

**CRC Report AV-10-09**

**JET FUEL “AROMATICS EFFECTS” AND  
“DISTILLATION SLOPE” RESEARCH  
SURVEY**

**FINAL REPORT**

**April 2012**



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## **FINAL REPORT**

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# **JET FUEL “AROMATICS EFFECTS” AND “DISTILLATION SLOPE” RESEARCH SURVEY**

## **EXECUTIVE SUMMARY**

A 2-year review has been made of current and recent research programs studying the fuel effects on elastomer performance and marginal combustion. The review sought to determine if these programs are addressing two major issues that are very important to the definition and approval of synthetic kerosenes for use as jet fuel:

- The need for a minimum aromatic content and what that minimum should be
- The need for constraints on the boiling point distribution

Ten programs were identified relating fuel aromatics to fuel-system elastomers performance. Most of these projects focused on conducting standard property tests to demonstrate that representative elastomers are compatible with synthetic kerosenes. No issues were identified, which is hardly surprising since the materials were formulated to be compatible with hydrocarbons in the kerosene boiling range. None of the completed projects have directly addressed the question of a minimum aromatic content. One new project sponsored by the US Air Force appears to address the question by working with aged elastomers that have taken compression set. Two other projects under the FAA/CLEEN program which have not yet started have objectives of determining minimum aromatic content.

One system that has not been adequately addressed is fuel composition effects on the performance of self-sealing fuel bladders. Two completed projects have been inconclusive. Details of a third project, which may have been successful, have not been made available.

A literature search on combustion yielded a large number of papers on ignition and LBO. The majority of these studies focused on combustor design effects. Very few previous studies have focused on fuel effects; most of those that did compared widely disparate fuels, e.g., JP-4 vs. JP-8 vs. diesel fuel. None of them investigated chemistry effects. Seven current or recent projects were identified and reviewed. The three completed combustion studies to evaluate fuel effects on ignition and lean blow-out (LBO) have provided relevant results that show consistency but are as yet incomplete. The combustion systems have represented both older and advanced-concept combustion systems. The results to date have shown that fuel chemistry and slope of the boiling point distribution are not significant factors compared to front-end volatility. Projects planned to be conducted in 2012 and 2013 show promise to providing definitive answers to this issue.

Future efforts should focus on volatility to determine the need for a control.

## **1. OBJECTIVE**

The overall objective of this project was to survey and review previous and current research programs that address the following two topics of importance to the approval process for emerging aviation fuels:

1. The effect of fuel aromatics on the performance of elastomeric seals and gaskets.
2. The effect of boiling-point distribution and chemistry on marginal combustion issues such as ignition, lean stability limits, and altitude relight.

The purpose was to evaluate these programs for appropriateness and completeness to answer the following two questions, respectively:

1. Are aromatics needed in jet fuel for seal and gasket performance in aircraft fuel systems, and if needed, what is the minimum aromatic requirement? A related question is whether other hydrocarbons, such as cyclo-paraffins, or additives can be used to provide the required performance?
2. Will fuels with relatively flat distillation curves or relatively heavy concentrations of specific hydrocarbon families in the more volatile fractions of the fuel adversely affect limits of ignition and lean extinction for combustion in gas turbine engines? To this end, are limits needed on the slope of the boiling point distribution and/or special limits on composition?

## **2. SCOPE**

The scope of this survey focused on current research on the two topics. Previous research projects were looked at but none were found that addressed the questions identified above.

Previous research on aromatics and elastomers was conducted in the early 1980's at UDRI by the U.S. Air Force while considering jet fuels from shale oil and in support of the JP-4 to JP-8 conversion. About the same time, similar studies were conducted by Southwest Research Institute, SwRI, for the U.S. Navy in the early 1980s under the direction of this author looking the potential problems of using diesel fuel in Navy aircraft to extend fuel supplies. Neither of these two studies addressed the issue of minimum aromatic content. More recently, there was a workshop moderated by Roger Organ on aromatics at the ASTM Aviation Fuels subcommittee meeting in December 1998; the workshop concluded there was insufficient data available to address the question of minimum aromatics.

With respect to combustion issues, the following resources were searched for relevant papers and reports on effects of jet fuel properties on ignition and lean blowout (LBO):

- AGARD reports
- Air Force reports
- AIAA Journal
- ASME Transactions
- ASME Journal of Energy for Gas Turbines and Power
- ASME Turbo-Expo conference papers
- Combustion and Flame
- Energy & Fuels
- NASA reports

- Navy reports
- Proc. Energy and Combustion Science
- Proceedings of the Combustion Institute

While there are a number of papers in the literature on ignition and LBO, the majority focus on combustor design effects such as atomization, fuel-air ratio, spark energy, velocity, etc. Very few studies focus on fuel effects; none of them investigated chemistry effects. A NASA study compared widely different fuels such as JP-4, Jet A, and diesel fuel. An Air Force program in the early 1980's included six JP-8s of different composition evaluated in a number of engine combustors. The Navy conducted a similar study with JP-5s.

These studies provided useful information on fuel effects on combustion, but were not parametric studies on boiling point distribution or composition. The general consensus of these studies was that atomization is more important than volatility, but this is not unanimous.

Due to the lack of relevant research in the past, this report focuses on current research projects.

### **3. APPROACH**

Initially the principal investigators (PI) of the known relevant research programs were contacted and informed of this survey and the information desired. The following questions were asked to initiate the survey:

1. Objectives
2. Scope
3. Approach
4. Test hardware
5. Matrix of test fuels
6. Status
7. Anticipated results
8. Anticipated completion

Based on the responses, a preliminary evaluation of each project was made as to its relevance to the Objectives stated in Section 1, and follow-up email exchanges were held with the PI to clarify any issues.

The projects were summarized in monthly progress reports as information became available. In hindsight, quarterly progress reports would have been more practical as there was rarely sufficient progress to report on a monthly basis.

This project was originally planned for a one-year effort. However, at the end of the first year, many of the identified projects had not been completed or, if completed, the final reports had not been approved for release. An interim report was submitted at the end of the first year with a request for a one-year, no-cost extension which was granted.

#### 4. PROJECTS IDENTIFIED

The projects identified that were addressing fuel effects on elastomeric materials are identified in Table 1. Similarly, the projects identified on fuel effects on combustion are identified in Table 2.

**Table 1. Projects on Fuel Effects on Elastomers**

| Project No. | Research Facility and Location                 | Sponsor              |
|-------------|------------------------------------------------|----------------------|
| F/E-1.      | Univ. of Dayton Research Institute, Dayton, OH | FAA/Boeing           |
| F/E-2.      | UDRI, Dayton, OH                               | US Air Force         |
| F/E-3.      | UDRI, Dayton, OH                               | USAF                 |
| F/E-4.      | US Army, Ft Eustis VA                          | USAF                 |
| F/E-5.      | US Navy, Pax River, MD                         | US Navy              |
| F/E-6.      | UDRI, Dayton, OH                               | Boeing               |
| F/E-7.      | Univ. of Cape Town, Cape Town, South Africa    | Sasol                |
| F/E-8.      | Univ. of Sheffield, Sheffield, UK              | FAA/Rolls-Royce & BA |
| F/E-9.      | Southwest Research Institute, San Antonio, TX  | US Army              |
| F/E-10.     | Honeywell, Phoenix, AZ                         | FAA/Honeywell        |

**Table 2. Projects on Fuel Effects on Combustion**

| Project No. | Research Facility and Location        | Sponsor                  |
|-------------|---------------------------------------|--------------------------|
| F/C-1.      | Univ. of Cape Town, South Africa      | Sasol                    |
| F/C-2.      | DLR <sup>1</sup> , Stuttgart, Germany | Sasol                    |
| F/C-3.      | Univ. of Sheffield, UK                | Shell                    |
| F/C-4.      | DLR <sup>1</sup> , Stuttgart, Germany | Shell, QSTP <sup>2</sup> |
| F/C-5.      | DLR <sup>1</sup> , Stuttgart, Germany | various                  |
| F/C-6.      | Honeywell, Phoenix, AZ                | FAA/Honeywell            |

Notes: 1. Institute for Combustion Technology of the German Aerospace Center

2. Qatar Science & Technology Park

#### 5. Project Summaries – Fuel Effects on Elastomeric Materials

The projects are summarized individually by their project number in Table 1.

##### **F/E-1.**

This project at UDRI was funded by Boeing as part of the FAA CLEEN program. The Principal Investigator was Dr. John Graham. The project is finished and a final report has been issued. [Ref.: Graham, John L., et al, Final Task Report on “Impact of SPK Fuels and Fuel Blends on Non-metallic Materials used in Commercial Aircraft Fuel Systems”, FAA OTA DTFAWA-10-C-0030 – Continuous Lower Energy, Emissions and Noise (CLEEN) Program, July 29, 2011.]

The objective of this study was to examine the overall effect of SPK and SPK fuel blends on non-metallic materials used in commercial aircraft fuel systems. The primary measure of performance was the volume swell of dry source materials immersed in fuel for 40 hours at room

temperature. Table 3 lists the materials evaluated, while Table 4 lists the primary test fuels and their aromatic content.

The four SPKs were tested both as neat fuels, i.e., 100%, and as 50/50 blends with one of the Jet A-1s. In addition, an evaluation was made of the effect of specific aromatic type by blending each of 10 different aromatics into one of the SPKs. The aromatics are listed in Table 5. They were selected to represent long-chain alkyl groups (1-3), short-chain methyl groups (4-6), cycloaromatics (one of which has an olefinic bond) (7-9), and a two-ring aromatic (10). The single-ring aromatics were blended to 8% and the naphthalene and methylindene were blended at 3% because they would not normally be present in jet fuel at higher concentrations. These fuels were selected to provide some fundamental metrics to describe the nature of the aromatics in addition to simply the aromatic content of the fuel, i.e., hydrogen bonding, molar volume, and polarity.

**Table 3. Test Materials**

| Component | Material                     |
|-----------|------------------------------|
| O-Rings   | Nitrile                      |
|           | Extracted nitrile*           |
|           | Fluorosilicone               |
|           | Low-temperature Fluorocarbon |
| Sealants  | Light-weight polysulfide     |
|           | Polythioether                |
| Coatings  | Epoxy(1)                     |
|           | Epoxy(2)                     |
| Films     | Nylon                        |
|           | Kaptan                       |

\* plasticizer extracted

**Table 4. Primary Test Fuels**

| #  | Fuel                | Aromatics, % | Naphthalenes, % |
|----|---------------------|--------------|-----------------|
| 1  | Jet A-1             | 8.7          | 0.2             |
| 2  |                     | 15.0         | 1.9             |
| 3  |                     | 15.5         | 0.2             |
| 4  |                     | 17.6         | 2.5             |
| 5  |                     | 17.6         | 1.4             |
| 6  |                     | 17.7         | 1.3             |
| 7  |                     | 17.7         | 1.3             |
| 8  |                     | 17.9         | 0.6             |
| 9  |                     | 18.1         | 0.6             |
| 10 |                     | 19.6         | 0.4             |
| 11 |                     | 19.9         | 1.4             |
| 12 |                     | 23.1         | 1.1             |
| 13 | Jatropha SPK (Jat)  | 0.0          | 0.0             |
| 14 | Camelina SPK (Cam)  | 0.0          | 0.0             |
| 15 | Jat/Cam/Algae blend | 0.0          | 0.0             |
| 16 | Bio-oil derived SPK | 0.0          | 0.0             |

**Table 5. Aromatics Evaluated**

| #  | Aromatic Hydrocarbon   | Carbon Number |
|----|------------------------|---------------|
| 1  | Propylbenzene          | 9             |
| 2  | Butylbenzene           | 10            |
| 3  | Pentabenzene           | 11            |
| 4  | 1,3,5-Trimethylbenzene | 9             |
| 5  | 1,2,4-Trimethylbenzene | 9             |
| 6  | 1,2,3-Trimethylbenzene | 9             |
| 7  | Tetralin               | 10            |
| 8  | Indan                  | 10            |
| 9  | Methylindene           | 10            |
| 10 | Naphthalene            | 10            |

As expected, the nitrile materials were the most sensitive to the aromatic content, swelling about 5.5 to 7% for a 10% increase in aromatic content. The two seals increased about 1 to 1.5% for a

10% increase in aromatic content. The other materials were relatively unaffected. The study of aromatic type showed that the volume swell of the nitriles was more sensitive to hydrogen bonding of the three metrics, and thus to lower molecular-weight materials among the single-ring aromatics, i.e., No's 4-6.

The results also showed that the 50/50 blends of the SPK with Jet A-1 produced sufficient swell to perform like the low-aromatic Jet A-1, confirming the minimum aromatic limit in D7566 is sufficient.

Author's comment: This study did not directly address the question that this CRC study is focusing on, namely whether a minimum aromatic limit is necessary and, if so, can it be lower than 8%. The information and the molecular metrics could be useful to address the question of adding aromatics synthesized from renewable sources.

#### **F/E-2.**

This project at UDRI was funded by the US Air Force. The Principal Investigator was Dr. John Graham. The project is finished and a poster paper was presented at the 2011 IASH meeting in Sarasota, FL. [Ref.: Graham, John L., et al, "The Effect of Aromatic Type on the Volume Swell of Nitrile Rubber in Selected Synthetic Paraffinic Kerosenes", 12th International Conference on Stability, Handling, and Use of Liquid Fuels, Sarasota, Florida USA, 16-20 October 2011.]

This project was very similar to that of F/E-1 except that the focus was only on nitrile O-rings and the reference fuels were JP-8s rather than commercial Jet As. Table 6 lists the basic test fuels and Table 7 lists the aromatic materials that were evaluated. Note that the benzene and toluene are not in the jet fuel boiling range and only very limited amounts of ethylbenzene and styrene could be present due to flash point considerations.

The stated objective of this study was to identify the most effective aromatics to add to SPKs to provide satisfactory swell of elastomeric seals. The study focused on the volume swell of nitrile O-rings using 7 reference JP-8s, 4 SPKs, and 11 different aromatic compounds. As with F/E-1, the primary metrics to represent fuel properties for their performance as swelling promoters were molar volume, polarity, and hydrogen bonding. Naphthalenes are also limited to 3.0%, and their presence is really not desirable.

Basically the results of this study showed that lower molecular weight aromatics are more effective at creating swell in nitrile materials. However, the most effective materials are not within the jet fuel boiling range; within the jet fuel boiling range the options for choice are rather limited.

Author's comment: This study complements F/E-1 by using different base fuels and aromatic additive while focusing only on nitrile O-rings, which were shown to be the most sensitive. It did not directly address the question that this CRC study is focusing on, namely whether a minimum aromatic limit is necessary and, if so, can it be lower than 8%. The information and the molecular metrics could be useful to address the question of adding aromatics synthesized from renewable sources.

**Table 6. Test Fuels**

| #  | Fuel             | Aromatic Content |
|----|------------------|------------------|
| 1  | JP-8             | 23.6             |
| 2  |                  | 15.9             |
| 3  |                  | 20.3             |
| 4  |                  | 16.9             |
| 5  |                  | 18.8             |
| 6  |                  | 10.9             |
| 7  | CTL SPK*         | 0                |
| 8  | Camelina SPK*    | 0                |
| 9  | GTL SPK*         | 0                |
| 10 | Beef Tallow SPK* | 0                |

\* Contained JP-8 additives

**Table 7. Aromatics Tested**

| #  | Aromatic Hydrocarbon   | Carbon Number |
|----|------------------------|---------------|
| 1  | Benzene                | 6             |
| 2  | Toluene                | 7             |
| 3  | Ethylbenzene           | 8             |
| 4  | Styrene                | 8             |
| 5  | Propylbenzene          | 9             |
| 6  | Butylbenzene           | 10            |
| 7  | Pentabenzene           | 11            |
| 8  | 1,2,3-Trimethylbenzene | 9             |
| 9  | 1,2,4-Trimethylbenzene | 9             |
| 10 | 1,3,5-Trimethylbenzene | 9             |
| 11 | Naphthalene            | 10            |

**F/E-3.**

This project at UDRI was funded by the US Air Force. The Principal Investigator was Dr. John Graham. A follow-on phase to this study is planned.

The primary objective of this study is to evaluate fuel compositional effects on aged elastomers. In order to do this, a standard way of aging O-rings had to be developed, that has the objective of the work that has just been completed. This was accomplished by using fuel-line couplings that contain O-ring seals and creating a plumbing system that could be placed in an environmental chamber that can be heated to 180°F in a heated oven to accelerate the aging, or chilled to -55°F to promote leakage. There are 48 couplings in the plumbing system. The investigators believe they have succeeded in developing the standard method for aging and are now in the process of conducting tests.

While developing the test protocol, nitrile and fluorosilicone O-rings were exposed to flowing fuel at 180°F for 2,4,6, and 8 weeks. The properties were then compared to similar O-rings soaked in the same fuel at ambient conditions for 8 weeks and dry materials. The condition of the O-rings was primarily monitored by measuring their volume swell, modulus (E), glass transition temperature (Tg), compression and compression set. As expected, the changes were greater with the nitrile O-rings. Also, the greatest change in the physical properties of the O-rings occurred during the initial exposure to fuel, and the prolonged exposure to 180°F had little effect on the extent of cure or the molecular structure of the polymeric materials.

Exposure time did, however, have an effect on compression and compression set. By the end of the exposure period the nitrile rubber O-rings exhibited an average of 33% compression set while the fluorosilicone O-rings showed an average of 27% compression set, indicating that the average sealing pressure of both types of O-rings declined by approximately 1/3rd during the course of the conditioning test. These results suggest that this approach may be a very promising way to determine the minimum aromatic requirement.

Phase I of the project has been completed, and an internal test report has been written, but not yet released. A second phase of the project is planned to look at the effect of fuel switch loading.

Author's comment: This first phase of the project has laid the groundwork for a continuation that could address the question of the minimum aromatic requirement since the question is driven by potential effects on aged elastomers that have taken plastic or compression set.

**F/E-4.**

This project was conducted at an Army test facility by a self-sealing bladder manufacturer and funded by the US Air Force, but in this project the objective was to evaluate the effect of SPKs on self-sealing fuel bladders using live fire tests. This project was completed in 2010, but a report has not been issued. The results were inconclusive due to variations in the way the rounds hit the test volume.

Author's comment: This could be an important subject since the mechanism or action and the relation to fuel composition could be fundamentally different than the swell of O-rings. Thus, the need for a minimum aromatic content could depend upon self-sealing fuel bladders rather than O-rings and seals. Continuation of this evaluation is considered important. Although self-sealing fuel bladders are not used in commercial aircraft, there is a desire for harmony among the specifications. Also, the Air Force is looking at converting to commercial Jet A. Therefore, it is considered likely that the same aromatic standard would be used in both commercial and military jet fuels.

**F/E-5.**

The US Navy has also conducted live-fire tests on self-sealing fuel bladders. Rick Kamin was the point of contact. Like the Air Force tests identified in F/E-4, the results were inconclusive due to the test variability, and no report has been issued.

Author's comment: It appears that a laboratory test needs to be developed that can evaluate the effects of fuels on the mechanism of self-sealing bladders. Hopefully, information will be obtained from F/E-6 that will address this need.

**F/E-6.**

This project was conducted at UDRI for Boeing St. Louis. Dr. John Graham was the Principal Investigator. This project also focused on self-sealing fuel bladders, but used laboratory tests instead of live-fire tests. The project has been completed. However, no report has been issued and information from Boeing about the results was not available at the time of this writing.

Author's comment: In light of the failure of live-fire tests to address the question of fuel effects on self-sealing bladders, information on the results of this project are considered important, and hopefully will become available in the near future.

**F/E-7.**

This project is being conducted in the Sasol Advanced Fuels Laboratory at the University of Cape Town (UCT), South Africa; it is sponsored by Sasol Technology. The objective is to study the effects of fuel chemistry on O-ring properties and to identify additives that could be used to provide swell in O-rings when using SPKs. This study is ongoing. The Principal Investigator is Dr. Chris Woolard. A Masters Thesis will result from this work, but the document has not been completed at the time of this writing.

The research was conducted using standard ASTM D471 seal swell methods as well as using an elastomer compression rig that was designed and built at UCT. Experiments were conducted on both new and conditioned nitrile O-ring samples; conditioning was accomplished by de-plasticizing the material to simulate aging. The test fuels included petroleum derived Jet A-1, two Fischer Tropsch derived synthetic kerosenes, and pure compounds including isomers of various paraffins, aromatics, and oxygenates. Table 8 provides a summary of the test fuels. The change in mass and volume measurements of the O-rings were used as metrics; the mass change was found to be more repeatable, it was noted that it does not take into account the varying density of the fuel/solvent. The basic approach was to compare the mass change with that of the reference Jet A-1 to evaluate the various concepts.

The results showed that different aromatics produced different amounts of change when added to a paraffinic kerosene at 8%, with aromatics of lower molecular weight producing more change. This has been shown several times by other investigators including F/E-1 and F/E-2 reported above.

**Table 8. Test Fuels, Solvents, and Additives Used in UCT Study**

| #  | Fuel, Solvents, and Additives | Carbon No. |
|----|-------------------------------|------------|
| 1  | Jet A-1                       | -          |
| 2  | Syntroleum R-8                | -          |
| 3  | Sasol IPK                     | -          |
| 4  | Toluene                       | 7          |
| 5  | Xylene                        | 8          |
| 6  | Mesitylene                    | 9          |
| 7  | Cumene                        | 9          |
| 8  | Naphthalene                   | 10         |
| 9  | Anisole                       | 7          |
| 10 | Benzyl alcohol                | 7          |
| 11 | Benzyl methyl ether           | 8          |
| 12 | Dibenzyl ether                | 14         |
| 13 | DIEGME                        | 5          |

The study also looked at using oxygenated solvents such as benzyl ether and benzyl alcohol as additives to produce seal swell. Benzyl alcohol in the range of 0.5 to 1.0% was sufficient to produce swell similar to Jet A-1. 4% of benzyl ether was found to provide both the same swell and density as 8% aromatics. However, the effects of benzyl alcohol varied with temperature of the experiment. At 23°C, 0.5% benzyl alcohol produced more swell than Jet A-1, but at 50°C, it produced much less. This result has questioned the possible use of benzyl alcohol as a fuel blend and therefore contradicting a number of previous studies.

Author's comment: This study did not address the critical issue of providing technical evidence for a minimum aromatic content in jet fuel. It did demonstrate that aromatics and certain oxygenated solvents could be added to SPK to generate seal swell in nitrile elastomers. At low concentrations, the oxygen content of the final mix might be low enough to be acceptable.

**F/E-8.**

This project is being conducted at the University of Sheffield, UK; it is sponsored by Rolls-Royce and British Airways under a program under the FAA/CLEEN program. The program manager at Rolls-Royce is Chris Lewis.

The objective of the project is to study the effects of alternative jet fuels on O-rings under compression:

- when the fuel is cycled, i.e., switch-loading
- high-life nitrile seals in legacy aircraft

Two different tests are available to the project: continuous compression/stress-relaxation tests and a more simple seal-leakage test. These tests can be conducted with flowing fuel at elevated temperatures (180°C at 500 psi) or ambient temperature; sub-ambient temperature capabilities are being developed. The advantage is that these are seal performance tests as opposed to elastomer property or compatibility tests.

No information on results was made available as the project is proprietary but will be reported when completed under the FAA/CLEEN program.

Author's comment: The concept of "performance tests" rather than fuel compatibility tests appears to have a better chance at addressing the questions of using fuel with low aromatics and is in line with the approach currently being taken at UDRI as discussed in F/E-3. Both are using aged elastomers.

**F/E-9.**

This project is being conducted in the US Army TARDEC Fuels and Lubricants Facility at SwRI for the US Air Force. The Principal Investigator is Dr. Nigil Jeyashekar.

This project differs from the other projects in that it employs a dynamic test rig whereas all the others are static immersions followed by property tests. The rig uses axial motion of a polished stainless steel rod through two O-rings. The surrounding housing is heated to a control temperature, which can be as high as 300F. The test fuel is located in a cavity between the two O-rings and pressurized to 80 psig. Fuel that leaks past the O-ring seals is collected in a vial; a photoelectric sensor is incorporated to stop the test after a certain volume of leaked fuel is collected in either of the vials. Failure criterion is defined as the time to collect a certain amount of fuel in either one of the vials.

Another feature of the test rig is that the test fuel can be switched while the test is running. Two pressurized fuel reservoirs are used, and valves and drains are used to flush and change the test fuel. The scope of the project calls for testing Syntroleum R-8 (from animal fat) and two HRJ fuels plus blends of each with the baseline JP-8. At the present there is no intent to look at varying aromatic content to address the question of minimum aromatic content.

This project just started recently, and only preliminary data are available on JP-8 and R-8; no data is available on HRJ, blends, or switch-loading. The data available shows a marked

reduction in O-ring “life” for R-8 as compared to JP-8 for both Buna-N and Viton O-rings. Fluorosilicone O-rings are also being tested and have shown much shorter life than the other two materials, which supports the reason why fluorosilicone O-rings are not used in dynamic applications.

This project is scheduled to finish November 30, 2012.

Author’s comment: It is too early to comment on this program. The ability to switch-load is a desirable capability; hopefully the investigator will be able to conduct parametric studies on aromatic content. It is not clear why fluorosilicone O-rings are being tested since they are not suitable for dynamic situations; perhaps that testing could be dropped in favor of parametric testing of aromatic content.

#### **F/E-10.**

This project is a part of Honeywell’s effort under the FAA/CLEEN program. Randy Williams is the Principal Investigator. This is a new project which has just recently been initiated so there are no results to report.

There are two main objectives:

- to determine a minimum aromatic limit, and
- to determine compatibility with fully renewable fuels, i.e., containing aromatics from renewable sources.

The initial fuel matrix will be a HEFA SPK doped with varying concentrations of petroleum-derived aromatics blended to match the composition of synthetic aromatics. Later testing will use the synthetic aromatics in varying concentrations in the HEFA SPK. The initial testing will use standard elastomer-fuel compatibility tests.

The testing is scheduled to start later this year after the test plan is finalized and a test site identified.

Author’s comment: It is too early to comment on this project. It does have a stated objective of addressing the minimum aromatic questions, but it is not clear how this will be accomplished using compatibility tests.

## **6. Project Summaries – Fuel Effects on Combustion**

#### **F/C-1.**

This combustion project was conducted in the Sasol Advanced Fuels Laboratory at the University of Cape Town in Cape Town South Africa; it was sponsored by Sasol Technology. The Principal Investigator was Dr. Andy Yates. It resulted in a Masters Thesis for Victor Burger. A technical paper on this research has been submitted to the 2012 ASME Turbo-Expo meeting.[Ref. Victor Burger et al, “Influence of Fuel Physical Properties and Reaction Rate on Threshold Gas Turbine Combustion”, ASME Paper GT2012-68153.]

This experimental research study investigated the relative influence of fuel evaporation rate and chemical reaction characteristics on lean blowout (LBO) limits in a gas turbine combustor. The test fuel matrix consisted of 17 fuels comprised of conventional and synthetic Jet A-1, synthetic iso-paraffinic kerosene, linear paraffinic solvents, aromatic solvents, and pure compounds. Pertinent properties and characteristics are summarized in Table 9. The matrix was designed to have high- and low-temperature boiling ranges, each with high and low flash points. Solvents were used to stress all four hydrocarbon families in the volatile fraction: n-paraffins, iso-paraffins, cyclo-paraffins, and aromatics. Also, the slope of the boiling point distribution was varied from typical to very flat. The distillation profiles were used as metrics for evaporation characteristics. Laminar flame speed and ignition delay were used to characterize the chemical reaction characteristics of the test fuels.

The combustor was an in-house simulation of the primary zone of a T63 combustor. (Secondary and dilution zones were eliminated to reduce the air-flow requirements.) Experiments were conducted at constant combustor pressure drop, i.e., air flow rate, across the fuel matrix to eliminate mixing rates as a factor in the results; overall, tests were conducted at six different pressure drops defining regimes in which LBO was evaporation/mixing limited and reaction rate limited. Laser diffraction methods were used to measure the atomization characteristics.

Table 10 summarizes the correlation coefficients for LBO with the various fuel properties and characteristics; the judgments on the correlations are those of the investigators.

**Table 9. Fuel matrix for Combustion Tests at UCT**

| #  | Description             | Blend Material | Flash Point °C | T <sub>10</sub> °C | T <sub>50</sub> °C | T <sub>50</sub> - T <sub>10</sub> , °C | T <sub>90</sub> - T <sub>10</sub> °C | Viscosity cSt | Density kg/l |
|----|-------------------------|----------------|----------------|--------------------|--------------------|----------------------------------------|--------------------------------------|---------------|--------------|
| 1  | Jet A-1 (petroleum)     | Clear          | 54.5           | 175.5              | 197.3              | 21.8                                   | 51.1                                 | 1.29          | 0.80         |
| 2  | Jet A-1                 | Dodecane       | 65.0           | 191.0              | 205.4              | 14.4                                   | 25.1                                 | 1.40          | 0.78         |
| 3  | Jet A-1                 | Clear          | 38.0           | 174.2              | 197.2              | 23.0                                   | 51.9                                 | 1.28          | 0.80         |
| 4  | Jet A-1                 | Dodecane       | 39.0           | 185.4              | 205.1              | 19.7                                   | 31.1                                 | 1.35          | 0.77         |
| 5  | FSJF (commercial)       | Clear          | 57.0           | 175.3              | 196.8              | 21.5                                   | 67.7                                 | 1.60          | 0.81         |
| 6  | FSJF                    | Clear          | 38.0           | 171.5              | 195.6              | 24.1                                   | 71.1                                 | 1.48          | 0.81         |
| 7  | FSJF                    | Decane         | 39.0           | 167.7              | 177.5              | 9.8                                    | 59.6                                 | 1.18          | 0.77         |
| 8  | Iso-Paraffinic Kerosene | Clear          | 55.0           | 175.3              | 182.2              | 6.9                                    | 29.7                                 | 1.26          | 0.76         |
| 9  | Iso-Paraffinic Kerosene | C9-C11 n-par   | 44.5           | 162.2              | 172.2              | 10.0                                   | 32.9                                 | 1.05          | 0.74         |
| 10 | Iso-Paraffinic Kerosene | C9-C11 c-par   | 47.0           | 170.6              | 175.2              | 4.6                                    | 23.0                                 | 1.19          | 0.78         |
| 11 | Iso-Paraffinic Kerosene | C9-C11 aro     | 51.0           | 167.2              | 174.3              | 7.1                                    | 32.8                                 | 1.05          | 0.79         |
| 12 | n-paraffin stream       | Clear          | 43.0           | 155.7              | 162.8              | 7.1                                    | 24.4                                 | 0.93          | 0.73         |
| 13 | Heavy naphtha stream    | Clear          | 50.0           | 163.3              | 166.7              | 3.4                                    | 12.1                                 | 0.95          | 0.75         |
| 14 | FSJF (certification)    | Clear          | 55.5           | 173.6              | 184.4              | 10.8                                   | 43.8                                 | 1.27          | 0.78         |
| 15 | Jet A-1 narrow cut      | Clear          | 75.0           | 207.0              | 215.6              | 8.6                                    | 21.3                                 | 1.71          | 0.82         |
| 16 | GTL kerosene            | Clear          | 39.5           | 155.6              | 168.1              | 12.5                                   | 28.7                                 | 0.97          | 0.73         |

**Table 10. LBO Correlation Coefficients with Fuel Properties**

| Fuel Parameter | T <sub>10</sub> | T <sub>50</sub> | T <sub>50</sub> -T <sub>10</sub> | T <sub>90</sub> -T <sub>10</sub> | Flash Point | Density @ 20°C | Viscosity @ 40°C | DCN <sup>1</sup> | Peak LFS <sup>2</sup> | SMD <sup>3</sup> |
|----------------|-----------------|-----------------|----------------------------------|----------------------------------|-------------|----------------|------------------|------------------|-----------------------|------------------|
| r <sup>2</sup> | 0.73            | 0.64            | 0.12                             | 0.14                             | 0.48        | 0.77           | 0.68             | 0.48             | 0.41                  | 0.44             |

Notes:1. DCN: Derived Cetane Number, ASTM D7170, a measure of ignition delay; higher DCN indicates shorter ignition delay

2. LFS: Laminar Flame Speed

3. SMD: Sauter Mean Diameter, a metric for atomization

|        |                    |                  |                |
|--------|--------------------|------------------|----------------|
| Legend | Strong correlation | Weak correlation | No correlation |
|--------|--------------------|------------------|----------------|

Observations by the researchers included the following:

- Fuels with lower density and viscosity had broader LBO limits; this was a relatively strong correlation.
- T10 and T50 were also found to have relatively strong correlation with LBO.
- Fuels with a lower flash point, had broader extinction limits, but the correlation was less than the correlations for T10 and T50.
- Correlations of LBO with laminar flame speed, ignition delay, and atomization were relatively weak.
- There was no correlation of LBO with [T50 – T10] or [T90 – T10].

Author's comment: It is surprising that viscosity was so important but that atomization, i.e., SMD, was only mildly important. Missing in the paper are actual LBO data to show the magnitude or significance of these fuel related changes. The matrix of fuels was well designed to look separately at composition and volatility. Problems with the combustor delayed and limited this study. This work was considered preliminary by the investigators. There are plans to continue this research with modern, lean-burn combustors at Rolls-Royce and Institute for Combustion Technology of the German Aerospace Center (DLR) during 2012. (See F/E-2)

#### **F/C-2.**

This project will be conducted at both Rolls-Royce in Derby, UK, and at DLR in Stuttgart, Germany. This research will be a follow-on to the research described in F/C-1 above. The research will result in a PhD Dissertation for Victor Burger and is slated to start in the spring of 2012.

#### **F/C-3.**

This experimental research project was conducted at the University of Sheffield, Sheffield, UK. It was sponsored by the Shell Petroleum Company. The Principal Investigator was Prof. Chris Wilson. [Ref. Rye L, Wilson C. "The Influence of Alternative Fuel Composition on Gas Turbine Ignition Performance. Fuel (2012), doi:10.1016/j.fuel.2011.12.047] The research was also the subject of a PhD Thesis for Lucas Rye.

The focus of this research was to determine the degree in which different fuel composition and volatility affect ignition and lean stability performance. Experimental ignition loops were obtained by conducting ignition tests at atmospheric pressure in both a can combustor, representing older designs, and an annular combustor section, representing a next-generation lean combustor. Both were fitted with air-blast atomizers.

The ignition tests were conducted on three fuels with distinctly different, but relevant, boiling point distributions (BPD). One fuel was a Jet A-1 fuel with a typical BPD. The second fuel was a light GTL kerosene that had a much flatter BPD than the Jet A-1. The third fuel was a diesel fuel that had a BPD with the same slope as the Jet A-1, but shifted about 75°C higher. Thus, the two jet fuels had about the same front end volatility and flash point, while the diesel fuel had a much higher flash point.

In both combustor systems, the diesel fuel required a much higher equivalence ratio to achieve ignition compared to the Jet A-1 and the GTL fuels, which were almost the same. The compromise exhibited by the diesel fuel was much greater in the advanced, lean combustor. The investigators concluded this was due to the lower amount of fuel present and hence less vaporized fuel.

Overall the research concluded that increasing fuel volatility, i.e., a lower initial boiling point, enhanced ignition because there was more fuel vapor in the vicinity of the igniter. Variations in fuel chemistry were not important as long as the fuel contained a sufficient amount of lower boiling point hydrocarbons. Increased fuel volatility was also found to increase the combustor stability limits.

Further analysis of experimental results and fuel composition – through two-dimensional gas chromatography techniques (GCxGC) – facilitated the development of a mathematical correlation between the primary zone ignition equivalence ratio and the calculated test fuel vapor pressure.

Author's comment: This was very interesting work, and very well done using both older and advanced design combustors. It would be very beneficial to conduct more tests with a broader range of parametric fuel blends to better separate volatility, atomization, and chemistry effects.

#### **F/C-4.**

This experimental project was conducted by DLR, Texas A&M in Qatar, Shell and Rolls-Royce, sponsored by Qatar Science and Technology Park. [Ref's. (1) Joanna M Bauldreay, Paul F Bogers and Ali Al-Sharshani, "Use of Surrogate Blends to Explore Combustion-Composition Links for Synthetic Paraffinic Kerosenes", 12th International Conference on Stability, Handling, and Use of Liquid Fuels, Sarasota, Florida USA, 16-20 October 2011. (2) D. Fyffe, J. Moran, K. Kannaiyan, R. Sadr & A. Al-Sharshani, "Investigation of GTL-like jet fuel composition on GT engine altitude ignition and combustion performance. Part I: Combustor operability", paper GT2011-45487, ASME Turbo Expo 2011, June 2011, Vancouver.]

The objective of this research was to evaluate the effect of hydrocarbon composition synthesized paraffinic kerosenes (SPK) on ignition, altitude relight, and emissions; the effect of carbon number and spread were also considered. A 3-dimensional design of experiments (DOE) matrix of six test fuels was defined based on iso-/normal ratio, cyclo-paraffins, and carbon-number spread. One of the six test fuels was a conventional Jet A-1. For the five synthetic fuels and blends, the slope of the boiling point distributions straddled the limits allowed by ASTM D7566 as shown in Table 11. Four of the test fuels had very flat distillation curves and did not meet the T50 – T10 requirements for final fuel blends (D7566 Table 1); one of the two SPKs failed to meet the T90 – T10 requirements for SPKs (D7566 Table A1.1). The flash points ranged from 40.5 to 49.

Altitude relight tests were conducted on these fuels using a multi-sector representation of a Rolls-Royce advanced, lean-burn, low-NOx gas turbine (GT) combustor, fitted with an advanced design coaxially fuel-staged, lean burn injector with air blast atomizer. Inlet air parameters simulated altitude conditions at 25k to 30k feet.

**Table 11. Boiling-Point-Distribution & Viscosity Characteristics of Test Fuels (D86)**

| Fuel Parameter    | D7566 Table 1 | D7566 Table A1.1 | Jet A-1 | SPK-1 | SPK-2 | Blend 1 | Blend 2 | Blend 3 |
|-------------------|---------------|------------------|---------|-------|-------|---------|---------|---------|
| T90 – T10         | ≥ 40°C        | ≥22°C            | 68.3    | 22.5  | 18.4  | 20.7    | 27.5    | 21.2    |
| T50 – T10         | ≥ 15°C        | --               | 28.5    | 16.6  | 9.4   | 8.4     | 10.0    | 8.4     |
| Flash Point       |               | ≥38.0            | 40.5    | 41.5  | 46.0  | 45.5    | 49.0    | 45.5    |
| Viscosity @ -20°C | ≤8.0 cSt      |                  | 3.792   | 2.552 | 3.237 | 3.27    | 3.642   | 2.985   |

The results showed little or no deterioration to the weak boundary of the ignition regime or the weak extinction limits, within the method precision, as compared with the Jet A-1. There were some indications of possible improved ignition performance at simulated altitude conditions with the two fuels SPK-1 and Blend-3. In the paper, it was suggested this might be due to the lower iso-/normal ratio of these two fuels.

Author’s comment: Overall, the results were not too surprising since the test fuels all had relatively low flash points. The reason the two fuels SPK-1 and Blend-3 had better altitude relight performance could have been due to the lower viscosity of these two fuels which would result in better atomization. The results would have been more useful to the question at hand if the fuel matrix had contained one more fuel that had a narrow or flat boiling point distribution but a high flash point, in the range of 60 to 70°C.

#### **F/C-5.**

Over the last couple years, a number of research projects have been conducted at DLR in support of SWAFEA. Dr. Patrick le Clercq has been the Principal Investigator, although he is currently on sabbatical at the University of California at Irvine. These research projects have resulted in a number of technical papers, the most relevant of which are listed below:

- An Experimental and Modeling Study on the Auto Ignition of Kerosene and Surrogate Fuel Mixture (AIAA-2008-97370)
- Validation of a Multicomponent-Fuel Model for Spray Computations (AIAA-2009-1188)
- Impact of Fischer-Tropsch Fuels on Aero-Engine Combustion Performance (AIAA-2010-613)
- Jet A-1 Fuel Spray Evaporation in a Turbulent Flow: Experimental Investigations and Validation of Numerical Models (AIAA-2011-790)
- On Surrogate Fuel Formulation (ASME-GT2009-60012)

While all of these papers address issues of alternative fuels, i.e., synthetic fuels for aircraft gas turbines, only the first of these papers is a combustion paper while the other four focus on the problem of calculating atomization, especially for surrogate fuels. The combustion paper compares calculations of ignition delay times for surrogate fuels with data from shock-tube experiments; it was found that the calculations for the several surrogate fuels did not accurately match that of an actual jet fuel. The atomization papers address the problem of calculating the drop-size distribution of fuel sprays so as to identify surrogate fuels that will mimic the

atomization of real jet fuels.

Author's comment: While none of these papers directly address the specific questions being addressed by this report, they appear to be a part of a larger research program that is leading toward these questions as evidenced by the two items, F/C-2 and F/C-4 discussed above.

#### **F/C-6.**

This project is a part of Honeywell's effort under the FAA/CLEEN program. Randy Williams is the Principal Investigator. This is a new project which has just recently been initiated so there are no results to report.

The objective is to evaluate fuel composition effects, primarily type and concentration of aromatics, on ignition and lean stability over a range of flight conditions. The test fuels will be a sub-set of the matrix used in the elastomer testing (F/E-10 above). The testing is scheduled to start early 2013.

Author's comment: It is premature to comment on the project as it has not started, other than to say that the stated objectives are in line with the questions being addressed by this report. Hopefully boiling point distribution will be addressed in the fuel matrix as well as composition.

## **7. Summary and Conclusions**

### **7.1 Aromatic Content**

None of the recently completed fuel-elastomer studies have addressed the question of the minimum aromatic content, i.e., is it necessary and, if so, what should it be. The efforts have primarily been directed toward conducting compatibility tests. The results have been positive in the sense that none of the SPKs or their 50/50 blends with conventional jet fuel have been shown to be incompatible with current fuel-system elastomers. This is not surprising since all of the elastomers used in engine and aircraft fuel systems were designed to be compatible with hydrocarbons in the kerosene boiling range. And the fuels being tested are just that, only the hydrocarbons did not come from petroleum.

The question now focuses on the potential problem of an aged seal having taken some degree of compression, i.e., plastic, set, and then shrinking too much when exposed to a low-aromatic fuel such that it can no longer seal against the fuel pressure. The current work at UDRI under US Air Force sponsorship, FE-3, appears to have developed a method to repeatably age O-rings so that they can be tested with varying levels of aromatics under switch-loading operation. This approach uses actual fuel-system hardware so it has the advantage of being a performance test rather than a fuel compatibility test. Another desirable feature is the ability to switch-load fuels with varying aromatic content.

Two other projects are performance based, FE-8 and FE-9, and employ switchloading. The project at Sheffield, FE-8, is a static test and has a stated objective of determining a minimum aromatic level. The project at SwRI, FE-9, is a dynamic test but focuses on compatibility and

does not currently have the determination of minimum aromatic content as an objective.

Current plans for the pending project at Honeywell, FE-10, call for using standard elastomer compatibility tests; future plans may change.

The evaluation of self-sealing fuel bladders is important since the mechanisms are different than seals, etc. They could be the critical system that determines the minimum required aromatic content for military fuels. It is unfortunate that repeatability of live-fire tests is inconsistent. Laboratory tests will probably be necessary to address this question.

## **7.2 Boiling Point Distribution**

The literature search did not identify any research projects that had studied the effect of boiling point distribution or chemistry of the fuel on ignition and LBO in a definitive manner. A number of current or pending research projects were identified and reviewed. The three completed projects with combustion experiments did not cover the same range of fuels or combustor technologies, but the results were consistent with each other. Fuel vapor pressure, i.e., front end volatility, seemed to be the most important fuel parameter. Fuel chemistry was not important, even when the front end of the boiling point distribution, i.e., the most volatile fraction, was heavily spiked with each of the four hydrocarbon families. Also, the slope of the boiling point distribution was not seen as important. The results should be validated in modern combustors. The need for a control on maximum flash point, or some other metric of fuel volatility, has not been addressed.

## **8. Recommendations**

Several projects have been identified that are just beginning or are about to begin. In general, it is recommended that the Principal Investigators make sure the objectives are in line with the needs and concerns of the aviation industry and not simply repeat work that has already been done. Specific recommendations are as follows by technical issue:

### **8.1 Aromatic Content**

It is recommended that the fuel-elastomer studies that are either pending or underway be evaluated by the Principal Investigators to make sure the objectives and approach are in line with the industry desire to define the minimum aromatic content for alternative jet fuels. It is thought that performance tests with the ability to switch-load test fuels, i.e., change fuels, provide a better opportunity to address this need than standard compatibility tests based on properties such as volume swell, hardness, etc. The projects identified at UDRI and the University of Sheffield, FE-3 continuation and FE-8, appear to meet these criteria and are supported. The project at SwRI, FE-9, is encouraged to consider adding tests with varying aromatic content to their matrix in lieu of testing fluorosilicone materials, which are not used in dynamic seals. Although the pending Honeywell study, FE-10, has the determination of minimum aromatic content as an objective, the information available is not sufficient to judge how they plan to meet that objective; here it is merely recommended that consideration be given to how that will be accomplished before initiating the effort.

It is recommended that one or more projects be undertaken to study the effect of fuel chemistry on the function of self-sealing fuel bladders. This mechanism is different than that of the seals and other materials that have been examined. This system could, therefore, be the system determines the minimum aromatic requirement for military fuels. This could become a moot point if information on the Boeing study at UDRI proves decisive.

It would be beneficial to know if there really are legacy aircraft still flying that have aged seals that would be prone to leakage if exposed to zero- or low-aromatic fuels, or if the community is being overly conservative based on anecdotal information. If, in fact, there are such seals in flying aircraft, knowing how much set they have taken and how much they would shrink would be very useful information towards perhaps establishing a minimum swell requirement for alternative fuels.

## **8.2 Boiling Point Distribution**

The specific need on fuel distillation is to determine whether or not a control on front-end volatility is necessary, e.g., a maximum flash point or minimum vapor pressure.

The fuel matrix at UTC, FC-1, was very comprehensive, but the combustion experiments were limited to LBO tests in a combustor simulating an older technology. The plans to use a similar fuel matrix for ignition and LBO testing using more modern combustors, FC-2, are supported. It is also recommended that the combustion research at Sheffield, FC-3, be continued using a fuel matrix similar to the one used at UCT, FC-1, as a means to further develop the robustness of their vapor pressure model. It would be very beneficial if both of these projects, FC-2 and a continuation of FC-3, should address some metric of fuel volatility, e.g., flash point and vapor pressure, to determine if a control is needed.

## **9. Acknowledgements**

The author thanks the Principal Investigators for their willingness to take their time to share the details of their projects on a continuing basis.