

Why Crude Oil Vapor Pressure Should Be Tested Prior to Rail Transport

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Received 16 April 2014; accepted 12 June 2014

Published online 24 June 2014

Abstract

Recent crude oil rail car accidents have forced US and Canadian authorities to issue Emergency Testing Orders to ensure safe transportation of crude oils. One crucial parameter in meeting these safety requirements is the testing of the vapor pressure (VP) of crude oil.

This paper explains the impact of highly volatile components inside the crude oil on the vapor pressure measurement. It describes typical VP measurement errors and discusses guidelines and technology for proper crude oil classification.

It offers measurement data to show the effect of sample outgassing and to describe the impact of temperature changes and the vapor-liquid ratio (V/L) on vapor pressure test results. The second part of the paper discusses methods to measure the True Vapor Pressure (TVP) and Bubble Point Pressure (BPP) of Crude Oils for safety purposes.

Key words: Crude oil; Volatility testing; Safety data sheet; Hazardous material regulations (HMR); Emergency testing order; Vapor pressure (VP); ASTM D6377; Reid vapor pressure (RVP); ASTM D323; True vapor pressure (TVP); Vapor-liquid ratio (V/L); Bubble point pressure (BPP); Floating piston cylinder (FPC)

Pichler, H., & Lutz, J. (2014). Why crude oil vapor pressure should be tested prior to rail transport. *Advances in Petroleum Exploration and Development*, 7(2), 58-63. Available from: URL: <http://www.cscanada.net/index.php/aped/article/view/5098>
DOI: <http://dx.doi.org/10.3968/5098>

INTRODUCTION

Recent developments have put crude oil transportation into public spotlight in the United States and Canada. The US Department of Transportation (DOT) has issued an Emergency Testing Order that requires all shippers to test crude oil from the Bakken region to ensure the proper characterisation of the crude oil before it is transported by rail.

The order is in response to a number of recent incidents involving the derailment of trains transporting crude oil from Canada to the United States. All shippers are required to comply with Hazardous Materials Regulations (HMR) that include testing of vapor pressure and flashpoint to ensure proper transportation and packing.

The number of rail carriages transporting crude oil from Canada to the United States has increased steeply. The oil industry has found building rail infrastructure for new shale oil and gas fields simpler and more flexible than pipelines. However, the increased use of rail transport also has resulted in an increase in the number of accidents and led to greater scrutiny. These accidents have caused significant environmental damage with an estimated cost of more than \$1 billion US^[1].

Accident investigations have highlighted the need for more accurate classification of crude oils. Classification has often been based solely on safety data sheets, many of them outdated. As a result of these investigations, US DOT issued several Emergency Testing Orders with the most recent amended version issued on March 6, 2014 and addressed to shippers of petroleum crude. The order specifically requires the flashpoint and boiling point testing of crude oils and endorses the requirement that crude oil shipments follow volatility testing defined by Hazardous Material Regulations. US DOT has defined draconic penalties of 175.00 US\$ for noncompliance with the Emergency Testing Order^[1].

In Canada, Trans Canada, which is legally responsible for enforcing the requirements for safe transportation of

crude oils, has implemented similar measures through the Protective Directive No. 31: Any crude oil shipped, handled or imported has to be tested immediately, unless it has undergone classification testing after July 7th, 2013^[1].

1. TESTING CRUDE OIL VAPOR PRESSURE

The proper testing of crude oil vapor pressure is critical for meeting Hazardous Material Regulations and in determining the requirements for safe packing for transport^[2]. The risk of pressure build up inside a rail car and crude oil boil increases significantly if the crude oil includes volatile components. In the discussion that follows, the term volatile components is used for crude oil components with a high tendency to evaporate, such as dissolved hydrocarbon gases, air or liquid components that begin to evaporate at a low temperature.

When testing crude oil samples, it is of utmost importance that the sample is properly handled to keep the volatile light ends in the crude oil prior to vapor pressure testing. Crude oils may be misclassified if hydrocarbon

volatiles are allowed to evaporate prior to sampling. One solution is to ensure that the crude sample is pressurized when delivered to the vapor pressure tester. Below are some of the most common errors in vapor pressure testing.

1.1 Measurement Error 1: Sample Outgassing Prior to Vapor Pressure Testing

“Live” crude oil typically is crude oil with sufficiently high vapor pressure that will boil if exposed to atmospheric pressure at room temperature. “Live” crude oil, especially Bakken shale oil, is known to contain a high level of volatile components. The vapor pressure of these components is a key parameter for the pressure build-up inside a rail carriage. In general, the more gas inside a crude oil, the higher its vapor pressure. To prevent evaporation of crude oil volatiles prior to vapor pressure testing, it is important that the samples are delivered in a pressurized container such as a floating piston cylinder (FPC). There is a noticeable difference in the vapor pressure when crude oil is delivered in a pressurized floating piston cylinder versus a bottle (Figure 1).

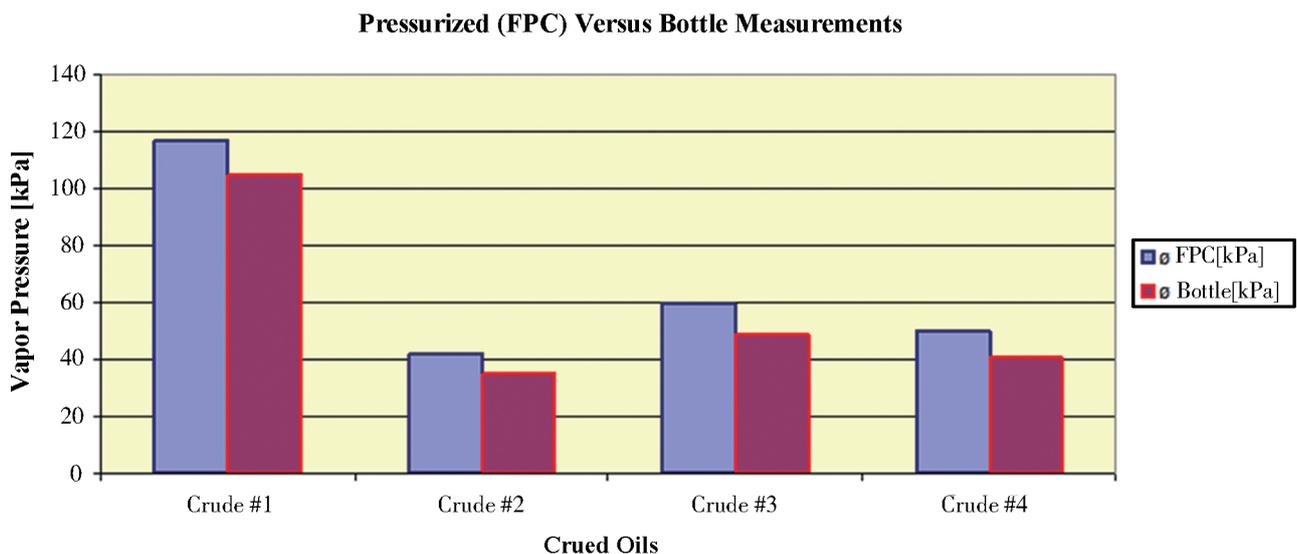


Figure 1
VP of Stabilized Crude Oil According to ASTM D6377 at 37.8 °C (100 °F) and a V/L = 4/1, Samples Delivered in Pressurized Floating Piston Cylinder Versus Bottle

Figure 1 shows that crude oil vapor pressure decreases if crude oil has been tested from an open bottle instead of a pressurized FPC, before they are being shipped in a rail cargo. If the sample is measured from an unsealed bottle, there is a risk that the actual vapor pressure of the crude oil inside the rail cargo will end up being significantly higher than the test results suggest. For best accuracy, therefore, it is important to make certain the crude oil sample is tested “as is”, including all the volatile components.

1.2 Measurement Error 2: Neglecting Temperature and Sample Composition

HMR requires that the vapor pressure is tested at one specific temperature. For an accurate risk assessment, it is useful, if the vapor pressure test also simulates the conditions, which the crude oil is subjected during transport. The temperature inside a rail cargo usually rises, as the rail carriage moves south from Canada into Washington State and the warmer regions of the United States, especially the Gulf Coast, where many US refineries are located. Vapor pressure is a function of temperature: The higher the temperature, the higher is the vapor pressure (Figure 2).

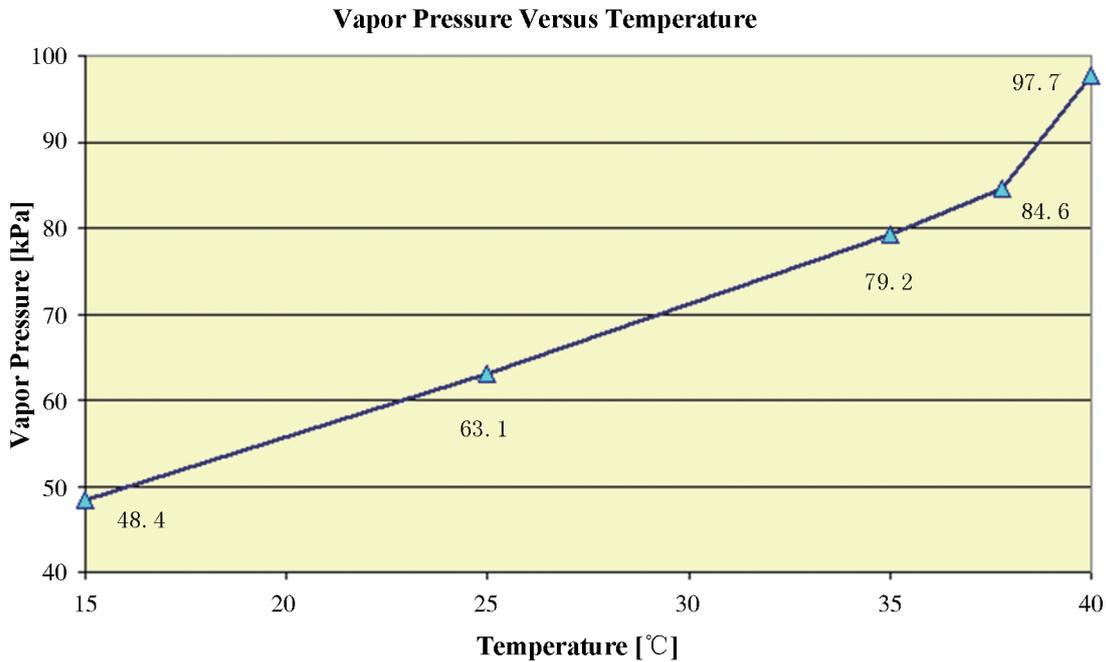


Figure 2
Increase of Crude Oil Vapor Pressure With Temperature, Measured With ASTM D6377 Method

Crude oil, especially shale oil, is a mixture of liquid and gaseous components. Special attention has to be paid to crude oils that contain a lot of components with a low carbon number (C4 or less), as these components start to boil below atmospheric pressure and ambient temperature.

The vapor pressure of a liquid and gaseous mixture can be displayed in a vapor pressure versus temperature curve, similar to Figure 2. This pressure curve is not predictable from a measurement at one specific temperature, unless the exact sample composition and the increase of the vapor pressure of these components with temperature are known. As a safety measure, transport specifications require that the vapor pressure is measured at an elevated temperature. This is a logical requirement, as the temperature in a closed rail cargo exposed to direct sunlight certainly may increase well beyond 50 °C.

Despite these obvious facts, the industry is accustomed to single temperature VP testing at 37.8 °C (100 °F). The vapor pressure at higher temperatures is then estimated through the API nomograph. This nomograph is based on a single 1950's artificially weathered Pennsylvania crude oil^[3]. At the time of its introduction it was an acceptable measure, because crude oil contained little to no volatiles. But as today's crude oils contain more highly volatile components, the use of a nomograph certainly is inadequate and potentially very risky.

1.3 Measurement Error 3: Neglecting the Ullage or Vapor-Liquid Ratio (V/L)

The ullage is the vapor space in a closed container. The vapor pressure of pure substances in general is not affected by the ullage level inside a container, if the sample contains no volatiles or air. On the other hand, if crude oil containing volatile components is put into a container, the gas will start to liberate into the vapor space above the liquid. As a general rule, if the ullage level is very low or almost non-existent, then the vapor pressure of crude oils usually becomes very high (Figure 3).

In vapor pressure testing, the ullage level in a closed container is referred to in terms of the vapor-liquid ratio (V/L). A V/L ratio of 4/1 is commonly used for testing petrochemicals and crude oils: The test is performed in a chamber containing four (4) parts vapor space versus one (1) part liquid space, as required for example by the ASTM D323 Reid Vapor Pressure (RVP) standard method. In terms of ullage, a V/L ratio of 4/1 corresponds to an ullage level of 80%. Another vapor pressure test method, the ASTM D2879 Isoteniscope method, can be used for mixtures with an ullage level of 40%, which corresponds to a V/L ratio of 2/3.

The resulting problem for transportation becomes obvious, if a tank is filled to the top with volatile crude. If the crude oil's VP has been measured either at a 40% or at a 80% ullage level, it is impossible to estimate the vapor pressure in a carriage, that has been filled almost up to the top unless there exists extensive knowledge of sample composition, especially with regards to the high volatiles.

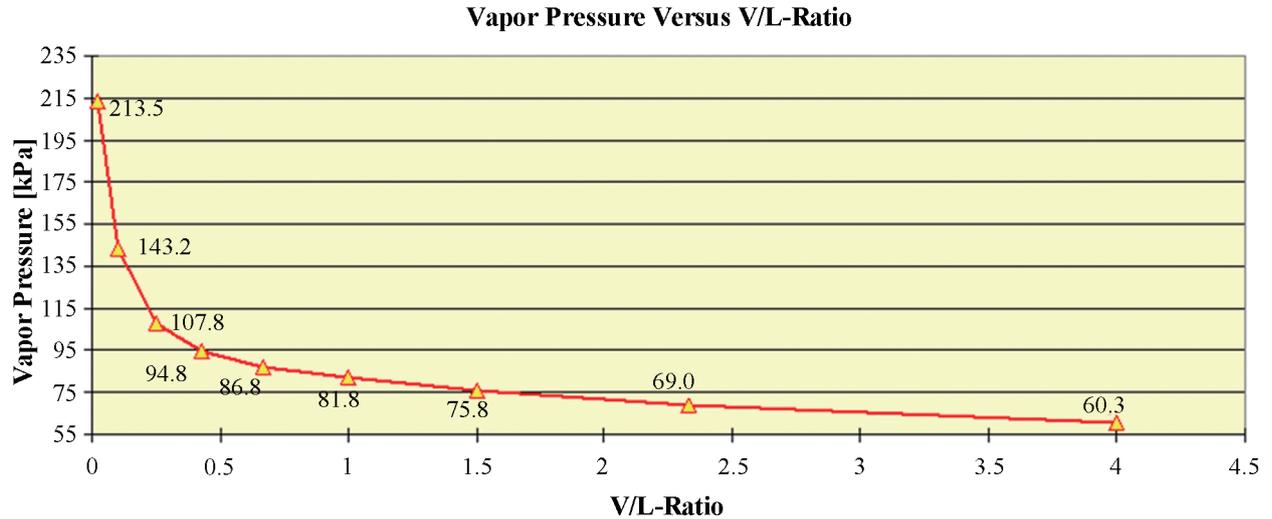


Figure 3
Vapor Pressure of Crude Oil at Different Vapor-Liquid Ratios at 37.8 °C (100 °F)

Figure 3 shows the steep increase of the vapor pressure of crude oil when the V/L ratio is reduced to a V/L ratio of 0.02/1, which is roughly corresponding to a 2% ullage level. For accurate risk assessment it is important that the vapor pressure at varying filling levels in tanks and rail

carriages can be measured. It is also important to know that not only hydrocarbon gases but also air saturation is a major contributor to the vapor pressure at very low V/L ratios (see Figure 4).

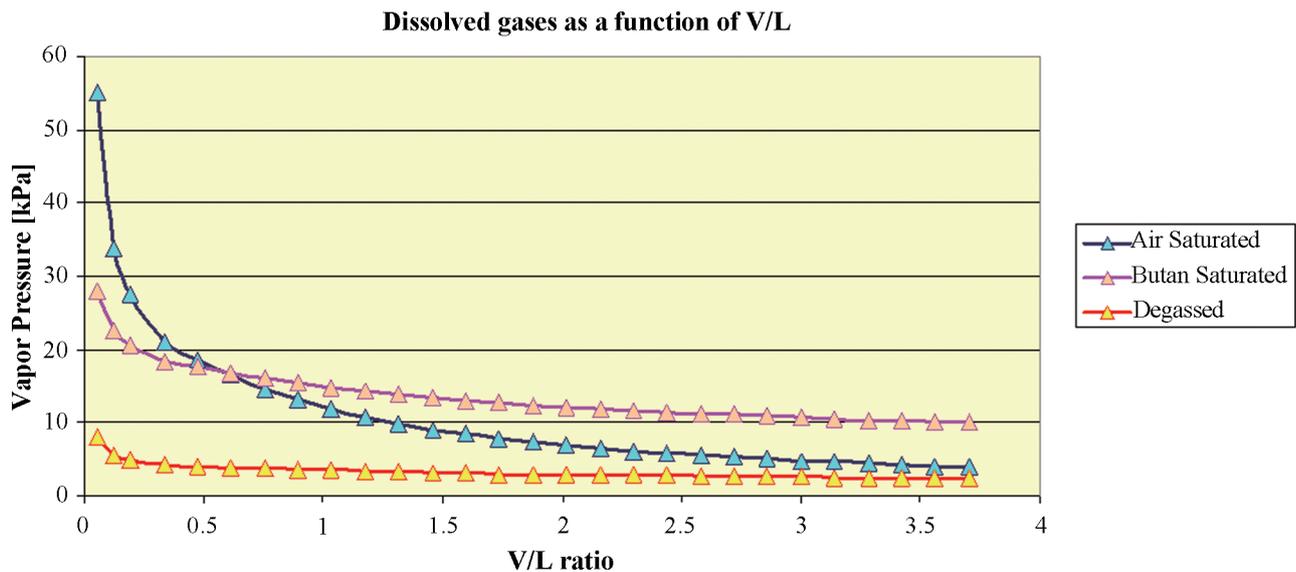


Figure 4
Influence of Amount and Types of Dissolved Gases in a Hydrocarbon Liquid as a Function of the Vapor-Liquid Ratio

1.4 Correct Measurement of Crude Oil Vapor Pressure

To eliminate these common measuring errors, a vapor pressure test method for crude oils should prevent sample outgassing and should allow the testing of samples at varying temperatures and V/L ratios. This way a temperature dependent vapor pressure build-up inside a rail carriage, which is encountered during transportation, can be estimated.

AMETEK Grabner Instruments has developed a proven method for effectively testing pressurized crude oils under varying transport conditions. The company offers a package for the safe, air-tight and pressurized transportation of crude oil to the vapor pressure tester. The crude oil with all of its light ends is captured inside a high-quality floating piston cylinder (FPC). Once this cylinder is connected to the MINIVAP VPXpert vapor pressure instrument, testing can begin immediately. This

versatile analyzer is able to test vapor pressures at temperatures ranging from 0 to 120 °C and at vapor-to-liquid ratios (V/L) ranging from 0.02/1 to 4/1 to simulate the various fill levels encountered during transportation. AMETEK Grabner Instruments also offers a process version of its vapor pressure analyzer for online monitoring that operates using the same principle as the laboratory version.

The Grabner method of measuring crude oil was standardized in 2003 as ASTM D6377 standard method. Since its introduction, the D6377 method has gained industry wide acceptance and quickly replaced the old manual Reid method ASTM D323. In 2013, the US Environmental Protection Agency approved ASTM D6377 as an alternative method of measuring the vapor pressure of crude oils^[4].

2. TRUE VAPOR PRESSURE

Another important parameter in vapor pressure testing is the True Vapor Pressure (TVP). The TVP term is used for at least two different specifications.

2.1 Air Pollution Protection (Title 40 CFR)

For emission prevention according to title 40 CFR, the TVP is defined as follows:

“True vapor pressure is the equilibrium partial pressure exerted by a volatile organic liquid, as defined by ASTM-D 2879 or as obtained from standard reference texts.”^[5]

Three methods can be used to measure the TVP according to title 40 CFR^[5]. First, from the D323 RVP measurement, the true vapor pressure is estimated via the API nomograph. Second the result of the D2879 Isotenoscope method is used for the true vapor pressure. And third, the ASTM D6377 method can be used according to the EPA approval^[4]. It has to be noted that EPA is not specifying a V/L ratio for a D6377 test, but the industry currently understands that the same V/L ratio of 4/1 shall be used as is required by the ASTM D323 RVP method.

2.2 Bubble Point Determination: Vapor Pressure at a V/L = 0

The TVP term is also used for safe transportation and storage and in order to prevent pumping cavitation or the overturn of floating roof tanks. In this context, the True Vapor Pressure (TVP) or Bubble Point Pressure (BPP) is defined by Sandia National Laboratories^[6] and maritime transportation guidelines^[7,8] as follows:

“The TVP or bubble-point vapour pressure is the equilibrium vapour pressure of a mixture when the gas/liquid ratio is effectively zero. It is the highest vapour pressure, which is possible at any specified temperature.”^[7]

“The true vapour pressure of a liquid is the absolute pressure exerted by the gas produced by evaporation from a liquid when gas and liquid are in equilibrium at the prevailing temperature and the gas liquid ratio is effectively zero.”^[8]

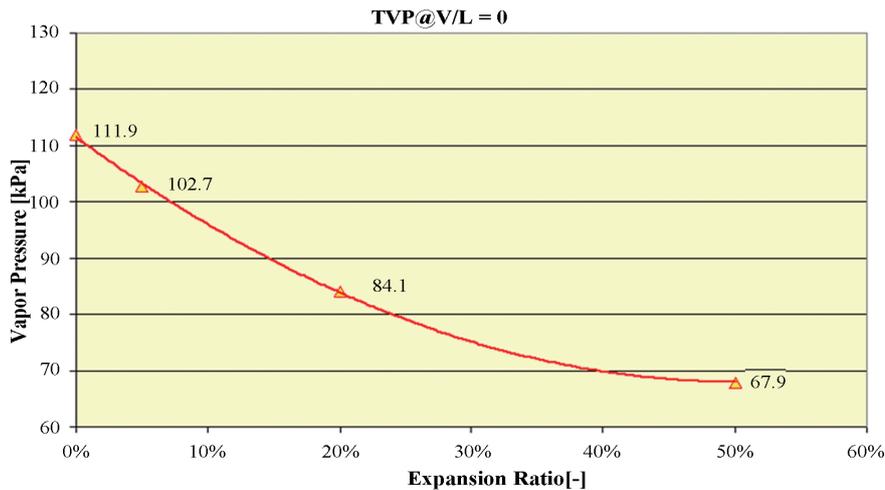


Figure 5
Three Step Measurement at Different V/L Ratios for TVP or Bubble Point Extrapolation

According to the definition of the International Maritime Organisation^[7], the TVP is equal to the BBP, it is the vapor pressure at a V/L = 0. Sandia National Laboratories^[6] also refer to the Bubble Point Pressure as the vapor pressure at a V/L = 0. The TVP or BPP can help to describe a “worst case” scenario during transportation of crude oils: The vapor pressure that can be expected at a certain temperature under the condition a tank is filled

completely to the top. It has to be noted, that the problem of thermal expansion of the liquid is not accounted for by TVP measurement. At a V/L = 0, even small increases in temperature will result in a massive pressure build-up, which can pose a severe risk for a container’s integrity.

AMETEK Grabner Instruments’ analyzers offer a TVP method that follows the requirement to test the vapor pressure at a V/L-ratio close to 0. With the automated

Grabner vapor pressure tester a V/L of 0.02/1 can be achieved, which is already a very good TVP estimate. Because of physical and technical limitations like the thermal expansion of the liquid, the TVP as the vapor pressure at a V/L = 0/1 cannot be measured directly, but has to be extrapolated. The TVP extrapolation method available in Grabner analyzers is based on research work from Hinkebein and Sandia National Laboratories^[6]. From three D6377 measurements at different V/L ratios the TVP of crude oil at a V/L = 0 is extrapolated (see Figure 5). The extrapolation function assumes that crude oil is composed of three components: very light components (e.g. methane, nitrogen or air), intermediate volatility components (e.g., C2 and higher) and a non-volatile fraction. This is a very accurate model for crude oils, and it was successfully demonstrated on large number of crude oil samples at the US Strategic Petroleum Reserve.

DISCUSSION

A number of questions need to be addressed to properly classify crude oils. Volatility testing as enforced by the US DOT Emergency Testing Order^[1] specifically requires testing of flashpoint and boiling point for classification of crude oils. But flashpoint testing is an atmospheric method and a crude oils light ends can evaporate during sample transfer. Distillation also is an atmospheric method. And, distillation will not detect volatile components, if those volatile components do not build a condensate that can be measured in the receiver.

Atmospheric methods, therefore, bear a high risk that the sample is not representative and that the test results are wrong. If volatiles are lost during sampling or if lower type carbons are not accurately determined, then the sample classification may also be wrong. On the other hand, vapor pressure testing allows samples to be tested "as is", by keeping volatiles inside a pressurized container -- a natural advantage compared with atmospheric methods. Vapor pressure testing is the first step in prevent accidents that may result from crude oil boiling over inside rail cars.

Based on the above discussion, here is a short list of do's and don'ts with regards to vapor pressure testing:

- (a) Don't use an open bottle to transport and test the crude oil sample. A pressurized container will prevent the evaporation of highly volatile crude oil components.

- (b) Do make sure that the vapor pressure is tested at the temperature required by HMR. There are obvious reasons why HMR requires higher test temperatures than 100 °F (37.8 °C).
- (c) If the V/L ratio is not defined by transportation regulations, do make sure to use a correct V/L ratio for vapor pressure testing, to simulate the filling level of your transportation medium.

All of the requirements that ensure accurate vapor pressure testing in the lab or in the field currently are fulfilled only by the Grabner ASTM D6377 test method.

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