VALIDATION OF TRUE VAPOUR PRESSURE MEASUREMENT IN CRUDE OIL AND REFINED PRODUCTS

Testing the vapour pressure of crude oil and refined products is critical for meeting strict safety requirements and for complying with environmental regulations. Vapour pressure is a very important parameter for assessing a fuel's performance, for maximising profits during blending operations, and for ensuring US Environmental Protection Agency (EPA) compliance at every custody transfer on its way to market.

This article explains the traditional, yet cumbersome, method of calculating true vapour pressure (TVP) and then describes the ability of new lab and online analysers to directly measure this parameter. Analyser technology has been developed that allows for the use of an inherently small sample size and short measuring interval. To perform this measurement, the analyser must use an expansion type measuring chamber. This will provide the various V/L ratios necessary for TVP extrapolation.

Measurement data showing the reliability of this method will be compared to calculations based on API Chapter 19 Section 2, as well as to an underlying model of the nature of vapour pressure in pure substances, refined products, and crude oils.

Background

Reid vapour pressure (RVP) and true vapour pressure (TVP) are two of the most closely monitored parameters of crude oil and finished gasoline. While the Reid method is performed at a fixed temperature of 37.8°C, true vapour pressure is measured as a function of temperature. The true vapour pressure method is used to understand how the sample's vapour pressure reacts to an increase or decrease in temperature. The API [3] calculation is the most recognised and practiced method today for reporting TVP. To use this method, two parameters need to be known: the RVP and the stock temperature of the sample. These values must be put into a complex mathematical equation to achieve the TVP. Separate equations are used for various vapour pressure ranges for both crude oil and finished gasoline.

Using expansion-type measuring chamber technology, it is possible to perform an analysis of TVP with a minimum sample. The pressure transducer permits the collection of vapour pressure readings at programmable expansion ratios, resulting in a TVP calculation within minutes. The section that follows shows the ability of the analyser to measure TVP through theoretical and real world data.

True Vapour Pressure (TVP)

According to International Safety Guide for Oil Tankers and Terminals (ISGOTT) [1] and the Internationale Maritime Organisation, the "True Vapour Pressure (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." According to this definition, the TVP is the vapour pressure at a

vapour-liquid ratio (V/L) = 0/1 at a specific temperature. Because of the V/L = 0/1, the True Vapour Pressure is a special condition of the Total Vapour Pressure.

Total Vapour Pressure

The term Total Vapour Pressure is commonly used to describe the sum of the vapour pressure of the liquid and the gases at a specific temperature and at a specific V/L ratio. Vapour pressure methods typically report a total vapour pressure at a V/L = 4/1.

It is important to note that dissolved air is one of the major contributors to vapour pressure for small V/L-ratios. The problem with dissolved air in the sample is that air cannot be separated from dissolved hydrocarbon gases like propane or butane. However, the problem of dissolved air and other gases, or the respective degassing process is not topic of this consideration, but is addressed in standardisation committee activity. Current ASTM work to review the ASTM D6377 crude oil method focuses on proper sample handling to prevent air saturation of the sample and loosing volatiles in the process of sampling.

It can be seen from the chart (Figure 1) that the total vapour pressure increases significantly for smaller V/L ratios, especially if light gases (C1-C3) or air is present in the sample. At a V/L = 4/1, methods are virtually blind to the presence of gases in the sample. This is due to the fact that a big vapour space allows
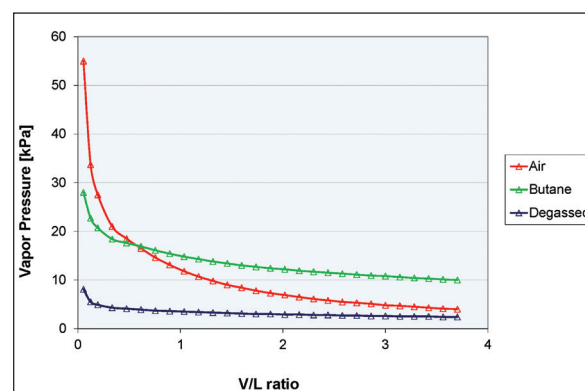
Fig 1. Influence of amount and types of dissolved gases in one hydrocarbon liquid as a function of vapour liquid ratio (V/L).

outgassing of the sample during testing, with only a marginal increase in pressure. At a lower V/L ratio the presence of gases has a significant effect on the measured total vapour pressure.

Figure 1 helps with understanding the problems faced by TVP measurement in testing high volatile crude oils. When the API calculation [3] was created, degassed (stabilised) samples that included only very little amounts of light gases were used to design the calculation. Because the calculation is based on that sample set, the API calculation will under predict the TVP for samples with high amounts of light gases and will tend to over predict the TVP for samples that do not contain C1-C3 gases at all.

Data in Figure 2 shows the increase in vapour pressure for V/L ratios down to zero for several samples, such as

• 2 different crude oil samples
• 2 gasoline samples
• 2 pure substances

Note that the crude oil samples have been stored at ambient pressure at zero centigrade. It can be assumed, that those samples are saturated with air, and some of the high volatiles may be lost

TVP Model

The TVP (True Vapour Pressure) model discussed will show how to use several Total vapour pressure measurements, tested at different V/L ratios, to extrapolate the TVP at a V/L =0/1.

The model uses the following assumptions: Assuming there is no decomposition of the samples, it is a good assumption that the vapour pressure of the liquid hydrocarbons are constant at a given temperature (Pliquid). It also can be assumed, that the vapour pressure of the substance is the sum of the contribution of the gas and the vapour pressure of the unchanged liquid. Assuming further, that the vapour pressure of the gas is well described by the ideal gas law (but including a volume of the dissolved gas in the liquid Va), the total pressure of the substance can be written as:

$$p_{tot} = \overline{p_{liquid}} + p_{vap} = p_{liquid} + \frac{A_1}{(V + V_a)}$$

(1)
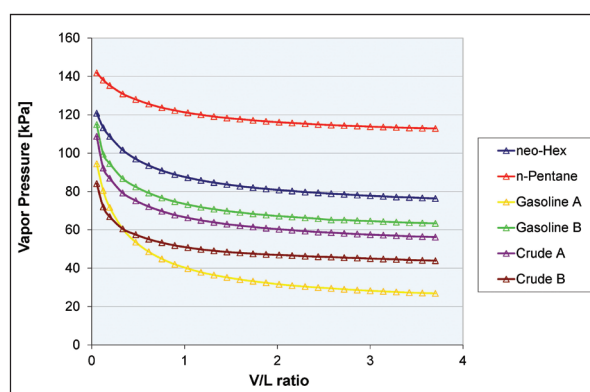
Fig 2. Total vapour pressure of different hydrocarbon mixtures as a function of vapour/liquid ratio.

Where Ptot = the total vapour pressure of the sample, which is comprised of Pliquid and Pvap

Pliquid = the absolute pressure of the liquid sample

Pvap = the pressure contribution of the dissolved gas

A1 = representation of the Ideal Gas Law (nRT)

V = the actual gas-volume in the test chamber

Va = the volume of the dissolved gas in the sample

Assuming that Va and nRT=const.=A1 are constants that only depend on the substance under consideration, will allow to have three independent and constant parameters (Pliquid, A1 and Va) to be fitted to the measured curve.

Testing this model against real measurements however reveals that decomposition of the sample happens, which can be corrected by introducing a linear increase of the vapour pressure of the liquid as the volume increases.

Assuming validity of Raoult's Law [5], it becomes evident that the more volatile components evapourate to a higher extent, shifting the composition stoichiometrics of the mixture. The larger the volume of the vapour space, the larger the shift. As Raoult's Law assumes a linear dependence of the vapour pressure versus mixing ratio, this results in a linear dependence of the vapour pressure with volume.

$$\overline{p_{liquid}} = p_{liquid} + A_2 \cdot V$$

(2)

Where P liquid = the modified vapour pressure of the liquid sample, written as the sum of the vapour pressure of the liquid (Pliquid) at a given V/L Ratio, and a term comprising of the vapour space volume of the test chamber (V) times a fit constant (A2). By introducing this into the equation of total vapour pressure, the new equation reads:

$$p_{tot} = \overline{p_{liquid}} + \overline{p_{vap}} = p_{liquid} + A_2 \cdot V + \frac{A_1}{(V + V_a)}$$

(3)

When performing a Curve-Fit using a Levenberg-Marquardt algorithm of above function to the measured vapour pressure versus volume plots, the differences between calculated and measured values can be shown (see Figure 3).
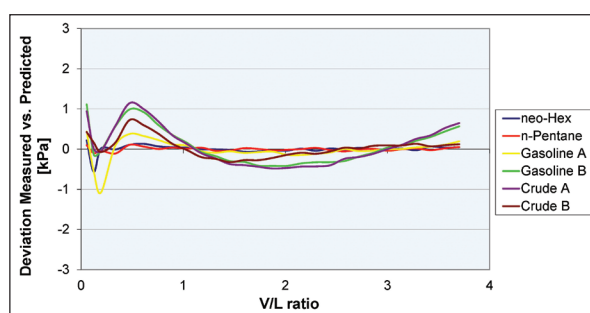

Fig 3. Difference (in kPa) between predicted and measured vapour pressure as a function of V/L ratio.

Using this theoretical curve, two parameters can be calculated easily:

1) The vapour pressure of the complete (not degassed) sample at V/L=0/1.

2) The vapour pressure of the (numerically) degassed sample – by skipping the Pvap contribution.

In the TVP mode, due to time constraints, analysers do not perform such a detailed multipoint expansion as shown in the graphs, but use much fewer points as well as a proprietary extrapolation procedure to obtain the vapour pressure at zero expansion [2]. In the TVP mode, three D6377 measurements at different V/L ratios are performed and the TVP at a V/L = 0/1 is extrapolated (see Fig. 4).
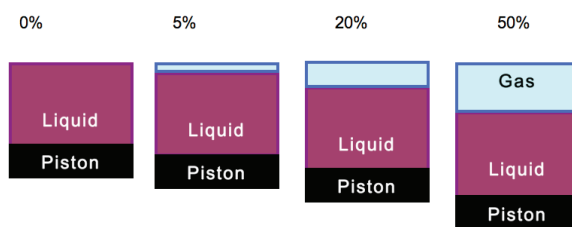

Fig 4. Schematic of the 3-step expansion sequence.

Validation of the TVP model

In the following section, actual measurements of the TVP analyser will be compared with the theoretical model and with results generated by the API TVP calculation.

Table 1 shows

• Results derived from the previously discussed theoretical TVP model, using a 28-point fit

• Results from TVP analyser measurements, using a 3-point fit

• Results from API calculation

The first section shows measured RVPE values. For crude oils, the measurement procedure and RVPE conversion as described in ASTM D6377 was used. For refined products, ASTM D5191 was used, using the conversion between Ptot and RVPE as described in CARB regulations.

The second section shows theoretical (28-point curve fit) and measured TVP results for not degassed samples. It can be seen, that inclusion of gases and air in the samples significantly increases the TVP.

The third section compares results calculated from the 28-point curve-fit (with numeric-degassing) and compares them to the results that can be expected when using API Chapter 19 Section 2 to convert from RVP to TVP [2, 3]. As these results are significantly lower, it is clear that the API conversion assumes degassing of the sample.

The following conclusions can be drawn from the results listed in Table 1:

1. The results from the theoretical 28-point curve fit model compare excellent to actually measured TVP data.

2. So it is not necessary to employ a 28-point curve fit to get accurate results. A 3-point curve fit yields comparable results to the more complex theoretical model.

3. Air saturation has a significant influence on the results, even for pure substances.

4. Assuming degassing, the results of the theoretical 28-point curve fit model are comparable to results from API Chapter 19 Section 2 conversion from RVP to TVP.

Summary

From the data shown, it can be stated that a vapour pressure analyser can be employed to measure true vapour pressure. By using robust hardware (expansion type measuring chamber) and proven extrapolation, a TVP measurement can be performed within minutes, reducing the API calculation to a cross-check.

One of the main advantages of the TVP analyser is that the TVP can be measured for degassed and not degassed samples. This is critical for the accurate measurement of today's highly volatile crude oils. As shown it is also of highest importance to prevent air saturation of the sample prior to the test, as full or partly air saturation will significantly alter test results. Air saturation can be prevented, if samples are measured directly in process or are transported in a sealed floating piston cylinder (FPC) or manual piston cylinder (MPC) from the sample source to the TVP analyser (see Fig. 5).

Fig 5. Laboratory TVP analyser with mounted Floating Piston Cylinder

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Vapor pressure [kPa]	Crude B	Crude A	Gasoline A w/o Aromats	Gasoline B	n-Pentan	neo-Hex
RVPE from ASTM D 6377-03	38,85	48,09				
RVPE from ASTM D5191			24,17	57,56	104,67	67,02
Results for not degassed samples						
TVP results from analyzer	100,67	125,49	106,87	127,56	144,91	123,79
TVP from Extrapolation (using 28 measured points down to 5%)	100,25	128,10	108,71	130,15	145,11	127,55
Results for degassed samples						
TVP from API 19 for crude oils	47,41	61,32				
TVP From API 19 for refined products			25,25	60,73	111,17	70,83
TVP from Extrapolation (assuming propper degassing, 28 points)	46,22	61,02	23,02	66,23	109,19	73,94

Table 1: Comparison of experimental and calculated data for different hydrocarbon mixtures and methods

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