Vapor Pressure Measurement Technology: Analysis of the Effects of Temperature on Vapor Pressure for Various Oil Samples

Koehler INSTRUMENT COMPANY, INC.

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Overview

Vapor pressure is important to measure in our industry, since a failure to account for a sample's vapor pressure can lead to accidents that impact the environment and human health. Volatile petroleum products can contribute to ground-level ozone, which is associated with numerous human health problems. To combat this, some governments regulate the vapor pressure of some petroleum products, such as gasoline, due to air pollution standards. For example, the EPA restricts the Reid vapor pressure of commercial gasolines during the summer to be less than a value of either 7.0, 7.8, or 9.0 psi, depending on the state and county. Therefore, vapor pressure testing is required to guarantee the gasoline meets the regional vapor pressure standard.

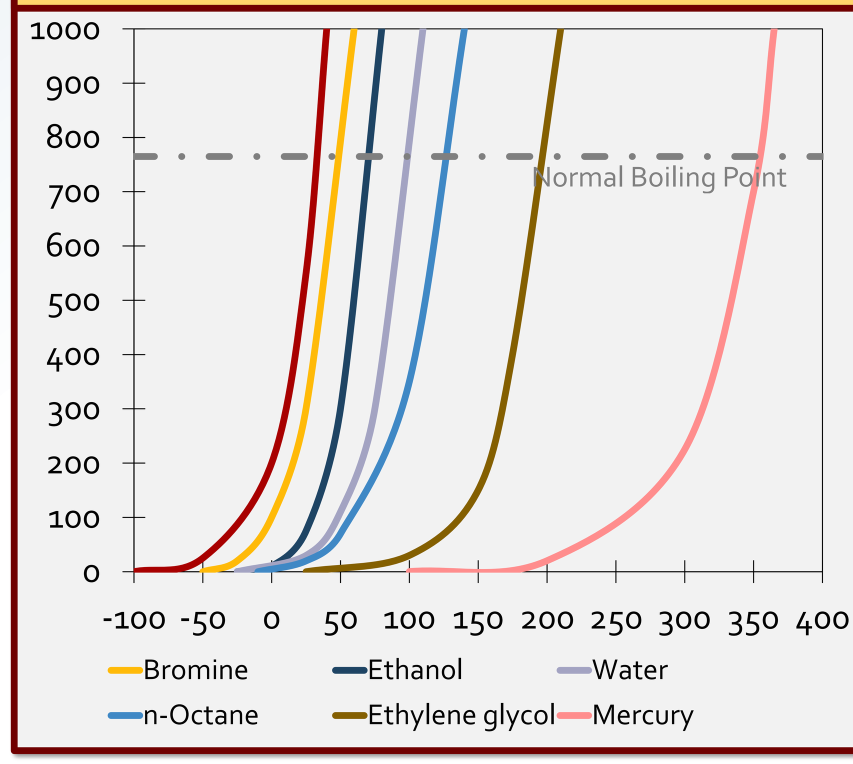
To determine the vapor pressure of a sample, there are various ASTM methods to follow. The Reid method for determining vapor pressure of petroleum products, described in ASTM D323, is the referee method, and was published in 1930. The method was developed by the German chemist Reid in 1927. In this method, a liquid chamber is filled with cooled sample and connected to a vapor chamber at 100°F, and the apparatus is help at a constant temperature of 100°F until a constant pressure is observed in the apparatus. The result of ASTM D323 is the Reid vapor pressure, or RVP. Over the years, ASTM D323 has served our industry well, however, in recent years there has been an interest by the market for newer methods, which require smaller sample volumes and easier procedures.

This push by the market has led to the development of new alternative methods for vapor pressure determination. In 1991, the mini method was developed, and is provided by ASTM D5191, and utilizes advanced technology compared to ASTM D323. In this method, 1 mL of sample is introduced into an evacuated test chamber, and then the test chamber is heated to 100°F, and the pressure in the chamber is measured. The result of ASTM D5191 is the dry vapor pressure equivalent, or DVPE.
Then in 1999, the triple expansion method for vapor pressure determination was developed, and is provided by ASTM D6378. This revolutionary method was developed by Dr. Grabner, and now serves as the new standard of vapor pressure testing in our industry. This method uses a piston to expand the test chamber, for a total of three expansions. At the end of each expansion, the total pressure in the chamber is measured. From the three pressure measurements along with the volume after each expansion, the partial pressure due to dissolved air is calculated. The vapor pressure (VPx) of the sample is then calculated by subtracting the partial pressure of air from the total pressure after the third expansion. ASTM D6378 also provides correlative equations to calculate the RVPE and DVPE.

References

- **ASTM D323-15a** "Standard Test Method for Vapor Pressure of Petroleum Products (Reid Method)"
- **ASTM D5191-15** "Standard Test Method for Vapor Pressure of Petroleum Products (Mini Method)"
- **ASTM D6378-10** "Standard Test Method for Determination of Vapor Pressure (VPx) of Petroleum Products, Hydrocarbons, and Hydrocarbon-Oxygenate Mixtures (Triple Expansion Method)"
- **Environmental Protection Agency** "Gasoline Reid Vapor Pressure" (United States)
- **Grabner Instruments** "The Standard for Vapor Pressure Testing of Gasoline and Crude Oil" (Austria)
- **Seta-Analytics** "Vapor Pressure Principle" (Granger, IN)
- **Bruce A. Averill, Patricia Eldredge** "The Vapor Pressure of Several Liquids as a Function of Temperature" (Principles of General Chemistry)

The Science of Vapor Pressure



These ASTM methods provide practical procedures to determine the vapor pressure of a sample. In scientific terms, the vapor pressure of a liquid is the pressure exerted by the liquid's vapor when the vapor and liquid are in equilibrium and is an indicator of a substance's volatility. The vapor pressure of a substance depends on the temperature and the composition of the substance, and the graph shown below is an example of how temperature and substance composition will affect the vapor pressure. The dependences on substance composition and temperature can be demonstrated in various equations to calculate the vapor pressure. The Antoine Equation is one of these equations and is shown below. In this equation, the constants A, B, and C depend on the substance, and T is the temperature in Kelvin.

Instrumentation

These new methods are successful in fulfilling the market demands, requiring only small amounts of sample and including automated procedures. Instrumentation for the new ASTM methods is smaller, making it easier to transport and use in the field or in the laboratory. These new methods are effective in simplifying the vapor pressure testing process and will efficiently serve the industry for years to come.

Koehler K11450

- ASTM D323
- 700 – 800 mL Required Sample
- 1 Hour Test Time
- 13.7 Gallon Bath
- Manual Unit

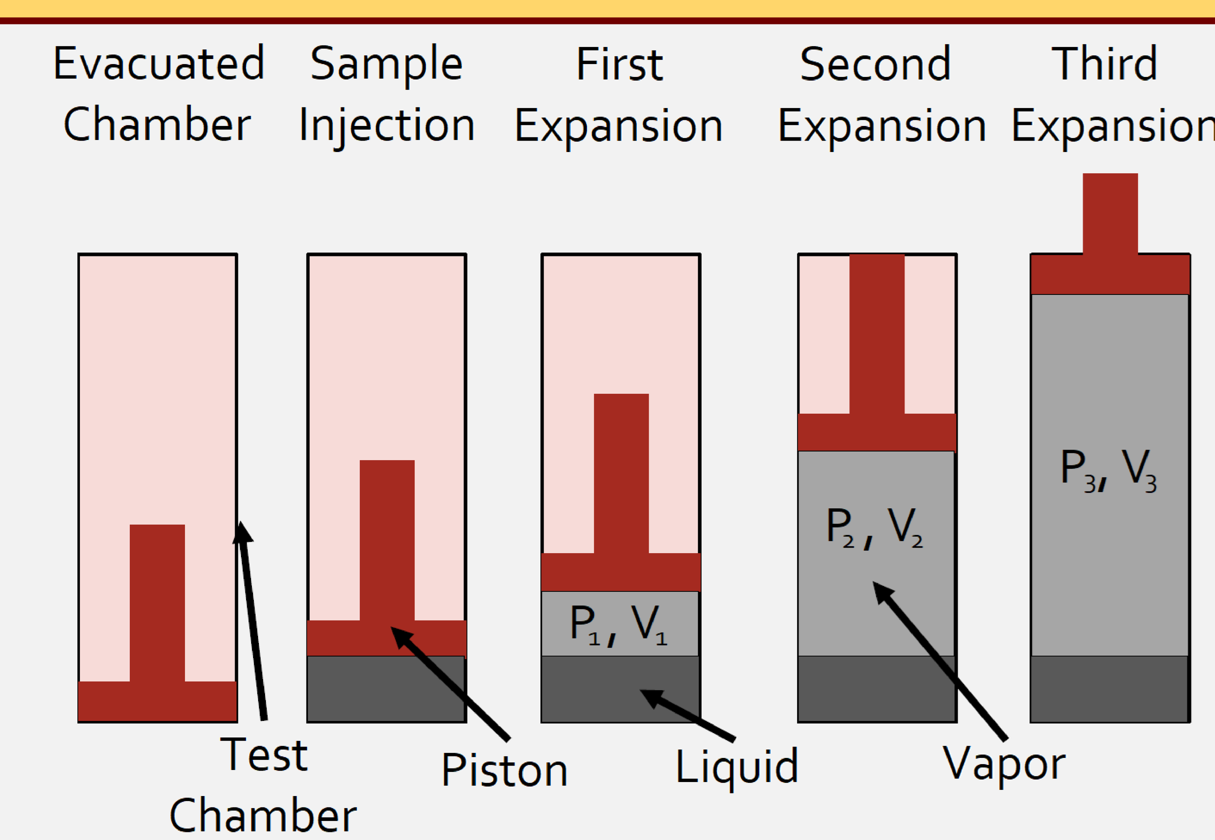
Koehler K24870

- ASTM D5191
- ASTM D6378
- 10 mL Required Sample
- 15 Minute Test Time
- Lightweight and Portable
- Automatic Unit

Operation of ASTM D6378

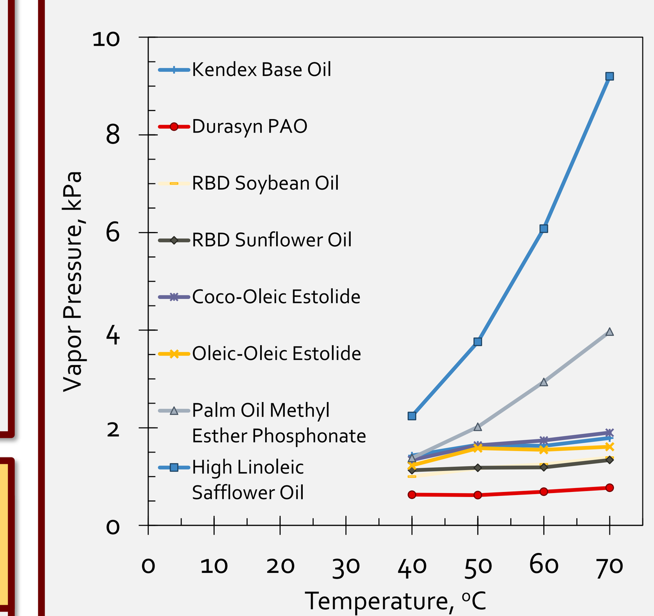
At the end of each expansion, the pressure and volume is measured. These values are used to calculate the sample's Vapor pressure with the following equation:

$$VP = P_3 - \frac{(P_1 - P3)(P_2 - P_3)}{\frac{V_3 - V_1}{V_2 - V_1}(P_1 - P_2) - (P_1 - P_3)}$$



Comparative Analysis

Various samples were tested to determine their vapor pressure with the Koehler K24870 unit. The samples were provided by the United States Department of Agriculture. The vapor pressure of each sample was measured as a function of temperature, under the guidelines of ASTM D6378. The results for the vapor pressure testing is shown in the table below in units of kPa.



Sample	40°C	50°C	60°C	70° C
Kendex Base Oil	1.43	1.65	1.63	1.79
Durasyn PAO	0.63	0.62	0.69	0.77
RBD Soybean Oil	1.00	1.17	1.25	1.39
RBD Sunflower Oil	1.13	1.18	1.19	1.34
Coco-Oleic Estolide	1.34	1.64	1.74	1.90
Oleic-Oleic Estolide	1.23	1.58	1.55	1.61
Palm Oil Methyl Esther Phosphonate	1.38	2.02	2.94	3.97
High Linoleic Safflower Oil Methyl Ester Phosphonate	2.24	3.76	6.08	9.20

The data expresses the theoretical relationship between the vapor pressure and temperature. Generally, as the temperature increases, the vapor pressure will increase exponentially. This is clearly shown in the results, especially for the Palm Oil and High Linoleic Safflower Oil Methyl Ester Phosphonate samples. The other samples express only a slight increase in vapor pressure with temperature, so perhaps to obtain a better curve, a higher temperature range should be used. This experiments shows the versatility of this vapor pressure instrument, as it can measure for a wide variety of samples. With ASTM D6378 as a basis of operation, the instrument can easily and quickly handle vapor pressure testing for many laboratory applications.

Conclusion

Vapor pressure is commonly tested for fuels, specifically gasolines, since it is an important specification for transportation and storage. From the moment the gasoline is produced to when it is sold, the vapor pressure must be determined at all stages of production. Since the gasoline must pass through various transportation containers and distribution centers, it would be ideal to have a quick test method that requires a small amount of sample. This is one industrial example where ASTM D6378 is a revolutionary test method, due to the small sample requirement and short test time. In addition, the instrumentation that conforms to ASTM D6378 is small, lightweight, and portable, allowing for vapor pressure testing to occur anywhere. The instrument used in this poster, the Koehler K24870, is one of such cutting-edge units in our industry. Overall, ASTM D6378 is an innovative method for vapor pressure testing and reduces the need for outdated methods, like ASTM D323. Instrumentation for ASTM D6378 is effective in improving the vapor pressure testing process by producing repeatable results with automatic procedures.