

Crude Oil Vapor Pressure Testing

Why a higher shaker speed improves the accuracy of ASTM D6377



Background

The VPCR (vapor pressure of crude oil) 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 vapor pressure.

For an ASTM D6377 crude oil measurement, the specimen is introduced into the measuring cell, the piston expands against vacuum adjusting a vapor 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 / 60 s 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 (vapor 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 vapor 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 vapor 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 of *minimum frequency* of 1.5 c/s. In contrast, modern instruments (e.g.: eralytics' ERAVAP) can apply much higher shaking speeds leading to the question of the influence of shaking speed on the ASTM D6377 measurement.

The intention of this application note 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 vapor 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

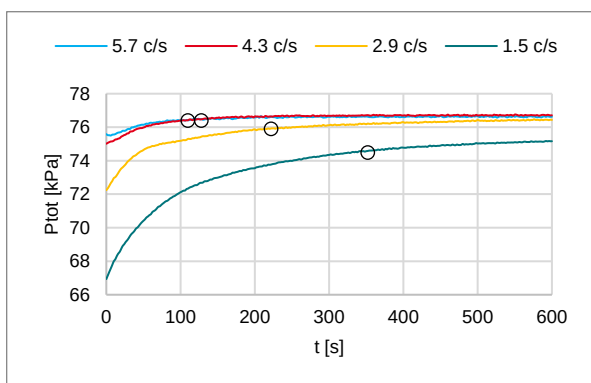
The following measurements were conducted on an ERAVAP EV10 with an integrated density meter module EV10-D4052. The density (ASTM D4052) and vapor pressure (ASTM D6377) were determined simultaneously for each sample.

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 ($\rho = 0.8364 \text{ g/cm}^3$) had a considerable fraction of volatiles and was stored in a FPC with a back pressure of 300 kPa. Crude oil 2 ($\rho = 0.8374 \text{ g/cm}^3$) 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 to 5.7 c/s and each measurement was repeated 2 times to verify the result.

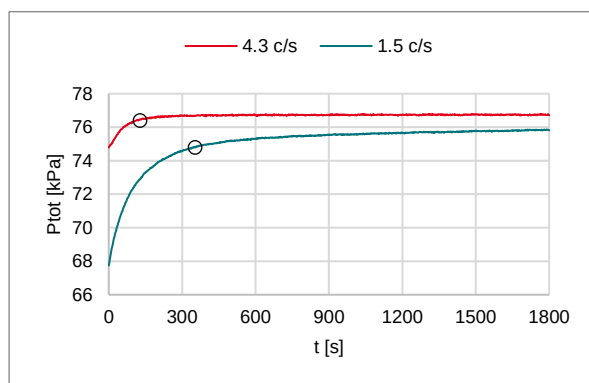
Note: In the initial version of this application note the conducted shaking speeds were reported as 1.5, 3.0, 4.5 & 6.0 c/s. Further investigation showed that for the higher shaking speeds these values had to be revised to 2.9, 4.3 & 5.7 c/s.

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 ($\rho = 0.9274 \text{ g/cm}^3$) features a significantly higher viscosity than the previous two samples and a vapor pressure comparable to crude oil 1. Crude oil 4 ($\rho = 0.8193 \text{ g/cm}^3$) showed a low viscosity while having an even higher vapor pressure than any of the other samples. Both crudes were kept in a FPC and the vapor pressure was determined at shaking speeds ranging from 1.5 c/s to 4.3 c/s.

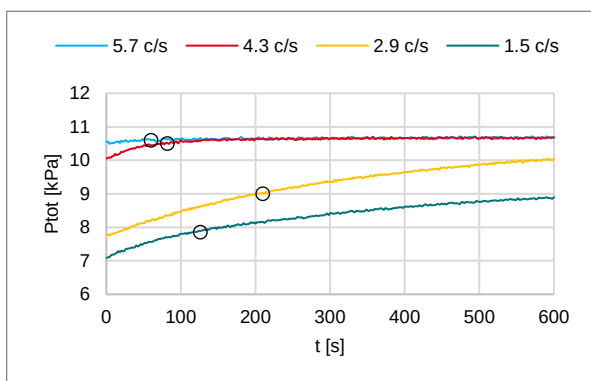
The measurement curves (graph 1-8) depict the pressure during the progressing measurement in dependence of the applied shaking speed, the point of the ASTM D6377 stability criterium is marked:



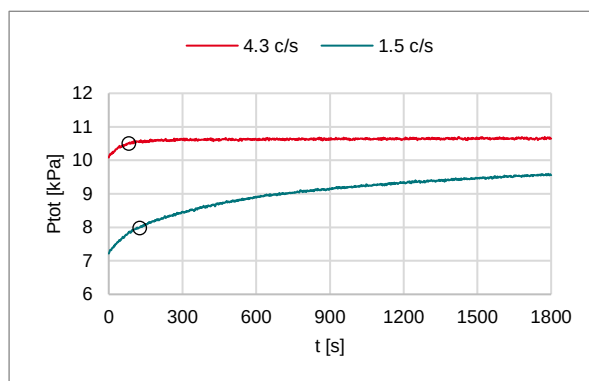
Graph 1: **Crude Oil 1** measured with a V/L ratio of 4.00 and variable shaking speeds between 1.5 c/s to 5.7 c/s. The equilibrium points according to ASTM D6377 are marked.



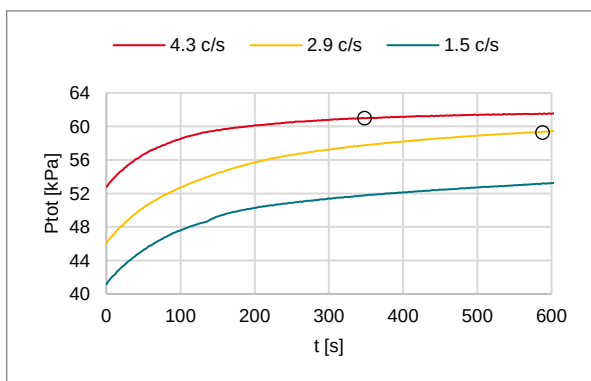
Graph 2: **Crude Oil 1** measured with a V/L ratio of 4.00 and variable shaking speeds of 1.5 c/s and 4.3 c/s up to 1800 s. The equilibrium points according to ASTM D6377 are marked.



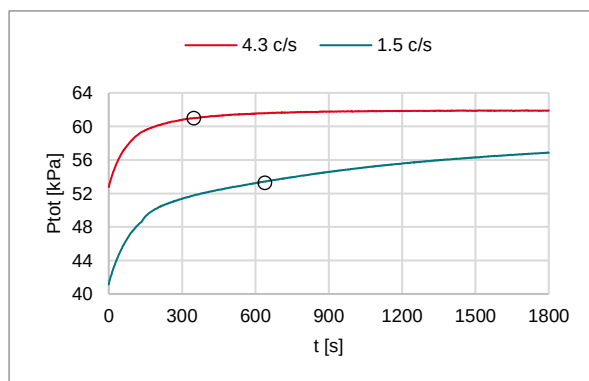
Graph 3: **Crude Oil 2** measured with a V/L ratio of 4.00 and variable shaking speeds between 1.5 c/s to 5.7 c/s. The equilibrium points according to ASTM D6377 are marked.



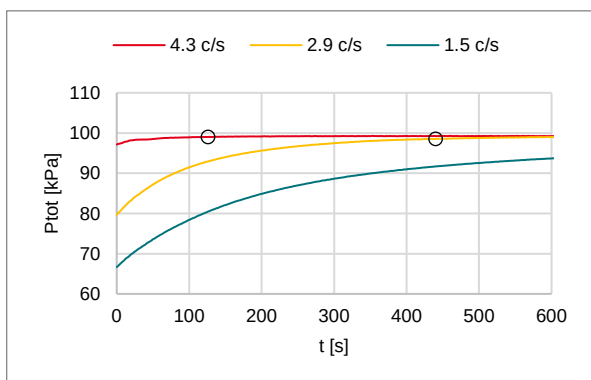
Graph 4: **Crude Oil 2** measured with a V/L ratio of 4.00 and variable shaking speeds of 1.5 c/s and 4.3 c/s up to 1800 s. The equilibrium points according to ASTM D6377 are marked.



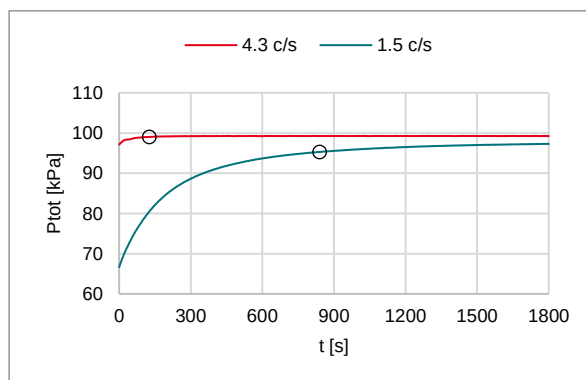
Graph 5: **Crude Oil 3** measured with a V/L ratio of 4.00 and variable shaking speeds between 1.5 c/s to 4.3 c/s. The equilibrium points according to ASTM D6377 are marked.



Graph 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.



Graph 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.



Graph 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.

Discussion

The measurements of the four different crude oils shown in figures 1-8 all demonstrate the strong impact of shaking speed on the vapor 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:

Sample	Measurement Parameter	Equilibrium: Time & Pressure				
		0 c/s	1.5 c/s	3 c/s	4.5 c/s	6 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: Time and pressure readings when the stability criterium of 0.3 kPa / 60 s (ASTM D6377) is reached and the bias to the final pressure.

Table 1 contains the time and VPCR results (i.e. pressure readings when the stability criterium 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 1 to 7.7 kPa (1.12 psi) for crude 3. Also significant is the difference in measurement time. The time for reaching the stability criterium 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 criterium is reached. This results in large difference between the VPCR result and the equilibrium vapor pressure. The bias between the VPCR and the actual equilibrium vapor pressure result (pressure at 1800 s with shaking speed of 4.3 c/s) can be as large as 8.6 kPa when a minimum shaking speed of 1.5 c/s is applied. For a shaking speed of 4.5 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 anymore. It can be argued that at this point a thermodynamic vapor pressure equilibrium has been achieved. In this regard a shaking frequency of 4.3 c/s can be considered as a critical threshold. When using slower shaking speed the formation of a thermodynamic vapor 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 anymore, 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 **7.7 kPa (1.12 psi)**.
- Applying shaking speeds of 4.3 c/s or above eventually lead to the **formation of a thermodynamic equilibrium vapor pressure**.
- A **VPCR result obtained at higher shaking speed (4.3 c/s or above) is closer to (or at) the actual thermodynamic equilibrium vapor 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 vapor pressure**.
- **Include the shaking speed** whenever comparing or reporting results. Many established vapor pressure testers **provide only limited shaking speed** (< 4.3 c/s) and will therefore **not reach thermodynamic equilibrium vapor pressure and report a too low VPCR result**.