An Early Evaluation Method of the Compatibility of Alternative Jet Fuels with Elastomer Seals

Master's Thesis

By

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ACKNOWLEDGEMENT

I would like to thank my supervisors Basel Al-Rudainy and Per-Johan Tolf as well as my examiner Ola Wallberg for all the help and support with this project. Thank you to the Deputy director of CESTAP, Elna Heimdal Nilsson for providing resources and connections. The methods section of this project would not have been possible without the fuels provided by Mattias Richter at Combustion Physics. Thank you all.

A special thanks to MathWorks MATLAB Answers that where a huge help when I was developing the MATLAB scripts used in this report.

Furthermore, thank you to the Chemical engineering division at LTH for making me feel welcome. It was a lot easier to work on this project knowing that I would always have coffee and fun conversations waiting at fika time.

A final thank you to Lunds University, LTH, K-sektionen, and Sydskånska nationen for making my years at university more fun and memorable than I ever would have imagined.

ABSTRACT

The aviation industry is a contributor to the global greenhouse gas emissions. Moving away from fossil-based fuels has proven to be more difficult than expected. One possibility for the aviation industry is the development of sustainable aviation fuels (SAFs), produced from renewable sources such as biomass and waste. Certain problems have been discovered with using SAFs, however. The fuels are usually not compatible with the elastomer seals in engines. The elastomer usually swells in contact with conventional fuels making it more compact and a better seal. Elastomer seals in contact with alternative fuels tend to shrink and harden, causing leakages. This issue has been traced to the inherent low content of aromatics in SAFs. The testing of the effect of fuels on materials in standards such as ASTM occurs after much fuel is already used. This study aimed therefore to find a rapid method of getting an early indication of the effect of a fuel on elastomer seals.

Previous studies on the subject have focused on the testing of volume change to determine the compatibility of fuels and materials. Volume change is a basic response for a material in contact with a fuel and many other properties will vary proportionally. The change in volume is determined by two processes, the material absorbing fuel components (causes swelling) and the fuel extracting components from the material (causes shrinking). Eventually an equilibrium is reached, and the volume remains constant. Volume swell is mostly tested by using Optical dilatometry, a method in which an elastomer is submerged in a fuel and images are taken at a specified time interval. These images are then analyzed, and the volume change is calculated by assuming isotropic volume change.

The optical dilatometry method was used to test the effect of fuels on a nitrile rubber O-ring. The fuels used were kerosene, HVO and RME. Every test used 10 mL of fuel in a volumetric flask, with a 2-3 mm cross-section of O-ring. Each fuel was tested in its pure form, tests were also done with a mix of kerosene and HVO. Pieces of elastomer were also aged in kerosene for 3 days and then switched to pure HVO and a blend of kerosene and HVO. All tests were done at room temperature. A Matlab script was used to detect the area of the elastomer in pixels.

The result of the tests showed that the kerosene fuel caused swelling immediately. The volume change reached a plateau of almost 12% volume swell within the first 24 hours. Testing of HVO showed some weak initial swelling and then consistent shrinking (about 1-2%). Testing of RME showed a swell of about 30-35%. The elastomer is assumed to have been dissolving in the fuel due to polar parts in both the elastomer and the fuel. Blends of HVO and kerosene showed similar swelling to that of pure kerosene but limited to around 5%. Aged elastomers showed a dramatic shrinking when switched to HVO and a blend of HVO and kerosene. This showed that a used elastomer is more strongly affected by a switch to a low aromatic fuel than a completely new elastomer.

It was concluded that testing volume swell by using optical dilatometry is a relatively simple way of testing material compatibility. Conclusions could be drawn from the results within the testing period. For faster results, higher temperatures could be used. Ageing the elastomers is necessary to see the effect of a new fuel on used elastomers. Other materials than nitrile rubber should also be tested.

POPULÄRVETENSKAPLIG SAMMANFATTNING

Klimatomställningar har gjorts inom de flesta delar av transportsektorn, som ofta pekas ut som boven i dramat när det kommer till utsläpp av koldioxid. Bilar som går på elektricitet är ett typiskt exempel. Denna omställning är svårare att göra när det gäller flygindustrin. Elektriska flygplan är inte realistiska just nu då batterierna hade behövt vara enorma.

Fördelen med flytande bränslen är att de bränns upp under resan, vilket gör flygplanet lättare med tiden. Därför har industrin börjat utveckla bränslen som produceras från förnybara resurser såsom växtolja, biomassa och avfall. Dessa bränslen har potential att vara klimatneutrala från en livscykelanalys. Det finns sådana bränslen som har godkänts för kommersiell användning, men de måste blandas med fossila bränslen för att få användas. Detta är för att rena biobränslen ofta inte är kompatibla med elastomera (en typ av polymer) tätningsmedel i flygmotorer. Fossila bränslen innehåller aromater (cykliska kolväten) som absorberas av elastomeren och orsakar svällning. Svällningen gör elastomeren mer kompakt vilket förbättrar dess förmåga att förhindra läckor. Biobränslen innehåller inte aromater vilket orsakar att bränslet i stället extraherar komponenter från elastomeren. Detta gör att elastomeren krymper, vilket i sin tur orsakar läckor. Syftet med denna studie var att hitta en snabb metod för att få en indikation av hur ett bränsle kommer påverka ett elastomeriskt tätningsmedel.

För att uppnå detta testades volymsvällningen genom att använda en metod som kallas optisk dilatometer. Volymsvällning är en grundläggande reaktion hos ett material i kontakt med bränslen och många andra egenskaper kommer att variera proportionerligt. Testmetoden går ut på att man skär upp en bit av en O-ring (som är ett vanligt elastomeriskt tätningsmedel), lägger den i ett kärl och häller i ett bränsle. Under kärlet placeras en kamera som tar bilder en gång i timmen. En lampa placeras ovanför kärlet.

Experimenten genomfördes i ca 3–4 dygn i rumstemperatur. Bilderna analyserades genom att använda ett datorprogram (MatLab). Volymändringen räknades ut genom att använda arean från bilderna i en ekvation som antar att volymändringen är likadan i alla riktningar. Tre olika bränslen användes, ett vanligt fossilt fotogen och två biodieslar (HVO och RME).

Hur bränslet påverkade materialet kunde observeras inom tiden för testning. Fotogenet orsakade svällning som planade av under det första dygnet. HVO orsakade krympning av elastomeren under hela testperioden. Elastomeren svällde upp till 35%, i RME, vilket misstänkts är på grund av att RMEn löser upp materialet. Tydligast effekt skedde i de tester där elastomeren först ”åldrades” i 3 dygn i fotogen och sedan testades med HVO. Då krympte elastomeren dramatiskt inom det första dygnet. Detta visade att tätningsmedel som redan varit i bruk kommer att påverkas mer av ett byte till ett lågaromatiskt biobränsle än ett helt nytt tätningsmedel.

Därför rekommenderas bränsleutvecklare att testa nya bränslen på båda nya och använda material. Dessutom bör de testa bränslet på flera olika material då dessa kan reagera olika. För snabbare metod, bör experiment utföras med högre temperatur.

LIST OF ABBREVIATIONS

AJF	Alternative jet fuels
AFRL	Air Force Research Laboratory
ASTM	American Society for testing and materials
ATJ	Alcohol-to-jet
CHJ	Catalytic hydrothermolysis jet
FT	Fischer-Tropsch
HC	Hydroprocessed hydrocarbons
HEFA	Hydroprocessed esters and fatty acids
HVO	Hydrotreated vegetable oil
RME	Rapeseed methyl ester
SAF	Sustainable aviation fuels
SIP	Synthetic isoparaffins
SPK	Synthetic paraffinic kerosene

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1. INTRODUCTION

Emissions from the aviation industry are a leading contributor to the global climate change. To mitigate the impact of climate change, many sectors need to reduce their carbon emissions, especially the transportation sector. Aviation stands for about 2% of global emissions of carbon dioxide. As other sectors lower their carbon footprint, this percentage will become higher and higher. The market demand does not seem to become lower either. Airplane travel has become much more available and easily accessible. Because of these reasons the aviation industry's relative emissions will become higher with time. [1] The aviation industry is aiming to achieve a 50% decrease in greenhouse gas emission by 2050 in comparison to the emissions in 2005. [2]

The next step into lowering the global gas emissions from the aviation industry is to create alternative jet fuels that have net-zero carbon dioxide emissions. This can be done by creating fuels made from renewable feedstocks such as plants or waste. These fuels are called Sustainable Aviation Fuels (SAF). There are many benefits to using SAFs instead of conventional fuels besides the environmental ones. They provide a stable and diverse source of energy. With fossil fuels being a finite resource, alternative fuels are an important subject for research. [1]

Certain problems with alternative jet fuels have been discovered, however. The testing of these fuels has revealed a compatibility issue with the elastomer seals in engines and airframes. The elastomers tend to shrink and cause leakage when an alternative fuel is used. This problem has been traced to the low or no aromatic content in alternative fuels. The low aromatic content causes alternative fuels to not be able to be used on their own and limits the blending ratio with conventional fuels. [3]

Previous research has determined that aromatics promote most of the swelling behavior in elastomeric seals. There is a minimum requirement of 8% aromatics content in a fuel for the swelling to be sufficient. This number is based on historical aromatic content in conventional fuels, not scientific determinations. Small, aromatic molecules with high polarity and potential for creating hydrogen bonds are most effective in causing seals to swell. [4]

The current infrastructure for air travel is based on conventional, fossil derived fuels. From refineries to airport distribution system and finally to refueling the aircraft. The previously mentioned material compatibility issues can become a huge issue. [5]

1.1 AIM

In this project we aim to find a method of rapidly testing the compatibility between a fuel and non-metallic materials. Many non-metallic materials are used in aircrafts, for various purposes. The scope of this study is limited to elastomer seals.

2. LITERATURE REVIEW

2.1 CONVENTIONAL AND ALTERNATIVE JET FUELS

Jet fuels are a kerosene-type fuel, originally developed from lamp oil. The turbine engine was developed during World War II. Since the war effort required all available gasoline, the jets used kerosene instead. Kerosene type fuels were considered to have the best combination of properties when the commercial jet industry was developing. To this day, kerosene-type fuels are used predominately in the aviation industry. [6]

Conventional jet fuels are produced by using petroleum sources. [6] Alternative jet fuels are fuels produced by using non-petroleum sources. These could still be fossil-based if coal or natural gas are used as a feedstock. For a fuel to be a Sustainable Aviation fuel (SAF), the feedstock should be something that can be renewed. For example, plant oil, algae, biomass, waste, and residues. Using these types of feedstock could lead to a reduced lifecycle greenhouse gas emission for the jet fuels. [7]

Petroleum jet fuels have been used for almost a century. The current engines, handling and transportation of jet fuels are adapted to the conventional jet fuels. It is preferred that new jet fuels are compatible with the infrastructure that already exist. The complete change of the infrastructure globally would be too costly. Research focuses on so called “drop-in fuels”, fuels that are directly compatible with existing infrastructure without having to change anything because they would essentially be identical to conventional fuels. These drop-in fuels can often be mixed in with conventional fuels, sometimes as high as a 50% blend. [5]

2.1.1 TESTING OF JET FUELS

There are several specifications for jet fuels globally. The ones this report focuses on are the specifications provided by the American Society for Testing and Materials (ASTM). Jet fuels from fossil fuels are produced according to the specification in *ASTM D1655, “Standard specification for Aviation Turbine Fuels”*. The testing of fuels is rigorous and expensive, but necessary from a safety aspect. The jet fuel has a critical role in the operation of an aircraft. Alternative jet fuels that are proven to be essentially identical to conventional fuels get approved as drop-in fuels in *ASTM D7566, “Standard Specification for Aviation Turbine Fuel Containing Synthesized Hydrocarbons”*. [5]

Alternative jet fuels have their own set of tests in *ASTM D4054 “Standard practice for evaluation of new aviation turbine fuels and fuel additives”*. This standard was created to compare the performance and properties of alternative jet fuels to conventional jet fuels. The D4054 gives manufacturers guidelines in how to test a fuel and what properties a fuel should have to be incorporated into other specifications. [1, 5, 8]

2.1.1.1 ASTM D4054 – STANDARD PRACTICE FOR EVALUATION OF NEW AVIATION TURBINE FUELS AND FUEL ADDITIVES

It is made clear in the standard that the D4054 is not an approval process. It is a guide to obtain comprehensive data for a new fuel that could then be used in an approval process. The testing is divided into four Tiers. [5, 8]

Tier 1: Specification properties

The fuel is tested to make sure that it meets the criteria for some basic fuel properties such as composition, combustion, stability, lubricity etc. The standard includes specifications of these properties. The properties tested are important for safe operation and must therefore be tested early. [5, 8]

Tier 2: Fit-for-Purpose properties

Fit-for-purpose properties are usually not routinely measured in conventional fuels since they are mostly inherent in petroleum fuels. Since alternative fuels are produced from unconventional feedstocks, these properties need to be tested. Some of these are chemical composition, electrical properties, and a preliminary testing of the compatibility with engine and seals. [5, 8]

Tier 3: Component/Rig/Materials testing

This tier tests the effect of the fuel on the engine and aircraft system. However, before the tier 3 testing can begin, the data from Tiers 1 and 2 are reviewed by a subcommittee. If the data is found acceptable, the rest of the testing can be performed. Tier 3 tests the fuels compatibility with engine seals, coatings and metal or testing the combustor. [5, 8]

Tier 4: Full scale engine testing

Tier 4 is a full-scale engine test where performance, operability, emissions etc. are evaluated. [5, 8]

Fuel requirements

Each tier requires a certain amount of fuel for testing. This is an estimation by ASTM:

- Tier 1 ≈ 40 L
- Tier 2 ≈ 300 L
- Tier 3 ≈ 40 000 L
- Tier 4 ≈ 850 000 L

In total, about 900 000 L of fuels are needed to gather data for a potential annexing into the ASTM D7566. A fuel that is shown to not be compatible with materials in engines in Tier 2 or Tier 3 means that a lot of fuel has been tested in vain. Any changes to the fuel would require the testing procedures to be performed again. An early indication of material compatibility is therefore beneficial. [8]

2.1.1.2 PRESCREENING OF JET FUELS

One method of determining if a jet fuel is suitable for use would be to determine the composition of the fuel by a pre-screening. Heyne et.al suggest an additional two Tiers of pre-screening. Tier α would use small volumes (milliliters) for testing to determine the composition of a fuel which in turn could reveal important information about the properties. A 2D GC could be used to determine the composition, while correlative modeling could determine properties. Tier β would use bigger volumes (150-500 ml) to directly measure specific properties. This can be used to confirm the model predictions made in Tier α. These methods are outside of the ASTM standard and aim to give an early insight into the chemistry of the fuel. [1]

2.1.2 APPROVED ALTERNATIVE JET FUELS

There are several alternative fuels that have been approved for use as jet fuels and annexed into the ASTM D7566. Specifics on the fuels can be seen in *Table 1* below. [9]

Table 1. ASTM D7566 Annexes described in terms of feedstock and maximum blending.

	TYPE	FEEDSTOCK	MAX BLEND
A1: FT-SPK	Fischer Tropsch synthetic paraffinic kerosene	Syngas (CO and H2) is synthesized through coal or gas.	50 vol%
A2: HEFA	Hydroprocessed esters and fatty acids SPK	Fatty-acids, lipids and fatty-acid esters from plants, animal fats, greases.	50 vol%
A3: SIP	Hydroprocessed fermented sugars to synthetic isoparaffins	Sugars	10 vol%
A4: FT-SPK/A	FT- SPK with aromatics	Same as FT-SPK. Light aromatics synthesized from non-petroleum sources	50 vol%
A5: ATJ	Alcohol-to-jet SPK	Ethanol and isobutanol from non-petroleum sources	50 vol%
A6: CHJ	Catalytic hydrothermolysis synthesized kerosene	Same as HEFA	50 vol%
A7: HC-HEFA	Hydroprocessed hydrocarbons, esters, and fatty acids SPK	Same as HEFA plus bio-derived hydrocarbons	10 vol%
A8: ATJ-SKA	Alcohol-to-Jet SPK with aromatics	Same as ATJ with added aromatics	50 vol%

None of these fuels can be used on their own, they must be mixed with a conventional fuel. A maximum fuel blend is 50 vol% of an AJF but can be as low as 10 vol%. Most of the fuels annexed after FT-SPK can be produced from renewable feedstocks, making them potential SAFs. Thorough life-cycle analyses would have to be made to determine the carbon footprint of such fuels. [5, 10]

2.1.3 COMPOSITION OF JET FUELS

The composition of jet fuels is very complex and not always fully understood. Some efforts have been made into defining the compositions as more alternative fuels are being developed and the need for understanding the chemistry becomes even more important. [11]

Most jet fuels have a composition made up of groups of paraffins, naphthenes, cycloparaffins and aromatics with small amounts of olefins present. The majority (70-85%) of a fuel's composition is made up of paraffins. Both normal straight chained and branched isoparaffins can be found in varying ratios. N- and isoparaffins have a high hydrogen to carbon ratio which causes a high heat to weight ratio and a clean burn. Aromatics make up less than 25% of the total fuel. They can contain one or more 6-carbon ring structures. [11]

Alternative jet fuels have been observed to contain mostly paraffins. These include mostly iso-paraffins but also some n-paraffins and cycloparaffins. These fuels have a consistent hydrogen to carbon ratio. Studies have shown that alternative fuels have very low sulfur content as compared to conventional fuel, which is also beneficial. [3, 10]

Most alternative jet fuels have a very low or no aromatic content (usually less than 1%), which can cause problems with materials in engines and airframes. [10, 12] However, aromatics in fuels also cause problems like inefficient combustion and emissions of soot. Fuels free of aromatics have higher combustion efficiency and increased energy content whilst also reducing the emission of NOx, CO, and soot. Finding a way to use fuels with low aromatics concentration would be beneficial. [4]

2.2 NON-METALLIC MATERIALS IN AIRCRAFTS

Polymers are used in many ways in aircrafts. Polymers are used as a glue to hold together fibers of high stiffness and high strength in polymer-fibre composites. The composites are used in both in the airframe and engine components. Polymers can also be used as adhesives to join aircraft components. [13]

Elastomers are used as seals in an aircraft fuel system to prevent fuel leakages, due to their low stiffness and high elasticity. These properties also make elastomers suitable for being used in tires, gaskets and hoses. [13] Elastomers are crucial components in the aviation industry and are therefore expected to operate without flaw while they are used. [14]

2.2.1 ELASTOMERS AS A SEAL

Elastomers are a type of polymer that have a molecular structure somewhere between a thermoplastic and a thermoset. There is some crosslinking between elastomer chains that are coiled like a spring which allows them to be stretched without permanent deformation. When the deformation load is removed, the elastomer will regain its original size and shape. [13]

O-rings are the most common elastomeric materials in aircraft engines. They are often shaped as a doughnut. The O-ring works as a seal by restricting the flow of fluid between two surfaces.[15] A simple schematic of the process can be seen in *Figure 1* below.

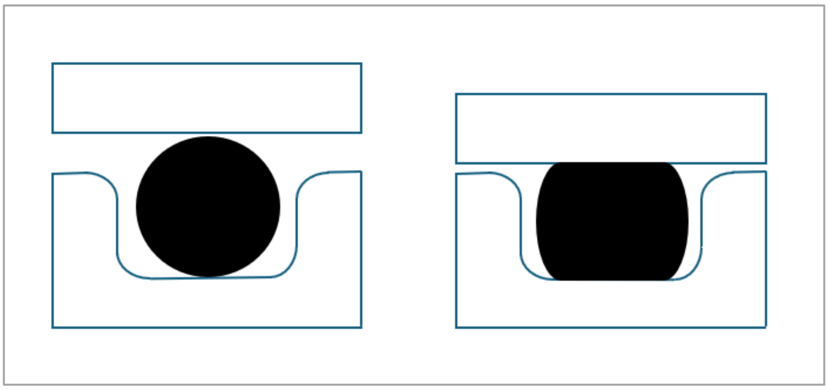


Figure 1. Schematic of the process of sealing with an O-ring.

The mechanical pressure causes the elastomer spread out in the cavity and creates a tight seal. Fluid that enters the cavity will push the elastomer to the side. If the O-ring can keep its sealing properties, fuel will not leak out. This also requires the O-ring to maintain its elastomeric properties and not shrink. [15]

Different types of elastomers are used in aircrafts, and they can be grouped into three main groups based on composition: nitrile group, fluorocarbon group and fluorosilicone group. The seal industry has previously used nitrile as the main material because of properties like high wear resistance, but has moved on to other materials in modern times. [14]

2.2.2 SWELLING BEHAVIOR OF ELASTOMERS

The volume change of a new polymer in contact with a fuel is determined by two processes. The polymer, or in this case elastomer, can either absorb components from the fuel (aromatics etc.) or the fuel extracts components from the material (plasticizers, solvents etc.). The first causes the polymer to swell which can improve the polymers sealing abilities and prevent leaks. The second can cause the elastomer to shrink and harden which causes cracks and therefore leakage. The balance of these processes will cause the overall volume change in the material. The swelling of polymers is an important characteristic in a sealing material. The swelling causes the material to become more packed and prevents leaking. The opposite, a sealant shrinking, causes more leaks. [7]

The process of polymers absorbing fuel can be described in several steps. First, individual fuel molecules will break the fuel-fuel intermolecular bonds to be able to leave the bulk fluid. The polymer must also be able to accept the fuel molecule. This is done by the breaking of polymer-polymer intermolecular bonds to create a cavity large enough for the fuel molecule to enter. Fuel-polymer bonds are created when the fuel molecule enters the cavity. The breaking of polymer-polymer bonds causes elastic strain around the cavity. [7]

Volume swell has been found to increase with a decrease in the molar volume of fuel components, i.e., smaller molecules contribute more to volume swell. The volume swell also increases as the fuel component’s polarity and hydrogen bonding increases. [7]

2.2.3 TESTING METHODS OF SEALS

The elastomeric seals used in aircrafts can be tested either statically or dynamically. The static testing observes the changes in physical properties of the elastomers. These tests are usually done by immersing the material in a fuel for a certain amount of time. The changes in properties are then analyzed. Static testing cannot determine the real-time changes that occur in a seal during usage. Dynamic testing subjects the seals to real-time working conditions. The changes to the elastomeric seals can be seen as they occur. [14]

TESTING OF PHYSICAL CHANGES

Stress relaxation is an important seal testing method for determining the lifetime of elastomers. These tests can simulate the real working conditions of seals by using desired temperatures and pressures. As describe in *Figure 1* above, the O-ring is subjected to a constant strain when it is being compressed by two mating faces. The deformation caused by the compression causes the elastomer to develop counter-responsive strain. This strain decays with time in a process called stress relaxation. Both physical and chemical changes occur during this process. Fuel penetrating the seal causes increase in seal volume and a temporary increase in relaxation ratio.[14]

Volume change can be measured dynamically through optical methods that record the elastomer submerged in fuels at short intervals. [14]

TESTING OF CHEMICAL CHANGES

Ways of testing chemical changes in elastomers would for example be to test the absorbed compounds through Gas chromatography-mass spectroscopy (GC-MS). By knowing the composition of the absorbed fuel, it can be determined which compounds promote volume swell.[14]

Absorption can also be tested by using thermogravimetric analysis (TGA). Mass is continuously measured while temperature is changed. This method can determine an elastomers capacity to absorb fuels. [14]

ASTM TESTING

ASTM D4054 lists all types of tests that need to be done on materials during Tier 2 & 3. Material tests during Tier 2 are preliminary tests performed on three types of O-rings: nitrile, fluorosilicone, and fluorocarbon. Aged and unaged O-rings are soaked for 7 days in the candidate fuel and then tested for volume swell, tensile strength, and hardness. [8]

Tier 3 tests many more materials, both metallic and non-metallic. The tests required for sealants are peel strength, hardness, tensile strength, elongation, and volume swell. The same tests are required for O-rings in gaskets. The materials are soaked in the candidate fuel for 28 days before testing. The values are then compared to the same material that has been tested in a baseline fuel. The ageing occurs at high temperatures (ca 70-90 ˚C). Because of this, the fuel is changed out after 14 days since the fuel's properties may change after being subjected to high temperatures for a long time. The D4054 does not specify how the material properties should be tested, only which properties. Specifications on methods of testing are found in other ASTM standards, such as D471. [8]

2.3 PREVIOUS RESEARCH

2.3.1 VOLUME SWELL

Previous research on materials compatibility with jet fuels has mostly been focused on volume swell. Volume swell is a property that is directly affected by a fuel's composition as mentioned before. Other physical properties will vary proportionally to a change in volume. [16]

The compatibility problem started being studied in the early 2000s by the U.S Air Force Research Laboratory (AFRL). They used an optical dilatometer to capture the volume change of an elastomer immersed in fuel. In this way, the changes in volume could be seen as they occur. A schematic of an optical dilatometer can be seen in *Figure 2* below. [16]

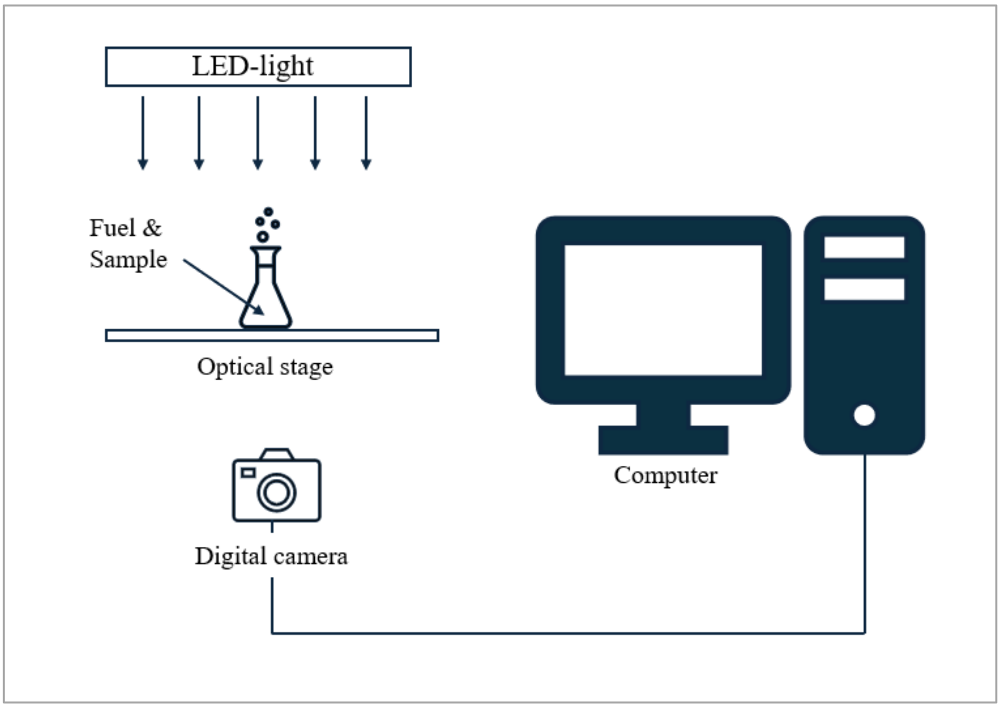


Figure 2. A simple schematic of an optical dilatometer set-up.

The digital camera is placed under an optical stage where the sample rests in an optical cell (or some other vessel). The stage is illuminated by a flat panel LED-light to get even lighting across the sample. The digital camera is connected to a computer that has some software that captures images on a specified time interval. [7]

The volume swell can be calculated by assuming isotropic volume change. [16]

EQ. 1

$$VS(\%) = \left[\left(\frac{A_i}{A_0}\right)^{\frac{3}{2}} - 1\right] \times 100$$

Where VS is the volume swell in percent, Ai is the cross-sectional area at t=i, and $A0$ is the cross-sectional area at t=0 hours.

Using an optical method like an optical dilatometer gives a dynamic way of testing the volume swell. The volume swell could be seen as a function of time. Statically testing an elastomer by submerging it into fuel and calculating the volume after a certain period, gives no information on how the elastomer has been affected by the fuel or if it has reached the equilibrium mentioned above. An optical dilatometer would show how the volume change has varied over the testing period.

2.3.2 SWELL PROMOTERS

Research has also been conducted on what kind of effect different types of aromatics have on volume swell. A short-term solution would be to add in aromatics to alternative jet fuels to promote swelling in materials, which some of the annexes in ASTM D7566 do. It is, therefore, beneficial to know which aromatics would cause the most efficient swelling.

Studies done by Graham et.al. have concluded that not all aromatics are as good at causing volume swell. The components that are most effective at causing volume swell are small aromatic molecules with a high polarity or capacity for hydrogen bonding. [7, 17]

The intermolecular bonding of fuel molecules and polymers can be expressed by Hansen solubility parameters (HSPs). The HSPs for fuel molecules show that alkenes tend to be large, non-polar molecules that do not participate in hydrogen bonds. Aromatics, however, are compact, more polar and can participate in weak hydrogen bonds. Diaromatics are also compact and exhibit significant polarity and ability to form hydrogen bonds. This means that diaromatics will have the strongest interactions with an elastomer whilst alkenes will have the weakest effect. The degree to which a fuel will interact with a material is very dependent on the material and the composition of the fuel. [7, 17]

There has also been research conducted on the possibility to eliminate the need of aromatics by using cycloparaffins as a swell promoter. Cycloparaffins produce less soot compared to aromatics (about 88% less) causing lower emissions.[18, 19] Studies have shown that cycloparaffins exhibit modest volume swell in materials, even though it is lower than that of aromatics. Addition of active cycloparaffins (cyclodecane or decalin) to the level that occurs in conventional jet fuels (circa 30 vol%) can elevate the volume swell in sealants of alternative jet fuels to near the level of jet fuels with lower aromatic contents. [7]

3. METHOD

The physical property selected to test for this thesis was volume swell, since the main purpose of the elastomers in an engine system is to prevent leakage and volume change affects this ability. It is an important property that can be analyzed simply and quickly. Moreover, volume swell is a basic response of a material in contact with a fuel, and many other physical properties will change with a change in volume.

3.1 OPTICAL DILATOMETRY

The method used to test the volume swell of the nitrile rings was an optical dilatometry set-up. A camera was placed under a glass disk. On the disk, a volumetric flask was placed with a cross-section of a Nitrile rubber O-ring. Above the flask there was an LED-lamp. Pictures of the set-up can be seen in *Figure 3* below.

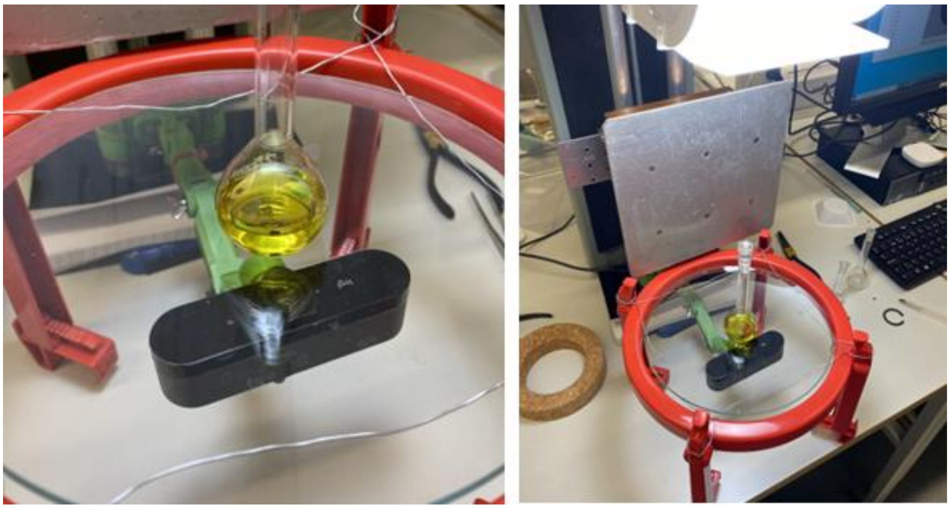


Figure 3. Simple optical dilatometry set-up.

The camera was connected to a computer program that took pictures at a specified time interval for a chosen period. An example of the images obtained can be seen in *Figure 4* below.

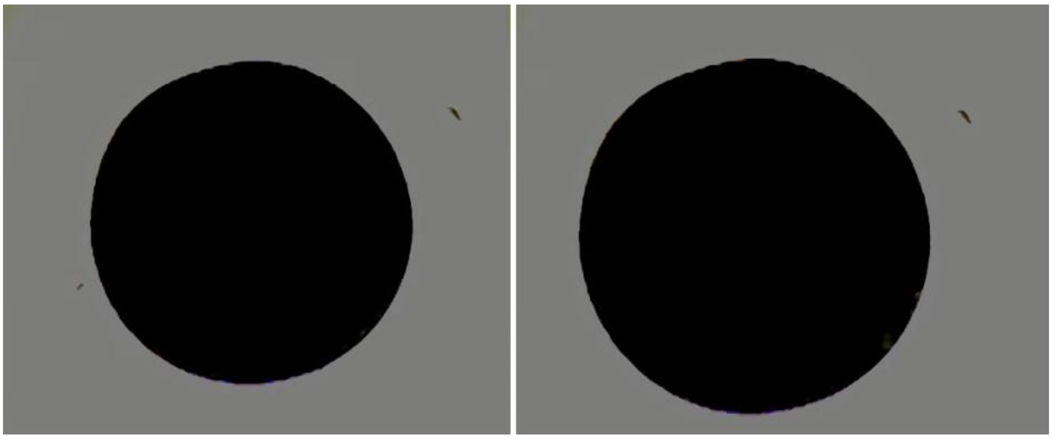


Figure 4. Example of image obtained from the set-up. This example is the first(left) and last(right) images obtained from experiment 7 (RME test).

3.2 O-RINGS

The O-rings used for testing were Nitrile butadiene rubber (NBR) produced by the Parker Hannifin Corporation and provided by SAAB. All O-rings came from the same batch, part number MS29513-215. Materials from the same batch tend to be near identical meaning that the changes occurring to the O-ring during testing can be attributed to the effect the jet fuel has on the material. Nitrile rubber was selected as a testing material because it is highly sensitive to compositional changes in fuels. The effect of the jet fuel will be seen clearly.

3.3 FUELS

The fuels used for the experiments were a conventional kerosene, HVO (hydrotreated vegetable oil) and RME (rapeseed methyl ester). The fuels were produced by Preem AB. The aromatic content of the kerosene fuel is not known but is most likely well within the specifications set by ASTM standards (8-25%) since the fuel is sold commercially. The other two fuels have a content of <1% aromatics according to Preem AB.

3.4 EXPERIMENTS

The experiments were conducted as follows. A section of O-ring was cut with a sharp knife. The width of the elastomer piece was 2-3 mm. The elastomer was transferred to a volumetric flask which was placed on the glass disc so that the camera could be adjusted to make sure that the image had the right focus, brightness and contrast before the fuel was added. 10 mL of fuel where then added to the volumetric flask carefully so that the elastomer did not move around. A stopper was put on the flask which was then transferred to the optical dilatometry set-up. When the image was clear and satisfactory the analysis was started. An image was taken at the start of the analysis and then every hour for a specific amount of time. Specifics on each experiment can be seen in *Table 2***Fel! Hittar inte referenskälla.** below.

Table 2.Specifics on each experiment performed.

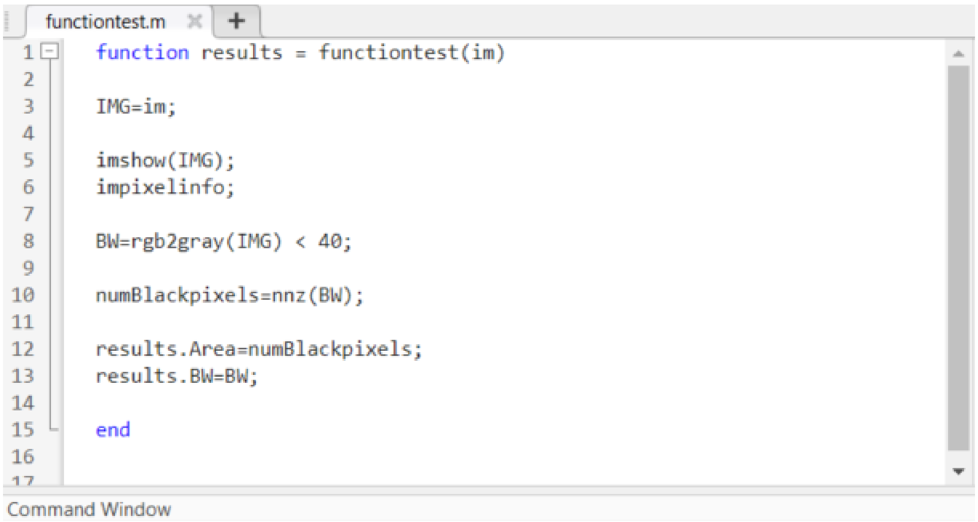
TEST	FUEL	TIME (H)	PREPARATION OF ELASTOMER	COMMENT
1	Kerosene	70	None	
2	HVO	71	Presoaked in kerosene for 70 h	Continuation of experiment 1
3	HVO	71	None	
4	HVO	71	None	Scrapped due to imaging issues
5	50/50 blend of kerosene and HVO	71	None	Fuels not mixed well enough before testing
6	HVO	71	None	
7	RME	92	None	
8	RME	94	None	
9	50/50 blend of kerosene and HVO	95	None	
10	Kerosene	72	None	
11	50/50 blend of kerosene and HVO	95	Presoaked in kerosene for 72 hours	Continuation of experiment 10

Note that the total volume of fuel was always 10 mL. When a blend was tested, 5 mL of each fuel was used.

3.5 AREA DETECTION AND CALCULATIONS

As can be seen in *Figure 4* above, the cross section of an O-ring is not always perfectly circular, making it difficult to approximate the area of the circle using mathematical equations. Instead, a MatLab-script was used to identify and count the number of black pixels in an image. The number of black pixels was used as the area of the circle and used in further calculations.

The Matlab application "Image Batch Processer" was used to process the images obtained from the optical dilatometry set-up. The app can run each individual image through a function that returns the area of the elastomer in pixels. The function can be seen in *Figure 5* below.



```
function results = functiontest(im)

IMG=im;

imshow(IMG);
impixelinfo;

BW=rgb2gray(IMG) < 40;

numBlackpixels=nnz(BW);

results.Area=numBlackpixels;
results.BW=BW;

end

```

Figure 5. Matlab function used to process images.

The function turs each image into a grayscale image and then detects each black pixel (grayscale < 40). Each pixel is counted, and the total is the area. The function also returns an inverse image, which shows which areas are included in the total area. Through this it can be made certain that only the area of the O-ring is counted.

Isotropic volume change was assumed when calculating the volume, since only data on the cross-sectional area was able to be extracted. The volume swell was calculated and then plotted against time, with t=0 as a start. Equation 1 was used to calculate volume change.

$$VS(\%) = \left[\left(\frac{A_i}{A_0}\right)^{\frac{3}{2}} - 1\right] \times 100$$

The unit used for the area is pixels. Images were taken every hour.

4. RESULTS AND DISCUSSION

The purpose of the experiments conducted was to determine if there is a rapid way of testing any jet fuels effect on sealants.

The result of the experiments showed that the equilibrium in volume change described in the literature review is reached during the testing period for elastomers in conventional fuels. For alternative fuels with low aromatic content, the equilibrium was not reached within the test time of about 72 hours, but the trend was clear within the test time.

Data on the obtained area in pixels and the calculated volume changes for every experiment can be seen in Appendix 1 and Appendix 2 respectively.

Some imaging issues occurred due to the experiments being conducted in a teaching laboratory, where there were some fluctuations in light conditions.

4.1 TESTING OF CONVENTIONAL JET FUELS

Experiment 1 and 10 were performed with a conventional kerosene fuel. The results of the experiments were plotted and are shown in *Figure 6* below.

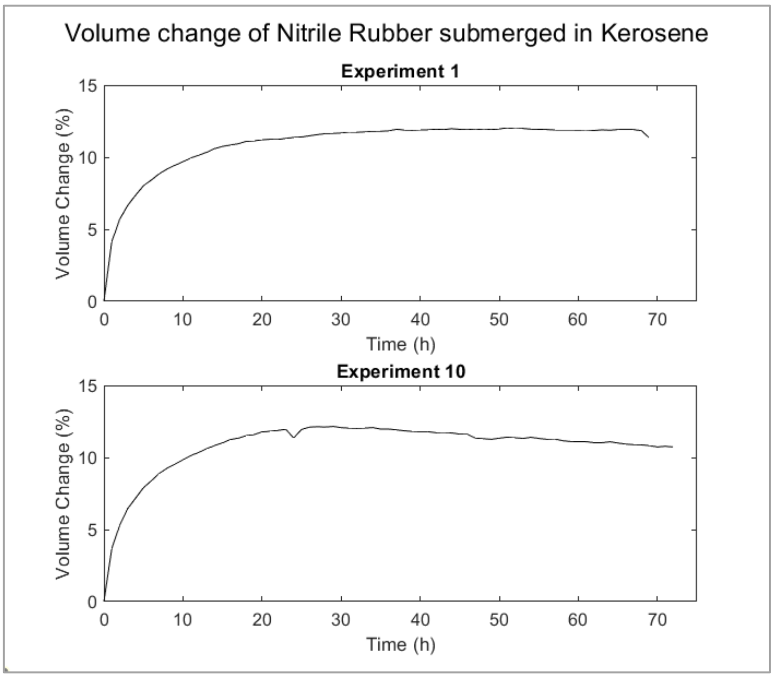


Figure 6. Two separate experiments on the volume change of a cross section of an O-ring submerged in 10 mL of Kerosene at room temperature.

The plots show an initial sharp increase in volume for the first 10 hours. The volume swell reaches an equilibrium after about 30 hours of testing for both tests. The sharp declines at the end for experiment 1 and at about 25 hours for experiment 10 are most likely due to some imaging issues.

There is no reason to expect the volume to change at any point after this test period since the system seems to have reached an equilibrium. Longer tests made by other studies have shown the volume swell plateauing after a few days and remaining similar for the rest of the testing period.[7]

4.2 TESTING OF ALTERNATIVE JET FUELS

4.2.1 HVO

Experiments 3,4 and 6 were conducted by using 100% HVO as the test fuel. Due to some imaging issues, the results from experiment 4 were inconclusive. Experiment 3 and 6 are plotted in *Figure 7* below.

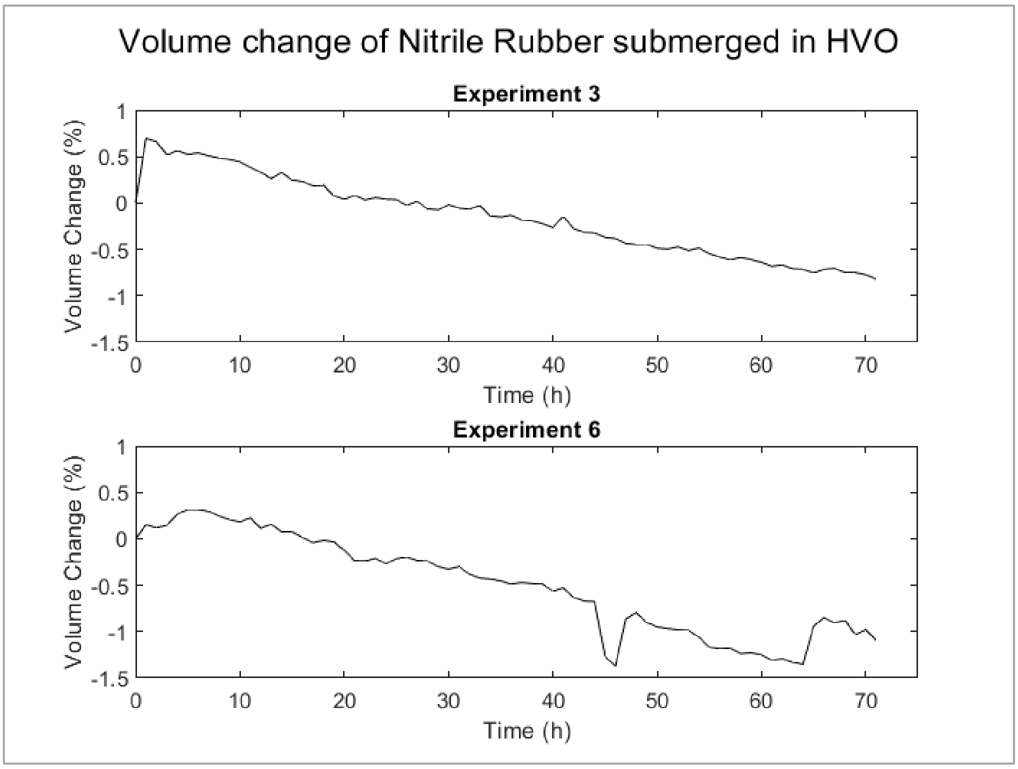


Figure 7. Two separate experiments on the volume change of a cross section of a Nitrile rubber O-ring submerged in 10 mL of 100% HVO for 71 hours at room temperature.

The figure shows a more erratic change in volume from hour to hour for both experiments. For experiment 3 there is some initial swelling in the first hour of testing. After 30 hours, the elastomer is back to its original size, but keeps shrinking. A similar trend can be seen for experiment 6. The two sharp peaks at about 45 h and 65 hours stem most likely from some fault with those images.

The volume change does not reach an equilibrium like experiment 1 described above, but a trend can be observed. The initial swelling is not sufficient for the purpose of preventing leakages. As can be seen from the plot, the swelling is only temporary, and the equilibrium shifts toward a shrinking of the material.

Previous research has seen some swelling of a nitrile rubber in synthetic paraffinic kerosene. Usually, a lot less than conventional fuels, but still some swell. [7] Why the nitrile rubber is consistently shrinking in HVO is unknown.

4.2.2 RME

Experiment 7 and 8 were conducted by using 100% RME as test fuel. The experiments are plotted in *Figure 8* below.

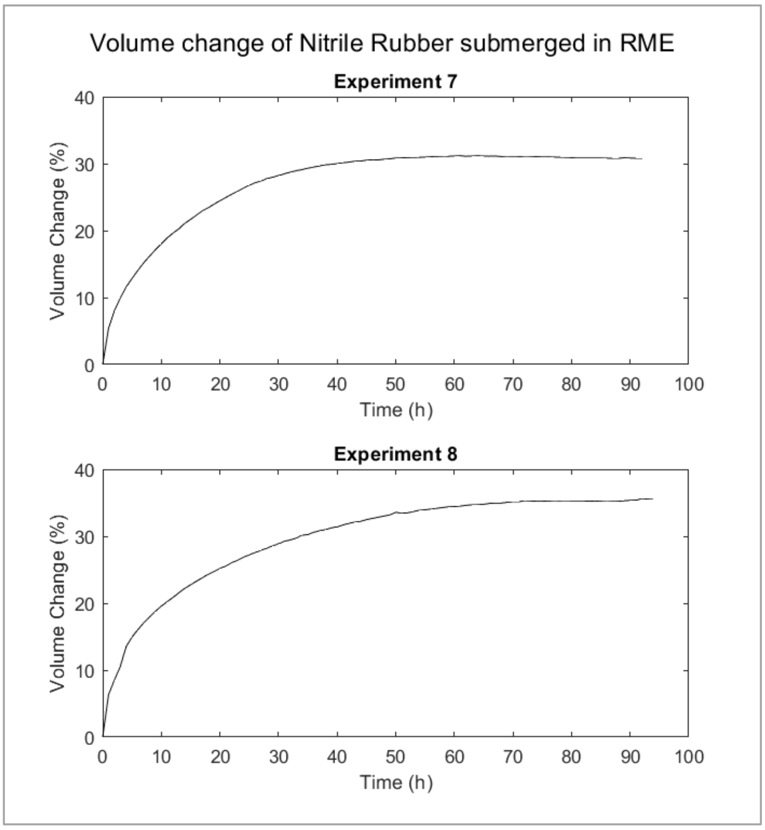


Figure 8. Two separate experiments on the volume change of a cross-section of O-ring submerged in 10 mL of RME for 91 hours at room temperature.

These experiments show an elastomer swelling to about 30-35% of its original size. Experiment 7 can be seen in *Figure 4*.The polymer is most likely dissolving in the RME. NBR is a copolymer of acrylonitrile and butadiene and is thus polar. The esters in RME interact with the polar parts of the NBR to dissolve the elastomer according to the “like dissolves like” principle. The dipole-dipole interactions between NBR and biodiesels have been observed to be stronger than those with diesel. This is thought to be because of the high polarity of fatty acid esters. [20]

RME is therefore not a suitable fuel to use with NBR since the fuel dissolves the elastomer with time.

4.3 TESTING OF FUEL BLENDS

Experiments 5 and 8 was conducted by using a 50/50 blend of kerosene and HVO (5 mL of each) as test fuel. The experiment is plotted in *Figure 9* below.

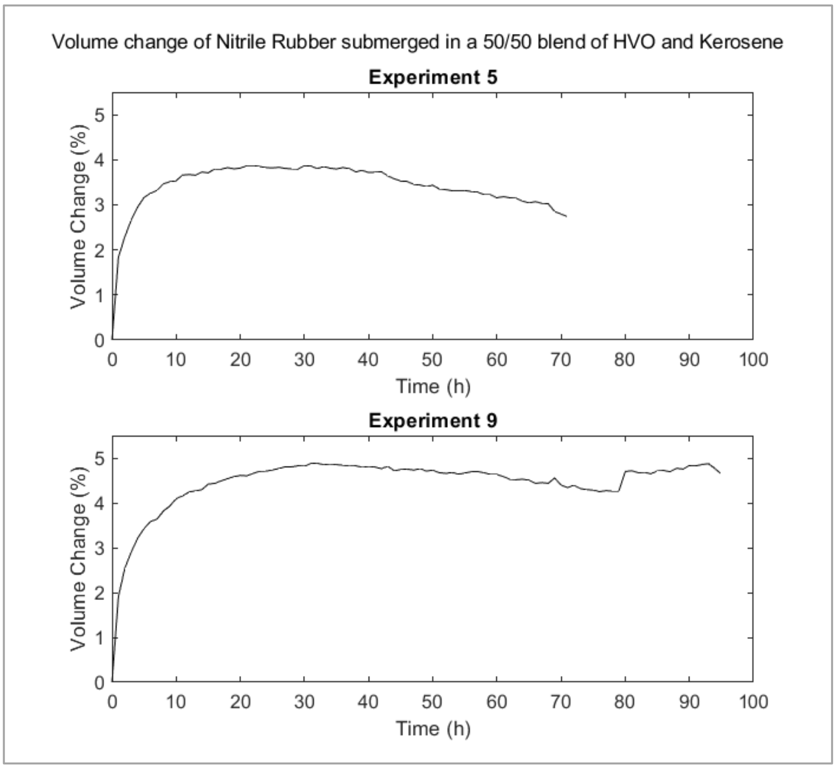


Figure 9. Two separate experiments on the volume change of a cross section of a Nitrile rubber O-ring submerged in a 10 mL blend of 50% kerosene and 50% HVO at room temperature. Experiment 7 was conducted for 71 hours and Experiment 9 for 93 hours.

The plot shows that the blend of kerosene and HVO reaches a total volume swell of about 5%. The volume swell effect of the blend is almost half that of the pure kerosene, but we can see that HVO does not prevent the elastomer from swelling. The sudden increase at 80h for experiment 9 is most likely an imaging issue. The two fuels were not pre-mixed in experiment 5, which is most likely why the curve is not as smooth as the other experiments. Like the experiments from with conventional fuels, an equilibrium is reached after about 30h. Although the insufficient mixing of the two fuels makes it less of a secure analysis.

4.4 TESTING OF PRESOAKED ELASTOMER IN KEROSENE

Elastomers that were presoaked in kerosene were used to simulate the effect of a fuel or fuel blend on an elastomer that has been in service. The pieces used in experiment 1 and 10 were quickly removed from the kerosene fuel, dried off with a paper towel and then immediately transferred to a new fuel.

4.4.1 100% KEROSENE TO 100% HVO

Experiment 2 was transferred from a 100% kerosene to a 100% HVO fuel. The result is plotted in *Figure 10* below.

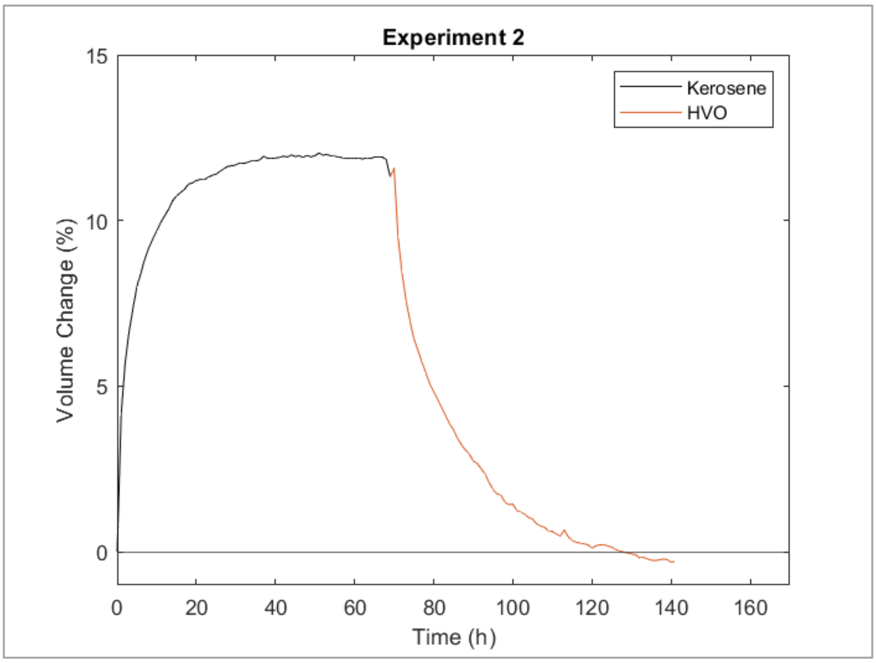


Figure 10. Volume change of a cross section of an O-ring that was first submerged in 10mL of kerosene for 69 hours at room temperature and then submerged in 10 mL of HVO for 72 hours at room temperature.

The presoaked elastomer shows a dramatic change in volume when switched to a low aromatic fuel from a conventional kerosene. If we compare the result from the experiment above to the results from using HVO on a new piece of elastomer (*Figure 7*), we see a clear difference that can be attributed to the state of the elastomer at the start of the test. An elastomer that has been in use with a conventional fuel will be more strongly affected by a switch to a low aromatic fuel than a completely new elastomer. The elastomer continues shrinking below the original size of the elastomer but seems to be reaching a lower degree of shrinking with time. As with the swelling of the polymer, most of the shrinking occurs in the first 24 hours of testing.

4.4.2 100% KEROSENE TO 50/50 BLEND OF HVO AND KEROSENE

Experiment 11 is the result of using the elastomer from experiment 10 and submerging it in a blend of 50/50 HVO and kerosene. The second part of the experiment was not zoomed in as much as the first part, so the obtained area had to be scaled up to be comparable. The result is plotted in *Figure 11* below.

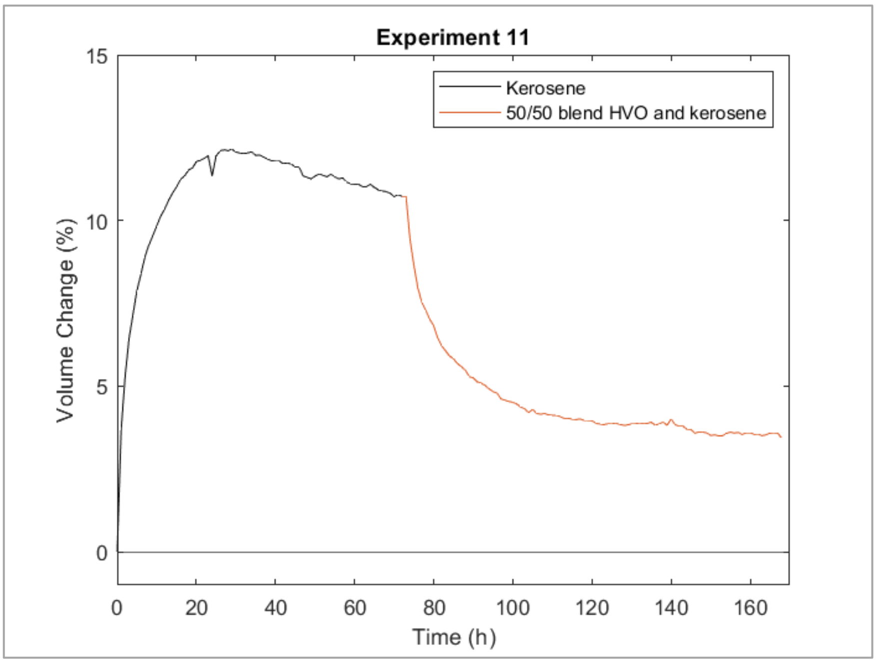


Figure 11. Volume change of a cross section of an O-ring that was first submerged in 10mL of kerosene for 73 hours at room temperature and then submerged in 10 mL of a 50/50 HVO and kerosene blend for 72 hours at room temperature.

As with experiment 2 shown above, the initial effect of the fuel on the pre-soaked material is dramatic compared to the HVO tests on new pieces of elastomers. Most of the shrinking occurs during the first 24 hours of testing and then plateaus. The shrinking does not reach the original size of the elastomer, instead the plateau is around a total of 5% volume swell. Switching to a fuel with a lower aromatic content than a conventional fuel will still have a shrinking effect on the elastomer.

5. CONCLUSION

From the literature review and the experiments conducted in this study we can conclude that an accurate determination of the effect of a jet fuel on a sealant can be obtained in a short amount of time. Volume swell is one of the most important properties of sealants. The equilibrium of volume change is reached quite quickly since most of the swelling occurs in the first 24 hours for fuels containing aromatics. For the HVO fuel, the equilibrium was not reached in the testing period, but we can still conclude that the fuel will not be compatible with the material by the continuous shrinking.

ASTM D4054 requires elastomers to be aged for 28 days through a soak test before testing most properties. It does not give instructions on how to test properties like volume swell. Ageing of a fuel was shown to be important in this study since the pre-soaked elastomers were dramatically affected by a change to a low aromatic fuel. The ageing was only done for a few days in this study (about 72 hours), but the result of switching fuels could still be seen.

The advantage of the optical dilatometry test is that it is simple to set up, uses small amounts of fuel (10 mL at a time) and can give a visualization of the effect of the fuel on the material with time. With a good image processing program, the analysis of the data will be fast.

It is however important to know the composition of both the fuel and the non-metallic materials. For tests with RME, one might have thought that the 30% in volume swell was a positive indication when in fact the elastomer was dissolving.

5.1 RECOMMENDED MODIFICATIONS OF THE METHOD

The set-up in this study was determined by what was available in the lab. It worked decently, but improvements can be made.

- The lamp in this study was quite far away from the volumetric flask which caused the lighting to be quite poor. This caused some imaging issues if other lamps in the room were turned on or off.
- The glass disc where the volumetric flask was placed, was not sturdy enough. Bumping into the table could cause it to move. A sturdier method of fastening the flask could be useful. For example, a utility clamp.
- All processes are limited in how rapid they are at room temperature. For a faster method, higher temperatures should be used.
- To avoid the assumption of isotropic volume swell, a second camera could be placed to take images of the thickness of an elastomer piece. Or whole O-rings could be tested instead.

5.2 RECOMMENDED PROCESS OF TESTING

It is recommended that testing of new jet fuels should be done on both new materials and aged materials. The results showed that the effect will be different on a used elastomer compared to a new one. Most likely, the O-rings in an engine will not be switched out before switching to a new fuel.

New fuels should also be tested on more materials, not just nitrile rubber. Especially since the aviation industry seems to be moving away from nitrile rubber O-rings.

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APPENDIX 1: Area in pixels for every experiment

Table 3. Obtained area in pixels for every experiment.

T(h)	EX1	EX2	EX3	EX5	EX6	EX7	EX8	EX9	EX10	EX11
0	39364	42344	48915	53189	52652	66874	62697	59925	48921	40801
1	40444	41813	49142	53840	52705	69279	65319	60686	50112	40487
2	40843	41544	49130	53997	52693	70420	66214	60937	50632	40288
3	41089	41333	49084	54130	52703	71229	67026	61079	51001	40119
4	41271	41173	49099	54231	52745	71943	68223	61202	51233	40013
5	41441	41035	49086	54305	52763	72486	68796	61287	51464	39951
6	41543	40949	49091	54338	52763	73005	69239	61348	51618	39885
7	41654	40856	49081	54359	52756	73487	69640	61368	51780	39836
8	41737	40772	49073	54410	52738	73914	69990	61440	51895	39747
9	41805	40685	49068	54427	52725	74317	70324	61484	51986	39687
10	41866	40622	49059	54435	52716	74688	70629	61549	52079	39648
11	41932	40564	49041	54479	52731	75057	70889	61574	52173	39610
12	41982	40501	49023	54483	52692	75364	71136	61607	52239	39589
13	42033	40437	49001	54478	52706	75632	71408	61618	52324	39552
14	42097	40372	49022	54502	52679	75973	71671	61628	52391	39529
15	42136	40326	48996	54497	52679	76219	71873	61677	52450	39503
16	42160	40260	48991	54526	52657	76485	72086	61684	52522	39454
17	42184	40210	48975	54524	52637	76746	72285	61705	52553	39444
18	42226	40168	48977	54537	52646	76941	72490	61725	52609	39415
19	42234	40135	48941	54527	52640	77165	72645	61743	52630	39406
20	42253	40081	48928	54533	52609	77378	72830	61753	52688	39387
21	42261	40062	48942	54552	52569	77574	72967	61750	52704	39362
22	42258	40021	48926	54553	52568	77782	73152	61771	52721	39341
23	42277	39978	48934	54546	52578	77963	73306	61789	52746	39330
24	42294	39912	48928	54537	52558	78151	73470	61791	52556	39287
25	42302	39857	48927	54535	52577	78331	73613	61801	52743	39276
26	42323	39823	48907	54539	52583	78491	73744	61814	52793	39267
27	42343	39813	48921	54531	52570	78596	73874	61829	52802	39261
28	42361	39757	48894	54527	52567	78740	73992	61828	52795	39247
29	42365	39738	48891	54525	52547	78829	74129	61839	52808	39224
30	42372	39742	48909	54552	52537	78932	74248	61835	52782	39211
31	42388	39691	48897	54549	52547	79034	74391	61858	52772	39183
32	42384	39680	48893	54530	52518	79138	74471	61861	52767	39206
33	42392	39663	48906	54545	52503	79226	74566	61847	52773	39178
34	42401	39637	48870	54532	52500	79292	74740	61853	52783	39170
35	42402	39624	48866	54526	52493	79379	74774	61848	52750	39177
36	42410	39586	48872	54537	52481	79455	74904	61843	52752	39165
37	42438	39570	48856	54529	52487	79515	74995	61835	52733	39162
38	42423	39559	48853	54503	52483	79589	75053	61838	52714	39161
39	42420	39532	48842	54516	52481	79610	75157	61824	52700	39152
40	42426	39526	48830	54499	52453	79659	75215	61833	52693	39139
41	42428	39506	48868	54501	52465	79714	75323	61826	52694	39140
42	42439	39490	48825	54505	52430	79748	75414	61813	52671	39133
43	42432	39538	48812	54472	52416	79806	75485	61833	52678	39130
44	42447	39485	48810	54450	52414	79815	75528	61794	52667	39135
45	42436	39456	48794	54432	52206	79870	75628	61805	52641	39124
46	42441	39441	48790	54430	52169	79893	75694	61809	52636	39124
47	42429	39435	48773	54407	52349	79887	75762	61800	52554	39121
48	42444	39427	48769	54401	52371	79926	75833	61813	52540	39102
49	42433	39421	48770	54390	52335	79953	75893	61792	52527	39096
50	42443	39395	48756	54400	52318	80000	76044	61799	52552	39091
51	42462	39413	48753	54371	52312	80008	75984	61778	52574	39099

52	42446	39420	48761	54366	52307	80026	76014	61771	52561	39097
53	42452	39421	48748	54358	52305	80037	76084	61779	52546	39103
54	42440	39411	48757	54359	52280	80040	76156	61765	52572	39094
55	42437	39402	48737	54359	52241	80057	76188	61774	52546	39086
56	42433	39383	48725	54351	52235	80077	76223	61786	52528	39089
57	42426	39374	48715	54346	52237	80095	76271	61788	52535	39097
58	42423	39364	48723	54327	52217	80105	76311	61777	52496	39098
59	42425	39355	48716	54326	52220	80104	76356	61762	52480	39104
60	42421	39348	48706	54303	52212	80126	76366	61762	52476	39098
61	42426	39342	48693	54311	52191	80141	76395	61744	52476	39101
62	42416	39318	48697	54302	52197	80107	76437	61719	52453	39110
63	42427	39321	48684	54299	52184	80123	76466	61716	52454	39087
64	42421	39309	48682	54276	52177	80144	76474	61720	52474	39098
65	42432	39299	48669	54263	52320	80117	76497	61712	52446	39111
66	42434	39296	48682	54272	52354	80112	76548	61684	52422	39086
67	42432	39301	48685	54259	52333	80121	76562	61690	52411	39135
68	42412	39308	48671	54256	52343	80086	76564	61684	52407	39092
69	42282	39304	48670	54195	52289	80105	76609	61731	52389	39079
70		39283	48663	54176	52307	80103	76644	61669	52360	39081
71		39291	48648	54154	52268	80092	76644	61646	52375	39057
72						80059	76703	61668	52360	39056
73						80065	76682	61638		39027
74						80086	76670	61628		39036
75						80067	76669	61625		39036
76						80072	76682	61611		39029
77						80056	76698	61620		39010
78						80049	76690	61615		39014
79						80036	76702	61615		39007
80						80023	76692	61788		39007
81						79999	76692	61794		39026
82						79999	76687	61778		39034
83						80000	76670	61780		39028
84						80002	76682	61768		39032
85						80001	76664	61793		39017
86						79990	76647	61797		39030
87						79981	76660	61786		39029
88						79984	76666	61816		39018
89						80018	76695	61809		39020
90						79999	76721	61839		39009
91						79985	76729	61837		39014
92						79985	76817	61850		39027
93							76789	61855		39030
94							76769	61813		39026
95								61765		38986

APPENDIX 2: Calculated volume change for every experiment

Table 4. Calculated volume change for every experiment. EQ1 was used for calculations.

T(h)	EX1	EX2	EX3	EX5	EX6	EX7	EX8	EX9	EX10	EX11
0	0,00%	11,57%	0,00%	0,00%	0,00%	0,00%	0,00%	0,00%	0,00%	10,73%
1	4,14%	9,48%	0,70%	1,84%	0,15%	5,44%	6,34%	1,91%	3,67%	9,45%
2	5,69%	8,42%	0,66%	2,29%	0,12%	8,06%	8,53%	2,54%	5,29%	8,65%
3	6,64%	7,60%	0,52%	2,67%	0,15%	9,93%	10,53%	2,90%	6,44%	7,96%
4	7,35%	6,97%	0,56%	2,95%	0,27%	11,58%	13,51%	3,21%	7,17%	7,54%
5	8,02%	6,43%	0,52%	3,16%	0,32%	12,85%	14,94%	3,43%	7,90%	7,29%
6	8,42%	6,10%	0,54%	3,26%	0,32%	14,06%	16,05%	3,58%	8,38%	7,02%
7	8,85%	5,74%	0,51%	3,32%	0,30%	15,19%	17,06%	3,63%	8,89%	6,82%
8	9,18%	5,41%	0,48%	3,46%	0,25%	16,20%	17,95%	3,82%	9,26%	6,46%
9	9,44%	5,08%	0,47%	3,51%	0,21%	17,15%	18,79%	3,93%	9,54%	6,22%
10	9,68%	4,83%	0,44%	3,53%	0,18%	18,03%	19,57%	4,09%	9,84%	6,07%
11	9,94%	4,61%	0,39%	3,66%	0,23%	18,91%	20,23%	4,16%	10,14%	5,91%
12	10,14%	4,36%	0,33%	3,67%	0,11%	19,64%	20,85%	4,24%	10,34%	5,83%
13	10,34%	4,12%	0,26%	3,66%	0,15%	20,27%	21,55%	4,27%	10,61%	5,68%
14	10,59%	3,87%	0,33%	3,73%	0,08%	21,09%	22,22%	4,29%	10,83%	5,59%
15	10,75%	3,69%	0,25%	3,71%	0,08%	21,68%	22,74%	4,42%	11,01%	5,49%
16	10,84%	3,43%	0,23%	3,79%	0,01%	22,31%	23,28%	4,44%	11,24%	5,29%
17	10,94%	3,24%	0,18%	3,79%	-0,04%	22,94%	23,79%	4,49%	11,34%	5,25%
18	11,10%	3,08%	0,19%	3,83%	-0,02%	23,41%	24,32%	4,54%	11,52%	5,13%
19	11,13%	2,95%	0,08%	3,80%	-0,03%	23,95%	24,72%	4,59%	11,59%	5,10%
20	11,21%	2,74%	0,04%	3,81%	-0,12%	24,46%	25,20%	4,61%	11,77%	5,02%
21	11,24%	2,67%	0,08%	3,87%	-0,24%	24,94%	25,55%	4,60%	11,82%	4,92%
22	11,23%	2,51%	0,03%	3,87%	-0,24%	25,44%	26,03%	4,66%	11,87%	4,84%
23	11,30%	2,35%	0,06%	3,85%	-0,21%	25,88%	26,43%	4,70%	11,95%	4,79%
24	11,37%	2,10%	0,04%	3,83%	-0,27%	26,33%	26,85%	4,71%	11,35%	4,62%
25	11,40%	1,88%	0,04%	3,82%	-0,21%	26,77%	27,22%	4,73%	11,94%	4,58%
26	11,48%	1,75%	-0,02%	3,83%	-0,20%	27,16%	27,56%	4,77%	12,10%	4,54%
27	11,56%	1,72%	0,02%	3,81%	-0,23%	27,41%	27,90%	4,80%	12,13%	4,52%
28	11,64%	1,50%	-0,06%	3,80%	-0,24%	27,76%	28,21%	4,80%	12,11%	4,46%
29	11,65%	1,43%	-0,07%	3,79%	-0,30%	27,98%	28,56%	4,83%	12,15%	4,37%
30	11,68%	1,44%	-0,02%	3,87%	-0,33%	28,23%	28,87%	4,82%	12,07%	4,32%
31	11,74%	1,25%	-0,06%	3,86%	-0,30%	28,48%	29,24%	4,88%	12,04%	4,21%
32	11,73%	1,21%	-0,07%	3,81%	-0,38%	28,73%	29,45%	4,88%	12,02%	4,30%
33	11,76%	1,14%	-0,03%	3,85%	-0,42%	28,95%	29,70%	4,85%	12,04%	4,19%
34	11,79%	1,04%	-0,14%	3,81%	-0,43%	29,11%	30,15%	4,86%	12,07%	4,15%
35	11,80%	0,99%	-0,15%	3,79%	-0,45%	29,32%	30,24%	4,85%	11,97%	4,18%
36	11,83%	0,85%	-0,13%	3,83%	-0,49%	29,51%	30,58%	4,84%	11,97%	4,13%
37	11,94%	0,79%	-0,18%	3,80%	-0,47%	29,65%	30,82%	4,82%	11,91%	4,12%
38	11,88%	0,74%	-0,19%	3,73%	-0,48%	29,84%	30,97%	4,83%	11,85%	4,12%
39	11,87%	0,64%	-0,22%	3,77%	-0,49%	29,89%	31,25%	4,79%	11,81%	4,08%
40	11,89%	0,62%	-0,26%	3,72%	-0,57%	30,01%	31,40%	4,81%	11,79%	4,03%
41	11,90%	0,54%	-0,14%	3,72%	-0,53%	30,14%	31,68%	4,80%	11,79%	4,04%
42	11,94%	0,48%	-0,28%	3,73%	-0,63%	30,22%	31,92%	4,76%	11,72%	4,01%
43	11,92%	0,66%	-0,32%	3,64%	-0,67%	30,37%	32,11%	4,81%	11,74%	4,00%
44	11,98%	0,46%	-0,32%	3,58%	-0,68%	30,39%	32,22%	4,71%	11,70%	4,02%
45	11,93%	0,35%	-0,37%	3,53%	-1,27%	30,52%	32,48%	4,74%	11,62%	3,97%
46	11,95%	0,29%	-0,38%	3,52%	-1,37%	30,58%	32,65%	4,75%	11,60%	3,97%
47	11,90%	0,27%	-0,44%	3,45%	-0,86%	30,57%	32,83%	4,73%	11,34%	3,96%
48	11,96%	0,24%	-0,45%	3,44%	-0,80%	30,66%	33,02%	4,76%	11,30%	3,88%
49	11,92%	0,22%	-0,44%	3,41%	-0,90%	30,73%	33,18%	4,71%	11,26%	3,86%
50	11,96%	0,12%	-0,49%	3,43%	-0,95%	30,84%	33,58%	4,73%	11,34%	3,84%
51	12,03%	0,19%	-0,50%	3,35%	-0,97%	30,86%	33,42%	4,67%	11,41%	3,87%

52	11,97%	0,21%	-0,47%	3,34%	-0,98%	30,91%	33,50%	4,66%	11,37%	3,86%
53	11,99%	0,22%	-0,51%	3,31%	-0,99%	30,93%	33,68%	4,68%	11,32%	3,89%
54	11,95%	0,18%	-0,48%	3,32%	-1,06%	30,94%	33,87%	4,64%	11,40%	3,85%
55	11,94%	0,14%	-0,55%	3,32%	-1,17%	30,98%	33,96%	4,66%	11,32%	3,82%
56	11,92%	0,07%	-0,58%	3,29%	-1,19%	31,03%	34,05%	4,69%	11,26%	3,83%
57	11,89%	0,04%	-0,61%	3,28%	-1,18%	31,08%	34,17%	4,70%	11,28%	3,86%
58	11,88%	0,00%	-0,59%	3,23%	-1,24%	31,10%	34,28%	4,67%	11,16%	3,87%
59	11,89%	-0,03%	-0,61%	3,22%	-1,23%	31,10%	34,40%	4,63%	11,11%	3,89%
60	11,87%	-0,06%	-0,64%	3,16%	-1,25%	31,15%	34,42%	4,63%	11,10%	3,87%
61	11,89%	-0,08%	-0,68%	3,18%	-1,31%	31,19%	34,50%	4,59%	11,10%	3,88%
62	11,85%	-0,18%	-0,67%	3,16%	-1,29%	31,11%	34,61%	4,52%	11,02%	3,92%
63	11,90%	-0,16%	-0,71%	3,15%	-1,33%	31,14%	34,69%	4,52%	11,03%	3,82%
64	11,87%	-0,21%	-0,71%	3,08%	-1,35%	31,20%	34,71%	4,53%	11,09%	3,87%
65	11,92%	-0,25%	-0,75%	3,04%	-0,94%	31,13%	34,77%	4,51%	11,00%	3,92%
66	11,92%	-0,26%	-0,71%	3,07%	-0,85%	31,12%	34,91%	4,44%	10,92%	3,82%
67	11,92%	-0,24%	-0,70%	3,03%	-0,91%	31,14%	34,94%	4,45%	10,89%	4,02%
68	11,84%	-0,21%	-0,75%	3,02%	-0,88%	31,05%	34,95%	4,44%	10,88%	3,84%
69	11,32%	-0,23%	-0,75%	2,85%	-1,03%	31,10%	35,07%	4,55%	10,82%	3,79%
70		-0,31%	-0,77%	2,80%	-0,98%	31,10%	35,16%	4,40%	10,73%	3,80%
71		-0,28%	-0,82%	2,73%	-1,09%	31,07%	35,16%	4,34%	10,78%	3,70%
72						30,99%	35,32%	4,39%	10,73%	3,70%
73						31,00%	35,26%	4,32%		3,59%
74						31,05%	35,23%	4,29%		3,62%
75						31,01%	35,23%	4,29%		3,62%
76						31,02%	35,26%	4,25%		3,59%
77						30,98%	35,30%	4,27%		3,52%
78						30,96%	35,28%	4,26%		3,53%
79						30,93%	35,31%	4,26%		3,51%
80						30,90%	35,29%	4,70%		3,51%
81						30,84%	35,29%	4,71%		3,58%
82						30,84%	35,27%	4,67%		3,61%
83						30,84%	35,23%	4,68%		3,59%
84						30,85%	35,26%	4,65%		3,60%
85						30,85%	35,21%	4,71%		3,55%
86						30,82%	35,17%	4,72%		3,60%
87						30,80%	35,20%	4,69%		3,59%
88						30,80%	35,22%	4,77%		3,55%
89						30,89%	35,29%	4,75%		3,56%
90						30,84%	35,36%	4,83%		3,51%
91						30,81%	35,38%	4,82%		3,53%
92						30,81%	35,62%	4,86%		3,59%
93							35,54%	4,87%		3,60%
94							35,49%	4,76%		3,58%
95								4,64%		3,42%