DETERMINATION OF FLASH POINT INSTRUMENTATION BASED ON APPLICATION

Flash point measurement is a critical test used to determine the lowest temperature at which a liquid can produce enough vapor to ignite in the presence of an ignition source. Whilst not the most exciting task run in the lab, this test is essential for ensuring safety while handling chemicals, fuels, and other flammable liquids. The flash point measurement provides valuable information for storage and transportation of hazardous materials.

The history of flash point measurement dates back to the early 18th century when the French chemist, Jean Hellot, described the use of a "fire test" to determine the flammability of oils. However, it wasn't until the mid-19th century that the first standardized methods for flash point measurement were developed.

In 1865, Abel's closed cup flash point test was developed in England by Sir Frederick Augustus Abel, a chemist and explosive expert. Abel's closed cup test was the first method for measuring the flash point of liquids and involved heating a small sample of liquid in a closed container and observing for the first sign of ignition.

In the 20th century, various other methods for measuring flash point were developed, including the Pensky-Martens closed cup test, Cleveland open cup test, and Tagliabue open cup test. These methods differed in terms of their testing conditions and apparatus, but each aimed to provide accurate flash point values.

Today, flash point measurements are standardized procedures which simulate applications in various industries, including petroleum, chemical, pharmaceutical, and transportation. Modern flash point measuring instruments employ a variety of techniques, including automated and manual heating and temperature sensing.

The most common methods for flash point measurement include the closed cup test and the open cup test. The closed cup test involves heating a small volume of liquid in a sealed container and slowly heating it until a flame is observed. The temperature at which the flame appears is the flash point of the liquid. The open cup test involves heating a small volume of liquid in an open container and observing the temperature at which the vapor ignites. The open cup test is preferred when testing liquids that have a higher flash point temperature.

Close cup measurement techniques include Pensky-Martens and Tag methods. Open cup measurement techniques include Cleveland and Tag. Each of these methods can be carried out following the corresponding standard test method by the American Society for Testing and Materials (ASTM). Koehler Instrument Company Inc. has developed a range of automatic and manual instruments to carry out these various flash point tests.

ASTM standards undergo a rigorous pre-publishing process comprised of five general steps. Even before consideration for the process, the proposed new work must illustrate novelty and a lack of representation in the specified application. Then, the five-step process begins:

1. Initiation of the Project: A new work item is approved to move forward as a standard project

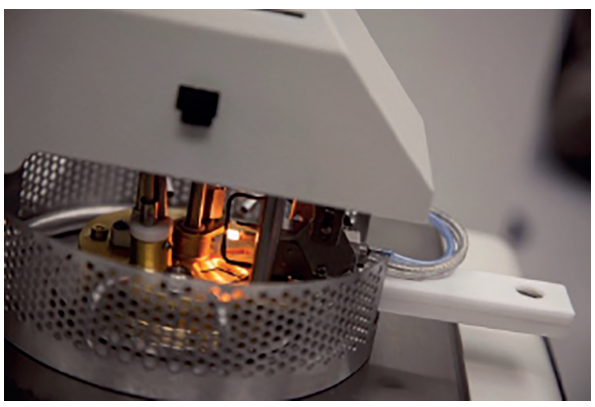
2. Standard Drafting: A subcommittee specialized in the technical subject is formed and the task group begins work on a standard draft, which includes Scope and Significance. These descriptors provide insight on the pertinence and purpose of the standard, respectively.

3.Review/Comment: The chairman of the formed task group leads the draft through several rounds of peer review, commenting, voting and revisions. This is performed in order to refine the draft and ensure it incorporates input from a spectrum of stakeholders, to include both industrial and governmental entities with interest in the work item and its impact on users.

4. Final Voting: The draft then enters committee ballot, where it typically receives multiple rounds of comments and revisions before obtaining final approval.

Finalization and Publication: After clearing peer review at 3 levels (subcommittee, main committee, and Society), the standard is given an alphanumeric designation and approved as an ASTM Standard [1].

All standards referenced in this paper have undergone this rigorous process and are accepted as ASTM standard methods [1].



Both closed and open cup tests mimic real-world conditions, with each reflecting a different application. Closed cup tests are meant to replicate storage conditions similar to lab spaces or warehouses. These are used to determine a fuel's behavior if an ignition source, or an applied source of heat which is used to ignite combustible materials or products, were to contact the material while stored in a closed container [2], [3]. These results provide a standard for laboratories and other storing facilities to use as a guide for regulating temperature conditions, significantly reducing the possibility of an accident [4]. These regulations can also be applied to the transportation of fuels, as probability of an accident greatly increases with constant movement or environmental heating and the increased likelihood of fuel contact with an ignition source.

On the other hand, open cup testing acts to simulate a leak in an open area, as well as the transportation or storage of materials in an open system [5]. Because open cup test methods involve vapors which are released into the surrounding environment, these methods allow for the determination of safe operating temperatures in the presence of spills [4]. Open cup testing results tend to correlate more to the fire point - the temperature to which a product must be heated under prescribed conditions to burn continuously when a mixture of a product vapors and air is ignited by a specified flame [6]. This effect is caused by the ignition source being over the surface of the liquid. The difference between the numerical results for the two methods is based on the closed cup test trapping vapor, while the open cup test releases vapor. The flash point will consistently be lower with closed cup tests, as a smaller volume is occupied by the vapors. In comparison, the release vapors during open cup tests can disperse across larger areas, diluting the concentration of the potentially flammable vapors. This leads to a higher temperature for ignition, since the same number of collisions of molecules in a larger volume necessitates a higher energy. This higher energy is facilitated by increased temperature. Necessary for safe use, storage, and transportation of potentially volatile materials, both open and closed tests are integral in the determination of flammability hazard of a fuel.

Flash point tests are conducted with manual or automatic instruments. Certain tests may not have both a manual and automatic method. For a manual test, the operator is controlling the test for its entire duration, including monitoring, stirring, setting the temperature, and recording the results [4]. An improperly trained operator can make a multitude of mistakes while testing, leading to drastically different results than the true characteristics of the sample. Incorrect test data can then lead to improper storage or lab conditions, creating potentially dangerous situations. With automated testing, the instrument and its corresponding software will perform the test in a controlled, calculated manner. In the case of flash point testing, automated tests merely require the user to fill the test cup and initiate the test. Therefore, the benefit of automatic flash point instrumentation is that human involvement and error is minimized. The automatic instrument will run the test via its pre-installed software, reducing human involvement in the testing process. [4]. Automatic testing produces not only produce more consistent results than manual testing, but also reduces the time needed for analysis. This improved efficiency is well-accepted by industry and is generally more cost effective than manual

methods requiring operator involvement.

The closed cup Tag flash point test (ASTM D56) is the oldest flash point method to date. For a sample to be appropriate for ASTM D56, certain requirements must be met. The sample should be a liquid with a viscosity below 5.5mm^2/s at 40℃ or a viscosity below 9.5mm^2/s at 25℃ [7]. Also, the expected flash point for the material should not exceed 93℃ [7]. In addition to fuels and oils, D56 is utilized for the solvents typically used in paints and coatings [5]. This method entails pouring the sample liquid into a precooled cup followed by heating at a constant rate. The rate of heating depends on the sample's expected flash point. If the expected flash point of a sample is below 60°C the heating rate should be set to 1℃ /min [7]. If the expected flash point is above 60℃ the rate of heating should be 3℃/min [7]. Once prepared, the ignition source is introduced into the cup, which is immediately brought to a temperature 5°C below the sample's expected flash point. The instrument's software then causes the ignition source to repeatedly ignite every 0.5℃ or 1℃. Koehler Instrument Company's Automatic Tag Closed Cup Flash Point Tester (K87700) is an automated flash point testing instrument, conforming to ASTM D56, and featuring a dual flash point detection system, the choice between gas or electric ignition, quick access to calibration parameters, and an automatic gas cut-off mechanism upon the end of the test.

Similarly, the Pensky-Martens test method (ASTM D93) is used to determine the closed cup flash point of a petroleum sample. Just as for the Tag method, specific conditions should be met utilizing the Pensky-Martens method. For example, samples must fit into a flash point temperature range, depending on the sample to be tested. For petroleum products, the expected flash point temperature should be between 40℃ to 370℃ [8]. For biodiesel, the expected flash point temperature should be between 60℃ to 190℃ [8]. Testing outside of the given temperature range is highly discouraged, as results may be inaccurate or may not meet method specifications for a given application. ASTM D93 details distinct procedures applicable to different types of fuel. One procedure, utilized for testing distillate fuels such as turbine fuel, entails filling the test cup to the inside mark first [8]. The sample is then stirred at 120 revolutions (rev)/min while experiencing a constant rate of heating (5-6℃/min) [8]. If the expected flash point is known, the ignition source is applied every increment of 1℃ if the expected flash point is less than or equal to 110℃, or every 2℃ if expected flash point is above 110℃ [8]. This application of ignition source only occurs once the temperature reaches 23℃ below the expected flash point of the sample, which is done to reduce wear on the instrument [8]. If the expected flash point is unknown, heat the sample initially to 15℃ and apply the ignition source for every 1-2℃ after the sample becomes visually viscous [8]. These two procedures both end upon ignition of the vapors, when the flash point is determined. Figure 2 below shows the K71000 Automatic Pensky-Martens Closed Cup Flash Point Analyzer. This automated instrument conforms to D93 and other related specifications. With flash point detection range of ambient to 405°C by thermocouple and ionization ring, this instrument offers software selectability, and an integrated dual fan system that directly cools the test cup and the surrounding environment.

Figure 2

K71000 Automatic Pensky-Martens Closed Cup Flash Point Analyzer

Notable open cup techniques include the Cleveland open cup method, which is designated as ASTM D92. This testing method can be used to determine flash points of all petroleum products with expected flash points above 79℃ and below 400℃ [9]. Additionally, solid petroleum products can also be measured after being heated to a liquid state. ASTM D92 states to first fill the test cup to the inside mark with sample and adjust the diameter of the test flame [9]. The heating rate is set initially to 17℃/min. Once the temperature of the sample reaches 56℃ below the expected flash point value (if known), the heating rate is decreased to 5-6℃/min. The test flame is then applied every 2℃ after the temperature reaches 28℃ below the flash point.

If the flash point of the sample is unknown, ASTM D92 instructs to initially heat the sample to no greater than 50℃. The sample is then heated at a rate of 5-6℃/min, and the test flame is applied at every 2℃ increments. The flash point is determined after a large flame appears on the surface of the sample [9]. Figure 3 below highlights the K72000 Automatic Cleveland Open Cup Flash Point Tester. This instrument provides simple automation routine for easy operation, and a fire suppression system that floods the instrument with inert gas in the event of a fire.

Figure 3

K72000 Automatic Cleveland Open Cup Flash Point Tester

In contrast to the previously discussed Tag closed cup test, the Tag open cup test, designated as ASTM D1310, is ideal for testing liquids with a flash or fire point between 18℃ and 165℃ [10]. This test is used on paints and resin solutions as well as fuels and oil as in correlation with its closed cup counterpart. The methodology is very similar to the closed cup version of the test with the main difference in the test cup. The Tag closed cup test features a brass test cup with a non-rusting metal lid [10]. The Tag open cup requires a test cup made of clear annealed glass that is heated at a rate of 1℃/min with no stirring [10]. While the two Tag tests are quite similar, the open cup features a higher range of flash point temperatures as well as a more hands-off methodology as stirring of the sample is eliminated. Additionally, the Tag open cup allows for testing with ASTM D3143, while closed cup test does not. ASTM D3143 allows for determining if an asphalt cutback has been properly prepared with solvents to meet proper flammability limits [11]. The test is conducted in the same way as ASTM D1310, but it is designed with the intent of safety precautions for asphalt materials, rather than oil or fuel.

While all the discussed test methods have been reviewed through the pre-publication process, these tests inherently contain potential sources of error. These include human error, unaccounted variations in pressure from atmospheric conditions, and "outgassing" [12]. Firstly, unaccounted variations in pressure may present error by introducing a nonstandard condition. As pressure decreases, the flash point of a petroleum product will decrease, much like boiling point. At a lower environmental pressure, molecules need a lower speed to escape from liquid to vapor. Therefore, if the pressure of the test environment is lower than atmospheric pressure, the flash point observed will be lower than an expected value. Conversely, a higher pressure yields a higher flash point value. If this deviation in pressure is left out of the report of the flash point, the true flash point is not obtained. Such a lack of precision will cause an inaccurate flash point determination and in turn an incorrect determination of the necessary storage and transport conditions. These incorrect conditions may lead to disastrous safety hazards, such as explosions and fire. These hazards can be avoided by using the conversions found in the calculation sections of the ASTM standards.

Additionally, "outgassing" is a serious source of error in the determination of flash point. "Outgassing" is the condition in a flash point in which nonflammable components of a liquid mixture act to inert the vapor space, while the gases emitted to the surroundings are ignitable [12]. Effectively, outgassing can hide the true flammable nature of the tested sample and may lead to the determination that a truly dangerously flammable sample in fact has a higher flash point or no flash point at all. This condition, much like the unaccounted variation in pressure, may cause an incorrect determination of storage conditions for potentially dangerous samples. This phenomenon is one way in which flash point testing can be improved in the future and provides a target for research. One current method to deal with the risk of outgassing samples is to determine flammability danger rating on multiple tests, rather than a single measurement.

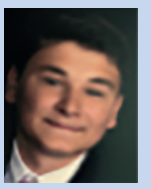
In short, these sources of error, if overlooked, can lead to mislabeling, incorrect storage of flammable samples, and possible explosions, fires, and other safety hazards.

In addition to the traditional methods, new technologies are being developed for flash point measurement. Some of these include the use of microscale systems, electrochemical sensors, and spectroscopic methods. The K24800 Automatic Microscale Continuously Closed Cup Flash Point Analyzer conforms to ASTM D6450 and ASTM D7094, while also having excellent correlation to ASTM D56, D93, D3278, D3828; IP 170; EN ISO 6379 / 3680; ISO 2719; SH/T 0768, SH/T 3077.1, SH/T 3077.2, DL/T 1354, GB/T 261, GB/T 21615, GB/T 5208, GB/T 21790. This unit uses 1 to 2 mL volume of sample while providing highly accurate results. With a temperature range of ±0.1 ℃, the instrument provides accurate, reliable measurement over a wide temperature range, while simultaneously reducing the amount of sample necessary to run individual tests.

The previously discussed ASTM D56, D92, and D93 methods were investigated to determine the effect of automatic versus

Dr. Raj Shah is a Director at Koehler Instrument Company in New York, where he has worked for the last 28 years. He is an elected Fellow by his peers at IChemE, CMI, STLE, AIC, NLGI, INSTMC, Institute of Physics, The Energy Institute and The Royal Society of Chemistry. An ASTM Eagle award recipient, Dr. Shah recently coedited the bestseller, "Fuels and Lubricants handbook", details of which are available at ASTM's Long-Awaited Fuels and Lubricants Handbook 2nd Edition Now Available (https://bit.ly/3u2e6GY). He earned his doctorate in Chemical Engineering from The Pennsylvania State University and is a Fellow from The Chartered Management Institute, London. Dr. Shah is also a Chartered Scientist with the Science Council, a Chartered Petroleum Engineer with the Energy Institute and a Chartered Engineer with the Engineering council, UK. Dr. Shah was recently granted the honourific of "Eminent engineer" with Tau beta Pi, the largest engineering society in the USA. He is on the Advisory board of directors at Farmingdale university (Mechanical Technology) , Auburn Univ (Tribology), SUNY, Farmingdale, (Engineering Management) and State university of NY, Stony Brook (Chemical engineering/ Material Science and engineering). An Adjunct Professor at the State University of New York, Stony Brook, in the Department of Material Science and Chemical engineering, Raj also has over 575 publications and has been active in the energy industry for over 3 decades. More information on Raj can be found at https://bit.ly/3QvfaLX

Contact: rshah@koehlerinstrument.com



William Streiber

Mr. William Streiber is part of a thriving internship program at Koehler Instrument company in Holtsville, and a student of Chemical Engineering at Stony Brook university, Long island, where Dr. Shah is the current chair of the external advisory board of directors.

manual testing [5]. It was determined when the tests are preformed correctly, both manual and automated testing yield equivalent results with no statistically significant differences [5]. All tests had a repeatability of 95% confidence with negligible differences within the confidence level [5]. Both methods yield consistently accurate results, yet manual testing requires considerably more labor to deliver the same values determined by an automatic instrument. Automatic testing generally requires a smaller amount of sample compared to manual tests. This is observed in the K24880 from Koehler Instrument Company Inc, which conforms to both ASTM D6450 and D7094. The results provided by this instrument correlate to both the closed Tag (ASTM D56) and Pensky-Martens (ASTM D93) tests. Normally requiring 50mL and 70mL respectively for an individual test, the K24880 allows conservation of samples and a larger number of tests to be run with the same sample volume.

Utilizing smaller sample volumes also reduces the risk of fire in a laboratory. In the case of a fire caused by measuring flash point, having less sample volume lends to easier control and extinguishment of a flame.

A summary of the test methods and requirements for each test is shown in Table 1 below.

The flash point measurement has become an essential safety requirement for flammable liquids, and various regulatory bodies, such as the United States Environmental Protection Agency (EPA) and the European Union (EU), have set standards for the safe handling and transportation of these materials.

In conclusion, flash point measurement is a critical test used to determine the flammability of liquids. From its early beginnings in the 18th century to the modern-day instruments, flash point testing has come a long way. With advancements in technology and increasing safety requirements, flash point measurement is likely to remain an essential tool for ensuring the safety of flammable liquids for years to come.

Table 1

Type of Flash Point Test	Closed or Open Cup	Qualifications to Run Test
Tag Closed Cup	Closed Cup	Sample should: 1. Be a liquid 2. Have a viscosity below 5.5mm²/s at 40℃ 3. Have a viscosity below 9.5mm²/s at 25℃. 4. Expected flash point below 93℃
Pensky-Marten	Closed Cup	Sample should: For petroleum products: 1. Have a temperature range of 40℃ to 370℃ For biodiesel: 1. Have a temperature range of 60℃ to 190℃
Cleveland	Open Cup	Sample should: 1. Have expected flash point between 79℃ and 400℃ 2. Sample could be solid or liquid. (Solid must be melted before testing)
Tag Open Cup	Open Cup	Sample should: 1. Have expected flash point of 18℃ to 165℃

Adapted from [7], [8], [9], [10]

Works Cited:

[1] ASTM Standards Development process. Standards Coordinating Body. (n.d.). Retrieved April 16, 2023, from https://www.standardscoordinatingbody.org/process-astm

[2] ISO 10093:1998. ISO. (2017, November 30). Retrieved April 16, 2023, from https://www.iso.org/standard/24991.html

[3] White, E. W. (2013). Practice of flash point determination: A laboratory resource. (R. G. Montemayor, Ed.).

[4]"What Is Flash Point Testing?" Scimed.Co.Uk, SciMed, 26 May 2020, https://www.scimed.co.uk/education/what-is-flash-point-testing/

[5]Montemayor, R.G., etc., Precision and Equivalence of Automatic Manual Flash Point Apparatus, Journal of Testing and Evaluation, January 2002

[6]Thangarasu, V., & Anand, R. (2019). Fire point. Fire Point - an overview | ScienceDirect Topics. Retrieved April 16, 2023, from https://www.sciencedirect.com/topics/earth-and-planetary-sciences/fire-point

[7]ASTM D56-16a, "Standard Test Method for Flash Point [4] by Tag Closed Cup Tester," Annual Book of ASTM Standards, ASTM International, West Conshohocken, PA

[8]ASTM D93-16a, "Standard Test Method for Flash Point by Pensky-Martens Closed Cup Tester," Annual Book of ASTM Standards, ASTM International, West Conshohocken, PA.

[9] ASTM D92-12b, "Standard Test Method for Flash and Fire Points by Cleveland Open Cup Tester," Annual Book of ASTM Standards, ASTM International, West Conshohocken, PA.

[10] ASTM D1310-01, "Standard Test Method for Flash Point and Fire Point of Liquids by Tag Open-Cup Apparatus," Annual Book of ASTM Standards, ASTM International, West Conshohocken, PA.

[11] ASTM D3143-19, "Standard Test Method for Flash Point of Cutback Asphalt with Tag Open-Cup Apparatus," Annual Book of ASTM Standards, ASTM International, West Conshohocken, PA.

[12] Gorbet, G. E., Kennedy, C., Kennedy, K. C., Kennedy, P. M., & Kennedy, J. A. (2018). Outgassing phenomenon in flash point testing for Fire Safety Evaluation. Fornesic File Analysis Institue. Retrieved April 16, 2023, from https://forensicfireinstitute.com/wp-content/uploads/2018/07/outgassing-phenomenon-in-flash-point-testing-for-fire-safety-evaluation-.pdf

Author Contact Details

Dr. Raj Shah, Koehler Instrument Company • Holtsvile, NY11742 USA • Email: rshah@koehlerinstrument.com • Web: www.koehlerinstrument.com