VAPOR PRESSURE TESTING AND REPORTING

Recent Developments and Clarifications

In Case You Weren't Aware

EPA document AP 42 *Compilation of Air Emissions Factors* is the primary compilation of EPA's emissions factors information. It contains emissions factors and process information for more than 200 air pollution source categories[1].

The Fifth Edition of AP-42 was published in January, 1995. Since then EPA has published supplements and updates to the 15 Chapters available in *Volume I, Stationary Point and Area Sources*[2].

Two chapters in this document are of particular interest:

Chapter 5 *Petroleum Industry*- Measurement and calculation of emissions during transport in vessels (rail cars/water-borne vessels), sale and marketing of finished products (service stations) and emissions from refinery process sources. Last Revision of this chapter was April, 2015.

Chapter 7 *Liquid Storage Tanks*- Particularly *Organic* liquid storage. Discussions of pure hydrocarbons as well as hydrocarbon mixtures such as gasoline, jet fuel, and crude oil. The most recent revision of this chapter was November 2019. Of specific interest are revisions regarding how the vapor pressure of crude oil should be measured and reported.

The Emissions Calculation Process

The calculations for emitted mass are based on conventional gas laws and direct measurements of the vapor or of the liquid composition. For very well-characterized fluids Raoult's Law may be used to derive the **Total Vapor Pressure** (P_{VA})[3].

True Vapor Pressure may be determined by ASTM D2879 (or ASTM D6377 for crude oils with a true vapor pressure greater than 3.6 psia).... For certain petroleum products, **True Vapor Pressure** may be predicted from **Reid vapor pressure**, which is the absolute vapor pressure of volatile crude oil products and non-viscous petroleum liquids, as determined by ASTM D 323. ASTM D 5191 may be used as an alternative method for petroleum products, however, *it should not be used for crude oils*[4] (emphasis mine).

What is TVP? Clarification, Please?

True Vapor Pressure is the sum of the partial pressures of each volatile component at a defined temperature at equilibrium. Entrained gases are vented or nulled.

Total Vapor Pressure is the sum of the partial pressures of each volatile component at a defined temperature at equilibrium. Entrained gases and very light hydrocarbons are not vented

Think about gasoline—manufactured product. Very little C3, and if it is present at all it is not by conscious desire to have it there. Little or no C1, C2, CO2, CO, Nitrogen, or **H2S** to impact VP results. O2 and N2 are nulled out in the sample prep.

Now think about crude oil- It is very likely to contain all of these components which may be partially or totally lost by aeration at 0 C.

TVP continued

RVP/DVPE is a good measure of True Vapor Pressure for products which generally do not contain *extremely* volatile components in measurable percentages.

True Vapor Pressure is the target parameter mandated by the EPA for calculating stationary emissions when a detailed analysis of the vapor in equilibrium with the liquid phase at a specified temperature is not available.

RVP/DVPE is a horrible measurement of True Vapor Pressure when intrinsic components have been lost during sample prep.

For crude oil however, Total Vapor Pressure = True Vapor Pressure

A Brief History

D323 (Reid Method) was developed as a performance specification for motor gasolines in the 1930s.

Optimized volatility for use in carbureted engines. The primary goal was to deliver a product with enough intrinsic volatility for cold-weather starting and operation without risking vapor lock at warmer temperatures or higher elevations.

Important indicator of suitability for the proper function and operation of gasoline-powered engines.

Much easier to perform than True Vapor Pressure measurement by isoteniscope (D2879).

Summary of Modifications and New Method Development

D323- Key test parameters such as test temperature, V/L ratio, and sample prep remain essentially static since WWII.

D4953-99- a key modification of the Reid procedure for gasoline and *gasoline-oxygenate blends*. Contact of the test specimen with water is not allowed. Product will not go 2-phase during testing.

D5188-91, D5190-91 and D5191-91 usher in the age of automatic testing for V/L ratio and vapor pressure of petroleum products. Much less dependent on operator technique.

D6377-99 and published as a means for determination of True Vapor Pressure in crude oil.

Brief History Continued

The Proposed Rulemaking of the Clean Air Act of 1990 initially mandated D323 for the determination of True Vapor Pressure in gasoline. Industry petitions for use of automatic analyzers and inundate EPA with correlation data. In the Final Rule issued in 1994 EPA allows use of automatic analyzers with a correlation factor derived in their labs. Introduction of term DVPE. Doesn't roll off the tongue like "RVP" And for gasoline they are basically equivalent numbers after correlation, so…..

D4953 was developed to counter impact of oxygenated gasoline blends reacting with the water/water vapor contained in a typical D323 cylinder.

D4953 found to be every bit as tedious as D323. Automatic analyzer sales surge.

Automatic and manual methods found to be inadequate for measuring True Vapor Pressure for crude oils. Some mitigation actions were tested (Shaking the analyzer to liberate dissolved gases) and found to be insufficient.

Crude Oil Prompts Further Method Research

Development and publication of D6377 – The Expansion Method

Key difference is in sample prep. No chilling or air saturation. Light components are not lost as quickly.

Retains the relative accuracy for measuring Total Vapor Pressure with the ease of the D5191 procedure.

Tariffs-Texas Style

The Texas Administrative Code[5]

(1)   & (2) Max 2.0% of basic sediment and water using "centrifugal machine"

(9) (Section C) Adjustments to quantities performed using API gravity corrected to nearest 0.5 API units.

(9) (Section D) A transfer of custody of crude between transporters is subject to measurement as agreed upon by the transporters.

That's it

Getting back to AP 42

Revision has been out for several months (November 2019).

Comments are extremely interesting, and the official response to each comment indicates thoughtful consideration and fact-based reasoning. Check them out at https://www.epa.gov/air-emissions-factors-and-quantification/ap-42-frequent-questions

Terminology When Discussing Vapor Pressure of Crude Oil

Don't reference Reid Vapor Pressure. Or RVP. Or even DVPE. Those are terms for refined products-not crude oil.

If your emissions software prompts you for an RVP value for estimating emissions from a crude oil tank—you most likely need new software. TANKS will not be updated. The conventional wisdom is that common calculation programs such as Excel are powerful enough to handle the calculations defined in AP 42.

Don't be lazy. If it means cleaning up some old spreadsheets, report formats, field procedures, lab procedures, tariffs....It's worth it to stop confusion when there is a direct impact on the integrity of your EPA reports.

Abbreviated Bibliography

1. https://www.epa.gov/air-emissions-factors-and-quantification/ap-42-compilation-air-emissions-factors.

2. Ibid.

3. *AP 42 Chapter 7 Section 7.1.3 pp 7.1-15 – 7.1-23.*

4. *Ibid p. 7.1-23 Note 2.*

5. The Texas Administrative Code (12/15/2019) Title 16, Part 1, Chapter 3.71.

Comments?