

Vapour Pressure Testing of Gasoline and Crude Oil - Regulatory Changes and Resulting Possibilities

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Regulatory changes and increasing safety concerns in recent years led to extensive adjustments in process and laboratory vapour pressure testing. In the past it was required to determine the RVP - Reid Vapour Pressure according to the ASTM D323 standard. However, due to the sample preparation required by this standard, process analysers were never able to comply with it, but can only offer correlating measuring methods. Additionally, with ASTM D323 it is not possible to address the actual situation during transport of live crude oils. Developments for crude oil measurements according to the advanced standard ASTM D6377 as well as recent Tier 3 regulatory changes for vapour pressure testing of gasoline lead to changes that for the first time allow using the same measurement principle for process as well as laboratory measurements.

Introduction

Vapour pressure is one of the key parameters measured in the gasoline blending process. Due to the increased use of ethanol in fuel the measurement of the Reid vapour pressure (RVP) is replaced by ASTM D5191 in the EPA "Tier 3 Motor Vehicle Emission and Fuel Standards", because "...ASTM D323...is not applicable to ethanol-blended gasoline. It is being replaced with an automated ASTM D5191..., which is appropriate for ethanol-blended gasoline" [1].

While most process vapour pressure testers, which use their own methods, can be correlated to RVP (ASTM D323), it is nearly impossible to perform process measurements exactly to this standard. With the piston based ASTM D5191 it is possible to perform high quality measurements according to the standard, but again the sample preparation as described in the standard cannot be done correctly. When performing a measurement according to ASTM D5191 it is necessary to cool the sample to a temperature of 0 °C to 1 °C and saturate the liquid with air. In between the multiple saturation steps it is required to let the sample cool again for approximately 2 minutes. These steps are necessary for reproducible measurements. During the measurement a single expansion is performed, thus just the total vapour pressure (a combination of the partial pressure of the dissolved air and the vapour pressure of the liquid) is accessible. This can lead to uncontrollable deviations caused by the user when the sample preparation is not performed as requested by the standard.

The solution for this is the use of ASTM D6378, which is based on the same measurement principle. However, this standard is based on a triple expansion step, which allows calculating the absolute vapor pressure of the liquid, as well as the partial pressure of the dissolved air. Cooling or air saturation is not necessary, thus making it the ideal solution for process measurements. For samples with a vapour pressure of ≤ 82 kPa ASTM D6378 has an even better repeatability than using ASTM D5191. For the reproducibility this value even increases to 92 kPa. This covers a large area of gasolines which have a common vapour pressure range of 48 kPa to 103 kPa [2]. Formulas are available in the corresponding standards to correlate the measurements according to ASTM D6378 with ASTM D5191 results. This formula was determined in an interlaboratory study (ILS) by ASTM.

When dealing with the vapour pressure of crude oils recent incidents showed that the currently used measurement methods are not sufficiently reflecting the conditions that occur during transportation or storage. This is especially true when using a vapour / liquid (V/L) ratio of 4 compared to more realistic values of e.g. 0.02 which would equal a tank filled to 98%. The Crude Oil Quality Association (COQA) and the Canadian Crude Quality Technical Association (CCQTA) are currently working on an extension of ASTM D6377 to express these conditions. With the "Mini Methods" it is possible to measure more than one V/L ratio within a single curve measurement thus combining multiple measurements in a single step. Current discussions indicate that these curves measurements should cover a V/L range of 0.1 or even 0.02 up to 4. The temperature will be kept at 37.8°C, but additional measurements at other temperatures might be necessary to cover changing ambient conditions during transportation or storage.

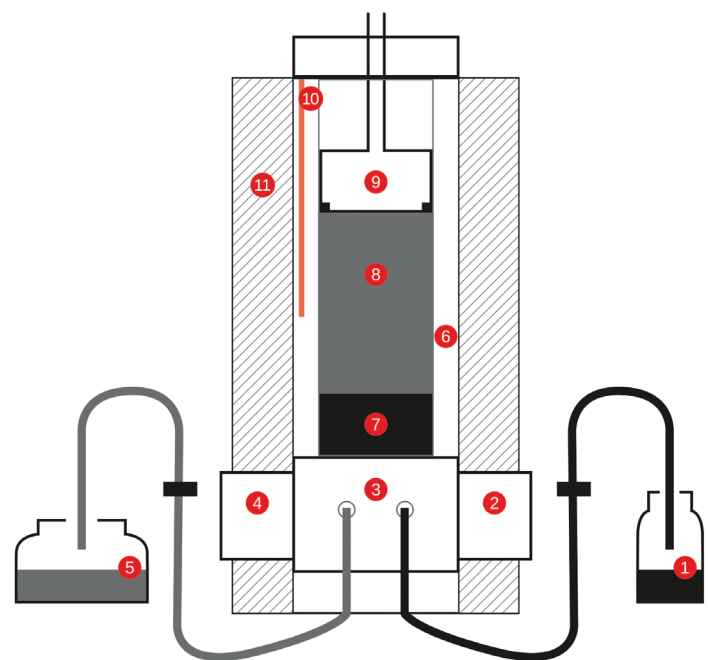
Within this publication we want to show the advantages using the "Mini Method" based ASTM D6378 and ASTM D6377 in terms of robustness and flexibility when analysing gasoline and crude oil.

Experimental

Piston based "Mini Methods"

The "Mini Methods" for vapour pressure testing of gasoline and crude oil are based on a piston inside a thermoelectrically stabilised measurement cell (figure 1). The piston is used to introduce the sample into the measurement cell. It incorporates a pressure sensor and is used to create the vacuum above the sample to determine the vapour pressure. This eliminates the need of a vacuum pump before or during the measurement. Depending on the sample volume and the position of the piston

after the expansion a wide range of V/L ratios can be selected. This allows to measure at realistic conditions e.g. when looking for vapour pressures that can be reached during transport and storage. The measurement cell is temperature controlled to allow measurements at a wide temperature range reaching from -20 °C to 120 °C independently from ambient temperature.



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|---------------|-------------------|-------------------------------|-----------------------|
| 1 sample | 4 outlet valve | 7 liquid phase | 10 temperature sensor |
| 2 inlet valve | 5 waste container | 8 gas phase | 11 insulation |
| 3 manifold | 6 measuring cell | 9 piston with pressure sensor | |

Figure 1: Measurement principle of the piston based vapour pressure analysers ERAVAP & ERAVAP ONLINE

Instruments & Samples

The gasoline measurements were performed using a typical Austrian gasoline blend. At the beginning of the measurements an infra red (IR) spectrum of the gasoline was recorded using eralytics FT-IR spectrometer ERASPEC. The spectrum is shown in figure 2 and some properties and parameters based on this spectrum are listed in table 1.

If not indicated otherwise the measurements were performed using the ERAVAP ONLINE (figure 3) process analyser from the Austrian manufacturer eralytics. During the measurements of gasoline ERAVAP ONLINE sampled one stream every 10 minutes for 50 hours. For comparison a sample was taken every hour (during daytime) and measured with eralytics laboratory vapour pressure tester ERAVAP (figure 4).

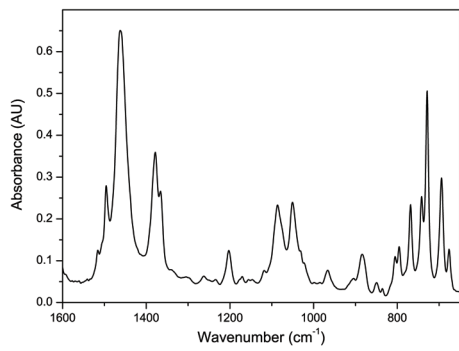


Figure 2: Absorbance spectrum of measured gasoline



Figure 4: ERAVAP vapour pressure tester



Figure 3: ERAVAP ONLINE vapour pressure tester with two sample conditioning systems

Table 1: Properties and parameters of the used gasoline (determined by ERASPEC from IR spectrum)

Properties		Parameters	
Density	0.7469 g/cm ³	Aromatics (sum)	29.2 v%
RON	97.1	Benzene	0.54 v%
MON	86.0	Toluene	8.35 v%
Vapour pressure	57 kPa	Xylene (o / m / p)	3.39 v% / 3.89 v% / 2.03 v%
IBP	34.8 °C	Ethanol	4.1 v%
T10	52.6 °C	Oxygenate	6.8 v%
T50	95.8 °C	Oxygen	1.91 w%
T90	147.9 °C	Olefines	8.8 v%
FBP	184.5 °C	ETBE	2.66 v%

The online and laboratory vapour pressure measurements of gasoline were performed at 37.8 °C. A triple expansion was used as mentioned in ASTM D6378 to measure the vapour pressure of the sample, the partial pressure caused by dissolved air and the total pressure. For a comparison of repeatability and reproducibility according to ASTM D5191 and D6378, the results of ASTM D6378 were converted to DVPE (dry vapour pressure equivalent) as described in the standard.

The crude oil measurements were performed with a Zarzaitine crude oil (density: 0.815 g/cm³). Typical compositions for crude oils of this region can be found in the literature [3] [4]. Due to transport and storage some of the light ends possibly were lost before the measurement, thus lowering the resulting vapour pressure, compared to literature values. When measuring the vapour pressure, the measurement cell was moved by a shaker as required by ASTM D6377. Curve measurements were performed with changing V/L ratios from 0.02 to 4 within a single measurement. Fresh crude oil was measured at various temperatures ranging from 0 °C to 75 °C.

Vapour Pressure Testing of Gasoline

During the measurement campaign with the process analyser the recorded vapour pressure remained in a stable region around 57.7 kPa. When comparing these results with the laboratory measurements an offset of 0.3 kPa can be seen (figure 4). When performing reference measurements using pentane, this effect was not visible. This shows that a small loss of volatile content happened during sampling. However, this offset was significantly lower than the reproducibility or even repeatability of ASTM D5191 and D6378, as indicated in figure 4.

This proves an easy and direct comparison between the process and laboratory vapour pressure tester. The process monitoring of the vapour pressure during blending is capable of performing trustfully measurements without the need of ongoing sampling for laboratory measurement. Additionally the triple expansion of ASTM D6378 eliminates the influence caused by different air saturation levels of gasoline during the process measurements.

Vapour Pressure Testing of Crude Oil

The results of multiple V/L curves at different temperatures are displayed in figure 5. For simplicity, just 2 states are indicated in the line plots showing the correlation between vapour pressure and temperature as well as vapour pressure and V/L ratio, respectively. Knowing the relation of V/L ratio, temperature and vapour pressure of different crudes is vital to judge the crudes behavior during transportation and storage at different conditions. When blending crudes of high viscosity with e.g. condensates for transportation the combined vapour pressure can be easily measured at the desired conditions.

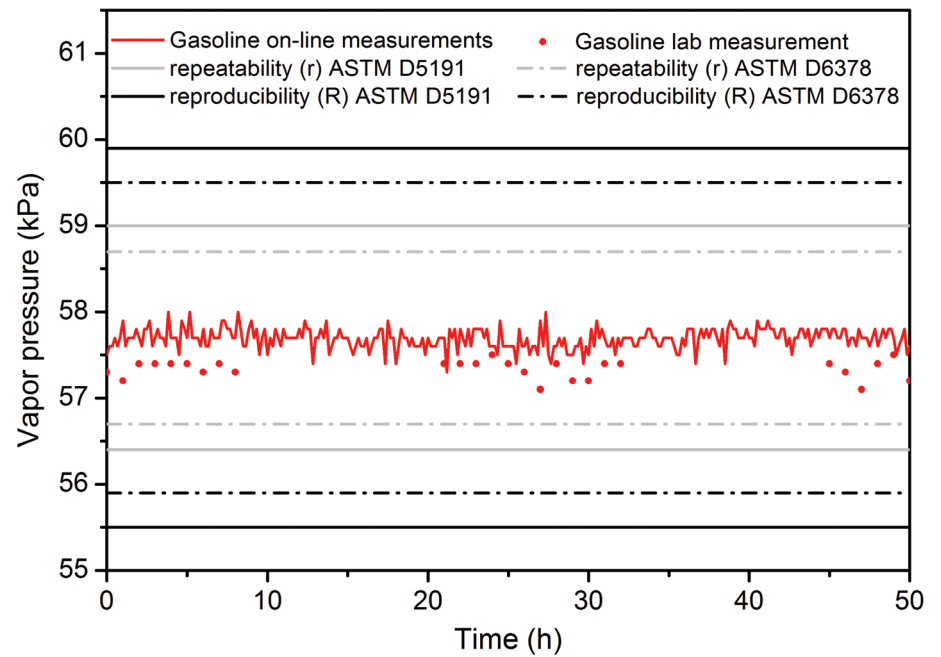


Figure 5: Online and laboratory vapour pressure measurements and limits for repeatability & reproducibility according to ASTM D5191 & D6378

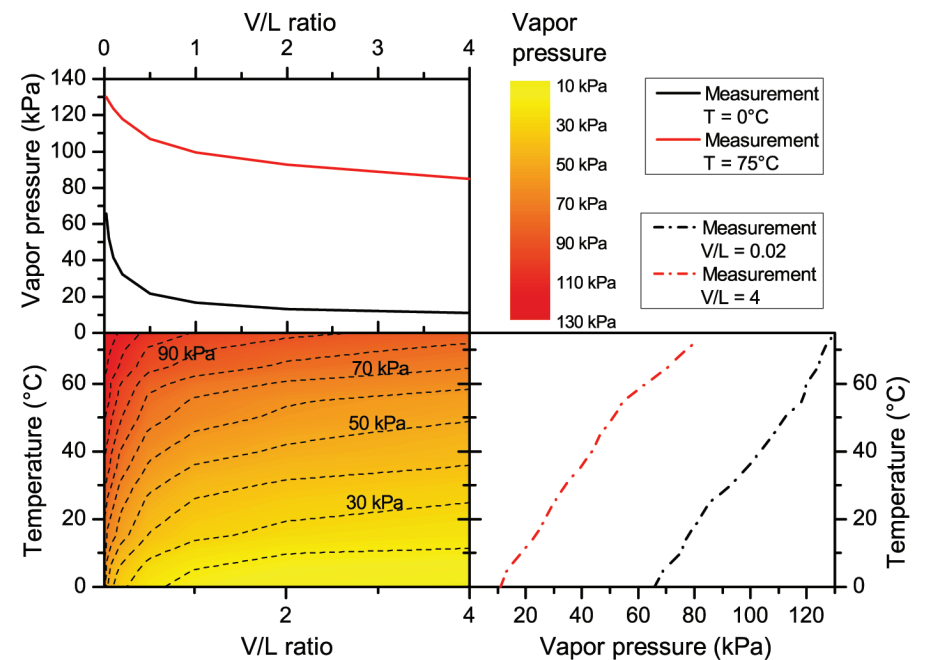


Figure 6: Vapour pressure of a sample crude oil at various temperatures and V/L ratios

The vapour pressure of the measured (dead) sample crude at standard conditions (V/L = 4, T = 37.8°C) was approximately 40 kPa. Considering the V/L ratio found in a tank increases the vapour pressure by a factor of approximately 2.5. Adding bright sunlight (T = 60 °C) into the equation increases the vapour pressure by a factor of 3 or more. Dealing with light crude oil containing high amounts of dissolved volatile hydrocarbons will increase the vapour pressure even further.

Summary

“Mini Methods” for vapour pressure testing like ASTM D5191, D6378 and D6377 are ideal to reflect current regulatory changes and safety concerns during transport and storage of petroleum products. For the first time the methods required by authorities, as well as the methods available for process (and laboratory) instruments are the same, allowing an easy comparison between laboratory and online measurements. This reduces the need for manual control measurements and allows higher automation for processes where vapour pressure is a key parameter.

Literature

- [1] United States Environmental Protection Agency, „Control of Air Pollution from Motor Vehicles: Tier 3 Motor Vehicle Emission and Fuel Standards Final Rule - Regulatory Impact Analysis (EPA-420-R-14-005),“ 2014.
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