Crude oil vapour pressure testing

Why a higher shaker speed improves the accuracy of measurement

CHRISTIAN SCHRÖDER-HOLZHACKER
eralytics

The vapour pressure of crude oil (VPCR) is a major safety parameter for storage, transport, and handling of crudes. Its reliable determination is of high interest in the petroleum industry, in particular for crude oils featuring a high vapour pressure.

For an ASTM D6377 crude oil measurement, the specimen is introduced into the measuring cell, the piston expands against vacuum adjusting a vapour to liquid ratio of 4:1, and the temperature is regulated to 37.8°C. When the pressure is stable within a maximum pressure variation of 0.3 kPa/60s the VPCR is determined.

Compared to simple spark ignition fuels or other petroleum based final products, crude oils have a much more complex composition, and their volatility (vapour pressure) may range from <1 kPa up to atmospheric pressure or even above. Furthermore, other crude oil properties like viscosity play an important role for vapour pressure measurement. A higher viscosity significantly influences the degassing process and delays the formation of a thermodynamic pressure equilibrium. Therefore, to improve repeatability and to speed up the measurement, shaking of the measurement cell during the measurement is mandatory in ASTM D6377.

The first vapour pressure instruments on the market could only shake the sample with about 1.5 cycles per second, and therefore ASTM D6377 required the relatively ambiguous shaking speed minimum frequency of 1.5 c/s. In contrast, modern instruments such as eralytics' Eravap can apply much higher shaking speeds, leading to the question of the influence of shaking speed on the ASTM D6377 measurement.

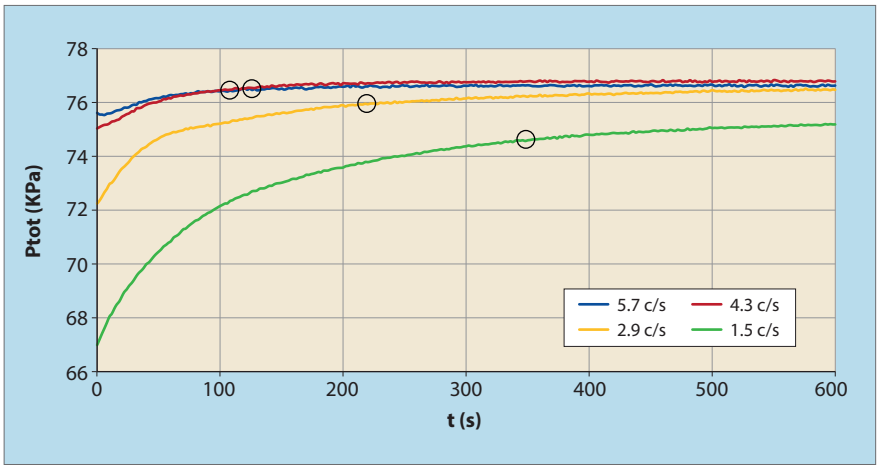

Figure 1 Crude oil 1 measured with a V/L ratio of 4.00 and variable shaking speeds between 1.5 c/s to 5.7 c/s. The equilibrium points according to ASTM D6377 are marked

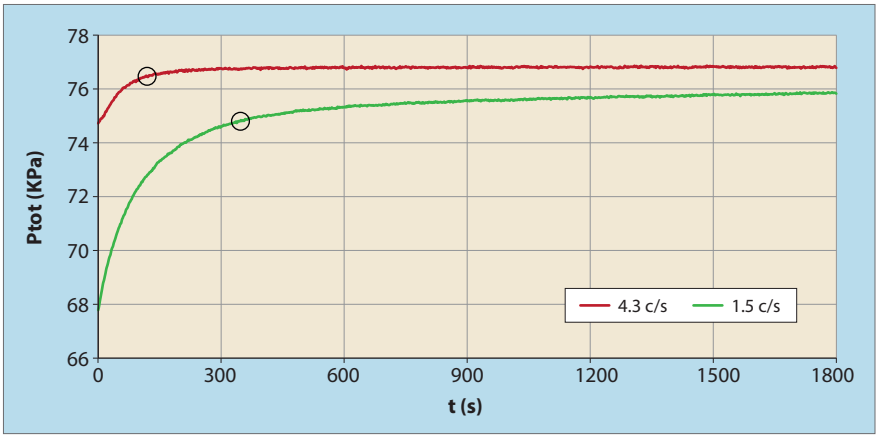

Figure 2 Crude oil 1 measured with a V/L ratio of 4.00 and variable shaking speeds of 1.5 c/s and 4.3 c/s up to 1800 s. The equilibrium points according to ASTM D6377 are marked

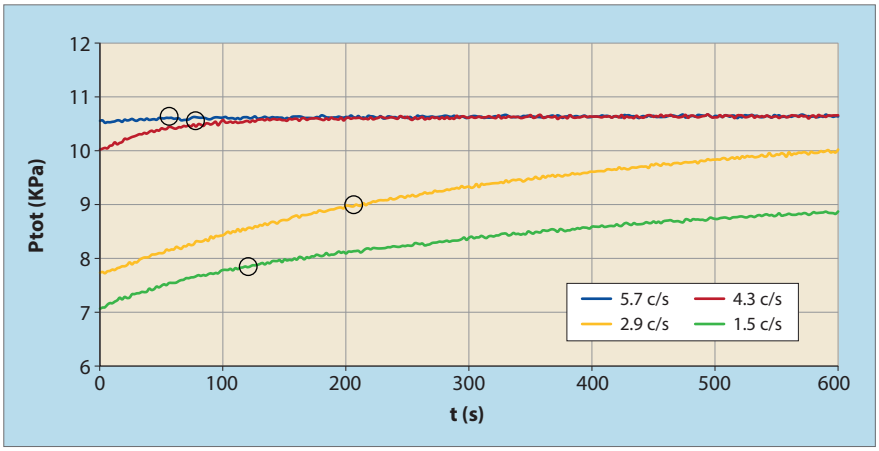

Figure 3 Crude oil 2 measured with a V/L ratio of 4.00 and variable shaking speeds between 1.5 c/s to 5.7 c/s. The equilibrium points according to ASTM D6377 are marked

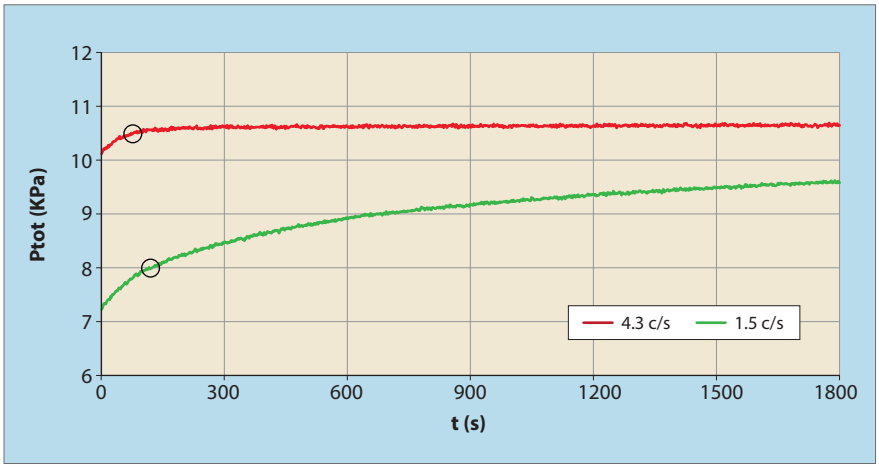

Figure 4 Crude oil 2 measured with a V/L ratio of 4.00 and variable shaking speeds of 1.5 c/s and 4.3 c/s up to 1800 s. The equilibrium points according to ASTM D6377 are marked

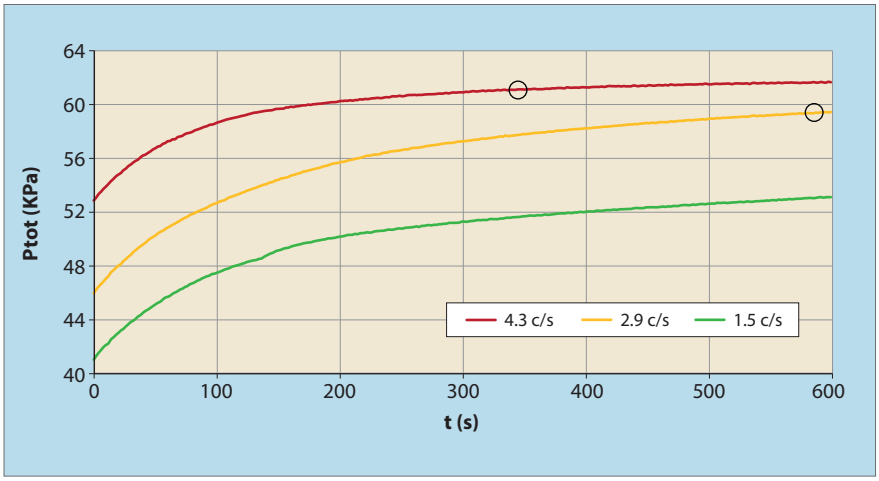

Figure 5 Crude oil 3 measured with a V/L ratio of 4.00 and variable shaking speeds between 1.5 c/s to 4.3 c/s. The equilibrium points according to ASTM D6377 are marked

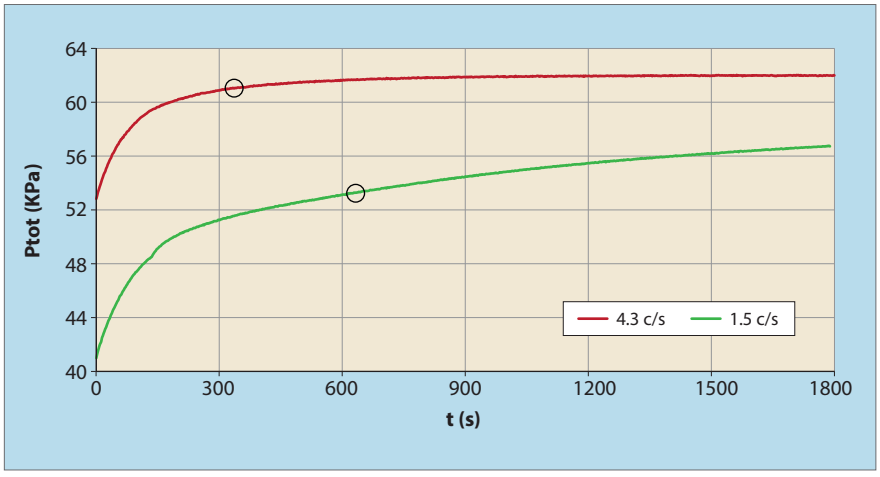

Figure 6 Crude oil 3 measured with a V/L ratio of 4.00 and variable shaking speeds of 1.5 c/s and 4.3 c/s up to 1800 s. The equilibrium points according to ASTM D6377 are marked

The intention of this article is to clarify the following questions:

- How is the VPCR result affected by changes in the shaking speed?
- Is there a bias between the VPCR and an "equilibrium vapour pressure result" and does this depend on the shaking speed?
- Does a higher shaking speed reduce the measurement time?
- Is there an optimum shaking speed?

Experimental

The following measurements were conducted on an Eravap EV10 with an integrated density meter module EV10-D4052. The density (ASTM D4052) and vapour pressure (ASTM D6377) were determined simultaneously for each sample.

To demonstrate the impact of shaking speed and measuring time, initially two different crude oils were measured with a V/L ratio of 4.00 at 37.8°C (100°F). Crude oil 1 (ϱ = 0.8364 g/cm³) had a considerable fraction of volatiles and was stored in a floating piston cylinder (FPC) with a back pressure of 300 kPa. Crude oil 2 (ϱ = 0.8374 g/cm³) can be considered as 'dead' and was sampled with a standard tube from an open sample container. Both crudes were measured at various shaking speeds, ranging from 0 c/s to 5.7 c/s and each measurement was repeated two times to verify the result.

Initially, the conducted shaking speeds were reported as 1.5, 3.0, 4.5, and 6.0 c/s. Further investigation showed that for the higher shaking speeds these values had to be revised to 2.9, 4.3, and 5.7 c/s.

To expand the investigation, two additional crude oils from Canada were investigated, as reports have indicated that these crudes show a particularly large sensitivity to shaking speed. Crude oil 3 (ϱ = 0.9274 g/cm³) features a significantly higher viscosity than the previous two samples and a vapour pressure comparable to crude oil 1. Crude oil 4 (ϱ = 0.8193 g/cm³) showed a low viscosity while having an even higher vapour pressure than any of the other samples. Both crudes were kept in an FPC and the vapour pressure was determined at shaking speeds ranging from 1.5 c/s to 4.3 c/s.

The measurement curves (see **Figures 1 to 8**) depict the pressure during the progressing measurement in dependence of the applied shaking speed. The point of the ASTM D6377 stability criterion is marked.

Discussion

The measurements of the four different crude oils shown in **Figures**

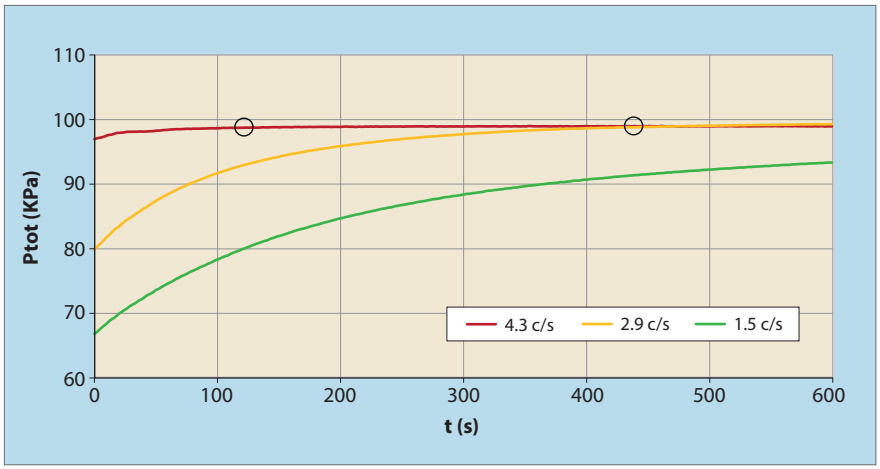

Figure 7 Crude oil 4 measured with a V/L ratio of 4.00 and variable shaking speeds between 1.5 c/s to 4.3 c/s. The equilibrium points according to ASTM D6377 are marked

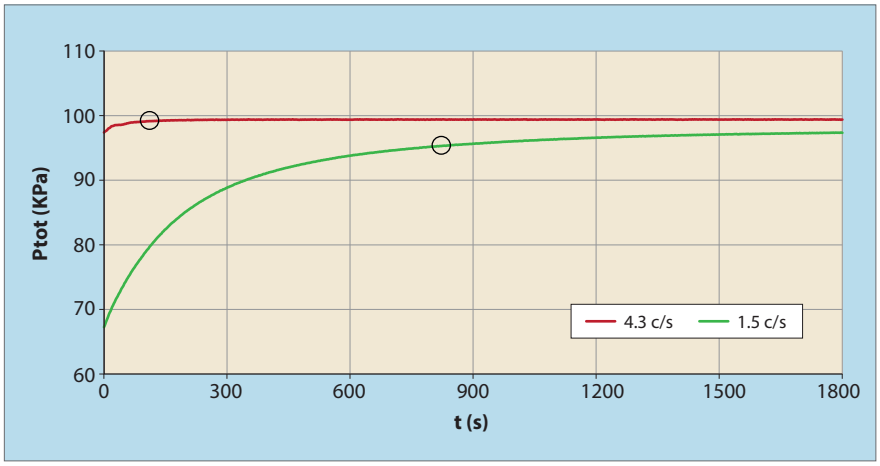

Figure 8 Crude oil 4 measured with a V/L ratio of 4.00 and variable shaking speeds of 1.5 c/s and 4.3 c/s up to 1800 s. The equilibrium points according to ASTM D6377 are marked

Time and pressure readings when the stability criterion of 0.3 kPa/60 s (ASTM D6377) is reached and the bias to the final pressure

Measurement		Equilibrium: time and pressure				
Sample	**Parameter**	**0 c/s**	**1.5 c/s**	**2.9 c/s**	**4.3 c/s**	**5.7 c/s**
Crude 1	Time (VPCR)	354 s	352 s	222 s	128 s	110 s
	VPCR	74.6 kPa	74.6 kPa	75.9 kPa	76.5 kPa	76.5 kPa
	Bias	2.1 kPa	2.1 kPa	1.8 kPa	0.2 kPa	0.2 kPa
	Time (eq.)	-	-	-	230 s	210 s
	Pressure (eq.)	-	-	-	76.7 kPa	76.7 kPa
Crude 2	Time (VPCR)	124 s	126 s	210 s	82 s	60 s
	VPCR	7.9 kPa	7.9 kPa	9.0 kPa	10.5 kPa	10.6 kPa
	Bias	2.7 kPa	2.7 kPa	1.6 kPa	0.1 kPa	0 kPa
	Time (eq.)	-	-	-	128 s	90 s
	Pressure (eq.)	-	-	-	10.6 kPa	10.6 kPa
Crude 3	Time (VPCR)	884 s	638 s	584 s	342 s	-
	VPCR	54.5 kPa	53.3 kPa	59.3 kPa	61.0 kPa	-
	Bias	7.4 kPa	8.6 kPa	2.6 kPa	0.9 kPa	-
	Time (eq.)	-	-	-	1240 s	-
	Pressure (eq.)	-	-	-	61.9 kPa	-
Crude 4	Time (VPCR)	866 s	840 s	440 s	124 s	-
	VPCR	95.1 kPa	95.3 kPa	98.5 kPa	99.0 kPa	-
	Bias	4.2 kPa	4.0 kPa	0.8 kPa	0.3 kPa	-
	Time (eq.)	-	-	856 s	354 s	-
	Pressure (eq.)	-	-	99.3 kPa	99.3 kPa	-

Table 1

1 to 8 all demonstrate the strong impact of shaking speed on the vapour pressure measurement. The higher the shaking speed, the higher the recorded pressures. Also, a higher shaking speed significantly speeds up the formation of a stable pressure.

Table 1 contains the time and VPCR results (the pressure readings when the stability criterion according to ASTM D6377 is reached). The difference between a VPCR result obtained with a shaking speed of 1.5 c/s 4.3 c/s ranges from 1.9 kPa (0.28 psi) for crude oil 1 to 7.4 kPa (1.07 psi) for crude oil 3. Also significant is the difference in measurement time. The time for reaching the stability criterion of ASTM D6377 correlates with the shaking speed and the viscosity: for crude oil 3, at the minimum frequency of 1.5 c/s this pressure stability is reached after 884 s, whereas at 4.3 c/s it takes only 342 s.

At the minimum shaking speed of 1.5 c/s, the pressure continues to rise significantly even after the ASTM D6377 cut-off criterion is reached. This results in a large difference between the VPCR result and the equilibrium vapour pressure. The bias between the VPCR and the actual equilibrium vapour pressure result (pressure at 1800 s with shaking speed of 4.3 c/s) can be as large as 7.4 kPa when a minimum shaking speed of 1.5 c/s is applied. For a shaking speed of 4.3 c/s, this bias is significantly smaller, implying a higher accuracy for these measurements.

Clearly visible for all four crudes at shaking speeds of 4.3 c/s (or above), the pressure eventually does not change any more. It can be argued that at this point a thermodynamic vapour pressure equilibrium has been achieved. In this regard, a shaking frequency of 4.3 c/s can be considered a critical threshold. When using a slower shaking speed, the formation of a thermodynamic vapour pressure equilibrium could not be observed within a reasonable measurement time. On the other hand, applying shaking speeds above 4.3 c/s does not change the final VPCR result any further, even though the final pressure level is reached slightly faster.

Conclusions

- A higher shaking speed leads to a higher VPCR.
- The difference between a VPCR result obtained with a shaking speed of 1.5 c/s and 4.3 c/s can be as large as 7.4 kPa (1.07 psi).
- Applying shaking speeds of 4.3 c/s or above eventually leads to the formation of a thermodynamic equilibrium vapour pressure.
- A VPCR result obtained at a higher shaking speed (4.3 c/s or above) is closer to (or at) the actual thermodynamic equilibrium vapour pressure, meaning this result is more accurate.
- The measurement time for ASTM D6377 can be reduced significantly by increasing the shaking speed.
- For Eravap, a shaking speed of 4.3 c/s (= "36" in the method parameters) was found to be the optimum setting for ASTM D6377 measurements.

Recommendations

- Always agitate the sample with the highest shaking speed possible. This results in a VPCR closer to (or at) the actual thermodynamic equilibrium vapour pressure.
- Include the shaking speed whenever comparing or reporting results. Many established vapour pressure testers provide only limited shaking speed (<< 4.3 c/s) and will therefore not reach thermodynamic equilibrium vapour pressure and report a too low VPCR result.

Christian Schröder-Holzhacker is a Product Manager with eralytics GmbH, Vienna, Austria. With prior experience in academia, his expertise is vapour pressure and flashpoint determination of various products throughout the petroleum industry. He holds a PhD in synthetic chemistry from the Vienna University of Technology, Austria.