RECENT ADVANCES IN THE REALM OF CLOUD POINT AND POUR POINT TESTING SPECIFICALLY AS IT RELATES TO BIOFUELS

Over the next 30 years, biofuels, including biodiesel and fuel ethanol, are expected to undergo an 18% rise in production, with the possibility of up to 55% in growth if crude oil prices continue to inflate [1]. Biofuel has proven to be an efficient and effective petroleum product substitute with numerous environmental benefits. However, one argument against biofuels is that their performance may be compromised in low temperature conditions.

Measuring properties such as the cloud and pour points of a biofuel can help to quantify its cold-weather characteristics. Understanding these properties and their effect on the biofuel sample is essential for the safe use of the product. Cloud point testing identifies the temperature in which a fuel begins to appear cloudy as solidified wax begins to form. Conversely, pour point testing identifies the point at which a liquid sample ceases to flow. Both points indicate a temperature at which the biofuel will stop performing as intended, either because the now-solidified wax changes the fuel into a two-phase system as opposed to its original single-phase system, or because the flow of the biofuel has halted. Under extreme temperatures, biofuels have been shown to be impractical for most low-temperature applications due to biofuel's tendency to have a high cloud point and pour point [2].

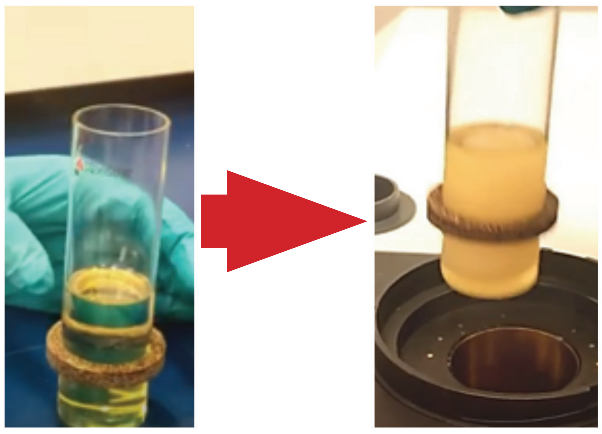

Figure 1a (Left). Freezing of Sample from Pour Point Test

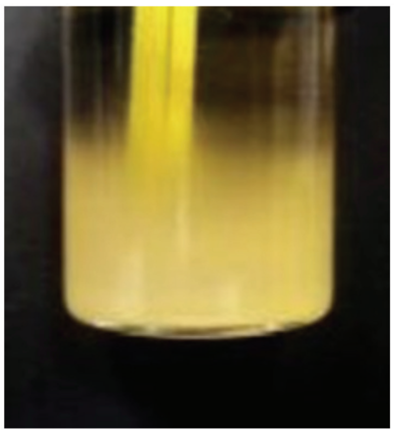

Figure 1b (Right). Formation of crystals in Sample from Cloud Point Test

Koehler Instrument Company's Automatic Cloud and Pour Point Analyzer, shown in Figure 2, is an automated test system capable of determining the cloud point of a fuel via optical detection and the pour point of a fuel using an automatic tilt method. ASTM D5771 is the test method that describes the detection of cloud point. In this test, the test specimen is constantly monitored by a reflective optical system which is composed of an optical fiber made light emitter and light receiver. Once the optical system detects the presence of solid wax, the temperature within 0.1°C is recorded [3]. The pour point is measured using the automatic tilt method which is in accordance with ASTM D5950. For this method, the test specimen is examined at 1°C or 3°C intervals using a light emitter and light receiver to detect any movement [4].

Figure 2. Koehler Instrument Company Automatic Cloud and Pour Point Analyzer [5]

A typical biofuel, such as biodiesel or fatty acid methyl ester (FAME), has a chemical structure similar to the one depicted in Figure 3. FAME fuels are produced by a transesterification reaction between ethanol and animal fat or vegetable oil. In the presence of a catalyst, the resulting product is a mixture of fatty acids, esters, and glycerols. After a cleaning step, the fatty acid esters are utilized for biodiesel fuel. The long alkane chain resembles the structure of typical petroleum diesel which allows biodiesel to perform similar functions in practice.

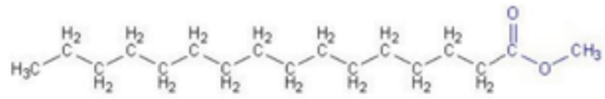

Figure 3. Typical Chemical Structure of Biodiesel [6]

Often, as a direct result of the production of biodiesels, these fuels show poor cold weather properties such as cloud point and pour point. Moreover, additional issues arise with biodiesel usage at low temperatures due to a biodiesel fuel's low sulfur content. These fuels have a higher affinity to water than traditional diesel. The high sulfur content helps diesel fuel by keeping the composition mixed evenly. This absence causes a greater potential for icing of water [7]. Because water freezes at a relatively high temperature compared to the alkanes in the fuel, before the fuel reaches its cloud point, frozen water can cause a plethora of issues including corrosion of components and engine sputtering. Another major reason biodiesel shows poor cold weather operability is due to the saturation of the alkane chain in a fuel. The average degree of unsaturation, or the number of double bonds plus aromatic rings in a fuel, has been shown to negatively correlate with cloud point [8]. The long alkane backbone of a fuel has a high molecular weight and when the alkanes are cooled, they become supersaturated, resulting in the precipitation of less soluble flat plate-like wax crystals. It is common that when wax continues to accumulate, an impermeable mass that can melt together forms [9]. Although there is no specific bias listed in the ASTM D5771 or ASTM D5950 documentation, based on regular diesel fuel results, a typical standard to follow to ensure safe use of the fuel for the cloud point is a value less than -10°C and for the pour point a value less than -30°C. Table 1 lists the cloud point and pour point measurements for biodiesel derived from different oils and it can be seen that none exhibit values within the standardized range for both properties. This makes fuel additives a necessity to reach these crucial thresholds.

Table 1. Cloud and Pour Point Values for Biodiesel Derived from Different Oils [10]

Vegetable Oil	Cloud Point (°C)	Pour Point (°C)
Corn	-1.1	-40.0
Cottonseed	+1.7	-15.0
Peanut	+12.8	-6.7
Rapeseed	-3.9	-31.7
Sesame	-3.9	-9.4
Soya bean	-3.9	-12.2
Sunflower	+7.2	-15.0
Tobacco oil	-7.8	-14.0
Tomato oil	-8.9	-16.1

As temperatures decrease in the winter months, users and manufacturers must consider the cold weather properties of their fuel. But, why are these properties important? When ambient temperatures approach the cloud point of a fuel, start-up and operability issues can arise. At the cloud point temperature, engine obstruction is the top concern. Some other concerns that begin to occur when the temperature reaches the cloud point of a fuel are injector coking, severe engine deposits, filter gumming, and piston ring sticking [11]. If temperatures continue to decrease, the cold filter plugging point (CFPP) will be reached. The CFPP is the lowest temperature a fuel can freely flow through a filter in a diesel engine before clogging. When an engine becomes clogged vehicle performance is greatly hindered. A few common occurrences that result from a clogged fuel filter include poor acceleration, strong exhaust odors, frequent engine stalling, and even the complete stopping of the engine. If temperatures continue to fall the fuel will continue to solidify until the pour point is reached. A fuel should never be stored in an environment where temperatures can reach the fuel's pour point as after the fuel solidifies it can be incredibly difficult to re-liquify the fuel. Although the pour point of a fuel should always be considered, system failures begin to occur once the cloud point is reached. Once the cloud point of a fuel is reached, there is a high chance of system failure. The most common cause, as previously mentioned, is clogging of the diesel filter by the solidified wax formed at the cloud point and beyond. This is unlike lubricants, which can still perform adequately at the cloud point but especially lose performance at the pour point. If a lubricant were to have an insufficient pour point, the lubricant would congeal to a near solid state under low temperatures, preventing lubrication from reaching all parts of the machine. Normal operation of most machines generates enough heat for the lubricant to spread enough in its liquid form this to be a non-issue. However, during startup, the lack of lubrication will cause excessive wear on the under lubricated components of the system. Increased friction due to under-lubricated parts will also generate an extreme amount of heat, so once lubrication flow begins the lubricants may break down and lose their useful properties after coming into contact with that heat leading to a ferocious cycle resulting in the entire system becoming under-lubricated [12]. Components being dysfunctional for just a few seconds can cause severe problems and lead to a loss of large amounts of money due to the high costs of industrial machinery. In order to prevent system failures and to save money on repairs or replacements, it is crucial to understand the cloud point and pour point of your fuel and lubricant.

To increase cold weather operability of fuels, pour point depressants are utilized. As temperatures lower to the cloud point and then further to the pour point, the individual paraffins from a fuel's composition each begin to gel. When the gel molecules come in contact with each other, they clump together in a matrix formation. Many pour point depressants are made from polymethacrylates. To understand the chemical structure of polymethacrylates, we must look at an ester group's structure, which is shown in Figure 4. Polymethacrylates consist of an ideally short alkane backbone with ester groups attached periodically along the backbone, from the R position of the ester, and a long alkane chain connects to the R' position as seen in Figure 5 [13]. These polymethacrylates intersect wax molecules, bordered by the yellow dots, and attach to them to prevent the clumping that will lead to the eventual failure of the system. A visual representation of the process can be seen in Figure 5.

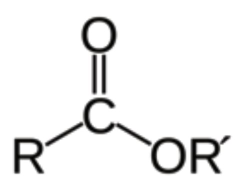

Figure 4. Ester Group Structure

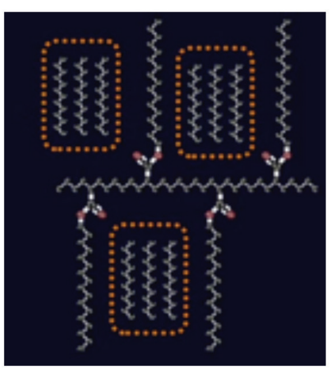

Figure 5. Polymethacrylate Wax Prevention [13]

In this study from early 2021, a pour point depressant known as fatty alcohol polyoxyethylene ether was used to alter the cold flow properties of a biodiesel sample [14]. The measured properties for cloud point, cold filter plugging point, and pour point for a biodiesel sample with and without additives are shown in Table 2 and Table 3. The pour point depressant (FAPE) is shown to lower all required properties successfully. While it does have a significantly greater effect on the cold filter plugging point and pour point of the biodiesel, the lowered cloud point value is still insufficient. In addition, the study showed that the pour point depressants have the property of inhibiting the aggregation of crystals, which in turn reduces the crystal size and shape, for example from plate-like to needle-like, which is also incredibly beneficial for improving the low-temperature performance of the fuel [14].

Table 2. Biodiesel Sample B20 Property Values Without Additives [14]

Properties	ASTM D7467	B20
CP (°C)	-	-2
CFPP (°C)	-	-4
PP (°C)	-	-14

Table 3. Biodiesel Sample B20 Property Values with a Pour Point Depressant [14]

Properties	B20 + PPDC-FAPE7
CP (°C)	-6
CFPP (°C)	-14
PP (°C)	-33

Testing for these key cold flow properties is of the utmost importance when a fuel is being used in freezing temperatures. If these properties go unchecked, it can be detrimental to the machinery. The costly consequences of the negligence of the cloud point and pour point is not worth how quickly testing can be done. Additionally, measuring the cloud point and pour point is now made simple with the new automated technologies in use. Be sure to check for these pivotal values of your desired fuel or oil the next time you approach operating machinery in extreme cold weather conditions.

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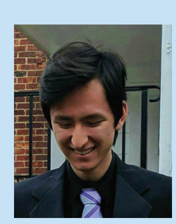

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