

## *Measuring Crude Oil Vapor Pressure On Line precisely and reliably.*

The determination of the vapor pressure in crude oils and petroleum products is without doubts one of the most important parameters in the initial process of evaluating and characterizing these hydrocarbons. It is important not only for establishing the best route for their refining strategic program but also for determining the hazards associated with their transportation especially by rail.

Many cases have been reported of safety concerns and serious accidents due to improper procedures, uncertainty and errors in the determination of vapor pressures in hydrocarbons.

To properly establish the mechanisms for its safe transportation Environmental Policies and Federal Regulations are more and more stringent demanding continuous monitoring of this physical property.

Crude Oil blending operations respond to the need to facilitate oil transportation together with addressing the safety concerns of their transportation; to bring the final product into specifications especially for optimum refining operations and in general to optimize their commercial value. Reid Vapor Pressure (RVP) is the most common property used to monitor and control these operations. Although regulations change depending on territory and products, The State of North Dakota for instance issued a rule limiting the RVP of Bakken Oil for transporting by rail to less 13.7 psi.

In addition to regulations set forward by environmental agencies and stakeholders, risks associated with asset protection such as from pump cavitation and risk to floating roof tanks is also a consideration.

On May 1<sup>st</sup> 2015 the U.S. Department of Transportation (DOT) issued its final Crude-by-rail rule, effective July 1<sup>st</sup> 2015, that mandates more stringent standards for operational controls under 49 CFR B Chapter 1 Sub-chapter C Part 173. 49 CFR 173.41 addresses all sampling and testing programs for unrefined petroleum-based products. These materials must be properly classed and described as prescribed in §173.22. The regulation also specifies the frequency of sampling and testing, the sampling and testing methods, and the classification of the material under the HMR. Each person who offers a hazmat for transportation shall certify as prescribed by §172.204 that the material is offered in accordance with this subchapter.

In consequence, the characterization of crude oils, blends and other hazardous hydrocarbon materials demands for more controlled, reliable and rigorous analytical procedures.



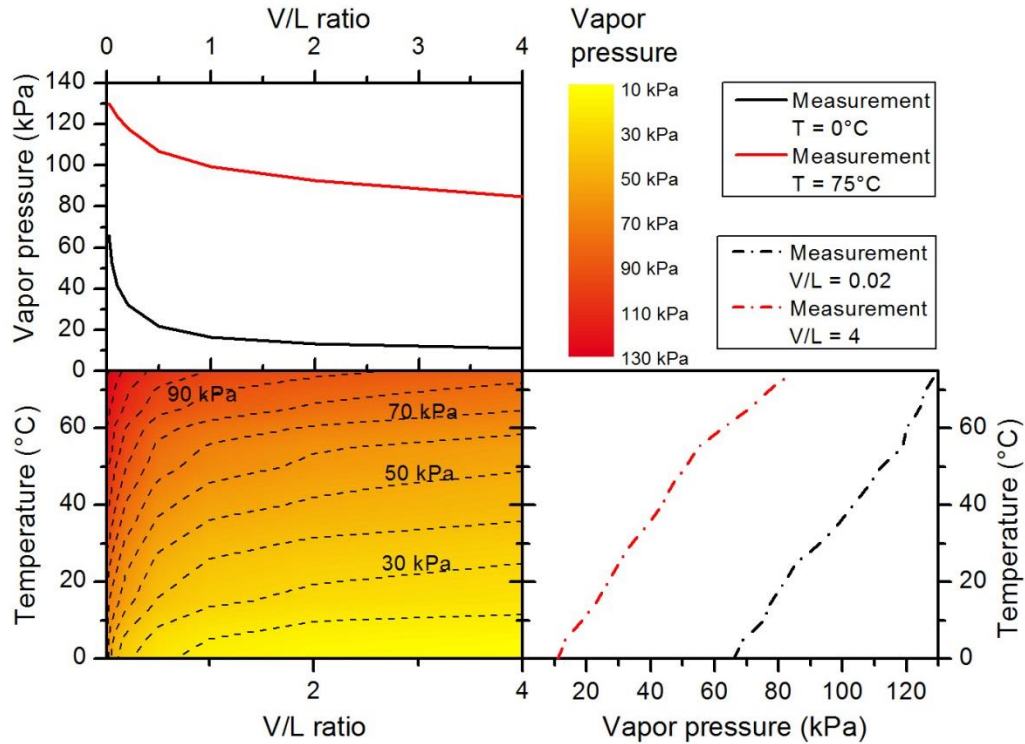
## **TVP and VPCR<sub>x</sub> for Blending Operations of Crude Oils**

Blending of C4 components into crude oils stocks has become an important profit driven process for many producers. Not only does this practice increase “followability” of heavier crude oils, but also increases the value of crude oils to a significant degree. By utilizing a relatively low cost blend stock such as butane, producers can create significant increased volumes and margin with ROI in less than a few months. Strict limits to blend ratios are typically defined by and agreed on between pipeline operators or between supplier/customer.

The analytical method used in most laboratories for certification of crude oil vapor pressure is ASTM D6377. This method reports a value that is equivalent to legacy ASTM methods such as ASTM D323, while reporting values with more precision and offering the ability to vary the vapor to liquid ratios used during testing. This ability is important as it has a great impact on the measured vapor pressure. The graphic below shows the increase of vapor pressure with smaller and smaller V/L ratios. Currently vapor pressure of crude oil is typically measured at a V/L ratio of 4. These measurements for example highly underestimate the pressure that can build up in a rail car which is typically filled to a V/L ratio of 0.1/1. Looking at floating roof tanks the situation gets even more extreme as the vapor pressure exponentially increases with decreasing V/L ratios. In the worst case the built up pressure inside a vessel exceeds the maximum safety pressure of it leading to a burst of the vessel with dramatic effects on the environment.

Consequently, the highest vapor pressure that can be reached for a given temperature will be measured at a V/L ratio of 0. This vapor pressure is called True Vapor Pressure (TVP) according to popular belief. Up till now, however, there is no official ASTM definition available.

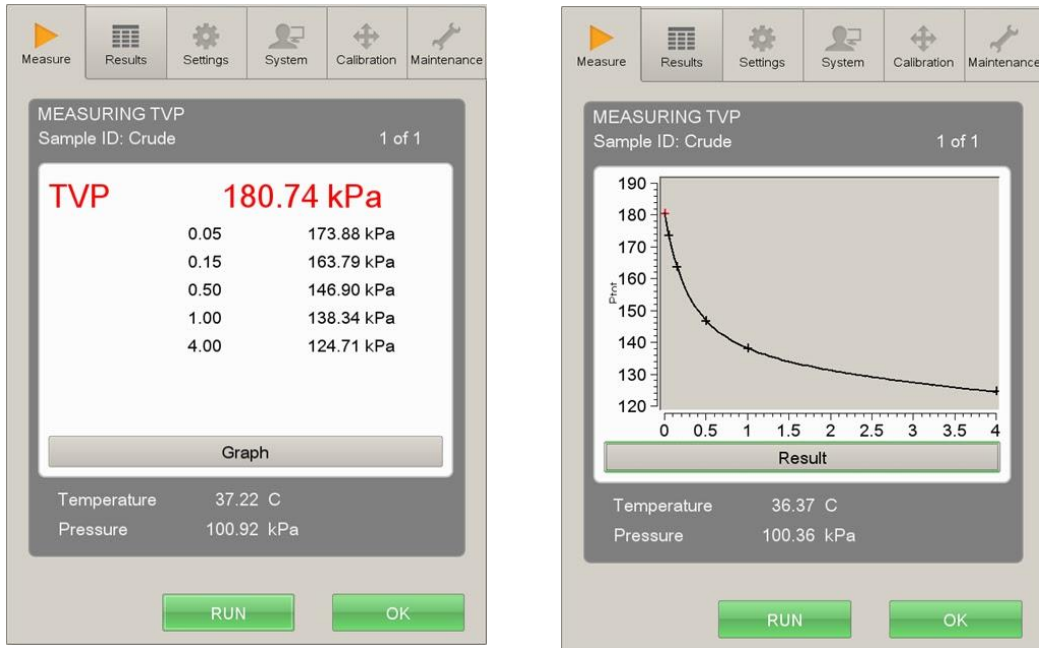
Caused by the measurement procedure it is not possible to measure the vapor pressure at such a V/L ratio and therefore the TVP value is extrapolated from at least three different V/L ratio measurements at the same temperature. See below for a graph that shows the evolution of the vapor pressure at different V/L ratios and temperatures to get a feeling of the various influences on the vapor pressure result.



What can be seen is that the vapor pressure rises the smaller the V/L ratio gets and the higher the temperature is. The slope of V/L vs vapor pressure curve is mainly determined by high volatile compounds contained in the sample.

Therefore it is a necessity to run crude oil samples only from floating piston cylinder sampling devices that have been pressurized all the time or directly from the process using a sample conditioning system. Measuring non pressurized samples or samples that have been exposed to air might underestimate the real TVP value of the sample as small hydrocarbons will degas from the sample altering its composition. Most samples will then give a TVP reading close to atmospheric pressure.

The default V/L ratios that have proven to work very well with ERAVAP ONLINE are 0.05, 0.15, 0.5, 1 and 4. The sample is drawn into the measurement chamber only once and the measurement starts at the smallest V/L ratio. Expanding the head space by each measurement finally gives all the needed measurement values to calculate the TVP result. It is possible to reduce the number of measurement points to three speeding up the measurement procedure having only little effect on the measurement accuracy. In this case it is recommend to use V/L 0.05, 0.15 and 0.5 to achieve good TVP results.



After the measurement the vapor pressures at all V/L ratios together with the TVP result are displayed.

Extrapolating data always heavily relies on accuracy and precision of the measurement data used for the extrapolation these parameters are more important than ever. ERAVAP Online performs at lab standards, fast, 24/7 and with minimum downtime during calibration, operation and preventive maintenance, due to its dual measurement cells. Its Piston-based measurement principle does not require an external vacuum pump. The built in sensors play an important role in the instrument stability rendering values of Repeatability of 0.3 kPa and Reproducibility of 0.7 kPa and a pressure resolution of 0.01 kPa possible for real life samples. This clearly shows the advantage over current standard methods. By having an instrument with this precision and performance it is possible to optimize blending operations not only in terms of product quality but also in the economy of the process as it allows for great savings reducing the quality giveaways.

ERAVAP Online fully complies with ASTM Standards D6377, D6378 and D6897. It also provides excellent correlation to other methods like D323, D5188, D5191 and EN 13016. ERAVAP Online, provides for up to eight control charts to monitor sample quality. All with the signification advantage of running reference referee ASTM methodologies for the utmost confidence in values.

Due to its active participation and collaboration with COQA and CCTQA associations ERALYTICS the manufacturer of ERAVAP Online contributes to the continuous improvement of measuring procedures, maximizing the safety of crude oil transportation.