AYALYTICAL INSTRUMENTS
Technical Application Science

Storage Tank Emissions

Air Pollutants as a Function of Vapor Pressure and the EPA's New Expansion of Regulations

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Abstract

The Environmental Protection Agency (EPA) recently amended the source performance standards for volatile organic liquid and petroleum liquid storage vessels. The EPA published the final rule in the Federal Register Citations (FRC) for new source performance standards (NSPS) on September 30th, 2024. The amendments and additions were added to the code of federal regulations (CFR) citations under 40 CFR Part 60 Subpart Kb with a new section known as Subpart Kc.

These new amendments reduced the vapor pressure applicability thresholds to a maximum true vapor pressure (MTVP) greater than or equal to 10.3 kPa and MTVP greater than or equal to 3.4 kPa depending on the volume in which they are stored. The NSPS also revised the general applicability thresholds for reporting to 1.7 kPa. With these new standards, new additional lower explosive limit (LEL) monitoring and design/operating requirements to ensure compliance have also been established specific to the infrastructure of the storage tanks. The technical methods for determining the vapor pressure have also been changed from ASTM D2879 to the D6277/D6378 methods. Among the above statutes within Subpart Kc, amendments to NSPS Subpart Kb have been established to apply to VOC liquid and petroleum liquid storage vessels and also add electronic reporting requirements. Affectability is highly specific to a wide variety of factors like geographic location, volume, and tank design so find the full specifications under EPA 40 CFR Part 60 Subpart Kb and Kc.

The goal of these revisions is to expand air pollution controls to a wider range of storage vessels than is currently regulated under the current NSPS. The finalized VOC standards achieve an industry-wide 98% control efficiency for VOCs compared to the most recent NSPS which requires only 95% control efficiency.

Volatility and Vapor Pressure

Volatility has always been a physical characteristic of note because it describes how readily a chemical vaporizes at a given temperature and pressure. A substance with high volatility also has high vapor pressure, but the two are not necessarily the same thing. Vapor pressure is the quantitative measure of the pressure exerted by the vapor of a substance in a closed system at a given temperature, whereas volatility is a qualitative descriptor describing vaporization tendency.

Regulatory agencies like the Environmental Protection Agency (EPA) are invested in vapor pressure and volatility because when these chemicals evaporate into the air and atmosphere, they contribute to adverse health effects on people and the environment. Because of the dangers associated with volatile organic compounds (VOCs) specifically, regulations are in place to limit the emission output of larger-scale operations. Highly volatile chemicals like gasoline are heavily regulated to ensure their emissions into the environment are limited. Even compounds with low vapor pressures can contribute to human health and environmental issues when they exist in high enough quantities. Due to their contributions to things like ground-level ozone which decreases air quality and damages forest and crop health, storage facilities with high-volume tanks containing both of these high and low vapor pressure compounds must calculate and report their emission output to comply with these regulatory agencies.

Regulatory Emission Factors

The EPA has an extensive document, AP-42, which is the chief compilation of the EPAs emission factor information. An emission factor is a representative value that attempts to relate the quantity of a pollutant with an activity associated with the release of the pollutant. Emission factors are fundamental tools in developing emission control strategies. Typically, the mass of the pollutant is divided by a unit volume, mass, distance, or duration of the activity emitting the pollutant. The general equation for these emission estimates is:

$$E = A \times EF\left(1 - \frac{ER}{100}\right)$$

Where:

E = emissions

A = activity rate

EF = emission factor

ER = overall emission reduction efficiency

These variables provide an estimate of the emission levels of pollutants from various sources or industries, in which AP-42 details extensively. Each chapter focuses on a specific type of source like biogenic sources or industries like the petroleum industry, and chapter seven revolves around the output of emissions from stationary organic liquid storage tanks. This chapter is becoming increasingly important due to the recent amendments and additional regulations that require the calculation of estimated emissions to maintain compliance for these extensive tank networks containing all types of compounds.

Organic Liquid Storage Tanks

The compounds that participate in atmospheric chemical reactions defined by the EPA (40 CFR 51.100) as volatile organic compounds (VOCs) are required in a state implementation plan (SIP) emission inventory. This SIP is a collection of regulations used by state or regional agencies to implement, maintain, and enforce the National Ambient Air Quality Standards (NAAQS) set forth by the EPA, and to comply with other requirements in the Clean Air Act (CAA). These organic compounds that can react with atmospheric constituents can have relatively high or even considerably low vapor pressures; both of which contribute to ground-level ozone and need to be reported by using emission factors to calculate their estimated emissions.

The formulas producing these emission estimates are fully outlined in chapter seven of the AP-42 and were developed by the American Petroleum Institute (API) and derived from publicly available data and information. They take into account every possible variable ranging from chemical composition of the pollutant to storage container color and even meteorological wind data for the region in which the tanks exist. With estimates comes some level of diminished accuracy. In order to hone in to the true value these equations are aiming to derive, there are six basic subsets delineated by the type of tank being used. Two umbrella classifications include fixed and floating roof tanks and the general emission factor equations for these types of tanks can be found below:

1. Fixed Roof Tanks

$$L_T = L_S + L_W$$

Where:

$L_T = total\ routine\ losses,\ lb/yr$

$L_S = standing\ losses,\ lb/yr$

$L_W = working\ losses,\ lb/yr$

Expanded:

$$L_T = \left(365\left(\frac{\pi}{4}D^2\right)H_{VO}\left(\frac{\left(\Sigma M_i\left(\frac{Px_i}{P_{VA}}\right)\right)P_{VA}}{RT_V}\right)\left(\frac{\Delta T_V}{T_{LA}} + \frac{\left(P_{VX}-P_{VN}\right)-\left(P_{BP}-P_{BV}\right)}{P_A-P_{VA}}\right)\left(\frac{1}{1+0.053P_{VA}H_{VO}}\right)\right) + \left(V_Q K_N K_P\left(\frac{\left(\Sigma M_i\left(\frac{Px_i}{P_{VA}}\right)\right)P_{VA}}{RT_V}\right)K_B\right)$$

2. Floating Roof Tanks

$$L_T = L_S + L_W$$

Where:

$$L_T = total\ routine\ losses,\ lb/yr$$

$$L_S = standing\ losses,\ lb/yr$$

$$L_W = withdrawal\ losses,\ lb/yr$$

Expanded:

$$L_T = \left(\left(K_{Ra} + K_{Rb}v^n\right)D\left(\frac{\frac{P_{VA}}{P_A}}{\left(1+\left[1-\left(\frac{P_{VA}}{P_A}\right)\right]^{0.5}\right)^2}\right)\left(\frac{\left(\Sigma M_i\left(\frac{Px_i}{P_{VA}}\right)\right)P_{VA}}{RT_V}\right)K_C\right) + \left(F_F\left(\frac{\frac{P_{VA}}{P_A}}{\left(1+\left[1-\left(\frac{P_{VA}}{P_A}\right)\right]^{0.5}\right)^2}\right)\left(\frac{\left(\Sigma M_i\left(\frac{Px_i}{P_{VA}}\right)\right)P_{VA}}{RT_V}\right)K_C\right) +$$

$$\left(K_D S_D D^2\left(\frac{\frac{P_{VA}}{P_A}}{\left(1+\left[1-\left(\frac{P_{VA}}{P_A}\right)\right]^{0.5}\right)^2}\right)\left(\frac{\left(\Sigma M_i\left(\frac{Px_i}{P_{VA}}\right)\right)P_{VA}}{RT_V}\right)K_C\right) + \left(\frac{0.943QC_S W_L}{D}\left(1 + \frac{N_C F_C}{D}\right)\right)$$

*These equations do not take into account or display filling, landing, purging, and flashing losses. Variable and derivative information can be found extensively in Chapter 7 of AP-42.

These equations are a function of tank capacity, vapor pressure of the stored liquid, utilization rate of the tank, and atmospheric conditions of the tank location. The equations are derived from a theoretical energy transfer model. Some default parameters were assigned values to simplify the calculations based on this energy transfer model. The accuracy of the resultant equations are dependent on the likeness in which the storage containers under review fit the assumptions made for that specific subdivision of tank type.

Vapor Pressure as Variables

As can be seen by the above equations, vapor pressure values (P_{VX}, P_{VN}, P_{VA}, and P) are a critical variable in emission output from these storage tanks.

P_{VX} = Vapor pressure at average daily maximum liquid surface temperature, psia.

P_{VN} = Vapor pressure at average daily minimum liquid surface temperature, psia.

P_{VA} = Vapor pressure at average daily liquid surface temperature, psia.

P = True vapor pressure, psia.

Vapor pressure clearly contributes to emission factors in an extensive manner. Containers and tanks storing high vapor pressure liquids like VOCs and petroleum liquids drastically contribute to air pollution and this is why these liquids are the focus of the EPA.

New Source Performance Standards (NSPS) - Subpart K

The EPA exists as the statutory authority over these regulations as granted by the CAA section 111. This section explains the notion of governance of standards of performance for stationary sources contributing to air pollution. These standards are referred to as new source performance standards (NSPS) and the EPA has the scope to define the source categories, determine the applicability of compounds, set regulation levels, and distinguish between categorical delineations within classes themselves. The EPA is required to review these standards every eight years, and revise if necessary.

To set or revise these standards, the EPA must analyze “the degree of emission limitation achievable through the application of the best system of emission reduction (BSER) which (taking into account the cost of achieving such reduction and any non-air quality health and environmental impact and energy requirements) the Administrator determines has been adequately demonstrated” (CAA section 111(a)(1)).

Current Subpart Kb

The first petroleum liquid storage NSPS was promulgated in 1974 under NSPS subpart K, and was amended multiple times leading up to 1980. VOC storage was not added to the vessels under regulation until it was proposed in 1984 and codified in 1987 under subpart Kb. NSPS subpart Kb has two sets of applicability thresholds: one for determining affected facilities and the other for determining which of these facilities require controls. Subpart Kb regulates storage vessels with a 20,000 gallon or more capacity with true vapor pressures of more than 15.0 kPa, and storage tanks with a 40,000 gallon or more capacity with a true vapor pressure value of more than 3.5 kPa. Controls are required for 20,000 gallon or more vessels with true vapor pressure values over 27.6 kPa, and from 40,000 or more gallon tanks with values greater than 5.2 kPa. These controls require the use of floating roofs: either internal or external roofs with supplemental vent systems and other control devices. Both require gaskets and rim seals to prevent vapor escape into the atmosphere.

Amendments and Additions to Subpart K

Following the scheduled review of subpart K, after using BSER assessments alongside predictive emission factor modeling using the equations above from chapter 7 of AP-42, and compared to the estimated cost effectiveness and impact on the environment and economy, the EPA proposed revisions to the NSPS subpart Kb alongside the addition of subpart Kc. The major revisions and additions can be found below:

1. Simplified Applicability Threshold

The first major proposal lowers the threshold for applicability to 1.7 kPa. This means any storage vessel greater than 20,000 gallons containing VOCs or petroleum liquids that has extremely low vapor pressures will not be subject to subpart Kc regulations without having to meet the prerequisite vapor pressure level. This amendment establishes a baseline for monitoring and recordkeeping in tanks that have very low vapor pressure emission properties.

2. Revision of Controls Applicability

Another major revision includes the lowering of the threshold for facilities to have controls in place. Vessels between 20,000 and 40,000 gallons with a true vapor pressure greater than or equal to 10.3 kPa and vessels above 40,000 gallons with a value of 3.4 kPa are required to have controls in place to further reduce emissions.

3. Storage Control Compliance

The EPA has also opted to include more specific requirements for vessel design to limit standing emissions. For tanks with a vapor pressure less than 76.5 kPa, an internal floating roof with enhanced rim seals is required. The equipment standard designates the vessel must have a liquid-mounted or mechanical shoe primary seal and rim-mounted secondary seal to be in compliance. Tanks in compliance with these standards were found to have 98% control efficiency. Some external floating roofs with extensive and adequate closed vents and controls can achieve the 98% control which can be used as an alternate form of compliance.

For tanks holding VOC and petroleum liquids with vapor pressures greater than 76.5 kPa, a closed vent system with a control device must be installed and also achieve 98% control efficiency.

4. Lower Explosive Limit Monitoring

The current standard only requires inspections of internal floating roof systems with dual seals every five years, but under the new guidelines, annual inspections must be performed alongside lower explosive limit (LEL) monitoring of the headspace to more readily identify malfunctioning vessels. This addition is a less subjective means to monitor and verify performance of the floating roofs.

5. Technical Methods for VP Determination

The current method for determining vapor pressure values for proper operation, monitoring, and reporting is designated as the American Society for Testing and Materials (ASTM) D2879. However, the new guidelines are switching the technical method for determining these values to ASTM D6378-22 and D6377-20. These methods are automated and produce more accurate vapor pressure measurements.

ASTM D6378-22 "Standard Test Method for Determination of Vapor Pressure (VPX) of Petroleum Products, Hydrocarbons, and Hydrocarbon-Oxygenate Mixtures (Triple Expansion Method)," is used for measuring vapor pressures between 7 kPa and 150 kPa.

ASTM D6377-20 "Standard Test Method for Determination of Vapor Pressure of Crude Oil: $VPCR_x$ (Expansion Method)," is used for measuring vapor pressures between 29 kPa and 180 kPa. For each analysis, you must use a 4:1 vapor to liquid ratio.

6. Electronic Reporting Requirements

Operators will also be required to submit monitoring reports electronically to the central data exchange which will enhance the usefulness of the information.

Affected Parties and Effective Outcomes

The EPA estimated that approximately 240 new storage vessels become subject to the NSPS subpart Kb every year, such that 1,200 new storage vessels could become subject to NSPS subpart Kc over the next five years if no change in thresholds is adopted.

It was projected that with lower vapor pressure thresholds, approximately 20 percent more storage vessels could become subject to the NSPS subpart Kc standards each year.

The lowered control applicability thresholds yield emission reductions at a cost of $6,000 to $7,000 per ton of VOC reduced.

The EPA estimates a reduction of VOC emission by 1,085 tons per year.

Based on 2022 values, the revision will cost approximately $20.6 million in total capital cost and result in total annualized savings of $4.48 million per year including product recovery.

Summary of Amendments

Under the new guidelines released by the EPA revising subpart Kb and adding subpart Kc, any VOC and petroleum liquid storage vessel over 20,000 gallons with a vapor pressure above 1.7 kPa is subject to monitoring and reporting emissions. The vapor pressure applicability threshold requiring storage vessels to have controls in place was also decreased from 15.0 kPa to 10.3 kPa for tanks with a volume between 20,000 and 40,000, with any vessel greater than 40,000 gallons requiring controls with a vapor pressure greater than 3.4 kPa (threshold decreased from 3.5 kPa). The equipment standard was also updated mandating 98% control efficiency (increase form 95%) using an internal floating roof with a dual seal system for vessels with vapor pressure values less than 76.5 kPa, and requiring a closed vent system with controls for tanks greater than 76.5 kPa. The revisions also mandate annual roof inspections with lower explosive limit (LEL) measurements. The technical method for the determination of vapor pressure values has also switched from ASTM D2879 to ASTM D6378-22 and D6377-20 in efforts to produce more accurate vapor pressure values. All monitoring values and data are also now required to be submitted electronically to the central data exchange.

For more information on all of the amendments and additions to the NSPS and other resources related to these standards, including how you specifically will be affected, navigate to the NSPS publication.