CAAFI Biennial General Meeting 2016

Key Qualification Challenges

Walter E. Washington Convention Center
Washington, D.C.

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Cert-Qual agenda

**Plenary**
SAJF Certification and Qualification

- Certification Overview
- SAJF Approval Status
- The Path Forward

**Unconference 1**
Enhancing Fuel Qualification Process

- OEM Review Process
- Stakeholder Engagement
- Approval Process Improvements

**Unconference 2**
Key Fuel Qualification Challenges

- Key Technical Issues
- SAJF Compositional Considerations

**Cert-Qual Breakout**

- Centralized Mgt of Test & Review Process
- Generic Spec
Challenges

- Resources (time and funding)
- Predictive capabilities (modeling?)
- Protocols/specs based on similarity (Cliff Moses)
- Property test methods (Melanie Thom)
- Slow contracting
- Centralized testing/coordination
- Management of OEM Management
- US vs Europe differences in processes/involvement
- Change of mind from producers late in the process
- Better control/tracking of samples used for data
- ...
Predictive capabilities

National Jet Fuel Combustion Program
* 5 OEMs, 10+ Univ, DoD, DoT, NASA
* Develop a protocol to get to kinetic models for a new fuel

Some challenges:
- To get to a model for a new fuel quickly
- Can a reliable model be practical in size?
- Develop a common format for all OEMs
- Are drop-in fuels similar enough that models can’t differentiate?
- Do differences observed in fundamental level tests matter at system level?
- Sub-model (e.g., spray) development?

Can we predict how combustion performance will be by using modeling?
Tests methods

- Inadequate (e.g., large variation, valid for diesel but not for kerosene, etc.), non-existent, existent and accurate but with no clearly defined pass/fail criteria or limits, obsolete, or adequate but not readily available
- Survey first; fix later if needed
- CRC Aviation AV-23-15 Project

How adequate is the set of test methods currently in spec & D4054 requirements?
- ASTM D7566 Annexes set-up per "process"
- Different process produce similar products
- Low blend ratio (10%) to lower the risk due to different process
- Focus on composition & Table 1 properties being favorable

Can we have a more generic spec to facilitate easier entry?
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Key Qualification Challenges
- ASTM Test Methods Survey

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Melanie Thom
Baere Aerospace Consulting, Inc.
Adequacy of Existing Test Methods for Aviation Jet Fuel and Additive Property Evaluation

- Contracted by the Coordinating Research Council 9/15/16
- Contract duration is 6 months

Review the specifications referenced in ASTM D1655, D7566, and D4054

- Why is it in the list, what is the goal, i.e. to control production, address a hardware issue, exclude something?
- Is it based on an older test method?
- Are there assumptions stated or implied in the use or the interpretation of results for jet fuel?
- Is the test likely, based on stated limitations or scientific principles, to be fuel chemistry dependent?

General Review of Testing Accessibility

- Not addressing any identified issues, just finding them
Definitions

* OEM – Original Equipment Manufacturer
* SME – Subject Matter Expert
* Tech – Technology

Next CRC Meeting – May 1-4, 2017, Portland OR
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Developing a Generic Annex to Safely Reduce the Effort to Approve Synthesized Fuels

Clifford Moses, PhD
Consultant

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◆ Cleared for public release

◆ All conclusions and recommendations are those of the author and not necessarily those of UTC or the US Air Force.
Pacing Factors

Key Issues identified at Certification/Qualification Panel meeting during 2014 CAAFI Annual Meeting: (from Mark Rumizen’s summary presentation)

◆ “ASTM D4054 Process too Lengthy and Costly”
  ➢ “Extensive Fuel Property and Engine/Aircraft Testing”
  ➢ “Repeating Same Tests Regardless of Compositional Similarities With Previous Fuel Approvals”
Background

- ~40 synthesized kerosenes and blends with conventional fuel have been evaluated
  - Conventional jet fuel
  - F-T & HEFA SPSKs
  - 2nd-generation renewable, w/wo aromatics
  - Synthesized kerosenes with aromatics

- **Independent of resource or processing:**
  - All have met Table 1 property requirements
  - All have bulk physical properties typical of conventional jet fuels
  - There have been no issues with materials compatibility
  - There have been no issues with combustor/engine/airframe performance or ground handling safety and storage
What is necessary to prove a synthesized fuel or semi-synthetic blend is fit-for-purpose?

- Demonstrate the candidate fuel has properties and characteristics that are typical of conventional jet fuel
  - Boiling point distribution
  - Chemistry
  - Bulk physical properties
  - Materials compatibility
  - Control of trace contaminants
  - Table 1
Boiling Point Distribution

- **Objective:** BPD like jet fuel, vis-s-vis single molecules/carbon numbers
- **Control developed in D7566 Annex 1 and continued in others**
  - T90 – T10 > 22C interim control
  - 4 contiguous carbon numbers each with more than 5% of the fuel
- **Recommend maximum flash point**
Chemistry: Distribution of Hydrocarbons (GCxGC)

- Iso- and normal paraffins
- Cyclo-paraffins
- Aromatics

Distributed across the boiling point range

GCxGC analyses
Conventional Fuel
Chemistry: Aromatics in CRC World Survey (GCxGC)

Aromatics are distributed across the boiling range:
- Alkyl benzenes (single ring): 50 to 80% of aromatic fraction
- Tetralins and indans: 10 to 40% of aromatic fraction
- Naphthalenes (double ring): 0 to 20% of aromatic fraction

Each are distributed

### Distribution of Aromatics

- Alkylbenzenes (66%)
- Tetralins & Indans (24%)
- Naphthalenes (10%)

### Concentration of Aromatic

- Alkyl-Benzenes
- Cyclo-Aromatics
- Naphthalenes
Chemistry “Box” of Conventional Jet Fuel

- CRC World Fuel Survey using GCxGC analysis
- Make synthesized HC kerosenes fit within the box for generic Annex independent of resource and processing

<table>
<thead>
<tr>
<th>Hydrocarbon Family</th>
<th>Typical Conventional Jet Fuel*</th>
</tr>
</thead>
<tbody>
<tr>
<td>n- plus iso-paraffins</td>
<td>50 to 90%</td>
</tr>
<tr>
<td>cyclo-paraffins</td>
<td>0 to 40%</td>
</tr>
<tr>
<td>aromatics (total fuel)</td>
<td>10 to 25%</td>
</tr>
<tr>
<td>single-ring (AF)**</td>
<td>50 to 90%</td>
</tr>
<tr>
<td>tetralins + indans (AF)**</td>
<td>10 to 45%</td>
</tr>
<tr>
<td>naphthalenes (AF)**</td>
<td>0 to 20%</td>
</tr>
</tbody>
</table>

* CRC World Fuel Survey
**AF: aromatic fraction only
D4054 Bulk Physical Properties

- Bulk physical properties of kerosenes containing synthesized hydrocarbons are the same as conventional jet of similar properties
  - Density
  - Viscosity (ASTM transformed)
    - Specific heat
    - Surface tension
    - Thermal conductivity
  - Speed of sound
  - Bulk Modulus
  - Air solubility
  - Water solubility
  - Dielectric constant?
Density vs. Temperature

Density is linear with temperature, and all fuels have the same slope.
Viscosity vs. Temperature

Viscosity/temperature dependence mimic the density results
D4054 Bulk Physical Properties

- Bulk physical properties of kerosenes containing synthesized hydrocarbons are typical of conventional jet fuels
  - X vs Temperature of all fuels and pure HCs are linear and parallel
  - Verified with pure hydrocarbons
  - Fundamental physical chemistry
  - Final value for fuel is simply the result of combining constituents

- All HC kerosenes with typical BPD and meeting Table 1 values for density and viscosity will have typical D4054 physical properties
Materials Compatibility Data Sets

◆ D4054 list of materials and tests based on Air Force protocol developed for Syntroleum S-8

- Multiple properties on “Short-short list” of D4054 tests
  - Typical service temperatures
  - Most syn-fuels
  - With/without synthetic aromatics

◆ O-ring tests at ambient temperature on F-T, HEFA, and 2nd-generation renewable fuels (SwRI)

- Volume swell vs. aromatic content on 9 classes of materials for conventional and F-T fuels at ambient temperature (UDRI)
Materials Compatibility

- Volume swell is considered to be the most sensitive to aromatic content (Graham et al)
- Nitrile materials are the most sensitive to aromatics
MATERIALS COMPATIBILITY RESULTS:
N0602 O-RINGS, 28 DAYS @ 265°F

Volume Change

Tensile Strength

Hardness

Compression Set
Materials Response to Aromatics

◆ Materials
  Ø O-rings
  Ø Sealants
  Ø Coatings
  Ø Adhesives
  Ø Hoses
  Ø Bladder liners
  Ø Films

◆ Fuels
  Ø Conventional jet
  Ø F-T paraffinic
  Ø Renewable w/wo aromatics

◆ Responses are linear; small scatter

◆ Materials respond to synthesized aromatics the same as aromatics in petroleum-derived jet fuel
Materials Compatibility Conclusions

◆ All synthesized jet fuels and blends with aromatics >8% have demonstrated materials compatibility typical of conventional fuels with similar aromatic content regardless of resource or processing
  ➢ All fuel system materials are developed and qualified to be compatible with hydrocarbon kerosenes (8 – 25% aromatics)
  ➢ We are evaluating hydrocarbon kerosenes with 8 – 25% aromatics.

◆ Minimum of 8% aromatics in final fuel is a necessary and sufficient condition for materials compatibility
Other issues

◆ Most other properties/issues are due to non-HC contaminants and can be addressed by additives and/or Annex specification table.
  ➢ Thermal stability
  ➢ Lubricity
  ➢ Electrical conductivity
  ➢ Storage stability
  ➢ Effects on filter/coalescers
  ➢ …
We are not making new fuels; we are making the same fuels from new resources

Source and processing don’t matter if there is sufficient downstream processing, i.e., hydrotreating, etc. (Dennis Hoskin)

- 325°C JFTOT breakpoint
Summary

- Defined chemistry box of conventional jet fuel
- Demonstrated that if a hydrocarbon kerosene meets Table 1 specification property requirements, the bulk physical properties have to be typical of conventional jet
- Shown that non-metallic materials respond to synthesized aromatics the same as aromatics in conventional jet fuels
  - Linear with aromatic content
  - 8% aromatics is necessary and sufficient condition to maintain desirable swell characteristics
- Other issues can be addressed by specification tables and/or additives
  - Table AX.1 Detailed Batch Requirements
  - Table AX.2 Other Detailed Requirements
Conclusions

Don’t need a separate evaluation and Annex for every new fuel resource/process.

- GCxGC to determine chemistry and distribution of carbon #s and isomers
  - Cyclo-paraffins: ≤ 30%
  - Aromatics: ≤ 20% of fuel and distributed
  - Tetralins and indans: < 30% of aromatics
  - Carbon numbers: ≥ 4 significant contiguous numbers

- ≥ 325°C JFTOT breakpoint
- Typical boiling point distribution, not distorted
- Add maximum flash point
- Tables AX.1 and AX.2
- ...

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Conclusions (cont.)

◆ We can safely develop a new generic Annex for synthesized kerosenes independent of resource or conversion process
  ➢ HC kerosenes typical of conventional fuel
  ➢ Focused controls beyond Table 1 on critical issues
  ➢ Allow up to 10% blend
  ➢ Forego further FFP and component testing

◆ Allow earlier entrance into production

◆ Approval efforts would focus on fuels that are not typical kerosenes to determine blending constraints with conventional jet fuel
  ➢ High concentrations of only a few molecules
  ➢ 1 or 2 carbon numbers
  ➢ Abnormal boiling point distributions
  ➢ JFTOT breakpoint < 325°C
Way Forward

- The US Air Force is funding a team to develop a generic Annex independent of resource and conversion processing
  - Tim Edwards, USAF
  - George Wilson, SwRI
  - Chris Lewis, consultant
  - Cliff Moses, consultant

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