Crude oil vapour pressure testing

Vapour pressure testing is an important safety check in the transport, storage and blending of crude oil

HANNES PICHLER and KLAUS HENSE Grabner Instruments, a subsidiary of AMETEK

t is very important for the true vapour pressure (TVP) and Reid vapour pressure (RVP) of crude oil to be tested when dealing with its production and storage. The vapour pressure indicates how the crude oil will perform during highlights handling, conditions under which bubbles are likely to build and shows where pressure build-ups of escaping light ends could happen. As such, vapour pressure measurement prevents costly damage to pipelines or vessels transporting crude oil. It also provides guidance on how transportation facilities need to be built to survive a worst-case scenario.

Pipeline operators determine TVP and bubble point before transporting the crude to a distribution point. With wellhead crude, gas has to be removed to meet pipeline, storage and tanker specifications. Excess gas can be separated or flared to regulate the vapour pressure and prevent any damage to the transportation medium. If the vapour pressure of the crude case is too high, two main safety issues can arise. The first is pumping cavitation during transfer operations and the second is vapour pressure in the pipeline, or in a vessel, which could rise because of temperature changes. Once the transportation medium is exposed to direct sunlight, the vapour pressure of the crude oil rises and, in the worst case scenario, causes damage. Hence, it is advisable for operators to be equipped with a vapour pressure analyser, to prevent costly damage and to provide evidence that the released crude is delivered according to specifications.

TVP measurement and bubble point determination

The exact definition of TVP and bubble point is a topic of wide discussion in the engineering community. First, it is worth mentioning that the bubble point refers to a temperature, whereas the bubble point vapour pressure refers to a pressure. According to the International Maritime Organisation, the TVP and bubble point pressure (BPP) are equal: "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. As the temperature of a petroleum mixture increases, its TVP also increases. If the TVP exceeds atmospheric pressure, the liquid commences to boil." (*IMO*, 2006, *p*140). In this definition, TVP is essentially the total vapour pressure (P_{tot}) of the crude oil minus the vapour pressure of air and the dissolved gases in the sample (P_{gas}) .

The resulting value is the absolute vapour pressure (P_{abs} or P_{liquid}) of the liquid, commonly referred to as TVP, as measured by ASTM D2879 (*US EPA, 2006*). The ASTM D2879 method should be used only for single-component substances. Crude oil in general is a multi-component liquid and thus requires a different form of analysis.

The equation TVP = BPP at a vapour-to-liquid ratio (V/L ratio) of 0/1 addresses the common practical problems for crude oil transportation. In floating roof tanks, the roof is placed directly on the liquid crude oil, while in pipelines the liquid crude oil is pressurised. In both

cases, the V/L ratio is effectively zero and the TVP measurement gives a precise indication of the bubble point pressure at a specified temperature.

In some cases, the equation is not sufficient. In multi-component mixtures, bubbles tend to build whenever the vapour pressure of the liquid exceeds the environmental pressure (IMO, 2006), independent of whether the V/L ratio is 0/1 or 100/1. Three factors have an influence on the bubble point: pressure, volume and temperature. A more accurate definition takes different temperatures and V/L ratios into account when determining the bubble point: in a multi-component mixture, the bubble point is the temperature at which the first bubbles appear at a fixed V/L ratio.

Pumping cavitation

One of the major risks when transporting crude oil is pumping cavitation. Cavitation happens when the TVP or bubble point vapour pressure at a V/L ratio near 0/1 is reached and usually has drastic effects. In a pumping system, the crude oil is accelerated, generating areas of low pressure. When the surrounding pressure is lower than the vapour pressure of the crude oil, bubbles build, grow, then collapse, generating high pressure and high temperatures at the bubble surface. Near a fixed surface, for instance in a pumping system, the collapse of the cavitation bubble will generate a shockwave directed to a nearby surface, which can damage the transportation system or the pump.

For correctly dimensioning new pipelines and pumping systems, and

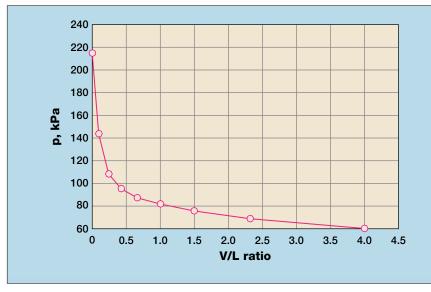


Figure 1 Vapour pressure of crude oil at different vapour-liquid ratios at 37.8°C (100°F)

for writing standard operating procedures, it is important to know the vapour pressure of the crude oil. To prevent bubble building and pumping cavitation in an installed transportation system, it is necessary to ensure that the pressure in the transportation system is higher than the vapour pressure of the crude for any expected condition.

If the vapour pressure is too high, pressure, volume or temperature have to be modified. The pressure in the transportation system can be increased to exceed the vapour pressure of the crude oil. Also, the vapour pressure of the crude oil can be reduced, for instance by the separation or burning of excess gases, which reduces the volume. As a third option, the temperature for transportation and thus the vapour pressure of the crude oil can be reduced. Lord & Rudeen suggest oil degasification or oil cooling to reduce the vapour pressure: "The degasification program removes gas from oil in selected caverns, which reduces its bubble point pressure and gas-oil ratio, which in turn significantly increases the predicted margin of system performance under the safety criteria."2

Crude oil producers face a complex problem here: when crude oil is extracted, it is not homogenous. The vapour pressure of the crude can change during oil production. Also, the presence of various amounts of natural gas in the crude changes the V/L ratio considerably

and increases the vapour pressure dramatically. Plus, highly viscous crude oil needs to be transported at a high temperature to guarantee a flow in the pumping system and in the pipeline. Temperature changes in turn affect the vapour pressure.

Depending on the amount of light ends delivered with the crude oil, the vapour pressure of the crude oil will be significantly higher for 60°C compared to the vapour pressure at 37.8°C. Most vapour pressure testers measure crude oil only at 37.8°C (100°F) and a V/L ratio of 4/1. But crudes can sometimes be transported at 85°C and at a V/L ratio close to 0/1. Under these extreme conditions, some volatiles might begin to dissolve even in "dead" crude oil and produce a gaseous mixture, causing a non-linear pressure increase. This risk cannot be foreseen if the vapour pressure is measured at 37.8°C and a V/L ratio of 4/1 only.

For adequate risk management regarding the bubble point, it is thus important to measure the vapour pressure at different temperatures and at a V/L ratio of 0/1. Only a vapour pressure analyser that can monitor vapour pressure at different temperatures and V/L ratios will allow the operator to regulate their transportation system immediately.

Vapour pressure increase in the transportation medium

Another potential problem when transporting crude oil is an

unexpected pressure increase in the pipeline or the tanker. Whereas "dead" crude oil is mostly unproblematic when transported, "live" crude oil contains volatiles. Volatiles such as natural gases increase the vapour pressure of the crude case. When the transportation medium for live crude - a pipeline or a tanker — is exposed to direct sunlight and heats up, the vapour pressure can increase considerably. The vapour pressure of live crude oil filled at 20°C can more than double if the temperature of the live crude oil is increased to 50°C.

The absolute pressure increase from temperature fluctuations is even higher if the live crude oil is transported at a very low V/L ratio. In Russia, it is necessary to test the vapour pressure of crude oil at a V/ L of 0.02/1 to simulate the conditions in a tanker or a pipeline. Typically, 98% of a tanker's volume is filled with crude oil. The increase in vapour pressure that results from this can be seen in Figure 1.

The testing of vapour pressure at different temperatures and V/L ratios answers many questions that arise from crude oil transportation:

• How much will the vapour pressure rise if the crude oil at a V/L of 0.02/1 (98% filled with liquid) is transported at 50°C rather than 37.8°C because the tanker is exposed to sunlight?

• Do control personnel need to reduce the vapour pressure prior to shipment or storage?

• Is it necessary for specific crude cases containing volatiles to fill a tanker up to only 90% to prevent damage to the tanker or air pollution by excessive outgassing?

• Is the vapour pressure low enough that it is possible to blend in some natural gas prior to shipment without risking damage?

Vapour pressure analyser

It is essential to continuously monitor vapour pressure, TVP and BPP at different V/L ratios to help operations regulate their transportation system immediately. The Minivap On-line vapour pressure process analyser from Grabner Instruments can measure TVP or BPP at different temperatures in the range of 20–60°C and to simulate TVP for even higher temperatures. It also enables measurement of a V/L ratio down to 0.02/1 in a pressure range of 0–1000 kPa.

The analyser incorporates the ASTM D 6377 method, which is the latest standard for the vapour pressure determination of crude oil without sample preparation. This method replaces the 80-year-oldplus ASTM D323 and is used to measure TVP or BPP in the analyser. With the vapour pressure process analyser's sample conditioning system, the pressurised crude oil is transferred directly to the measuring chamber and the vapour pressure is measured against a vacuum by a single expansion of a built-in piston. A three-point expansion sequence is performed at different V/L ratios, then a curve fit is performed for assessing the TVP at a V/L of 0/1(see also Lord & Rudeen, 2010).

The Minivap On-line also incorporates the triple expansion method for vapour pressure measurement according to ASTM D6378, which allows for direct measurement of the total vapour pressure (P_{tot}) of the sample, and the vapour pressure of both the liquid (Pabs or P_{liquid}) and the gases (P_{gas}) in the sample (see Figure 2). Based on the fact that the vapour pressure of liquids remains constant and that all components such as dissolved air follow the ideal gas equation, $(p^*V)/T = constant$, an expansion is performed in three steps at a constant temperature. Three total pressure values are determined, and from these the partial pressure of the air, the solubility factor of the liquid and the absolute vapour pressure of the liquid are calculated. Results for the TVP (P_{tot}) of the sample, the pressure of the liquid $(P_{abs} \text{ or } P_{liquid})$ and the pressure of the gas (P_{gas}) are available every five to seven minutes. The precision of this measurement is ASTM Round Robin proven and significantly better than that of classical vapour pressure test methods.

Crude blending

An analyser that can be used to measure both TVP and RVPE will repay its cost in a short time. Usually, suppliers and refiners agree

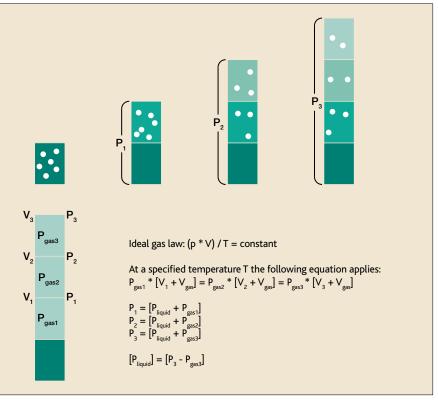


Figure 2 Vapour pressure measurement using the triple expansion method

over the maximum vapour pressure limits of crude oil delivered to a plant or terminal. This is necessary to ensure safety for transportation and storage, and to guarantee that the refiner receives crude of a certain quality. In this process, crude oil blending is a means of increasing the sales price or facilitating the processing of crude oil. By blending lower-grade crude oil with highergrade crude oil or natural gas to reach, but not exceed, target specifications, the price valuation of crudes can be increased significantly. Profits are earned if target specifications are reached by blending the minimum amount of high-grade crude oil with low-cost hydrocarbons.

The addition of these hydrocarbons is limited by the maximum RVP. Depending on the RVP prior to blending, typically ratios of 1–5% hydrocarbons are blended into the crude. The highest accuracy in vapour pressure tests according to standards is the ultimate goal of every blending facility because it increases the possible blending ratio.

The precision of the Minivap Online allows for close C_4 blending to RVP limits and the highest profit generation. With a measurement method that fully complies with the strictest ASTM, EN and IP standards, as well as US EPA regulations for vapour pressure testing of crude oil, gasoline and LPG, no further testing in the laboratory needs to be done to certify the accuracy of the measurement.

References

1 Specialized Training for Oil Tankers, International Maritime Organisation, Model Course 1.02, Edition (TB102E), London, 2006.

2 Lord D L, Rudeen D K, *Strategic Petroleum Reserve Crude Oil Equation of State Model Development - Current Performance Against Measured Data*, Research Report, Sandia National Laboratories, Albuquerque, NM & Livermore, CA, 2010.

3 Organic Liquid Storage Tanks, *Compilation of Air Pollutant Emission Factors*, Emission Factor Documentation for AP-42, 5th ed, I, 7.1, Office of Air Quality Planning and Standards Office of Air and Radiation, US EPA, Durham, NC, 2006.

Hannes Pichler is a Product Marketing Manager with Grabner Instruments, a subsidiary of automatic petroleum testing equipment developer AMETEK. He holds a MSc degree in natural sciences from the University of Vienna. *Email: hannes.pichler@ametek.at*

Klaus Hense is Head of R&D at Grabner Instruments, where he focuses on the development and improvement of measuring methods for the chemical and petrochemical industry. He holds a PhD in physics from the Technical University in Vienna. *Email: klaus.hense@ametek.at*