

# Vapor Pressure of Heavy Petroleum Liquids for Estimating Emissions

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## Introduction

This technical report will provide a methodology to predict the vapor pressure for heavy petroleum liquids (i.e. having vapor pressure below 1 psi) over a range of temperatures by evaluating the results of simulated distillation tests in process simulation software. The term “vapor pressure,” for purposes of this report, refers to the sum of the equilibrium partial pressures exerted by the components of a volatile organic liquid at a given temperature.



# Vapor Pressure of Heavy Petroleum Liquids for Estimating Emissions

## 1 Scope

This technical report provides a methodology to predict the vapor pressure for heavy petroleum products over a range of temperatures by evaluating the results of simulated distillation tests in process simulation software.

## 2 Terms, Definitions, Acronyms, and Abbreviations

### 2.1 Terms and Definitions

There are no terms and definitions specified for the purposes of this document. Terms of more general use can be found in the API *Manual of Petroleum Measurement Standards (MPMS)* Chapter 1 *Terms and Definitions* online database.

### 2.2 Acronyms and Abbreviations

|      |                                                  |
|------|--------------------------------------------------|
| API  | American Petroleum Institute                     |
| ASTM | American Society for Testing and Materials       |
| EPA  | US Environmental Protection Agency               |
| GC   | gas chromatograph                                |
| MPMS | <i>Manual of Petroleum Measurement Standards</i> |
| MW   | molecular weight                                 |
| RVP  | Reid vapor pressure                              |
| SG   | specific gravity                                 |
| TBP  | true boiling point                               |
| VOC  | volatile organic compound                        |

## 3 Executive Summary

### 3.1 Statement of Purpose

Currently, there are limited vapor pressure data available for use in estimating tank emissions for heavy petroleum liquids. The limited data provided in API *MPMS* Chapter 19.4 are likely outdated, as discussed in 4.3. As discussed in Section 4, a method is needed for obtaining more representative vapor pressure data over a range of temperatures to improve emissions estimation from tanks storing these heavy stocks.

This project was initially tasked with collecting and evaluating existing vapor pressure or distillation curve data for heavy (low-volatility) petroleum liquids. However, collection of vapor pressure data was not successful because there was not a reliable test method available for determining vapor pressure for heavy stocks. The project then focused on developing a methodology for predicting vapor pressure of heavy stocks from distillation curve data.

This technical report presents methodology for predicting the vapor pressure of heavy stocks over a range of temperatures by evaluating the results of simulated distillation tests in process simulation software. The protocol for the method is provided in Annex A.

### 3.2 Method for Predicting Vapor Pressure

#### 3.2.1 General

The method presented in this report for predicting vapor pressure of a stock involves the following steps.

- Perform simulated distillation tests on at least three samples of the petroleum liquid in question.
- Enter the results of the simulated distillation tests into process simulation software to determine the predicted vapor pressure at multiple temperatures that span the range of typical storage temperatures.
- Perform a regression analysis of the vapor pressure versus temperature data to obtain vapor pressure constants that can be used to predict the vapor pressure at any given temperature.

These steps are described in more detail below.

### 3.2.2 Perform Simulated Distillation

Companies reported that simulated distillation is routinely performed on samples of heavy refinery streams for process purposes. Simulated distillation involves introducing a liquid sample into a gas chromatograph (GC), and the boiling point temperature of each fraction is then predicted from the retention time of that fraction in the column of the chromatograph. The array of boiling points thus obtained is then compiled into a distillation curve. In that the distillation curve is a function of the volatility of the compounds making up these liquid mixtures, it was hypothesized that characterization of the stream from the distillation data would allow prediction of the vapor pressure.

Simulated distillation results are typically reported as the temperature at 0.5 % distilled, 5 % distilled, 10 % distilled, and then at increments of 10 % distilled. ASTM methods D2887 and D7169 for simulated distillation both specify 0.5 % distilled as the initial boiling point, which accounts for initial vaporization from wetting of the distillation equipment as the apparatus heats up. Assignment of 0.5 % distilled as the initial boiling point also minimizes the impact of entrained gases, corresponding to the use of a vapor-to-liquid ratio of 4:1 in a Reid vapor pressure (RVP) test.

The vapor pressure of the stock, for purposes of estimating emissions, is the sum of the equilibrium partial pressures of the constituent compounds. The heavier compounds of these heavy stocks contribute very little to the sum of the constituent vapor pressures, and thus the vapor pressure of the stock is largely determined by the first fractions to boil. The traditional reporting convention, however, reports only 3 data points for the first 10 % distilled as shown in Figure 1.

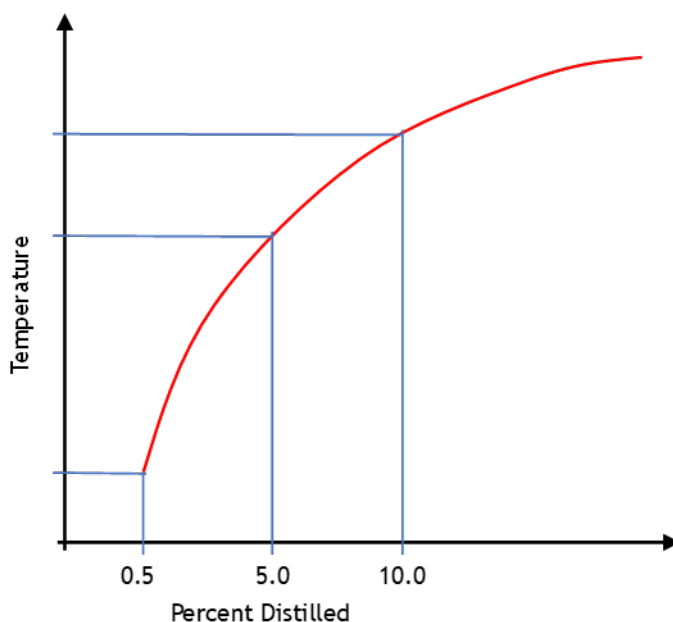


**Figure 1—Simulated Distillation Traditional Reporting Convention for the First 10 % Distilled**

It was determined that a single data point for the fraction below 5 % distilled (i.e. the temperature at 0.5 % distilled) did not provide sufficient detail to reasonably characterize this fraction. To achieve greater granularity in the characterization of the most volatile fractions, it was determined from trial runs that these fractions were adequately characterized by reporting the distillation temperature at increments of 0.1 % distilled for the range of 0.5 % distilled to 10 % distilled, as represented in Figure 2. The simulated distillation tests should be reported in this manner for each of the three samples from the stock in question, and the results then compared to evaluate repeatability as specified in Annex A.

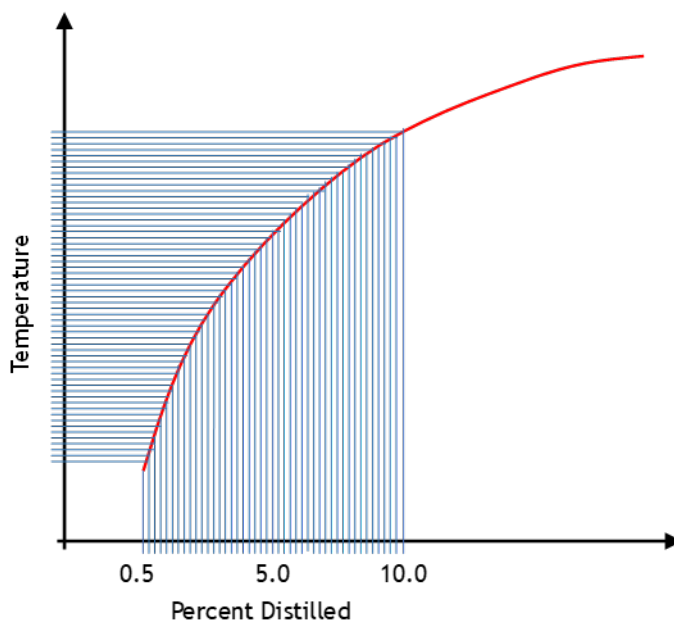


**Figure 2—Simulated Distillation Results Reported in Small Increments for the First 10 % Distilled**

### 3.2.3 Evaluate with Process Simulation Software

Simulated distillation data that meet the specified repeatability criteria are then entered into process simulation software, along with the stock density, to create a model of the heavy stock. Process simulation software creates a set of hypothetical components, sometimes referred to as pseudo components, to represent the full distillation curve. The properties associated with the pseudo components are estimated using correlations available in the software. As with the reporting of simulated distillation results, the assignment of pseudo components to mole fractions representing the heavy stock should be done in a manner that will result in adequate granularity so as to reasonably characterize the most volatile fractions. That is, enough pseudo components should be used to represent the front end of the distillation curve to ensure a good match of the process simulation model with the distillation data.

For example <sup>1</sup>, if the difference between the temperature at 0.5 % distilled and the temperature at 5.0 % distilled is 200 °F, and pseudo components are assigned at increments of 40 °F, then the 45 data points reported from the simulated distillation for this range will be represented by only five pseudo components in the process simulation software. This is illustrated in Figure 3, where each horizontal bar represents a pseudo component assigned to a given range of temperature.

<sup>1</sup> The following are merely examples for illustration purposes only. (Each company should develop its own approach.) They are not to be considered exclusive or exhaustive in nature. API makes no warranties, express or implied, for reliance on or any omissions from the information contained in this document.

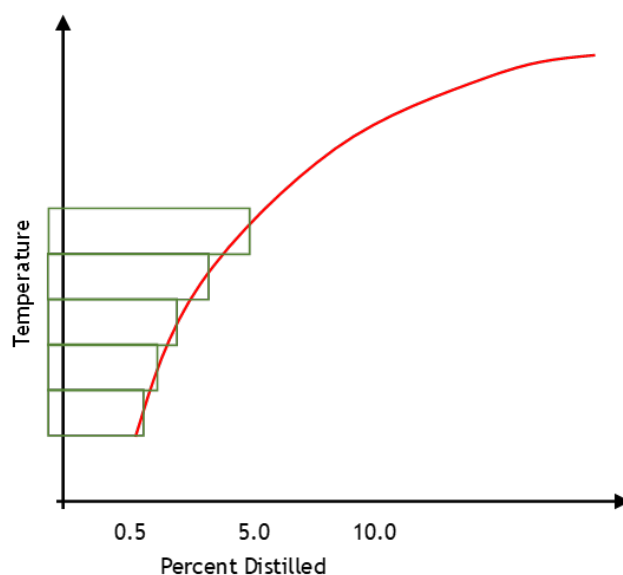


**Figure 3—Pseudo Components Assigned to Relatively Large Ranges of Temperature**

To prevent this from occurring and to retain the desired granularity in the process simulation software model of the heavy stock, it was determined from trial runs that pseudo components should be assigned in temperatures range increments of not greater than 5 °F for the fraction from 0.5 % to 10.0 % distilled. This limitation of the temperature range represented by each pseudo component will result in a better representation of the distillation curve, as shown in Figure 4.

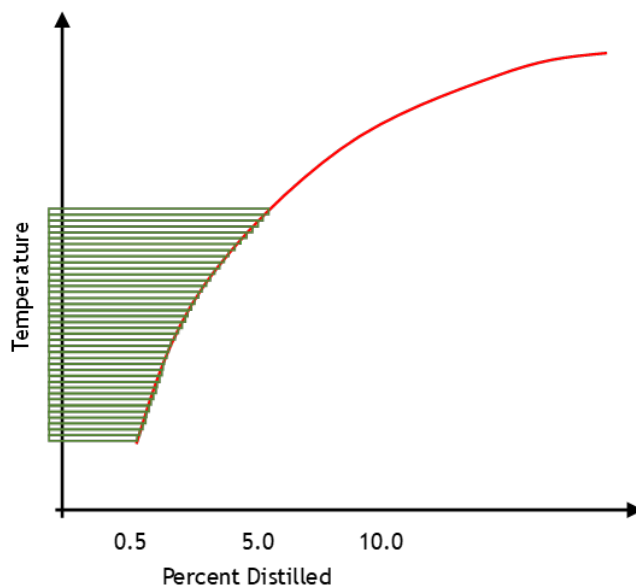


**Figure 4—Pseudo Components Assigned to Relatively Small Ranges of Temperature**

Having modelled the heavy stock in the process simulation software by the assignment of pseudo components to represent the fractions determined from the simulated distillation, the process simulation software can then report predicted vapor pressure values for given levels of temperature.

### 3.2.4 Perform a Regression Analysis

For pure substances over a sufficiently small temperature range, the change in vapor pressure has been shown to be reasonably approximated by the exponential Clausius-Clapeyron equation given as Equation (5) in API *MPMS* Chapter 19.4, and this same dependency has also been applied empirically to mixtures:

$$P_{VA} = \exp \left[ A - \frac{B}{T_{LA}} \right] \quad (1)$$

where

$P_{VA}$  is the stock true vapor pressure (psia);

$T_{LA}$  is the daily average liquid surface temperature (degrees Rankine);

$A$  and  $B$  are the vapor pressure constants.

Generically stating vapor pressure as  $P$  and temperature as  $T$  gives:

$$P = \exp \left[ A - \frac{B}{T} \right] \quad (2)$$

This can be restated as:

$$\ln(P) = A - B \left( \frac{1}{T} \right) \quad (3)$$

This expression can be evaluated as the linear equation:

$$y = A - B(x) \quad (4)$$

where

$$y = \ln(P);$$

$$x = \left( \frac{1}{T} \right).$$

Given sets of values for  $P$  and  $T$  from the process simulation software, linear regression can then be employed to solve for  $A$  and  $B$ . Having thus obtained values for  $A$  and  $B$ , the Clausius-Clapeyron equation can be used to predict the vapor pressure of the stock at a given temperature.

## 4 Background

### 4.1 Earlier Study in API *MPMS* Chapter 19.4—Annex G

API *MPMS* Chapter 19.4 <sup>2</sup> Annex G, which was added to API *MPMS* Chapter 19.4 in the Third Edition, contains a report of a study to obtain data on the true vapor pressure and the hazardous air pollutant

<sup>2</sup> API *Manual of Petroleum Measurement Standards* Chapter 19.4, *Evaporative Loss Reference Information and Speciation Methodology*, Third Edition, Washington, DC, October 2012.

concentrations for heavy fuel oils, such as No. 6 Fuel Oil and Bunker C marine fuel, and to develop improved technical guidance for these physical properties.

The three refineries that participated each reported manufacturing heavy fuel oil as a blend of vacuum residual oil and a cutter stock. Each participating refinery provided samples of their vacuum residual oil, their cutter stock, and their blended heavy fuel oil. Blend ratios included a 4:1 blend of vacuum residual oil with a cutter stock similar to kerosene (i.e. 20 % kerosene) and a 3:1 blend of vacuum residual oil with a cutter stock similar to diesel (i.e. 25 % diesel).

Various approaches were applied to the estimation of the true vapor pressure of these heavy fuel oils, including ASTM method D2879.<sup>3</sup> ASTM D2879 has been historically specified in the US Environmental Protection Agency (EPA) air regulations as an acceptable method to use for determining the true vapor pressure of stocks for purposes of determining rule applicability.

Data were also obtained by applying the HOST method<sup>4</sup>, which was developed specifically for determining the vapor pressure of heavy crude oils. Another approach calculated the vapor pressure of the heavy fuel oil as the partial pressure of the cutter stock.

The results of these evaluations suggested that the default values for vapor pressure in the earlier edition of API *MPMS* Chapter 19.4<sup>5</sup> were too low to be deemed reasonably representative of a typical blended heavy fuel oil. Table 1 below shows a comparison of vapor pressure values predicted at 150 °F by various approaches. A temperature of 150 °F is above the range at which these heavy fuel oil products are typically stored, and it is selected here only as a basis for comparing the various approaches employed.

**Table 1—No. 6 Fuel Oil in the First Study—True Vapor Pressure (psia) at 150 °F**

| Temperature (°F) | Average ASTM D2879 | HOST Method | 20 % Kerosene Partial Pressure | 25 % Diesel Partial Pressure | API <i>MPMS</i> Chapter 19.4, Second Edition |
|------------------|--------------------|-------------|--------------------------------|------------------------------|----------------------------------------------|
| 150              | 0.06               | 0.02        | 0.02                           | 0.02                         | 0.0008                                       |

API *MPMS* Chapter 19.4—Annex G reported the ASTM D2879 test results at 150 °F as ranging from 0.0352 psia to 0.0912 psia. While this represents a range of more than  $\pm 40$  %, these results are relatively consistent with each other and with the other approaches taken in this study as compared to the old default value of 0.0008 psia. That is, each approach taken in this study to evaluate the vapor pressure of No. 6 Fuel Oil resulted in values at 150 °F in the hundredths of a psia, whereas the value from the Second Edition of API *MPMS* Chapter 19.4 was nearly two orders of magnitude lower.

Given the relative consistency of results from the study, it was concluded that the vapor pressure of No. 6 Fuel Oil should be in the hundredths of a psia at 150 °F. It was further concluded that ASTM D2879 was a reasonable, albeit potentially conservative, method for determining vapor pressure for heavy fuel oils.

<sup>3</sup> ASTM D2879, *Standard Test Method for Vapor Pressure-Temperature Relationship and Initial Decomposition Temperature of Liquids by Isoteniscope*.

<sup>4</sup> "Test Method for Vapor Pressure of Reactive Organic Compounds in Heavy Crude Oil Using Gas Chromatography," May 28, 2002 (see Annex E to *MPMS* 19.4, Third Edition, October 2012). (Note that this method was approved by EPA as alternative method ALT-090 for determining vapor pressure, but such approval is specific to crude oils with an API gravity of 26 or less: Broadly Applicable Approved Alternative Test Methods, US Environmental Protection Agency, <https://www.epa.gov/emc/broadly-applicable-approved-alternative-test-methods>).

<sup>5</sup> API *Manual of Petroleum Measurement Standards* Chapter 19.4, *Recommended Practice for Speciation of Evaporative Losses*, Second Edition, September 2005.