Considerations for Using Existing Standards as Part of Alternative Fuels Approval and Deployment

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Adequacy of Testing Methods for Aviation Fuels and Additives

Executive Summary


The work entailed reviewing all of the standards and specifications referenced in ASTM D-1655 Standard Specification for Aviation Turbine Fuels, ASTM D7566, Standard Specification for Aviation Turbine Fuels Containing Synthesized Hydrocarbons, and ASTM D4054, Standard Practice for Qualification and Approval of New Aviation Turbine Fuels and Fuel Additives to determine what, if any, impact a change in the fuel composition or in how the standard was used might have on the results.

The purpose of the study was to assess the continued adequacy of the referenced test standards for use with: fuels prepared in manners other than those used with traditional petroleum crude; D7566 blendstocks which may not be fluids meeting the traditional kerosene distillation profile; and additives. It was considered beyond the scope of the program to assess how potential issues and concerns were evaluated or addressed, and it was beyond the scope of the project to evaluate the constraints provided by the parent documents on the quantitative values.

The results indicated of the 348 individual documents reviewed, 140 documents were identified as being test methods. Of those 140 documents, 70 showed no indications of impact, 27 indicated reasons for more careful review, and 6 showed reasons for probable concern. An additional 10 documents were specifically used in relational analyses.

Only the six documents of probable concern are presented in this summary.
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Introduction

Over the last 75 years, there has been an evolution in three areas of aviation fuel testing: changes in the needs of the aircraft hardware, changes in the technology of the test methods, and changes in the fuel chemistry composition.

Because of the interrelationship of the fuel with the aircraft engines and fuel systems, changes in the aircraft hardware meant changes in the specific types of data and related fuel properties required by the designers in the fuel specification. The changing requirements over time were observed as changes in the ASTM D1655 Table 1 properties, both in absolute values and in the properties specified.

While the standards, data requirements, and methods continuously evolved over the last 75 years, this evolution revolved around traditional petroleum derived kerosene distillation range jet fuels. Test methods and requirements were added to control the traditional jet fuel. Active data collection was driven by experience with traditional jet fuel. All of the development efforts were directed at changing hardware and designs with the fuel as a fixed variable.

First encountered during the evaluations of the +100 thermal stability additive, and later with the introduction of alternative jet fuels, the assumptions on what was known about fuel needed to be reconsidered. The industry began to encounter the extent of the assumptions related to fuel properties and performance embodied in the requirements. With research into alternatively derived and alternatively composed fuels, the standards were being employed to measure the properties and performances of fuels that might not be kerosene distillation range hydrocarbons. Test methods that had not been routinely performed were being resurrected. Data that had not been routinely considered were being collected and reviewed.

This raised the question, are these methods still adequate? Do they report data that are meaningful? Accurate? Precise? Useful? Applicable? To explore these questions, the Coordinating Research Council, Inc. (CRC) funded a review of the specifications and standards referenced by the aviation fuel community. The goal was to begin a conversation on the methods, not to conclude them.

This paper summarizes those findings and their potential implications.
Background

The basic concern is that existing ASTM standards are being used to assess alternatively produced and alternatively composed jet fuels, but offerors do not know if the data developed by this testing are “correct” or sufficient. It is most expedient to use existing standards and specifications and directly compare resulting data between traditional jet fuel and alternatives. The industry is familiar with the tests and with the data, but the comparison is useful only if the data are instructive.

The concern is three-fold. First there is a concern that over time the requirements specified by the standard have been driven by needs that are based on the interaction of aircraft engines and fuel systems (hardware) with traditional petroleum-based kerosene boiling range fuels. Are the needs the same if the fuel is not a traditional jet fuel? The second concern is that analytical chemistry techniques have evolved over time and the fundamental assumptions involved in developing the methods may or may not be appropriate for their use on alternative fuels. The third concern is if the properties required by the standards, that are devised to control the production of petroleum fuels, are suitable for controlling fuels derived from alternative production methods.

These concerns have raised questions regarding three potential data gaps; 1) that test methods and accuracy statements were developed specifically for petroleum derived kerosene range jet fuels and the validity of their use on alternatively produced and composed fuels is not known, 2) that the test methods have evolved or been superseded based on test parameter assumptions from the original test method performance with petroleum based kerosene jet fuels and those assumptions may not be valid for other types of fuels, and 3) there is an inference of fuel performance from an absolute data value that may or may not correspond when the fuel is produced by alternative means. This third data gap may be because the performance only relates to an absolute value from a fuel with a specific formula, or because assumptions of data at a single test parameter are assumed to be a predictor of test performance across a range of parameters and when the fuel formula changes this assumption is not correct.

As fuel technology has evolved, the emerging situation is a state where the aircraft engine and airframe manufacturers using the fuel in their hardware do not necessarily know what is specifically needed from the fuel, only that the fuel needs to do what it has always done. Because it is not known which requirements are primary, relating to performance and which are secondary, like controlling refining, compliance to all the properties is required. These restrictions may constrain technology change. A fluid is required to give the same data on all the tests even if the result is non-applicable, non-valid or makes no sense. The first step in stretching into new technologies is to relearn what the data are capable of telling us and why it should be considered.
Review Process

The review performed for CRC provided the following deliverables:

- A list of standards that are/will be imminently obsoleted by the industry
- List of any identified industry standards not specified in the three target standards
- A list of standards that display a technology gap
- A short summary on each standard reviewed
- Where possible, a list of how data are used by OEM’s, especially when the use diverges from the goal/purpose of the test
- Identification of where tests can be done
- List of references used, including previous surveys

These deliverables are provided in the CRC report AV-23-15 and are not in this report.

To understand where the technology gaps were, it was necessary to understand what each test method was for, why it was run, and what the data were purported to indicate. To collect this information, the following process was used.

❖ Review all the tests referenced in ASTM D1655, D7566, and D4054.
   ➢ What were they ostensibly to do?
   ➢ Why did they exist in the standard?
     ▪ Are they controlling a process, installed to address a specific challenge in production or use, or to address a hardware issue?
   ➢ Were they or could they be run at an average testing laboratory?
   ➢ Were there indications that the test was no longer available, or required measurable effort to procure?
   ➢ Were they built on any technical assumptions, or did the answer require a correction based on the use?
     ▪ Was the assumption built specifically on petroleum-based chemistry or did it have specific restrictions?
     ▪ Could the assumptions be validated for contemporary fuel chemistries?
   ➢ What/how were other test methods being used in design?
     ▪ Were they being used in coordination with or in spite of ASTM test methods?
- Were they manufacturer specific; and with or without standard?
  - Were there similar methods used in related industries?

The review was conducted considering three potential end products; 1) a final, fully formulated jet fuel that would still be a kerosene boiling range fuel; 2) a blendstock for use in a fully formulated jet fuel or a final fuel that met fit-for-purpose but could be measurably different than a normal kerosene boiling range fuel in some way; 3) done for approval of a fuel additive.

It was determined that, with the exception of the critically impacted tests, it was impractical within the time and resource limits of the program to develop historical discussions on why a specific test or value was required for all of the reviewed standards. There were several ASTM monographs which provided comprehensive discussions on a measurable subset of the standards reviewed, making these discussions here less value-added. A listing of the references was included in the CRC report.

The review process is graphically shown in Figure 1.
To categorize the standards uniformly, a review system was developed with the following criteria.

Green – There were no limitations or restrictions, either overt or implied, which directly prevented the use of the test method related to the target composition. This did not negate the value of confirming data, particularly related to the precision and bias statement, but there was nothing about the test method that the process, chemistry, or physics would suggest as a concern.

Yellow - There was something in the test method that suggested a concern. While the method did not overtly restrict the use based on the composition of the sample, there was content which, based on the method or based on the SME evaluation, suggested a reason that the offeror should perform additional work to document the method was acceptable for use. This included items such as changes to the precision and bias statement, a
conversion of data to a calculated output, or an assumption of correlation based on the output. This also included concerns of limitations on the fundamental test based on subject matter expertise, including in some cases how the data were used. With the exception of specific restrictions from the standard, these concerns were not likely to be observed with kerosene boiling range fuels even though they were semi or fully synthetic in origin.

Red - There was a reason to believe the test method would not work, would not work appropriately, had limitations or restrictions that would prohibit its use, or was based on a fundamental assumption that was not believed to be valid for different chemical compositions. More significant validation of the method for use with non-traditional samples was encouraged. While precision and bias statement inadequacies contributed to a “red” assessment, more than just a concern for the precision and bias statement was required to be assessed red.

**Results**

There were 318 individual standards identified in the parent documents that were reviewed. The documents were sorted as Practice, Guide, Specification, Method, and unidentified (Figure 2). After the downselect, 130 standards and specifications were determined to be test methods and were subjected to the in-depth review (Figure 3).
Figure 2 - Breakdown of Standard Type

Figure 3 - First Downselect from All Referenced Standards
After the review of each of the 130 identified standards, it was determined that:

- 70 standards were identified as having no anticipated impact based on the application, scope, or precision and bias statement limitations ("green").
- 27 standards were identified as having a specific concern and warranted further reviews ("yellow"). Most of the concerns are related to the precision and bias statements, potential deviations in software interpretations, or subsequent application of the data.
- 6 standards were identified as having a probable unacceptable impact ("red").

With the exception of the standards assessed as having a probable unacceptable impact, the individual reviews are not included in this report. Readers wishing to explore the reviews further are directed to the Coordinating Research Council, Inc. to request CRC Report No. AV-23-15, “Adequacy of Existing Test Methods for Aviation Jet Fuel and Additive Property Evaluation”.

**Standards Raising Concerns – “Yellow”**

Following the review, 27 individual standards or 19% of the total were identified as having a concern. These were standards which had some content which raised a specific concern about the potential impact of the fuel composition on either the method or the results of the test. Standards which covered methods that were not themselves likely to be sensitive to the chemical composition but which had post-data usage which could be sensitive were also designated as Yellow.

**Table 1 - Reviewed Standards - Yellow, Possible Impact**

<table>
<thead>
<tr>
<th>Yellow Standard</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASTM D130</td>
<td>Standard Test Method for Corrosiveness to Copper from Petroleum Products by Copper Strip Test</td>
</tr>
<tr>
<td>ASTM D1319</td>
<td>Standard Test Method for Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption</td>
</tr>
<tr>
<td>ASTM D1740</td>
<td>Standard Test Method for Luminometer Numbers of Aviation Turbine Fuel</td>
</tr>
<tr>
<td>ASTM D240</td>
<td>Standard Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter</td>
</tr>
<tr>
<td>ASTM D2624</td>
<td>Standard Test Methods for Electrical Conductivity of Aviation and Distillate Fuels</td>
</tr>
<tr>
<td>ASTM D3240</td>
<td>Standard Test Method for Undissolved Water In Aviation Turbine Fuels</td>
</tr>
<tr>
<td>Standard Test Method or Practice</td>
<td>Description</td>
</tr>
<tr>
<td>---------------------------------</td>
<td>-------------</td>
</tr>
<tr>
<td>ASTM D341</td>
<td>Standard Practice for Viscosity-Temperature Charts for Liquid Petroleum Products</td>
</tr>
<tr>
<td>ASTM D3701</td>
<td>Standard Test Method for Hydrogen Content of Aviation Turbine Fuels by Low Resolution Nuclear Magnetic Resonance Spectrometry</td>
</tr>
<tr>
<td>ASTM D3343</td>
<td>Standard Test Method for Estimation of Hydrogen Content of Aviation Fuels</td>
</tr>
<tr>
<td>ASTM D4308</td>
<td>Standard Test Method for Electrical Conductivity for Liquid Hydrocarbons by Precision Meter</td>
</tr>
<tr>
<td>ASTM D5001</td>
<td>Standard Test Method for Measurement of Lubricity of Aviation Turbine Fuels by the Ball-on-Cylinder Lubricity Evaluator (BOCLE)</td>
</tr>
<tr>
<td>ASTM D5190</td>
<td>Heat of Vaporization, Latent</td>
</tr>
<tr>
<td>ASTM D5191</td>
<td>Standard Test Method for Vapor Pressure of Petroleum Products (Mini Method)</td>
</tr>
<tr>
<td>ASTM D5972</td>
<td>Standard Test Method for Freezing Point of Aviation Fuels (Automatic Phase Transition Method)</td>
</tr>
<tr>
<td>ASTM D7153</td>
<td>Standard Test Method for Freezing Point of Aviation Fuels (Automatic Laser Method)</td>
</tr>
<tr>
<td>ASTM D7154</td>
<td>Standard Test Method for Freezing Point of Aviation Fuels (Automatic Fiber Optical Method)</td>
</tr>
<tr>
<td>ASTM D7524</td>
<td>Standard Test Method for Determination of Static Dissipater Additives (SDA) in Aviation Turbine Fuel and Middle Distillate Fuels—High Performance Liquid Chromatograph (HPLC) Method</td>
</tr>
<tr>
<td>ASTM E411</td>
<td>Standard Test Method for Trace Quantities of Carbonyl Compounds with 2,4-Dinitrophenylhydrazine</td>
</tr>
<tr>
<td>ASTM E2071</td>
<td>Calculating Heat of Vaporization from Vapor Pressure data</td>
</tr>
</tbody>
</table>
Standards with Probable Impact - “Red”

Following the review, six individual standards or 5% of the total were identified as having probable impact. These were standards which had a high probability of impact due to the chemical composition of the material. These standards had a direct limitation or prohibition on the chemistry, presented a methodology or other developmental restriction, or used post collection data modification, formulaic or correlational, that suggested a limitation. These assessments were based on data where possible; however, some reviews were based on professional opinion and should be the start of the conversation on applicability, not the conclusion.

Table 2 - Reviewed Standards - Red, Probable Impact

<table>
<thead>
<tr>
<th>Red Standards</th>
<th>Guide for Use of the Petroleum Measurement Tables</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASTM D1405</td>
<td>Standard Test Method for Hydrocarbon Types in Middle Distillates by Mass Spectrometry</td>
</tr>
<tr>
<td>ASTM D4529</td>
<td>Standard Test Method for Dissipation Factor (or Power Factor) and Relative Permittivity (Dielectric Constant) of Electrical Insulating Liquids</td>
</tr>
<tr>
<td>ASTM D924</td>
<td>Standard Test Method for Calculated Cetane Index of Distillate Fuels</td>
</tr>
</tbody>
</table>

The results of the reviews of these six standards are provided below.

Red Standards

**ASTM D924-15 – Dielectric Constant**

Use: Electrical Insulating Liquids

Concern:

- The precision and bias statement was developed using mineral oil and as such may not be applicable to traditional aviation turbine fuel, much less to alternatively prepared fuels.

- The dielectric constant is related to density and the speed at which the atoms respond to the electric field. The first becomes part of the analysis. The second can be foundational to the results.

- The method was not originally developed for measuring fuel capacitance. The data were determined to provide a useful means of measuring fuel volume and by relationship calculation, determining density, and therefore mass of fuel. As such there are a number of testing variables that are points of discussion within the industry: the K-cell vs. a 3 terminal cell;
the frequency at which the test is run; the relative density terms used for calculations (vacuum or air, dry or ambient, matched temperature or ambient).

- While capacitance and its measurement are foundational physics properties, the testing parameters and how the data are used ARE fuel chemistry dependent. This is because how the atoms respond in the electric field under different test conditions will be affected by the fuel chemistry. The method, as written, was developed for mineral oil. Discussions with the OEMs and with researchers performing the test indicated that kerosene boiling range fuels need different testing parameters because of differences in chemical composition as compared to mineral oil.

- There are enough variables and calculations involved to suggest that the test method is sensitive to chemical composition.

*ASTM D976-06 (2016) – Calculated Cetane Index
Use: Distillate Fuels
Concern: Document has a published limitation that the method is not applicable to pure hydrocarbons, synthetic fuels, alkylates or coal tar products. This suggests compositional sensitivity.

- This method is NOT applicable to jet fuel and is specifically invalid by the published property range limitations. The results will be affected by the chemical composition of the sample.

*ASTM D1250-08 (2013) – Use of Petroleum Measurement Tables
Use: Petroleum Products
Concern: Note: these concerns are less likely to be encountered for fuels in the normal kerosene boiling range. However, as chemical composition, especially of the blendstocks diverge from normal kerosene, the following concerns should be considered.

- The use of the Petroleum Tables is no longer in the hands of the analyst. It is completely a software exercise requiring inputting the “correct” values. It assumes that all petroleum products follow the same correlations, and it assumes that the analyst selects the appropriate “class” to access the correct equation.

- Given the dependence on data from naturally occurring petroleum products to generate the software, there is a concern that the correlations
may not be the same for synthetically or alternatively produced hydrocarbon fuels that are not traditional kerosene boiling range fuels or for the blendstocks used to prepare final fuels. These variations may actually be small; however, there is a natural predilection to ascribe inappropriate accuracy and precision to a value reported from computer-based output that may be at odds with the precision and accuracy of the actual correlations.

- Because volume changes are part of the calculations to convert from °API or relative density at one temperature to another, especially with the use of a hydrometer, there is a potential for diversion from historical data if the rate of volume change is different.
- These diversions from historical are potentially even more problematic for other outputs of the Petroleum Tables, such as volume vs weight calculations, and thermal expansion calculations used by the fuel handling and distribution industries.
- The table for conversion of observed gravity to the gravity at 60/60 has already accounted for the change in volume with temperature. If the chemical composition results in measurable deviations to this relationship, the conversion could be affected.

ASTM D2425-04 – Hydrocarbon Types by Mass Spectroscopy

Use: Middle Distillates with the boiling range 204 to 343 °C (400 to 650 °F)

Concern:
- Per the method, the composition should be paraffinic in the C_{10} to C_{18} with an average between C_{12} and C_{16}.
- As the alternatively prepared jet fuel sources result in more skewed, narrowed, or limited carbon number ranges, and less traditional composition, concerns for the applicability of the method as developed and described increase.
- The work developing the summation scheme may be impacted by the chemical composition of the sample. Moving to new sources may require changes to the scheme due to shifts in the carbon number distributions. The way this method is designed, an analyst has to have at least some knowledge of from where one is starting to confirm a) samples are in the target carbon number range, with the expected average carbon number, and b) expected carbon mass fragments that may or should be seen.
- In addition, testing to date has shown that reproducibility error increases as the paraffinic content increases. This means it is not a good choice of
method for alternatively produced fuels, many of which have a very high paraffinic composition.

- Experts in the field have expressed concern the equipment is obsolete, is hard to run well, and is hard to find a source to run it.

**ASTM D1405-08 – Estimation of Net Heat of Combustion**

*Use:* Aviation Fuels

*Concern:* • Per the stated limitations, the method is only valid for liquid hydrocarbon fuels derived by normal refining processes from conventional crude oil. It is not valid for synthetic or other petrochemical compositions.

• Per the stated limitations, the method is not applicable to pure hydrocarbons. This means that the results reported for fuel chemistries based on pure hydrocarbons, or blends with significantly less compositional complexity than traditional fuels will be incorrect.


*Use:* Aviation fuels

*Concern:* • Per the standard, the method is purely empirical, and is applicable only to liquid hydrocarbon fuels derived by normal refining processes from conventional crude oil.

• “The estimation of the net heat of combustion of a hydrocarbon fuel from its aniline point temperature and density is justifiable only when the fuel belongs to a well-defined class for which a relationship between these quantities has been derived from accurate experimental measurement on representative samples of that class.”
  
  □ The aniline point, density and sulfur contents are determined experimentally and correlations are based on articles from the 1950s and 60s.

**Conclusion**

In general, the majority of the standards were assessed as appropriate for use from the standpoint of the mechanics of the method. The standard methods were not being misapplied and the data developed were not influenced by the fuel composition. The majority of the specifications assessed as yellow were assessed as such due to potential creep in the statistics related to the repeatability and reproducibility, not due to a specific problem with the method itself. This could be problematic for absolute data values near the extremes of specification requirements. Even the standards identified as having a
probable impact should be considered as a beginning in reviewing the methods, not as a summary conclusion of impact.

This review is not an assessment of how the data are applied to operations. The test methods provide quantitative results. How these results are applied to form, fit and function on the aircraft must still be considered during the engineering review. Absolute values that are not the same as contemporary values need to be considered with respect to use to determine if the divergence impacts operational considerations.