Recent Improvements for ASTM D86 Distillation Testing including the Development of a New Hydrocarbon Synthetic Standard

Dr. Raj Shah[1], PhD; Cindy Klager[1]; Gary Lew[2]

[1]Koehler Instrument Company, Inc.; [2]Spectrum Standards

Abstract

ASTM D86 is the Standard Test Method for Distillation of Petroleum Products and Liquid Fuels at Atmospheric Pressure and has been used across the industry for decades. It is one of the oldest test methods under the ASTM D02 Jurisdiction and we are continuously looking for ways to improve the method. This poster will take a look at some of the most recent improvements and work being done to improve the precision, usability and overall robustness of ASTM D86.

The ASTM D02 subcommittee on Volatility has launched a ruggedness study to begin testing new options for ASTM D86. With this study the committee hopes to eliminate the use of Mercury thermometers, which has been a widely discussed topic across ASTM D02, with Gallium thermometers. Another main goal of this ruggedness study is to test the newly developed Synthetic Reference Fluid. Currently toluene is used as a verification fluid for calibration and hexadecane is used at higher temperatures. The recently developed synthetic hydrocarbon standard will cover a wider range than what is currently being used. It is another goal of ASTM to harmonize standards with comparable international organization standards. In the case of ASTM D86 it is requested to harmonize it with the ISO 3405 test method for distillation. ISO recently conducted a study using higher level biodiesel blends (B30) which offered results that lie within the current precision statement. ISO will be adding distillate fuels containing up to 30% biodiesel to the scope of ISO 3405 which will also have to be taken into account during the study within ASTM in order to harmonize the methods. All of the aforementioned changes will bring overall improvements to the ASTM D86 test method.

Introduction

In ASTM D86, the sample is characterized as either a Group 1, 2, 3, or 4 substance, based on its composition, vapor pressure, and expected boiling points. The substance's group will define the apparatus' parameters and arrangements. The following table is used to determine the substance's group.

	Group 1	Group 2	Group 3	Group 4
Sample characteristics				
Distillate type				
Vapor pressure at				
37.8 °C, kPa	≥65.5	<65.5	<65.5	<65.5
100 °F, psi	≥9.5	<9.5	<9.5	<9.5
(Test Methods D323, D4953, D5190, D5191, D5842, IP 69 or IP 394)				
Distillation, IBP °C			≤100	>100
°F			≤212	>212
EP °C	≤250	≤250	>250	>250
°F	≤482	≤482	>482	>482

In the procedure, a 100 mL sample is distilled under conditions dictated by its group. The distillation occurs at ambient pressure. Observations of temperature readings and volumes of condensate are made. The results are typically reported as percent recovered as a function of temperature, either in a table or a graph. Both manually and automatic procedures exist for ASTM D86. The following picture shows an example of automated instrumentation for ASTM D86.

Introduction

In the procedure, a 100 mL sample is distilled under conditions dictated by its group. The distillation occurs at ambient pressure. Observations of temperature readings and volumes of condensate are made. The results are typically reported as percent recovered as a function of temperature, either in a table or a graph. Both manually and automatic procedures exist for ASTM D86. The following picture shows an example of automated instrumentation for ASTM D86.

Recent discussion for changes to ASTM D86 involve safe and logistical concerns. The currently used Mercury thermometer is undergoing a possible change to a Gallium thermometer and the chilling requirement for Group 1 fuels may be removed.

Gallium behaves predictably in the same way as mercury in regards to changes in temperature However, gallium is more sensitive to temperature changes than mercury. Mercury is also three times as heavy as gallium, so more gallium than mercury will fit into a small thermometer. These two characteristics make gallium a better material to be detect small temperature changes and produce more accurate readings.

The chilling requirement is being considered for removal because the new synthetic calibration compound will provide a better simulation for Group 1 fuels.

The downside of this method is that it requires the operator to manually extract between 100-300 mL of the sample, insert it into the chamber and run the test for several hours. In industry, the time it takes to run these tests is so long that it is not affordable and efficient.

Revision of Precision Statements

Additional changes are mostly in regards to revision of the precision statements. In addition, a study determining the precision of higher level biodiesel blends (B30) by the ISO 3405 distillation method was conducted and concluded with promising results. The study showed similar precision therefore, ISO 3405 can be applied to distillate fuels containing up to 30% biodiesel. The next steps are to harmonize D86 with ISO 3405 by expanding its scope to include these fuels.

ASTM Ruggedness Study

A joint ruggedness study for D86 reference fuels and gallium thermometers is set to begin in 2019. We anticipate that the studies will lead to the replacement of the mercury thermometers in the method, and the addition of distillate fuels containing up to 30% biodiesel to the scope of the method.

Other prospective changes to the D86 method as briefly mentioned before in the introduction is new synthetic hydrocarbon calibration standards. The current materials used for calibration do not produce an adequate range for Group 1 and Group 4 fuels. The new synthetic seeks to provide a qualifier for the instrument that will offer the desired range.

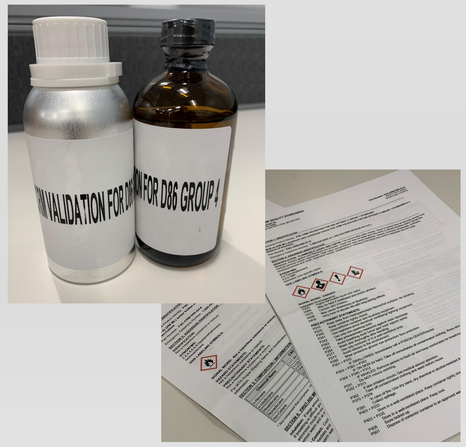
New Reference Material

Currently toluene is used as a verification fluid for calibration. Hexadecane is used at higher temperatures. At the request of the ASTM D86 committee, new synthetic hydrocarbon calibration standards are being developed for the method. These standards will cover a wider range than the current toluene. This poster deals with the development and preliminary tests of these standards.

The synthetic mixes will bring a consistency to the calibration for both Group 1 and Group 4 fuels. This will be better than the single calibration that is currently done. These mixes are intended to mimic diesel and gasoline.

The mixes or Certified Reference Materials (CRM's) are currently not approved. The material has been sent to ASTM in roughly mid April. It is too soon for any conclusive results to be presented in this poster.

The materials will had initial tests done in a Pilot Study that was recently completed before the ASTM D02 committee meetings in June. The results of this study are expected within the upcoming months.



Conclusions

D86 is undergoing several potential changes to the equipment used in its procedure and its precision statements. The current Mercury thermometry is considered to be replaced with the more temperature sensitive and less denser alternative, the Gallium thermometer. The chilling requirement for Group 1 fuels is also potentially being removed as a necessary step. A study that determined the precision of higher level biodiesel blends (B30) by the ISO 3405 distillation method was conducted and concluded with promising results. D86 will be harmonized with ISO 3405 to include these fuels in its scope. Discussion on the possible ILS would include ethanol and biodiesel samples. There are still questions of what levels of blends would be needed and if determining the ARVs for the suggested ASTM D86 reference materials could take place during the same study. The new synthetic hydrocarbon calibration in development intends to bring a consistency to the calibration of Group 1 and 4 fuels and to mimic diesel and gasoline better than the current toluene and hexadecane used. The synthetic is currently in testing process and the timeline for its approval and integration into the D86 test method is unclear.

References

- ASTM D86-17 "Standard Test Method for Distillation of Petroleum Products and Liquid Fuels at Atmospheric Pressure." (West Conshohocken, PA)
- ASTM International "Report of Subcommittee 08 to D02 Main Committee" June, 27th 2019 (Denver, CO)

Acknowledgements

Koehler Instrument Company, Inc.
85 Corporate Drive Holtsville, NY 11742
631-589-3800
www.koehlerinstrument.com
Dr. Raj Shah: rshah@koehlerinstrument.com
Cindy Klager: cklager@koehlerinstrument.com

Spectrum Quality Standards
17360 Groeschke Road, Houston, TX 77084
281-578-7575
sqs@spectrumstandards.com
www.spectrumstandards.com