THE DEVELOPMENT OF FLASH POINT TESTING: A HIGHLY NUANCED AND EXACT SCIENCE

Safety is one of the most important considerations when handling various petroleum products due to their chemical nature and tendency towards flammability. The need for assessing the safety of liquid fuels, liquid lubricants, and their mixtures has led to the development of flash point testing. The flash point of a liquid is defined as the minimum temperature, corrected to a barometric pressure of 101.3 kPa, at which the vapors of the liquid will briefly ignite given a nearby ignition source. The term "flashing" of a liquid has been defined as when a flame appears and spreads itself across the vapor formed by the liquid [1]. In some asphalt samples, flame may not spread itself but be localized at the occurrence of flash point. There is a similar characteristic to flash point called the "fire point," where the flame that is generated after the ignition of the flammable vapors is sustained for at least five seconds. At the flash point temperature, the vapor is flammable enough to ignite briefly but the flame is not usually sustained for more than five seconds. Although the flame is not usually sustained at the flash point, it is still a very important temperature to recognize because even the very brief ignition of vapors can lead to catastrophic results with regard to safety in transporting and storing the liquid petroleum products. In this article, we will go over the primary methods that have been developed to test flash point and highlight what makes them different from each other. We will mainly attempt to address the question of why there are so many different flash point testers and methods and why one method cannot be used to cover every different type of flammable product.

Abel Closed-Cup Test (ISO 13736)

In the UK during the 19th century, Parliament passed the Petroleum Act in 1862, which declared that liquids with a flash point temperature below 37.7°C were flammable. This was developed due to a number of fires resulting from kerosine blending with lighter hydrocarbons. Recognizing the necessity of accurate testing for flash point of various liquids to comply with the Petroleum Act, Sir Frederick Abel designed his own apparatus, which was established by Parliament in 1879. The apparatus is a closed-cup apparatus with a brass test cup of 14 mm thickness, 55-57 mm depth, and a sample size of around 78 mL. The close-fitting cover and stirrer are also made of brass and the heating vessel is made of copper. The heating device can be anything, such as a gas flame or electric heater, that is suitable to heat the vessel at the prescribed rate. The procedure describes a heating rate of 1°C/min and a stirring rate of around 30 rpm [2,3]. The manual version of this tester is shown in Figure 1.

Tag Closed-Cup Test (ASTM D56)

The first method to be standardized by ASTM International was the Tag Test, issued in 1918 by ASTM Committee D02. The apparatus was designed by an American scientist named Charles J. Tagliabue. The apparatus is a closed-cup apparatus with a brass test cup of 0.9 mm thickness and 54.5 mm depth, a lid made of any nonrusting metal, a heater of any type, and a liquid bath made of brass or copper. The test procedure calls for a heating rate of 1°C/min for lower flash points or 3°C/min for higher flash points. A sample size of at least 50 mL is required. It is important to note that there is no stirring in this method [2,4].

Cleveland Open-Cup Test (ASTM D92)

The Cleveland open-cup test was approved by ASTM in 1921. This apparatus consists of a test cup usually made of brass, a heating plate (as opposed to liquid bath), and either a gas or electric heater. The test cup does not have a uniform thickness, but rather the sides are 2.25-2.5 mm thick and the base is 2.8-3.5 mm thick. The procedure is to keep the heating rate at 5 to 17°C/min and then decrease the heating rate to 5 to 6°C/min when the test specimen is around 56°C below the expected flash point. This method does not involve any stirring and the sample size is around 70 mL [2,5].

Figure 1. Manual Abel Closed Cup Tester (Koehler Instrument Company).

Flash and Fire Point of Asphalt by Cleveland Open Cup (COC) Tester (ASTM D8254-19)

Published by ASTM in June 2019, ASTM D8254 describes the determination of flash and fire point of skin-forming and non-skin-forming asphalts by a manual or automated Cleveland open cup apparatus. It is applicable to products with flash points above 79 oC and below 400 oC. Determination of the flash point of asphalt samples that form a skin during the course of the test presents unique challenges. ASTM D92 suggests skimming or removal of the skin prior to passing the test flame over the test sample surface. Using a technique for prevention of skin-formation which was first introduced by ASTM under an Appendix of D92 produces flash point results which are lower than those obtained by skimming or removal of the skin. This technique, embodied in ASTM Method D8254, provides added safety and convenience particularly for those performing the D92 test on asphalt samples manually. Under D8254, asphalt sample is poured into a COC flash cup that is previously prepared for the test with a single-holed qualitative filter paper and restraining ring in its base. The test procedure is generally similar to D92.

Pensky-Martens Closed-Cup Test (ASTM D93)

In 1921, ASTM also added the Pensky-Martens Closed-Cup Test, which was based on an apparatus designed by Adolf Martens and Berthold Pensky in Germany. The apparatus consists of a test cup usually made of brass (55.75-56 mm depth, 1 mm side thickness, 2.29-2.54 mm base thickness), a brass cover and shutter, a flame-type or electric resistance-type heater, an air bath, and a stirrer which is mounted in the center of the cover. There are three different Procedures (A, B, & C) that can be used depending on the type of specimen that is tested. Procedure C is specifically for biodiesel and only describes an automatic tester. Each procedure has its own stirring and heating rate and as opposed to previous methods, all procedures start stirring while the test specimen is heating and then stop stirring whenever testing for the flash point. This method requires around 75 mL of sample [2,6]. An automatic version of the tester is shown in Figure 2.

Tag Open-Cup Test (ASTM D1310)

The Tag Open-Cup Test was adopted by ASTM Committee D01 in 1952. This method is open-cup, unlike D56, but also differs from that method by having a test cup made of clear, annealed glass. The test cup here has a depth of approximately 47.6 mm the heating rate generally stays at about 1°C/min with no stirring. The sample in the cup is about 90 mL [2,7].

Small-Scale Closed-Cup Test (ASTM D3828)

In 1979, ASTM Committee D02 approved the use of a “small-scale” tester which allowed for the use of a smaller sample size. The sample size here can be either 2 or 4 mL and the test cup has a depth of only 9.7-10 mm and a diameter between 49.4 and 49.7 mm. The test cup is made of either aluminum alloy or another metal with suitable conductivity. These dimensions and the procedure in this method allow for thermal equilibrium testing of flash point, where the vapor and liquid are at the same temperature during ignition. This method also has a procedure for determining flash/no-flash at a specified test temperature and a separate procedure for determining flash point more traditionally [2,8].

Continuously Closed-Cup Test (ASTM D6450/D7094)

The method using a continuously closed-cup apparatus was approved by ASTM in 1999. The apparatus contains a solid brass lid and a sample cup made of nickel-plated aluminum or another metal with similar conductivity. The cup has a volume of 4 mL and accommodates only 1 mL of sample for the test. Because of the sample size, it has been much safer to conduct compared with the sample sizes in excess of 50 mL in previously approved methods. The ignition source is a high voltage electric arc and a pressure transducer is used to determine the flash point. The flash point is recorded when there is a sudden increase in pressure inside the cup of at least 20 kPa above barometric pressure. There is also an air supply which introduces about 1.5 mL of air into the test cup after each ignition. A method known as the modified continuously closed-cup test (ASTM D7094) was introduced in 2004. This method uses the same apparatus but it features a 7 mL sample cup with a sample size of 2 mL and also uses a different heating rate [2,9].

Why are there many different flash point tests?

The section above is not meant to be an exhaustive list of all the different methods in use. There are a few more that are widely used, and more information on these can be found in *The Practice of Flash Point Determination: A Laboratory Resource* published by ASTM International [2]. However, from the sections above, it is clear that the different methods that have been developed all have detailed parameters that are unique to each, such as test cup material, test cup dimensions, heating rate, stirring rate, sample size, and so on. This is one of the reasons why flash point testing is not a “one size fits all” endeavor. There are test specimens which would benefit more from a certain set of operating conditions than another. For example, a very viscous liquid might be better tested in a method with a faster stirring rate. This is why some of the methods outline in their scope that they are most useful for liquids within a specific viscosity range.

One of the most important considerations in flash point testing is using an open-cup vs. closed-cup apparatus. The reason both open-cup and closed-cup tests exist is to attempt to recreate certain conditions that may be encountered in the real world. Closed-cup testing is meant to simulate what would happen if an ignition source were introduced accidentally into a sealed container or other type of closed system containing the test specimen. Open-cup testing is meant to simulate the event of either a spill of the test specimen in an open area or to simulate storage/transport conditions in an open system. Regarding the methods of the tests, there is not a significant difference in procedures when looking at open vs. closed-cup testing and there are no special considerations to be made when using one method or the other. What is important to understand is that open-cup tests will always give a higher flash point than closed-cup tests for a given substance. This is because in an open-cup test, a significant amount of flammable vapor that emerges from the test specimen is able to leave the immediate area above the liquid surface. At the time of ignition, there is a lower concentration of flammable vapor in the test cup then there would be in a closed cup. In closed-cup testing, the vapor is not given much chance to escape and there will always be a higher concentration of flammable vapor in the test cup, which means that it does not require as much heating to reach a temperature where the vapor will ignite. This phenomenon also results in closed-cup tests usually having better precision than open-cup tests, which is why closed-cup tests are usually recommended in specifications for products [10].

Another consideration in flash point testing that has developed over time is the option of using manual vs. automatic testers. Back when these methods were first developed and approved, all of the testers were manual, which meant the operator had to execute every step of the procedure by hand and also needed to determine a flash by eyesight. Most of the methods now have automated testers that have been designed according to the materials and dimensions outlined for the manual apparatus. This development came to fruition largely due to safety concerns in addition to the operator’s convenience. With automated testers, the operator no longer needs to apply the ignition source and is free to do other tests in the lab during the brief time that the test is taking place in the automated tester. Most of the methods specifically state that an automated tester is acceptable to use as long as it is able to perform all of the detailed and specific steps from the manual procedure and There have also been numerous studies and tests which have shown that there is no statistically significant difference between the results obtained by manual testers and their automated counterparts [2]. These are the reasons why automated testers have become very popular over the years. However, in cases of dispute, it is typically preferred to carry out a test with a manual apparatus so that the operator can confirm that every step took place correctly and that an appropriate flash was observed at a certain temperature [10].

Figure 2. The latest automatic Pensky-Martens Closed Cup Tester (Koehler Instrument Company).

A note should also be made about the question of whether results from one method can be directly compared or correlated with results from another method, or if methods can just be substituted between each other. Due to the fact that the various apparatus designs and procedures in each method are very specific and they are each unique, it is not recommended that two different methods be compared directly. Most of the methods under the jurisdiction of ASTM Committee D02 begin with the following message which addresses the issue:

“Flash point values are a function of the apparatus design, the condition of the apparatus used, and the operational procedure carried out. Flash point can therefore only be defined in terms of a standard test method, and no general valid correlation can be guaranteed between results obtained by different test methods, or with test apparatus different from that specified.” [4-6]

This is the reason why whenever a value for flash point is listed on a specification or datasheet, it should always be listed along with the method that was used to obtain the value.

How do we know which method to use?

When we are trying to decide which method to use for a specific product, it is very important to know how that product is classified and to know as many physical characteristics about that product as possible. Each method will usually outline which different types of test specimen it can accommodate and also it may give information about testing within a specific range of flash point or within a specific range of viscosity. These guidelines which are on the method itself can be used to help make a choice on which method to use. While the methods themselves can be referred to, it is usually known exactly what type of product is being tested. In this case, the operator should refer first to the specification for that product (usually published by ASTM International). The specification will list the value of the minimum flash point that the product can have and will also list the method that should be used to get that value. If a product with a certain specification is being tested, then it is not recommended to replace the method outlined in the specification with another method, unless there are very special circumstances or there is approval for this to happen. Not all specifications contain a minimum required flash point and there are also some specifications where certain grades have a minimum flash point and some other grades do not. These are usually the products that have the lowest flash points and are normally quite volatile, such as liquefied petroleum gas (LPG) and automotive spark ignition fuels [2].

Here we will go over some of the major classes of products and discuss which methods have been approved for them. The methods that have been approved for diesel fuels (specified in ASTM D975) are ASTM D93, D56, and D3828. The reference method is D93 and the other two have been approved as alternate methods. ASTM D3941, which is a closed-cup equilibrium method, may be acceptable in certain cases to better understand the flammability characteristics under controlled lab conditions. For normal fuel oils (specified in ASTM D396), ASTM D93 is the reference method for all grades and ASTM D3828 has been approved as an alternate for all grades. ASTM D7094 can also be used for all grades. ASTM D56 can be used as an alternate in Grades 1 & 2. For kerosene (specified in ASTM D3699), ASTM D56 is the reference method and both ASTM D3828 and D7094 can be used as alternates. For lubricating oils, the significance of flash point is mainly about determining contamination by more volatile substances, as opposed to determining fire hazards. ASTM D92 is mostly used as the reference method in lubricating oil specifications but closed-cup methods (ASTM D93 and D56) can be used as well. One such example is the U.S. Department of Transportation, which instead considers ASTM D93 to be the reference method for lubricating oils. When choosing between one of the closed-cup methods, the choice will largely depend on the specific physical properties of the test specimen. More information on specifications not mentioned here can be found in *Significance of Tests for Petroleum Products,* published by ASTM International, and also in Appendix 5 of reference [2]. This discussion is meant to serve as a guide but the specifications themselves should always be the primary source for the most up-to-date information [2,11]. When looking at the various specifications, it is clear that ASTM D93 is one of the most popular methods, especially when considering fuels. We can also see that for certain fuels, ASTM D7094 has been approved as an alternate method to D93. This is because there have been experiments which show very high correlation between D7094 and D93, with results from a test shown in Figure 3 [12]. The continuously closed-cup methods were developed not as a way to test new types of products, but more as a way to test our existing products in a safer and more convenient way. These newer methods allow for fully automatic testing and much smaller sample sizes than the traditional methods. As of now, ASTM D7094 has only been approved for fuel oils and a few other types of fuels, but it has not been approved yet for lubricants. If more studies are done that can show strong correlation between the newer continuously closed-cup methods and other more traditional methods, then D6450 and D7094 could potentially end up getting approved on a wider variety of specifications. If this happens, then there is a potential for an entire new generation of safer and more efficient flash point testing for the petroleum industry.

Hopefully, this article can provide a good reference for people both new to this science and experienced with these tests, and can also clear up some confusion that may arise in discussions. Flash point testing is not going anywhere and it is as important today as it always was before. It may even be more important today considering the current development of new types of fuels and lubricants to conform to stricter environmental and safety regulations. It is clear that flash point testing is a constantly changing and evolving field, with methods spanning from ISO 13736, created in the late 19th century, all the way to ASTM D7074 with its inception in at the turn of the 21st century. Given this long and eventful timeline, it is fairly certain that more methods to determine the flash point of flammable liquids will be developed and approved in the future. For anybody in the petroleum industry, keeping up with the developments in flash point testing will be essential. However, in order to fully understand the new developments, it will be imperative to always refer back to the basic guiding principles upon which flash point testing is built.

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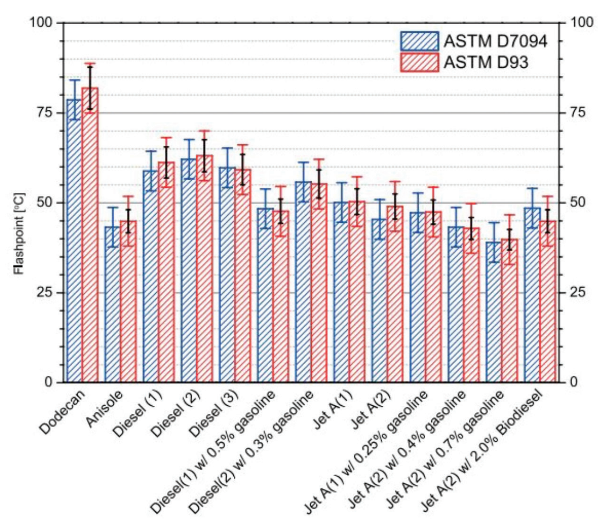

Figure 3. A chart of the average values obtained from multiple participants in a round robin test (RR-D02-1581) conducted by ASTM International. The colored bars are the reproducibility values from this round robin test and the black bars are the reproducibility values calculated from ASTM D93 [12].

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