


Fig. 5. Structures of the compounds studied.

Table 3

Volume swell percent values for o-ring seals immersed in CHCJ, a 50:50 blend by volume of Jet A and HEFA, neat Sasol IPK or Sasol IPK doped with different organic compounds at 8% by volume, except for naphthalene, phenol and 2,6-di(*tert*-butyl)-4-methylphenol that were used at lower volume percents.

Organic mixtures/compounds used to swell o-ring seals	Volume swell percent <sup>a</sup>	Molar mass of dopant (g/mol)	Molar volume of dopant (ml/mol)
CHCJ	5.5 ± 0.3%	N/A <sup>b</sup>	N/A <sup>b</sup>
Jet A/HEFA	2.2 ± 0.2%	N/A <sup>b</sup>	N/A <sup>b</sup>
Sasol IPK	0.05 ± 0.04%	N/A <sup>b</sup>	N/A <sup>b</sup>
<b>Aromatic dopants</b>			
ethylbenzene	3.1 ± 0.2%	106.168	122.45
indane	2.8 ± 0.1%	118.179	122.47
tetralin	2.1 ± 0.1%	132.206	135.74
<i>n</i> -propylbenzene	1.9 ± 0.2%	120.195	139.44
naphthalene <sup>c</sup>	1.6 ± 0.2%	128.174	125.53
isopropylbenzene	1.6 ± 0.1%	120.195	139.44
<i>n</i> -butylbenzene	1.4 ± 0.1%	134.222	156.07
1,3,5-trimethylbenzene	1.0 ± 0.1%	120.195	139.12
<i>sec</i> -butylbenzene	0.9 ± 0.1%	134.222	156.44
<i>tert</i> -butylbenzene	0.7 ± 0.1%	134.222	154.81
1,2,4,5-tetramethylbenzene	0.29 ± 0.02%	134.222	151.15
<b>Nonaromatic dopants</b>			
cyclohexene	1.7 ± 0.1%	82.143	101.29
1,5-hexadiene	1.5 ± 0.2%	82.143	118.70
1-methylcyclohexene	0.6 ± 0.1%	96.173	118.59
cyclohexane	0.4 ± 0.1	84.162	108.04
<i>n</i> -hexane	0.02 ± 0.03	86.178	130.77
<b>Heteroatomic dopants</b>			
Phenol <sup>d</sup>	1.5 ± 0.2	94.113	87.96
2,6-di( <i>tert</i> -butyl)-4-methylphenol <sup>d</sup>	0.04 ± 0.07	220.351	209.86

<sup>a</sup> Values are reported as an average of three measurements. The standard deviation ( $\mu \pm 1\sigma$ ) was also determined.

<sup>b</sup> Not applicable.

<sup>c</sup> Approximately 1.14 g of naphthalene was dissolved in Sasol IPK to obtain a total volume of 100 mL.

<sup>d</sup> Approximately 24 mg of phenol or 2,6-di(*tert*-butyl)-4-methylphenol were dissolved individually in 100 mL of Sasol IPK.

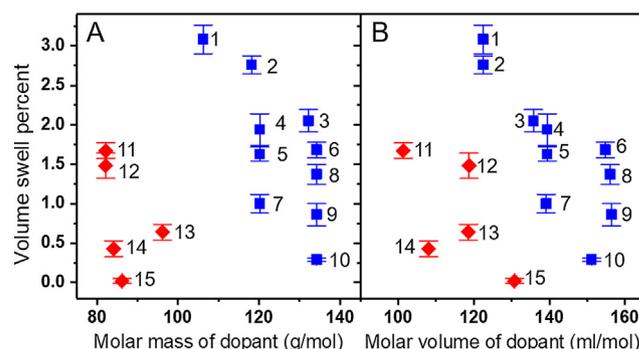


Fig. 6. Volume swell percent values for o-ring seals immersed in Sasol IPK doped with different organic compounds at 8% by volume vs the dopant molar mass (A) and molar volume (B). The identities of the compounds is as follows: ethylbenzene 1, indane 2, tetralin 3, *n*-propylbenzene 4, isopropylbenzene 5, *n*-butylbenzene 6, 1,3,5-trimethylbenzene 7, *sec*-butylbenzene 8, *tert*-butylbenzene 9, 1,2,4,5-tetramethylbenzene 10, cyclohexene 11, 1,5-hexadiene 12, 1-methylcyclohexene 13, cyclohexane 14 and *n*-hexane 15. The red diamonds indicate data measured for aliphatic compounds and the blue squares for aromatic compounds (for interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

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<sub>10</sub>H<sub>14</sub> 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. Therefore, molar volume is not the only parameter controlling o-ring swelling.

Finally, the swelling ability of naphthalene was also examined. Due to its poor solubility in Sasol IPK, it could only be doped at 1% by volume. Nevertheless, it swelled o-rings very effectively (Table 3).

Despite its effectiveness, it has a greater yield sooting index (YSI) than alkylbenzenes and upon combustion contributes to large particulates [29]. Therefore, it is not a desirable component in fuels.

The dependence of the volume swell percent values of the molar mass and molar volume of the dopant organic compounds was explored by preparing plots for each set of data. When all compounds are considered, no correlations are found in these plots (Fig. 6A and B). However, when the compounds are separated into the aromatic compound class and aliphatic compound class, nonlinear correlations are found between the volume swell percent and the molar mass of the compounds, in agreement with literature [8].

The above structural trends 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 [15,31]. The partition coefficients for these and some additional compounds into the o-rings 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 reduce the diffusivity and the partition coefficients of the compounds into the polymers in o-ring seals. This reasoning may explain why 1,3,5-trimethylbenzene and 1,2,4,5-tetramethylbenzene swell o-rings least effectively among their isomers despite having the smallest molar volume.

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/1000 mL or 0.002% in volume) [35]. The sterically hindered phenol did not swell the o-ring seals. On the other hand, phenol swelled 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 that exhibited hydrogen-bonding (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 [8,14,30]. However, the concentrations of these dopants were approximately 400 times the maximum amount specified by ASTM D1655 [14,35]. Therefore, although small phenols with little steric hindrance swell o-ring seals effectively, they are not suitable dopants to increase the o-ring swelling properties of aviation fuels.

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]. 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 Fig. 7. With the exception of ethylbenzene (data point 1) and phenol (data point 9; a lower concentration was used than for the other dopants), a nonlinear correlation appears to exist for the three parameters (Fig. 7). The low steric effects, small molar mass and small molar volume of ethylbenzene may explain why it is the most effective compound tested in this study. On the other hand, phenol was found to swell o-ring seals with great efficiency, despite of its low volume percent (0.02%) in Sasol IPK. The solubility of phenol in o-ring seals is facilitated by the favorable intermolecular forces of the phenol functional group with the fuel-resistant polar polyacrylonitrile chains.

#### 4.3. Swelling of o-ring seals by alternative aviation fuel Jet/HEFA and CHCJ fuel

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) [37]. The mass percent of aromatic compounds in this alternative fuel is approximately 11% as determined here by GC × GC/FID measurements (data in Supporting Information). The volume swell percent for o-ring seals immersed in Jet A/HEFA was measured to be  $2.2 \pm 0.2$ . This value is smaller than that measured for o-ring seals immersed in Sasol IPK doped with ethylbenzene and indane (3.1 and 2.8%, respectively; the corresponding mass percent values in Sasol IPK were 10% and 11%, 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.

CHCJ fuel is an alternative biofuel produced by utilizing a supercritical water process that converts oils from algae, plants, and animals into a product that is subsequently hydrotreated via a proprietary catalyst to reduce olefins and remove oxygen atoms [38]. The treated product is fractionated to produce the jet fuel. The chemical composition of the CHCJ alternative fuel sample employed was determined here (data in Supporting Information). The volume swell percent for o-ring seals immersed in 100% CHCJ was measured to be  $5.5 \pm 0.3$ . This value is the largest measured in this study. The mass percent of aromatic compounds in CHCJ is approximately 22% (data in Supporting Information). Hence, the large total aromatic content in CHCJ likely explains its highly efficient swelling of seals.

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

Aromatic compounds have been shown to extract plasticizers and processing aids from o-ring seals [8]. Loss of these components may affect the structural integrity of the seals. Hence, it is imperative to not only identify specific aromatic compounds that swell o-ring seals effectively but also make sure that they do not degrade and weaken 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 [39]. However, correlations between the extent of swelling and 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 Fig. 8. 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 caused a decrease in the ultimate tensile strength and ultimate elongation percent of the 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 *sec*-butylbenzene or 1,2,4,5-tetramethylbenzene, the two compounds that caused the least amount of swelling, retained the largest ultimate tensile strength and ultimate elongation percent after immersion.

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

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 influenced by the exact structure of the aromatic compound. However, the decrease in the strength of the seals may not necessarily mean that the

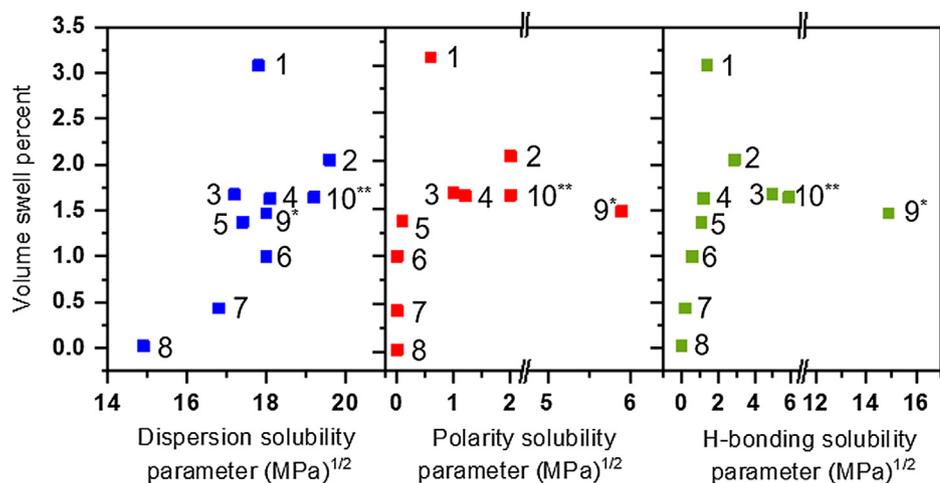


Fig. 7. Volume swell percent versus (A) dispersion solubility parameter, (B) polarity solubility parameter and (C) H-bonding solubility parameter. The identity of the organic compounds is as follows: ethylbenzene 1, tetralin 2, cyclohexene 3, isopropylbenzene 4, n-butylbenzene 5, 1,3,5-trimethylbenzene 6, cyclohexane 7, n-hexane 8, phenol 9 and naphthalene 10. The parameter values were taken from Ref. [36]. Please note that as opposed to the other compounds (doped at 8% by volume), phenol\* and naphthalene\*\* were doped only at 0.02% and 1% by volume, respectively, in Sasol IPK.

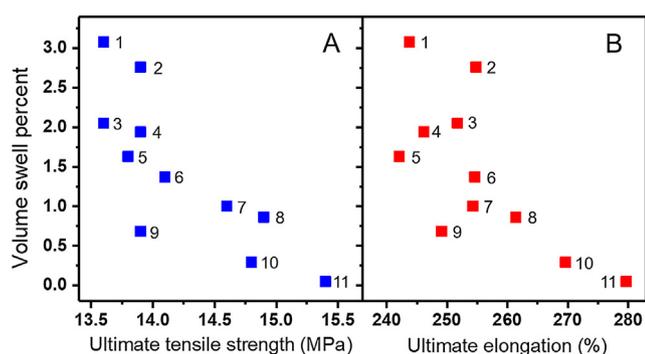


Fig. 8. Volume swell percent vs ultimate tensile strength (A) and ultimate elongation percent (B). The identity of the compounds is as follows: ethylbenzene 1, indane 2, tetralin 3, *n*-propylbenzene 4, isopropylbenzene 5, *n*-butylbenzene 6, 1,3,5-trimethylbenzene 7, *sec*-butylbenzene 8, *tert*-butylbenzene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

aromatic compounds are weakening the seals through extraction of plasticizers, 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) if the intermolecular bonds of the polymer chains can reform, allowing the seals to regain their strength and withstand greater mechanical loads. To test this hypothesis, o-ring seals were immersed in a consecutive manner in two different solutions, first in Sasol IPK doped with ethylbenzene for 48 h and then in neat Sasol IPK for 96 h. 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 as a function of time (at the beginning and after 4, 8, 24, 48, 72 and 96 h of immersion) by using GC  $\times$  GC/FID (Fig. 9A). The volume swell percent of o-ring seals was found to decrease for the first 48 h and then gradually level off after about 50 h. The volume swell percent after 96 h was  $0.8 \pm 0.2$  compared to  $0.05 \pm 0.04\%$  for o-ring seals immersed only in neat Sasol IPK and to  $3.1 \pm 0.2\%$  for o-rings immersed in Sasol IPK doped with ethylbenzene for 48 h (Table 3). Therefore, the volume swelling of o-ring seals is reversible.

Further, the concentration of ethylbenzene in neat Sasol IPK was found to increase for the first 48 h of o-ring immersion and to gradually level off after about 50 h (Fig. 9A). This finding suggests that since neat Sasol IPK has only low aromatic content, ethylbenzene diffused out of the o-ring seals into Sasol IPK until a new equilibrium was 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 h, and to level off after about 50 h (Fig. 9B). After 96 h 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 o-ring seals. Hence, the seals can now withstand greater mechanical forces. These findings suggest that no permanent damage occurred to the o-ring seals upon interactions

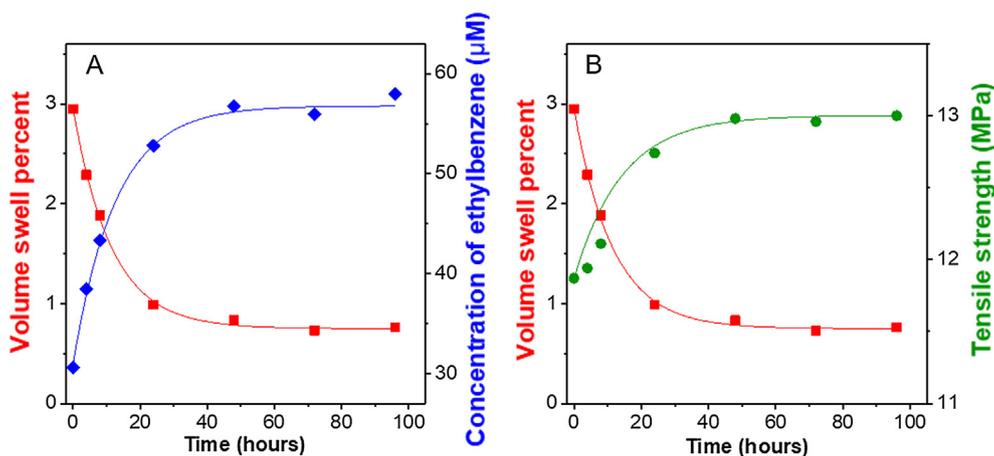


Fig. 9. (A) Volume swell percent of o-ring seals (red) and concentration of the ethylbenzene (blue diamonds) (quantified by using GC  $\times$  GC FID) in Sasol IPK after diffusion out of o-ring seals as a function of time and (B) the volume swell percent of o-rings (red squares) and tensile strength of o-ring seals (green circles) as a function of time (for interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

with the aromatic dopants in Sasol IPK as the changes to the o-ring seals are reversible.

## 5. Conclusions

The volume swell percent of Buna-N o-ring seals was shown to be influenced by the exact structure of aromatic and nonaromatic dopants in Sasol IPK. Steric effects (*e.g.*, branching in alkyl chains, the length of alkyl chains, and the number of alkyl chains attached to a benzene ring) affect the propensity of the compounds to swell o-ring seals. Further, cyclic compounds swell the seals more effectively than acyclic compounds with the same number of carbon atoms (*e.g.*, cyclohexane swells o-ring seals more effectively than *n*-hexane, and cyclohexene swells the seals more effectively than 1,5-hexadiene). The presence of benzene rings or C=C bonds appeared to increase the ability of organic compounds to swell o-ring seals. Naphthalene with two fused benzene rings swelled the o-rings very efficiently. Further, nonlinear correlations were found between the volume swell percent of seals and the molar mass and the molar volume of compounds, in agreement with literature [8]. However, steric effects appear to attenuate the propensity of the compounds to swell the seals despite of having a small molar mass and a small molar volume. Nonlinear correlations were found also for the volume swell percent and the Hansen solubility parameters if aliphatic and aromatic compounds were considered separately.

The ultimate tensile strength and ultimate elongation percent 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, exposure to organic compounds does not appear to cause irreversible damage to the o-rings. The intermolecular bonds of polymer chains that were disrupted by the dopants can reform 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 at 8% by volume swells o-ring seals more effectively than an alternative aviation fuel Jet A/HEFA.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.fuel.2018.10.103>.

## References

- [1] White House, Blueprint for a Secure Energy Future, Washington, DC: Executive Office of the President, March 2011.
- [2] Lamprecht D. Fischer-Tropsch fuel for use by the U.S. military as battlefield-use fuel of the future. *Energy Fuels* 2007;21:1448–53.

- [3] Gormley RJ, Link DD, Baltrus JP, Zandhuis PH. Interactions of jet fuels with nitrile o-rings: petroleum-derived versus synthetic fuels. *Energy Fuels* 2009;23:857–61.
- [4] Striebich RC, Shafer LM, Adams RK, West ZJ, DeWitt MJ, Zarbarnick S. Hydrocarbon group-type analysis of petroleum-derived and synthetic fuels using two-dimensional gas chromatography. *Energy Fuels* 2014;28:5696–706.
- [5] Benoit J, Perry D, Mondal K. Fischer-Tropsch synthesis in supercritical CO<sub>2</sub> – inhibition of CO<sub>2</sub> selectivity for enhanced hydrocarbon production. *Fuel* 2017;209:383–93.
- [6] Yang R, Zhou L, Gao J, Hao X, Wu B, Yang Y, et al. Effects of experimental operations on the Fischer-Tropsch product distribution. *Catal Today* 2017;298:77–88.
- [7] Caldwell L, Van Vuuren DS. On the formation and composition of the liquid phase in Fischer-Tropsch reactors. *Chem Eng Sci* 1986;41:89–96.
- [8] Graham JL, Striebich RC, Myers KJ, Minus DK, Harrison WE. Swelling of nitrile rubber by selected aromatics blended in a synthetic jet fuel. *Energy Fuels* 2006;20:759–65.
- [9] Balster LM, Corporan E, DeWitt MJ, Edwards JT, Ervin JS, Graham JL, et al. Development of an advanced, thermally stable, coal-based jet fuel. *Fuel Process Technol* 2008;89:364–78.
- [10] Fu J, Turn SQ. Effects of aromatic fluids on properties and stability of alternative marine diesels. *Fuel* 2018;171–80.
- [11] Anderson BE, Beyersdorf AJ, Hudgins CH, Plant JV, Thornhill KL, Winstead EL, et al. Alternative aviation fuel experiment [AAFEX] NASA/TM-2011-217059 2011.
- [12] Corporan E, Edwards T, Shafer L, DeWitt MJ, Klingshirn C, Zabarnick S, et al. Chemical, thermal stability, seal swell, and emissions studies of alternative jet fuels. *Energy Fuels* 2011;25:955–66.
- [13] Flory PJ. *Principles of Polymer Chemistry*. Ithaca, NY: Cornell University Press; 1953.
- [14] Link DD, Gormley RJ, Baltrus JP, Anderson RR, Zandhuis PH. Potential additives to promote seal swell in synthetic fuels and their effect on thermal stability. *Energy Fuels* 2008;22:1115–20.
- [15] Mathai AE, Singh RP, Thomas S. Transport of substituted benzenes through nitrile rubber/natural rubber blend membranes. *J Membr Sci* 2002;202:35–54.
- [16] Joseph A, Mathai AE, Thomas S. Sorption and diffusion of methyl substituted benzenes through cross-linked nitrile rubber/poly(ethylene co-vinyl acetate) blend membranes. *J Membr Sci* 2003;220:13–30.
- [17] Bhowmick AK, Stephens HL, editors. *Handbook of Elastomers*. 2nd ed. New York: Marce; Dekker; 2007.
- [18] Roberts J. O-rings. Lockheed Martin Service News, A service publication of Lockheed Martin Aeronautical Systems. Vol. 22 No 4 and Vol. 23 No 1. Pages 1 – 36. October 1995 – March 1996.
- [19] DeWitt MJ, Corporan E, Graham J, Minus D. Effects of aromatic type and concentration in Fischer-Tropsch fuel on emissions production and material compatibility. *Energy Fuels* 2008;22:2411–8.
- [20] Standard Test Method for Rubber Property-Effect of Liquids; Designation No. ASTM D471 – 16 a; ASTM International: West Conshohocken, PA; 2016.
- [21] Standard Test Methods for Rubber O-Rings; Designation No. D1414 – 15; ASTM International: West Conshohocken, PA; 2015.
- [22] Standard Test Methods for Rubber O-Rings, Designation No. ASTM D1414-15, ASTM International, West Conshohocken, PA, 2015.
- [23] Vozka P, Mo H, Šimáček P, Kilaz G. Middle distillates hydrogen content via GCxGC-FID. *Talanta* 2018;140–6.
- [24] Luning Prak DJ, Romanczyk M, Wehde KE, Ye S, McLaughlin M, Luning Prak PJ, et al. Analysis of catalytic hydrothermal conversion jet fuel and surrogate mixture formulation: components, properties, and combustion. *Energy Fuels* 2017;31:13802–14.
- [25] Turbine Fuel, Kerosine Type, Jet A-1; Defence Standard 91-91/Issue 7, Ministry of Defence: U.K.; 2015.
- [26] Beyersdorf AJ, Timko MT, Ziembra LD, Bulzan D, Corporan E, Herndon SC, et al. Reductions in aircraft particulate emissions due to the use of Fischer-Tropsch fuels. *Atmos Chem Phys* 2014;14:11–23.
- [27] Timko MT, Yu Z, Onasch TB, Wong HW, Miake-Lye RC, Beyersdorf AJ, et al. Particulate emissions of gas turbine engine combustion of a Fischer-Tropsch synthetic fuel. *Energy Fuels* 2010;24:5883–96.
- [28] Xue X, Hui X, Singh P, Sung CJ. Soot formation in no-premixed counterflow flames of conventional and alternative fuels. *Fuel* 2017;210:343–51.
- [29] Das DD, McEnally CS, Kwan TA, Zimmerman JB, Cannella WJ, Mueller CJ, et al. Sooting tendencies of diesel fuels, jet fuels, and their surrogates in diffusion flames. *Fuel* 2017;197:445–58.
- [30] “Final Report for Alternative Fuels Task: Impact of SPK Fuels and Fuel Blends on Non-metallic Materials used in Commercial Aircraft Fuel Systems,” FAA Office of Environment and Energy under CLEEN OTA Number: DTFAWA-10-C-0030, December, 2013.
- [31] Mathai AE, Thomas SJ. Transport of aromatic hydrocarbons through crosslinked nitrile rubber membranes. *J Macromol Sci Phys* 1996;B35:229–53.
- [32] Jennerwein MK, Eschner M, Gröger T, Wilhamr T, Zimmerman R. Complete group-type quantification of petroleum middle distillates based on comprehensive two-dimensional gas chromatography time-of-flight mass spectrometry (GCxGC-TOFMS) and visual basic scripting. *Energy Fuel* 2014;28:5670–81.
- [33] Kehimkar B, Hoggard JC, Marney LC, Billingsley MC, Fraga CG, Bruno TJ, Synovec RE. Correlation of rocket propulsion fuel properties with chemical composition using comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry followed by partial least squares regression analysis. *J Chromatogr A* 2014;1327:132–40.
- [34] Bernabei M, Reda R, Galiero R, Bocchinfuso G. Determination of total polycyclic aromatic hydrocarbons in aviation fuel. *J Chromatogr A* 2003;985:197–203.
- [35] Standard Specification for Aviation Turbine Fuels; Designation No. D1655 – 18a;

- ASTM International: West Conshohocken, PA; 2018.
- [36] Hansen CM. Hansen Solubility Parameters: A User's Handbook. 2nd ed. Boca Raton, FL: CRC Press; 2007.
- [37] Gawron B, Białeczki T. Impact of a Jet A-1/HEFA blend on the performance and emission characteristics of a miniature turbojet engine. *Int J Environ Sci Technol* 2018;15:1501–8.
- [38] ARA. <https://www.ara.com/capabilities/advanced-biofuels-and-renewable-chemicals> (accessed December 28, 2016).
- [39] Maciel V, Machado JC, Pasa VM. The effect of temperature on the properties of NBR/PVC blend exposed to ethanol fuel and different gasolines. *Fuel* 2013;113:679–89.