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E-Futures

Mini-project summary report

**How low can you go? Aviation fuel needs
to reduce its aromatic content - but by
how much?**

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Abstract: The stress relaxation behaviour of nitrile o-rings, immersed in a synthetic gas to liquid Fischer-Tropsch derived aviation fuel (GTL) blended with varying quantities of the synthetic aromatics toluene and naphthalene, was experimentally determined. The results were compared with the stress relaxation behaviour observed for nitrile o-rings in a pure GTL and a Jet A1 type fuel, so as to determine the effect both the concentration and type of aromatics has on the degree of stress relaxation. The degree of stress relaxation appeared dependent on both the concentration and hydrogen bond donor ability of the aromatics present in the fuel. But in all cases significantly more stress relaxation was observed with the GTL aromatic blends when compared to a Jet A1 type fuel. This further emphasizes current concerns as to the compatibility of nitrile o-rings and synthetic aviation fuels.

1. Background

Whilst aviation currently contributes around just 2% of the worlds carbon dioxide (CO₂) emissions, [1] the ever increasing demand for civilian and freight air travel means this figure is predicted to rise to 15-20% by 2050, should the use of traditional, petroleum sourced aviation fuels e.g. Jet A1, be maintained. [2]

Whilst carbon dioxide is generally perceived as the major environmental threat, it is not the only environmentally degrading pollutant produced as a result of aviation. The high temperatures generated within an aircrafts engine can lead to the formation of nitrogen oxides (NO_x) through the reaction of atmospheric nitrogen and oxygen. Whilst the combustion of other chemical species present in the fuel e.g. disulphides and heteroaromatics, can lead to the production of sulphur oxides (SO_x), unburnt hydrocarbons and particulates, all of which can have just as significant an impact on global warming. [3-5]

These environmental concerns combined with economic and socio-political aspects, such as the increased volatility in oil price and concerns over supply chain security, has led to an interest in jet fuel obtained from non petroleum sources. [6-7]

Alternative aviation fuels can be obtained from a wide range of sources; however the desire to have a “drop in” replacement i.e. an alternative fuel that requires no modification to current technology, aircraft operations and transport limits these options. As such a great deal of interest has focussed on the production of synthetic kerosene type aviation fuels using the Fischer-Tropsch (FT) process. One such example is that of a natural gas to liquid FT fuel (GTL).

Whilst such fuels have many advantageous properties over Jet A1 type fuels e.g. better thermal stability, cleaner combustion etc. They are

currently not approved for commercial use without individual approval and a minimum aromatic content of 8% volume. This is due to compatibility issues surrounding nitrile o-ring seals present in an aeroplanes jet engine/fuel system. This is generally believed to be due to the absence of aromatics and heteroatoms in a synthetic FT aviation fuel.

The current requirement of a minimum 8.0% volume of aromatics in any aviation fuel with a synthetic component, appears purely to be a value which is known to ensure adequate performance. [8] Whether this value represents the true limit for elastomer compatibility remains unknown. Since it is both uneconomical and detrimental to the environment to add aromatics to a synthetic FT aviation fuel, determining whether this is the limit is of great importance.

As such this study investigates the stress relaxation behaviour of nitrile o-rings immersed in variety of GTL aromatic blends and performs a comparison with that observed in a pure GTL and a Jet A1 type fuel. The aromatics of choice were toluene and naphthalene, both known to be present in Jet A1 type fuels.

2. Stress Relaxation

When a constant strain is applied to an elastomeric material, the force required to maintain the strain is not constant, it decreases over time. This phenomenon is known as stress relaxation. [9]

Stress relaxation tests can be performed in either tension (stretching the elastomer) or compression (squashing the elastomer) modes. In this study stress relaxation under compression was used as it is more representative of the conditions found in a jet engine. Further to this it also effectively allows the sealing force of nitrile o-rings immersed in different fuel blends to be measured. For this study, stress relaxation tests were performed using the Elastocon Relaxation Tester EB 02 (Figure 1).



Figure 1 – The Elastocon Stress Relaxation Tester EB02. [10]

3. Experimental

Fuel blends containing 2,4,6 and 8% toluene (volume %) or naphthalene (weight %) in GTL were prepared using standard laboratory glassware and stored in air tight, epoxy lined fuel drums cleaned in accordance with ASTM D4306. [11] Prior to testing the drums were vigorously shaken for ~1 minute to ensure the blend was fully mixed.

All stress relaxation tests were performed at the test temperature of $30 \pm 0.5^\circ\text{C}$. When the cell oven had reached the test temperature the Elastocon Relaxation Tester EB 02 rigs were removed, nitrile o-rings inserted between the two compression plates and held in place with a force of ~10N. These were then immersed in 150ml of the fuel blend and the rigs returned to the cell oven and allowed to re-equilibrate to the test temperature. When the test temperature was reached, the o-ring in each rig was compressed by 20% of its original dimensions and the data logging software activated.

For each rig, the temperature and counterforce required to maintain the deformation were logged at minutely intervals throughout the test using the Elastocon software package CombiLab. Tests were run for a minimum of 120 hours by which time the counterforce appeared in all cases to be decaying naturally. When a test was complete the o-rings were removed and stored in sealed glass jars containing the corresponding test fuels for any further analysis.

4. Results and Discussion

Baseline Tests

The stress relaxation profile for a nitrile o-ring with no fuel present was observed to have three stages;

Stage 1 (0-3hours) – An initial period where the counterforce required to maintain constant deformation decays rapidly.

Stage 2 (~3-40 hours) – An equilibrium period where the counterforce remains relatively constant.

Stage 3 (>40 hours) – A period of gradual counterforce decay observed to the end of the test.

Initial tests, performed with a pure GTL, a Jet A1 type fuel and with no fuel present, further emphasize why there are concerns regarding the use of nitrile o-rings with synthetic FT aviation fuels (Figure 2). For the o-ring immersed in pure GTL, stage 2 was observed to be much shorter than in the other scenarios and the decay process in stage 3 much faster. This can be attributed to the GTL fuel acting as a solvent and extracting any plasticizers or fillers present in the o-ring. This isn't observed with o-rings immersed in the Jet A1 type fuel, in fact an increase in the counterforce was actually observed during stage 2. This can be attributed to the aromatics present in a Jet A1 type fuel diffusing into the o-ring, replacing any extracted species and causing the o-ring to swell. Overall significantly more stress relaxation was observed with the GTL fuel indicating a weaker sealing force would likely be obtained.

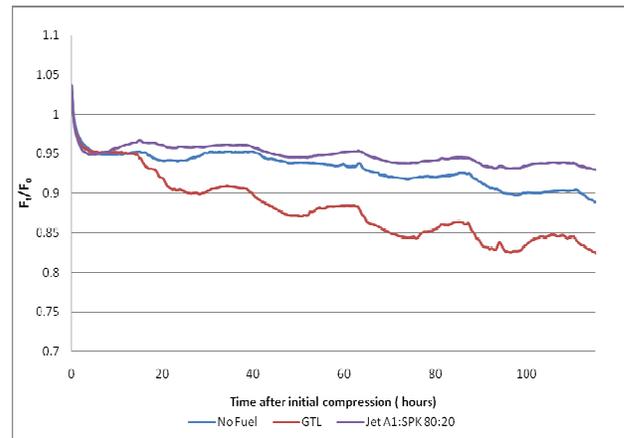


Figure 2 – Stress relaxation profile for nitrile o-rings in 100% GTL, Jet A1 SPK 80:20 and with no fuel.

GTL Aromatic Blends

The addition of the mono-cyclic aromatic, toluene, in concentrations of up to 8% volume, appeared to have no major effect on the stress relaxation behaviour of nitrile o-rings immersed in GTL. The equilibrium period (stage 2) remained short and the decay process in stage 3 fairly rapid in comparison to the Jet A1 type fuel. There was also no significant increase in the counterforce observed during stage 2, indicating the addition of toluene imparted minimal swelling of the o-ring.

In contrast, the addition of the di-cyclic aromatic naphthalene, at concentrations >2% weight, did affect the stress relaxation behaviour of nitrile o-rings immersed in GTL. Above this concentration the equilibrium period was observed to last much longer, ~3-40 hours, equivalent to that observed with the Jet A1 type fuel. Further to this a significant increase in the counterforce was observed in stage 2 indicating the

addition of naphthalene imparted a significant degree of swell on the nitrile o-rings. However the decay process in stage 3 remained much more rapid than that observed with the Jet A1 type fuel and as such the percent stress relaxation that occurred over the duration of the test (R_{120}) was greater, indicating a weaker sealing force would still be obtained (Table 1).

Table 1 – Percent stress relaxation of GTL aromatic blends and Jet A1:SPK^a 80:20.

Fuel Composition	Toluene	Naphthalene
	R_{120}	R_{120}
GTL	19.11	19.11
GTL 2% aromatic	16.74	15.88
GTL 4% aromatic	16.54	13.25
GTL 6% aromatic	19.17 ^b	10.88
GTL 8% aromatic	18.48 ^b	10.29 ^b
Jet A1:SPK 80:20	7.61	7.18

a – Tallow derived synthetic paraffinic kerosene.

b – Tests performed as part of different run and therefore potentially exposed to fuel for a longer period of time before initial compression, effect of the test method.

These results tend to suggest that as the aromatic content of the fuel is increased the percent stress relaxation generally decreases. This appears logical as a higher aromatic content will favour the diffusion of aromatic molecules into the o-ring, resulting in increased swell and less stress relaxation i.e. a better sealing force. It is also clearly evident that the addition of naphthalene imparts significantly more swell on the o-ring than toluene. This suggests naphthalene diffuses more favourably into the o-ring. As naphthalene has a larger molar volume than toluene this can only be attributed to a specific interaction with the nitrile polymer. Yamada et al.[12] suggest the most likely/theoretically favourable interaction is a hydrogen bond between the sp^2 C-H of the aromatic and the $C\equiv N$ of the nitrile polymer. Naphthalene is more highly aromatic than toluene and therefore its hydrogen bond donor ability is greater, hence naphthalene interacts more strongly with the nitrile polymer and its diffusion into the o-ring is more favourable.

5. Conclusions

The application of stress relaxation tests in compression mode provides a more realistic means of assessing the compatibility of elastomer o-rings with differing fuel compositions. The work performed in this study confirms why there is significant concern regarding the compatibility of nitrile o-rings and synthetic Fischer-Tropsch derived aviation fuels such as GTL. The degree of stress relaxation observed for nitrile o-rings in a GTL fuel was considerably larger than that observed in a Jet A1 type fuel. This implies the sealing force imparted by nitrile o-rings would be

significantly less if a GTL fuel was to replace traditional petroleum derived kerosene.

It cannot be concluded from this study alone as to whether the current limit, of a minimum 8% volume aromatics in any aviation fuel with a synthetic component, represents the true limit. It does however provide some evidence to suggest this may not be the case. Whilst results indicate the degree of stress relaxation observed with nitrile o-rings generally decreases with increasing aromatic content of the fuel. It also highlights the stress relaxation behaviour of nitrile o-rings is dependent on the specific type of aromatics present. Whilst the addition of toluene had little effect on the stress relaxation behaviour of nitrile o-rings immersed in GTL, the presence of naphthalene at concentrations >2% weight resulted in stress relaxation behaviour more comparable to that observed with a Jet A1 type fuel. On this basis it can be concluded that the strength of the interaction between the polymer and the aromatic is of more importance than the molar volume, with regards to the uptake of aromatics by the o-ring. As such any potential additive should be good hydrogen bond donor. This suggests that it may not purely be the aromatic content of traditional petroleum derived jet fuels which provide their compatibility with nitrile o-rings. It could in fact be due to a combination of the aromatics, polar species and heteroaromatics typically found in a petroleum derived jet fuel.

6. Future Work

As such, any future work in the area should focus on identifying species which are likely to interact strongly with the nitrile polymer at a molecular level. A starting point would be to identify such species present in a Jet A1 type fuel or alternatively Sasol Synfuels approved fully synthetic jet fuel. A survey of the literature suggests polar aromatics such as phenols or benzyl alcohol in particular may make good additives.

7. References

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