API TECHNICAL REPORT 25XX

XXXXX 2024

Vapor Pressure of Petroleum Liquids

For Estimating Emissions

Special Notes

Boiler plate

Foreword

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Vapor Pressure of Petroleum Liquids for Estimating Emissions

1. SCOPE

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

2. TERMS AND DEFINITIONS

For the purposes of this document, the following terms and definitions apply. Terms of more general use can be found in the API *MPMS* Chapter 1 *Online Terms and Definitions Database.* Acronyms are defined in the text at first use.

3. EXECUTIVE SUMMARY

3.1. Statement of Purpose

There are currently limited vapor pressure data available for use in estimating tank emissions for heavy stocks at high temperatures. The limited data provided in API *MPMS* Chapter 19.4 are likely outdated. 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 is currently not a reliable test method 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 attached as Annex A to this report.

3.2. Method for Predicting Vapor Pressure

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.

3.2.1. Perform Simulated Distillation

Companies reported that simulated distillation is routinely performed on samples of heavy refinery streams for process purposes. 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 (designated as the initial boiling point), 5 % distilled, 10 % distilled, and then at increments of 10 % distilled. 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.
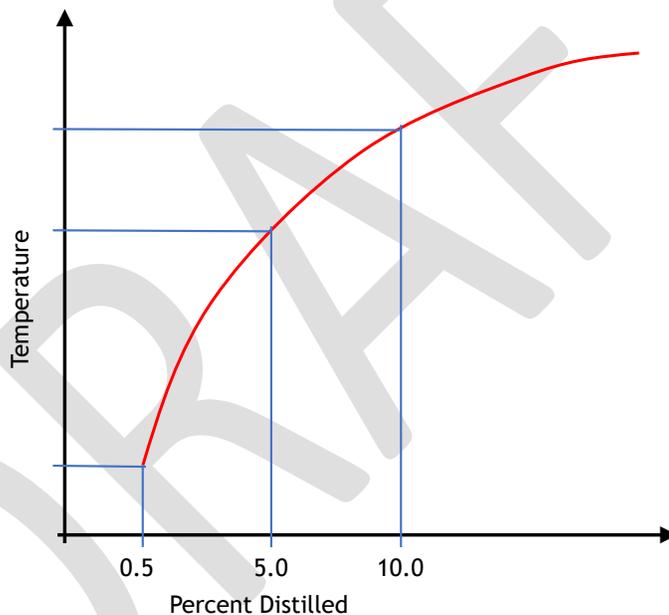
Figure 1. Simulated Distillation Traditional Reporting Convention for the First 10 % Distilled.

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. In order to achieve greater granularity in the characterization of the most volatile fractions, it was decided to report 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 are to be reported in this manner for each of the three samples from the stock in question, and the results are to then be compared to evaluate repeatability.
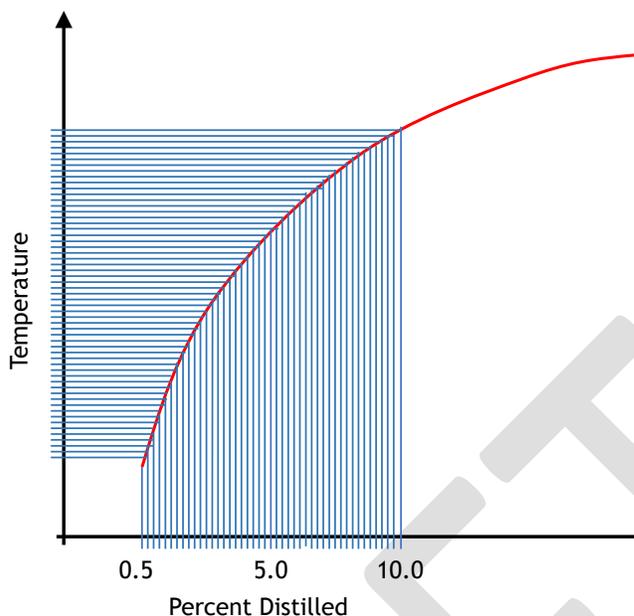
Figure 2. Simulated Distillation Results Reported in Small Increments for the First 10 % Distilled.

3.2.2. 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, 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.
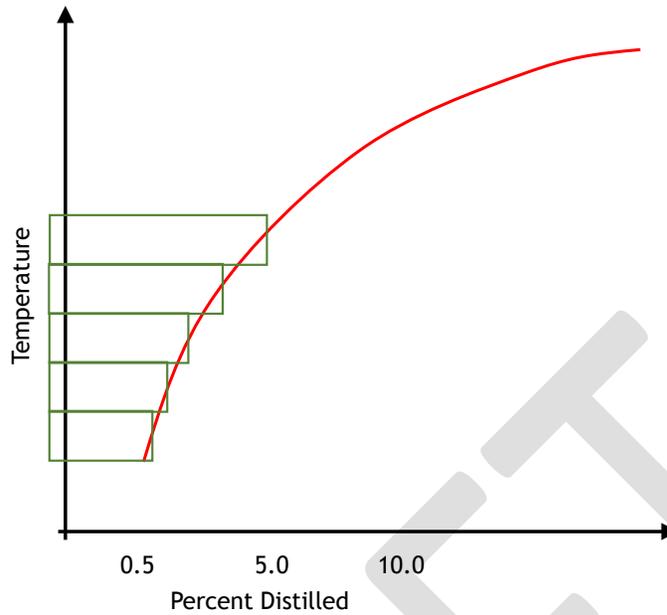
Figure 3. Pseudo Components Assigned to Relatively Large Ranges of Temperature.

In order to prevent this from occurring and to retain the desired granularity in the process simulation software model of the heavy stock, it was determined that pseudo components should be assigned in temperatures range increments of not greater than five degrees Fahrenheit 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.
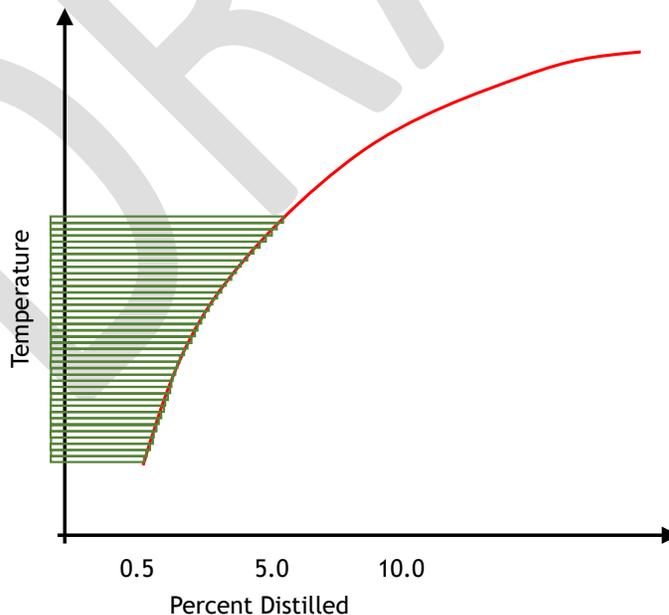

Figure 4. Pseudo Components Assigned to Relatively Small Ranges of Temperature.

Having modeled 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.

3.2.3. Perform a Regression Analysis

The relationship of temperature to vapor pressure can be described by the form of the Clausius-Clapeyron equation given as equation 5 in API *MPMS* Chapter 19.4:

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

where:

P_V is the stock true vapor pressure (psia),

T_{LA} is the daily average liquid surface temperature (degrees Rankine), and

A and B are vapor pressure constants.

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

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

This can be restated as:

$$\ln(P) = A - B(1/T)$$

This expression can be evaluated as the linear equation:

$$y = A - B(x)$$

where:

$y = \ln(P)$, and

$x = (1/T)$.

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[1] 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 (HAP) 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

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[1] American Petroleum Institute, *Evaporative Loss Reference Information and Speciation Methodology*, Manual of Petroleum Measurement Standards, Chapter 19.4, Third Edition, Washington, D.C., October 2012.

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 and a 3:1 blend of vacuum residual oil with a cutter stock similar to diesel.

Various approaches were applied to the estimation of the true vapor pressure of these heavy fuel oils, including ASTM method D2879.[2] ASTM D2879 has been historically specified in 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,[3] 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[4] 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 First Study – True Vapor Pressure (psia) at 150 °F

Temp (°F)	Average ASTM D2879	HOST Method	20 % kerosene partial pressure	25 % diesel partial pressure	API *MPMS* Chapter 19.4 [2nd Ed.]
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 +/– 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.

API *MPMS* Chapter 19.4 Annex G accordingly included the following recommendations for determining the true vapor pressure of No. 6 Fuel Oil (or related products, such as Bunker C, IBF 180, *etc*. made by blending a residual stream with a cutter stock):

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[2] ASTM D2879 *Standard Test Method for Vapor Pressure-Temperature Relationship and Initial Decomposition Temperature of Liquids by Isoteniscope*.

[3] "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, 3rd ed., 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 EPA)

[4] American Petroleum Institute, *Recommended Practice for Speciation of Evaporative Losses*, Manual of Petroleum Measurement Standards, Chapter 19.4, Second Edition, Washington, D.C., September 2005.

1) Have samples of the product analyzed in accordance with ASTM D2879. This might be a conservative (over predicting) approach, or

2) Determine the blend ratio and the properties of the cutter stock, and calculate the vapor pressure as a corresponding percentage of the vapor pressure of the cutter stock, or

3) If no specific information is available about the product, use the following vapor pressure constants (which are based on a 20 % kerosene or 25 % diesel blend with vacuum residual oil):

A	B
10.781	8933

4.2. Subsequent International Liquid Terminals Association (ILTA) Testing

After the recommendation by API to use ASTM D2879 to determine vapor pressure values for heavy fuel oil, ILTA coordinated the collection of samples for testing. Variability among the results was to be expected as there is a wide range of mixtures that can be characterized as No. 6 Fuel Oil. Nevertheless, as shown in Figure 5 the vapor pressure determined for all but one of the samples fell in the same order of magnitude at 150 °F as predicted from the API study (*i.e.*, between 0.01 and 0.1 psia). These data further reinforced the conclusions of the API study.
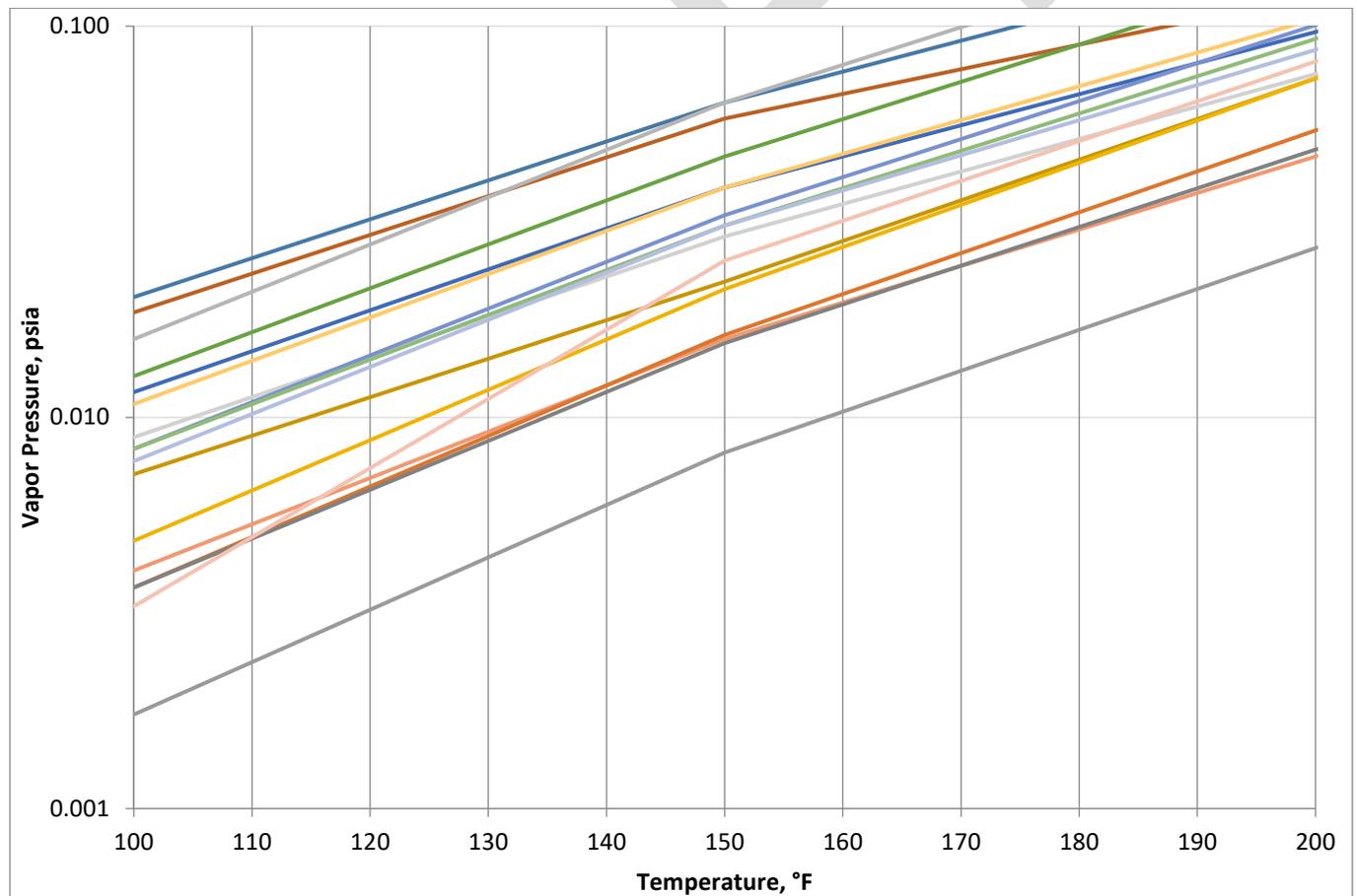

Figure 5: No. 6 Fuel Oil – True Vapor Pressure (psia) versus Temperature (°F)

4.3. Subsequent Loss of Confidence in ASTM D2879

The ASTM D2879 testing for the studies noted above was conducted by Phoenix Chemical Laboratory in Chicago, Illinois, where Dr. Arthur Krawetz had developed the method. Dr. Krawetz is now deceased and ASTM D2879 is now conducted by other laboratories with an apparent loss of consistency in the results. ILTA subsequently sponsored a round robin study of the method, sending twenty samples to the four known laboratories that then offered ASTM D2879 testing. Upon receiving results of this testing, one of the four laboratories was excluded due to excessive variability and seven of the samples were excluded due to incomplete or inconsistent results. Despite excluding the poorest results, the study concluded that ASTM method D2879 as conducted by these laboratories had very poor precision.

Accordingly, EPA's subsequent revision of AP-42 Chapter 7.1, *Organic Liquid Storage Tanks*,[5] contains the following caution:

> "Caution should be exercised when considering ASTM D 2879 for determining the true vapor pressure of certain types of mixtures. Vapor pressure is sensitive to the lightest components in a mixture, and the de-gassing step in ASTM D 2879 can remove lighter fractions from mixtures such as No. 6 fuel oil if it is not done with care (i.e. at an appropriately low pressure and temperature). In addition, any dewatering of a sample prior to measuring its vapor pressure must be done using a technique that has been demonstrated to not remove the lightest organic compounds in the mixture."

Since the passing of Dr. Krawetz, then, there has been a loss in confidence in the use of ASTM D2879 for the determination of vapor pressure for heavy fuel oils.

4.4. Consideration of ASTM D6378

EPA has subsequently approved ASTM method D6378[6] as an alternative to ASTM D2879 for purposes of determining the vapor pressure of petroleum liquids for regulatory purposes, but that approval is expressly limited to use within the vapor pressure range specified in the scope of the method. In that the vapor pressure range specified in the method is 1.0 psi to 21 psi, ASTM D6378 is not applicable to heavy stocks such as No. 6 Fuel Oil for which the vapor pressure at typical storage temperatures is well below 1.0 psi.

5. CURRENT STUDY

5.1. Initial Scope

Given the loss of confidence in ASTM D2879 for the determination of vapor pressure for heavy fuel oils and the inapplicability of ASTM D6378 to these low volatility stocks, API embarked on a second vapor pressure study for heavy fuel oils and this time included low volatility intermediate refinery streams such as heavy gas oils and residual oils as shown in the schematic attached as Annex B. The heavy fuel oils and low volatility intermediate streams will be referred to herein

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[5] U.S. Environmental Protection Agency, 7.1 "Organic Liquid Storage Tanks," in *Compilation of Air Pollutant Emission Factors*, USEPA Report No. AP-42, June 2020.

[6] ASTM D6378 *Standard Test Method for Determination of Vapor Pressure (VPX) of Petroleum Products, Hydrocarbons, and Hydrocarbon-Oxygenate Mixtures (Triple Expansion Method)*. (Note that D6378 was approved by EPA under alternative method ALT-137 for determining vapor pressure, but such approval is specific to petroleum products that exert a vapor pressure greater than 1.0 psi: Broadly Applicable Approved Alternative Test Methods | US EPA)

collectively as "heavy stocks." The initial scope of this project involved conducting a survey to collect vapor pressure data for these heavy stocks.

It became apparent from the survey responses, however, that vapor pressure data were not available for these heavy stocks. The properties that refineries typically measure for these heavy stocks are distillation temperatures and liquid density. Furthermore, with the loss of confidence in ASTM D2879, it was concluded that the study should pivot from data collection to test method development.

5.2. Revised Scope

In that companies reported simulated distillation being routinely performed on samples of heavy refinery streams for process purposes, and 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.

The scope of the study was revised to read:

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

Given this scope, it would be helpful to provide a brief discussion of simulated distillation and process simulation software.

5.3. Brief Discussion of Simulated Distillation and Process Simulation

The method presented in this report uses the distillation curve obtained from simulated distillation tests to predict the vapor pressure of heavy stocks. Heavy stocks, like any mixture of hydrocarbons, contain molecules of some compounds that are lighter than the overall mixture, and some that are heavier. When a mixture is distilled, its liquid is exposed to increasingly elevated temperatures. As the temperature increases to the initial boiling point of the mixture, molecules in the mixture begin to evaporate. Molecules of the lighter or more volatile compounds in the liquid tend to evaporate first, at relatively lower temperatures, followed by the heavier compounds at relatively higher temperatures. The relationship between how much (what fraction) of a liquid has evaporated, and what temperature is required to evaporate that fraction, is referred to as the "distillation curve" of the liquid.

The portion of the distillation curve at which a given fraction of the liquid mixture evaporates is described as the boiling point of that fraction. Boiling point is related to vapor pressure in that the boiling point of a liquid is the temperature at which the vapor pressure of that liquid reaches ambient pressure. It is therefore possible to use the distillation curve to estimate the vapor pressure characteristics of each fraction of a liquid mixture and thereby predict the overall vapor pressure of the mixture.

Vapor pressure, as that term is used for purposes of estimating emissions and determining regulatory applicability for storage tanks, refers to the sum of the equilibrium partial pressures of the constituent compounds. Characterizing the overall vapor pressure of a liquid mixture as the sum of the partial pressures of the constituent compounds assumes ideal behavior of each constituent compound. That is, it assumes there is negligible molecular interaction between compounds that would affect the effective vapor pressure of molecules of an individual

compound, and thus molecules of each constituent compound evaporate as they would if only that compound were present.

In a mixture, any given constituent compound represents only a fraction of the total aggregate of molecules in the mixture. This is referred to as the mole fraction of that compound. If the liquid is well mixed, then the mole fraction of a compound in the mixture also describes the fraction of that compound's molecules among the total molecules available for evaporation at the liquid surface.

Thus, even though an individual molecule of a given constituent compound is assumed to evaporate in the same manner from the surface of the mixture as it would if the liquid contained only that compound, the effective vapor pressure and overall evaporation rate of that constituent compound will be diminished in the mixture due to there being fewer molecules of that compound at the liquid surface of the mixture than there would be if only that compound were present. The effective vapor pressure of each constituent compound, then, is described by its vapor pressure if only that compound were present factored by the mole fraction of that compound in the mixture. This is what is meant by the equilibrium partial pressure of the compound.

When certain constituent compounds are significantly more volatile than the rest of the mixture, the overall vapor pressure will be largely determined by these more volatile compounds. For example, if a mixture contains a 0.05 mole fraction of hydrocarbon A with a vapor pressure of 0.2 psia at a given temperature and a 0.95 mole fraction of hydrocarbon B with a vapor pressure of 0.0001 psia at that temperature, then the sum of partial pressures would be (0.05*0.2) + (0.95*0.0001) or 0.0101 psia. In this example, the overall vapor pressure of the mixture is described almost entirely by the partial pressure of the lighter 5 % fraction, with insignificant contribution from the heavier 95 % fraction. It is evident, then, that accuracy of the characterization of the lightest fraction is critical to predicting the vapor pressure of such mixtures.

While the heavy stocks under consideration in this study are made up of far more than two compounds, these stocks tend to contain small amounts of compounds that are much more volatile than the rest of the mixture. The accuracy of predicting the effective vapor pressure of these heavy stocks from simulated distillation data, then, will depend heavily on the characterization of the lightest fractions.

In practice, refineries often determine the distillation curve using a "simulated distillation," in which a liquid sample is introduced into a gas chromatograph, and the boiling point temperature of each fraction is predicted from the retention time of that fraction in the column of the chromatograph. The array of boiling points thus obtained are then compiled into a distillation curve.

The distillation curve data generated from this simulated distillation are then input to a process simulation software tool. Process simulation software creates a model of a mixture by assigning properties to fractions of the mixture. The properties to be assigned come from a library in the software containing sets of hypothetical compounds referred to as "pseudo components." Once a mixture has been modeled in the process simulation software as a combination of pseudo components, the software can be used to report the mole fraction of each pseudo component representing the distillation curve. With the assignment of a boiling point for a given pseudo component, the vapor pressure of that pseudo component can then be determined. Vapor pressures are determined at different temperatures for each pseudo component using the

equation by Van Westen and Van Ness.[7] Given the vapor pressures determined for the pseudo components, the process simulation software can then predict the vapor pressure of the overall mixture.

5.4. Development of the Method

5.4.1. Member Company Participation

The pursuit of a method to predict the vapor pressure of heavy stocks from simulated distillation was enabled by the participation of an API member company that performed simulated distillation tests and process simulation evaluations in support of the project. The process simulation software utilized was HYSYS. A summary report of that company's work is attached as Annex C.

5.4.2. Required Granularity for the Simulated Distillation Test Reports

As noted above, the accuracy of vapor pressure prediction for heavy stocks is sensitive to the characterization of the lightest fractions. However, typical practice for process purposes at refineries is to report the temperature at 0.5 % distilled (designated as the initial boiling point), 5 % distilled, 10 % distilled, and then at increments of 10 % distilled. For the range below 10 % distilled, then, only two data points are typically reported.

It was found that this limited reporting practice was not a limitation of the simulated distillation methods, but rather was a convention appropriate for the purposes for which the data were used in managing refinery processes. That is, the simulated distillation methods support reporting results with greater granularity if requested, but this is typically not needed for refinery process purposes. It was determined, however, that more data points would be required to adequately characterize the stock for purposes of predicting stock vapor pressure.

After some trial-and-error evaluations it was concluded that, for purposes of using the data to predict the vapor pressure of heavy stocks, distillation temperatures in the range below 10 % distilled should be reported at increments of 0.1 % distilled and above 10 % distilled should be reported at increments of 5 % distilled.

5.4.3. Required Granularity for the Process Simulation Software

As noted above, a hydrocarbon mixture can be modeled in process simulation software by the assignment of pseudo components to fractions of the mixture. It was found, however, that default behavior of the software can assign a given pseudo component to a range of temperature that includes many values from the granular report of the distillation curve, resulting in a loss of granularity in the process simulation model.

For example, 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 for this range from the simulated distillation test will be represented by only five pseudo components in the process simulation software. In order to prevent this consolidation of data from occurring and to retain the desired granularity in the process simulation software model of the heavy stock, it was determined that pseudo components

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[7] Van Nes K. and Van Westen H.A. Aspects of the Constitution of Mineral Oils. Houston-Amsterdam: Elsevier Publishing Company, 1951.

should be assigned in temperatures ranges of not greater than five degrees Fahrenheit for the fraction from 0.5 % to 10.0 % distilled.

5.4.4. Results for No. 6 Fuel Oil Samples

In the earlier study discussed in 1.1 above, simulated distillation tests had been performed on the samples and the data reported in increments of 0.1 % distilled. As noted in Annex C below, the procedure labeled SimDist A assigned pseudo components with greater granularity than did the procedure labeled SimDist B. The predictions of vapor pressure at 150 °F for the samples from the earlier study, evaluated using SimDist A, ranged from 0.008 psia to 0.046 psia. The average value was 0.028 psia.

Similar to the ASTM D2879 results discussed in 1.1 above, these results for predicting vapor pressure from simulated distillation data exhibit a wide range on a percentage basis. However, the results are relatively consistent with each other and with the values obtained by multiple methods in the earlier study as compared to the old default value of 0.0008 psia as shown below in Table 2.

Table 2: Initial Set of No. 6 Fuel Oil Samples – True Vapor Pressure (psia) at 150 °F

Temp (°F)	Results from First Study Samples			New and Old Defaults	
	Average Simulated Distillation	Average ASTM D2879	HOST Method	25 % diesel partial pressure	API *MPMS* Chapter 19.4 [2nd Ed.]
150	0.028	0.06	0.02	0.02	0.0008

A separate set of six No. 6 Fuel Oil samples was made available to this study and evaluated by SimDist A by the participating member company, with results at 150 °F ranging from 0.011 psia to 0.063 psia with an average of 0.030 psia. These results show a similar range as other results in these studies, see Table 3, and the average value continues to be consistent with results from other tests.

Table 3: No. 6 Fuel Oil With Additional Samples – True Vapor Pressure (psia) at 150 °F

Temp (°F)	Average Simulated Distillation Results from Second Study Samples	Results from First Study Samples			New and Old Defaults	
		Average Simulated Distillation	Average ASTM D2879	HOST Method	25 % diesel partial pressure	API *MPMS* Chapter 19.4 [2nd Ed.]
150	0.030	0.028	0.06	0.02	0.02	0.0008

Given the relative consistency of the average values from the simulated distillation approach with average values from other tests, it was concluded that the simulated distillation approach was a reasonable method for predicting the vapor pressure of heavy stocks when conducted with the indicated level of granularity. Given the variability of results among individual tests, however, it was concluded that the method should always be based on the average of the results from testing at least three samples.

5.4.5. Comparison Testing with Jet Fuel

As noted above, ASTM D6378 is approved by EPA for determining the true vapor pressure of petroleum products, but the scope of this method does not extend to the low vapor pressure range of heavy stocks. ASTM D6378 does, however, have repeatability and reliability values for

jet fuel. It was decided to further evaluate the simulated distillation approach by applying both it and ASTM D6378 to jet fuel and comparing the results.

This testing was conducted by the participating member company, and the test report is attached as Annex D. A comparison of the results at 100 °F is shown in Table 4:

Table 4: Jet Fuel Comparison – True Vapor Pressure (psia) at 100 °F

Sample No.	Temp (°F)	ASTM D6378	Simulated Distillation
1	100	0.05	0.05
2	100	0.05	0.05
3	100	0.02	0.05
4	100	0.00	0.05
5	100	0.04	0.04
6	100	0.05	0.05

Two of the ASTM D6378 tests (samples 3 & 4) had unexplained low results, but the other four ASTM D6378 tests and all six results from the simulated distillation approach fell within the range of 0.04 to 0.05 psia when expressed to two decimal places. These results further reinforced the conclusion that simulated distillation data can be used to reasonably predict the vapor pressure of heavy stocks.

6. CONCLUSION

The first API study of the vapor pressure of heavy stocks, reported in Annex G of the Third Edition of API *MPMS* Chapter 19.4, concluded that the vapor pressure of No. 6 Fuel Oil at 150 °F is typically 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. The default vapor pressure constants for No. 6 Fuel Oil in the Second Edition of API *MPMS* Chapter 19.4 were therefore deemed to not be representative of typical blended No. 6 Fuel Oil, but rather to be perhaps appropriate for straight vacuum residual oil. New default vapor pressure constants were recommended for No. 6 Fuel Oil, and it was further concluded that ASTM D2879 was an acceptable method for determining vapor pressure for heavy fuel oils.

Due to subsequent loss of confidence in ASTM D2879, API embarked on a second study which investigated the use of simulated distillation data to predict the vapor pressure of heavy stocks such as distillate fuel oils, residual fuel oils, and heavy intermediate refinery streams. This study concluded that the simulated distillation approach is a reasonable method for predicting the vapor pressure of these heavy stocks when conducted with the indicated level of granularity and when based on the average of the results from at least three samples. The recommended procedure for predicting vapor pressure from simulated distillation data is presented in Annex A.

Annex A
(informative)
Method for Predicting Vapor Pressure from Simulated Distillation

A.1 Purpose

The following protocol is intended to provide specific guidance for making vapor pressure estimates for petroleum products and refinery intermediates with initial boiling points in the range of 150 °F to 1330 °F. The estimated vapor pressures obtained from this protocol are intended to be used in conjunction with API *MPMS* Chapter 19 or EPA's AP-42 Chapter 7.1 to estimate VOC emissions from storage tanks.

A.2 Technical Approach.

The protocol references a variety of test procedures published by ASTM, estimating techniques published in peer reviewed journals, and commercially available process simulation software.

> *ASTM D2887-16a, Standard Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography*: The method is applicable to petroleum based liquids with an initial boiling point greater than 100 °F and less than 1,000 °F. This test procedure is commonly applied to petroleum products and refinery intermediates such as diesel fuels, jet fuels, fuel oils, and gas oils. For atmospheric and vacuum distillation residues use ASTM method D7169, a closely related method intended to estimate boiling points as high as 1330 °F.

D2887 is performed using a gas chromatograph (GC). Individual hydrocarbon compounds are retained on the chromatographic column according to their boiling points. The higher the boiling point, the longer the compound is retained. The gas chromatograph is calibrated with a mixture of hydrocarbon compounds with known boiling points. A relationship is established between the time each compound elutes from the GC column and the boiling point of that compound.

Sample mixtures are then tested by injecting a small volume of the sample onto the GC column. The data are divided into slices. Each of the slices should be adjusted such that the total cumulative area at the end of each slice divided by the total area of all peaks represents cumulative 0.1 wt % increments (*e.g.*, 0.5 %, 0.6 %, 0.7 %, …). The time at the end of each slice is then associated with a boiling point using the calibration curve.The final paired data of weight % and boiling point temperature looks similar to the data in Table A.1 below which was produced in an analysis of a distillate range cutter stock.

Table A.1: Paired Data of Weight Percent and Boiling Point

Wt %	Boiling Point (°F)
0.50	241.8
0.60	244.1
0.70	250.2
0.80	257.5
0.90	258.3
1.00	259.2
1.10	266.7
1.20	268.7
1.30	270.8
1.40	273.7
1.50	276.3
1.60	277.9
1.70	280.3
1.80	281.0
1.90	281.6
2.00	282.6

A.3 Procedure for Simulated Distillation Testing

Collect at least 3 liquid samples from the stream in question.

Measure density as API Gravity (API) using ASTM D287, or D7777 and convert the value to a specific gravity (SG) as follows:

$$SG = \frac{141.5}{°API + 131.5}$$

(A.1)

Measurement of the API gravity of the three samples should not vary by more than 0.5 ° API. Repeat measurements if necessary to achieve agreement or remove outlier samples from the average API gravity value.

For materials having a boiling range between 100 °F and 1,000 °F use ASTM D2887, or similar method for simulated distillation (SimDist). Use ASTM D7169 for materials with final boiling points as high as 1330 °F.

Report the SimDist results in increments of 0.1 % by weight for the range of 0.5 % (*e.g.*, 0.5 %, 0.6 %, 0.7 %…) to 10.0 % distilled, and in increments of 5.0 % above 10 % (*e.g.*, 10 %, 15 %, 20 %...) distilled.

For the weight increments from 0.5 % to 10 % the reported temperatures of the three samples should meet the following conditions:

- Should not vary by more than 2 °F when the reported temperatures are less than 400 °F.

- Should not vary by more than 3 °F when the reported temperatures are greater than 400 °F.

If the three samples meet the conditions, average the three reported values for each wt % increment.

If one sample does not meet the conditions above, average the two samples that do meet the conditions. If all samples do not meet the conditions, consider repeating the chromatographic measurements.

A.4 Procedure for Process Simulation Modeling

Enter the SimDist increments and measured density into a process simulation software package such as Hysys/Petro-SIM/Unisim/ProII. The default range covered by each boiling fraction selected by these simulation software packages tends to be too big for accurate representation of the initial 10 wt % of the hydrocarbon stream of interest. Between the initial boiling point and the 10 wt % of the distillation curve, ensure that the difference in boiling point temperature assigned to each consecutive pseudo component is not more than 5 °F. Essentially, a single pseudo component is used to represent each 5 degree F increment in the distillation curve up to 10 wt %. After 10 wt %, each pseudo component can represent 20 °F - 40 °F increment of the distillation curve. This is the typical range for general process simulation work. Since molecular weight (MW) of pseudo components are estimated by the simulation software package, it is important to select the appropriate correlation used in the estimation. Twu's method is the recommended correlation for estimating MW.

Once the characterization of the stream is done by the process simulation software, the output contains a list of the mole fraction for each pseudo component. The mole fraction (X_i) of each pseudo component is selected such that the distillation curve matches the data provided.

A.5 Procedure for Determination of Vapor Pressure Constants

The next step is estimating the vapor pressure of each of the pseudo components. Depending on the simulation software, one could extract the constants for a vapor pressure equation such as the Antoine equation. However, in cases where the constants are not available, but the boiling point of each pseudo component is known, one can alternatively use the equation by Van Westen and Van Nes[8] to estimate the vapor pressure of each pseudo component. The equation is as follows:

$$Log_{10}(P_T) = 3.2401 * \left(1 - 0.998 * \left(\frac{T_b - 41}{T - 41}\right) * \frac{(1393 - T)}{(1393 - T_b)}\right)$$

(A.2)

P_T is the vapor pressure at the temperature of interest and T_b is the normal boiling point of the pseudo component. Note that all temperatures are in Kelvin (K) and pressures are in Bar.

With the mole fraction and vapor pressure (P_{vp}) of each pseudo component available at a temperature of interest using the equation described above, one can then easily calculate the partial pressure of each pseudo component as:

$$P_i = X_i * P_{vp}$$

(A.3)

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[8] Van Nes K. and Van Westen H.A. Aspects of the Constitution of Mineral Oils. Houston-Amsterdam: Elsevier Publishing Company, 1951.

Then the summation of all the P_i's gives the vapor pressure of the stream at the temperature of interest. This calculation should be repeated for multiple temperatures spanning the range of temperature at which the given stock is typically stored. Having thus obtained vapor pressure values for given levels of temperature, vapor pressure constants can be obtained for the form of the Clausius-Clapeyron equation given as equation 5 in API *MPMS* Chapter 19.4:

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

(A.4)

where:

P_V is the stock true vapor pressure (psia),

T_{LA} is the daily average liquid surface temperature (degrees Rankine), and

A and *B* are vapor pressure constants.

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

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

(A.5)

This can be restated as:

$$\ln(P) = A - B(1/T)$$

(A.6)

This expression can be evaluated as the linear equation:

$$y = A - B(x)$$

(A.7)

where:

$y = \ln(P)$, and

$x = (1/T)$.

From the calculated sets of values for *P* and *T*, linear regression can 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.

Annex B
(informative)
Schematic of Heavy Stocks in a Refinery
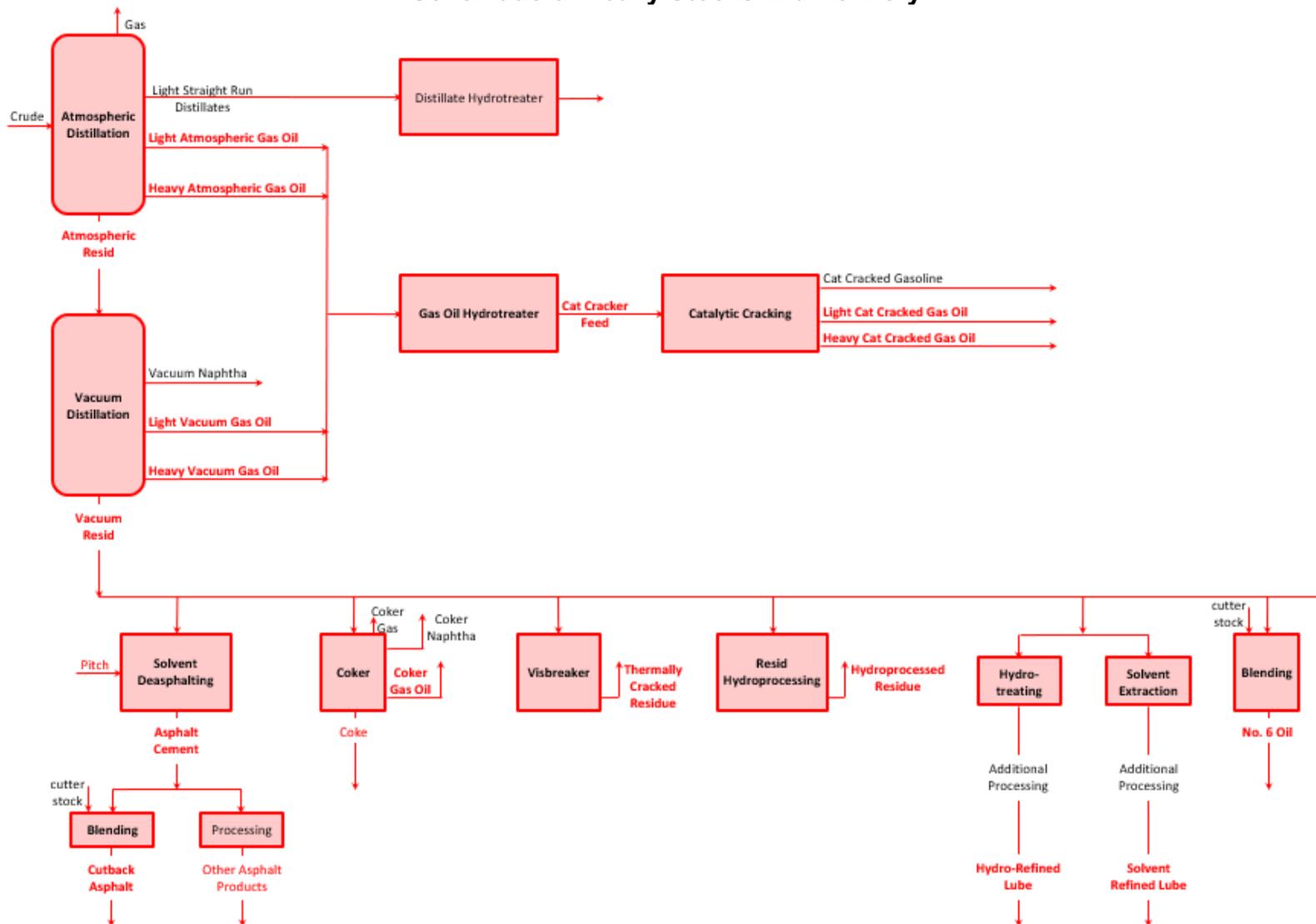

Figure B.1: Schematic of Heavy Stocks in a Refinery

NOTE   Heavy stocks are shown in red font.

Annex C
(informative)
Member Company Report on the Simulated Distillation Approach

C.1 Estimating Vapor Pressure of Heavy Refinery Streams

C.1.1 Background

Refinery streams contain many different chemical components. Most refineries do not measure vapor pressure for streams beyond light gas product streams, and the availability of vapor pressure data for the heavier streams is quite limited in the literature. However, most refiners typically measure the distillation curve and density of kerosene, diesel, and heavier refinery streams. These measurements are readily available in labs at refineries, and the vapor pressure of a stream is strongly associated with these qualities.

In process simulation modelling, characterization of hydrocarbon streams is done with the use of these readily available distillation curves and bulk stream densities. Based on these two pieces of information, one can use correlations available in commercial process simulation software (e.g., Hysys, ProII, Petro-SIM, Unisim, etc.) to generate a set of pseudo components to represent the measured distillation curve. In general, this approach assumes that an overall characterization named Watson K remains relatively constant across the boiling range of the pseudo components used to represent the distillation curve. The bulk Watson K is used to generate a density curve based on the distillation curve and bulk density. Watson K is defined as follows:

$$Watson\ K = \frac{T_b^{\frac{1}{3}}}{SG}$$

(C.1)

T_b is the normal boiling point and SG is the specific gravity of the specific pseudo component. The results from the characterization of a hydrocarbon stream from the process simulation software contain the mole fraction of each pseudo component in representing the distillation curve provided by the user. Based on Dalton's Law, the vapor pressure exerted by a hydrocarbon stream is the sum of the partial pressures from each of the individual components or pseudo components. In addition, Raoult's Law states that for ideal solutions (when activity coefficients are approximately in unison), the equilibrium partial pressure of each component is the product of (a) the mole fraction of that product in the liquid phase and (b) the equilibrium vapor pressure of the pure component. Hence, for each component, the equilibrium partial pressure can be calculated as follows:

$$P_i = X_i * Vapor\ Pressure\ of\ pseudo\ component\ i$$

(C.2)

X_i is the mole fraction of component i in the liquid phase. Then, the vapor pressure of the hydrocarbon stream is calculated as:

$$Stream\ Vapor\ Pressure = P_i + \cdots + P_n$$

(C.3)

The use of the approach described above has been reported by API Petroleum HPV Testing Group and CONCAWE.

The vapor pressure of a hydrocarbon stream is very much affected by values reported in the front end of the distillation curve, particularly the first 5 % distilled. Hence, having more granularities between the initial boiling point and the 5 % point of the hydrocarbon stream is important in generating a set of pseudo components representing the first 5 % of the hydrocarbon stream. Since there are many species of molecules representing the front end of the distillation curve, it is important to ensure that there are several pseudo components used to represent this part of the distillation curve such that the composition of the pseudo components used to calculate the vapor pressure can provide a good representation of the true chemical species. In addition, the vapor pressure of each pseudo component is used in the calculation of partial pressure. Hence, instead of using one single lumped component as a representative component to estimate the vapor pressure of the first 5 % of the distillation curve, using multiple components to represent the first 5 % of the distillation curve provides a more rigorous approach in estimating the true vapor pressure of the stream of interest.

This approach was applied to data collected in the development of API *MPMS* Chapter 19.4, Annex G. Distillation data submitted in that study for 4 cutter stocks of No. 6 Fuel Oils were used to calculate the vapor pressure at 100 °F. Below is a summary of the approaches used in estimating the vapor pressure, comparing the D2879 and HOST Method[9] results in API *MPMS* Chapter 19.4 Annex G to two sets of simulated distillation results. The value of the vapor pressure listed in the first four columns of Table C.1 is in psi; the units of the True Boiling Point (TBP) distillation temperature are degrees Fahrenheit.

Table C.1: Vapor Pressure Values from Various Methods

	D2879 (psi)	HOST (psi)	SimDist A (psi)	SimDist B (psi)	TBP Wt 5 % (°F)
A	0.0715	0.0060	0.0510	0.0450	317.6
B	0.0735	0.0140	0.0077	0.0020	437.2
C	0.0222	0.0060	0.0233	0.0082	391.9
D	0.0309	0.0600	0.0043	0.0022	436.0

It would be expected that stocks with significantly different TBP curves would have significantly different vapor pressures. As shown in Table C.1 above, however, both the D2879 and HOST

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[9] "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, 3rd ed., October 2012). (Note that Section 1.2 of this method identifies that the useful range of the method is a ROC vapor pressure range of 0.05 psia to 10 psia, that "ROC" is defined as excluding dissolved methane, ethane, and CO_2., and that results are for a V/L ratio of 4.)

methods can potentially generate vapor pressure data that are quite similar even though the TBP 5 wt % points differ by more than 70 °F (Stocks A and C). In the case of the two SimDist methods, the predicted results have the expected direct correlation on the measured TBP 5 wt % temperature.

The difference between SimDist A and SimDist B is the number of pseudo components used in the representation of the first 5 % of the TBP curve. SimDist A used more than 30 pseudo components to represent the first 5 % of the TBP curve. As a result, the measured TBP curve was matched very tightly even at 1 % of the TBP curve. In the case of SimDist B, about 10 pseudo components were used to represent the first 5 % of the TBP curve. The TBP at 1 % was not matched very well. The mismatches among the 4 cutter stocks evaluated by SimDist B for measured TBP at 5 % were between 5 °F and 10 °F.

To estimate vapor pressure, it is important to match the TBP curve 1 % and 5 % points very closely. Hence, the use of more than 10 pseudo components is necessary. In addition, most labs do not report TBP distillation data in 0.1 % increments. Instead, most TBP data are reported at IBP (Initial Boiling Point, typically designated as the 0.5 % point), 5 %, 10 %, etc. For accurate estimation of vapor pressure, it is necessary to get smaller increments of data (such as 0.1 % increments) from the lab. This then provides better guidance on how the front end of the distillation curve changes shape during the characterization step instead of using a cubic spline to connect the 1 % and 5 % points for example.

C.1.2 Proposed Protocol

C.1.2.1 Purpose

The following protocol is intended to provide specific guidance for making vapor pressure estimates for petroleum products and refinery intermediates with initial boiling points in the range of 150 °F to 1330 °F. The estimated vapor pressures obtained from this protocol are intended to be used in conjunction with API *MPMS* Chapter 19 or EPA's AP-42 Chapter 7.1 to estimate VOC emissions from storage tanks.

C.1.2.2 Technical Approach

The protocol references a variety of test procedures published by ASTM, estimating techniques published in peer reviewed journals, and commercially available process simulation software.

> *ASTM D2887-16a, Standard Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography*: The method is applicable to petroleum based liquids with an initial boiling point greater than 100 °F and less than 1,000 °F. This test procedure is commonly applied to petroleum products and refinery intermediates such as Diesel fuels, jet fuels, fuel oils, and gas oils. For atmospheric and vacuum distillation residues use ASTM method D7169, a closely related method intended to estimate boiling points as high as 1330 °F.

D2887 is performed using a gas chromatograph (GC). Individual hydrocarbon compounds are retained on the chromatographic column according to their boiling points. The higher the boiling point, the longer the compound is retained. The gas chromatograph is calibrated with a mixture of hydrocarbon compounds with known boiling points. A graph of typical gas chromatograph results is shown in Figure 5 of ASTM D2887. A relationship is established between the time

each compound elutes from the GC column and the boiling point of that compound. A typical calibration curve is shown in Figure 2 of ASTM D2887.

Sample mixtures are tested by injecting a small volume of the mixture onto the GC column. An example chromatogram of a sample mixture is shown in Figure 9 of ASTM D2887. The data are divided into slices. Each of the slices should be adjusted such that the total cumulative area at the end of each slice divided by the total area of all peaks represents cumulative 0.1 wt. % increments (e.g., 0.5 %, 0.6 %, 0.7 %, …). The time at the end of each slice is then associated with boiling point using the calibration curve. The final paired data of weight % and boiling point temperature looks similar to the data in Table C.2 below which was produced in an analysis of a distillate range cutter stock.

Table C.2: Paired Data of Weight Percent and Boiling Point Temperature

Wt %	Boiling Point (°F)
0.50	241.8
0.60	244.1
0.70	250.2
0.80	257.5
0.90	258.3
1.00	259.2
1.10	266.7
1.20	268.7
1.30	270.8
1.40	273.7
1.50	276.3
1.60	277.9
1.70	280.3
1.80	281.0
1.90	281.6
2.00	282.6

Collect at least 3 liquid samples from the stream in question.

Measure density API Gravity (API) using ASTM D287, or D7777 and convert the value to a specific gravity (SG) as follows:

$$SG = \frac{141.5}{°API + 131.5}$$

(C.4)

Measurement of the API gravity of the three samples should not vary by more than 0.5 °API. Repeat measurements if necessary to achieve agreement or remove outlier samples from the average API gravity value.

For materials having a boiling range between 100 °F and 1,000 °F use ASTM D2887, or similar method for simulated distillation (SimDist). Use ASTM D7169 for materials with final boiling points as high as 1330 °F.

Report the SimDist results in increments of 0.1 % by weight for the range of 0.5 % (e.g., 0.5 %, 0.6 %, 0.7 %, …) to 10.0 % distilled, and in increments of 5.0 % above 10 % (e.g., 10 %, 15 %, 20 %, ...) distilled.

For the weight increments from 0.5 % to 10 % the reported temperatures of the three samples should meet the following conditions:

• Should not vary by more than 2 °F when the reported temperatures are less than 400 °F.

• Should not vary by more than 3 °F when the reported temperatures are greater than 400 °F.

If the three samples meet the conditions, average the three reported values for each wt % increment.

If one sample does not meet the conditions above, average the two samples that do meet the conditions. If all samples do not meet the conditions, consider repeating the chromatographic measurements.

Enter the SimDist increments and measured density into a process simulation software package such as Hysys/Petro-SIM/Unisim/ProII. The default range covered by each boiling fraction selected by these simulation software packages tends to be too big for accurate representation of the initial 10 wt % of the hydrocarbon stream of interest. Between the initial boiling point and the 10 wt % of the distillation curve, ensure that the difference in boiling point temperature assigned to each consecutive pseudo component is not more than 5 °F. Essentially, a single pseudo component is used to represent each 5 degree F increment in the distillation curve up to 10 wt %. After 10 wt %, each pseudo component can represent 20 °F – 40 °F increment of the distillation curve. This is the typical range for general process simulation work. Since molecular weight (MW) of pseudo components are estimated by the simulation software package, it is important to select the appropriate correlation used in the estimation. Twu's method is the recommended correlation for estimating MW.

Once the characterization of the stream is done by the process simulation software, the output contains a list of the mole fraction for each pseudo component. The mole fraction (Xi) of each pseudo component is selected such that the distillation curve matches the data provided.

The next step is estimating the vapor pressure of each of the pseudo components. Depending on the simulation software, one could be able to extract the constants for a vapor pressure equation such as the Antoine equation. However, in cases where the constants are not available, but the boiling point of each pseudo component is known, one can alternatively use the equation by Van Westen and Van Nes[10] to estimate the vapor pressure of each pseudo component. The equation is as follows:

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[10] Van Nes K. and Van Westen H.A. Aspects of the Constitution of Mineral Oils. Houston-Amsterdam: Elsevier Publishing Company, 1951.

$$Log_{10}(P_T) = 3.2401 * \left(1 - 0.998 * \left(\frac{T_b - 41}{T - 41}\right) * \left(\frac{1393 - T}{1393 - T_b}\right)\right)$$

(C.5)

P_T is the vapor pressure at the temperature of interest and T_b is the normal boiling point of the pseudo component. Note that all temperatures are in Kelvin (K) and pressures are in Bar.

With the mole fraction and vapor pressure (P_{vp}) of each pseudo component available at a temperature of interest using the equation described above, one can then easily calculate the partial pressure of each pseudo component as:

$$P_i = X_i * P_{vp}$$

(C.6)

Then the summation of all the P_i's gives the vapor pressure of the stream at the temperature of interest.

Annex D
(informative)
Member Company Report on Testing of Jet Fuel

D.1 Comparison of measured vapor pressure to simulated distillation method for Jet Fuel.

D.1.1 Background

One of the key parameters in estimating hydrocarbon emissions from storage tanks is the vapor pressure of the liquid being stored. A refinery can have over a hundred storage tanks containing material ranging from crude oil to finished products with vapor pressures that can vary by orders of magnitude. Furthermore, there can be limited data in the literature on vapor pressure for a feed or product stream and if data exists it could be based on only a few data points. Refineries do not typically measure vapor pressures for heavier streams but often do measure the distillation curves and density.

In order to address these issues, a procedure to model vapor pressure from simulated distillation data is being investigated by the American Petroleum Institute (API) Committee on Evaporative Loss Estimation (CELE). The simulation procedure has been compared to measured vapor pressure data for #6 Oil and additional comparison was sought for Jet Fuel. Jet Fuel contains a variety of compounds with carbon chain lengths from 4 to 16.

D.1.2 Published Jet Fuel Vapor Pressure

Shepherd et al. published two correlations for jet fuel vapor pressure, shown in the equations below, where vapor pressure is given in mbar and the temperature is given in Kelvin.

$$P_\sigma = 2.256 * 10^{6 - \frac{3899}{T}}$$ Shepherd et al. Correlation

(D.1)

$$P = 6.465 * 10^{6 - \frac{4243.3}{T}}$$ Woodrow et al. Correlation

(D.2)

Figure D.1 below shows the Jet Fuel vapor pressure calculated from these two correlations in units of psi, over the range of 32 °F to 212 °F. Reid Vapor Pressure (RVP) is the vapor pressure at 100 °F, and the two correlations give RVPs of 0.12 psi and 0.11 psi.
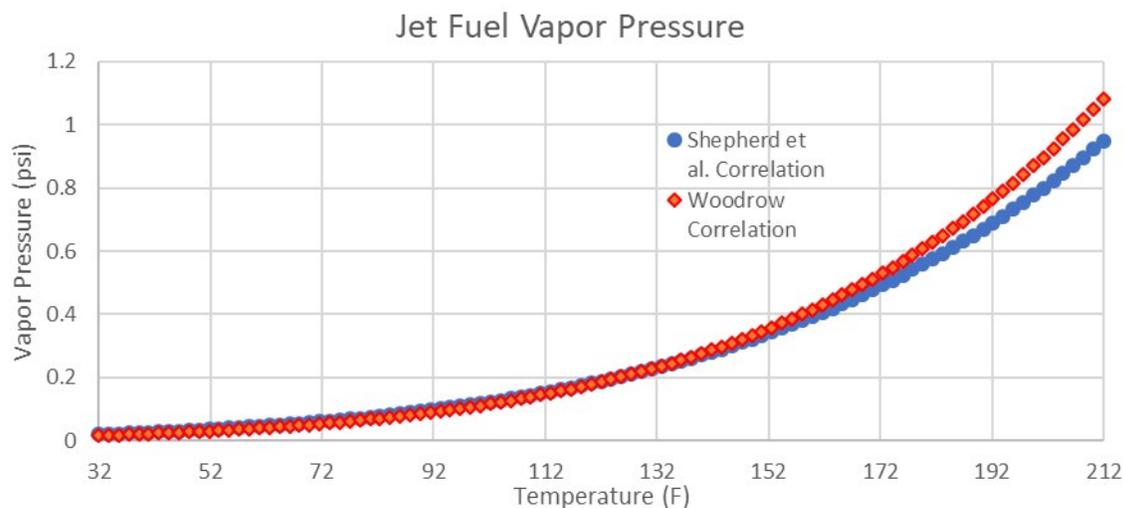
Figure D.1: Jet Fuel Vapor Pressure Correlation Data

D.1.3 Measured Jet Fuel Vapor Pressure

ASTM published a standard test method D6378-18a for automated vapor pressure instruments that determines the vapor pressure of aviation turbine fuels with boiling points over 32 °F that exert a vapor pressure between zero and 15.5 psi at a vapor-to-liquid ratio of 4:1 in the temperature range from 77 °F to 212 °F. A laboratory instrument that follows the D6378-18a method was used to analyze six refinery jet fuel samples, along with the API Gravity which is needed for the modeling process in the API procedure.

The measured jet fuel vapor pressure at 100 °F (RVP) and API Gravity are shown in Table D.1 below. Two samples show RVPs below the other 4 which have RVPs in the 0.04 psi to 0.05 psi range. The measured RVPs are of the same order as the RVP obtained in the correlations shown above, approximately 0.05 psi compared to 0.11 psi.

Table D.1: Measured Jet Fuel Reid Vapor Pressure

Sample Number	Measured API Gravity	Measured RVP (psi)
1	40.00	0.05
2	40.01	0.05
3	39.70	0.02
4	40.00	0.00
5	39.80	0.04
6	39.60	0.05

D.1.4 Simulated Distillation

ASTM published a standard test method D2887-19a to determine the boiling range distribution for petroleum fractions by gas chromatography. The test method is applicable to petroleum products having a final boiling point of 1000 °F or lower, with a boiling range greater than 100 °F and having a vapor pressure low enough to sample at ambient temperature.

An Agilent 7890A GC instrument that can automatically run simulated distillations of jet fuel samples using the D2887-19a method was used to analyze the six jet fuel samples, with each sample run five times. The replicates were performed to determine the uncertainty with the D2887-19a method. Figure D.2 below shows the results for the first sample with the five runs showing identical behavior.
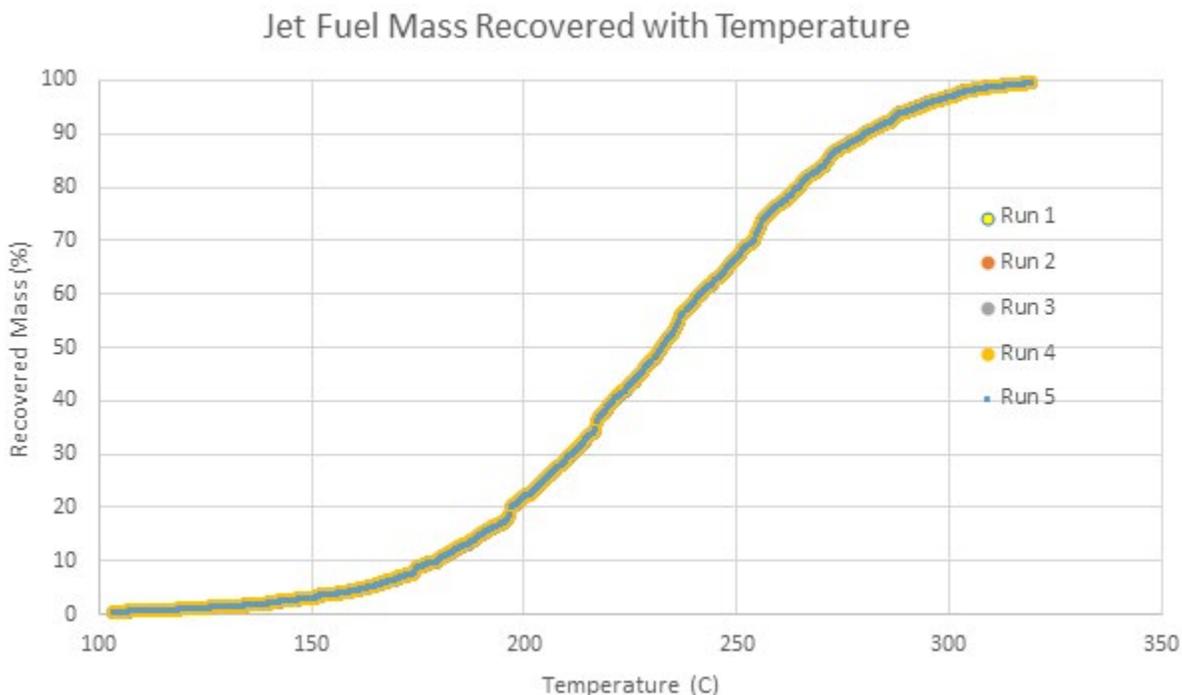

Figure D.2: Variation of simulated distillations for one Jet Fuel sample

In order to use the simulated distillation data to model the jet fuel vapor pressure only the first 10 % of recovered mass is needed, with this fraction provided in slices of 0.5 % of recovered mass to provide enough data for modelling. This required modifying the typical simulated distillation procedure which normally reports temperatures for recovered mass in 5 % increments.

One key point for the D2887-19a method is that the first data point is reported when 0.5 % of the mass has been recovered. In the jet fuel samples analyzed the temperature for 0.5 % recovered mass was 103 °C (217 °F). There is no boiling point data for the most volatile fraction that was determined using this methodology and therefore no way to gather data on the composition of the most volatile fraction of the jet fuel.

D.1.5 Process Simulation Modelling

Process simulation modelling uses the measured distillation curve to develop pseudo components that match the measured density and boiling curves. A single pseudo component is used for each 5 °F increment in the distillation curve up to the 10 % recovered mass. The vapor

pressure of the pseudo component is calculated using the Van Westen and Van Ness equation and the vapor pressure of the mixture at a temperature is calculated using the vapor pressure for each pseudo component and the mole fraction of each pseudo component.

This procedure was followed for each jet fuel sample and Table D.2 below shows the modelled RVP and the measured RVP.

Table D.2: Comparison of Measured and Modelled Jet Fuel RVP

Sample Number	Measured RVP (psi)	Modelled RVP (psi)
1	0.05	0.0489
2	0.05	0.0476
3	0.02	0.0481
4	0.00	0.0548
5	0.04	0.0431
6	0.05	0.0466

D.1.6 Summary

Six jet fuel samples were analyzed using ASTM D6378-18a to obtain the RVP and density of each. The same six samples were analyzed to obtain the simulated distillation with increments of 0.5 % and the data used in a process simulation model to develop pseudo components that match the simulated distillation.

The process simulation model used the pseudo components to calculate the vapor pressure of the mixture and the modelled RVP. The modelled data and four of the six measured samples had RVPs in the 0.04 psi to 0.05 psi range.

The D2887-19a method does not collect data until the first 0.5 % of the mass has been recovered. This means that there is limited information being collected on the most volatile components in any hydrocarbon mixture. This could have a large effect when considering the emissions from storage tanks at ambient temperature.

The data reported is for a small number of jet fuel samples and the vapor pressures obtained should not be considered as representative of the entire jet fuel category.

Bibliography

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[4] ASTM D2879, *Standard Test Method for Vapor Pressure-Temperature Relationship and Initial Decomposition Temperature of Liquids by Isoteniscope*

[5] ASTM D2887, *Standard Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography*

[6] ASTM D2887-16a, *Standard Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography*

[7] ASTM D2887-19a, *Standard Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography*

[8] ASTM D6378, *Standard Test Method for Determination of Vapor Pressure (VPX) of Petroleum Products, Hydrocarbons, and Hydrocarbon-Oxygenate Mixtures (Triple Expansion Method)*

[9] ASTM D6378-18a, *Standard Test Method for Determination of Vapor Pressure (VPX) of Petroleum Products, Hydrocarbons, and Hydrocarbon-Oxygenate Mixtures (Triple Expansion Method)*

[10] ASTM D7169, *Standard Test Method for Boiling Point Distribution of Samples with Residues Such as Crude Oils and Atmospheric and Vacuum Residues by High Temperature Gas Chromatography*

[11] ASTM D7777, *Standard Test Method for Density, Relative Density, or API Gravity of Liquid Petroleum by Portable Digital Density Meter*

[12] HOST Method, *Test Method for Vapor Pressure of Reactive Organic Compounds in Heavy Crude Oil Using Gas Chromatography*, May 28, 2002 (see Annex E to API MPMS Chapter 19.4, 3rd ed., 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) https://www.epa.gov/emc/broadly-applicable-approved-alternative-test-methods

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[16] *Estimating Vapor Pressure of Heavy Refinery Streams,* R. Ferry, K. Lau, D. Ringwald