eraflash & Liquid Waste

Safety without compromise:

Why continuously closed cup flash point analyzers are the definitive standard for liquid waste applications.

Introduction

The flash point is one of the oldest parameters measured for petroleum based products, dating back to as early as the 1860's. A flash point is defined as the lowest temperature at which the vapors of a volatile material can be ignited when given an external ignition source. It is used as a safety indicator – the lower the flash point, the higher the flammability risk. According to the specifications of modern petroleum-based products a minimum flash point of 38°C for jet fuel (ASTM D1655) or up to 55°C for diesel (ASTM D975, EN 590) is required to allow for the safe handling of these liquid fuels. For fuel testing the operator desires a precise test result. Not only to comply with the fuel specification, but also because the closer the flash point can be adjusted to the specification limit (without the risk of exceeding it), the more profit is achieved with the product.

Apart from petroleum-based products, the flash point is also an essential parameter for transport regulations, recycling and waste management, for which there is an ever-increasing demand in our modern society with limited resources. The main task for liquid waste flash point testing is to assign the sample to a flammability category. The actual limits and category names may slightly differ between authorities,. The table below shows the current categories as defined by US-OSHA (Occupational Safety and Health Administration) and EU-CLP (Regulation for Classification, Labeling and Packing):

US-OSHA	EU-CLP	Flash point	Initial boiling point	Classification
Category 1	Category 1	< 23°C	≤ 35°C	extremely flammable
Category 2	Category 2	< 23°C	> 35°C	highly flammable
Category 3	Category 3	23°C to 60°C	> 35°C	flammable
Category 4	-	60°C to 93°C	> 35°C	flammable

Figure 1: Categories of hazardous materials

A typical example for category 1 with a boiling point of < 35°C would be something similar to LPG, which is hardly found as liquid waste under normal circumstances. There are two questions about liquid waste which the flash point measurement answers:

1. Is my sample highly flammable?
2. If this is not the case, does it have a flash point above 60°C?

In cases of doubt or if the flash point is found to be at a limit, the lower category (higher flammability) is assumed for safety reasons. In this regard, the two applications fuel vs. waste are very different. Of course a lower category makes transport and handling of waste more hazardous and therefore expensive, but not impossible. An off-spec flash point renders jet fuel or diesel pretty much useless, because it cannot be sold at all.

The flash point of unknown samples

While for fuel applications the sample is homogeneous and its flash point is approximately known prior to the measurement, this is not the case for waste samples. It is possible to encounter highly volatile wastes like gasoline or solvents, non-volatile used oils, suspensions or even aqueous solutions which may not even exhibit a flash point at all. Such samples may exhibit a flash point anywhere from -40°C up to 250°C.

It is ironic that the flash point as a parameter is used for risk assessment, while the flash point measurement itself can pose considerable risks, because it involves:

- Flammable materials
- Open ignition source
- Hot surfaces
- Harmful fumes
- etc.

Only in rare cases an apparatus malfunction is responsible for fire accidents in the lab. In the vast majority such accidents are caused by human error, e.g. a highly flammable sample is measured by mistake because the user mixed up the diesel sample container with another one containing gasoline. That risk – getting highly flammables into the analyzer – can be reduced for fuel measurements, but is unavoidably present for liquid waste due to the very nature and variety of these samples.

Therefore, the most important aspect of liquid waste flash point measurements is not having a good precision (it is a “nice-to-have” nevertheless), but to ensure safety throughout the whole measurement process. In other words – when the author of this application note interviewed a lab manager working in a waste management company about his first and foremost suggestion for improving flash point testing, he said:

“I wanna see less explosions in my lab.”

That is a reasonable request. One approach could be using an automatic fire extinguishing system, and some Pensky-Martens (ASTM D93) flash point testers are in fact equipped with such features. But why not use a test method designed to exclude the formation of an open fire in the first place? The danger when testing potentially highly flammable materials is that the test specimen catches fire and keeps burning due to continued supply of oxygen. 70 mL of fuel on fire produces large quantities of heat, and is difficult to extinguish, so it can damage the equipment in mere seconds. Not to mention that an uncontrolled fire quickly leads to severe disasters in any lab.

Continuously closed cup flash point test methods

The modern MCCCFP test method (Modified Continuously Closed Cup Flash Point) ASTM D7094 has been designed to cope with these main challenges:

- A sample volume of only 2 mL is required. Less hazardous material = less risk
- The cup is *continuously* closed during the measurement. Oxygen is immediately consumed during the flash = no continuous fire is possible.

These two advantages make D7094 the uniquely suitable test method for waste applications. And apart from the fire hazard, the small sample volume and thermal mass in general additionally allow for rapid cooling prior to the actual measurement. A successful ignition requires not only sufficient oxygen in the sample cup head space, but also a sample concentration within the substance-specific flammability limits, see the figure below:

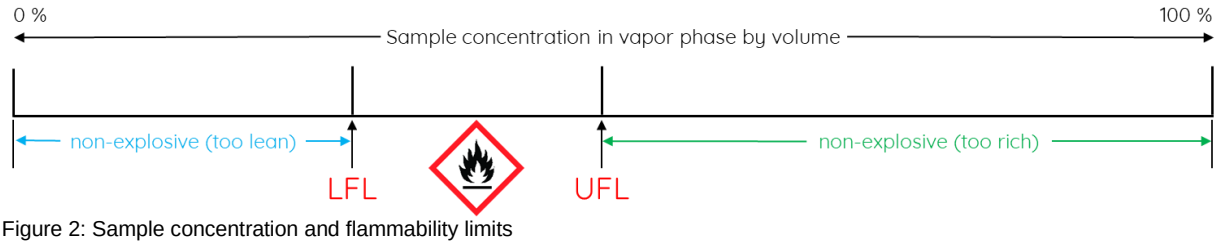

Figure 2: Sample concentration and flammability limits

For normal fuel samples with a flash point between 30°C and 70°C, e.g. diesel, the concentration in the vapor phase is far below the lower flammability limit at room temperature. During every flash point measurement the sample is slowly heated to increase the concentration until the lower flammability limit (LFL) is reached. For highly flammable substances, even the upper flammability limit (UFL) can already be exceeded at room temperature. Meaning that any ignition done at room temperature will either cause a violent reaction (a fire out of control), or, in extreme cases, may even choke the flash point due to oversaturation.

Measuring highly flammable waste samples with era**flash**

To avoid a violent ignition and oversaturation, the sample must be cooled down below the upper flammability limit prior to the actual measurement. The most volatile materials which may be encountered as liquid waste samples exhibit a flash point or flammability limits similar to gasoline. Extensive tests have shown that an initial starting temperature of -15°C is sufficiently low to cover even the UFL of gasoline. Pre-cooling the sample container in a refrigerator is often difficult, and in any case time-consuming. A typical sample container has a volume of 100 mL to 250 mL, in some cases up to 2 L. Cooling down the whole sample is not even necessary. Instead, only the test specimen of 2 mL needs to be cooled down to -15°C, which is achieved much faster. Along with its unique temperature range in the stand-alone configuration of -15°C up to 120°C, era**flash lt** offers a semi-automatic measurement procedure for this application. According to ASTM D7094 the approximate flash point of the sample must be known, which is apparently not the case for waste samples. As an alternative, the test method SCAN uses a faster heating rate and a larger ignition interval, and is therefore suitable for testing an unknown sample over a wide temperature range:

Test method	Heating rate	Ignition step	Advantage
ASTM D7094	2.5 °C/min	1°C	excellent precision
SCAN	10 °C/min	5°C	fast result on a wide range

Figure 3: Comparison table of ASTM D7094 vs. SCAN with era**flash**

On the user interface of the analyzer a temperature measuring range of -15°C to 93°C is applied in a pre-defined profile for assigning the flammability category to an unknown waste sample. The semi-automatic measurement procedure works as described below:

(1) The measurement is started with an empty sample cup placed in the measuring chamber.

(2) The empty cup is cooled down to -15°C, and upon reaching the starting temperature a pop-up message signals the user to fill the cup.

(3) After pressing “OK” on the screen, the user removes the pre-cooled cup from the chamber and quickly fills it with 2 mL of test specimen.

(4) The filled sample cup is installed into the analyzer, and the actual measurement is started.

(5) As soon as the cup is lifted up to the heating plate, a quick ignition is performed to check for highly volatiles.

(6) This *immediate ignition* triggers a flash point if high volatiles are present, and the measurement is stopped.

Commercially available gasoline according to EN 228 (“Sample 1”) was used as an example for a highly flammable waste sample. The immediate ignition triggered a flash point even before the actual measurement was undertaken, and the sample was safely assigned to the flammability category 2:

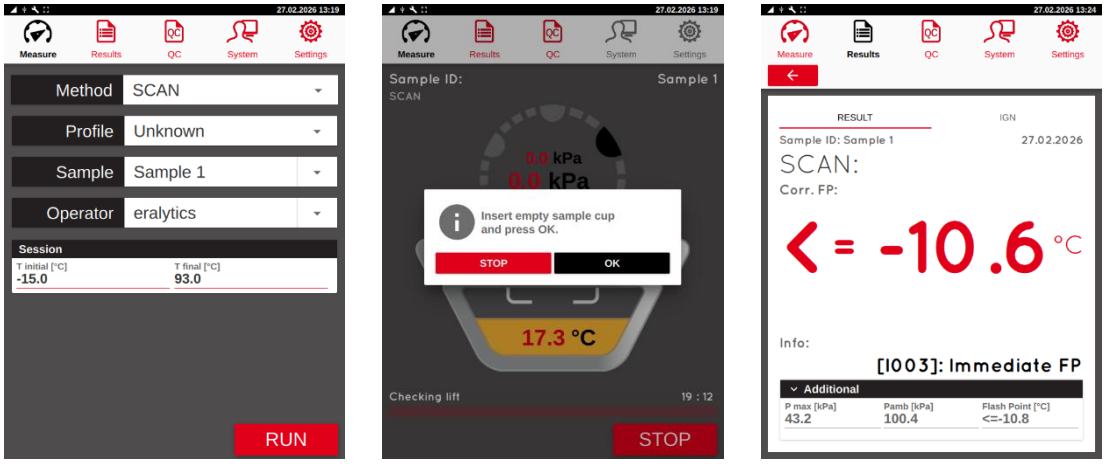

Figure 4: Screenshots during the measurement of the highly flammable “Sample 1” (gasoline)

As a second example, jet fuel according to ASTM D1655 (“Sample 2”) was measured with identical settings. The immediate ignition did not trigger a flash point in this case, the measurement could be continued and the sample was assigned to the flammability category 3 due to its flash point of ~45°C:

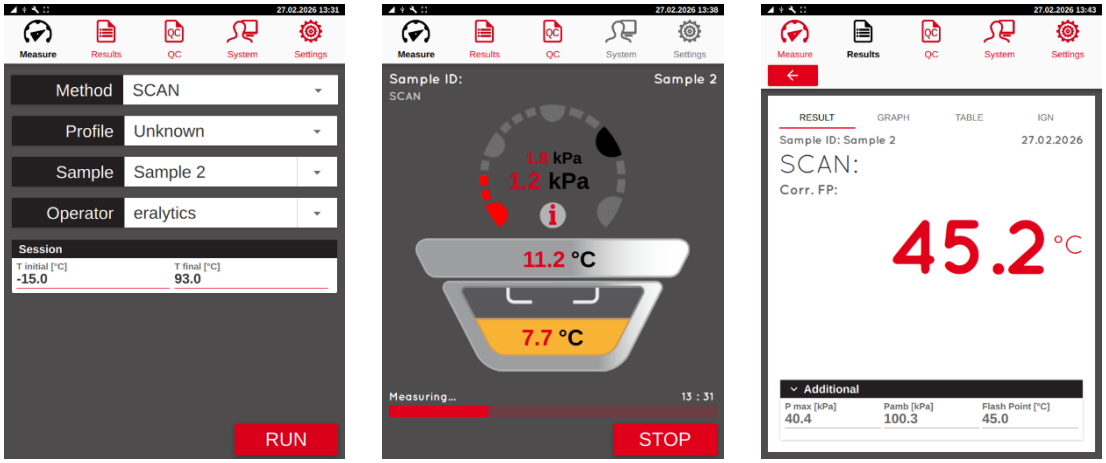

Figure 5: Screenshots during the measurement of “Sample 2” (jet fuel)

Conclusions

- era**flash** provides an inherently safe and reliable apparatus design, eliminating fire hazard and the need for fire extinguishing precautions for flash point testing.
- The wide temperature range of **era**lytics flash point tester model era**flash lt** allows for a starting temperature as low as -15°C, even in the stand-alone configuration.
- The measurement is completed in a short time, typically within 5 to 8 min.
- Due to the small sample volume of only 2 mL the amount of hazardous waste is minimized, and the cleaning of the equipment after a measurement is completed in a matter of seconds.
- The convenient software interface provides pre-configured profile settings, keeping the operation simple and independent of the sample type.