THE SIGNIFICANCE OF EVALUATING THE HIGH AND LOW TEMPERATURE CHARACTERISTICS OF PETROLEUM DERIVED PRODUCTS

Raw petroleum, or crude oil, is typically refined into a wide range of products used to fuel vehicles, heat buildings, and produce electricity. In the US, petroleum usage accounts for a significant portion of the country's total annual energy production, with an average consumption of 18.12 million barrels per day in 2020 [1]. Gasoline and distillate fuel oil, which includes diesel fuel and heating oil, are the most commonly used petroleum products in the US, which should not come as a surprise considering that about two-thirds of the US' petroleum consumption stems from the transportation sector [1]. Lubricants are another category of petroleum products used extensively in transportation, ensuring proper operation of moving surfaces in mutual contact and protecting these components from friction and wear.

However, petroleum products are known to experience deterioration and performance declines under extreme temperature conditions. The volatility and flammability of petroleum products also makes them susceptible to accidental combustion at sufficiently high temperatures [2]. Whereas, at low temperatures, solidified wax can begin to form from diesels, which can cause fuel filter plugging or fouling. In addition, low ambient temperatures can severely hamper the flow characteristics of lubricants, which increases their viscosity and compromises lubricant functionality [3]. In order to avoid these complications, various types of petroleum testing equipment are used to determine the flash, cloud, and pour points of petroleum products, so that appropriate measures can be taken to ensure their performance.

Figure 1: The ignition of ethanol fuel at a sufficiently high temperature [5]

Assessing the Flammability of Volatile Fuels at High Temperatures

Due to the volatile nature of flammable and combustible liquids, it is vital to determine the flash point of these products. Flash point is defined as the lowest temperature at which the vapor of a volatile liquid will briefly ignite, or flash, given the presence of an ignition source [2]. This is crucial information to have when handling volatile substances during transportation or storage, so that appropriate precautions can be taken to avoid accidental ignition. Also, flash point is a characteristic that is used to differentiate between flammable fuels, such as gasoline, and combustible fuels, such as diesel. Flammable fuels have a flash point less than 100°F (38.8°C), while combustible fuels have flash points that exceed that temperature [4]. The fire hazard and explosive risks associated with volatile fuels requires the determination of minimum flash points. Flash point can also be used to indicate the presence of highly volatile and flammable materials in a conventionally nonvolatile and nonflammable substances.

Flash point is often found as a parameter to be satisfied in numerous national and local regulations regarding the transportation, storage, and use of flammable and combustible liquids. For example, the National Fire Prevention Association (NFPA) have developed classifications that use flash point to indicate the relative hazard of liquids [6]. The measurement of flash point for volatile liquids is conducted in accordance to ASTM Test Methods D56, D93, D3278, or D3828, depending on the viscosity of the liquid, the range of the flash point, and whether the liquid contains suspended solids or tends to form a surface film. Also, the ASTM Committee D02 on Petroleum Products and Lubricants uses flash point as one of the requirements for their 11 fuel specifications, 4 specifications for lubricating oils and hydraulic fluids, and 1 miscellaneous specification [6]. Beyond the petroleum industry, the paint and coatings industry frequently use flash point in their regulations for the shipping, handling, and transportation of paint and coating products. Typically, ASTM D56, D1310, and D3941 are used for these applications over ASTM D93, due to the difficulty of cleaning paint residue from the instrument after flash point measurement [7,8,9].

There are two primary methods for flash point measurement, which are known as the open cup test and closed cup test.

The open cup test involves placement of a liquid sample in an uncovered container that is open to the environment [10]. Above the opening of the exposed cup, an ignition source is used to increase the sample's temperature towards its flash point. The measured flash point can vary depending on the height of the flame above the surface of the liquid sample. In contrast, the closed cup test differs in that it uses a closed vessel, instead of an open one [10]. As a result, the ignition of vapors occurs within the closed vessel at a much closer proximity to the sample. Typically, closed cup tests are preferred over their open cup counterparts, as they tend to yield lower flash points due to the closer proximity between the ignition source and liquid sample. It is common practice in the industry to label the minimum flash point of combustible liquids on the lower side in order to err on the side of caution. The K71000 Automatic Pensky-Martens Closed Cup Flash Point Tester, manufactured by Koehler Instrument Company, is a commercially available instrument for the flash point determination of biodiesels, distillate fuels, new lubricating oils, and residual fuel oils [11]. The instrument conforms to specifications of ASTM D93 Procedure A, B, and C, along with other closed cup standards [12].

Several other test methods exist for flash point determination, such ASTM D56, D92, D3828, and ISO 13736. The Tag test, as specified in ASTM D56, is a closed cup test method that is meant to test low viscosity fluids, with viscosities lower than 5.5 mm^2/s at 40°C or 9.5 mm^2/s at 25°C, and flash points below 93°C [7]. The Cleveland test, which is outlined in ASTM D92, is an open cup test designed

Figure 2: The K71000 Automatic Pensky-Martens Closed Cup Flash Point Tester, capable of measuring flash point as per ASTM D93 [11]

Figure 3: The formation of solid wax crystals from diesel use at cold temperatures, leading to the plugging of the fuel filter [19]

Figure 4: The K77000 Automatic Cloud and Pour Point Analyzer, which is capable of measuring both cloud and pour point [20]

to measure the flash point and fire point of petroleum products, excluding fuel oils, with flash points between 79°C and 400°C [13]. ASTM D3828 details a small-scale closed cup test that only requires 2-4 mL of a sample, as opposed to ASTM D93, D56, and D92, which require sample sizes of 75 mL, 50 mL, and 70 mL, respectively [7,12,13,14]. This test is applicable for a variety of petroleum products and biodiesel fuels at temperatures ranging between -30°C and 300°C and has a test duration of only 1-2 minutes. In contrast, the Abel test, which is standardized as ISO 13736, is a closed cup test that covers a narrow range of combustible liquids with flash points between -30°C and 75°C, and limited precision only for liquids between 8.5°C and 75°C [15]. Due to the variety of flash point test methods that exist and the different results that can be obtained from these tests, it is imperative to use the appropriate test method for flash point determination as cited in the respective specification or regulation [6]. Similarly, testing for operability parameters at low temperature, such as cloud point and pour point, is important for petroleum products used in colder environments.

Determining the Low Temperature Properties of Fuels and Lubricants

In colder climates, such as the northern parts of the US, Europe, and Canada, petroleum products are expected to function under extreme negative temperatures, especially during winter months. Consequently, the determination of the low temperature properties, such as cloud point and pour point, of various fuels and lubricants is crucial to evaluating their suitability for these conditions. Cloud point refers to the temperature at which wax, or paraffins, begins to separate from the oil and develops a cloudy appearance in the diesel [16]. This occurs in biodiesels as well, with the formation of biowax as the precipitate. The solidification of waxes causes the diesel fuel to thicken and can potentially clog fuel filters and injectors in engines. In addition, the accumulation of precipitate on cold surfaces can form emulsions with water and lead to fouling in pipelines and heat exchangers [17]. On the other hand, pour point refers to the lowest temperature at which an oil becomes too viscous and loses its flow characteristics [18]. Lubricants that drop below their pour point will restrict oil flow to bearings and other mechanical components. As a result of inadequate lubrication, the excessive friction within the system could lead to component damage or complete engine failure [3].

The complications that may result from the selection of fuels or lubricants with poor low temperature characteristics necessitates the measurement of the cloud point and pour point. These two characteristics are often measured together, as they both serve as important indicators of practical performance in automotive applications at low temperatures [16]. The K77000 Automatic Cloud and Pour Point Analyzer, developed by Koehler Instrument Company, is an example of an instrument that is capable of both cloud point and pour point testing in a single unit [20]. The instrument features an interchangeable wireless head for automatic determination of cloud point via the optical detection stepped cooling method (ASTM D5771) and automatic determination of pour point via the automatic tilt method (ASTM D5950) [21,22].

Conclusion

Assessing the thermal properties of petroleum products at high and low temperatures is imperative for the development of industry-wide standards for storage, transportation, and application of fuels. The measurement of the cloud point of diesels and biodiesels ensures that the appropriate fuels are selected for certain cold temperature applications, to avoid plugging and fouling caused by the formation of wax precipitates. Similarly, having the knowledge of the pour point of a lubricant is crucial in selecting the right lubricant to maintain its lubricity even at the coldest temperatures. Beyond the factors of product choice, these low temperature properties can be used to determine the appropriate additives needed to improve the functionality of particular products in extreme temperature conditions. Lubricity-enhancing low temperature diesel fuel additives are to improve the cold flow characteristics of diesel fuels and suppress the gelling effect of paraffins in diesel [3,23].

When dealing with volatile substances, such as flammable and combustible fuels, the measurement of flash point is critical for safety. Ensuring that certain fuels are stored, transported, and used at temperatures well below their respective flash points is necessary to avoid the catastrophic occurrence of a fire or explosion. Evaluating the lower flammability limits of volatile liquids with the proper test method and instrumentation is necessary in the modern fuels industry. Commercial petroleum derived products must have their flash points determined in order to comply with the flash point requirements outlined in various product specifications and regulations for flammable and combustible materials. Similarly, this principle applies to the determination of low temperature characteristics. Acquiring accurate measurements for the cloud point, pour point, and flash point of commercial petroleum products is integral to ensuring consumers are able to choose the appropriate product for their intended use at specific operating temperatures.

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