

Evaluating Methods for Determining the Vapor Pressure of Heavy Refinery Liquids

AQRP Project 16-007

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*Quality Assurance Requirements
Audits of Data Quality: 10% Minimum, Required*

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In Memoriam



Russell R. Nettles
(1967 – 2017)

This report is dedicated to the memory and work of Russ Nettles, a passionate, dedicated, loyal Technical Specialist in the Emissions Assessment Section of the Air Quality Division at the Texas Commission on Environmental Quality. Those of us who had the pleasure of working with Russ will remember him for the significant impacts he had on improving air quality in Texas, which has and will continue to benefit millions who never met him, through the studies and projects he conceived, initiated and managed for the TCEQ. This project is one, and probably the last, of these many projects.

Russ was an innovative thinker who combined vision with a pragmatic approach to solving problems. He had a great sense of humor, loved life, supported his community and unselfishly helped colleagues and contractors in any way he could. He often shared with us one of his favorite sayings: “a smart man learns from his mistakes, a wise man learns from the mistakes of others.” Russ, thank you for helping us employ wisdom in identifying and implementing solutions to air quality challenges.

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Executive Summary

This project's purpose was to identify a reliable means of measuring the vapor pressure of heavy refinery liquids. These liquids include commercial materials such as fuel oil no. 6, which is used as a marine fuel and less often for heating or power generation, and liquid asphalt, whose uses include paving and roofing. Heavy refinery liquids also include intermediate streams and blend stock, such as vacuum residual. These materials are generally stored at elevated temperatures because they are too viscous to be pumped at ambient temperatures. For example, fuel oil no. 6 is typically stored near 120°F and liquid asphalt near 200°F.

Background

The vapor pressure of these materials is a key parameter when estimating emissions of volatile organic compounds from storage tanks (US EPA 2006), but their vapor pressures are not well understood. The properties of these materials (e.g., low vapor pressure, high viscosity, high opacity) can create challenges when measuring their vapor pressure, and measurements are rarely attempted. Vapor pressure default values are only available for vacuum residual and fuel oil no. 6 (API 2012 with addendum dated 2013; US EPA 2006), and there is no body of data that shows whether or not these default values bear any resemblance to typical vapor pressures for these materials. Results from direct measurement (US EPA 2015) and remote sensing techniques used to estimate volatile organic compound (VOC) emissions from heated storage tanks suggest that heated storage tanks might be responsible for some of the gap between estimated emissions of VOCs and observed concentrations of VOCs in some locations. If this is the case, it could be that estimated emissions are low because unrealistically low values for vapor pressure were used in the equations that are used to estimate VOC emissions from storage tanks.

Heavy refinery liquids are complex mixtures and their composition varies from source to source and from time to time at the same source. Fuel oil no. 6 and liquid asphalt are particularly complex, as they generally consist of a very heavy refinery stream that is blended with a somewhat lighter refinery stream to create the desired properties. These materials are not uniform; they vary in their physical properties and in their chemical composition.

It is the light ends in these liquids that drive vapor pressure, but accurately measuring the composition of the light ends is made difficult by the properties of the streams. Even if accurate concentrations of light ends in the streams could be obtained, the mixtures are far from ideal and an unknown amount of uncertainty would be introduced if Raoult's law were to be used to estimate the vapor pressure of these materials.

Approach

There is no gold standard for measuring the vapor pressure of a mixture, so there is no way to determine the accuracy of measured results by comparing them to a value that is known

to be correct. In this project, this difficulty was addressed by applying a number of potentially appropriate methods to the study materials and by including study materials whose vapor pressure was either reasonably well understood or documented. The vapor pressure methods employed include:

At commercial laboratories:

- ASTM D2879 (2010a) (vapor pressure by isoteniscope; this is the method the US EPA (2006) refers to as defining the vapor pressure of volatile organic liquids for which vapor pressures from default values or standard reference texts are not available; it was conducted at three labs)
- ASTM E1719 (2012) (vapor pressure by ebulliometry)
- ASTM D323 Procedure A (2015) (Reid vapor pressure; in this method, the vapor pressure of an air- and water-saturated sample is taken at 100°F and its results are expected to represent an upper bound on measured vapor pressures of the study materials at 100°F)

Using two makes of automated mini method instruments (Grabner and Eralytics):

- ASTM D6378 (2010b) (triple expansion method), which can be conducted in single point mode, where a separate triple expansion is conducted for each measured temperature, and in multi point (Grabner) or curve (Eralytics) mode, where results from a triple expansion at one temperature are applied to the same sample at other temperatures
- methods based on ASTM D6378 that had instrument hardware modifications intended to make them more suitable for measuring the vapor pressure of heavy refinery liquids (Eralytics refers to this as their “low VP” method and Grabner refers to it as their “VOC” method)

The study materials were

- a “known” recipe (80 mol % n-nonadecane and 20 mol % octane) whose modeled vapor pressure can be reasonably expected to be accurate to within 10%
- a hydraulic fluid whose manufacturer provided detailed vapor pressure data
- three fuel oil no. 6 samples designated as MM, MB, and BT

Analysis of Results

Figures ES-1 through ES-5 show the results of the vapor pressure measurements for each of the five study materials in the temperature range of interest for heated storage tanks. Some of the results from commercial labs fall outside this temperature range. All of the data points can be viewed in figures in the analysis section of the main report.

In Figures ES-1 through ES-5, the y-axis is the vapor pressure in psi on a log scale and temperature is on the x-axis. The gold, yellow, and orange lines are the ASTM D2879 (vapor pressure by isoteniscope) results for three commercial labs, which are presented as measurements (large circular markers connected by a thin line) and values calculated by the labs from a curve fit of inverse absolute temperature to base 10 logarithm of pressure for the data points obtained at higher temperatures (dotted lines). This curve fit procedure is described in ASTM (2010a). The red dotted lines represent the lab’s calculated results

and the red circular markers connected by thin red lines represent measured results from ASTM E1719 (vapor pressure by ebulliometry). The calculated results for ASTM E1719 are obtained from a curve fit of inverse absolute temperature to base 10 logarithm pressure, as described by ASTM (2012). The green circular markers are the low VP single point readings from the Eralytics instrument, and the blue line and blue circles are from Grabner multipoint ASTM D6378 readings and Grabner VOC single point readings, respectively. “First” Grabner refers to the first Grabner instrument used in the project and “second” Grabner is the second instrument.

The black dashed line in Figure ES-1, the “known” recipe chart, is the vapor pressure for that mixture as modeled using the Soave-Redlich-Kwong equation of state. The black dashed line in Figure ES-2 (for the hydraulic fluid) represents the manufacturer’s vapor pressure values. The black dashed lines in Figures ES-3 through ES-5 (for the three fuel oil no. 6 samples) represent the API (2012 with addendum dated November 2013) default value for fuel oil no. 6.

Because there is a fair amount of confidence in the modeled expectations for the vapor pressure of the “known” recipe, it is an interesting test case for the various methods. Figure ES-1 shows that along with the Eralytics instrument’s results from the low VP single point method and the ASTM D2879 results produced by Lab 3, the Grabner ASTM D6378 multipoint curve (obtained on the first instrument) and single point VOC method results (obtained on the second instrument) are in good agreement with modeled expectations above 100°F for this material. Note that lab 3, the lab whose ASTM D2879 measurements are in good agreement with the modeled vapor pressures, is the only lab that is accredited for ASTM D2879. This figure shows that in this temperature range, there were no instances where a measured vapor pressure using ASTM D2879 by any of the three commercial labs that applied this method exceeded the modeled vapor pressure. It is possible that this lower bound on vapor pressure from ASTM D2879 holds true for all of the study materials because when conducting this method the likelihood of unknowingly obtaining mistakenly high readings is low. Of the results produced by commercial laboratories (both ASTM D2879 and ASTM E1719), the best agreement with the modeled expectations for vapor pressure were the results for ASTM D2879 (vapor pressure by isoteniscope) from Lab 3 and the poorest agreement were the results for ASTM D2879 from Lab 1. The mini method instrument results show better agreement with modeled expectations for vapor pressure at the higher temperatures of the small temperature range over which they were conducted. Most of the measured values for ASTM E1719 (vapor pressure by ebulliometry), many of which were obtained over a tight temperature range above typical storage temperatures for heavy refinery liquids and do not appear in Figure ES-1, were within 10% of the modeled values.

Figure ES-2, for the hydraulic fluid, shows that the vapor pressure values from the calculated (curve-fit) results for ASTM D2879 from all the commercial labs are in very good agreement with each other and are about 1.5 to ten times higher than the manufacturer’s values, with less agreement at lower temperatures. The ASTM D2879 measured results for all three labs agree at around 175°F. Labs 2 and 3 also agree at 120°F. The Grabner multipoint ASTM D6378 values and the ASTM E1719 calculated results are also in good

agreement with each other, but not with the calculated ASTM D2879 results. They are also higher than the manufacturer's values, from several hundred times higher at the lowest temperatures that can be compared to seven times higher at the highest temperature values from the Grabner instrument and 1.5 times higher for the E1719 calculated results at 300°F. For this material, the ASTM E1719 measured results were all taken at temperatures above 190°F and thus do not appear in this chart. Also, measurements taken using the Eralytics instrument are not shown in this chart because they were made using instrument methods that relied on algorithms that were later found to be in error.

Figure ES-3, for the MM fuel oil no. 6 sample, shows that the ASTM D2879 results from Labs 2 and 3 seem to be in fairly good agreement with each other but fall nearly an order of magnitude above the API default vapor pressure value. The three pairs of low VP single point readings taken on the Eralytics instrument vary across nearly an order of magnitude at 120°F and 140°F but are similar to each other at 160°F. Figure ES-3 shows that at 140°F, there are measured instrument readings, ASTM D2879 measured values for Labs 2 and 3, and the curve fit for ASTM D2879 for Labs 2 and 3, and all are on the order of a tenth of a psi. The default value (API 2012 with addendum dated November 2013) at 140°F is 0.016 psi. The lower of the two Eralytics single point readings at 140°F falls between the measured values obtained by labs 2 and 3 at this temperature. This is a wet vapor pressure measurement but this material was analyzed for water content using ASTM D95 (water by distillation) and was reported to be 0.00 vol % water. For this material, the ASTM E1719 measured results were all taken at temperatures above 190°F and thus do not appear in this chart. Also, there are no Grabner mini method instrument results for this material because the Grabner instruments ceased operating before they could be used to test this material.

In Figure ES-4, for the MB fuel oil no. 6 sample, all of the ASTM D2879 measured results from Lab 3 fall above the default vapor pressure values, and except for the upper end of the temperature range, so do the ASTM D2879 measured results for Lab 1. Only three single point readings for the low VP method were obtained using the Eralytics instrument for this material: one at 120°F, one at 140°F, and one at 160°F. The value at 140°F falls below the values at 120°F and 160°F; in reality, the vapor pressure would increase with increasing temperature. The mini method readings, all of the ASTM D2879 measured values for Lab 3 (which begin at 176°F), and all of the measured values for Lab 1 above 140°F are 0.1 psi or higher. The default value (API 2012) reaches a value of 0.1 psi at 223°F. The lower of the two Eralytics single point readings at 140°F falls between the measured values obtained by Labs 2 and 3 at this temperature. This is a wet vapor pressure measurement but this material was analyzed for water content using ASTM D95 (water by distillation) and was reported to be 0.00 vol % water. For this material, the ASTM E1719 measured results were all taken at temperatures above 190°F and thus do not appear in this chart. Also, there are no Grabner results for this material because the Grabner instruments ceased operating before they could be used to test this material. Lab 2 did not provide ASTM D2879 results for this material because they were unable to analyze this material using ASTM D2879.

Figure ES-5, for the BT fuel oil no. 6 sample, shows that all of the ASTM D2879 measured results from Lab 3 fall well above the default vapor pressure values, sometimes two orders

of magnitude higher. As with the MB fuel oil no. 6 sample, except for the upper end of the temperature range, the ASTM D2879 measured results for Lab 1 also fall above the default values. Five single point readings for the low VP method were obtained using the Eralytics instrument: two at 120°F, two at 140°F, and one at 160°F. The value at 160°F falls below the values at 140°F and 120°F; in reality, the vapor pressure would increase with increasing temperature. Four of the five mini method readings, all of the ASTM D2879 measured values for Lab 3 (which begin at 140°F), and all of the measured values for Lab 1 above 140°F are 0.1 psi or higher. The default value (API 2012) reaches a value of 0.1 psi at 223°F. One of the two mini method instrument readings at 140°F is nearly two orders of magnitude lower than the other four instrument readings. For this material, the ASTM E1719 measured results were all taken at temperatures above 190°F and thus do not appear in this chart. Also, there are no Grabner mini method instrument results for this material because the Grabner instruments ceased operating before they could be used to test this material. Lab 2 did not provide ASTM D2879 results for this material because they were unable to analyze this material using ASTM D2879.

The ASTM D323 result for each of the five study materials was < 0.2 psi. This method measures the vapor pressure of a water- and air-saturated sample at 100°F, and the results from ASTM D323 are expected to be higher than results from the other methods at 100°F. The only method that returned a value higher than 0.2 psi at 100°F for any of the materials was the “known” recipe, where the calculated result for ASTM E1719 is higher than 0.2 psi.

Discussion and Conclusions

This project demonstrated that mini method instruments can process samples of heavy refinery liquids and that there is often order of magnitude agreement in measured vapor pressures of heavy refinery liquids using mini method instruments and the commercial lab results of this study. For both ASTM D2879 (vapor pressure by isoteniscope) and the mini method instruments, it appears that accounting for or removing dissolved air in the material being analyzed can be an important source of error in the results. For ASTM D2879, potential opportunities for overcoming this hurdle include conducting the degassing step at very low pressure at the lowest possible temperature and seeding the boil. For the mini method instruments, careful measurement of the vapor volumes and total pressures at the three expansions, along with steps to ensure that pressure measurements are made after equilibrium is established, are potential opportunities for overcoming this hurdle.

ASTM D2879 (vapor pressure by isoteniscope) results from different commercial labs disagreed by more than an order of magnitude in some cases in this project. It is likely that the conditions of the degassing step in this method are a primary cause of disagreement in results at different labs. The only lab accredited for this method produced measurements very near the modeled vapor pressure of a mixture containing a volatile compound and a nonvolatile compound (the “known” recipe), indicating that this method may be appropriate for heavy refinery liquids if the conditions of the degassing step are carefully controlled. None of the measured values of the “known” recipe that were taken using this

method by any of the commercial labs were larger than the estimated vapor pressure, indicating that perhaps the measured values taken using this method represent a lower bound on vapor pressure.

The measured results for ASTM E1719 (vapor pressure by ebulliometry) were taken at temperatures higher than the temperatures of interest for estimating emissions from heated storage tanks holding fuel oil no. 6. The measured results of this method were in agreement with the estimated vapor pressure of the “known” recipe. This method generates calculated values for vapor pressure across a wide range of temperatures from measurements taken in a fairly tight band of temperatures, and these calculated values had a flatter slope than any other method’s results for all five study materials.

This project showed that the mini method instruments tested in this study show great promise as tools for measuring the vapor pressure of heavy refinery fuel oils. However, great care and understanding of the operation of the instrument and factors affecting the vapor pressure measurement of these fluids must be exercised when conducting these measurements. The results of the fuel oil no. 6 samples were very sensitive to the values for pressure and volume that were obtained at each of the expansions conducted by the instruments.

Method performance could only be assessed for the “known” recipe because there is no means of verifying the accuracy of measurements taken for any of the other study materials. A summary of method performance for the “known” recipe for temperatures ranging from 60°F to 190°F is given in Table ES-1. ASTM D2879 results from Lab 3 most closely matched the modeled expectations for this material, followed by the mini method instruments. Measured results for ASTM E1719 were in very good agreement with modeled expectations but were only made at the upper end of this temperature range and the curve-fit results for this method ranged from fair to poor. ASTM D2879 results for Lab 1 had the poorest agreement with modeled expectations, ranging from fair to poor, and ASTM D2879 results for Lab 2 ranged from fair to good.

At 100°F and above (which would include typical storage temperatures) the single point mini method results using methods intended for heavy refinery fluids were in every case near the estimated results for the “known” recipe. Except for one measurement at 140°F for the BT fuel oil no. 6 sample, the vapor pressures of the fuel oil no. 6 samples taken using the Eralytics instrument were between 0.1 and 1 psi. In addition, at least some of the Eralytics mini method results were within an order of magnitude of measured results from at least one commercial lab for each of the study’s fuel oil no. 6 materials.

ASTM D95 (water by distillation) was performed on the three fuel oil no. 6 samples. The MM and MB fuel oil no. 6 samples were found to contain 0.00 volume % water, but the BT fuel oil no. 6 did contain water at 0.1 or 0.2 volume %. The contribution of water to the vapor pressure of this material was estimated by applying the results from simulation of mixtures of water and hypothetical compounds that were developed based on boiling point distribution and specific gravity of heavy fuel oils. Using this method, the estimated contribution of water at these concentrations to the vapor pressure of a fuel oil no. 6 with

the density of this sample ranges from 0.01 to 0.03 psi at 100°F, from 0.02 to 0.06 psi at 120°F, and from 0.04 to 0.10 psi at 140°F. The contribution of water to the measured vapor pressures obtained during this study for this material (including all methods) were 17 to 42% at 100°F, 3 to 63% at 120°F, and 9 to >100% at 140°F.

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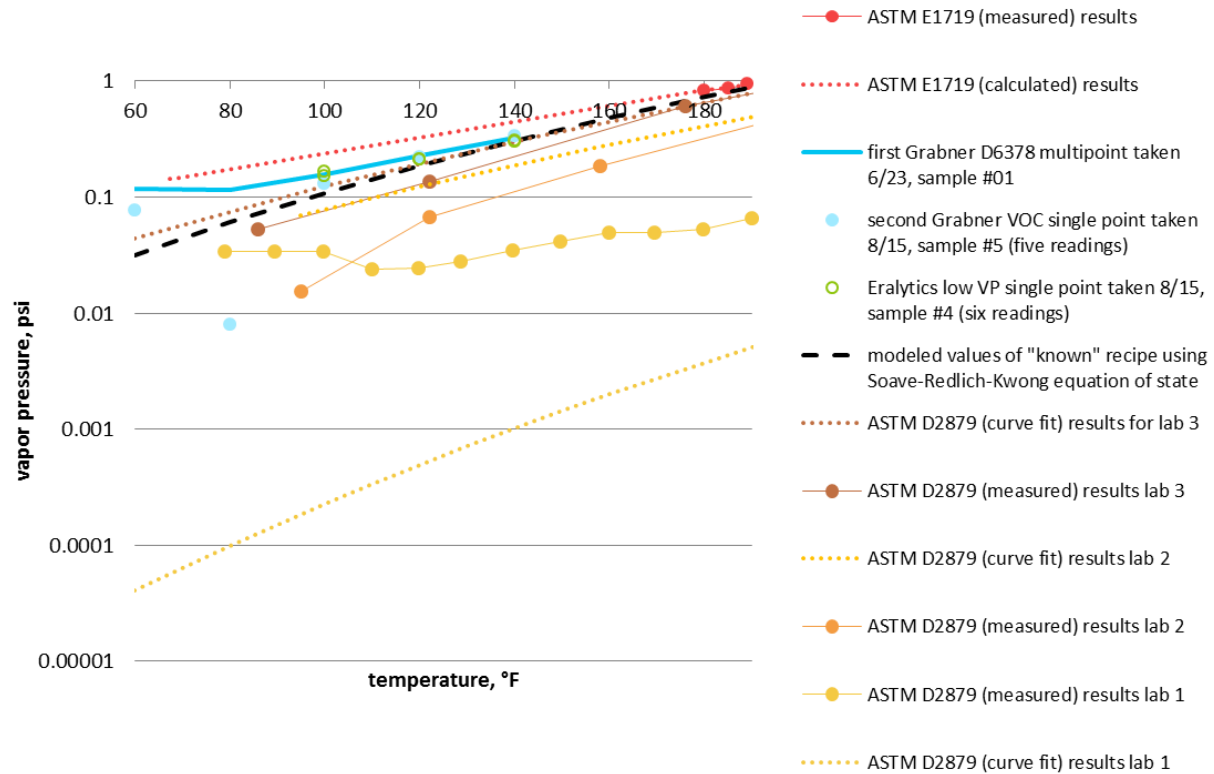
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KR2

Figure ES-1. “Known” recipe vapor pressure values from 60°F to 190°F. For the Grabner D6378 multipoint method, the values presented are the average after omitting the first injection of each syringe, per the instrument manufacturer’s instructions.

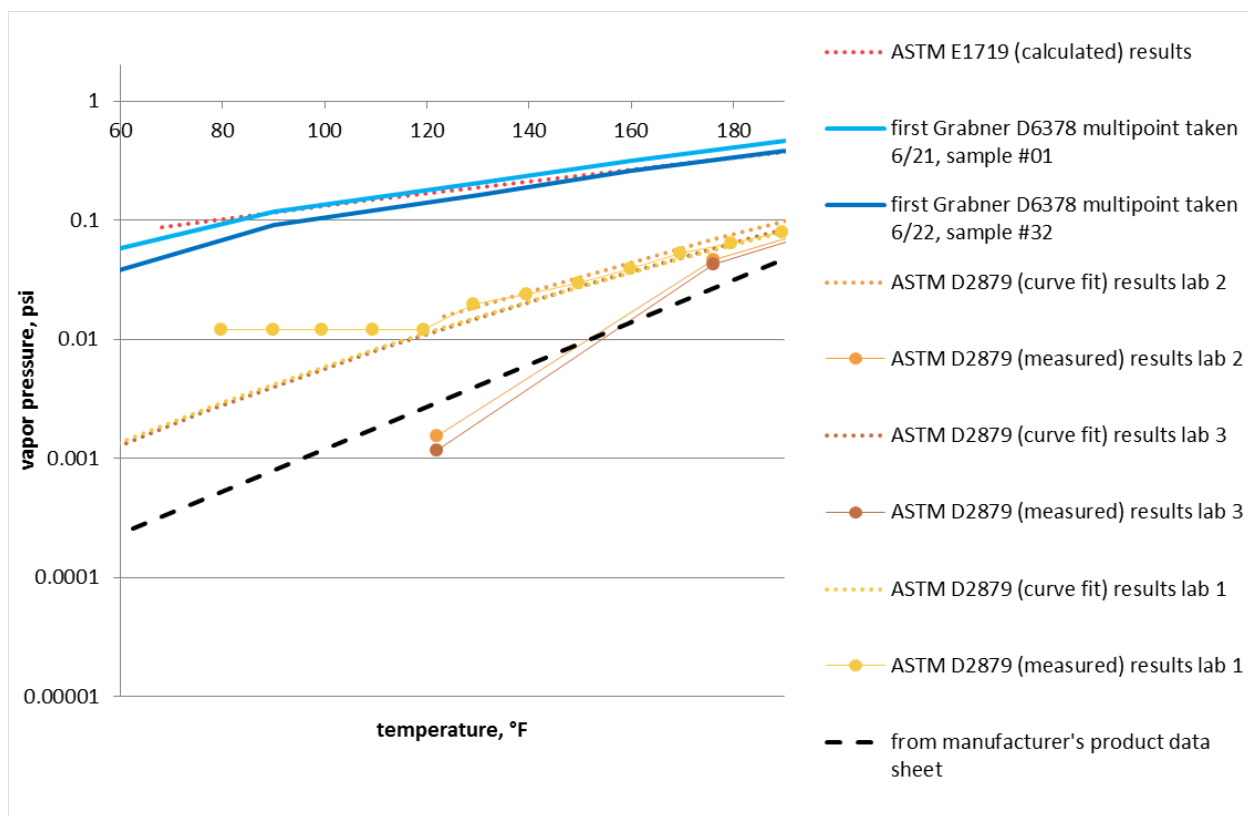


Figure ES-2. Hydraulic fluid vapor pressure values from 60°F to 190°F. For the Grabner D6378 multipoint method, the values presented are the average after omitting the first injection of each syringe, per the instrument manufacturer's instructions.

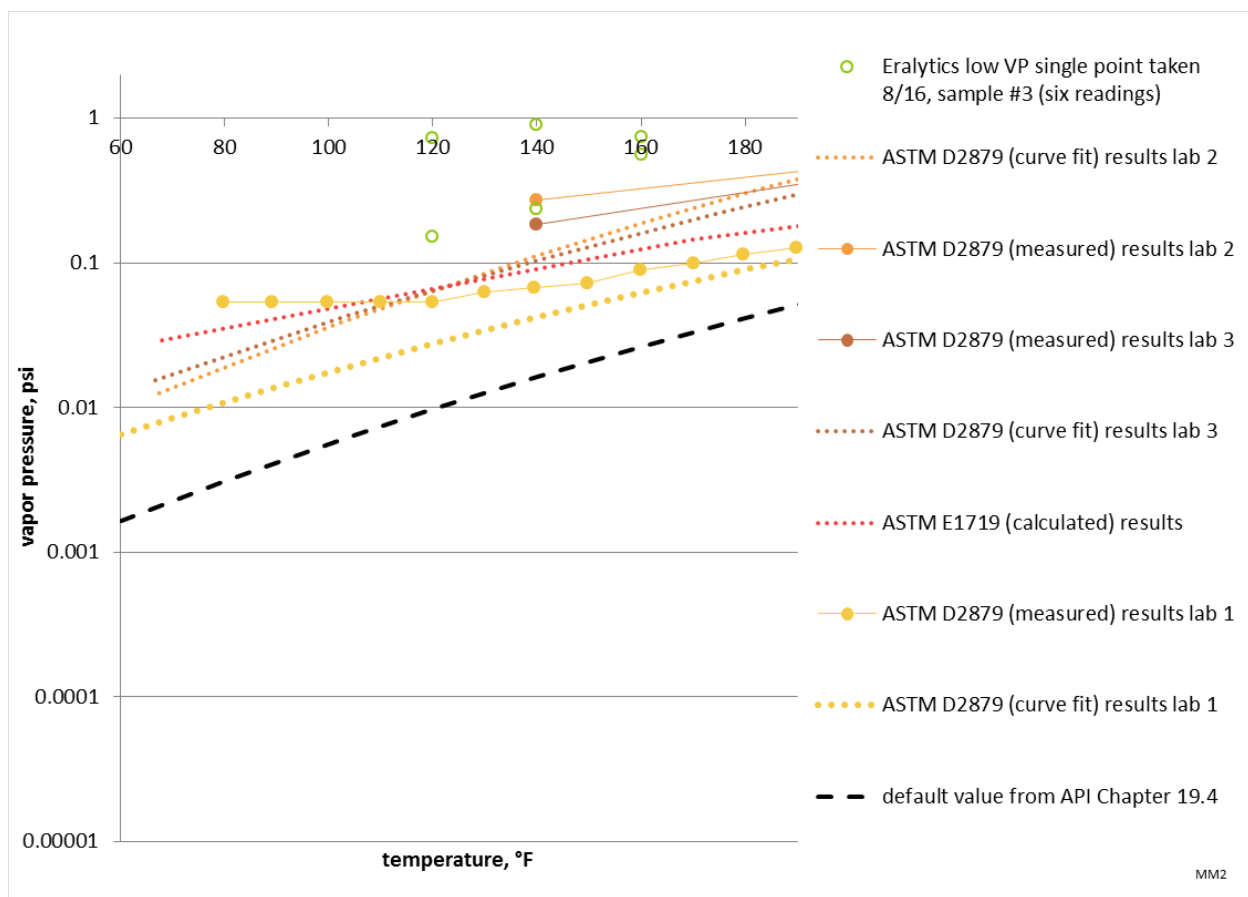
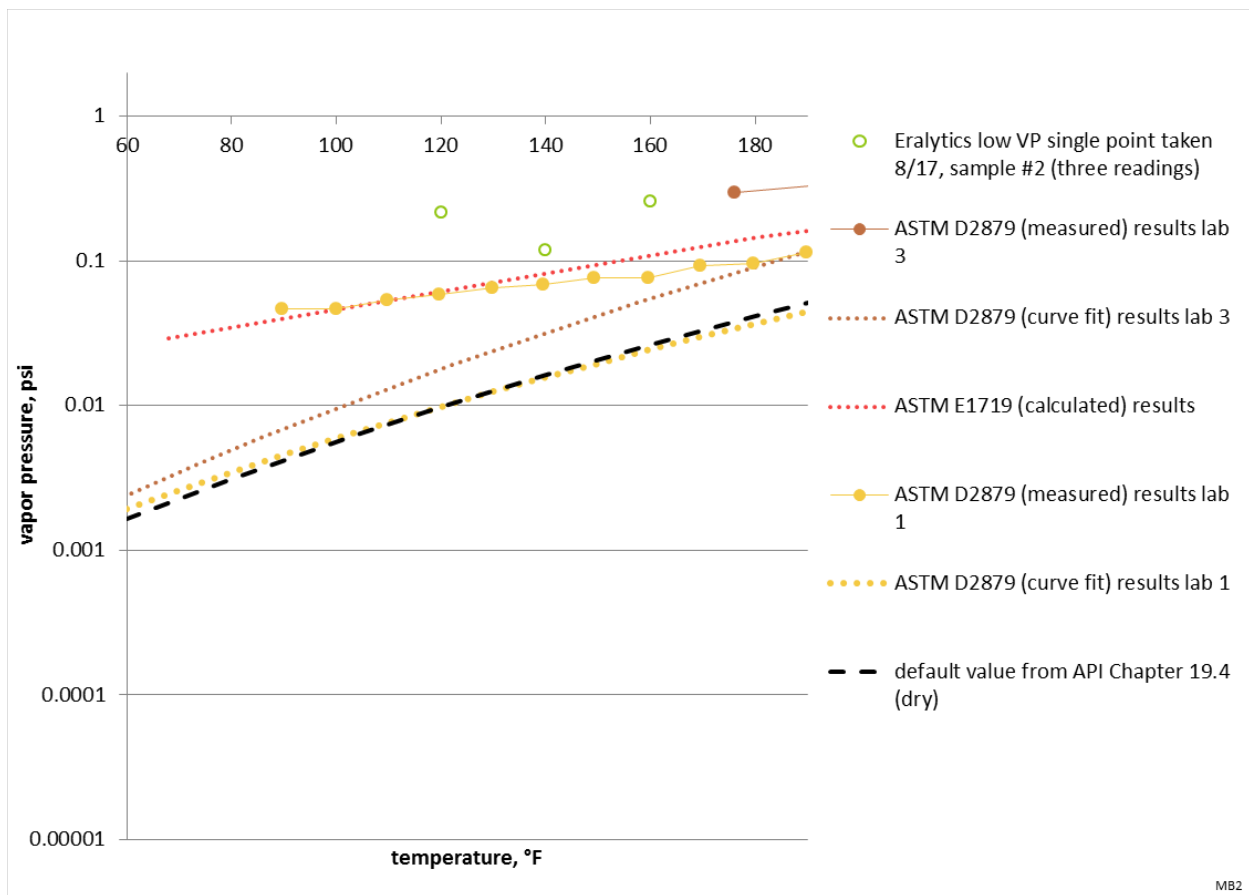
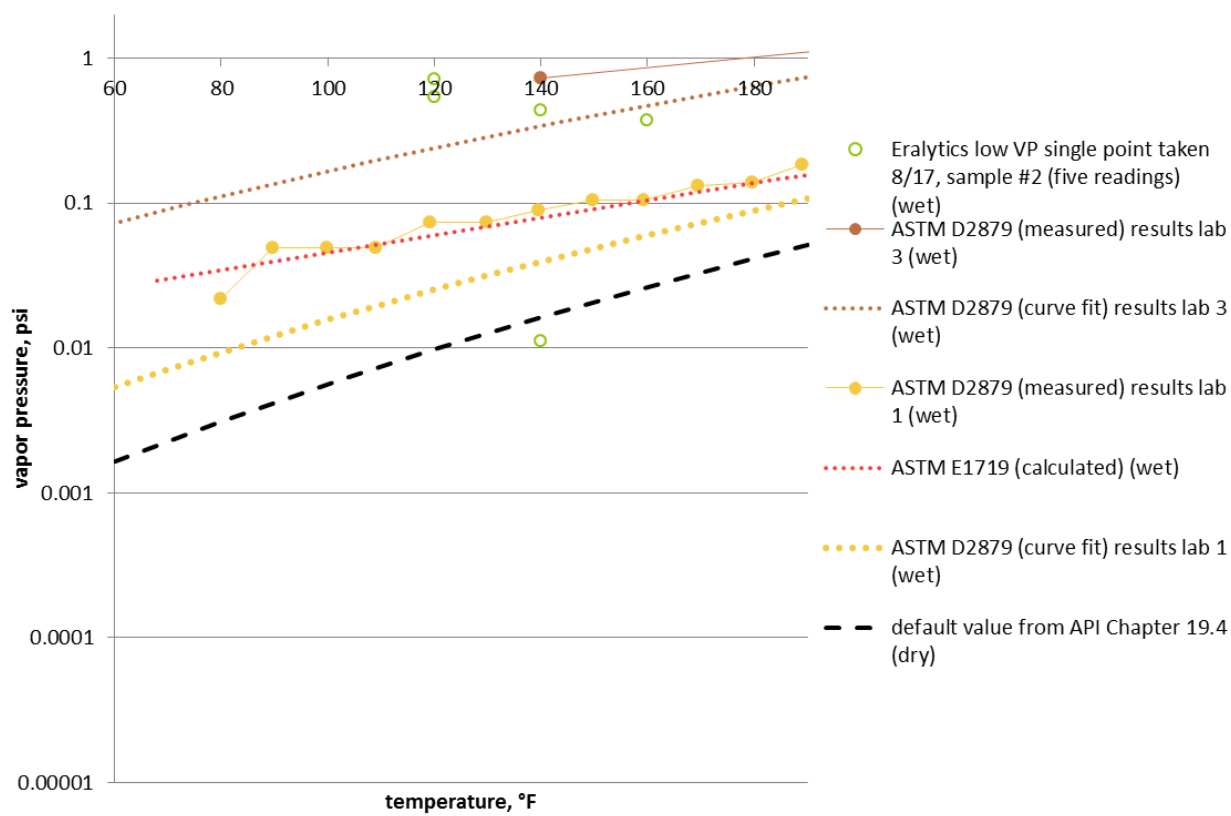


Figure ES-3. MM fuel oil no. 6 vapor pressure values from 60°F to 190°F.



MB2

Figure ES-4. MB fuel oil no. 6 vapor pressure values from 60°F to 190°F.



BT2

Figure ES-5. BT fuel oil no. 6 vapor pressure values from 60°F to 190°F.

Table ES-1. Agreement between modeled values and mini method and commercial lab vapor pressure results for the “known” recipe.

Key:

- The darkest green cells indicate very good agreement (method agrees with modeled value to within 10%)
- The medium green cells indicate good agreement (method agrees with modeled value to within 30%)
- The light green cells indicate fair agreement (method agrees with modeled value to within 90%)
- The white cells indicate poor agreement (not within 90%)
- The grey cells indicate no method value for comparison is available at this temperature

Temperature, °F	Mini method instruments			ASTM D2879 (vapor pressure by isoteniscope)						ASTM E1719 (vapor pressure by ebulliometry)	
	First Grabner ASTM D6378 multipoint taken 6/23, sample #01 ^a	Second Grabner VOC single point taken 8/15, sample #5 (five readings)	Eralytics low VP single point taken 8/15, sample #4 (six readings)	Lab 1 ^b measured	Lab 1 curve fit	Lab 2 measured	Lab 2 curve fit	Lab 3 measured	Lab 3 curve fit	Measured	Curve fit
60											
79											
80											
86											
95											
100											
100.04											
120											
122											
140											
158											
160											
176											
180											
185											
189											

Note: VP=vapor pressure; VOC=volatile organic compound

^aThese values are the average omitting the first injection of each syringe.

^bLab 1 provided vapor pressure measurements at 58 temperatures; only a sampling is provided in this table.

1. Introduction

During the last five years, crude oil and natural gas production and petroleum refinery operations have seen an increased focus on their emissions of volatile organic compounds (VOCs), especially those from storage tanks (US EPA, 2011a; US EPA, 2011b; US EPA, 2015a; US EPA, 2015b; US CFR, 2015a; US CFR, 2015b; US CFR, 2015c). These actions have been taken by the United States Environmental Protection Agency (US EPA) “because EPA and state investigations have identified Clean Air Act compliance concerns regarding significant emissions from storage vessels, such as tanks or containers at onshore oil and natural gas production facilities” (US EPA, 2015a) and to “collect information on processing characteristics, crude slate, emission inventories, and limited source testing to fill information gaps” (US EPA, 2011b).

The primary objective of this project is to identify the most accurate, reliable, convenient, and reasonably priced means of measuring the vapor pressure of heavy refinery liquids at temperatures in the range of the typical temperatures of the liquid surfaces in refinery storage tanks. The purpose of this research is to improve the ability to estimate VOC emissions from storage tanks holding heavy refinery liquids by identifying methods that can be used to measure the vapor pressure of heavy refinery liquids in storage tanks. These tanks are found at storage terminals and refineries and are frequently heated in order to reduce the viscosity of their contents and make them pumpable. Evidence is mounting that the emissions from these tanks are underreported. For example, a study of four tanks holding heavy refinery liquids in Maine revealed that reported emissions of VOCs fell far short of measured emissions (US EPA, 2015c). This underreporting of emissions from heavy refinery liquid storage tanks may be one of the factors contributing to the VOC inventory gap in some areas of Texas (areas where known sources of VOCs are insufficient to account for the concentrations of VOCs measured in the air).

Federal New Source Performance Standards for storage tanks have various control requirements depending upon whether the storage tanks meet the affected source criteria specified in the rule. If emissions from storage tanks are not estimated correctly, these standards will not be suitably applied.

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idx?SID=06714a14ef2109ecb0a5737178b04165&mc=true&node=sp40.7.60.oooo&rgn=div6 accessed February 2016.

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2. Background

Heavy refinery liquids are complex mixtures of many chemical species, and properties important to the generation of their storage emissions are not well understood. For example, the range of vapor pressures for two common heavy refinery liquids, fuel oil no. 6 and liquid asphalt, are not known with any certainty. For fuel oil no. 6 at 100°F, potential values range from a default value of 0.006 psi to a measured value of 0.55 psi. (The only default vapor pressure values available for heavy refinery liquids are for fuel oil no. 6, with a default value of 0.002 psi at 60°F, and vacuum residual oil, with a default value of 0.00004 psi at 60°F (API, 2012 with addendum dated 2013).) In tanks holding fuel oil no. 6, there is a potential for actual emissions to be much larger than emissions estimated using the default vapor pressure values. The Texas Commission on Environmental Quality (TCEQ) funded two projects recently (Rosselot and Torres, 2014; Rosselot and Allen, 2015) to better understand the composition and properties of heavy refinery liquids and the most appropriate method of determining their vapor pressure.

While heavy refinery liquids such as fuel oil no. 6 and liquid asphalt are primarily composed of very heavy stock, such as vacuum tower residual, whose vapor pressure would be expected to be extremely low, they are often mixed or “cut” with more volatile materials in order to reduce their viscosity so that they can be pumped. Even small traces (ppb concentrations) of volatile species can have partial pressures several times greater than the major component of a high molecular weight sample (Bruno and Mayrath, 1997). Thus, the volatility of the most volatile components in heavy refinery liquids can have a significant effect on the vapor pressure of these liquids, even when their concentration in the liquid is quite low.

Direct measurement of emissions from storage tanks is inherently inexact and expensive. The direct measurement method approved by the US EPA is a temporary total enclosure (TTE) through which a known airflow is blown. The known airflow coupled with the concentration of pollutants in the air stream is used to estimate emissions. It is impossible to construct an enclosure around a tank without potentially disturbing the emission mechanisms that would be in place without the enclosure and the accuracy of the results depends on whether emissions from the storage tank without the enclosure are significantly different from emissions with the enclosure (US CFR, 2011). The accuracy also depends on the accuracy with which the concentration of pollutants is measured.

Because of the difficulties inherent in directly measuring the emissions from storage tanks, TTEs are not used to estimate emissions for reporting purposes. They are instead used only under special circumstances, such as when they are required by a consent decree. Hence, reported emissions from storage tanks are in nearly every case based on equations that predict emissions based partly on thermodynamic principles and partly on empirically obtained values (US EPA, 2006). The value used for the vapor pressure in these equations has a profound impact on the results. In a modeling exercise that applied the approved equations for estimating emissions, applying a vapor pressure value of 0.4 psi instead of 0.5 psi for a fixed-roof storage tank reduced the estimated standing emissions from that tank

by 35%, while applying a vapor pressure value of 0.6 psi instead of 0.5 psi increased the estimated standing emissions by 60% (Rosselot and Allen, 2015). These are relatively small perturbations in vapor pressure; in practice, a heavy liquid's vapor pressure at the temperature of the liquid surface in the tank is not measured and a default value that may be in error by several orders of magnitude is often assumed when making emission estimates.

The vapor pressure of many pure substances is available in reference books and databases (Green, 2008; Weast, 1974). For a simple mixture of ideal liquids whose components have known vapor pressure, the mixture's vapor pressure can be estimated using Raoult's Law (US EPA, 2006). Most heavy refinery liquids, however, are complex mixtures of many chemicals whose vapor pressures are not necessarily known (Rosselot et al, 2014; US EPA 1988) and that may have non-ideal behavior. In addition, over time, the composition of the liquids can vary. Because of this, using Raoult's Law to obtain estimates of the vapor pressure of these liquids is infeasible.

The methods used to establish the default values for the vapor pressure of fuel oil no. 6 and vacuum residual are not described in public documents. ASTM standard test methods include a scope of applicability, and there is no ASTM standard test method whose scope includes vapor pressures as low as the API default vapor pressure value for vacuum residual oil. The only standard test method whose scope explicitly includes pressures as low as the default vapor pressure value for fuel oil no. 6 is ASTM E1719 (vapor pressure by ebulliometry).

In many cases (e.g., US EPA, 2006), ASTM D2879 (vapor pressure by isoteniscope) (ASTM, 2010a) is recommended as a method for measuring the vapor pressure of organic liquids whose vapor pressures do not appear in the literature or for which default values are not available. The appropriateness of applying ASTM D2879 to measure the vapor pressure of heavy refinery liquids is questionable for several reasons. It is a difficult method to apply and few laboratories offer this method of analysis (Calhoon 2015, Grace 2015). As of this writing, no refineries have been located that apply the method themselves. It has no precision statement (ASTM, 2010a), so its repeatability, reproducibility, and bias are unknown. An additional weakness of this method is that it involves a degassing step (ASTM, 2010a) that is intended to remove air from the sample, and because heavy liquids at refineries tend to contain a mixture of substances with highly varying vapor pressures, this degassing step could drive off lighter components of the mixture and provide values for the vapor pressure that are lower than the actual vapor pressure (Ferry 2013). In his presentation at the 4C Conference in 2016, Fuchs (2016) noted that for ASTM D2879, the experience level of the chemist performing the test is important to ensure accurate results. He also noted that ASTM D2879 is a labor-intensive method in which heavy, viscous products are the most difficult to test, and dark products like heavy refinery liquids that cling to the glass make the test even more difficult to perform because they obscure the meniscuses that must be sighted in order to obtain accurate results. In its guidelines for testing the vapor pressure of chemicals, the Organisation for Economic Co-operation and Development (OECD, 2006) noted that isoteniscope are usually not suitable for measuring

the vapor pressure of multicomponent systems (ASTM D2879 makes use of an isoteniscope).

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Terminology and numerical specifications for heavy fuel oils

Materials classified as the heaviest grade of fuel oil vary widely in their composition and cover a range of physical properties. Much of this fuel oil is used as marine fuel, but it is also used for space heating and power generation. The power sector in the United States has all but eliminated the use of heavy fuel oil for power generation, as shown in Figure 1, but this is not true of countries throughout the globe.

The heaviest grade of fuel oil is referred to using many terms, including fuel oil no. 6, which is the term used in this work. The many terms can be confusing because sometimes the terms are used to include materials that are lighter than fuel oil no. 6 and many of the terms have no official definition or specifications. Diesel 6 (D6) and six oil are synonymous with fuel oil no. 6. Terms that are sometimes treated as synonymous with fuel oil no. 6 are heavy fuel oil (HFO), intermediate fuel oil (IFO), residual fuel oil (RFO), bunker C, black oil, and Navy heavy.

There are numerical specifications or definitions for some of these terms and this section compares a set of materials that have numerical specifications. The terms for which there are numerical specifications are fuel oil no. 6 (ASTM 2016), HFO (IEA 2017), bunker fuels (Platts 2016), and residual marine fuels (ISO 2017). The Platts (2016) and ISO (2017) specifications include materials that do not meet the viscosity specifications for ASTM (2016) for fuel oil no. 6; only the materials that meet the ASTM (2016) specifications for fuel oil no. 6 are discussed here.

All of the numerical standards include a specification for kinematic viscosity and a specification for flash point. Kinematic viscosity is strongly a function of the temperature at which it is measured. Specifications that were encountered measured kinematic viscosity at three different temperatures (50°C, 80°C, and 100°C). Estimates of the kinematic viscosity specifications at a consistent reference temperature had to be made in order to identify areas of overlap among the specifications. These estimates were generated using Shell's BunkerCalc program (2005), which has a module that uses the kinematic viscosity at a given reference temperature to estimate the kinematic viscosity at another temperature. Table 1 provides the results of BunkerCalc estimates at all the relevant temperatures and kinematic viscosities.

Table 2 is a condensed summary of the numeric standards that exist for these materials. A blank entry in the table indicates that a numeric standard is not given in the listed source document. Where needed, an estimate of the kinematic viscosity at 50°C was made using Shell (2005). Note that the standards may specify non-numeric qualities as well, such as homogeneity, and contain details not included in this table. Note that the ISO standard is for fuels used in marine diesel engines and boilers, while the ASTM and IEA specifications do not apply solely to marine uses.

Figure 2 is a qualitative visualization of the information from Table 2. Several ISO materials (RMG and RMK 380, 500, and 700) also conform with standards set by ASTM for

fuel oil no. 6, and a subset of ISO's RME and RMG 180 would also conform with the ASTM standard for fuel oil no. 6. The Platts IFO 380 and 500 materials conform to the ASTM standard for fuel oil no. 6 and so does a subset of the Platts IFO 180 material. Much of the material that meets the IEA's definition for HFO would also meet the ASTM specifications for fuel oil no. 6 but IEA's HFO also includes materials that have a lower flash point and a lower viscosity than is specified by the ASTM standard for fuel oil no. 6.

Acronyms

D6	Diesel 6
HFO	Heavy fuel oil
IEA	International Energy Agency
IFO	Intermediate fuel oil
IMO	International Maritime Organization
ISO	International Organization for Standardization
MARPOL	Marine pollution
RFO	Residual fuel oil
RM	Residual marine

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Tables and Figures

Table 1. Kinematic viscosities found in specifications for heavy fuel oil and corresponding estimates of kinematic viscosities at other temperatures. Specifications are in boldface type and estimates at other temperatures (from Shell 2005) are in italics.

Kinematic viscosity, cSt		
50°C (ISO 8217)	80°C (IEA)	100°C (ASTM)
<i>25</i>	10	<i>6.3</i>
80*	<i>24</i>	<i>13</i>
<i>97</i>	<i>28</i>	15
180	<i>44</i>	<i>22</i>
380	<i>76</i>	<i>35</i>
500	<i>93</i>	<i>41</i>
<i>680</i>	<i>120</i>	50
700	<i>120</i>	<i>51</i>

*This is the maximum viscosity for RMD 80, which is not a heavy fuel oil but is the next less viscous material identified in the ISO 8217 standard and identifies a potential lower bound for the viscosity of RME and RMG 180.

Table 2. Summary of several numeric standards for heavy residual fuel oils (for details consult referenced documents).

Parameter	Type of Limit	ISO 8217: 2017	Platts	ISO 8217: 2017	ISO 8217: 2017	Platts	ISO 8217: 2017	ISO 8217: 2017	ISO 8217: 2017	ISO 8217: 2017	Platts	ISO 8217: 2017	ASTM D396-16	IEA
		RME 180	IFO 180	RMG 180	RMG 380	IFO 380	RMG 500	RMG 700	RMK 380	RMK 500	IFO 500	RMK 700	Fuel Oil No. 6	HFO
kinematic viscosity at 50°C, mm ² /s	max	180.0	180	180.0	380.0	380	500.0	700.0	380.0	500.0	500	700.0	680 (est.; actual standard is 50 mm ² /s at 100°C)	
kinematic viscosity at 50°C, mm ² /s	min												97 (est.; actual standard is 15 mm ² /s at 100°C)	25 (est.; actual standard is 10 mm ² /s at 80°C)
density at 15°C, kg/m ³	max	991.0		991.0	991.0		991.0	991.0	1010.0	1010.0		1010.0		
density, temperature not specified, kg/m ³	min													900
calculated carbon aromaticity index (CCAI)	max	860		870	870		870	870	870	870		870		
flash point, °C	min	60.0	60	60.0	60.0	60	60.0	60.0	60.0	60.0	60	60.0	60	50
sulfur, mass %	max		3.5			3.5					3.5			
hydrogen sulfide, mg/kg	max	2.00		2.00	2.00		2.00	2.00	2.00	2.00		2.00		
acid number, mg KOH/g	max	2.5		2.5	2.5		2.5	2.5	2.5	2.5		2.5		
total sediment, mass %	max	0.10		0.10	0.10		0.10	0.10	0.10	0.10		0.10	0.50	
water, volume %	max	0.50	0.5	0.50	0.50	0.5	0.50	0.50	0.50	0.50	0.5	0.50	2.00 (water + sediment may not exceed this value)	
carbon residue, mass %	max	15.00		18.00	18.00		18.00	18.00	20.00	20.00		20.00		

Parameter	Type of Limit	ISO 8217: 2017	Platts	ISO 8217: 2017	ISO 8217: 2017	Platts	ISO 8217: 2017	ISO 8217: 2017	ISO 8217: 2017	ISO 8217: 2017	Platts	ISO 8217: 2017	ASTM D396-16	IEA
		RME 180	IFO 180	RMG 180	RMG 380	IFO 380	RMG 500	RMG 700	RMK 380	RMK 500	IFO 500	RMK 700	Fuel Oil No. 6	HFO
pour point (winter/summer), °C	max	30/30	30/30	30/30	30/30	30/30	30/30	30/30	30/30	30/30	30/30	30/30		
ash, mass %	max	0.070	0.10	0.100	0.100	0.15	0.100	0.100	0.150	0.150	0.15	0.150		
vanadium, mg/kg	max	150	200	350	350	300	350	350	450	450	600	450		
sodium, mg/kg	max	50		100	100		100	100	100	100		100		
aluminum + silicon, mg/kg	max	50	80	60	60	80	60	60	60	60	80	60		
used lubricating oil, mg/kg	not allowed	Ca>30 and Zn>15 or P>15		Ca>30 and Zn>15 or P>15	Ca>30 and Zn>15 or P>15		Ca>30 and Zn>15 or P>15	Ca>30 and Zn>15 or P>15	Ca>30 and Zn>15 or P>15	Ca>30 and Zn>15 or P>15		Ca>30 and Zn>15 or P>15		

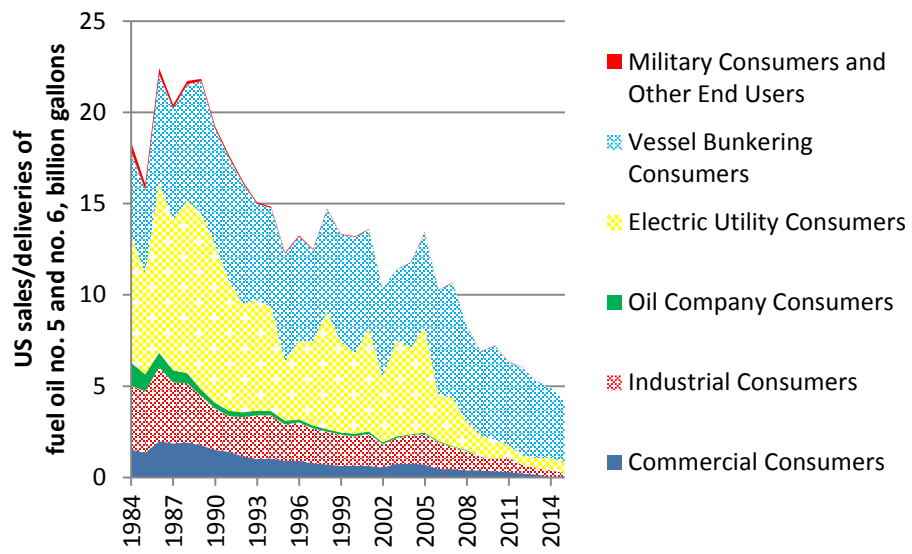


Figure 1. Trends in residual oil consumption in the United States. Data used to create this figure are from US EIA (2016).

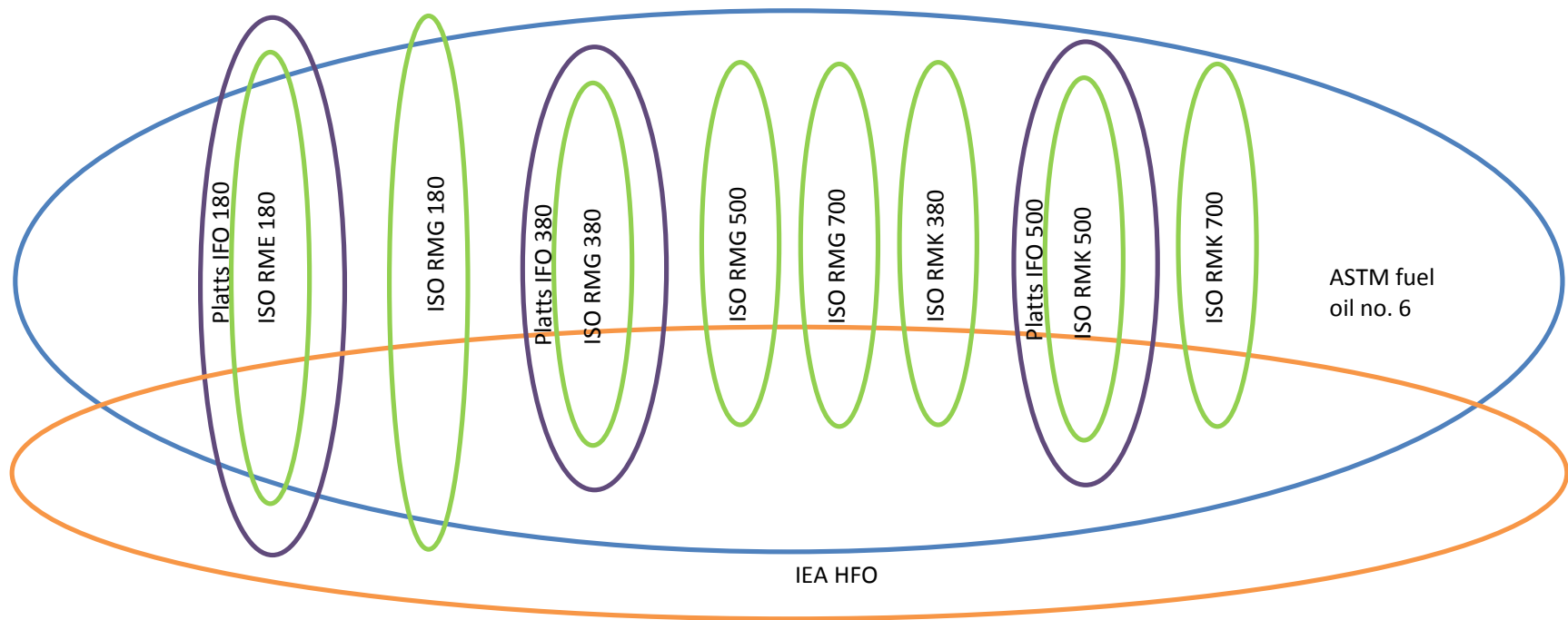


Figure 2. Venn diagram showing the overlap between 13 numeric standards for heavy fuel oil.

3. Approach

The approach used in this project was to measure the vapor pressure of five study materials using three standardized vapor pressure test methods that would be performed by multiple commercial labs and two automated mini method instruments designed to measure vapor pressure. The study materials are a “known” recipe (a mixture whose vapor pressure can be reliably modeled), a hydraulic fluid whose vapor pressure is documented by the manufacturer, and three samples of fuel oil no. 6, which is a heavy refinery liquid.

The commercial lab methods chosen for the study are ASTM D2879 (vapor pressure by isoteniscope), ASTM E1719 (vapor pressure by ebulliometry), and ASTM D323 Procedure A (Reid vapor pressure). ASTM D2879 was selected for the study because when estimating emissions from storage tanks, it is the method that US EPA refers to as defining the VP of volatile organic liquids for which vapor pressures from default values or standard reference texts are not available (US EPA, 2006). ASTM E1719 was selected because the scope of the method includes the anticipated vapor pressures of heavy refinery liquids and because it uses an entirely different analytical approach than the approach of ASTM D2879. ASTM D323 Procedure A was selected as a comparison method; because this method is used to measure the vapor pressure of a water- and air-saturated sample at 100°F, its results are expected to be equal to or greater than the results of the other methods at 100°F. The commercial labs chosen for the study and the basis for selection of these labs are provided later in this section.

At the time of the project, the only known automated mini method instruments that were recommended for measuring the VP of heavy refinery liquids were the Grabner MiniVap VP Vision and the Eralytics Eravap EV10 instruments. The methods intended for use on these instruments for the purposes of the study are ASTM D6378 (triple expansion method for measuring vapor pressure) and a method that applies the principles of ASTM D6378 but has modifications designed to accommodate measuring the vapor pressure of heavy refinery liquids. Eralytics refers to its instrument’s modified ASTM D6378 method, which it recommends for heavy refinery liquids as its low VP method, while Grabner refers to its instrument’s modified ASTM D6378 method for heavy refinery liquids as the VOC method. Originally, it was anticipated that correlations for converting ASTM D6377 results from the mini method instruments could be used to estimate ASTM D323 results that could be compared to ASTM D323 commercial lab results, but the correlations could not be applied to heavy refinery liquids, so ASTM D6377 was not applied.

The methods of the study and some of their characteristics are shown in Table 3, along with the rationale for selection of each method.

References

U.S. Environmental Protection Agency, 2006, AP-42, Fifth Edition, Volume I Chapter 7: Liquid Storage Tanks, available at <http://www3.epa.gov/ttn/chief/ap42/ch07/final/c07s01.pdf>.

Table 3. Measurement methods used in the study.

Method	Performed by Several Commercial Labs	Performed by One Commercial Lab Each		Grabner MiniVap VP Vision		Eralytics Eravap EV10	
	ASTM D2879	ASTM E1719	ASTM D323 Procedure A	ASTM D6378	VOC Method	ASTM D6378	low VP method
Description and rationale	This method makes use of an isoteniscope (a submerged manometer with one leg attached to a container holding the material being analyzed and the other leg connected to a source of inert gas and a pressure measuring device). This is the method recommended by the EPA for measuring vapor pressures that are otherwise unavailable for making emission estimates from storage tanks; there is no precision statement for this method so there is no assurance that it has reasonable repeatability or reproducibility.	This method applies ebulliometry to measure vapor pressure; it measures boiling point at different pressures to determine vapor pressure so is entirely unlike ASTM D2879. Will not work for mixtures that "bump" when they boil or that contain non-condensable gases.	This method measures the vapor of a water- and air-saturated sample and vapor pressure results using other methods are expected to be no higher than the results from this method.	Standardized automated mini method for determining the vapor pressure of petroleum products, hydrocarbons, and hydrocarbon-oxygenate mixtures. Uses triple expansion to provide a vapor pressure result that does not include the contribution of dissolved air.	Intended by the manufacturer to be a substitute for ASTM D2879. Unlike ASTM D2879, does not have a degassing step that can alter a sample's composition; instead uses triple expansion to provide a vapor pressure result that does not include the contribution of dissolved air.	Standardized automated mini method for determining the vapor pressure of petroleum products, hydrocarbons, and hydrocarbon-oxygenate mixtures. Uses triple expansion to provide a vapor pressure result that does not include the contribution of dissolved air.	Intended by the manufacturer to be a substitute for ASTM D2879. Unlike ASTM D2879, does not have a degassing step that can alter a sample's composition; instead uses triple expansion to provide a vapor pressure result that does not include the contribution of dissolved air.
Scope of method (temperature, °C)	< ambient to 475°C	12°C to 300°C (atmospheric boiling point of sample)	37.8°C	0°C to 100°C (precision statement applies at 37.8°C)	0°C to 120°C (per the manufacturer)	0°C to 100°C (precision statement applies at 37.8°C)	0°C to 120°C (per the manufacturer)
Scope of method (vapor pressure, kPa)	.133 kPa to 101.3 kPa	1 kPa to 100 kPa	<180 kPa (precision statement available for the 0 kPa to 35 kPa range)	<500 kPa (precision statement applies to samples with vapor pressure of 7 kPa to 150 kPa at 37.8°C)	0 - 2000 kPa (per the manufacturer)	<500 kPa (precision statement applies to samples with vapor pressure of 7 kPa to 150 kPa at 37.8°C)	0 kPa to 1000 kPa (per the manufacturer)

Identifying and selecting commercial labs

An attempt was made to use accredited labs, but not very many commercial labs offer the methods selected for this study and even fewer are accredited. Table 4 shows the accreditation entities and which labs were accredited for each method.

Table 5 lists the labs that performed measurements per the methods prescribed by this study. Of these labs, Petro-Lubricant Testing Laboratories, Inc. (Petrolubricant) was selected as one of three labs that would perform ASTM D2879 (vapor pressure by isoteniscope) because they were the only lab accredited for this method. Petrolubricant was also selected to conduct characterization of the project's fuel oil no. 6 samples, which was done in order to provide assurance that the samples meet ASTM specifications for fuel oil no. 6 (ASTM D396, 2016). These tests are for viscosity (ASTM D445), flash point (ASTM D93), and water (ASTM D95). ASTM D2622, which measures sulfur content, was also performed by Petrolubricant.

It was desirable to blind the vapor pressure results obtained using ASTM D2879 from the lab conducting ASTM E1719, and vice versa. Analytical Testing Services, Inc. was the only lab that was found that could perform ASTM E1719 (vapor pressure by ebulliometry), so it was not selected for ASTM D2879. This left three labs that could perform ASTM D2879. Of those three, Alcor Petrolab and Savant Labs were selected based on price considerations. In addition to performing ASTM D2879 for the project, Savant performed vapor pressure measurements per ASTM D323 (Reid vapor pressure method).

Results from the commercial laboratories are given in the next section of this report. Alcor Petrolab is referred to as Lab 1, Savant as Lab 2, and Petrolubricant as Lab 3 in the sections that follow.

References

ASTM International (ASTM), 2016. ASTM D396-16, Standard Specification for Fuel Oils. West Conshohocken, PA, www.astm.org.

Tables and figures

Table 4. Accredited labs for ASTM D2879, ASTM E1719, and ASTM D323

Type of accreditation	Search method	D2879	E1719	D323
National Environmental Laboratory Accreditation Program (NELAP)	lams.nelac-institute.org/search	No labs	No labs	No labs
Perry Johnson Laboratory Accreditation, Inc. (PJLA)	www.pjllabs.com/search-accredited-labs	Petro Lubricant Testing Laboratory, Inc.	No labs	No labs
National Voluntary Laboratory Accreditation Program (NVLAP)	www-s.nist.gov/niws/index.cfm?event=productlist.search#no-back	No labs	No labs	No labs
American Association for Lab Accreditation (A2LA)	www.a2la.org/dirsearchnew/newsearch.cfm	No labs	No labs	No labs
International Accreditation Service, Inc. (IAS)	www.iasonline.org/More/search.html	No labs	No labs	No labs
Laboratory Accreditation Bureau (L-A-B)	search.l-a-b.com/	No labs	No labs	U.S. Customs and Border Protection Laboratories and Scientific Services Directorate - San Francisco Laboratory
ANSI-ASQ National Accreditation Board (ACLASS & FQS)	This is the same as Laboratory Accreditation Bureau now.	See L-A-B	See L-A-B	See L-A-B
AASHTO Accreditation Program (AAP)	aashtoresource.org/aap/accreditation-directory	No labs	No labs	No labs

Table 5. List of labs that offer the methods used in this project

Lab	Source of info	D2879	E1719	D323
Alcor Petrolab/Phoenix Chemical Laboratory	www.alcorpetrolab.com/testing-info/heat-transfer-fluids/33-tests/227-astm-d2879	Yes	No	No
Chilworth Technology, Inc. - a DEKRA company	www.chilworth.com/laboratory-testing/astm-tests	Yes	No	No
Savant Labs	www.savantlab.com/images/Savant_Labs_Test_List_by_Method_Jan_2015.pdf	Yes	No	Yes
Analytical Testing Services, Inc.	wetestit.com/testing_list.htm	Yes	Yes	Yes
Petro Lubricant Testing Laboratory, Inc.	requests.petrolube.com/#!/	Yes*	No	Yes
American Testing Technologies, Inc.	www.astm.org/LABS/filtrexx40.cgi?+-P+ACCTNO+1942149+template.frm	No	No	Yes
Fesco	web form query	No	No	Yes

* this lab is accredited for this method

Determination of the “known” recipe

For this project, several commercial labs measured the vapor pressure of the study materials using ASTM methods, and for each material the vapor pressure was also measured using one or two mini method instruments. All of the materials are mixtures and there is no gold standard for measuring the vapor pressure of a mixture. (Strictly speaking, the term “vapor pressure” only applies to pure substances; this is because the vapor over a mixture is not the same composition as the liquid. However, the “vapor pressure” of mixtures is commonly referred to in industry and in the regulatory community and this terminology is used in this report.)

Because there is no gold standard for measuring the vapor pressure of mixtures, it is not possible to say which, if any, of the methods used to measure vapor pressure is obtaining accurate results. Therefore, the approach used in this study was to include materials whose vapor pressures were documented or could be accurately predicted. A hydraulic fluid whose manufacturer provided detailed vapor pressure information was included as a study material, as was a mixture prepared from pure substances. The latter material is referred to as the “known” recipe in this project because its vapor pressure could be estimated computationally. Ideally, this material would have a vapor pressure that is about the same order of magnitude as fuel oil no. 6 at typical storage temperatures and contain

compounds similar to those found in fuel oil no. 6. It is essential that there be a high level of confidence in the estimated vapor pressure of this material. It is also essential that the ingredients be reasonably easy to procure.

Fuel oil no. 6 is usually a blend of a very heavy refinery residual stream and cutter stock that is often an off-spec comparatively light stream or other low value lighter stream. It is generally stored at around 120°F; at ambient temperatures it is too viscous to be pumpable. The vapor pressure at the typical temperature of the liquid surface in a storage tank is used for estimating emissions from storage tanks, and while the surface temperature depends on factors including ambient conditions, equations provided by the US EPA (2006) generally estimate the liquid surface temperature of fuel oil no. 6 stored at 120°F to be in the neighborhood of 100°F. The API (2012 with addendum dated November 2013) vapor pressure default value for fuel oil no. 6 at 100°F is 0.0056 psi. API provides the August equation constants for both this material and for vacuum residual, which can be used to calculate default values for the vapor pressure of these materials at any temperature of interest. The US EPA (2006) vapor pressure default value for fuel oil no. 6 at 100°F is 0.00019 psi. Default vapor pressures at temperatures above 100°F are not given by the US EPA, but could be calculated from an August (or Antoine, etc.) equation curve fit of the values that are provided. No other heavy refinery liquids besides fuel oil no. 6 and vacuum residual have been assigned default vapor pressure values.

The range of values that might be expected for the vapor pressure of fuel oil no. 6 is not well understood. When default values provided by the US EPA (2006) or by the American Petroleum Institute (API October 2012 with addendum dated November 2013) are applied to the US EPA's (2006) methodology for estimating emissions from storage tanks, the estimates fall far short of field measurements of a tank holding fuel oil no. 6 in Maine. This could be partly due to errors in EPA's estimation methodology and/or partly due to inaccuracies inherent in field measurements. In addition, degassing and dewatering steps typically applied to these streams when the method that is most commonly recommended for measuring the vapor pressures of these streams (ASTM D2879) is used can remove the light ends in fuel oil no. 6 that would otherwise dominate the vapor pressure value that was obtained.

The API currently expects that the vapor pressure of fuel oil no. 6 would be on the order of a hundredth of a psi at 100°F (API 2012 with addendum dated November 2013). It was determined that the vapor pressure of the "known" recipe should be in the low tenths of a psi range at 100°F.

Fuel oil no. 6 contains straight chain hydrocarbons, branched hydrocarbons, cyclic compounds, and aromatic compounds. It also has organic sulfur and sometimes oxygen. Initially, three recipes were investigated:

1. n-octane and n-nonadecane
2. n-octane, n-nonadecane, and o-xylene
3. 2,2,4-trimethylpentane, n-nonadecane, and o-xylene

In order to be confident of the actual vapor pressure of the mixtures, vapor pressure values for the three recipes were calculated using Raoult's Law and the NIST-modified UNIFAC

model and were found to be within 10% of each other. However, the Peng-Robinson equation of state (with no binary interaction parameters) produced vapor pressure values that were 30-50% higher than the NIST-modified UNIFAC model for the cases with o-xylene (Cardoso 2017).

More equations of state were tested using ChemSep LITE (V7.15 with default models for properties and ignoring temperature ranges), taking care to ensure that the same expressions for the vapor pressure of the pure ingredients were used for Raoult's Law as for the NIST-modified UNIFAC model. As shown in Table 6, substituting another cyclic compound for o-xylene did not sufficiently tighten the range of calculated vapor pressures for the mixture. A mixture of ethylbenzene, octane, and nonadecane had the narrowest band of values for mixtures that included a cyclic compound, but in that case the lowest vapor pressure estimate (from the NIST-modified UNIFAC model) was 40% lower than the estimate using either the Peng-Robinson 76 or Peng-Robinson 78 equations of state with binary interaction parameters.

Because of this, the idea of including a cyclic compound in the recipe for the "known" recipe was abandoned and the selected "known" recipe consists of 20 mol % n-octane and 80 mol % n-nonadecane. Table 7 shows the results of the estimation methods for this mixture. The expectation is that the true value of the vapor pressure of this mixture at 310.9°C is very likely to lie between 0.10 and 0.12 psi.

Table 8 shows the sensitivity of Raoult's Law results for this mixture to the source of the information about the vapor pressure of the pure components. All of these results agree to within 10%. Note that the results when using Antoine's constants from NIST WebBook do not exactly match the results when using Antoine's constants from the ChemSep LITE pure components data because the Antoine's constants from those two resources are not exactly the same.

Table 6. Results of several vapor pressure estimation methods for mixtures containing cyclic compounds. All mixtures were 15 mol % n-octane, 70 mol % nonadecane, and 15 mol % cyclic compound. Results of all methods except NIST-modified UNIFAC were calculated using ChemSep LITE (V7.15).

Estimation method	Bubble point of mixture (psi) at 310.9K for cyclic compound				
	o-Xylene	m-Xylene	p-Xylene	Ethylbenzene	Ethylcyclohexane
Raoult's Law	0.12	0.13	0.13	0.14	0.15
Soave-Redlich-Kwong	0.14	0.15	0.15	0.16	0.17
Soave-Redlich-Kwong modified by API	0.14	0.15	0.15	0.16	0.17
Peng-Robinson '76 no binary interaction parameters	0.15	0.16	0.16	0.17	0.19
Peng-Robinson '76 with binary interaction parameters	0.16	0.17	0.17	0.18	0.19
Soave-Redlich-Kwong using universal mixing rule	0.17	0.19	0.20	0.17	0.15
Peng-Robinson '76 using universal mixing rule	0.18	0.20	0.21	0.17	0.16
Peng-Robinson '78 with binary interaction parameters	0.16	0.16	0.17	0.18	0.19
Peng-Robinson '78 with binary interaction parameters predicted by group contribution theory	a	a	a	0.14	0.16
Soave-Redlich-Kwong with binary interaction parameters predicted using modified Huron-Vidal first-order mixing rule	0.13	0.14	0.15	0.15	0.15
NIST-modified UNIFAC	0.11	0.12	0.12	0.13	0.14

^aThese runs generated the error message "PR78 ID not available for <cyclic>"

Table 7. Results of several vapor pressure estimation methods for the selected “known” recipe: 20 mol % n-octane and 80 mol % nonadecane. Results of all methods except NIST-modified UNIFAC were calculated using ChemSep LITE (V7.15).

Estimation method	Bubble point of mixture at 310.9K (psi)
Raoult's Law using T correlations	0.11
Soave-Redlich-Kwong	0.11
Soave-Redlich-Kwong modified by API	0.11
Peng-Robinson '76 no binary interaction parameters	0.12
Peng-Robinson '76 with binary interaction parameters	0.12
Soave-Redlich-Kwong using universal mixing rule	0.11
Peng-Robinson '76 using universal mixing rule	0.11
Peng-Robinson '78 with binary interaction parameters	0.12
Peng-Robinson '78 with binary interaction parameters predicted by group contribution theory	0.11
Soave-Redlich-Kwong with binary interaction parameters predicted using modified Huron-Vidal first-order mixing rule	0.11
NIST-modified UNIFAC	0.099

Table 8. Results of several sources of pure component vapor pressure information when using Raoult’s law to estimate the vapor pressure of the selected “known” recipe: 20 mol % n-octane and 80 mol % nonadecane. Results of all information sources except NIST WebBook Antoine’s constants and ChERIC were calculated using ChemSep LITE (V7.15).

Source of vapor pressure of pure components	Raoult’s Law bubble point at 310.9K (psi)
NIST WebBook Antoine's constants	0.10
CHERIC	0.11
Twu	0.11
Riedel	0.11
Lee Kessler	0.10
Antoine's constants	0.11
T correlations	0.11

References

American Petroleum Institute (API). October 2012 with addendum dated November 2013. Manual of petroleum measurement standards, Chapter 19.4 Evaporative loss reference information and speciation methodology, 3rd ed. with addendum 1. Washington, DC.

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Chemical Engineering and Materials Research Information Center (CHERIC). Accessed at www.cheric.org/research/kdb/hcprop/cmpsrch.php.
ChemSep LITE (V7.15). Accessed at www.chemsep.org/program/index.html.

National Institute of Standards and Technology Chemistry WebBook (NIST WebBook). Accessed at webbook.nist.gov/chemistry/name-ser.html.

U.S. Environmental Protection Agency, 2006, AP-42, Fifth Edition, Volume I Chapter 7: Liquid Storage Tanks, available at:
<http://www3.epa.gov/ttn/chief/ap42/ch07/final/c07s01.pdf>.

Obtaining sample materials

The materials tested for this project were a hydraulic fluid, a “known” recipe, and three samples of fuel oil no. 6.

“Known” recipe ingredients

The “known” recipe was generated in the lab at The University of Texas by mixing 1054.2 g nonadecane with 112.2 g octane. This mixture was then blended and dispensed into more manageable sample sizes.

Hydraulic fluid

The hydraulic fluid (Castrol Brayco Micronic 756) is used in aircraft, missile and ordnance. Information about its vapor pressure across a range of temperature was available from the manufacturer. It arrived in a 5-gallon pail and was dispensed into smaller sized aliquots before analysis.

Fuel oil no. 6

The fuel oil no. 6 samples were not easily sourced. Three materials were received in five shipments from mid-November to mid-June. Usually arriving in 1-quart containers, the five shipments were divided into three blending batches and then dispensed into more manageable sample sizes.

MM fuel oil no. 6

The MM fuel oil no. 6 samples were the second of two sets of samples obtained from a UT contractor who performs lab accreditations and testing. These samples were described as coming from a tank holding fuel oil no. 6 at a shipping terminal.

MB fuel oil no. 6

The MB fuel oil no. 6 sample was a blend of the first sample obtained from the same individual as the MM fuel oil. no. 6 samples and the BT fuel oil no. 6. It was necessary to blend the materials because there was not enough of the second sample obtained from the individual who provided the MM fuel oil no. 6 sample to conduct all the analyses for the project.

BT fuel oil no. 6

This sample was drawn from a tank holding fuel oil no. 6 at a storage terminal while two members of the study team observed.

Sample dispensing and shipping

The materials analyzed in this project came in containers ranging in volume from about one to 19 liters. The project required that smaller samples ranging from 10 mL to 500 mL be shipped to several different laboratories and that 30 mL samples be available for analysis by mini method instruments at the UT facilities. Four of the five study materials did not flow easily at room temperature and needed to be heated before being dispensed into smaller containers. This section describes the steps that were taken to ensure that samples were appropriately dispensed and safely shipped.

Sample dispensing

Because of the need to have all the samples of each material be uniform with respect to vapor pressure, a consistent and rapid method of handling, preparing, and dispensing the samples to be analyzed was developed. A dispensing apparatus was especially designed for the project. The dispensing procedure, described in Appendix A, minimized the potential for loss of any volatile components.

The hydraulic fluid flowed easily without being heated and was dispensed using the apparatus described in Appendix A without a heated oil bath on May 30. The dispensing apparatus was used to blend and heat the “known” recipe using an oil bath and this material was dispensed on June 6. On June 7, as the same apparatus was being used to dispense the BT fuel oil no. 6 material, the sample jar broke, resulting in a loss of the sample in the heating oil.

As a result, the dispensing apparatus was modified to eliminate the oil bath, as shown in Figure 3. Between June 8 and June 20 all the fuel oil samples were dispensed using this revised apparatus.



Figure 3. Revised dispensing scheme.

Containers filled and sample labeling

Table 9 lists the sizes of containers that were filled along with the vapor pressure method for which they were intended. When dispensing each study material, ten of the 30-ml vials were filled first and then when all the other containers were filled except the leftover material containers, 30 ml vials were filled. This is because the 30 ml vials were used for mini method instrument testing and the ability to test samples on the mini method instruments from both the beginning and end of the dispensing procedure in order to verify uniformity of samples was desired. To ensure that any necessary re-tests could be made, twice as many samples were dispensed as were thought to be needed. Note that after the sample bottle of BT fuel oil no. 6 shattered during dispensing, there was not enough of some of the fuel oil no. 6 samples to fill a reserve 125-ml container.

Tables and figures

Table 9. Dispensed samples

Size, mL	# of containers per material*	# of materials dispensed	Materials dispensed	Total # of containers	For ASTM method
10	8	3	3 fuel oil no. 6 materials	36	D2879 (three labs) BP study
	6	2	1 "known" recipe 1 hydraulic fluid		D2879 (three labs)
30	22	5	3 fuel oil no. 6 materials 1 "known" recipe 1 hydraulic fluid	110	Mini methods (5 reads per vial, 4 methods on the Grabner and 1 method on the Eralytics, collect ten vials at beginning and at least ten at end of dispensing)
50	4	3	3 fuel oil no. 6 materials	12	D445 (viscosity) D2622 (sulfur)
100	4	3	3 fuel oil no. 6 materials	12	D93 Procedure B (flash point) D95 (water)
125	2	5	3 fuel oil no. 6 materials 1 "known" recipe 1 hydraulic fluid	10	D323 Procedure A
200	2	5	3 fuel oil no. 6 materials 1 "known" recipe 1 hydraulic fluid	10	E1719
500	1	1	For storing leftover fuel oil no. 6 material	1	n/a
750	1	1	For storing leftover fuel oil no. 6 material	1	n/a

Shipments to commercial laboratories

The hydraulic fluid samples were shipped with a safety data sheet from Castrol. The “known” recipe and the fuel oil no. 6 samples were shipped with safety data sheets created for the project using information taken from existing safety data sheets for similar materials/ingredients and registered substances information maintained by the European Chemicals Agency. The safety data sheets are given in Appendix B.

Samples were sent to commercial labs in 1-gallon friction lid can combination packaging from Hazmatpac. These packages were certified to meet or exceed the rigorous DOT requirements for the transportation of hazardous goods. Although perhaps more durable than necessary, the UN packaging is considered to be a safe option for sending hazardous liquids. The known sample was shipped under the designation UN 1262 “Octanes mixture” and the fuel oil no. 6 samples were shipped under the designation UN 3082 “Environmentally hazardous substance, liquid, n.o.s.” All sample bottles were packed in absorbent vermiculite and all reached their designated delivery addresses without any breakage or loss.

4. Results

Quality Assurance and Audits of Data

In addition to the attempt to use labs that are accredited for the ASTM methods selected for the project and the standard operating procedure for making vapor procedure measurements using the mini method instruments, 100% of the data provided by the commercial labs and generated using the mini method instruments were audited by one or more of the project team members. The audit procedures are described in Appendix C.

Vapor pressure results from mini method instruments

Quality assurance measures taken when using the mini method instruments

The University laboratory used two key measurements to assure that the mini method instruments were performing correctly before analyzing samples. The first measurement was a test of the measurement of ambient pressure by the instrument's pressure transducer. The nominal ambient pressure for Austin, TX is 14.3 psiA. Beginning July 13 the station pressure at the point of the instrument was recorded with an electronic barometer with a resolution of 0.01 in Hg at least once per operating day. Acceptance criteria for this metric were determined to be a difference of +/- 0.05 psia from the station pressure.

Beginning on July 27, a second measurement was added to verify instrument performance. This was the vapor pressure of n-pentane. According to ASTM D6378 the acceptable testing range for the vapor pressure of n-pentane using the ASTM D6378 single point method at 100°C is 15.48 psi to 15.82 psi.

If for any reason these two requirements were not met, analysis would stop and the operator would follow the manufacturer's recommended troubleshooting steps to correct the issue. Of the results that are presented in this section of the report, the only measurements that were not bracketed by an ASTM D6378 single point analysis of n-pentane at 100°C were two ASTM D6378 curves for hydraulic fluid and one ASTM D6378 curve for the "known" recipe, both taken using the first Grabner instrument.

Quality assurance for the two mini method instruments was handled in a two-step process that formed the basis of the Vapor Pressure Analysis Using Minivap Method Standard Operating Procedure (Appendix D) used during all sample analyses. This procedure also incorporated critical instrument operating instructions and guidelines provided in the instrument application note provided by Grabner (Appendix E) and the operating instructions received from Eralytics (Appendix F). Laboratory personnel would verify that the samples were processed before sending them to another project team member for validation.

A gas tight syringe was used to introduce samples to the mini method instruments instead of the manufacture-provided syringe because vapors could be seen escaping the provided

syringe while injecting pentane and other lighter materials into the instrument. The gas tight syringe was used to avoid loss of lighter end components from the study materials.

The hydraulic fluid was the least viscous of the study materials and samples of this material were simply loaded from 30-ml vials into a 50 mL syringe. The headspace was carefully evacuated from the sample by inverting the syringe and pressing on the plunger. Then, the syringe was placed on the instrument for analysis. Only minor pressure was used on the plunger to overcome the friction of the gas tight seal against the internal cylinder of the syringe body.

The “known” recipe is a solid at room temperature but melts just above room temperature. Samples were heated to 100°F, then poured into an opened and preheated syringe. The headspace was removed, the syringe was capped, self-adhesive toe warmers were attached, and the assembly was placed back into the heated oven for 10 minutes while the instrument was readied for analysis. Fuel oil no. 6 samples were too viscous to flow easily at room temperature and the same procedure was followed for introducing them to the mini method instrument as the “known” recipe, except that they were warmed to 140°F. The toe warmers kept the more viscous samples liquefied while multiple injections into the instrument were made. A complete description of the sample preparation protocol can be found in Appendix B.

Grabner instruments

With this instrument, the D6378 and D6378 curve methods are pre-programmed single injection/single temperature point method and single injection/multi-temperature point measurement that conform to ASTM D6378. The VOC single point and multi-point methods are the same as the D6378 methods except that the piston speed is slowed to accommodate the slower place of a viscous fluid through the instrument’s tubing, and the sample chamber is shaken to speed up the establishment of vapor-liquid equilibrium.

We received a MiniVap VP Vision (VP/V) mini method instrument (Appendix G) from Grabner on April 20. The Gulf Coast Sales Manager for Ametek/Petrolabs helped the laboratory staff unpack, install, and power up the instrument. The first run attempted was a pentane sample. It was quickly determined that the solenoid-activated sample valve was stuck in the closed position. The sales representative took the instrument back for repair at their Tulsa, OK facility.

On May 8, the repaired instrument was returned. On May 10, we ran an octane test to confirm the instrument was functioning. On May 11, the sales representative approved using the instrument to test the more difficult samples. The week of May 15, we ran two pentane curve methods to familiarize ourselves with the proper operation of the instrument. The next week an analysis of hydraulic fluid was attempted. The instrument produced squeaking sounds and did not draw the sample into the sample port during the injection cycle. Per the manufacturer, the typical viscosity of the hydraulic fluid is 13.2 cSt at 40°C (104°F), so the sample’s viscosity was not expected to be the cause of the instrument’s breakdown. The manufacturer conducted troubleshooting on May 24 and

determined that the instrument needed repair. It was returned to the repair facility the next day. A setscrew on the internal plunger mechanism of the instrument had come loose. The technicians applied Loctite and retightened the setscrew.

On June 10, we received the instrument for the third time. Between June 19 and June 23 the laboratory conducted a preliminary ASTM D6378 curve measurement of the hydraulic fluid, then two ASTM D6378 curve readings of the hydraulic fluid (13 injections read at five temperatures each from two different syringes) and one ASTM D6378 curve method reading for the “known” recipe (seven injections read at five temperatures from one syringe). Subsequent measurements of the vapor pressure of pentane on June 26 and 27 showed that the instrument was not operating properly again; this time it was replaced by the manufacturer.

On August 15, the second Grabner instrument was used to obtain 5 single point readings of the “known” recipe using the single point VOC method. Two successful operational checks using pentane were conducted using ASTM D6378 and nonane was also analyzed using the single point VOC method. After that, the instrument failed to correctly measure atmospheric pressure when open to the atmosphere and was returned to the manufacturer.

Eralytics instrument

There were four different methods used on the Eralytics Eravap EV10 (Appendix G) to analyze sample and QA runs for this project.

1. D6378
2. D6378 Curve
3. Low VP
4. Low VP Curve

As with the Grabner instrument, the D6378 and D6378 curve methods on the Eralytics instrument are pre-programmed single injection/single temperature point method and single injection/multi-temperature point measurement that conform to ASTM D6378. The low VP single point and curve methods are the same as the D6378 methods except that the tubes leading to the sample chamber are heat-traced, the piston speed is slowed to accommodate the slower place of a viscous fluid through the instrument’s tubing, and the sample chamber is shaken to speed up the establishment of vapor-liquid equilibrium.

Analysis on the Eravap began on June 12 with several practice analyses to familiarize the laboratory personnel to the new equipment. Between June 15 and June 26, 23 injections of four different hydraulic fluid and “known” recipe samples were analyzed on the Eravap for a total of 115 temperature point vapor pressure measurements with the D6378 curve method (See Table 10). From June 27 to July 27, one “known” recipe, three hydraulic fluid samples, and seven fuel oil no. 6 samples were analyzed on the Eravap using the custom low VP curve method for a total of 58 injections and 290 individual vapor pressure measurements. From August 15 to August 17, one “known” recipe sample and all three types of fuel oil no. 6 were analyzed for a total of 20 injections and 20 individual vapor

pressure measurements. Including all sample and QA runs, a total of 139 injections and 463 individual vapor pressure measurements were generated. The results of these analyses as reported by the instrument are found in Tables 10 through 14.

Table 10. Raw results from D6378 Curve analysis of “known” recipe and hydraulic fluid samples.

Date	Time	Operator	SN	Sample ID	No.	Info	Comment	Tm	Pabs	Pgas	Ptot	Pabs Calculated	rate	[T]	[P]	Volume [ml]	T fill
6/23/2017	22:05	Spinhirne	EVP71157440	KR-060617-02	#00024			140	0.6721	0.2587	0.9309		0	°F	psi	1000	100
6/23/2017	21:59	Spinhirne	EVP71157440	KR-060617-02				120	0.5525	0.2501	0.8026		0	°F	psi	1000	100
6/23/2017	21:54	Spinhirne	EVP71157440	KR-060617-02				100	0.4759	0.2415	0.7174		0	°F	psi	1000	100
6/23/2017	21:48	Spinhirne	EVP71157440	KR-060617-02				80	0.4242	0.2328	0.657		0	°F	psi	1000	100
6/23/2017	21:43	Spinhirne	EVP71157440	KR-060617-02				60	0.3816	0.2415	0.6231		0	°F	psi	1000	100
6/23/2017	21:23	Spinhirne	EVP71157440	KR-060617-02	#00023			140	0.6555	0.2896	0.9451		0	°F	psi	1000	100
6/23/2017	21:17	Spinhirne	EVP71157440	KR-060617-02				120	0.5324	0.28	0.8124		0	°F	psi	1000	100
6/23/2017	21:12	Spinhirne	EVP71157440	KR-060617-02				100	0.4546	0.2703	0.7249		0	°F	psi	1000	100
6/23/2017	21:07	Spinhirne	EVP71157440	KR-060617-02				80	0.4057	0.2606	0.6663		0	°F	psi	1000	100
6/23/2017	21:01	Spinhirne	EVP71157440	KR-060617-02				60	0.358	0.2703	0.6283		0	°F	psi	1000	100
6/23/2017	20:42	Spinhirne	EVP71157440	KR-060617-02	#00022			140	0.6535	0.2939	0.9474		0	°F	psi	1000	100
6/23/2017	20:36	Spinhirne	EVP71157440	KR-060617-02				120	0.5317	0.2841	0.8158		0	°F	psi	1000	100
6/23/2017	20:30	Spinhirne	EVP71157440	KR-060617-02				100	0.4531	0.2743	0.7274		0	°F	psi	1000	100
6/23/2017	20:25	Spinhirne	EVP71157440	KR-060617-02				80	0.4057	0.2645	0.6702		0	°F	psi	1000	100
6/23/2017	20:19	Spinhirne	EVP71157440	KR-060617-02				60	0.3578	0.2743	0.6321		0	°F	psi	1000	100
6/23/2017	19:59	Spinhirne	EVP71157440	KR-060617-02	#00021			140	0.6526	0.2885	0.9412		0	°F	psi	1000	100
6/23/2017	19:54	Spinhirne	EVP71157440	KR-060617-02				120	0.5342	0.2789	0.8131		0	°F	psi	1000	100
6/23/2017	19:48	Spinhirne	EVP71157440	KR-060617-02				100	0.4513	0.2693	0.7205		0	°F	psi	1000	100
6/23/2017	19:42	Spinhirne	EVP71157440	KR-060617-02				80	0.4034	0.2597	0.6631		0	°F	psi	1000	100
6/23/2017	19:37	Spinhirne	EVP71157440	KR-060617-02				60	0.3503	0.2693	0.6196		0	°F	psi	1000	100
6/23/2017	19:17	Spinhirne	EVP71157440	KR-060617-02	#00020			140	0.6921	0.2489	0.941		0	°F	psi	1000	100
6/23/2017	19:12	Spinhirne	EVP71157440	KR-060617-02				120	0.5727	0.2406	0.8132		0	°F	psi	1000	100
6/23/2017	19:06	Spinhirne	EVP71157440	KR-060617-02				100	0.4883	0.2323	0.7205		0	°F	psi	1000	100
6/23/2017	19:01	Spinhirne	EVP71157440	KR-060617-02				80	0.4407	0.224	0.6647		0	°F	psi	1000	100
6/23/2017	18:55	Spinhirne	EVP71157440	KR-060617-02				60	0.3901	0.2323	0.6224		0	°F	psi	1000	100
6/23/2017	1:33	Spinhirne	EVP71157440	HY-053017-31	#00019			190	0.5476	0.2326	0.7802		0	°F	psi	1000	77
6/23/2017	1:27	Spinhirne	EVP71157440	HY-053017-31				160	0.4194	0.2218	0.6412		0	°F	psi	1000	77
6/23/2017	1:22	Spinhirne	EVP71157440	HY-053017-31				129.9999	0.3282	0.2111	0.5393		0	°F	psi	1000	77

Date	Time	Operator	SN	Sample ID	No.	Info	Comment	Tm	Pabs	Pgas	Ptot	Pabs Calculated	rate	[T]	[P]	Volume [ml]	T fill
6/23/2017	1:17	Spinhirne	EVP71157440	HY-053017-31				90	0.2486	0.1968	0.4454		0	°F	psi	1000	77
6/23/2017	1:11	Spinhirne	EVP71157440	HY-053017-31				50	0.178	0.2004	0.3784		0	°F	psi	1000	77
6/23/2017	0:45	Spinhirne	EVP71157440	HY-053017-31	#00018			190	0.5636	0.236	0.7996		0	°F	psi	1000	77
6/23/2017	0:40	Spinhirne	EVP71157440	HY-053017-31				160	0.433	0.2251	0.658		0	°F	psi	1000	77
6/23/2017	0:35	Spinhirne	EVP71157440	HY-053017-31				129.9999	0.3426	0.2142	0.5568		0	°F	psi	1000	77
6/23/2017	0:29	Spinhirne	EVP71157440	HY-053017-31				90	0.262	0.1997	0.4617		0	°F	psi	1000	77
6/23/2017	0:24	Spinhirne	EVP71157440	HY-053017-31				50	0.1915	0.2033	0.3948		0	°F	psi	1000	77
6/22/2017	23:57	Spinhirne	EVP71157440	HY-053017-31	#00017			190	0.5599	0.248	0.8079		0	°F	psi	1000	77
6/22/2017	23:52	Spinhirne	EVP71157440	HY-053017-31				160	0.4295	0.2365	0.666		0	°F	psi	1000	77
6/22/2017	23:47	Spinhirne	EVP71157440	HY-053017-31				129.9999	0.332	0.2251	0.5571		0	°F	psi	1000	77
6/22/2017	23:42	Spinhirne	EVP71157440	HY-053017-31				90	0.2575	0.2098	0.4673		0	°F	psi	1000	77
6/22/2017	23:36	Spinhirne	EVP71157440	HY-053017-31				50	0.183	0.2136	0.3967		0	°F	psi	1000	77
6/22/2017	23:05	Spinhirne	EVP71157440	HY-053017-31	#00016			190	0.5594	0.2627	0.8221		0	°F	psi	1000	77
6/22/2017	23:00	Spinhirne	EVP71157440	HY-053017-31				160	0.4279	0.2506	0.6785		0	°F	psi	1000	77
6/22/2017	22:54	Spinhirne	EVP71157440	HY-053017-31				129.9999	0.3319	0.2384	0.5703		0	°F	psi	1000	77
6/22/2017	22:49	Spinhirne	EVP71157440	HY-053017-31				90	0.2538	0.2223	0.476		0	°F	psi	1000	77
6/22/2017	22:44	Spinhirne	EVP71157440	HY-053017-31				50	0.1834	0.2263	0.4097		0	°F	psi	1000	77
6/22/2017	22:18	Spinhirne	EVP71157440	HY-053017-31	#00015			190	0.5618	0.2359	0.7977		0	°F	psi	1000	77
6/22/2017	22:12	Spinhirne	EVP71157440	HY-053017-31				160	0.4279	0.225	0.653		0	°F	psi	1000	77
6/22/2017	22:07	Spinhirne	EVP71157440	HY-053017-31				129.9999	0.3315	0.2141	0.5456		0	°F	psi	1000	77
6/22/2017	22:02	Spinhirne	EVP71157440	HY-053017-31				90	0.2542	0.1996	0.4538		0	°F	psi	1000	77
6/22/2017	21:56	Spinhirne	EVP71157440	HY-053017-31				50	0.1815	0.2033	0.3848		0	°F	psi	1000	77
6/22/2017	21:30	Spinhirne	EVP71157440	HY-053017-31	#00014			190	0.5699	0.2605	0.8303		0	°F	psi	1000	77
6/22/2017	21:25	Spinhirne	EVP71157440	HY-053017-31				160	0.429	0.2485	0.6775		0	°F	psi	1000	77
6/22/2017	21:20	Spinhirne	EVP71157440	HY-053017-31				129.9999	0.3323	0.2364	0.5687		0	°F	psi	1000	77
6/22/2017	21:15	Spinhirne	EVP71157440	HY-053017-31				90	0.2468	0.2204	0.4672		0	°F	psi	1000	77
6/22/2017	21:09	Spinhirne	EVP71157440	HY-053017-31				50	0.1731	0.2244	0.3975		0	°F	psi	1000	77
6/21/2017	22:27	Spinhirne	EVP71157440	HY-053017-02	#00013			190	0.5588	0.2525	0.8113		0	°F	psi	1000	77
6/21/2017	22:22	Spinhirne	EVP71157440	HY-053017-02				160	0.426	0.2409	0.6669		0	°F	psi	1000	77
6/21/2017	22:17	Spinhirne	EVP71157440	HY-053017-02				129.9999	0.3385	0.2292	0.5677		0	°F	psi	1000	77

Date	Time	Operator	SN	Sample ID	No.	Info	Comment	Tm	Pabs	Pgas	Ptot	Pabs Calculated	rate	[T]	[P]	Volume [ml]	T fill
6/21/2017	22:11	Spinhirne	EVP71157440	HY-053017-02				90	0.2607	0.2137	0.4744		0	°F	psi	1000	77
6/21/2017	22:06	Spinhirne	EVP71157440	HY-053017-02				50	0.1885	0.2176	0.4061		0	°F	psi	1000	77
6/21/2017	21:39	Spinhirne	EVP71157440	HY-053017-02	#00012			190	0.5652	0.2383	0.8035		0	°F	psi	1000	77
6/21/2017	21:34	Spinhirne	EVP71157440	HY-053017-02				160	0.4345	0.2273	0.6618		0	°F	psi	1000	77
6/21/2017	21:29	Spinhirne	EVP71157440	HY-053017-02				129.9999	0.3376	0.2163	0.5539		0	°F	psi	1000	77
6/21/2017	21:23	Spinhirne	EVP71157440	HY-053017-02				90	0.2604	0.2016	0.4621		0	°F	psi	1000	77
6/21/2017	21:18	Spinhirne	EVP71157440	HY-053017-02				50	0.1874	0.2053	0.3928		0	°F	psi	1000	77
6/21/2017	20:47	Spinhirne	EVP71157440	HY-053017-02	#00011			190	0.546	0.2543	0.8003		0	°F	psi	1000	77
6/21/2017	20:42	Spinhirne	EVP71157440	HY-053017-02				160	0.4136	0.2425	0.6562		0	°F	psi	1000	77
6/21/2017	20:37	Spinhirne	EVP71157440	HY-053017-02				129.9999	0.318	0.2308	0.5488		0	°F	psi	1000	77
6/21/2017	20:31	Spinhirne	EVP71157440	HY-053017-02				90	0.242	0.2151	0.4572		0	°F	psi	1000	77
6/21/2017	20:26	Spinhirne	EVP71157440	HY-053017-02				50	0.1727	0.2191	0.3917		0	°F	psi	1000	77
6/21/2017	20:00	Spinhirne	EVP71157440	HY-053017-02	#00010			190	0.5535	0.2291	0.7826		0	°F	psi	1000	77
6/21/2017	19:55	Spinhirne	EVP71157440	HY-053017-02				160	0.413	0.2185	0.6315		0	°F	psi	1000	77
6/21/2017	19:49	Spinhirne	EVP71157440	HY-053017-02				129.9999	0.3255	0.2079	0.5334		0	°F	psi	1000	77
6/21/2017	19:44	Spinhirne	EVP71157440	HY-053017-02				90	0.243	0.1938	0.4369		0	°F	psi	1000	77
6/21/2017	19:39	Spinhirne	EVP71157440	HY-053017-02				50	0.1706	0.1974	0.368		0	°F	psi	1000	77
6/21/2017	19:13	Spinhirne	EVP71157440	HY-053017-02	#00009			190	0.5432	0.2609	0.8041		0	°F	psi	1000	77
6/21/2017	19:08	Spinhirne	EVP71157440	HY-053017-02				160	0.4134	0.2489	0.6622		0	°F	psi	1000	77
6/21/2017	19:02	Spinhirne	EVP71157440	HY-053017-02				129.9999	0.3201	0.2368	0.5569		0	°F	psi	1000	77
6/21/2017	18:57	Spinhirne	EVP71157440	HY-053017-02				90	0.2416	0.2208	0.4624		0	°F	psi	1000	77
6/21/2017	18:52	Spinhirne	EVP71157440	HY-053017-02				50	0.1717	0.2248	0.3965		0	°F	psi	1000	77
6/21/2017	18:26	Spinhirne	EVP71157440	HY-053017-02	#00008			190	0.5869	0.2711	0.858		0	°F	psi	1000	77
6/21/2017	18:21	Spinhirne	EVP71157440	HY-053017-02				160	0.4337	0.2586	0.6923		0	°F	psi	1000	77
6/21/2017	18:16	Spinhirne	EVP71157440	HY-053017-02				129.9999	0.3257	0.2461	0.5717		0	°F	psi	1000	77
6/21/2017	18:10	Spinhirne	EVP71157440	HY-053017-02				90	0.2408	0.2294	0.4702		0	°F	psi	1000	77
6/21/2017	18:05	Spinhirne	EVP71157440	HY-053017-02				50	0.1702	0.2336	0.4038		0	°F	psi	1000	77
6/19/2017	22:26	Spinhirne	EVP71157440	HY-03-HY	#00007			190	0.6216	0.2475	0.8691		0	°F	psi	1000	77
6/19/2017	22:20	Spinhirne	EVP71157440	HY-03-HY				160	0.464	0.2361	0.7001		0	°F	psi	1000	77
6/19/2017	22:14	Spinhirne	EVP71157440	HY-03-HY				129.9999	0.3468	0.2246	0.5714		0	°F	psi	1000	77

Date	Time	Operator	SN	Sample ID	No.	Info	Comment	Tm	Pabs	Pgas	Ptot	Pabs Calculated	rate	[T]	[P]	Volume [ml]	T fill
6/19/2017	22:08	Spinhirne	EVP71157440	HY-03-HY				90	0.2579	0.2094	0.4673		0	°F	psi	1000	77
6/19/2017	22:03	Spinhirne	EVP71157440	HY-03-HY				50	0.178	0.2132	0.3912		0	°F	psi	1000	77
6/19/2017	21:36	Spinhirne	EVP71157440	HY-03-HY	#00006			190	0.6375	0.239	0.8765		0	°F	psi	1000	77
6/19/2017	21:30	Spinhirne	EVP71157440	HY-03-HY				160	0.4686	0.2279	0.6965		0	°F	psi	1000	77
6/19/2017	21:24	Spinhirne	EVP71157440	HY-03-HY				129.9999	0.3476	0.2169	0.5645		0	°F	psi	1000	77
6/19/2017	21:18	Spinhirne	EVP71157440	HY-03-HY				90	0.2606	0.2022	0.4628		0	°F	psi	1000	77
6/19/2017	21:12	Spinhirne	EVP71157440	HY-03-HY				50	0.1817	0.2059	0.3875		0	°F	psi	1000	77
6/19/2017	20:45	Spinhirne	EVP71157440	HY-03-HY	#00005			190	0.6587	0.2541	0.9129		0	°F	psi	1000	77
6/19/2017	20:39	Spinhirne	EVP71157440	HY-03-HY				160	0.4889	0.2424	0.7313		0	°F	psi	1000	77
6/19/2017	20:33	Spinhirne	EVP71157440	HY-03-HY				129.9999	0.367	0.2307	0.5977		0	°F	psi	1000	77
6/19/2017	20:27	Spinhirne	EVP71157440	HY-03-HY				90	0.2725	0.215	0.4875		0	°F	psi	1000	77
6/19/2017	20:22	Spinhirne	EVP71157440	HY-03-HY				50	0.1931	0.2189	0.4121		0	°F	psi	1000	77
6/19/2017	19:55	Spinhirne	EVP71157440	HY-03-HY	#00004			190	0.6725	0.2737	0.9462		0	°F	psi	1000	77
6/19/2017	19:49	Spinhirne	EVP71157440	HY-03-HY				160	0.4933	0.2611	0.7543		0	°F	psi	1000	77
6/19/2017	19:43	Spinhirne	EVP71157440	HY-03-HY				129.9999	0.3732	0.2484	0.6216		0	°F	psi	1000	77
6/19/2017	19:37	Spinhirne	EVP71157440	HY-03-HY				90	0.2763	0.2316	0.5079		0	°F	psi	1000	77
6/19/2017	19:31	Spinhirne	EVP71157440	HY-03-HY				50	0.1932	0.2358	0.429		0	°F	psi	1000	77
6/19/2017	19:05	Spinhirne	EVP71157440	HY-03-HY	#00003			190	0.7281	0.2929	1.0211		0	°F	psi	1000	77
6/19/2017	18:59	Spinhirne	EVP71157440	HY-03-HY				160	0.5199	0.2794	0.7993		0	°F	psi	1000	77
6/19/2017	18:53	Spinhirne	EVP71157440	HY-03-HY				129.9999	0.3723	0.2659	0.6382		0	°F	psi	1000	77
6/19/2017	18:46	Spinhirne	EVP71157440	HY-03-HY				90	0.2665	0.2478	0.5143		0	°F	psi	1000	77
6/19/2017	18:40	Spinhirne	EVP71157440	HY-03-HY				50	0.1833	0.2524	0.4357		0	°F	psi	1000	77
6/15/2017	21:26	Spinhirne	EVP71157440	HY-02-HY	#00002			190	0.8035	0.282	1.0855		0	°F	psi	1000	68
6/15/2017	21:21	Spinhirne	EVP71157440	HY-02-HY				160	0.5788	0.269	0.8477		0	°F	psi	1000	68
6/15/2017	21:16	Spinhirne	EVP71157440	HY-02-HY				129.9999	0.4186	0.2559	0.6746		0	°F	psi	1000	68
6/15/2017	21:11	Spinhirne	EVP71157440	HY-02-HY				90	0.3014	0.2386	0.54		0	°F	psi	1000	68
6/15/2017	21:05	Spinhirne	EVP71157440	HY-02-HY				50	0.2189	0.2429	0.4618		0	°F	psi	1000	68

Table 11. Raw results from Low VP Curve analysis of “known” recipe, hydraulic fluid, and fuel oil no. 6 samples.

Date	Time	Operator	SN	Sample ID	No.	Info	Comment	Tm	Pabs	Pgas	Ptot	Pabs Calculated	rate	[T]	[P]	Volume [ml]	T fill
6/26/2017	20:41	Spinhirne	EVP71157440	KR-060617-31	#00005			140	0.4228	0.5768	0.9996		0	°F	psi	1000	100
6/26/2017	20:36	Spinhirne	EVP71157440	KR-060617-31				120	0.3054	0.5576	0.863		0	°F	psi	1000	100
6/26/2017	20:31	Spinhirne	EVP71157440	KR-060617-31				104	0.2439	0.5422	0.7861		0	°F	psi	1000	100
6/26/2017	20:26	Spinhirne	EVP71157440	KR-060617-31				80.0001	0.2019	0.5191	0.721		0	°F	psi	1000	100
6/26/2017	20:21	Spinhirne	EVP71157440	KR-060617-31				60.0001	0.1633	0.5384	0.7017		0	°F	psi	1000	100
6/26/2017	20:02	Spinhirne	EVP71157440	KR-060617-31	#00004			140	0.4175	0.5636	0.9812		0	°F	psi	1000	100
6/26/2017	19:57	Spinhirne	EVP71157440	KR-060617-31				120	0.2978	0.5448	0.8427		0	°F	psi	1000	100
6/26/2017	19:52	Spinhirne	EVP71157440	KR-060617-31				104	0.2356	0.5298	0.7654		0	°F	psi	1000	100
6/26/2017	19:47	Spinhirne	EVP71157440	KR-060617-31				80.0001	0.1939	0.5072	0.7011		0	°F	psi	1000	100
6/26/2017	19:42	Spinhirne	EVP71157440	KR-060617-31				60.0001	0.161	0.5261	0.687		0	°F	psi	1000	100
6/26/2017	19:23	Spinhirne	EVP71157440	KR-060617-31	#00003			140	0.4214	0.5712	0.9926		0	°F	psi	1000	100
6/26/2017	19:18	Spinhirne	EVP71157440	KR-060617-31				120	0.3016	0.5522	0.8538		0	°F	psi	1000	100
6/26/2017	19:13	Spinhirne	EVP71157440	KR-060617-31				104	0.2428	0.537	0.7797		0	°F	psi	1000	100
6/26/2017	19:08	Spinhirne	EVP71157440	KR-060617-31				80.0001	0.1986	0.5141	0.7127		0	°F	psi	1000	100
6/26/2017	19:03	Spinhirne	EVP71157440	KR-060617-31				60.0001	0.162	0.5332	0.6952		0	°F	psi	1000	100
6/26/2017	18:43	Spinhirne	EVP71157440	KR-060617-31	#00002			140	0.4191	0.5559	0.9749		0	°F	psi	1000	100
6/26/2017	18:38	Spinhirne	EVP71157440	KR-060617-31				120	0.3084	0.5373	0.8457		0	°F	psi	1000	100
6/26/2017	18:33	Spinhirne	EVP71157440	KR-060617-31				104	0.2406	0.5225	0.763		0	°F	psi	1000	100
6/26/2017	18:28	Spinhirne	EVP71157440	KR-060617-31				80.0001	0.2014	0.5002	0.7017		0	°F	psi	1000	100
6/26/2017	18:23	Spinhirne	EVP71157440	KR-060617-31				60.0001	0.1602	0.5188	0.6791		0	°F	psi	1000	100
6/26/2017	18:01	Spinhirne	EVP71157440	KR-060617-31	#00001			140	0.432	0.5659	0.9979		0	°F	psi	1000	100
6/26/2017	17:56	Spinhirne	EVP71157440	KR-060617-31				120	0.3125	0.547	0.8595		0	°F	psi	1000	100
6/26/2017	17:51	Spinhirne	EVP71157440	KR-060617-31				104	0.2474	0.5319	0.7793		0	°F	psi	1000	100
6/26/2017	17:46	Spinhirne	EVP71157440	KR-060617-31				80.0001	0.2045	0.5093	0.7137		0	°F	psi	1000	100
6/26/2017	17:41	Spinhirne	EVP71157440	KR-060617-31				60.0001	0.1709	0.5282	0.6991		0	°F	psi	1000	100
7/27/2017	22:02	Spinhirne	EVP71157440	MB-061717-34	#00063			140	1.8995	0.5323	2.4319				°F	psi	140
7/27/2017	21:56	Spinhirne	EVP71157440	MB-061717-34				120	0.8653	0.5146	1.3799				°F	psi	140
7/27/2017	21:50	Spinhirne	EVP71157440	MB-061717-34				104	0.4809	0.5004	0.9813				°F	psi	140

Date	Time	Operator	SN	Sample ID	No.	Info	Comment	Tm	Pabs	Pgas	Ptot	Pabs Calculated	rate	[T]	[P]	Volume [ml]	T fill
7/27/2017	21:45	Spinhirne	EVP71157440	MB-061717-34	#00062			80.0001	0.1201	0.4791	0.5992					°F psi	140
7/27/2017	21:39	Spinhirne	EVP71157440	MB-061717-34				60.0001	-0.1314	0.4969	0.3655					°F psi	140
7/27/2017	21:17	Spinhirne	EVP71157440	MB-061717-34				140	1.832	0.5712	2.4031					°F psi	140
7/27/2017	21:11	Spinhirne	EVP71157440	MB-061717-34				120	0.7976	0.5521	1.3497					°F psi	140
7/27/2017	21:05	Spinhirne	EVP71157440	MB-061717-34				104	0.4215	0.5369	0.9584					°F psi	140
7/27/2017	21:00	Spinhirne	EVP71157440	MB-061717-34	#00061			80.0001	0.0795	0.514	0.5935					°F psi	140
7/27/2017	20:54	Spinhirne	EVP71157440	MB-061717-34				60.0001	-0.175	0.5331	0.3581					°F psi	140
7/27/2017	20:32	Spinhirne	EVP71157440	MB-061717-34				140	1.4378	0.8963	2.3341					°F psi	140
7/27/2017	20:26	Spinhirne	EVP71157440	MB-061717-34				120	0.4717	0.8664	1.3381					°F psi	140
7/27/2017	20:21	Spinhirne	EVP71157440	MB-061717-34				104	0.0946	0.8425	0.9371					°F psi	140
7/27/2017	20:15	Spinhirne	EVP71157440	MB-061717-34	#00060			80.0001	-0.2248	0.8066	0.5817					°F psi	140
7/27/2017	20:10	Spinhirne	EVP71157440	MB-061717-34				60.0001	-0.4914	0.8365	0.3452					°F psi	140
7/27/2017	19:48	Spinhirne	EVP71157440	MB-061717-34				140	1.9666	0.5355	2.5021					°F psi	140
7/27/2017	19:42	Spinhirne	EVP71157440	MB-061717-34				120	0.8716	0.5176	1.3892					°F psi	140
7/27/2017	19:37	Spinhirne	EVP71157440	MB-061717-34				104	0.503	0.5033	1.0063					°F psi	140
7/27/2017	19:31	Spinhirne	EVP71157440	MB-061717-34	#00059			80.0001	0.1205	0.4819	0.6023					°F psi	140
7/27/2017	19:26	Spinhirne	EVP71157440	MB-061717-34				60.0001	-0.1363	0.4998	0.3635					°F psi	140
7/27/2017	19:03	Spinhirne	EVP71157440	MB-061717-34				140	2.1023	0.4279	2.5302					°F psi	140
7/27/2017	18:58	Spinhirne	EVP71157440	MB-061717-34				120	1.1403	0.4136	1.5539					°F psi	140
7/27/2017	18:52	Spinhirne	EVP71157440	MB-061717-34				104	0.6889	0.4022	1.0911					°F psi	140
7/27/2017	18:47	Spinhirne	EVP71157440	MB-061717-34	#00058			80.0001	0.2501	0.3851	0.6351					°F psi	140
7/27/2017	18:41	Spinhirne	EVP71157440	MB-061717-34				60.0001	-0.0166	0.3994	0.3828					°F psi	140
7/27/2017	18:20	Spinhirne	EVP71157440	MB-061717-34				140	2.6371	0.1579	2.795					°F psi	140
7/27/2017	18:13	Spinhirne	EVP71157440	MB-061717-34				120	1.5637	0.1527	1.7164					°F psi	140
7/27/2017	18:08	Spinhirne	EVP71157440	MB-061717-34				104	1.0954	0.1484	1.2438					°F psi	140
7/27/2017	18:02	Spinhirne	EVP71157440	MB-061717-34	#00057			80.0001	0.5877	0.1421	0.7298					°F psi	140
7/27/2017	17:57	Spinhirne	EVP71157440	MB-061717-34				60.0001	0.3241	0.1474	0.4715					°F psi	140
7/26/2017	21:00	Spinhirne	EVP71157440	BT-062017-33				140	2.1538	0.606	2.7598					°F psi	140
7/26/2017	20:53	Spinhirne	EVP71157440	BT-062017-33				120	0.9831	0.5858	1.5689					°F psi	140
7/26/2017	20:48	Spinhirne	EVP71157440	BT-062017-33				104	0.5218	0.5696	1.0914					°F psi	140

Date	Time	Operator	SN	Sample ID	No.	Info	Comment	Tm	Pabs	Pgas	Ptot	Pabs Calculated	rate	[T]	[P]	Volume [ml]	T fill
7/26/2017	20:42	Spinhirne	EVP71157440	BT-062017-33	#00056			80.0001	0.0601	0.5453	0.6054					°F psi	140
7/26/2017	20:37	Spinhirne	EVP71157440	BT-062017-33				60.0001	-0.2033	0.5656	0.3623					°F psi	140
7/26/2017	20:15	Spinhirne	EVP71157440	BT-062017-33				140	2.27	0.4199	2.6899					°F psi	140
7/26/2017	20:09	Spinhirne	EVP71157440	BT-062017-33				120	1.1237	0.4059	1.5296					°F psi	140
7/26/2017	20:03	Spinhirne	EVP71157440	BT-062017-33				104	0.6494	0.3947	1.0441					°F psi	140
7/26/2017	19:58	Spinhirne	EVP71157440	BT-062017-33	#00055			80.0001	0.235	0.3779	0.6129					°F psi	140
7/26/2017	19:52	Spinhirne	EVP71157440	BT-062017-33				60.0001	-0.0211	0.3919	0.3709					°F psi	140
7/26/2017	19:30	Spinhirne	EVP71157440	BT-062017-33				140	2.4726	0.2829	2.7556					°F psi	140
7/26/2017	19:25	Spinhirne	EVP71157440	BT-062017-33				120	1.369	0.2735	1.6426					°F psi	140
7/26/2017	19:19	Spinhirne	EVP71157440	BT-062017-33				104	0.8811	0.266	1.1471					°F psi	140
7/26/2017	19:13	Spinhirne	EVP71157440	BT-062017-33	#00054			80.0001	0.3715	0.2546	0.6261					°F psi	140
7/26/2017	19:08	Spinhirne	EVP71157440	BT-062017-33				60.0001	0.1172	0.2641	0.3813					°F psi	140
7/26/2017	18:46	Spinhirne	EVP71157440	BT-062017-33				140	2.5142	0.2804	2.7946					°F psi	140
7/26/2017	18:40	Spinhirne	EVP71157440	BT-062017-33				120	1.3576	0.271	1.6286					°F psi	140
7/26/2017	18:34	Spinhirne	EVP71157440	BT-062017-33				104	0.8924	0.2636	1.156					°F psi	140
7/26/2017	18:29	Spinhirne	EVP71157440	BT-062017-33	#00053			80.0001	0.3771	0.2523	0.6295					°F psi	140
7/26/2017	18:23	Spinhirne	EVP71157440	BT-062017-33				60.0001	0.1181	0.2617	0.3799					°F psi	140
7/26/2017	18:01	Spinhirne	EVP71157440	BT-062017-33				140	2.3169	0.4548	2.7717					°F psi	140
7/26/2017	17:56	Spinhirne	EVP71157440	BT-062017-33				120	1.2229	0.4396	1.6626					°F psi	140
7/26/2017	17:50	Spinhirne	EVP71157440	BT-062017-33				104	0.7503	0.4275	1.1779					°F psi	140
7/26/2017	17:44	Spinhirne	EVP71157440	BT-062017-33	#00052			80.0001	0.2287	0.4093	0.638					°F psi	140
7/26/2017	17:39	Spinhirne	EVP71157440	BT-062017-33				60.0001	-0.0529	0.4245	0.3716					°F psi	140
7/26/2017	17:17	Spinhirne	EVP71157440	BT-062017-33				140	2.7806	0.1528	2.9334					°F psi	140
7/26/2017	17:11	Spinhirne	EVP71157440	BT-062017-33				120	1.6639	0.1477	1.8117					°F psi	140
7/26/2017	17:05	Spinhirne	EVP71157440	BT-062017-33				104	1.1356	0.1437	1.2792					°F psi	140
7/26/2017	17:00	Spinhirne	EVP71157440	BT-062017-33	#00051			80.0001	0.5618	0.1375	0.6994					°F psi	140
7/26/2017	16:57	Spinhirne	EVP71157440	BT-062017-33				60.0001	0.3303	0.1426	0.473					°F psi	140
7/26/2017	0:12	Spinhirne	EVP71157440	BT-062017-01				140	2.762	0.2589	3.0209					°F psi	140
7/26/2017	0:06	Spinhirne	EVP71157440	BT-062017-01				120	1.5522	0.2502	1.8024					°F psi	140
7/26/2017	0:01	Spinhirne	EVP71157440	BT-062017-01				104	0.9464	0.2433	1.1897					°F psi	140

Date	Time	Operator	SN	Sample ID	No.	Info	Comment	Tm	Pabs	Pgas	Ptot	Pabs Calculated	rate	[T]	[P]	Volume [ml]	T fill
7/26/2017	0:12	Spinhirne	EVP71157440	BT-062017-01	#00051			140	2.762	0.2589	3.0209					°F psi	140
7/26/2017	0:06	Spinhirne	EVP71157440	BT-062017-01				120	1.5522	0.2502	1.8024					°F psi	140
7/26/2017	0:01	Spinhirne	EVP71157440	BT-062017-01				104	0.9464	0.2433	1.1897					°F psi	140
7/25/2017	23:55	Spinhirne	EVP71157440	BT-062017-01				80.0001	0.4059	0.233	0.6389					°F psi	140
7/25/2017	23:50	Spinhirne	EVP71157440	BT-062017-01				60.0001	0.1394	0.2416	0.381					°F psi	140
7/25/2017	23:28	Spinhirne	EVP71157440	BT-062017-01	#00050			140	2.8121	0.1991	3.0113					°F psi	140
7/25/2017	23:22	Spinhirne	EVP71157440	BT-062017-01				120	1.6096	0.1925	1.8021					°F psi	140
7/25/2017	23:17	Spinhirne	EVP71157440	BT-062017-01				104	1.034	0.1872	1.2212					°F psi	140
7/25/2017	23:11	Spinhirne	EVP71157440	BT-062017-01				80.0001	0.4797	0.1792	0.6589					°F psi	140
7/25/2017	23:05	Spinhirne	EVP71157440	BT-062017-01				60.0001	0.207	0.1859	0.3929					°F psi	140
7/25/2017	22:44	Spinhirne	EVP71157440	BT-062017-01	#00049			140	2.8038	0.2406	3.0443					°F psi	140
7/25/2017	22:38	Spinhirne	EVP71157440	BT-062017-01				120	1.6183	0.2326	1.8508					°F psi	140
7/25/2017	22:32	Spinhirne	EVP71157440	BT-062017-01				104	1.0115	0.2261	1.2376					°F psi	140
7/25/2017	22:27	Spinhirne	EVP71157440	BT-062017-01				80.0001	0.4544	0.2165	0.6709					°F psi	140
7/25/2017	22:22	Spinhirne	EVP71157440	BT-062017-01				60.0001	0.171	0.2245	0.3955					°F psi	140
7/25/2017	22:00	Spinhirne	EVP71157440	BT-062017-01	#00048			140	2.8715	0.1811	3.0526					°F psi	140
7/25/2017	21:54	Spinhirne	EVP71157440	BT-062017-01				120	1.659	0.175	1.834					°F psi	140
7/25/2017	21:48	Spinhirne	EVP71157440	BT-062017-01				104	1.0763	0.1702	1.2465					°F psi	140
7/25/2017	21:43	Spinhirne	EVP71157440	BT-062017-01				80.0001	0.5147	0.1629	0.6776					°F psi	140
7/25/2017	21:37	Spinhirne	EVP71157440	BT-062017-01				60.0001	0.2467	0.169	0.4157					°F psi	140
7/25/2017	21:16	Spinhirne	EVP71157440	BT-062017-01	#00047			140	2.8471	0.2214	3.0686					°F psi	140
7/25/2017	21:10	Spinhirne	EVP71157440	BT-062017-01				120	1.6198	0.214	1.8339					°F psi	140
7/25/2017	21:04	Spinhirne	EVP71157440	BT-062017-01				104	0.9908	0.2081	1.1989					°F psi	140
7/25/2017	20:59	Spinhirne	EVP71157440	BT-062017-01				80.0001	0.4737	0.1993	0.673					°F psi	140
7/25/2017	20:53	Spinhirne	EVP71157440	BT-062017-01				60.0001	0.2176	0.2067	0.4242					°F psi	140
7/24/2017	22:04	Spinhirne	EVP71157440	MB-061717-01	#00046			140	1.2669	0.1181	1.385					°F psi	140
7/24/2017	21:58	Spinhirne	EVP71157440	MB-061717-01				120	0.8091	0.1142	0.9233					°F psi	140
7/24/2017	21:53	Spinhirne	EVP71157440	MB-061717-01				104	0.5499	0.111	0.6609					°F psi	140
7/24/2017	21:47	Spinhirne	EVP71157440	MB-061717-01				80.0001	0.34	0.1063	0.4463					°F psi	140
7/24/2017	21:42	Spinhirne	EVP71157440	MB-061717-01				60.0001	0.2634	0.1102	0.3736					°F psi	140

Date	Time	Operator	SN	Sample ID	No.	Info	Comment	Tm	Pabs	Pgas	Ptot	Pabs Calculated	rate	[T]	[P]	Volume [ml]	T fill
7/24/2017	21:15	Spinhirne	EVP71157440	MB-061717-01	#00045			140	1.3248	0.1272	1.452					°F psi	140
7/24/2017	21:10	Spinhirne	EVP71157440	MB-061717-01				120	0.8862	0.123	1.0092					°F psi	140
7/24/2017	21:04	Spinhirne	EVP71157440	MB-061717-01				104	0.596	0.1196	0.7156					°F psi	140
7/24/2017	20:58	Spinhirne	EVP71157440	MB-061717-01				80.0001	0.3434	0.1145	0.4579					°F psi	140
7/24/2017	20:53	Spinhirne	EVP71157440	MB-061717-01				60.0001	0.265	0.1187	0.3838					°F psi	140
7/24/2017	20:04	Spinhirne	EVP71157440	MB-061717-01	#00044			140	1.5076	0.1931	1.7007					°F psi	140
7/24/2017	19:58	Spinhirne	EVP71157440	MB-061717-01				120	1.0068	0.1867	1.1935					°F psi	140
7/24/2017	19:53	Spinhirne	EVP71157440	MB-061717-01				104	0.6875	0.1815	0.8691					°F psi	140
7/24/2017	19:47	Spinhirne	EVP71157440	MB-061717-01				80.0001	0.4031	0.1738	0.577					°F psi	140
7/24/2017	19:42	Spinhirne	EVP71157440	MB-061717-01				60.0001	0.2855	0.1803	0.4657					°F psi	140
7/21/2017	21:47	Spinhirne	EVP71157440	MM-060817-37	#00043			140	0.9831	0.0923	1.0755					°F psi	140
7/21/2017	21:41	Spinhirne	EVP71157440	MM-060817-37				120	0.7019	0.0892	0.7912					°F psi	140
7/21/2017	21:36	Spinhirne	EVP71157440	MM-060817-37				104	0.5383	0.0868	0.6251					°F psi	140
7/21/2017	21:31	Spinhirne	EVP71157440	MM-060817-37				80.0001	0.3647	0.0831	0.4477					°F psi	140
7/21/2017	21:25	Spinhirne	EVP71157440	MM-060817-37				60.0001	0.2743	0.0862	0.3604					°F psi	140
7/21/2017	21:03	Spinhirne	EVP71157440	MM-060817-37	#00042			140	0.983	0.1129	1.0959					°F psi	140
7/21/2017	20:58	Spinhirne	EVP71157440	MM-060817-37				120	0.7031	0.1091	0.8122					°F psi	140
7/21/2017	20:52	Spinhirne	EVP71157440	MM-060817-37				104	0.5385	0.1061	0.6445					°F psi	140
7/21/2017	20:47	Spinhirne	EVP71157440	MM-060817-37				80.0001	0.3399	0.1016	0.4415					°F psi	140
7/21/2017	20:41	Spinhirne	EVP71157440	MM-060817-37				60.0001	0.252	0.1053	0.3574					°F psi	140
7/21/2017	20:19	Spinhirne	EVP71157440	MM-060817-37	#00041			140	1.0189	0.0924	1.1113					°F psi	140
7/21/2017	20:14	Spinhirne	EVP71157440	MM-060817-37				120	0.7342	0.0893	0.8235					°F psi	140
7/21/2017	20:08	Spinhirne	EVP71157440	MM-060817-37				104	0.566	0.0868	0.6528					°F psi	140
7/21/2017	20:03	Spinhirne	EVP71157440	MM-060817-37				80.0001	0.3752	0.0831	0.4583					°F psi	140
7/21/2017	19:58	Spinhirne	EVP71157440	MM-060817-37				60.0001	0.2814	0.0862	0.3677					°F psi	140
7/21/2017	19:35	Spinhirne	EVP71157440	MM-060817-37	#00040			140	1.0391	0.1026	1.1417					°F psi	140
7/21/2017	19:30	Spinhirne	EVP71157440	MM-060817-37				120	0.7387	0.0992	0.8379					°F psi	140
7/21/2017	19:24	Spinhirne	EVP71157440	MM-060817-37				104	0.5631	0.0964	0.6595					°F psi	140
7/21/2017	19:19	Spinhirne	EVP71157440	MM-060817-37				80.0001	0.3686	0.0923	0.4609					°F psi	140
7/21/2017	19:13	Spinhirne	EVP71157440	MM-060817-37				60.0001	0.2757	0.0958	0.3714					°F psi	140

Date	Time	Operator	SN	Sample ID	No.	Info	Comment	Tm	Pabs	Pgas	Ptot	Pabs Calculated	rate	[T]	[P]	Volume [ml]	T fill
7/21/2017	18:52	Spinhirne	EVP71157440	MM-060817-37	#00039			140	1.0586	0.1786	1.2372					°F psi	140
7/21/2017	18:46	Spinhirne	EVP71157440	MM-060817-37				120	0.7583	0.1727	0.931					°F psi	140
7/21/2017	18:40	Spinhirne	EVP71157440	MM-060817-37				104	0.5717	0.1679	0.7395					°F psi	140
7/21/2017	18:35	Spinhirne	EVP71157440	MM-060817-37				80.0001	0.3479	0.1607	0.5086					°F psi	140
7/21/2017	18:32	Spinhirne	EVP71157440	MM-060817-37				60.0001	0.2529	0.1667	0.4196					°F psi	140
7/19/2017	21:58	Spinhirne	EVP71157440	MM-060817-02	#00038			140	0.7658	1.1826	1.9484					°F psi	140
7/19/2017	21:52	Spinhirne	EVP71157440	MM-060817-02				120	0.5004	1.1432	1.6436					°F psi	140
7/19/2017	21:46	Spinhirne	EVP71157440	MM-060817-02				104	0.3777	1.1116	1.4893					°F psi	140
7/19/2017	21:40	Spinhirne	EVP71157440	MM-060817-02				80.0001	0.2502	1.0643	1.3145					°F psi	140
7/19/2017	21:35	Spinhirne	EVP71157440	MM-060817-02				60.0001	0.1026	1.1038	1.2064					°F psi	140
7/19/2017	21:13	Spinhirne	EVP71157440	MM-060817-02	#00037			140	1.1447	0.1183	1.263					°F psi	140
7/19/2017	21:07	Spinhirne	EVP71157440	MM-060817-02				120	0.8126	0.1143	0.9269					°F psi	140
7/19/2017	21:02	Spinhirne	EVP71157440	MM-060817-02				104	0.6084	0.1112	0.7195					°F psi	140
7/19/2017	20:56	Spinhirne	EVP71157440	MM-060817-02				80.0001	0.3844	0.1064	0.4908					°F psi	140
7/19/2017	20:51	Spinhirne	EVP71157440	MM-060817-02				60.0001	0.2802	0.1104	0.3906					°F psi	140
7/19/2017	20:29	Spinhirne	EVP71157440	MM-060817-02	#00036			140	1.1416	0.0834	1.225					°F psi	140
7/19/2017	20:23	Spinhirne	EVP71157440	MM-060817-02				120	0.8324	0.0806	0.913					°F psi	140
7/19/2017	20:17	Spinhirne	EVP71157440	MM-060817-02				104	0.6224	0.0784	0.7008					°F psi	140
7/19/2017	20:12	Spinhirne	EVP71157440	MM-060817-02				80.0001	0.4018	0.0751	0.4769					°F psi	140
7/19/2017	20:06	Spinhirne	EVP71157440	MM-060817-02				60.0001	0.29	0.0778	0.3678					°F psi	140
7/19/2017	19:44	Spinhirne	EVP71157440	MM-060817-02	#00035			140	1.1151	0.0881	1.2032					°F psi	140
7/19/2017	19:38	Spinhirne	EVP71157440	MM-060817-02				120	0.8241	0.0852	0.9092					°F psi	140
7/19/2017	19:33	Spinhirne	EVP71157440	MM-060817-02				104	0.6272	0.0828	0.71					°F psi	140
7/19/2017	19:27	Spinhirne	EVP71157440	MM-060817-02				80.0001	0.3921	0.0793	0.4714					°F psi	140
7/19/2017	19:22	Spinhirne	EVP71157440	MM-060817-02				60.0001	0.281	0.0822	0.3632					°F psi	140
7/19/2017	19:00	Spinhirne	EVP71157440	MM-060817-02	#00034			140	1.1437	0.1004	1.2441					°F psi	140
7/19/2017	18:53	Spinhirne	EVP71157440	MM-060817-02				120	0.829	0.097	0.9261					°F psi	140
7/19/2017	18:48	Spinhirne	EVP71157440	MM-060817-02				104	0.634	0.0944	0.7284					°F psi	140
7/19/2017	18:42	Spinhirne	EVP71157440	MM-060817-02				80.0001	0.3996	0.0903	0.4899					°F psi	140
7/19/2017	18:37	Spinhirne	EVP71157440	MM-060817-02				60.0001	0.2841	0.0937	0.3778					°F psi	140

Date	Time	Operator	SN	Sample ID	No.	Info	Comment	Tm	Pabs	Pgas	Ptot	Pabs Calculated	rate	[T]	[P]	Volume [ml]	T fill
7/19/2017	18:15	Spinhirne	EVP71157440	MM-060817-02	#00033			140	1.1776	0.0954	1.273					°F psi	140
7/19/2017	18:09	Spinhirne	EVP71157440	MM-060817-02				120	0.8197	0.0922	0.9119					°F psi	140
7/19/2017	18:06	Spinhirne	EVP71157440	MM-060817-02				104	0.6502	0.0896	0.7398					°F psi	140
7/19/2017	18:01	Spinhirne	EVP71157440	MM-060817-02				80.0001	0.3986	0.0858	0.4844					°F psi	140
7/19/2017	17:58	Spinhirne	EVP71157440	MM-060817-02				60.0001	0.2991	0.089	0.3881					°F psi	140
7/19/2017	17:36	Spinhirne	EVP71157440	MM-060817-02	#00032			140	1.214	0.1156	1.3296					°F psi	140
7/19/2017	17:30	Spinhirne	EVP71157440	MM-060817-02				120	0.8891	0.1117	1.0008					°F psi	140
7/19/2017	17:24	Spinhirne	EVP71157440	MM-060817-02				104	0.6769	0.1086	0.7855					°F psi	140
7/19/2017	17:19	Spinhirne	EVP71157440	MM-060817-02				80.0001	0.42	0.104	0.524					°F psi	140
7/19/2017	17:14	Spinhirne	EVP71157440	MM-060817-02				60.0001	0.293	0.1079	0.4009					°F psi	140
7/19/2017	16:52	Spinhirne	EVP71157440	MM-060817-02	#00031			140	1.1181	0.2024	1.3204					°F psi	140
7/19/2017	16:46	Spinhirne	EVP71157440	MM-060817-02				120	0.8091	0.1956	1.0047					°F psi	140
7/19/2017	16:41	Spinhirne	EVP71157440	MM-060817-02				104	0.6101	0.1902	0.8003					°F psi	140
7/19/2017	16:35	Spinhirne	EVP71157440	MM-060817-02				80.0001	0.3773	0.1821	0.5594					°F psi	140
7/19/2017	16:30	Spinhirne	EVP71157440	MM-060817-02				60.0001	0.2533	0.1889	0.4422					°F psi	140
7/18/2017	23:46	Spinhirne	EVP71157440	MM-060817-01	#00030			140	0.9881	0.4621	1.4502					°F psi	140
7/18/2017	23:39	Spinhirne	EVP71157440	MM-060817-01				120	0.6389	0.4467	1.0856					°F psi	140
7/18/2017	23:34	Spinhirne	EVP71157440	MM-060817-01				104	0.4183	0.4344	0.8527					°F psi	140
7/18/2017	23:28	Spinhirne	EVP71157440	MM-060817-01				80.0001	0.2641	0.4159	0.6799					°F psi	140
7/18/2017	23:23	Spinhirne	EVP71157440	MM-060817-01				60.0001	0.1675	0.4313	0.5989					°F psi	140
7/18/2017	23:01	Spinhirne	EVP71157440	MM-060817-01	#00029			140	1.2224	0.1638	1.3863					°F psi	140
7/18/2017	22:55	Spinhirne	EVP71157440	MM-060817-01				120	0.8878	0.1584	1.0462					°F psi	140
7/18/2017	22:50	Spinhirne	EVP71157440	MM-060817-01				104	0.6684	0.154	0.8224					°F psi	140
7/18/2017	22:44	Spinhirne	EVP71157440	MM-060817-01				80.0001	0.4244	0.1474	0.5719					°F psi	140
7/18/2017	22:39	Spinhirne	EVP71157440	MM-060817-01				60.0001	0.2934	0.1529	0.4463					°F psi	140
7/12/2017	22:56	Spinhirne	EVP71157440	HY-053017-30	#00023			140	0.2654	0.5154	0.7807					°F psi	77
7/12/2017	22:51	Spinhirne	EVP71157440	HY-053017-30				120	0.2257	0.4982	0.7239					°F psi	77
7/12/2017	22:46	Spinhirne	EVP71157440	HY-053017-30				104	0.2051	0.4844	0.6895					°F psi	77
7/12/2017	22:41	Spinhirne	EVP71157440	HY-053017-30				80.0001	0.1646	0.4638	0.6284					°F psi	77
7/12/2017	22:36	Spinhirne	EVP71157440	HY-053017-30				60.0001	0.1043	0.481	0.5854					°F psi	77

Date	Time	Operator	SN	Sample ID	No.	Info	Comment	Tm	Pabs	Pgas	Ptot	Pabs Calculated	rate	[T]	[P]	Volume [ml]	T fill
7/12/2017	21:58	Spinhirne	EVP71157440	HY-053017-30	#00022			140	0.2585	0.5038	0.7623					°F psi	77
7/12/2017	21:53	Spinhirne	EVP71157440	HY-053017-30				120	0.2238	0.487	0.7108					°F psi	77
7/12/2017	21:48	Spinhirne	EVP71157440	HY-053017-30				104	0.2007	0.4736	0.6743					°F psi	77
7/12/2017	21:43	Spinhirne	EVP71157440	HY-053017-30				80.0001	0.1625	0.4534	0.616					°F psi	77
7/12/2017	21:38	Spinhirne	EVP71157440	HY-053017-30				60.0001	0.1068	0.4703	0.5771					°F psi	77
7/12/2017	21:16	Spinhirne	EVP71157440	HY-053017-30	#00021			140	0.27	0.5097	0.7797					°F psi	77
7/12/2017	21:11	Spinhirne	EVP71157440	HY-053017-30				120	0.2271	0.4927	0.7198					°F psi	77
7/12/2017	21:06	Spinhirne	EVP71157440	HY-053017-30				104	0.204	0.4791	0.6831					°F psi	77
7/12/2017	21:01	Spinhirne	EVP71157440	HY-053017-30				80.0001	0.1673	0.4587	0.626					°F psi	77
7/12/2017	20:56	Spinhirne	EVP71157440	HY-053017-30				60.0001	0.1064	0.4758	0.5822					°F psi	77
7/12/2017	19:55	Spinhirne	EVP71157440	HY-053017-30	#00020			140	0.2649	0.501	0.7659					°F psi	77
7/12/2017	19:50	Spinhirne	EVP71157440	HY-053017-30				120	0.2232	0.4843	0.7075					°F psi	77
7/12/2017	19:46	Spinhirne	EVP71157440	HY-053017-30				104	0.2049	0.471	0.6759					°F psi	77
7/12/2017	19:40	Spinhirne	EVP71157440	HY-053017-30				80.0001	0.1649	0.4509	0.6158					°F psi	77
7/12/2017	19:35	Spinhirne	EVP71157440	HY-053017-30				60.0001	0.1054	0.4677	0.573					°F psi	77
7/12/2017	19:13	Spinhirne	EVP71157440	HY-053017-30	#00019			140	0.2677	0.5208	0.7884					°F psi	77
7/12/2017	19:08	Spinhirne	EVP71157440	HY-053017-30				120	0.228	0.5034	0.7314					°F psi	77
7/12/2017	19:03	Spinhirne	EVP71157440	HY-053017-30				104	0.2038	0.4895	0.6933					°F psi	77
7/12/2017	18:58	Spinhirne	EVP71157440	HY-053017-30				80.0001	0.1682	0.4687	0.6369					°F psi	77
7/12/2017	18:53	Spinhirne	EVP71157440	HY-053017-30				60.0001	0.1073	0.4861	0.5934					°F psi	77
7/12/2017	18:31	Spinhirne	EVP71157440	HY-053017-30	#00018			140	0.2776	0.5329	0.8105					°F psi	77
7/12/2017	18:26	Spinhirne	EVP71157440	HY-053017-30				120	0.2384	0.5151	0.7535					°F psi	77
7/12/2017	18:21	Spinhirne	EVP71157440	HY-053017-30				104	0.2127	0.5009	0.7136					°F psi	77
7/12/2017	18:16	Spinhirne	EVP71157440	HY-053017-30				80.0001	0.1725	0.4796	0.6521					°F psi	77
7/12/2017	18:11	Spinhirne	EVP71157440	HY-053017-30				60.0001	0.1124	0.4974	0.6097					°F psi	77
6/28/2017	21:47	Spinhirne	EVP71157440	HY-053017-03	#00017			140	0.2334	0.5088	0.7422					°F psi	77
6/28/2017	21:42	Spinhirne	EVP71157440	HY-053017-03				120	0.2012	0.4918	0.693					°F psi	77
6/28/2017	21:37	Spinhirne	EVP71157440	HY-053017-03				104	0.1831	0.4783	0.6614					°F psi	77
6/28/2017	21:32	Spinhirne	EVP71157440	HY-053017-03				80.0001	0.1429	0.4579	0.6007					°F psi	77
6/28/2017	21:27	Spinhirne	EVP71157440	HY-053017-03				60.0001	0.0918	0.4749	0.5667					°F psi	77

Date	Time	Operator	SN	Sample ID	No.	Info	Comment	Tm	Pabs	Pgas	Ptot	Pabs Calculated	rate	[T]	[P]	Volume [ml]	T fill
6/28/2017	21:05	Spinhirne	EVP71157440	HY-053017-03	#00016			140	0.2442	0.5574	0.8016					°F psi	77
6/28/2017	21:00	Spinhirne	EVP71157440	HY-053017-03				120	0.2135	0.5388	0.7523					°F psi	77
6/28/2017	20:55	Spinhirne	EVP71157440	HY-053017-03				104	0.1924	0.5239	0.7163					°F psi	77
6/28/2017	20:50	Spinhirne	EVP71157440	HY-053017-03				80.0001	0.1537	0.5016	0.6553					°F psi	77
6/28/2017	20:45	Spinhirne	EVP71157440	HY-053017-03				60.0001	0.0931	0.5202	0.6134					°F psi	77
6/28/2017	20:23	Spinhirne	EVP71157440	HY-053017-03	#00015			140	0.2565	0.7333	0.9897					°F psi	77
6/28/2017	20:18	Spinhirne	EVP71157440	HY-053017-03				120	0.222	0.7088	0.9309					°F psi	77
6/28/2017	20:13	Spinhirne	EVP71157440	HY-053017-03				104	0.204	0.6893	0.8933					°F psi	77
6/28/2017	20:08	Spinhirne	EVP71157440	HY-053017-03				80.0001	0.1665	0.6599	0.8264					°F psi	77
6/28/2017	20:02	Spinhirne	EVP71157440	HY-053017-03				60.0001	0.0955	0.6844	0.7799					°F psi	77
6/28/2017	19:30	Spinhirne	EVP71157440	HY-053017-03	#00014			140	0.2334	0.4896	0.723					°F psi	77
6/28/2017	19:25	Spinhirne	EVP71157440	HY-053017-03				120	0.2028	0.4733	0.676					°F psi	77
6/28/2017	19:20	Spinhirne	EVP71157440	HY-053017-03				104	0.1804	0.4602	0.6406					°F psi	77
6/28/2017	19:15	Spinhirne	EVP71157440	HY-053017-03				80.0001	0.1487	0.4406	0.5893					°F psi	77
6/28/2017	19:10	Spinhirne	EVP71157440	HY-053017-03				60.0001	0.0887	0.457	0.5456					°F psi	77
6/28/2017	18:47	Spinhirne	EVP71157440	HY-053017-03	#00013			140	0.247	0.5291	0.7761					°F psi	77
6/28/2017	18:42	Spinhirne	EVP71157440	HY-053017-03				120	0.2122	0.5114	0.7236					°F psi	77
6/28/2017	18:37	Spinhirne	EVP71157440	HY-053017-03				104	0.1928	0.4973	0.6901					°F psi	77
6/28/2017	18:32	Spinhirne	EVP71157440	HY-053017-03				80.0001	0.1558	0.4761	0.6319					°F psi	77
6/28/2017	18:27	Spinhirne	EVP71157440	HY-053017-03				60.0001	0.0965	0.4938	0.5903					°F psi	77
6/28/2017	18:05	Spinhirne	EVP71157440	HY-053017-03	#00012			140	0.2446	0.5595	0.8041					°F psi	77
6/28/2017	18:00	Spinhirne	EVP71157440	HY-053017-03				120	0.2074	0.5408	0.7483					°F psi	77
6/28/2017	17:55	Spinhirne	EVP71157440	HY-053017-03				104	0.1872	0.5259	0.7132					°F psi	77
6/28/2017	17:50	Spinhirne	EVP71157440	HY-053017-03				80.0001	0.1507	0.5035	0.6543					°F psi	77
6/28/2017	17:45	Spinhirne	EVP71157440	HY-053017-03				60.0001	0.091	0.5222	0.6132					°F psi	77
6/28/2017	17:22	Spinhirne	EVP71157440	HY-053017-03	#00011			140	0.272	0.7715	1.0435					°F psi	77
6/28/2017	17:17	Spinhirne	EVP71157440	HY-053017-03				120	0.2286	0.7458	0.9744					°F psi	77
6/28/2017	17:13	Spinhirne	EVP71157440	HY-053017-03				104	0.2101	0.7252	0.9354					°F psi	77
6/28/2017	17:07	Spinhirne	EVP71157440	HY-053017-03				80.0001	0.1696	0.6943	0.864					°F psi	77
6/28/2017	17:02	Spinhirne	EVP71157440	HY-053017-03				60.0001	0.0947	0.7201	0.8148					°F psi	77

Date	Time	Operator	SN	Sample ID	No.	Info	Comment	Tm	Pabs	Pgas	Ptot	Pabs Calculated	rate	[T]	[P]	Volume [ml]	T fill
6/28/2017	0:54	Spinhirne	EVP71157440	KR-060617-30	#00010			140	0.4124	0.5224	0.9348					°F psi	100
6/28/2017	0:48	Spinhirne	EVP71157440	KR-060617-30				120	0.2942	0.505	0.7992					°F psi	100
6/28/2017	0:42	Spinhirne	EVP71157440	KR-060617-30				104	0.2346	0.491	0.7256					°F psi	100
6/28/2017	0:36	Spinhirne	EVP71157440	KR-060617-30				80.0001	0.1937	0.4701	0.6638					°F psi	100
6/28/2017	0:31	Spinhirne	EVP71157440	KR-060617-30				60.0001	0.1588	0.4876	0.6464					°F psi	100
6/28/2017	0:12	Spinhirne	EVP71157440	KR-060617-30	#00009			140	0.4076	0.5152	0.9227					°F psi	100
6/28/2017	0:06	Spinhirne	EVP71157440	KR-060617-30				120	0.2884	0.498	0.7864					°F psi	100
6/28/2017	0:01	Spinhirne	EVP71157440	KR-060617-30				104	0.2306	0.4842	0.7149					°F psi	100
6/27/2017	23:55	Spinhirne	EVP71157440	KR-060617-30				80.0001	0.1893	0.4636	0.653					°F psi	100
6/27/2017	23:49	Spinhirne	EVP71157440	KR-060617-30				60.0001	0.1566	0.4808	0.6374					°F psi	100
6/27/2017	23:30	Spinhirne	EVP71157440	KR-060617-30	#00008			140	0.4167	0.5192	0.9359					°F psi	100
6/27/2017	23:24	Spinhirne	EVP71157440	KR-060617-30				120	0.2911	0.5019	0.7931					°F psi	100
6/27/2017	23:19	Spinhirne	EVP71157440	KR-060617-30				104	0.2325	0.4881	0.7205					°F psi	100
6/27/2017	23:13	Spinhirne	EVP71157440	KR-060617-30				80.0001	0.1919	0.4673	0.6592					°F psi	100
6/27/2017	23:08	Spinhirne	EVP71157440	KR-060617-30				60.0001	0.1564	0.4846	0.6411					°F psi	100
6/27/2017	22:48	Spinhirne	EVP71157440	KR-060617-30	#00007			140	0.416	0.5102	0.9262					°F psi	100
6/27/2017	22:43	Spinhirne	EVP71157440	KR-060617-30				120	0.2951	0.4932	0.7883					°F psi	100
6/27/2017	22:37	Spinhirne	EVP71157440	KR-060617-30				104	0.2312	0.4796	0.7108					°F psi	100
6/27/2017	22:32	Spinhirne	EVP71157440	KR-060617-30				80.0001	0.1902	0.4592	0.6493					°F psi	100
6/27/2017	22:26	Spinhirne	EVP71157440	KR-060617-30				60.0001	0.1569	0.4762	0.6331					°F psi	100
6/27/2017	22:07	Spinhirne	EVP71157440	KR-060617-30	#00006			140	0.4269	0.5226	0.9494					°F psi	100
6/27/2017	22:01	Spinhirne	EVP71157440	KR-060617-30				120	0.3046	0.5051	0.8097					°F psi	100
6/27/2017	21:56	Spinhirne	EVP71157440	KR-060617-30				104	0.24	0.4912	0.7311					°F psi	100
6/27/2017	21:50	Spinhirne	EVP71157440	KR-060617-30				80.0001	0.1946	0.4703	0.6649					°F psi	100
6/27/2017	21:45	Spinhirne	EVP71157440	KR-060617-30				60.0001	0.1645	0.4877	0.6522					°F psi	100

Table 12. Raw results from Low VP analysis of “known” recipe, nonane, and fuel oil no. 6 samples.

p1	p2	Date	Time	Operator	SN	Sample ID	No.	Info	Comment	Tm	Pabs	Pgas	Ptot	[T]	[P]	T fill
2.5186	1.5853	8/17/2017	19:46	Spinhirne	EVP71157440	MB-061717-02	#00031			160	0.257	0.6023	0.8594	Å°F	psi	140

p1	p2	Date	Time	Operator	SN	Sample ID	No.	Info	Comment	Tm	Pabs	Pgas	Ptot	[T]	[P]	T fill
1.4048	0.8656	8/17/2017	19:28	Spinhirne	EVP71157440	MB-061717-02	#00030			140	0.1182	0.3361	0.4543	Â°F	psi	140
1.1473	0.7442	8/17/2017	18:59	Spinhirne	EVP71157440	MB-061717-02	#00029			120	0.2147	0.2341	0.4487	Â°F	psi	140
3.5321	3.043	8/17/2017	17:24	Spinhirne	EVP71157440	BT-062017-02	#00028			140	0.4395	1.781	2.2205	Â°F	psi	140
2.2243	1.8571	8/17/2017	17:11	Spinhirne	EVP71157440	BT-062017-02	#00027			120	0.5376	0.8066	1.3442	Â°F	psi	140
5.6011	4.9065	8/17/2017	16:55	Spinhirne	EVP71157440	BT-062017-02	#00026			160	0.3708	3.2682	3.639	Â°F	psi	140
3.5183	3.03	8/17/2017	16:40	Spinhirne	EVP71157440	BT-062017-02	#00025			140	0.0111	2.1462	2.1573	Â°F	psi	140
2.2832	1.8897	8/17/2017	16:27	Spinhirne	EVP71157440	BT-062017-02	#00024			120	0.7102	0.6816	1.3918	Â°F	psi	140
4.5242	2.415	8/17/2017	15:38	Spinhirne	EVP71157440	Nonane081717	#00023			100	0.2609	0.8811	1.142	Â°F	psi	68
2.9241	2.0537	8/16/2017	19:37	Spinhirne	EVP71157440	MM-060817-03	#00021			160	0.5616	0.7188	1.2804	Â°F	psi	140
1.6919	1.1879	8/16/2017	19:22	Spinhirne	EVP71157440	MM-060817-03	#00020			140	0.2361	0.4732	0.7094	Â°F	psi	140
1.186	0.7622	8/16/2017	19:08	Spinhirne	EVP71157440	MM-060817-03	#00019			120	0.1517	0.2779	0.4296	Â°F	psi	140
2.9598	2.0926	8/16/2017	18:52	Spinhirne	EVP71157440	MM-060817-03	#00018			160	0.7346	0.6352	1.3697	Â°F	psi	140
1.8991	1.4421	8/16/2017	18:24	Spinhirne	EVP71157440	MM-060817-03	#00017			140	0.8922	0.2365	1.1287	Â°F	psi	140
1.5148	1.1721	8/16/2017	18:11	Spinhirne	EVP71157440	MM-060817-03	#00016			120	0.727	0.196	0.923	Â°F	psi	140
4.5011	2.3949	8/16/2017	16:56	Spinhirne	EVP71157440	Nonane081617	#00015			100	0.2696	0.8662	1.1358	Â°F	psi	68
3.1858	1.6811	8/15/2017	23:41	Spinhirne	EVP71157440	KR-060617-04	#00014			140	0.3017	0.5466	0.8483	°F	psi	100
3.0443	1.5605	8/15/2017	23:23	Spinhirne	EVP71157440	KR-060617-04	#00013			120	0.2101	0.534	0.744	°F	psi	100
2.8161	1.4211	8/15/2017	22:56	Spinhirne	EVP71157440	KR-060617-04	#00012			100	0.153	0.5013	0.6543	°F	psi	100
3.2335	1.7045	8/15/2017	22:34	Spinhirne	EVP71157440	KR-060617-04	#00011			140	0.3039	0.5549	0.8588	°F	psi	100
3.013	1.5525	8/15/2017	22:16	Spinhirne	EVP71157440	KR-060617-04	#00010			120	0.2113	0.5317	0.743	°F	psi	100
2.8662	1.4566	8/15/2017	21:59	Spinhirne	EVP71157440	KR-060617-04	#00009			100.04	0.1647	0.5119	0.6766	°F	psi	100
4.5192	2.4223	8/15/2017	19:50	Spinhirne	EVP71157440	Nonane081517	#00008			100.04	0.2696	0.8819	1.1515	°F	psi	68
4.5746	2.4452	8/15/2017	19:26	Spinhirne	EVP71157440	Nonane081517	#00007			100.04	0.2631	0.8935	1.1565	°F	psi	68

Table 13. Raw results from D6378 single point analysis of QA samples.

Date	Time	Operator	SN	Sample ID	No.	Info	Comment	Tm	Pabs	Pgas	Ptot	Corr.	DVPE 6378	DVPE EPA	RVPE CARB	Corr.A	Correlation Formula	form1	form2	form3	form4	[T]	[P]	Volume [ml]	T fill
7/27/2017	16:31	Spinhirne	EVP71157440	Pentane072717	#00093			100	15.6466	0.4114	16.058	15.5008	15.5008	15.6267	15.4182	15.6466	DVPE 6378 = Pabs -0.146	DVPE 6378 = Pabs -0.146	DVPE EPA = Pabs -0.020	RVPE CARB = Pabs -0.228	FREE = Pabs	°F	psi	1000	68
7/27/2017	16:20	Spinhirne	EVP71157440	Pentane072717	#00092			100	15.6209	0.4277	16.0486	15.4751	15.4751	15.601	15.3924	15.6209	DVPE 6378 = Pabs -0.146	DVPE 6378 = Pabs -0.146	DVPE EPA = Pabs -0.020	RVPE CARB = Pabs -0.228	FREE = Pabs	°F	psi	1000	68
7/26/2017	16:07	Spinhirne	EVP71157440	Pentane072617	#00091			100	15.6475	0.4066	16.0541	15.5017	15.5017	15.6276	15.419	15.6475	DVPE 6378 = Pabs -0.146	DVPE 6378 = Pabs -0.146	DVPE EPA = Pabs -0.020	RVPE CARB = Pabs -0.228	FREE = Pabs	°F	psi	1000	68

Date	Time	Operator	SN	Sample ID	No.	Info	Comment	Tm	Pabs	Pgas	Ptot	Corr.	DVPE 6378	DVPE EPA	RVPE CARB	Corr.4	Correlation Formula	form1	form2	form3	form4	[T]	[P]	Volume [ml]	T fill
7/26/2017	15:39	Spinhirne	EV71157440	Pentane072617	#00090			100	15.6271	0.4047	16.0318	15.4813	15.4813	15.6072	15.3987	15.6271	DVPE 6378 = Pabs -0.146	DVPE 6378 = Pabs -0.146	DVPE EPA = Pabs -0.020	RVPE CARB = Pabs -0.228	FREE = Pabs	*F	psi	1000	68
7/25/2017	19:42	Spinhirne	EV71157440	Pentane072517	#00089			100	15.6776	0.4511	16.1287	15.5318	15.5318	15.6577	15.4491	15.6776	DVPE 6378 = Pabs -0.146	DVPE 6378 = Pabs -0.146	DVPE EPA = Pabs -0.020	RVPE CARB = Pabs -0.228	FREE = Pabs	*F	psi	1000	68
7/25/2017	19:25	Spinhirne	EV71157440	Pentane072517	#00088			100	15.6758	0.4658	16.1416	15.53	15.53	15.6559	15.4474	15.6758	DVPE 6378 = Pabs -0.146	DVPE 6378 = Pabs -0.146	DVPE EPA = Pabs -0.020	RVPE CARB = Pabs -0.228	FREE = Pabs	*F	psi	1000	68
7/25/2017	17:03	Spinhirne	EV71157440	Pentane072517	#00087			100	15.7853	0.3866	16.1719	15.6396	15.6396	15.7655	15.5569	15.7853	DVPE 6378 = Pabs -0.146	DVPE 6378 = Pabs -0.146	DVPE EPA = Pabs -0.020	RVPE CARB = Pabs -0.228	FREE = Pabs	*F	psi	1000	68
7/24/2017	18:29	Spinhirne	EV71157440	Pentane072417	#00086			100	15.818	0.4532	16.2712	15.6722	15.6722	15.7981	15.5896	15.818	DVPE 6378 = Pabs -0.146	DVPE 6378 = Pabs -0.146	DVPE EPA = Pabs -0.020	RVPE CARB = Pabs -0.228	FREE = Pabs	*F	psi	1000	68
7/24/2017	18:11	Spinhirne	EV71157440	Pentane072417	#00085			100	15.8134	0.4725	16.2859	15.6676	15.6676	15.7935	15.585	15.8134	DVPE 6378 = Pabs -0.146	DVPE 6378 = Pabs -0.146	DVPE EPA = Pabs -0.020	RVPE CARB = Pabs -0.228	FREE = Pabs	*F	psi	1000	68
7/24/2017	17:50	Spinhirne	EV71157440	Pentane072417	#00084			100	15.9573	0.4505	16.4079	15.8116	15.8116	15.9375	15.7289	15.9573	DVPE 6378 = Pabs -0.146	DVPE 6378 = Pabs -0.146	DVPE EPA = Pabs -0.020	RVPE CARB = Pabs -0.228	FREE = Pabs	*F	psi	1000	68
7/24/2017	17:38	Spinhirne	EV71157440	Pentane072417	#00083			100	15.8873	0.4579	16.3452	15.7416	15.7416	15.8674	15.6589	15.8873	DVPE 6378 = Pabs -0.146	DVPE 6378 = Pabs -0.146	DVPE EPA = Pabs -0.020	RVPE CARB = Pabs -0.228	FREE = Pabs	*F	psi	1000	68
7/24/2017	15:46	Spinhirne	EV71157440	Pentane072417	#00082			100	14.1668	0.0013	14.168	14.021	14.021	14.1469	13.9383	14.1668	DVPE 6378 = Pabs -0.146	DVPE 6378 = Pabs -0.146	DVPE EPA = Pabs -0.020	RVPE CARB = Pabs -0.228	FREE = Pabs	*F	psi	1000	68
7/21/2017	17:28	Spinhirne	EV71157440	Pentane072117	#00081			100	15.6937	0.376	16.0696	15.5479	15.5479	15.6738	15.4652	15.6937	DVPE 6378 = Pabs -0.146	DVPE 6378 = Pabs -0.146	DVPE EPA = Pabs -0.020	RVPE CARB = Pabs -0.228	FREE = Pabs	*F	psi	1000	68
7/21/2017	17:11	Spinhirne	EV71157440	Pentane072117	#00080			100	15.7132	0.3771	16.0904	15.5675	15.5675	15.6934	15.4848	15.7132	DVPE 6378 = Pabs -0.146	DVPE 6378 = Pabs -0.146	DVPE EPA = Pabs -0.020	RVPE CARB = Pabs -0.228	FREE = Pabs	*F	psi	1000	68
7/19/2017	15:13	Spinhirne	EV71157440	Pentane071917	#00079			100	15.6486	0.3937	16.0422	15.5028	15.5028	15.6287	15.4201	15.6486	DVPE 6378 = Pabs -0.146	DVPE 6378 = Pabs -0.146	DVPE EPA = Pabs -0.020	RVPE CARB = Pabs -0.228	FREE = Pabs	*F	psi	1000	68
7/19/2017	14:56	Spinhirne	EV71157440	Pentane071917	#00078			100	15.6437	0.4023	16.046	15.498	15.498	15.6239	15.4153	15.6437	DVPE 6378 = Pabs -0.146	DVPE 6378 = Pabs -0.146	DVPE EPA = Pabs -0.020	RVPE CARB = Pabs -0.228	FREE = Pabs	*F	psi	1000	68
7/18/2017	16:58	Spinhirne	EV71157440	Pentane071817	#00077			100	15.6343	0.3895	16.0238	15.4886	15.4886	15.6145	15.4059	15.6343	DVPE 6378 = Pabs -0.146	DVPE 6378 = Pabs -0.146	DVPE EPA = Pabs -0.020	RVPE CARB = Pabs -0.228	FREE = Pabs	*F	psi	1000	68
7/18/2017	16:16	Spinhirne	EV71157440	Pentane071817	#00076			100	15.6338	0.3784	16.0122	15.488	15.488	15.6139	15.4053	15.6338	DVPE 6378 = Pabs -0.146	DVPE 6378 = Pabs -0.146	DVPE EPA = Pabs -0.020	RVPE CARB = Pabs -0.228	FREE = Pabs	*F	psi	1000	68
7/13/2017	0:00	Spinhirne	EV71157440	Pentane071217	#00073		End of day	100	15.6495	0.3676	16.0171	15.5038	15.5038	15.6296	15.4211	15.6495	DVPE 6378 = Pabs -0.146	DVPE 6378 = Pabs -0.146	DVPE EPA = Pabs -0.020	RVPE CARB = Pabs -0.228	FREE = Pabs	*F	psi	1000	68
7/12/2017	17:20	Spinhirne	EV71157440	Pentane071217	#00072		Start of day	100	15.6744	0.3566	16.0311	15.5287	15.5287	15.6546	15.446	15.6744	DVPE 6378 = Pabs -0.146	DVPE 6378 = Pabs -0.146	DVPE EPA = Pabs -0.020	RVPE CARB = Pabs -0.228	FREE = Pabs	*F	psi	1000	68
7/12/2017	17:08	Spinhirne	EV71157440	Pentane071217	#00071		Start of day	100	15.6538	0.3619	16.0157	15.508	15.508	15.6339	15.4253	15.6538	DVPE 6378 = Pabs -0.146	DVPE 6378 = Pabs -0.146	DVPE EPA = Pabs -0.020	RVPE CARB = Pabs -0.228	FREE = Pabs	*F	psi	1000	68
6/28/2017	15:21	Spinhirne	EV71157440	Pentane062817	#00069			100	15.6386	0.342	15.9806	15.4928	15.4928	15.6187	15.4101	15.6386	DVPE 6378 = Pabs -0.146	DVPE 6378 = Pabs -0.146	DVPE EPA = Pabs -0.020	RVPE CARB = Pabs -0.228	FREE = Pabs	*F	psi	1000	68
6/28/2017	15:11	Spinhirne	EV71157440	Pentane062817	#00068			100	15.6415	0.3442	15.9857	15.4957	15.4957	15.6216	15.413	15.6415	DVPE 6378 = Pabs -0.146	DVPE 6378 = Pabs -0.146	DVPE EPA = Pabs -0.020	RVPE CARB = Pabs -0.228	FREE = Pabs	*F	psi	1000	68
6/27/2017	15:39	Spinhirne	EV71157440	Pentane06271702	#00067			100	15.6309	0.3637	15.9946	15.4851	15.4851	15.611	15.4025	15.6309	DVPE 6378 = Pabs -0.146	DVPE 6378 = Pabs -0.146	DVPE EPA = Pabs -0.020	RVPE CARB = Pabs -0.228	FREE = Pabs	*F	psi	1000	68
6/27/2017	15:06	Spinhirne	EV71157440	Pentane062717	#00066			100	15.634	0.3731	16.0071	15.4883	15.4883	15.6141	15.4056	15.634	DVPE 6378 = Pabs -0.146	DVPE 6378 = Pabs -0.146	DVPE EPA = Pabs -0.020	RVPE CARB = Pabs -0.228	FREE = Pabs	*F	psi	1000	68
6/12/2017	22:23	Spinhirne	EV71157440	NP-01-NP	#00065			100.04	15.6112	0.8979	16.5091	15.4654	15.4654	15.5913	15.3827	15.6112	DVPE 6378 = Pabs -0.146	DVPE 6378 = Pabs -0.146	DVPE EPA = Pabs -0.020	RVPE CARB = Pabs -0.228	FREE = Pabs	-F	psi	1000	68

Table 14. Raw results from Low VP analysis of QA samples

p1	p2	Date	Time	Operator	SN	Sample ID	No.	Info	Comment	Tm	Pabs	Pgas	Ptot	Corr.	DVPE 6378	DVPE EPA	RVPE CARB	Corr.4	Correlation Formula	form 1 DVP E 6378 = Pabs -	form 2 DVP E EPA = Pabs -	form 3 RVP E CAR B = Pabs -	form 4 FREE = Pabs	[T]	[P]	Volume [ml]	T fill
17.8027	16.6361	8/17/2017	18:15	Spinhirne	EV71157440	Pentane081717	#00103			100	15.6247	0.3945	16.0192	15.4789	15.4789	15.6048	15.3963	15.6247	DVPE 6378 = Pabs -0.146	0.146	0.020	0.228	FREE = Pabs	Å° F	psi	1000	68

p1	p2	Date	Time	Operator	SN	Sample ID	No.	Info	Comment	Tm	Pabs	Pgas	Ptot	Corr.	DVPE 6378	DVPE EPA	RVPE CARB	Corr.4	Correlation Formula	form 1 DVP E 6378 = Pabs - 0.146	form 2 DVP E EPA = Pabs - 0.020	form 3 RVP E CARB = Pabs - 0.228	form 4	[T]	[P]	Volume [ml]	T fill
4.5288	2.0791	8/17/2017	15:22	Spinhirne	EVP71157440	Nonane0817	#00102			100	0.2757	0.6724	0.9481	0.1299	0.1299	0.2558	0.0473	0.2757	DVPE 6378 = Pabs - 0.146	0.146	0.020	0.228	FREE = Pabs	Å° F	psi	1000	68
17.8975	16.7033	8/17/2017	14:52	Spinhirne	EVP71157440	Pentane081717	#00101			100	15.6661	0.4047	16.0708	15.5203	15.5203	15.6462	15.4377	15.6661	DVPE 6378 = Pabs - 0.146	0.146	0.020	0.228	FREE = Pabs	Å° F	psi	1000	68
18.1152	16.8393	8/17/2017	14:39	Spinhirne	EVP71157440	Pentane081717	#00100			100	15.6628	0.467	16.1298	15.5171	15.5171	15.643	15.4344	15.6628	DVPE 6378 = Pabs - 0.146	0.146	0.020	0.228	FREE = Pabs	Å° F	psi	1000	68
18.1936	16.863	8/16/2017	16:30	Spinhirne	EVP71157440	Pentane081617	#00099			100	15.674	0.4677	16.1417	15.5283	15.5283	15.6542	15.4456	15.674	DVPE 6378 = Pabs - 0.146	0.146	0.020	0.228	FREE = Pabs	Å° F	psi	1000	68
17.8861	16.6791	8/16/2017	16:14	Spinhirne	EVP71157440	Pentane081617	#00098			100	15.6411	0.4039	16.045	15.4953	15.4953	15.6212	15.4127	15.6411	DVPE 6378 = Pabs - 0.146	0.146	0.020	0.228	FREE = Pabs	Å° F	psi	1000	68
17.8458	16.6866	8/15/2017	18:49	Spinhirne	EVP71157440	Pentane081517	#00097			100	15.6708	0.3974	16.0682	15.5251	15.5251	15.651	15.4424	15.6708	DVPE 6378 = Pabs - 0.146	0.146	0.020	0.228	FREE = Pabs	*F	psi	1000	68
17.7979	16.6457	8/15/2017	18:39	Spinhirne	EVP71157440	Pentane081517	#00096			100	15.6393	0.3933	16.0326	15.4936	15.4936	15.6195	15.4109	15.6393	DVPE 6378 = Pabs - 0.146	0.146	0.020	0.228	FREE = Pabs	*F	psi	1000	68

Vapor pressure results from commercial labs

Vapor pressure measurements using three methods were obtained from commercial laboratories: ASTM D323 (Reid vapor pressure), ASTM D2879 (vapor pressure by isoteniscope), and ASTM E1719 (vapor pressure by ebulliometry). ASTM D2879 was conducted by three labs.

ASTM D2879 and ASTM D323: Vapor pressure by isoteniscope and Reid vapor pressure

Alcor Petrolab (Lab 1)

The ASTM D2879 (vapor pressure by isoteniscope) results for all five study materials from Lab 1 are given in Figures 4 through 8. This information was also provided by the lab in the form of Excel files, which are given in Attachment A to this report. The Excel files have information about the degassing step that Figures 4 through 8 do not have. In each case, the evacuation/nitrogen purge (ASTM D2879-10, §8.1) was performed at room temperature (approximately 22°C) and degassing (ASTM D2879-10, §8.2) was performed using an alcohol lamp. Pressure was determined using a digital pressure transducer with a 0 - 1000 mm Hg range and 32-bit resolution. The final degassing pressures were 1.7, 2.8, 2.8, 2.2, and 2.5 torr for the “known” recipe, the hydraulic fluid, the MM fuel oil no. 6, the MB fuel oil no. 6, and the BT fuel oil no. 6, respectively.

Figures

CERTIFICATE OF ANALYSIS

The University of Texas
CEER, Bldg. 133,
10100 Burnet Rd.
Austin, TX 78758

Report Date: 8/1/2017
Laboratory Number: P170718A2
Sample Type: Solid
Sample ID: KR-0600617-11

Vapor Pressure by Isoteniscope - ASTM D2879

Temperature (°C)	Temperature (°F)	Vapor Pressure - Curve Fit (torr)	Vapor Pressure - Curve Fit (psia)	Vapor Pressure - measured temperature (°C)	Vapor Pressure - measured pressure (torr)
15.6	60	0	0.000		
21.1	70	0	0.000		
26.7	80	0	0.000	26.1	1.8
32.2	90	0	0.000	31.9	1.7
37.8	100	0	0.000	37.6	1.7
43.3	110	0	0.000	43.3	1.2
48.9	120	0	0.000	48.8	1.3
54.4	130	0	0.001	53.7	1.5
60.0	140	0	0.001	59.8	1.8
65.6	150	0	0.001	65.3	2.2
71.1	160	0	0.002	71.0	2.6
76.7	170	0	0.003	76.3	2.5
82.2	180	0	0.004	82.1	2.7
87.8	190	0	0.005	87.8	3.4
93.3	200	0	0.007	93.1	3.8
98.9	210	0	0.009	98.8	4.2
104.4	220	1	0.012	104.1	4.8
110.0	230	1	0.016	110.0	5.3
115.6	240	1	0.020	115.3	6.1
121.1	250	1	0.026	121.0	7.1
126.7	260	2	0.033	126.5	7.2
132.2	270	2	0.042	131.9	9.0
137.8	280	3	0.053	137.6	10.2
143.3	290	3	0.067	143.3	11.4
148.9	300	4	0.083	148.5	13.1
154.4	310	5	0.103	153.9	14.7
160.0	320	7	0.127	159.8	16.4
165.6	330	8	0.156	165.5	18.8
171.1	340	10	0.190	171.0	21.0
176.7	350	12	0.231	176.5	23.2
182.2	360	14	0.279	181.9	26.5
187.8	370	17	0.336	187.5	30.1
193.3	380	21	0.402	192.9	33.9
198.9	390	25	0.479	198.6	38.5
204.4	400	29	0.569	204.4	43.8
210.0	410	35	0.673	209.6	49.2
215.6	420	41	0.794	215.4	55.8
221.1	430	48	0.932	221.1	63.9
226.7	440	56	1.090	226.4	71.9
232.2	450	66	1.270	231.8	80.5
237.8	460	76	1.476	237.5	91.3
243.3	470	88	1.710	243.2	102.8
248.9	480	102	1.974	248.6	115.4
254.4	490	117	2.272	254.3	130.5
260.0	500	135	2.607	259.7	145.9
265.6	510	154	2.984	265.5	165.5
271.1	520	176	3.406	271.1	186.7
276.7	530	200	3.876	276.4	208.2
282.2	540	228	4.401	282.1	234.5
287.8	550	258	4.984	287.6	261.7
293.3	560	291	5.630	293.2	293.8
298.9	570	328	6.345	298.6	326.3
304.4	580	369	7.134	304.4	368.8
310.0	590	414	8.004	309.6	410.3
315.6	600	463	8.960	315.3	460.7
321.1	610	518	10.010	320.7	511.5
326.7	620	577	11.159	326.4	573.5
332.2	630	642	12.416	332.0	641.1
337.8	640	713	13.787	337.7	713.4
341.2	646	760	14.695	341.2	760.8

Evacuation/N₂ purge performed at room temperature, approx 22 °C (ASTM D2879-10, §8.1)
Degassing performed using alcohol lamp (ASTM D2879-10, §8.2)
Pressure determined using digital pressure transducer, 0 - 1000 mm Hg range, 32 bit resolution

Final Degassing Pressure

1.7 torr

Report Prepared by,



Joe Burack, Lab Technician

Report Reviewed by,



Stuart Ramsdale, Lab
Manager

Figure 4. Lab 1 reported ASTM D2879 results for the “known” recipe.

CERTIFICATE OF ANALYSIS

The University of Texas
CEER, Bldg. 133,
10100 Burnet Rd.
Austin, TX 78758

Report Date: 8/1/2017
Laboratory Number: P170718A1
Sample Type: Hydraulic fluid
Sample ID: HY-053017-09

Vapor Pressure by Isoteriscope - ASTM D2879

Temperature (°C)	Temperature (°F)	Vapor Pressure - Curve Fit (torr)	Vapor Pressure - Curve Fit (psia)	Vapor Pressure - measured temperature (°C)	Vapor Pressure - measured pressure (torr)
15.6	60	0	0.006		
21.1	70	0	0.008		
26.7	80	1	0.011	26.5	2.8
32.2	90	1	0.014	31.7	2.8
37.8	100	1	0.018	37.6	2.8
43.3	110	1	0.022	43.3	2.8
48.9	120	1	0.027	48.9	2.8
54.4	130	2	0.034	54.3	3.2
60.0	140	2	0.042	59.8	3.5
65.6	150	3	0.051	65.3	3.7
71.1	160	3	0.062	71.0	4.6
76.7	170	4	0.075	76.7	5.1
82.2	180	5	0.089	82.1	5.9
87.8	190	6	0.106	87.7	6.6
93.3	200	7	0.126	92.9	7.2
98.9	210	8	0.149	98.5	8.6
104.4	220	9	0.174	104.3	9.9
110.0	230	11	0.204	109.8	11.3
115.6	240	12	0.237	115.3	12.0
121.1	250	14	0.274	120.9	14.8
126.7	260	16	0.316	126.3	16.5
132.2	270	19	0.363	132.1	19.4
137.8	280	21	0.416	137.7	22.0
143.3	290	25	0.474	143.0	24.8
148.9	300	28	0.539	148.7	28.1
154.4	310	32	0.610	154.4	31.6
160.0	320	36	0.689	159.9	35.4
165.6	330	40	0.775	165.5	40.2
171.1	340	45	0.870	170.9	44.3
176.7	350	50	0.973	176.3	49.7
182.2	360	56	1.086	181.9	56.0
187.8	370	62	1.208	187.7	62.6
193.3	380	69	1.342	193.1	69.1
198.9	390	77	1.486	198.7	76.0
204.4	400	85	1.641	204.1	83.3
210.0	410	94	1.809	209.7	91.2
215.6	420	103	1.990	215.5	100.8
221.1	430	113	2.183	220.8	108.7
226.7	440	124	2.391	226.5	120.2
232.2	450	135	2.614	231.8	130.7
237.8	460	147	2.851	237.7	142.5
243.3	470	161	3.105	242.9	154.6
248.9	480	174	3.374	248.6	168.8
254.4	490	189	3.661	254.4	184.1
260.0	500	205	3.965	259.7	198.5
265.6	510	222	4.288	265.4	218.3
271.1	520	239	4.629	270.8	235.7
276.7	530	258	4.990	276.6	257.2
282.2	540	278	5.371	282.2	277.9
287.8	550	299	5.773	287.8	301.4
293.3	560	320	6.195	293.0	325.7
296.6	566	334	6.454	296.6	345.4

Evacuation/N₂ purge performed at room temperature, approx 22 °C (ASTM D2879-10, §8.1)
Degassing performed using alcohol lamp (ASTM D2879-10, §8.2)
Pressure determined using digital pressure transducer, 0 - 1000 mm Hg range, 32-bit resolution

Final Degassing Pressure

2.8 torr

Report Prepared by,



Joe Burock, Lab Technician

Report Reviewed by,



Stuart Ramsdale, Lab
Manager

Figure 5. Lab 1 reported ASTM D2879 results for hydraulic fluid.

CERTIFICATE OF ANALYSIS

The University of Texas
CEER, Bldg. 133,
10100 Burnet Rd.
Austin, TX 78758

Report Date: 8/1/2017
Laboratory Number: P170718B1
Sample Type: Liquid
Sample ID: MM-060817-12

Vapor Pressure by Isoteniscope - ASTM D2879

Temperature (°C)	Temperature (°F)	Vapor Pressure - Curve Fit (torr)	Vapor Pressure - Curve Fit (psia)	Vapor Pressure - measured temperature (°C)	Vapor Pressure - measured pressure (torr)
15.6	60	0	0.006		
21.1	70	0	0.008		
26.7	80	1	0.011	26.5	2.8
32.2	90	1	0.014	31.7	2.8
37.8	100	1	0.018	37.6	2.8
43.3	110	1	0.022	43.3	2.8
48.9	120	1	0.027	48.9	2.8
54.4	130	2	0.034	54.3	3.2
60.0	140	2	0.042	59.8	3.5
65.6	150	3	0.051	65.3	3.7
71.1	160	3	0.062	71.0	4.6
76.7	170	4	0.075	76.7	5.1
82.2	180	5	0.089	82.1	5.9
87.8	190	6	0.106	87.7	6.6
93.3	200	7	0.126	92.9	7.2
98.9	210	8	0.149	98.5	8.6
104.4	220	9	0.174	104.3	9.9
110.0	230	11	0.204	109.8	11.3
115.6	240	12	0.237	115.3	12.0
121.1	250	14	0.274	120.9	14.8
126.7	260	16	0.316	126.3	16.5
132.2	270	19	0.363	132.1	19.4
137.8	280	21	0.416	137.7	22.0
143.3	290	25	0.474	143.0	24.8
148.9	300	28	0.539	148.7	28.1
154.4	310	32	0.610	154.4	31.6
160.0	320	36	0.689	159.9	35.4
165.6	330	40	0.775	165.5	40.2
171.1	340	45	0.870	170.9	44.3
176.7	350	50	0.973	176.3	49.7
182.2	360	56	1.086	181.9	56.0
187.8	370	62	1.208	187.7	62.6
193.3	380	69	1.342	193.1	69.1
198.9	390	77	1.486	198.7	76.0
204.4	400	85	1.641	204.1	83.3
210.0	410	94	1.809	209.7	91.2
215.6	420	103	1.990	215.5	100.8
221.1	430	113	2.183	220.8	108.7
226.7	440	124	2.391	226.5	120.2
232.2	450	135	2.614	231.8	130.7
237.8	460	147	2.851	237.7	142.5
243.3	470	161	3.105	242.9	154.6
248.9	480	174	3.374	248.6	168.8
254.4	490	189	3.661	254.4	184.1
260.0	500	205	3.965	259.7	198.5
265.6	510	222	4.288	265.4	218.3
271.1	520	239	4.629	270.8	235.7
276.7	530	258	4.990	276.6	257.2
282.2	540	278	5.371	282.2	277.9
287.8	550	299	5.773	287.8	301.4
293.3	560	320	6.195	293.0	325.7
296.6	566	334	6.454	296.6	345.4

Evacuation/N₂ purge performed at room temperature, approx 22 °C (ASTM D2879-10, §8.1)
Degassing performed using alcohol lamp (ASTM D2879-10, §8.2)
Pressure determined using digital pressure transducer, 0 - 1000 mm Hg range, 32-bit resolution

Final Degassing Pressure

2.8 torr

Report Prepared by,



Joe Burock, Lab Technician

Report Reviewed by,



Stuart Ramsdale, Lab
Manager

Figure 6. Lab 1 reported ASTM D2879 results for MM fuel oil no. 6.

CERTIFICATE OF ANALYSIS

The University of Texas
CEER, Bldg. 133,
10100 Burnet Rd.
Austin, TX 78758

Report Date: 8/1/2017
Laboratory Number: P170718B2
Sample Type: Liquid
Sample ID: MB-061717-12

Vapor Pressure by Isoteniscope - ASTM D2879

Temperature (°C)	Temperature (°F)	Vapor Pressure - Curve Fit (torr)	Vapor Pressure - Curve Fit (psia)	Vapor Pressure - measured temperature (°C)	Vapor Pressure - measured pressure (torr)
15.6	60	0	0.002		
21.1	70	0	0.003		
26.7	80	0	0.003		
32.2	90	0	0.005	32.0	2.4
37.8	100	0	0.006	37.7	2.4
43.3	110	0	0.008	43.2	2.8
48.9	120	1	0.010	48.6	3.0
54.4	130	1	0.012	54.3	3.4
60.0	140	1	0.016	59.8	3.6
65.6	150	1	0.020	65.2	3.9
71.1	160	1	0.024	70.9	4.0
76.7	170	2	0.030	76.4	4.7
82.2	180	2	0.037	82.1	5.0
87.8	190	2	0.045	87.7	5.9
93.3	200	3	0.054	93.0	6.3
98.9	210	3	0.065	98.8	7.1
104.4	220	4	0.078	104.1	7.2
110.0	230	5	0.092	109.9	8.4
115.6	240	6	0.109	115.2	10.0
121.1	250	7	0.129	121.1	11.1
126.7	260	8	0.151	126.6	12.2
132.2	270	9	0.177	131.9	13.5
137.8	280	11	0.206	137.8	15.1
143.3	290	12	0.238	143.0	16.6
148.9	300	14	0.275	148.8	18.1
154.4	310	16	0.316	154.1	19.8
160.0	320	19	0.362	159.8	22.0
165.6	330	21	0.414	165.5	24.8
171.1	340	24	0.471	170.9	27.0
176.7	350	28	0.534	176.7	30.3
182.2	360	31	0.604	181.9	33.4
187.8	370	35	0.681	187.6	37.4
193.3	380	40	0.766	193.2	41.8
198.9	390	44	0.859	198.7	46.1
204.4	400	50	0.960	204.3	51.2
210.0	410	55	1.071	209.8	56.5
215.6	420	62	1.192	215.4	61.8
221.1	430	68	1.323	220.8	68.7
226.7	440	76	1.465	226.5	75.3
232.2	450	84	1.618	232.2	83.9
237.8	460	92	1.784	237.6	91.9
243.3	470	102	1.963	243.3	101.1
248.9	480	111	2.155	248.7	110.6
254.4	490	122	2.362	254.4	121.6
260.0	500	134	2.583	259.6	133.2
265.6	510	146	2.820	265.3	145.7
271.1	520	159	3.073	271.1	161.1
276.7	530	173	3.343	276.6	175.3
282.2	540	188	3.630	281.8	191.3
287.8	550	204	3.936	287.5	210.8
292.4	558	217	4.205	292.4	228.5

Evacuation/N₂ purge performed at room temperature, approx 22 °C (ASTM D2879-10, §8.1)
Degassing performed using alcohol lamp (ASTM D2879-10, §8.2)
Pressure determined using digital pressure transducer, 0 - 1000 mm Hg range, 32-bit resolution

Final Degassing Pressure

2.2 torr

Report Prepared by,



Joe Burck, Lab Technician

Report Reviewed by,



Stuart Ramsdale, Lab
Manager

Figure 7. Lab 1 reported ASTM D2879 results for MB fuel oil no. 6.

CERTIFICATE OF ANALYSIS

The University of Texas
CEER, Bldg.133,
10100 Burnet Rd.
Austin, TX 78758

Report Date: 8/1/2017
Laboratory Number: P17071803
Sample Type: Liquid
Sample ID: BT-062017-12

Vapor Pressure by Isoteniscopes - ASTM D2879

Temperature (°C)	Temperature (°F)	Vapor Pressure - Curve Fit (torr)	Vapor Pressure - Curve Fit (psia)	Vapor Pressure - measured temperature (°C)	Vapor Pressure - measured pressure (torr)
15.6	60	0	0.005		
21.1	70	0	0.007		
26.7	80	0	0.009	26.6	1.1
32.2	90	1	0.012	32.1	2.5
37.8	100	1	0.016	37.7	2.5
43.3	110	1	0.020	42.8	2.5
48.9	120	1	0.025	48.5	3.8
54.4	130	2	0.032	54.3	3.8
60.0	140	2	0.039	59.7	4.6
65.6	150	3	0.049	65.4	5.4
71.1	160	3	0.060	70.7	5.4
76.7	170	4	0.073	76.4	6.8
82.2	180	5	0.088	82.1	7.2
87.8	190	6	0.107	87.2	9.6
93.3	200	7	0.128	93.2	10.7
98.9	210	8	0.152	98.9	11.7
104.4	220	9	0.181	104.4	14.4
110.0	230	11	0.213	109.7	16.0
115.6	240	13	0.250	115.3	17.2
121.1	250	15	0.293	121.1	19.3
126.7	260	18	0.341	126.3	22.2
132.2	270	20	0.395	131.9	25.3
137.8	280	24	0.456	137.5	28.7
143.3	290	27	0.525	143.2	31.1
148.9	300	31	0.601	148.7	34.5
154.4	310	36	0.687	154.2	38.6
160.0	320	40	0.781	159.6	44.1
165.6	330	46	0.886	165.2	48.3
171.1	340	52	1.002	171.0	53.0
176.7	350	58	1.130	176.7	58.9
182.2	360	66	1.270	182.1	65.9
187.8	370	74	1.423	187.7	74.5
193.3	380	82	1.591	193.1	82.9
198.9	390	92	1.774	198.4	90.7
204.4	400	102	1.973	204.3	100.9
210.0	410	113	2.188	209.6	109.8
215.6	420	125	2.422	215.2	121.1
221.1	430	138	2.674	221.0	137.3
226.7	440	152	2.947	226.4	150.0
232.2	450	168	3.240	232.0	166.4
237.8	460	184	3.555	237.6	180.1
243.3	470	201	3.892	243.2	201.2
248.9	480	220	4.254	248.6	219.1
254.4	490	240	4.640	254.3	241.3
260.0	500	261	5.053	259.6	256.5
265.6	510	284	5.492	265.4	286.3
271.1	520	308	5.960	270.9	308.6
276.7	530	334	6.456	276.4	331.3
282.2	540	361	6.983	282.1	359.8
287.8	550	390	7.541	287.4	386.3
293.3	560	421	8.132	293.2	405.7
298.9	570	453	8.755	298.5	445.2
304.4	580	487	9.414	304.2	482.5
310.0	590	523	10.107	309.7	519.9
315.6	600	560	10.838	315.3	556.7
321.1	610	600	11.606	321.0	586.3
326.7	620	642	12.412	326.3	643.7
332.2	630	686	13.258	332.1	676.4
337.8	640	732	14.145	337.4	722.9
341.1	646	760	14.686	340.9	755.4

Evacuation/N₂ purge performed at room temperature, approx 22 °C (ASTM D2879-10, §8.1)
Degassing performed using alcohol lamp (ASTM D2879-10, §8.2)
Pressure determined using digital pressure transducer, 0 - 1000 mm Hg range, 32-bit resolution

Final Degassing Pressure

2.5 torr

Report Prepared by,



Joe Burock, Lab Technician

Report Reviewed by,



Stuart Ramsdale, Lab
Manager

Figure 8. Lab 1 reported ASTM D2879 results for BT fuel oil no. 6.

Savant (Lab 2)

The ASTM D2879 (vapor pressure by isoteniscope) results for three of the study materials and ASTM D323 (Reid vapor pressure) results for all five of the study materials are given in Figures 10 through 15.

Lab 2 reported difficulties in analyzing the fuel oil no. 6 samples using method ASTM D2879 (Kanar 2017), saying that these samples

“are basically still bottoms. They contain a high content of bituminous material. This makes it very difficult to get them into the isoteniscope...the material doesn’t flow well upon heating...very high temperatures are required to get them to flow which then causes separation and coking of the sample which coats the isoteniscope making it difficult if not nearly impossible to see the meniscus in order to balance pressure. The degassing step is problematic for the same reason and has the added difficulty due to separation of the bituminous material from the lighter material owing to the very divergent range in molecular weight distribution. Sample integrity is also an issue because of these difficulties. Owing to great variability in bitumen content, molecular weight distribution, and viscosity, some samples can be less problematic and be tested relatively well, while others are extremely difficult and would yield questionable results at best if they can be tested at all.”

In the end, Lab 2 did not report ASTM D2879 results for the MB or BT fuel oil no. 6 samples, stating that “Due to the inhomogeneity of the samples, we experienced challenges in obtaining reliable data. Despite our attempts, we were only confident in reporting the data on the MM sample” (Dasbach 2017).

References

Dasbach, T. 2017. Savant Labs Operations Manager. Personal Communication. Midland, MI.

Kanar, N. 2017. Savant Labs Marketing and Sales Manager. Personal Communication. Midland, MI.

Figures



A World of Lubrication Understanding

4800 James Savage Road
Midland, MI 48642

989-496-2301

savant@savantgroup.com

SavantLab.com

Savant Laboratory Report	
Report Number	UTX01001-20170801-1 Final
Purchase Order/ Project Reference	2017A22081
Requestor(s)	Jarret Spinhirne Kirsten Rosselot Vince Torres
Requestor(s) Email(s)	spinhirne@mail.utexas.edu ksrosselot@processprofiles.com vmtorres@mail.utexas.edu
Company	University of Texas at Austin, CEER
Billing Address	10100 Burnet Road, Bldg. 133 Austin, TX 78758-4445
Sample Received Date	20170718
Report Date	20170808

Technical Development Report: Not Requested

Quality is the epicenter of all we do. Savant Labs rigorously adheres to ASTM and other industry standard test methods. It is our responsibility to execute the tests within the precision of the method(s). The interpretation and/or any actions considered or taken based on the results is the responsibility of the client. Test results are not a proxy for official licensing processes for lubricants and do not warranty or imply suitability of a lubricant for a specific or general application.



Our laboratory's Quality Management System is ISO 9001:2008 approved and our services are utilized on a global scale. Satisfaction is essential for every customer and our service group is eager to assist. For questions please call 989-496-2301 or email savant@savantgroup.com.



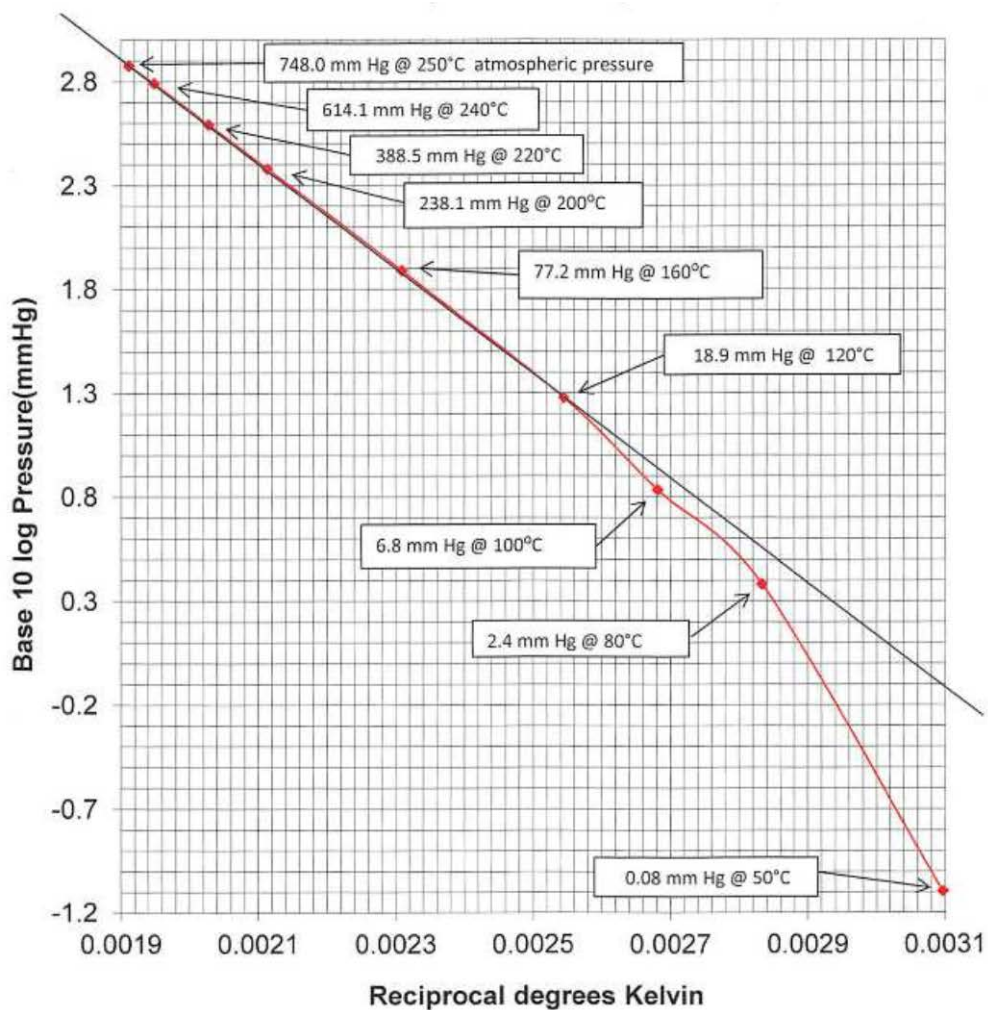
For a copy of the certificate or a complete list of testing that is ISO/IEC 17025:2005 approved, please visit SavantLab.com or email savant@savantgroup.com. Assessment was completed by PJLA for Chemical and Mechanical Tests under Accreditation No. 84229.

Figure 9. Lab 2 reported ASTM D2879 and ASTM D323 results for the “known” recipe and hydraulic fluid (part 1 of 4).

Savant Laboratory Report

Vapor Pressure by Isoteniscope ASTM D2879

Sample ID:	Savant ID:
HY-053017-10 (10 ml vial)	S170718R



Note: Sample degassed at -12.0 mm Hg at -112°C.

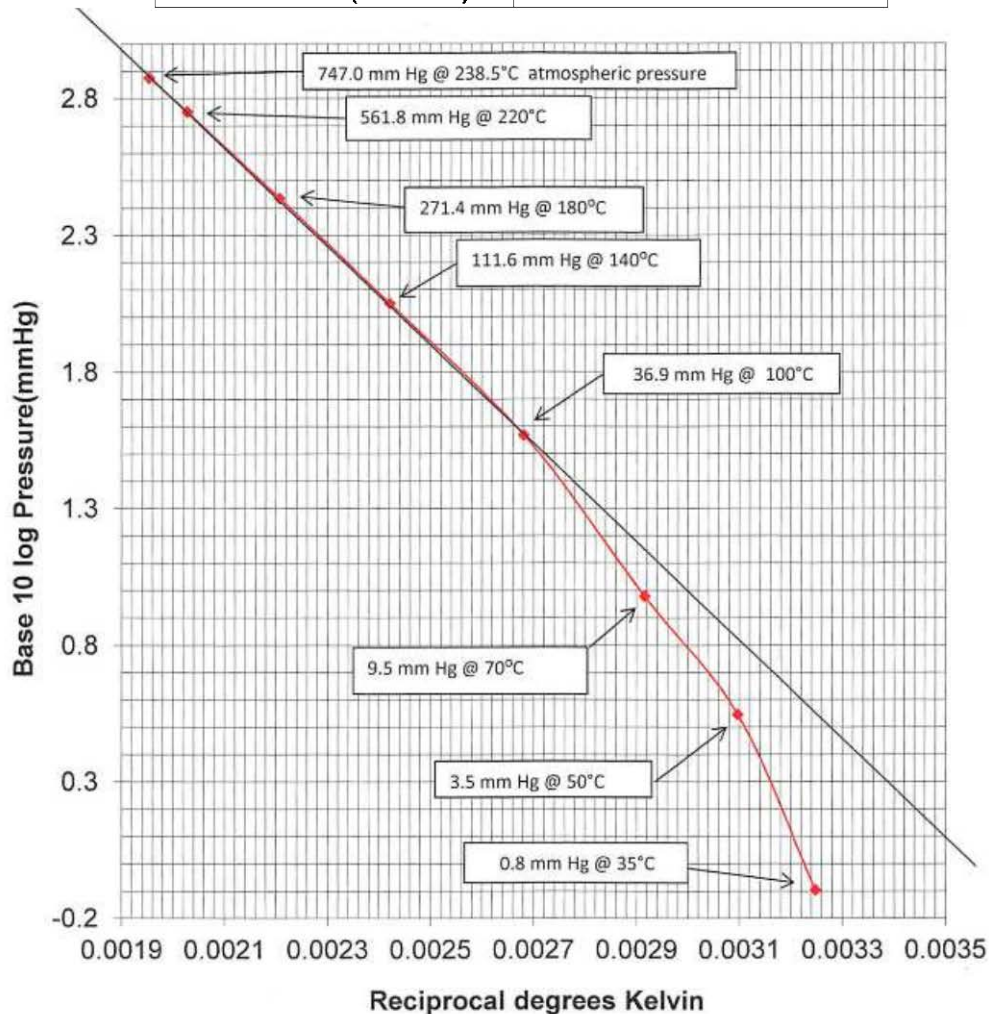
Report Number UTX01001-20170801-1 Final 2 of 4

Figure 10. Lab 2 reported ASTM D2879 and ASTM D323 results for the “known” recipe and hydraulic fluid (part 2 of 4).

Savant Laboratory Report

Vapor Pressure by Isoteniscope ASTM D2879

Sample ID:	Savant ID:
KR-060617-09 (10 ml vial)	S170718S



Note: Sample degassed at -19.0 mm Hg at -112°C.

Report Number UTX01001-20170801-1 Final 3 of 4

Figure 11. Lab 2 reported ASTM D2879 and ASTM D323 results for the “known” recipe and hydraulic fluid (part 3 of 4).

Savant Laboratory Report

Vapor Pressure ASTM D323 Reid Vapor Pressure

Sample ID:	Savant ID:	(psi)
HY-053017-15 (125 ml vial)	S170718T	<0.20
KR-060617-15 (125 ml vial)	S170718U	<0.20

Comments and Observations:

D2879 Comments: A mercury manometer was used for pressure readings above 10 mm Hg with correction multiplier of 0.996 and actual data points are reported on the graphs with no further corrections or extrapolations. A mercury McLeod gauge was used for pressure readings below 10 mm Hg.

Tina Dasbach Ph.D.

Tina Dasbach, Ph.D.
Operations Manager

Report Number UTX01001-20170801-1 Final 4 of 4

Figure 12. Lab 2 reported ASTM D2879 and ASTM D323 results for the “known” recipe and hydraulic fluid (part 4 of 4).



A World of Lubrication Understanding

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Savant Laboratory Report	
Report Number	UTX01001-20170801-2 Updated
Purchase Order/ Project Reference	2017A22081
Requestor(s)	Jarret Spinhirne Kirsten Rosselot Vince Torres
Requestor(s) Email(s)	spinhirne@mail.utexas.edu ksrosselot@processprofiles.com vmtorres@mail.utexas.edu
Company	University of Texas at Austin, CEER
Billing Address	10100 Burnet Road, Bldg. 133 Austin, TX 78758-4445
Sample Received Date	20170718
Report Date	20171009

Technical Development Report: Not Requested

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For a copy of the certificate or a complete list of testing that is ISO/IEC 17025:2005 approved, please visit SavantLab.com or email savant@savantgroup.com. Assessment was completed by PJLA for Chemical and Mechanical Tests under Accreditation No. 84229.

Report Number UTX01001-20170801-2 Updated

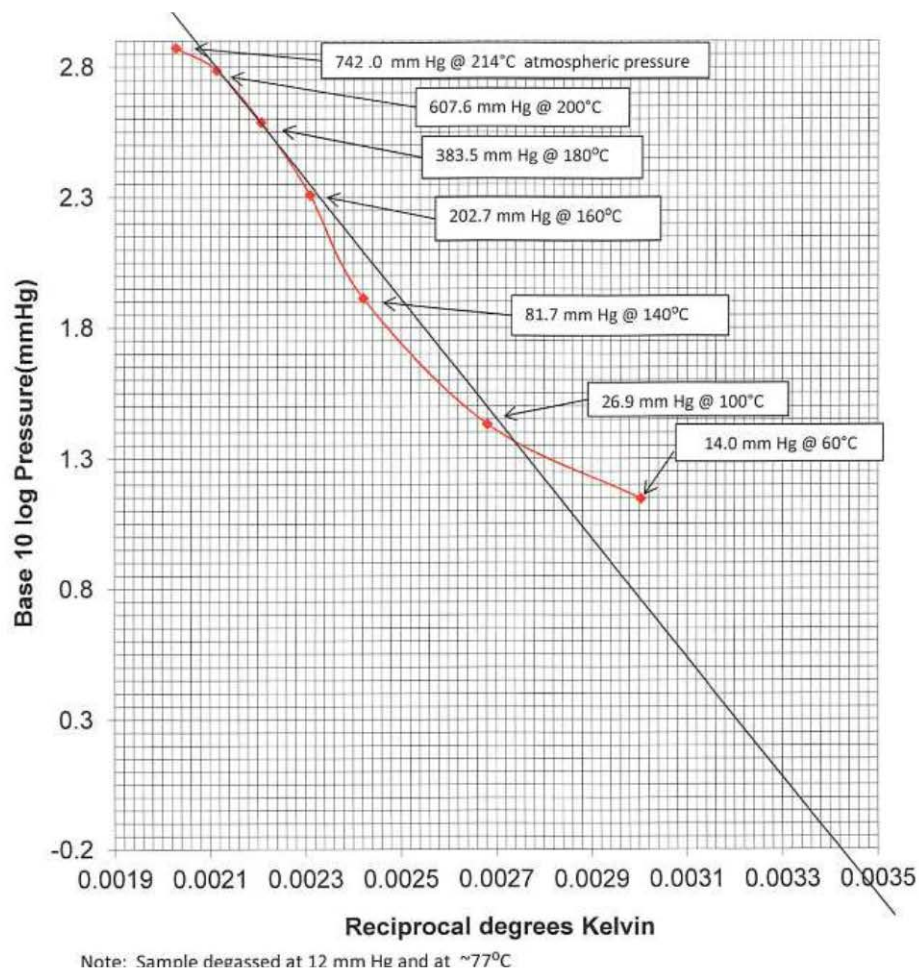
1 of 3

Figure 13. Lab 2 reported ASTM D2879 and ASTM D323 results for the fuel oil no. 6 samples (part 1 of 3).

Savant Laboratory Report

Vapor Pressure by Isoteniscope ASTM D2879

Sample ID:	Savant ID:
MM-060817-10 (10 ml vial)	S170718V



Report Number UTX01001-20170801-2 Updated

2 of 3

Figure 14. Lab 2 reported ASTM D2879 and ASTM D323 results for the fuel oil no. 6 samples (part 2 of 3).

Savant Laboratory Report

Vapor Pressure by Isoteniscope ASTM D2879

Sample ID:	Savant ID:	Results
MB-061717-10 (10 ml vial)	S170718W	Unable to test.
BT-062017-10 (10 ml vial)	S170718X	Unable to test.

Vapor Pressure ASTM D323 Reid Vapor Pressure

Sample ID:	Savant ID:	(psi)
MM-060817-25 (125 ml vial)	S170718Y	<0.20
MB-061717-25 (125 ml vial)	S170718Z	<0.20
BT-062017-23 (125 ml vial)	S170718AA	<0.20

Comments and Observations:

After further attempts, sample S170718V was successfully tested and reported. Unfortunately, S170718W and S170718X were not able to be tested.


Tina Dasbach, Ph.D.
Operations Manager

Figure 15. Lab 2 reported ASTM D2879 and ASTM D323 results for the fuel oil no. 6 samples (part 3 of 3).

Petro-Lubricant Testing Laboratories (Lab 3)

The ASTM D2879 (vapor pressure by isoteniscope) results for all five of the study materials are given in Figures 16 through 22.

Figures

PETRO-LUBRICANT TESTING LABORATORIES, INC.

Member A.S.T.M.

116 Sunset Inn Road
PO Box 300 Lafayette, N.J. 07848
fax 973-579-9447
phone 973-579-3448

September 25, 2017

Test Report 17071804

Page 1 of 2

The University of Texas
CEER
Pickle Research Campus, Building 133
10100 Burnet Road
Austin, TX 78758

ATTN: Mr. Jarett Spinhirne

RE: Your samples of Purchase Order No.:2017A21987

Final Report

Dear Sir.,

Analysis of your samples has been completed. The results are as follows:

SAMPLE: KR-060617-10
Lab # 17071804

<u>TEST METHOD</u>	<u>DESCRIPTION</u>	<u>RESULTS</u>
ASTM D2879	Vapor Pressure by Isoteniscope (60°F to Boiling Point) Multi Point Graph	Graph Attached

SAMPLE: MM-060817-11
Lab # 17071817

<u>TEST METHOD</u>	<u>DESCRIPTION</u>	<u>RESULTS</u>
ASTM D2879	Vapor Pressure by Isoteniscope (60°F to Boiling Point) Multi Point Graph	Graph Attached

SAMPLE: MB-061717-11
Lab # 17071818

<u>TEST METHOD</u>	<u>DESCRIPTION</u>	<u>RESULTS</u>
ASTM D2879	Vapor Pressure by Isoteniscope (60°F to Boiling Point) Multi Point Graph	Graph Attached

Figure 16. Lab 3 reported ASTM D2879 results for all five study materials (part 1 of 7).

PETRO-LUBRICANT TESTING LABORATORIES, INC.

Member A.S.T.M.

116 Sunset Inn Road
PO Box 300 Lafayette, N.J. 07848
fax 973-579-9447
phone 973-579-3448

September 25, 2017 Test Report 17071804
The University of Texas
RE: Your samples of Purchase Order No.:2017A21987

Page 2 of 2

Final Report

SAMPLE: BT-062017-11
Lab # 17071819

<u>TEST METHOD</u>	<u>DESCRIPTION</u>	<u>RESULTS</u>
ASTM D2879	Vapor Pressure by Isoteniscope (60°F to Boiling Point) Multi Point Graph	Graph Attached

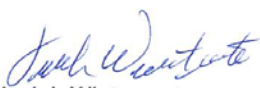
SAMPLE: HY-053017-11
Lab # 17071820

<u>TEST METHOD</u>	<u>DESCRIPTION</u>	<u>RESULTS</u>
ASTM D2879	Vapor Pressure by Isoteniscope (50°F to Boiling Point) Multi Point Graph	Graph Attached

Comments: A mercury manometer was used for pressure readings above 10 mm Hg with correction multiplier of 0.996 and actual data points are reported on the graphs with no further corrections or extrapolations. A mercury McLeod gauge was used for pressure readings below 10 mm Hg.

Please call if you have any questions regarding this report.

Respectfully submitted,


Josiah Wintermute
Chief Chemist

JW:em

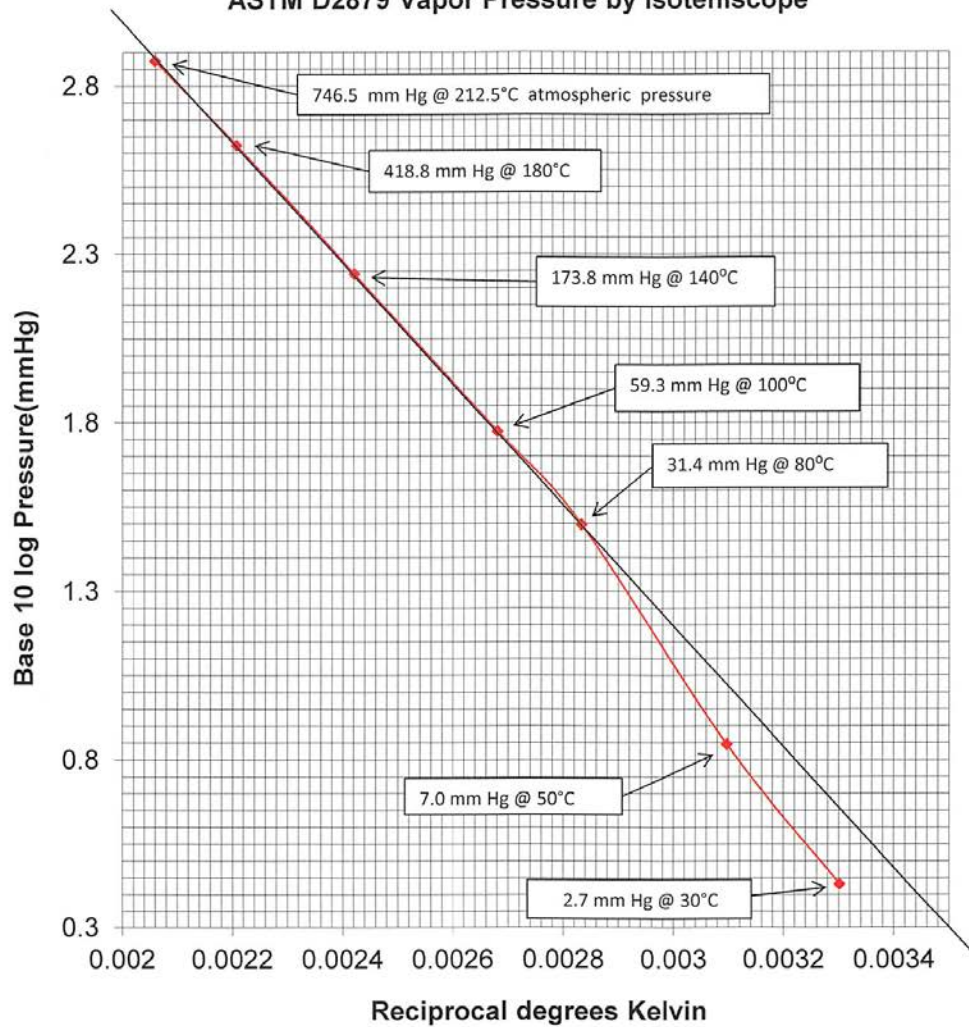
Attachment (5 ASTM D2879 graphs)

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Figure 17. Lab 3 reported ASTM D2879 results for all five study materials (part 2 of 7).

The University of Texas

ASTM D2879 Vapor Pressure by Isoteniscope



Note: sample degassed at 20 mm Hg and at 70°C

Sample: KR060617-10

September 20, 2017

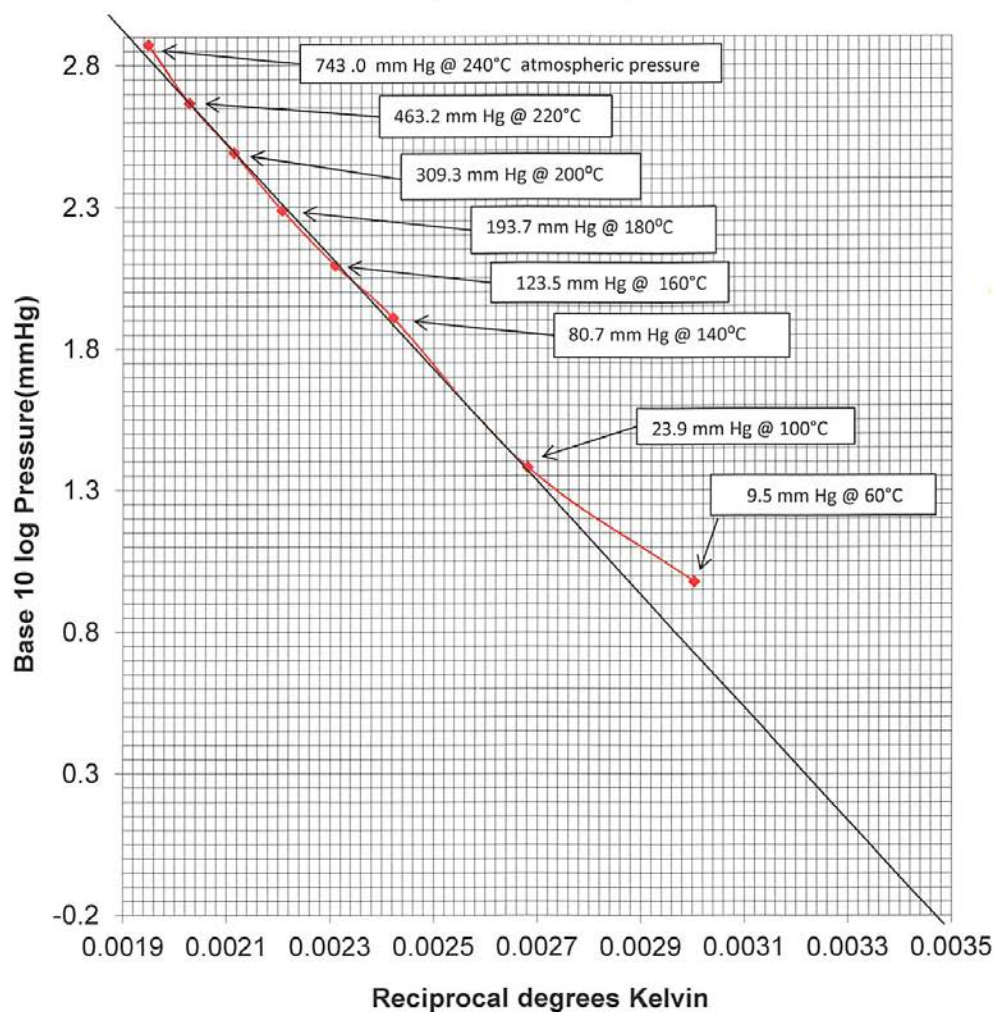
Lab# 17071804

Figure 18. Lab 3 reported ASTM D2879 results for all five study materials (part 3 of 7).

Petro-Lubricant Testing Laboratories, Inc.

The University of Texas

ASTM D2879 Vapor Pressure by Isoteniscope



Note: Sample degassed at 30 mm Hg and at 108°C

Sample: MM-060817-11

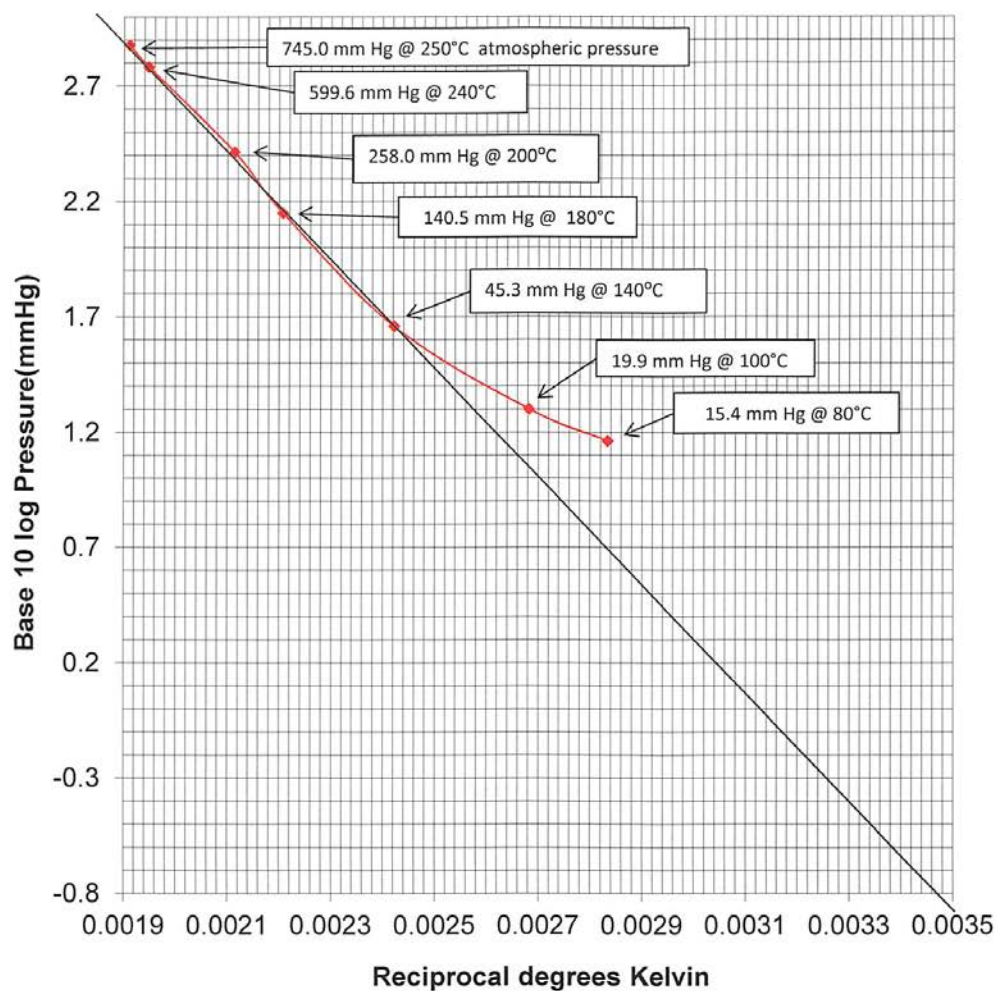
September 20, 2017

Lab# 17071817

Figure 19. Lab 3 reported ASTM D2879 results for all five study materials (part 4 of 7).

Savant

ASTM D2879 Vapor Pressure by Isoteniscope



Note: Sample degassed at 32 mm Hg and at 124°C

Sample: MB-061717-11

September 22, 2017

Lab# 17071818

Figure 20. Lab 3 reported ASTM D2879 results for all five study materials (part 5 of 7).

ASTM D2879 Vapor Pressure by Isotenoscope

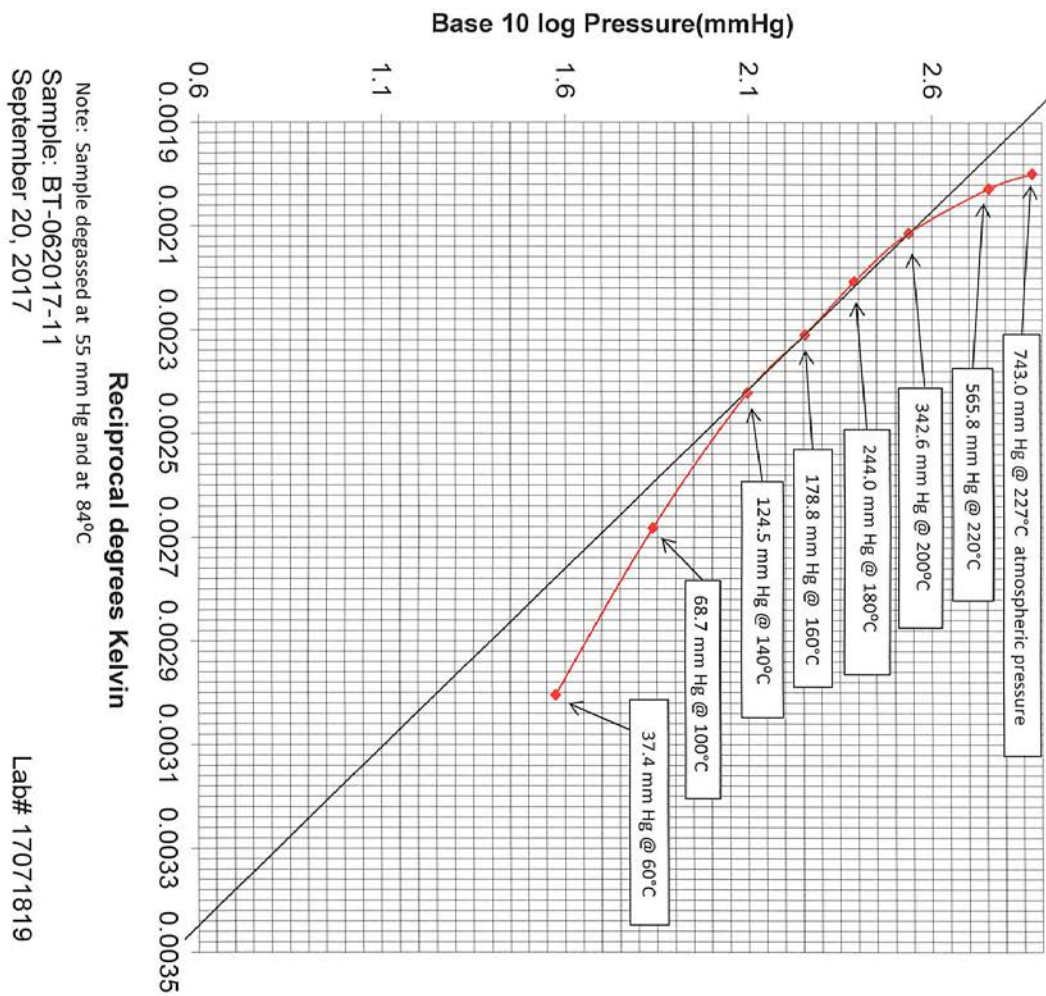
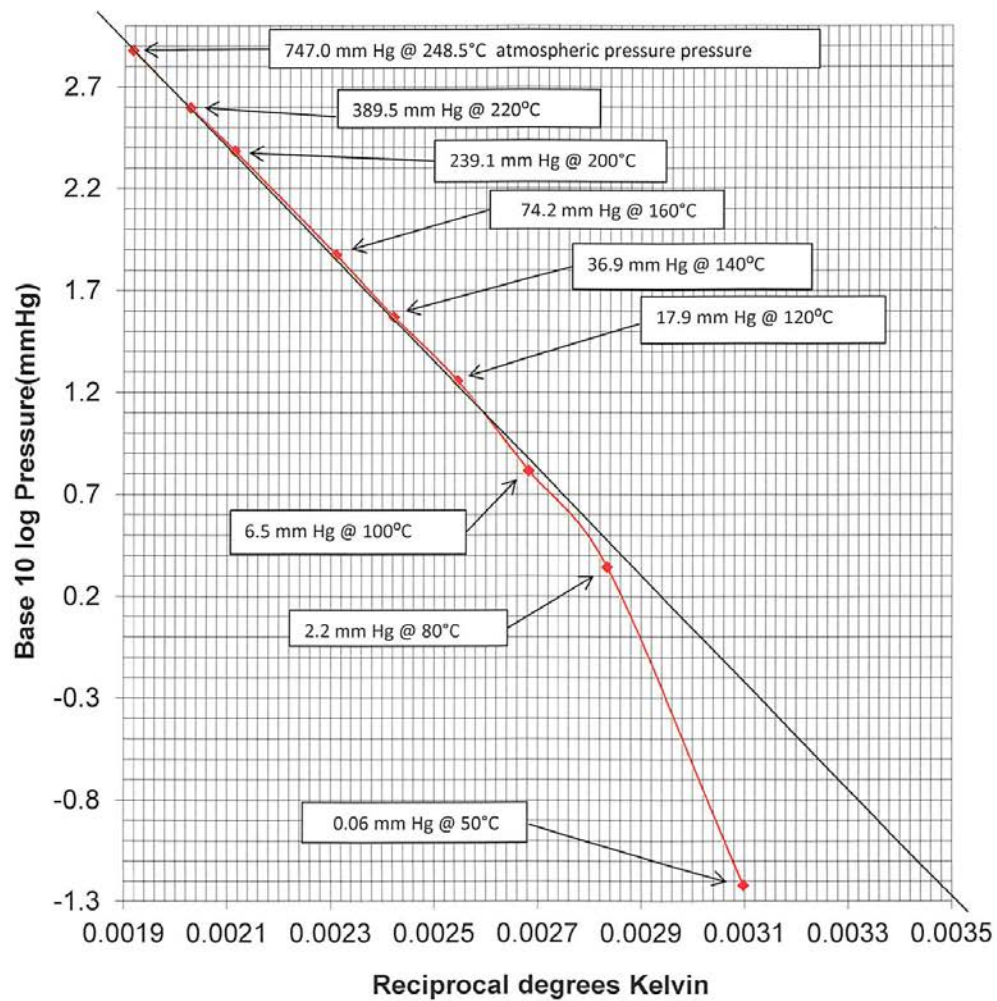


Figure 21. Lab 3 reported ASTM D2879 results for all five study materials (part 6 of 7).

Petro-Lubricant Testing Laboratories, Inc.

University of Texas

ASTM D2879 Vapor Pressure by Isoteniscope



Note: Sample degassed at 8 mm Hg and at 105°C

Sample: HY-053017-11

September 22, 2017

Lab# 17071820

Figure 22. Lab 3 reported ASTM D2879 results for all five study materials (part 7 of 7).

ASTM E1719: Vapor pressure by ebulliometry

The ASTM E1719 (vapor pressure by ebulliometry) results for the five study materials are given in Figures 23 through 27.

Figures



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Correspondence: PO Box 61 Franklin, PA 16323 • Shipping: 190 Howard St. Suite 404 Franklin, PA 16323

August 7, 2017

Jarett Spinhirne
University of Texas Austin
10100 Burnet Rd, Bldg 133
Austin, TX 78758

The following are the results of the analyses performed on the samples submitted.

Reference: ATS Sample ID:..... 104967
UTA ID:..... KR-060617-17

Methodology: ASTM E1719 – Vapor Pressure by Ebulliometry

Linear Regression of $1/T$ vs $\log(P)$

R squared 0.995

Experimental				
Temperature		Pressure kPa		
°C	°K	Exp	Calc	Delta
82.2	355.2	5.73	5.70	0.03
85.0	358.0	6.00	6.07	-0.07
87.2	360.2	6.53	6.38	0.15
92.2	365.2	7.07	7.12	-0.06
96.1	369.1	7.60	7.74	-0.14
98.9	371.9	8.13	8.21	-0.08
101.1	374.1	8.67	8.60	0.07
104.4	377.4	9.20	9.20	0.00
106.7	379.7	9.73	9.62	0.11

Calculated			
Pressure		Temperature	
kPa	torr	C	°K
1.0	7.5	19.6	292.6
10.0	75.0	108.6	381.6
30.0	225.0	173.3	446.3
70.0	525.0	240.5	513.5
101.3	760.0	276.7	549.7
1.0	7.6	20.0	293.0

Data from a 125 ml charge to a Stirred Flask
Ebulliometer

Thank you for the opportunity to be of service to you, and if we can assist you in the future, please feel free to contact us.

Sincerely,

Richard M. Eakin,
President

Reference: Final Report Emailed to Jarett Spinhirne at spinhirne@mail.utexas.edu on Aug-07-2017.

Figure 23. Reported ASTM E1719 results for the “known” recipe.



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August 7, 2017

Jarett Spinhirne
 University of Texas Austin
 10100 Burnet Rd, Bldg 133
 Austin, TX 78758

The following are the results of the analyses performed on the samples submitted.

Reference: ATS Sample ID:..... 104966
 UTA ID:..... HV-053017-17

Methodology: ASTM E1719 – Vapor Pressure by Ebulliometry

Linear Regression of 1/T vs log(P)

R squared 0.982

Experimental				
Temperature		Pressure kPa		
°C	°K	Exp	Calc	Delta
95.0	368.0	3.07	2.97	0.09
101.7	374.7	3.33	3.34	0.00
113.9	386.9	3.87	4.08	-0.21
116.7	389.7	4.27	4.26	0.00
121.7	394.7	4.53	4.61	-0.07
125.6	398.6	4.80	4.88	-0.09
128.3	401.3	5.07	5.09	-0.03
130.0	403.0	5.33	5.22	0.11
132.2	405.2	5.60	5.39	0.21

Calculated			
Pressure		Temperature	
kPa	torr	C	°K
1.0	7.5	42.1	315.1
10.0	75.0	179.7	452.7
30.0	225.0	299.0	572.0
70.0	525.0	444.8	717.8
101.3	760.0	534.7	807.7
0.6	4.2	20.0	293.0

Data from a 125 ml charge to a Stirred Flask
 Ebulliometer

Thank you for the opportunity to be of service to you, and if we can assist you in the future, please feel free to contact us.

Sincerely,

Richard M. Eakin,
 President

Reference: Final Report Emailed to Jarett Spinhirne at spinhirne@mail.utexas.edu on Aug-07-2017.

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 Samples are retained thirty (30) days.

Figure 24. Reported ASTM E1719 results for the hydraulic fluid.



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August 7, 2017

Jarett Spinhirne
 University of Texas Austin
 10100 Burnet Rd, Bldg 133
 Austin, TX 78758

The following are the results of the analyses performed on the samples submitted.

Reference: ATS Sample ID:..... 104970
 UTA ID:..... MM-060817-27

Methodology: ASTM E1719 – Vapor Pressure by Ebulliometry

Linear Regression of 1/T vs log(P)

R squared 0.973

Experimental				
Temperature		Pressure kPa		
°C	°K	Exp	Calc	Delta
155.0	428.0	4.67	4.43	0.23
167.2	440.2	5.33	5.33	0.00
176.7	449.7	5.73	6.11	-0.37
182.2	455.2	6.40	6.60	-0.20
187.2	460.2	6.93	7.06	-0.13
192.2	465.2	7.47	7.55	-0.08
196.7	469.7	8.00	8.00	0.00
200.0	473.0	8.53	8.34	0.19
202.8	475.8	9.07	8.64	0.42

Calculated			
Pressure		Temperature	
kPa	torr	C	°K
1.0	7.5	76.7	349.7
10.0	75.0	214.7	487.7
30.0	225.0	327.8	600.8
70.0	525.0	458.7	731.7
101.3	760.0	535.6	808.6
0.2	1.6	20.0	293.0

Data from a 125 ml charge to a Stirred Flask
 Ebulliometer

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Sincerely,

Richard M. Eakin,
 President

Figure 25. Reported ASTM E1719 results for the MM fuel oil no. 6.



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August 7, 2017

Jarett Spinhirne
 University of Texas Austin
 10100 Burnet Rd, Bldg 133
 Austin, TX 78758

The following are the results of the analyses performed on the samples submitted.

Reference: ATS Sample ID:..... 104969
 UTA ID:..... MB-061717-28

Methodology: ASTM E1719 – Vapor Pressure by Ebulliometry

Linear Regression of 1/T vs log(P)

R squared 0.972

Experimental				
Temperature		Pressure kPa		
°C	°K	Exp	Calc	Delta
136.7	409.7	3.07	2.85	0.22
152.8	425.8	3.60	3.69	-0.09
162.8	435.8	4.13	4.30	-0.16
172.8	445.8	4.67	4.96	-0.30
179.4	452.4	5.20	5.44	-0.24
184.4	457.4	5.73	5.83	-0.09
188.9	461.9	6.27	6.18	0.09
193.3	466.3	6.80	6.55	0.25
197.2	470.2	7.33	6.88	0.45

Calculated			
Pressure		Temperature	
kPa	torr	C	°K
1.0	7.5	82.3	355.3
10.0	75.0	228.7	501.7
30.0	225.0	351.4	624.4
70.0	525.0	496.6	769.6
101.3	760.0	583.5	856.5
0.2	1.4	20.0	293.0

Data from a 125 ml charge to a Stirred Flask
 Ebulliometer

Thank you for the opportunity to be of service to you, and if we can assist you in the future, please feel free to contact us.

Sincerely,

Richard M. Eakin,
 President

Reference: Final Report Emailed to Jarett Spinhirne at spinhirne@mail.utexas.edu on Aug-07-2017.

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Figure 26. Reported ASTM E1719 results for the MB fuel oil no. 6.



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August 7, 2017

Jarett Spinhirne
 University of Texas Austin
 10100 Burnet Rd, Bldg 133
 Austin, TX 78758

The following are the results of the analyses performed on the samples submitted.

Reference: ATS Sample ID:..... 104968
 UTA ID:..... BT-062017-24

Methodology: ASTM E1719 – Vapor Pressure by Ebulliometry

Linear Regression of 1/T vs log(P)

R squared 0.986

Experimental				
Temperature		Pressure kPa		
°C	°K	Exp	Calc	Delta
136.7	409.7	3.07	2.94	0.12
147.8	420.8	3.60	3.58	0.02
157.8	430.8	4.13	4.23	-0.09
167.2	440.2	4.67	4.91	-0.24
173.3	446.3	5.20	5.39	-0.19
178.9	451.9	5.73	5.86	-0.13
182.8	455.8	6.27	6.21	0.06
186.7	459.7	6.80	6.56	0.24
191.7	464.7	7.33	7.04	0.29

Calculated			
Pressure		Temperature	
kPa	torr	C	°K
1.0	7.5	84.3	357.3
10.0	75.0	218.1	491.1
30.0	225.0	325.0	598.0
70.0	525.0	445.6	718.6
101.3	760.0	514.9	787.9
0.2	1.2	20.0	293.0

Data from a 125 ml charge to a Stirred Flask
 Ebulliometer

Thank you for the opportunity to be of service to you, and if we can assist you in the future, please feel free to contact us.

Sincerely,

Richard M. Eakin,
 President

Reference: Final Report Emailed to Jarett Spinhirne at spinhirne@mail.utexas.edu on Aug-07-2017.

These services are rendered without any warranty or liability, since they are based on sample and information supplied by others.
 Samples are retained thirty (30) days.

Figure 27. Reported ASTM E1719 results for the BT fuel oil no. 6.

Characterization of the fuel oil no. 6 samples

In addition to performing ASTM D2879 analyses of all five study materials, Lab 3 conducted analyses of sulfur content, water content, flash point, and viscosity on the fuel oil no. 6 samples. The results are shown in Table 15.

In addition to the values in Table 15, results from analyses of the BT sample conducted by Inspectorate on March 31, 2017 were provided to the study team. An image of the reported values for these analyses is provided in Figure 28.

References

Almaraz, P. 2017. Kinder Morgan General Manager – Gulf Central Region. Personal communication.

ASTM International (ASTM), 2016. ASTM D396-16, Standard Specification for Fuel Oils. West Conshohocken, PA, www.astm.org.

Tables and figures

Table 15. Characterization of fuel oil no. 6 samples (conducted by Lab 3).

Method	Result			Fuel oil no. 6 specification (ASTM 2016)
	MM fuel oil no. 6	MB fuel oil no. 6	BT fuel oil no. 6	
ASTM D93 Standard Test Methods for Flash Point by Pensky-Martens Closed Cup Tester (Procedure B)	84.5°C	102.5°C	96.5°C	≥60°C
ASTM D445 Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity) (at 100°C)	28.08 cSt	51.63 cSt	31.60 cSt	≥15.0 mm ² /s and ≤50 mm ² /s
ASTM D95 Standard Test Method for Water in Petroleum Products and Bituminous Materials by Distillation	0.00 volume %	0.00 volume %	0.12 volume %	Water by ASTM D95 plus sediment by ASTM D473: ≤2.00% by volume with sediment by ASTM D473 ≤.50% by mass
ASTM D2622 Standard Test Method for Sulfur in Petroleum Products by Wavelength Dispersive X-ray Fluorescence Spectrometry	157 ppm (by mass)	842 ppm (by mass)	25,331 ppm (by mass)	Not specified

<u>Method</u>	<u>Test</u>	<u>Result</u>	<u>Units</u>
ASTM D4052	Gravity by Digital Density Meter		
	API Gravity @60°F	11.3	°
	Density @15°C	990.3	kg/m³
ASTM D445	Kinematic Viscosity @122°F/50°C	340.6	cSt
ASTM D4294	Total Sulfur Content	2.51	%wt
ASTM D93B	Flash Point (Fuel Oil)	> 230	°F
ASTM D97	Pour Point	21.2	°F (calc)
ASTM D95	Water % (V/m)	0.20	% v/m
ASTM D1796	Water and Sediment	0.05	
ASTM D482	Ash Content	0.090	mass%
ASTM D4530	Micro Method Carbon Residue	12.6	%wt
ASTM D4740	Cleanliness Rating	1	
IP501	Aluminum Content	33	ppmw
IP501	Silicon Content	40	ppmw
IP501	Aluminum + Silicon Content	73	ppmw
IP501	Vanadium Content	202	ppmw
IP501	Sodium Content	29	ppmw
IP501	Calcium Content	20	ppmw
IP501	Zinc Content	6	ppmw
IP501	Phosphorus Content	16	ppmw

Figure 28. Results of analyses of the BT fuel oil no. 6 sample conducted by Inspectorate on March 31, 2017 (Almaraz, 2017).

5. Analysis of Measurements

In this section, the vapor pressure results from the commercial laboratories and mini method instruments for the five study materials are summarized, compared, and displayed graphically.

“Known” recipe

As described in an earlier section of the report, the vapor pressure of the “known” recipe (a mixture of 20 mol % octane and 80 mol % nonadecane) can be modeled and the recipe was selected such that the modeled vapor pressure is expected to provide similar results regardless of which model is used or which sources of vapor pressure information on the ingredients are used. This makes the “known” recipe an interesting test case for the various methods. This mixture has a low vapor pressure and is a solid unless slightly above room temperature, but it is otherwise unlike heavy refinery liquids. For example, once melted, it is clear, not viscous, and not sticky. These qualities made it easier to handle and analyze than the fuel oil no. 6 samples.

As Figure 29 shows, the vapor pressure of the “known” recipe was measured using both makes of mini method instruments. It was also measured using ASTM D2879 (vapor pressure by isoteniscope) at three commercial labs, using ASTM E1719 (vapor pressure by ebulliometry) at one lab, and using ASTM D323 (Reid vapor pressure) at one lab. The y-axis in this figure is on a logarithmic scale and the entire range of values provided by commercial labs is given.

The black dashed line is the vapor pressure of the mixture as modeled using the Soave-Redlich-Kwong equation of state and version 7.15 of ChemSep Lite (Kooijman and Taylor, 2016), using the default models for physical properties. There is uncertainty in the vapor pressure of the mixture and this black dashed line represents only one of several methods for estimating the mixture’s vapor pressure. As explained in the section about determining the “known” recipe, the expectation is that the true vapor pressure of the mixture is probably within 10% of the values used to construct the black dashed line.

The gold, yellow, and orange lines are the ASTM D2879 (vapor pressure by isoteniscope) results for three commercial labs, which are presented as measurements (large circular markers connected by a thin line) and calculated values (dotted lines). The red lines represent results from ASTM E1719 (vapor pressure by ebulliometry). The open green circular markers are the low VP single point readings from the Eralytics instrument, and the blue line and blue circles are from Grabner multipoint ASTM D6378 readings and Grabner VOC single point readings, respectively. “First” Grabner refers to the first Grabner instrument used in the project and “second” Grabner is the second instrument.

Figure 29 shows that along with the Eralytics instrument’s results from the low VP single point method and the ASTM D2879 results produced by Lab 3, the Grabner ASTM D6378 multipoint curve (obtained on the first instrument) and single point VOC method results

(obtained on the second instrument) are in good agreement with modeled expectations at the higher temperature readings for this material. Note that lab 3 is the only lab that is accredited for ASTM D2879. The curve obtained using ASTM E1719 is flatter than any of the ASTM D2879 curves; this phenomenon was noted for all of the study materials. A discussion of the technique used to obtain the curves for ASTM D2879 and ASTM E1719 is included in section 6.

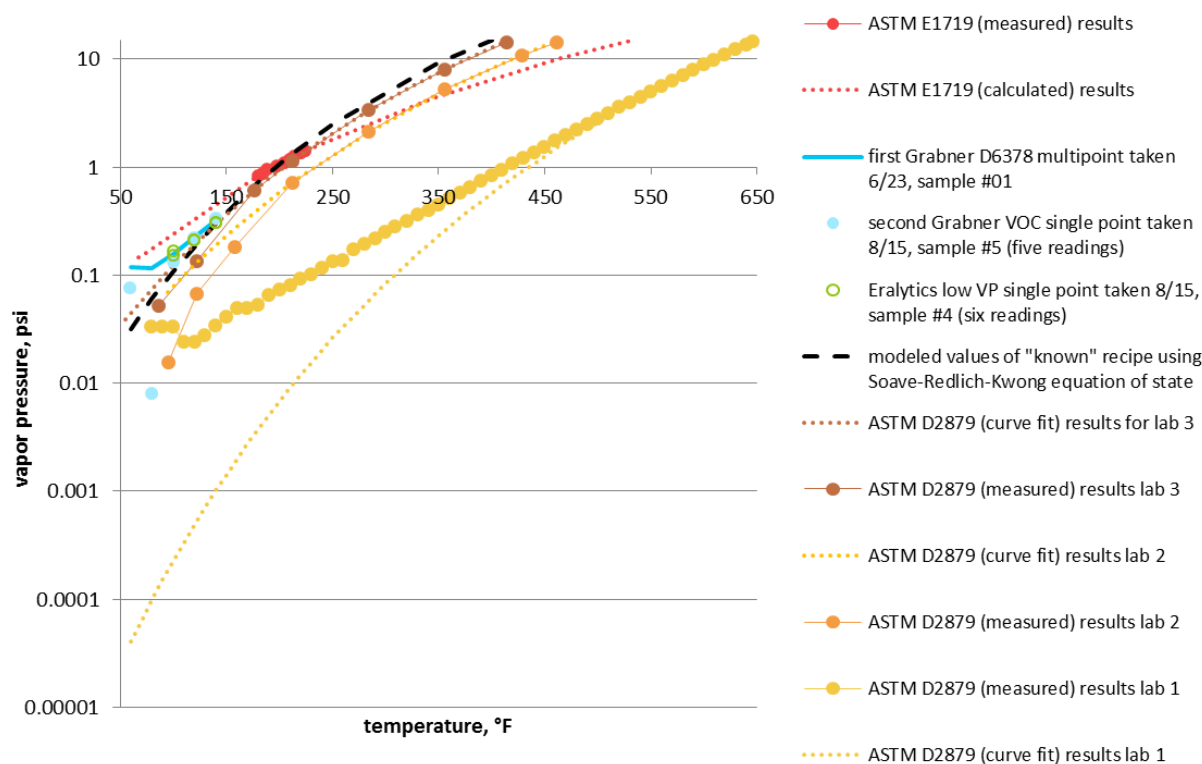
Figure 30 allows a closer look at the “known” recipe results for all of the methods at temperatures that are most representative of the temperature region of interest when estimating emissions from storage tanks holding heavy refinery fluids (fuel oil no. 6 is typically held at 120°F and liquid asphalt is typically held at 200°F). The color scheme is as before. The second single point VOC method measurement taken for the “known” recipe on the Grabner instrument, at 80°F, returned a result that was much lower than the neighboring values at 60°F and 100°F. The agreement of the Grabner readings with the modeled expectations is better at higher temperatures, where the vapor pressure readings are higher.

Figure 30 shows that in this temperature range, there were no instances where a measured vapor pressure using ASTM D2879 by any of the three commercial labs that applied this method exceeded the modeled vapor pressure.

The ASTM D323 result for the “known” recipe was < 0.2 psi. This method measures the vapor pressure of a water- and air-saturated sample at 100°F, and the results from ASTM D323 are expected to be higher than results from the other methods at 100°F. The only method that returned a value higher than 0.2 psi at 100°F for the “known” recipe was the calculated result for ASTM E1719.

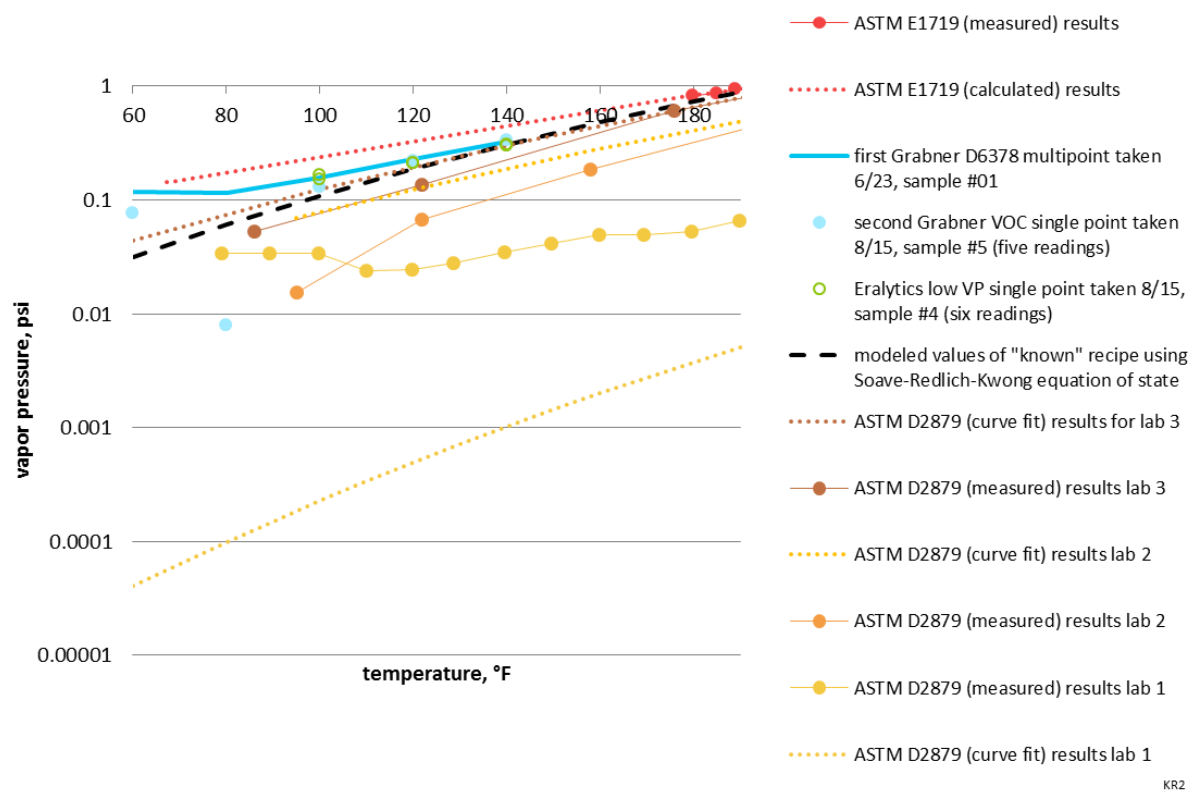
The mini method and commercial lab results for the “known” recipe are tabulated in Table 16. This table shows that of the results produced by commercial laboratories (both ASTM D2879 and ASTM E1719), the best agreement with modeled expectations for vapor pressure were the results for ASTM D2879 (vapor pressure by isoteniscope) from Lab 3 and the poorest agreement were the results for ASTM D2879 from Lab 1. The mini method instrument results show better agreement with modeled expectations for vapor pressure at the higher temperatures of the small temperature range over which they were conducted. Most of the measured values for ASTM E1719 (vapor pressure by ebulliometry) were within 10% of the modeled values.

Figures and tables



KR1

Figure 29. The full range of measured and reported vapor pressure values for the “known” recipe. For the Grabner D6378 multipoint method, the values presented are the average after omitting the first injection of each syringe, per the instrument manufacturer’s instructions.



KR2

Figure 30. "Known" recipe vapor pressure values from 60°F to 190°F. For the Grabner D6378 multipoint method, the values presented are the average after omitting the first injection of each syringe, per the instrument manufacturer's instructions.

Table 16. Modeled values along with mini method and commercial lab vapor pressure results for the “known” recipe, psi. The darkest green cells agree with the modeled value to within 10%, the medium green cells agree to within 30%, and the light green agree to within 90%.

Temperature, °F	Modeled values using Soave-Redlich-Kwong	Mini method instruments			ASTM D2879 (vapor pressure by isoteniscope)						ASTM E1719 (vapor pressure by ebulliometry)		ASTM D323 (Reid vapor pressure)
		First Grabner ASTM D6378 multipoint taken 6/23, sample #01 ^a	Second Grabner VOC single point taken 8/15, sample #5 (five readings)	Eralytics low VP single point taken 8/15, sample #4 (six readings)	Lab 1 ^b measured	Lab 1 curve fit	Lab 2 measured	Lab 2 curve fit	Lab 3 measured	Lab 3 curve fit	Measured	Curve fit	
60	0.032	0.12	0.076			0.000040		0.028		0.045		0.13	
79	0.058				0.034	0.000095		0.047		0.074		0.18	
80	0.060	0.12	0.008			0.000099		0.048		0.076		0.18	
86	0.072					0.00013		0.056	0.052	0.089		0.20	
95	0.094					0.00019	0.015	0.069		0.11		0.24	
100	0.11	0.16	0.13	0.15	0.034	0.00023		0.078		0.12		0.26	<0.2
100.04	0.11			0.16		0.00023		0.079		0.13		0.26	
120	0.19	0.23	0.22	0.21 0.21	0.024	0.00049		0.12		0.20		0.36	
122	0.19					0.00053	0.068	0.13	0.14	0.21		0.37	
140	0.30	0.32	0.34	0.30 0.30	0.034	0.0010		0.19		0.30		0.48	
158	0.46					0.0019	0.18	0.27		0.43		0.62	
160	0.48				0.049	0.0020		0.29		0.45		0.64	
176	0.67					0.0033		0.39	0.61	0.61		0.79	
180	0.73				0.053	0.0038		0.42		0.66	0.83	0.83	
185	0.80					0.0044		0.45		0.72	0.87	0.88	
189	0.87					0.0049		0.49		0.77	0.95	0.93	
198	1.0					0.0064		0.57		0.90	1.0	1.0	
200	1.1				0.074	0.0068		0.59		0.93		1.1	
205	1.2					0.0079		0.64		1.0	1.1	1.1	
210	1.3				0.082	0.0090		0.70		1.1	1.2	1.2	
212	1.3					0.0096	0.71	0.72	1.1	1.1		1.2	
214	1.4					0.010		0.75		1.2	1.3	1.3	
220	1.5					0.012		0.83		1.3	1.3	1.3	
224	1.6					0.013		0.88		1.4	1.4	1.4	
250	2.5				0.14	0.026		1.3		2.1		1.9	
284	4.1					0.058	2.2	2.1	3.4	3.3		2.6	
350	9.3				0.45	0.23		4.8		7.5		4.6	
356	10					0.26	5.2	5.2	8.1	8.0		4.8	

Temperature, °F	Modeled values using Soave- Redlich- Kwong	Mini method instruments			ASTM D2879 (vapor pressure by isoteniscope)						ASTM E1719 (vapor pressure by ebulliometry)		ASTM D323 (Reid vapor pressure)
		First Grabner ASTM D6378 multipoint taken 6/23, sample #01 ^a	Second Grabner VOC single point taken 8/15, sample #5 (five readings)	Eralytics low VP single point taken 8/15, sample #4 (six readings)	Lab 1 ^b measured	Lab 1 curve fit	Lab 2 measured	Lab 2 curve fit	Lab 3 measured	Lab 3 curve fit	Measured	Curve fit	
414.5	18					0.73		9.5	14.43	15		7.3	
428	20					0.90	11	11		17		8.0	
449	24				1.6	1.3		13		20		9.2	
450	24					1.3		13		21		9.3	
461.3	27					1.5	14	14.7		23		9.9	
550	50				5.1	5.0		30		46		16	
646	88				14.71	14.7		57		88		26	
650	90					15		58		90		26	

Note: VP=vapor pressure; VOC=volatile organic compound

^aThese values are the average omitting the first injection of each syringe.

^bLab 1 provided vapor pressure measurements at 58 temperatures, only a sampling is given in this table.

Hydraulic fluid

Castrol's Brayco Micronic 756 was selected as a study material for the project because it has a very low vapor pressure and the manufacturer documents its vapor pressure across a range of temperatures from -65°F to 300°F (Castrol 2000). A Castrol representative stated that the method used to produce the vapor pressure results was ASTM D2879 (vapor pressure by isoteniscope) (Haspert 2016). While there is no gold standard method for measuring the vapor pressure of a mixture, and thus no means of verifying the accuracy of the vapor pressure results published by Castrol, this material represents an interesting opportunity for comparison between the methods.

While this material has a low vapor pressure, it has a kinematic viscosity of 13.2 cSt at 40°C, so it is much less viscous than fuel oil no. 6. Also, it is not sticky. Like the "known" recipe, it is easier to analyze for vapor pressure than the fuel oil no. 6 samples.

The vapor pressure of the hydraulic fluid was measured using both makes of mini method instruments but the measurements made using the Eralytics instrument had to be abandoned because they were taken using the instrument's D6378 curve and Low VP curve methods and there was an error in the instrument's algorithms for the curve methods. (Here, the word "curve" is Eralytics' nomenclature for a variation of ASTM D6378 that allows the contribution of dissolved air at one temperature to be based on the contribution of dissolved air at another temperature and the ideal gas law, as described in ASTM 2010 Appendix X2. It corresponds to what Grabner calls "multi point" methods and does not involve fitting a curve to data.) It was also measured using ASTM D2879 at three commercial labs, using ASTM E1719 (vapor pressure by ebulliometry) at one lab, and using ASTM D323 (Reid vapor pressure) at one lab.

Figure 31 shows the full range of vapor pressure values obtained for hydraulic fluid along with all of the manufacturer-reported results and the results from the Grabner mini method instrument. As with the "known" recipe, the y-axis in this figure is on a logarithmic scale. Also, the color scheme is the same as for the "known" recipe charts except that the black dashed line represents the manufacturer's vapor pressure results.

Figure 31 shows that the vapor pressure results produced by the commercial laboratories (all labs conducting ASTM D2879 as well as ASTM E1719) appear to converge in the vicinity of 300°F. The curve result from ASTM E1719 has a smaller slope than the ASTM D2879 slopes from any of the labs.

Figure 31 is meant to show the full range of all the results, but because of the spread of temperature and vapor pressure for this material, it is difficult to make out how the methods compare from this chart. Figure 32 shows a close-up for a more restricted range of temperature. The axes in Figure 32 match the axes of Figure 30; each of the materials is plotted on these axes in order to show how the cluster of readings for the different methods compare across the different study materials.

Figure 32 shows that the vapor pressure values from the curve methods for ASTM D2879 from all the commercial labs are in very good agreement with each other and are about 1.5 to ten times higher than the manufacturer's values, with less agreement at lower temperatures. The Grabner multipoint ASTM D6378 values and the ASTM E1719 calculated results are also in good agreement with each other, but not with the ASTM D2879 results. They are also higher than the manufacturer's values, from several hundred times higher at the lowest temperatures that can be compared to seven times higher at the highest temperature values from the Grabner instrument and 1.5 times higher for the E1719 calculated results at 300°F.

The ASTM D323 result for the hydraulic fluid was < 0.2 psi. This method measures the vapor pressure of a water- and air-saturated sample at 100°F, and the results from ASTM D323 are expected to be higher than results from the other methods at 100°F. None of the study methods returned a value higher than 0.2 psi at 100°F for the hydraulic fluid.

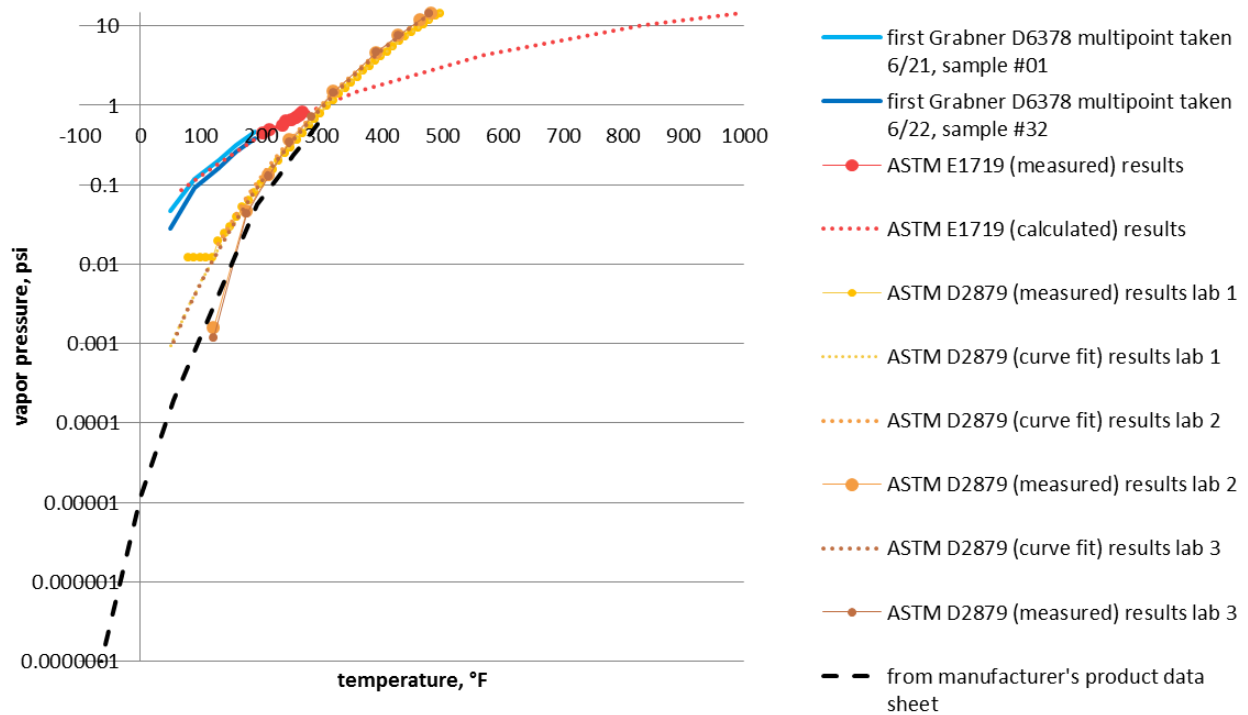
References

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Castrol Industrial North America Inc. 2000. Castrol Brayco® Micronic 756 Product Data Sheet. Downers Grove, IL.

Haspert, J. 2016. Castrol Senior Corporate Engineer/Chemist. Personal communication. Naperville, IL.

Figures



HY1

Figure 31. The full range of measured and reported vapor pressure values for the hydraulic fluid. For the Grabner D6378 multipoint method, the values presented are the average after omitting the first injection of each syringe, per the instrument manufacturer's instructions.

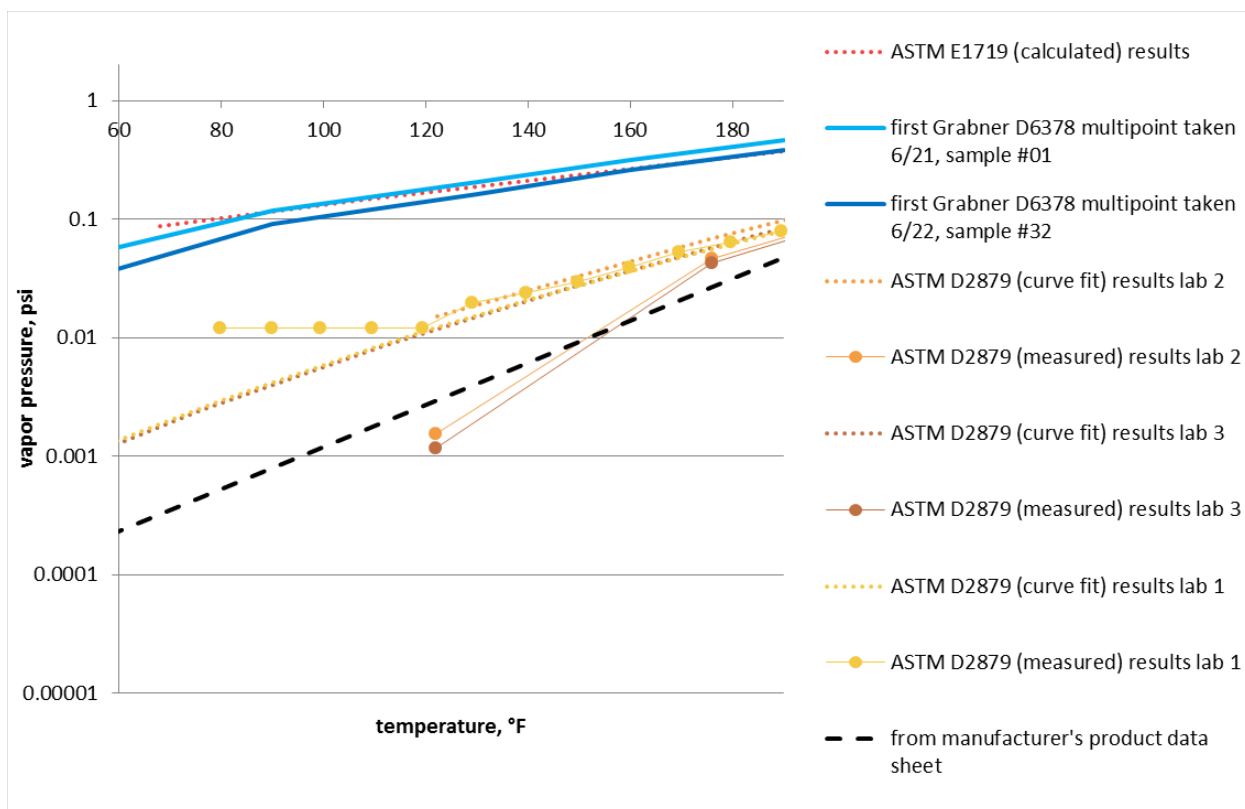


Figure 32. Hydraulic fluid vapor pressure values from 60°F to 190°F. For the Grabner D6378 multipoint method, the values presented are the average after omitting the first injection of each syringe, per the instrument manufacturer's instructions.

Fuel oil no. 6

Results of ASTM D2879 from two labs for two of the fuel oil no. 6 samples and from three labs for the remaining fuel oil no. 6 sample, ASTM E1719 results for all three samples, and single point VOC method readings from the Eralytics instrument for all three samples are given in this section, along with the default vapor pressure for fuel oil no. 6 from API Chapter 19.4 (API 2012).

Note that the second Grabner instrument broke down before it could be used to analyze any fuel oil no. 6 samples. Also, as described in the results section of this report, Lab 2 reported difficulties in analyzing the fuel oil no. 6 samples using method ASTM D2879 and ultimately only provided results for MM fuel oil no. 6.

MM fuel oil no. 6

Figure 33 shows the entire range of vapor pressure values for MM fuel oil no. 6 from the commercial labs and from the Eralytics mini method instrument. The color scheme is the

same as for the “known” recipe and hydraulic fluid charts except that the black dashed line represents the default vapor pressure for fuel oil no. 6 from API Chapter 19.4 (API 2012).

The ASTM D2879 results from Labs 2 and 3 seem to be in fairly good agreement with each other but generally fall nearly an order of magnitude above the default vapor pressure value. The ASTM D2879 results from Lab 1 have a less steep slope than the slope of the lab 2 and 3 results, and the slope of the curve obtained using ASTM E1719 is smaller than the slope of the curves for any of the three labs that conducted ASTM D2879. The default value, the Lab 1 ASTM D2879 measured results, and the ASTM E1719 measured results are in good agreement with each other and are several factors lower than the ASTM D2879 results from Labs 2 and 3 in the vicinity of 400°F. The three pairs of low VP single point readings taken on the Eralytics instrument vary across nearly an order of magnitude at 120°F and 140°F but are similar to each other at 160°F.

Note that when applied to the “known” recipe, none of the ASTM D2879 measured results exceeded the modeled vapor pressure. This could mean that the largest measured ASTM D2879 results are likely to represent a lower bound for actual vapor pressure values.

Figure 33 is meant to show the full range of all the results. Figure 34 focuses only on 60°F to 190°F temperature range. The axes on this chart are the same as the axes for Figures 30 and 32 so that the cluster of values for each material can be compared.

Figure 34 shows that at 140°F, there are measured instrument readings, ASTM D2879 measured values for Labs 2 and 3, and the curve fit for ASTM D2879 for Labs 2 and 3, and all are on the order of a tenth of a psi. The default value (API 2012) at 140°F is 0.016 psi. The lower of the two Eralytics single point readings at 140°F falls between the measured values obtained by labs 2 and 3 at this temperature. This is a wet vapor pressure measurement but this sample was analyzed for water content using ASTM D95 (water by distillation) and was found to be 0.00 vol % water.

The variation in the pairs of single point readings taken at 120°F and 140°F on the Eralytics instrument is apparent in Figure 34. The readings taken at 160°F are in good agreement with each other. A discussion of the challenges inherent in using a mini method instrument to obtain vapor pressure values for heavy refinery liquids is given in Appendix H of this report.

The vapor pressure values from all of the study methods for MM fuel oil no. 6 from 60°F to 190°F fall in a tighter cluster than the values for either the “known” recipe or the hydraulic fluid across the same temperature, ranging over three orders of magnitude instead of four or five.

The ASTM D323 result for the MM fuel oil no. 6 was < 0.2 psi. This method measures the vapor pressure of a water- and air-saturated sample at 100°F, and the results from ASTM D323 are expected to be higher than results from the other methods at 100°F. None of the study methods returned a value higher than 0.2 psi at 100°F for the MM fuel oil no. 6 sample, but it should be noted that measurements of the vapor pressure of this material

using the Eralytics mini method instrument were not conducted below 120°F, and Labs 2 and 3 did not make any ASTM D2879 measurements at temperatures below 140°F for this material.

Figures

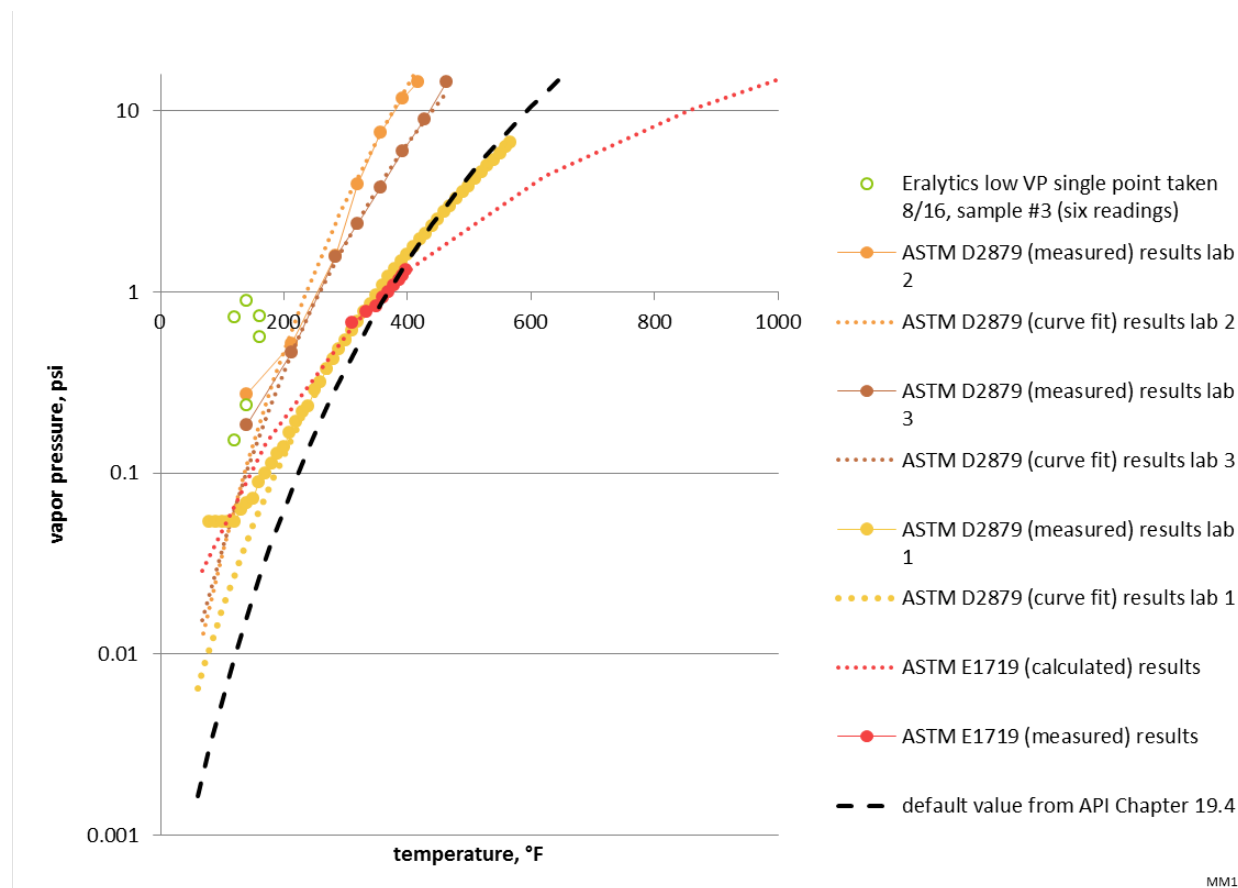


Figure 33. The full range of measured and default values for the vapor pressure of MM fuel oil no. 6.

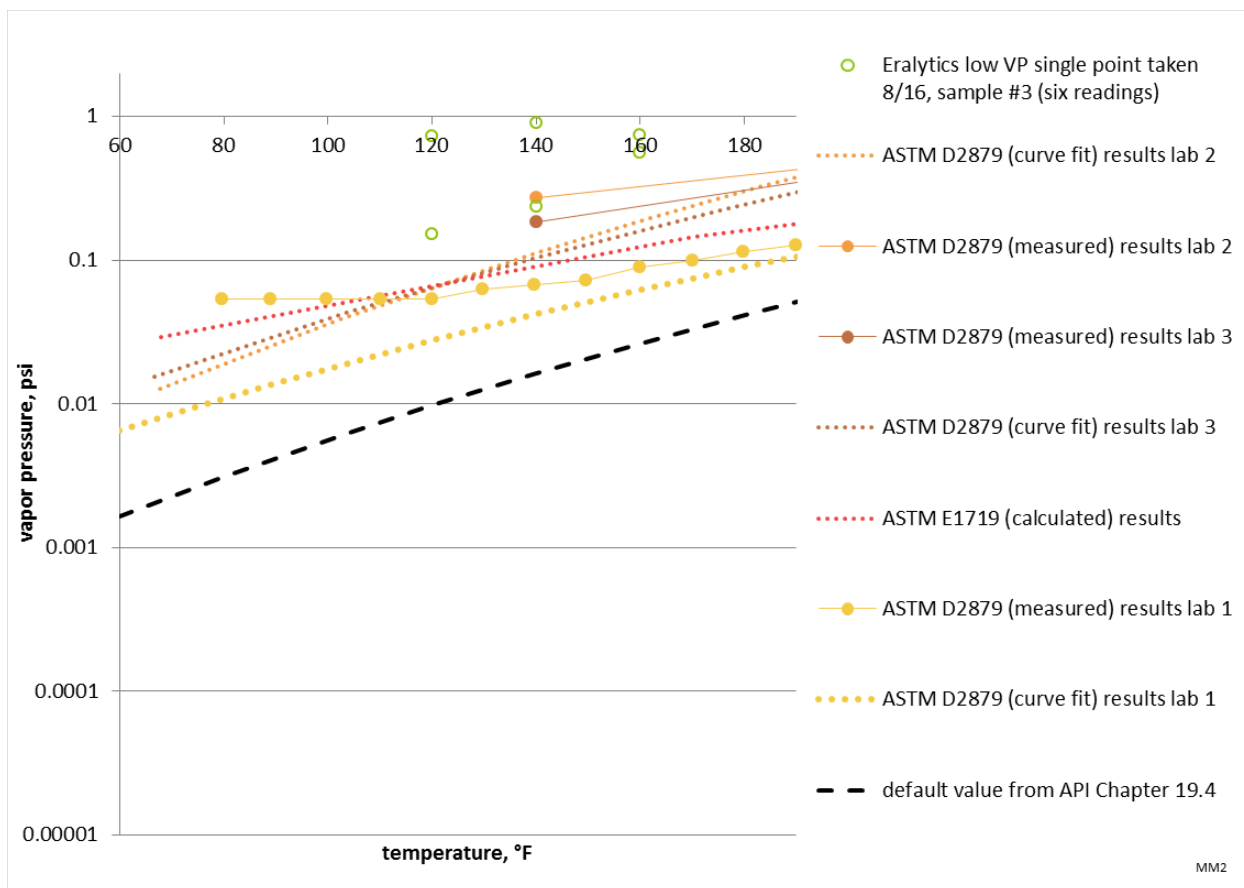


Figure 34. MM fuel oil no. 6 vapor pressure values from 60°F to 190°F.

MB fuel oil no. 6

Figure 35 shows the entire range of vapor pressure values for MB fuel oil no. 6 from the commercial labs and from the Eralytics mini method instrument. The color scheme is the same as for the “known” recipe and hydraulic fluid charts except that the black dashed line represents the default vapor pressure for fuel oil no. 6 from API Chapter 19.4 (API 2012).

All of the ASTM D2879 measured results from Lab 3 fall above the default vapor pressure values, and except for the upper end of the temperature range, so do the ASTM D2879 measured results for Lab 1. The ASTM D2879 curve results from Lab 1 have a less steep slope than the slope of the Lab 3 curve results, and the slope of the curve obtained using ASTM E1719 is smaller than the slope of the curves for either of the labs that conducted ASTM D2879. Only three single point readings for the low VP method were obtained using the Eralytics instrument: one at 120°F, one at 140°F, and one at 160°F. The value at 140°F falls below the values at 120°F and 160°F; in reality, the vapor pressure would increase with increasing temperature.

As noted in the previous section describing the MM fuel oil no. 6 results, none of the ASTM D2879 measured results exceeded the modeled vapor pressure when applied to the “known” recipe. This could mean that the largest measured ASTM D2879 results are likely to represent a lower bound for actual vapor pressure values.

Figure 35 is meant to show the full range of all the results. Figure 36 focuses only on 60°F to 190°F temperature range. The axes on this chart are the same as the axes for Figures 30, 32, and 34 so that the cluster of values for each material can be compared.

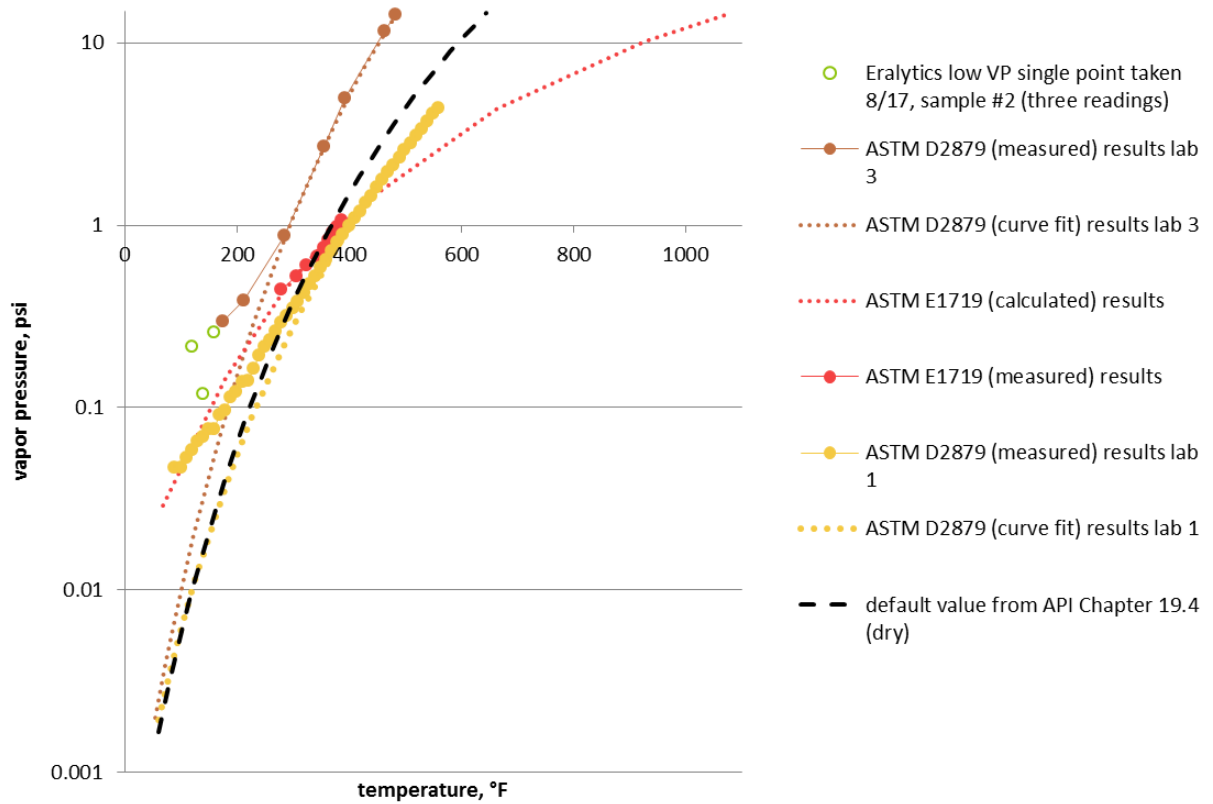
Figure 35 and Figure 36 show that the mini method readings, all of the ASTM D2879 measured values for Lab 3 (which begin at 176°F), and all of the measured values for Lab 1 above 140°F are 0.1 psi or higher. The default value (API 2012) reaches a value of 0.1 psi at 223°F.

The lower of the two Eralytics single point readings at 140°F falls between the measured values obtained by Labs 2 and 3 at this temperature. This is a wet vapor pressure measurement but this material was found to have no water when ASTM D95 was used to measure its water content.

As with MM fuel oil no. 6, all of the vapor pressure values for MB fuel oil no. 6 from 60°F to 190°F fall in a tighter cluster than the values for either the “known” recipe or the hydraulic fluid across the same temperature, ranging over three orders of magnitude instead of four or five.

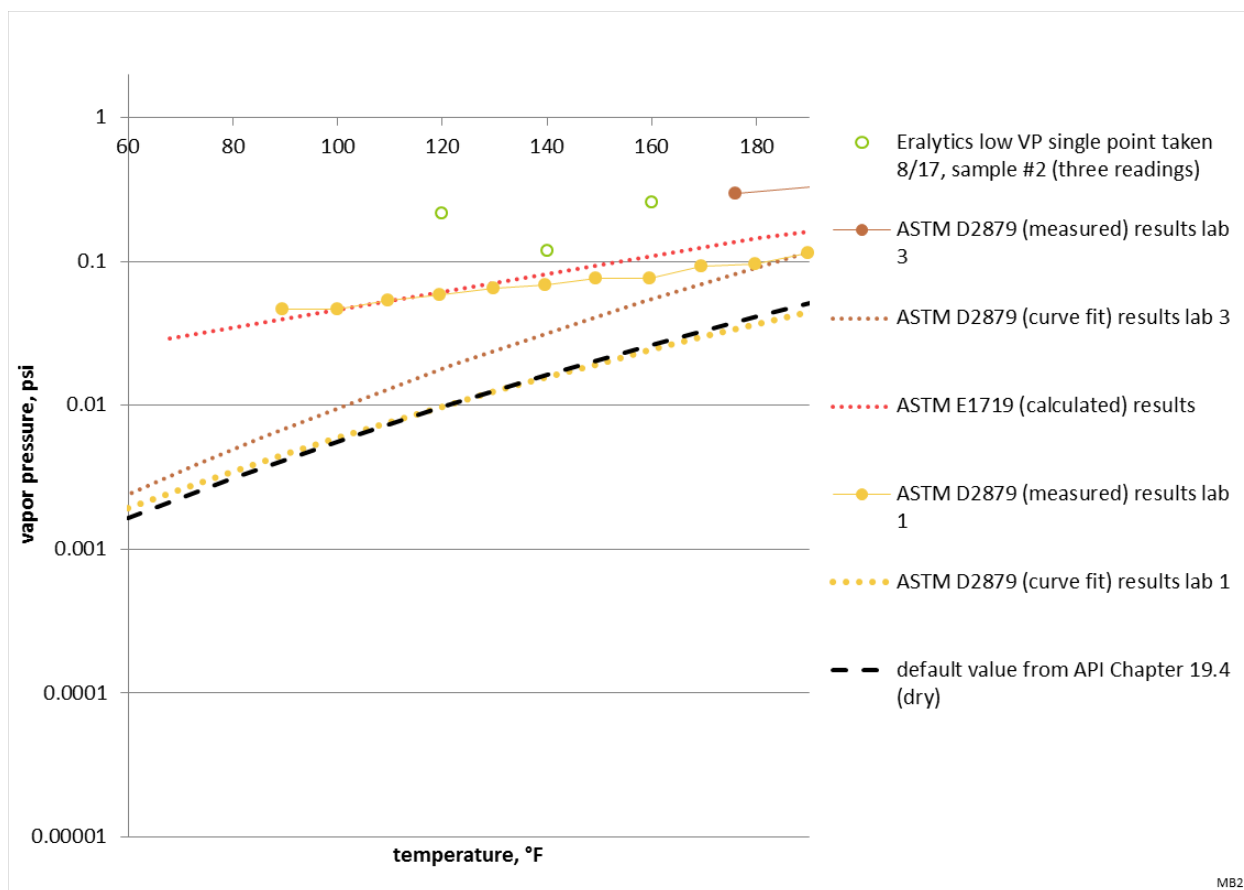
The ASTM D323 result for the MB fuel oil no. 6 was < 0.2 psi. This method measures the vapor pressure of a water- and air-saturated sample at 100°F, and the results from ASTM D323 are expected to be higher than results from the other methods at 100°F. None of the study methods returned a value higher than 0.2 psi at 100°F for the MB fuel oil no. 6 sample, but it should be noted that measurements of the vapor pressure of this material using the Eralytics mini method instrument were not conducted below 120°F, and Lab 3 did not make any ASTM D2879 measurements at temperatures below 176°F for this material.

Figures



MB1

Figure 35. The full range of measured and default values for the vapor pressure of MB fuel oil no. 6.



MB2

Figure 36. MB fuel oil no. 6 vapor pressure values from 60°F to 190°F.

BT fuel oil no. 6

Figure 37 shows the entire range of vapor pressure values for BT fuel oil no. 6 from the commercial labs and from the Eralytics mini method instrument. The color scheme is the same as for the “known” recipe and hydraulic fluid charts except that the black dashed line represents the default vapor pressure for fuel oil no. 6 from API Chapter 19.4 (API 2012).

All of the ASTM D2879 measured results from Lab 3 fall well above the default vapor pressure values, sometimes two orders of magnitude higher. As with the MB fuel oil no. 6 sample, except for the upper end of the temperature range, the ASTM D2879 measured results for Lab 1 also fall above the default values. The ASTM D2879 curve results from Lab 1 have a less steep slope than the slope of the Lab 3 curve results, and the slope of the curve obtained using ASTM E1719 is smaller than the slope of the curves for either of the labs that conducted ASTM D2879. Five single point readings for the low VP method were obtained using the Eralytics instrument: two at 120°F, two at 140°F, and one at 160°F. The value at 160°F falls below the values at 140°F and 120°F; in reality, the vapor pressure would increase with increasing temperature.

As noted in the previous sections describing the MM and MB fuel oil no. 6 results, none of the ASTM D2879 measured results exceeded the modeled vapor pressure when applied to the “known” recipe. This could mean that the largest measured ASTM D2879 results are likely to represent a lower bound for actual vapor pressure values.

Figure 37 is meant to show the full range of all the results. Figure 38 focuses only on 60°F to 190°F temperature range. The axes on this chart are the same as the axes for Figures 30, 32, 34, and Figure 38 so that the cluster of values for each material can be compared.

Figure 37 and Figure 38 show that four of the five mini method readings, all of the ASTM D2879 measured values for Lab 3 (which begin at 140°F), and all of the measured values for Lab 1 above 140°F are 0.1 psi or higher. The default value (API 2012) reaches a value of 0.1 psi at 223°F.

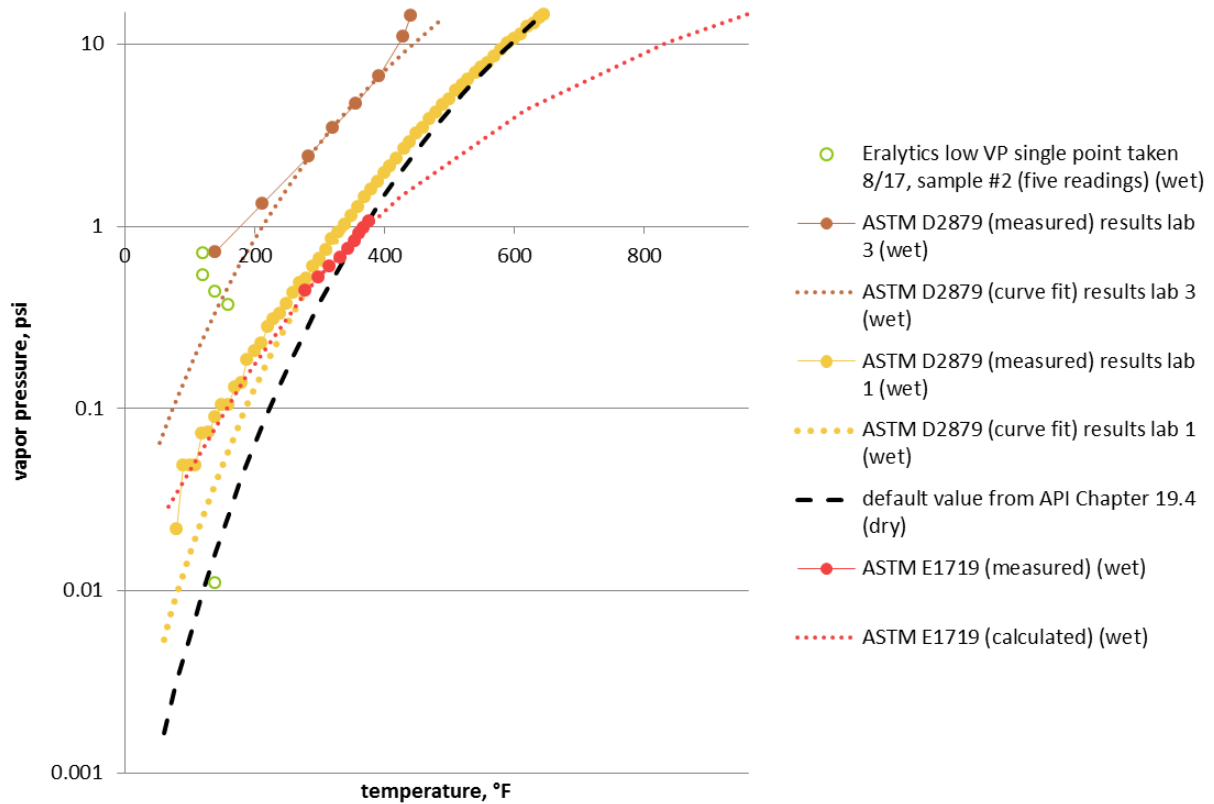
One of the two mini method instrument readings at 140°F is nearly two orders of magnitude lower than the other four instrument readings.

The commercial lab and mini method instruments returned “wet” vapor pressure measurements (i.e., there was a contribution to vapor pressure due to the presence of water in the sample). The water content of BT fuel oil no. 6 was measured using ASTM D95 (water by distillation) at two different labs and was found to be 0.1 vol % at one lab and 0.2 vol % at the other. In the discussion section of this report, there is a subsection about the effects of water on vapor pressure and one means of assessing the potential contribution of water is used to show what portion of the measured vapor pressure values for this material were due to the water it contained.

As with MM and MB fuel oil no. 6 samples, all of the vapor pressure values for BT fuel oil no. 6 from 60°F to 190°F fall in a tighter cluster than the values for either the “known” recipe or the hydraulic fluid across the same temperature, ranging over three orders of magnitude instead of four or five.

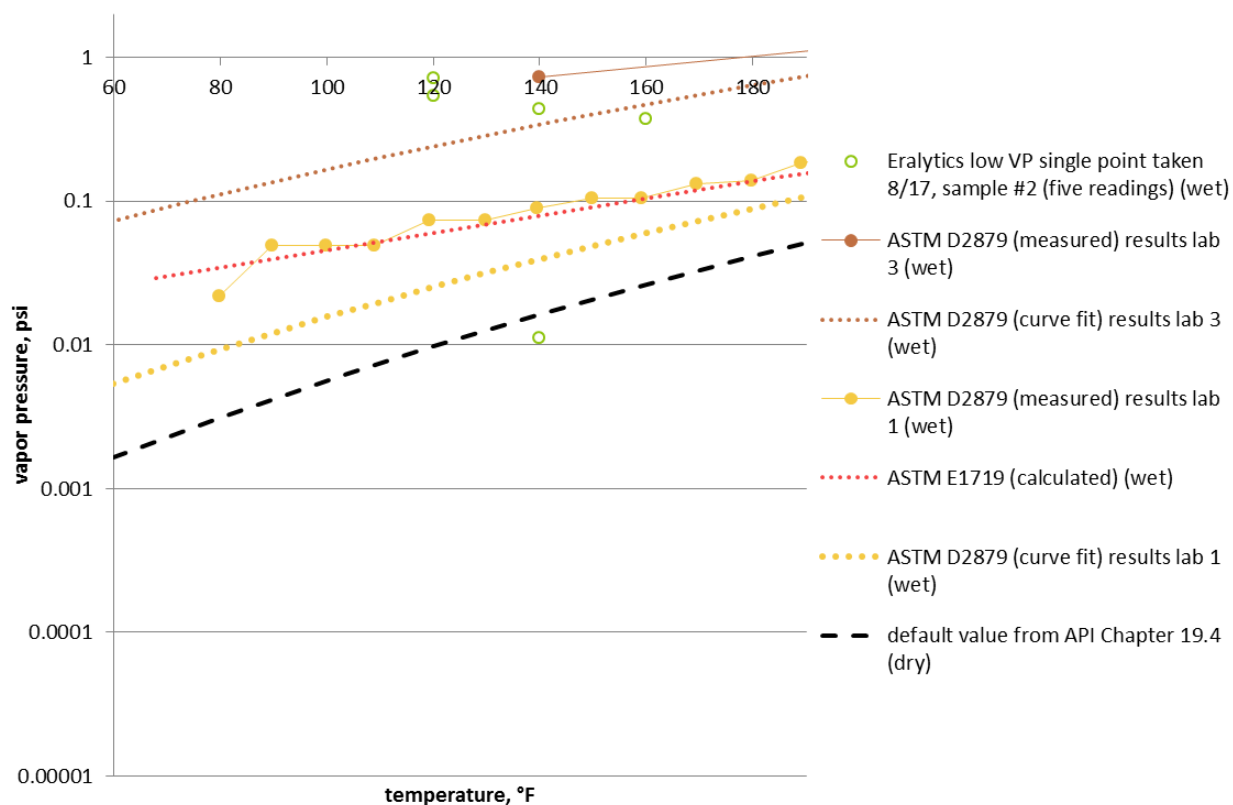
The ASTM D323 result for the BT fuel oil no. 6 was < 0.2 psi. This method measures the vapor pressure of a water- and air-saturated sample at 100°F, and the results from ASTM D323 are expected to be higher than results from the other methods at 100°F. None of the study methods returned a value higher than 0.2 psi at 100°F for the BT fuel oil no. 6 sample, but it should be noted that measurements of the vapor pressure of this material using the Eralytics mini method instrument were not conducted below 120°F, and Lab 3 did not make any ASTM D2879 measurements at temperatures below 140°F for this material.

Figures



BT1

Figure 37. The full range of measured and default values for the vapor pressure of BT fuel oil no. 6.



BT2

Figure 38. BT fuel oil no. 6 vapor pressure values from 60°F to 190°F.

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6. Discussion of methods for determining vapor pressure

Commercial lab results (ASTM D2879 and ASTM E1719)

Figure 29 and Figure 30 show that the ASTM D2879 curves from Labs 1 and 2 deviate substantially from the modeled expectation for the “known” recipe. A number of potential explanations for this exist. One explanation is that there is a degassing step in ASTM D2879 that is intended to remove dissolved air from the sample. If conditions are not carefully controlled during this degassing step, lighter ends contained in a mixture are lost as well as dissolved air.

The potential for degassing interfering with ASTM D2879 was explored by plotting the Lab 1 and Lab 2 results against pure octane, pure nonadecane, the modeled expectations for the “known” recipe, and a recipe that contains less octane than the “known” recipe. These plots are shown in Figure 39 (for Lab 1) and Figure 40 (for Lab 2). Figure 39 shows that many of the measurements taken by Lab 1 coincide with modeled expectations for a mixture that contains only 0.7 mol % octane (the “known” recipe is 20 mol % octane). Figure 40 shows that many of the measurements taken by Lab 2 coincide with modeled expectations for a mixture that contains 10 mol % octane. This suggests that octane may have been lost during the degassing step at both of these labs, but more so from Lab 1.

An escape of vapor into the inert gas used to balance the pressure in an isoteniscope is another mechanism that could cause ASTM D2879 vapor pressure readings to be low, because the vapor lost would be relatively high in light ends. There is also the possibility of accidentally introducing a bubble of the inert gas used to balance the pressure into the vapor space in the isoteniscope, which would cause vapor pressure readings to be too high. A final source of error when using an isoteniscope to measure vapor pressure is that when performing this method, the pressure is determined by balancing the pressure of the inert gas so that the menisci in the two vertical tubes of the isoteniscope are at the same level. If it is difficult to sight the menisci, it is difficult to determine the right level of inert gas pressure. Fuel oil no. 6 is a very sticky, dark substance and clings to the glass of the isoteniscope, making the menisci particularly difficult to sight. This effect is worse at lower temperatures than higher temperatures, making it even more difficult to sight the menisci and get the right pressure reading at lower vapor pressures.

Another factor that influences the accuracy of determining the curve for the ASTM D2879 method is that the curve is obtained by drawing a line through a plot of the log of the higher-temperature vapor pressure measurements vs. the inverse of the absolute temperature. The relationship of vapor pressure and temperature is more complicated than this and the temperature over which a linear relationship between the log of the vapor pressure and the inverse of the absolute temperature is not wide enough to include all of the results obtained by the labs.

This is illustrated in Figure 41, which plots all of the curves found in Figure 29 and Figure 30 using the axes specified for developing the curves in ASTM D2879 and ASTM E1719. As

shown in this figure, the modeled expectations for the vapor pressure of the “known” recipe and the vapor pressures of octane and nonadecane are not linear over the full range of temperatures in this figure; they arc slightly downwards as the inverse of absolute temperature increases (i.e., as temperature decreases).

Figure 39 shows that measured values for the “known” recipe using ASTM D2879 for Labs 2 and 3 arc downwards more steeply at lower temperatures than the modeled expectations predict, while the measured values for Lab 1 arc upwards. A possible explanation for less agreement at lower temperatures is that it may be harder to detect when equilibrium is reached at lower temperatures. Also, oftentimes there is larger relative error in pressure gauge readings at lower temperatures. It could also be that the modeled expectations are less accurate at lower temperatures.

ASTM E1719 applies the same methodology as ASTM D2879 for finding the curve (a plot of the log of vapor pressure vs. the inverse absolute temperature through the measured values). The measured values for the “known” recipe using ASTM E1719 were all obtained at a fairly narrow range of temperature, from 180°F to 225°F. This narrow band of values was extrapolated to a range that goes from 60°F to 530°F.

Both ASTM E1719 and ASTM D2879 were developed before computers were widely available. Now that computers are ubiquitous, it would be a simple matter to perform a regression of the measured values to create a formula that is more likely to express the true behavior of vapor pressure as a function of temperature, such as this form of Antoine’s equation:

$$\ln(p) = A - B/(T + C)$$

In this equation, A, B, and C are constants that are fitted from measured data points via regression, p is vapor pressure, and T is absolute temperature. However, when the measured values from ASTM E1719 are fit to this form, the regression returns a value of -687.5 R for the constant C. This creates a discontinuity in the vapor pressure curve at $T = 687.5 \text{ R}$ (227.8°F).

Figures

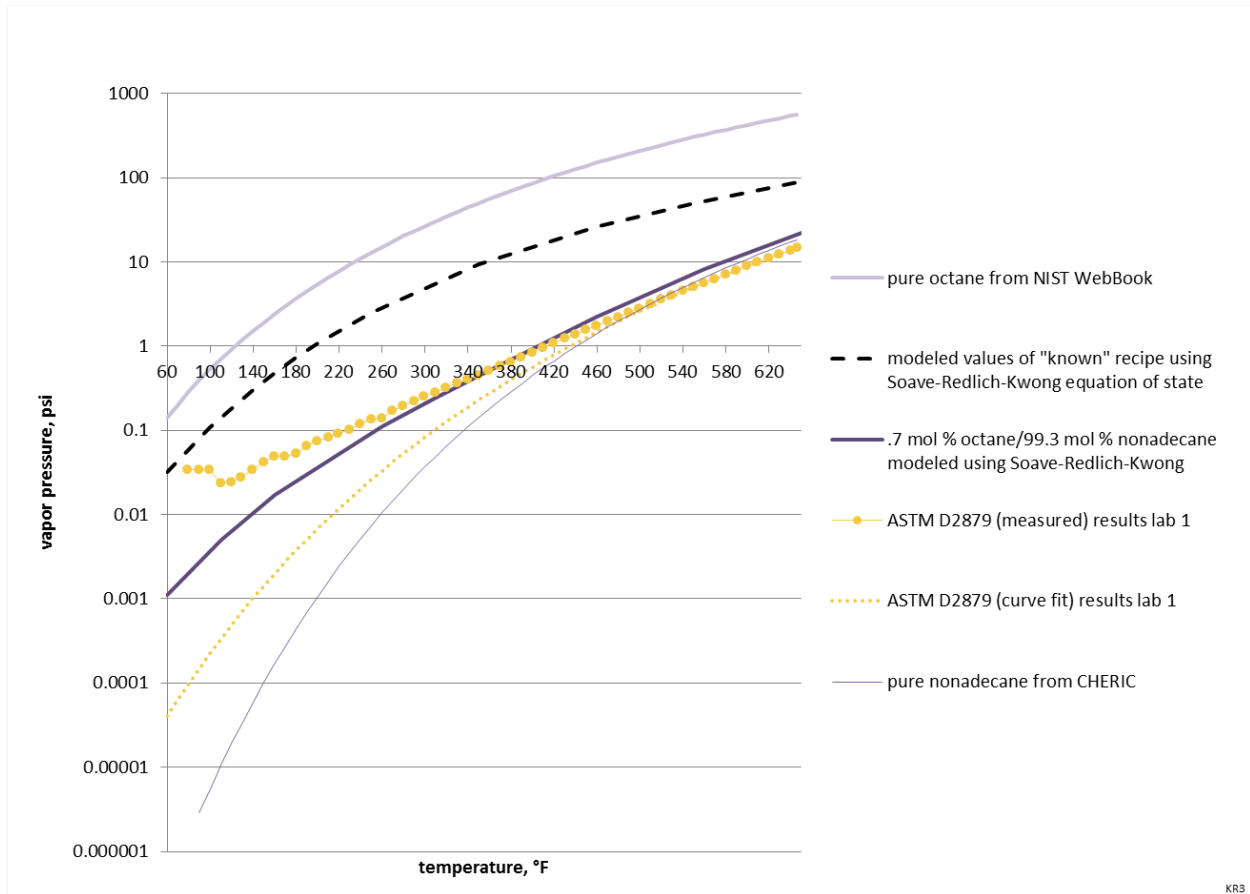
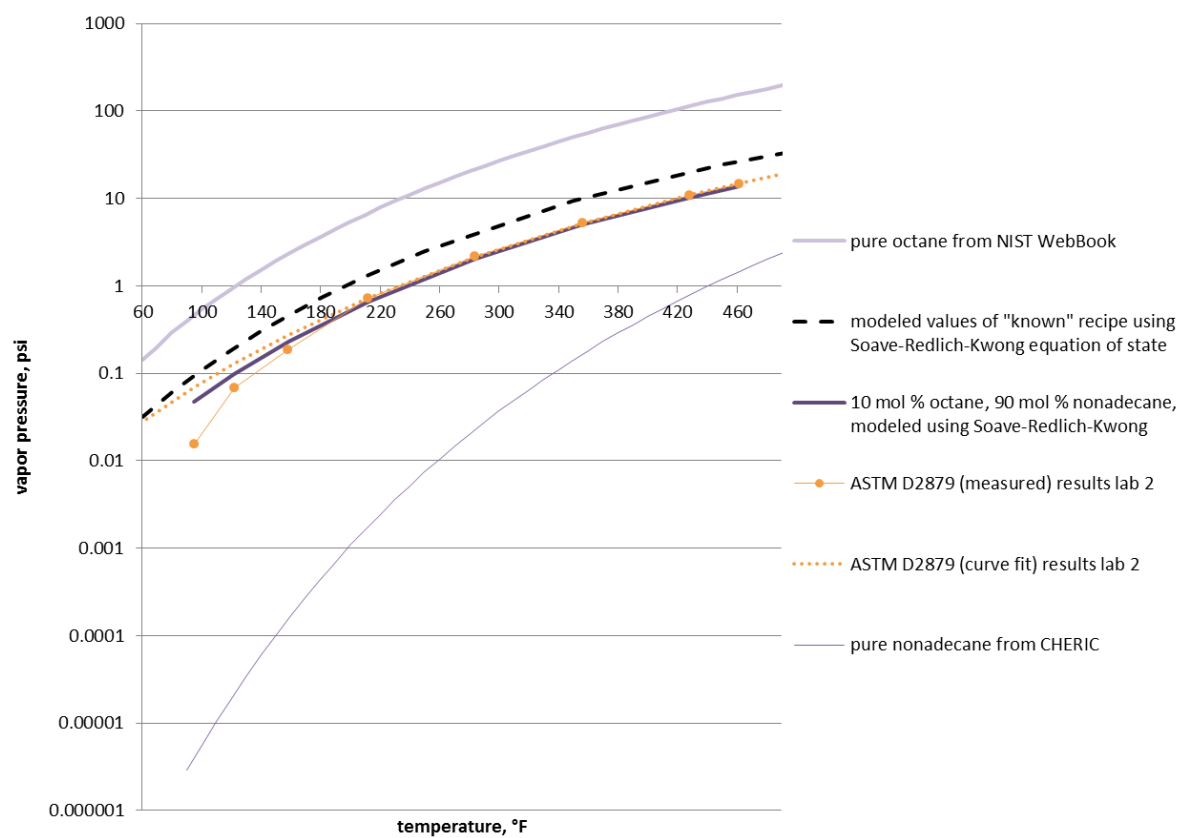
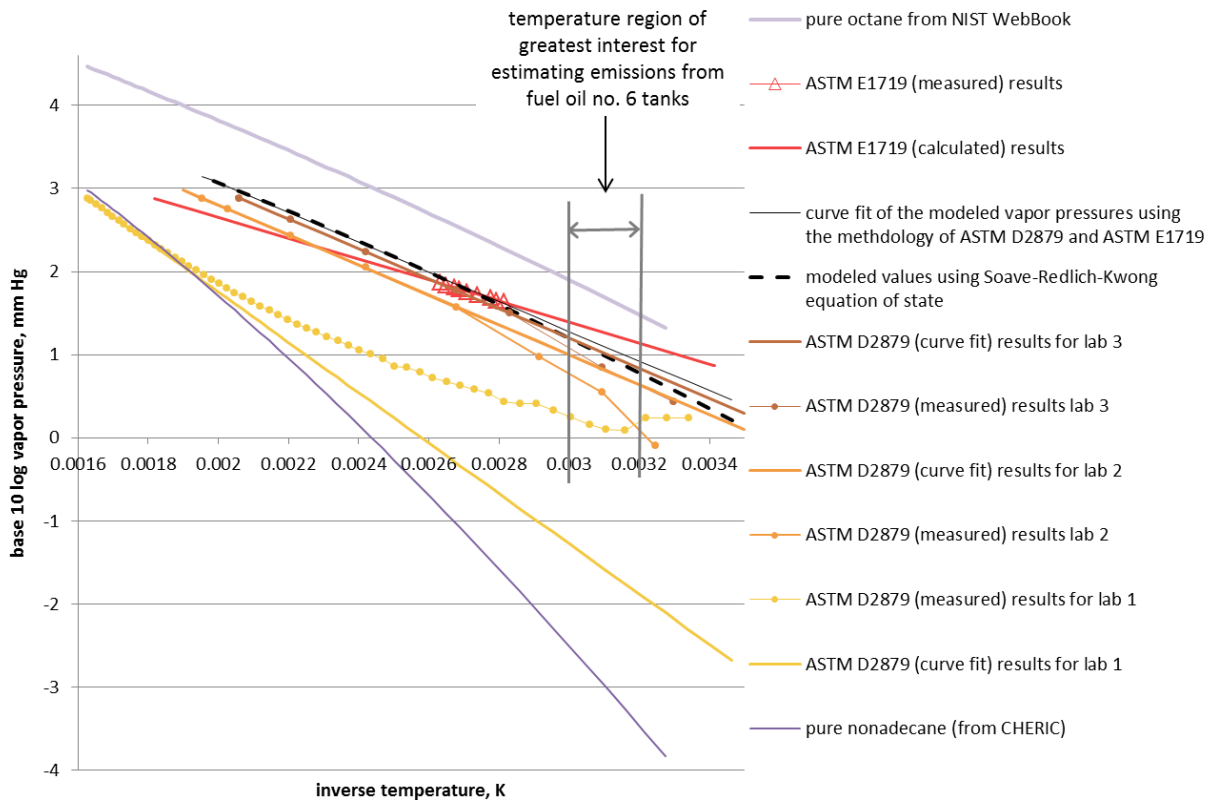


Figure 39. Comparison between Lab 1's ASTM D2879 results for the "known" recipe and an alternate recipe containing less octane than the "known" recipe.



KR4

Figure 40. Comparison between Lab 2's ASTM D2879 results for the "known" recipe and an alternate recipe containing less octane than the "known" recipe.



KR5

Figure 41. Curve fits for the “known” recipe for ASTM D2879 (vapor pressure by isoteniscope) and ASTM E1719 (vapor pressure by ebulliometry).

Mini method instruments

At the outset of the project, the strategy for using the instruments was to start with materials that flowed easily, such as pentane. Then, the hydraulic fluid would be analyzed, followed by the “known” recipe and the fuel oil no. 6 samples. As in commerce, the fuel oil no. 6 samples analyzed for this project varied in their ease of handling, with the MM sample being the easiest to analyze and the MB sample the most difficult.

Originally, before experience showed that getting vapor pressure readings for viscous materials and cleaning the instruments between runs could be quite time-consuming, the instruments were going to be used to analyze all of the study materials using several methods. Some measurements using ASTM D6378 were made before deciding to focus on the methods that were in principle like ASTM D6378, but that had hardware modifications intended to accommodate heavy refinery liquids. For the Grabner instrument, these modifications were to shake the sample chamber to speed the development of equilibrium and to slow the piston speed to accommodate the slow movement of these viscous fluids through the instrument’s tubes. In addition to these modifications, the tubes in the

Eralytics instrument were heat-traced. These heavy refinery liquid methods were called the “VOC” method for the Grabner instrument and the “low VP” method for the Eralytics instrument. These methods could be run in either curve/multi-point or single point mode, with the curve/multi-point mode producing vapor pressure results at multiple temperatures for each injected sample and the single point mode producing one vapor pressure result at one temperature for each injection. The instrument manufacturers recommended the curve/multi-point mode, and measurements were taken using this mode.

In measurements of one of the fuel oil no. 6 samples taken at the end of July using the “low VP curve” method, the Eralytics instrument returned some negative values for Pabs. Earlier runs using the same method on the same material had not produced negative Pabs results. It was noted that the lower temperature readings were particularly affected.

Further investigation revealed some factors to consider when applying a triple expansion method for measuring the vapor pressure of heavy refinery liquids (described in Appendix H). These factors include theoretical issues (e.g., a simplification allowed by the method) and instrumentation issues (e.g., the sensitivity of vapor pressure to the pressure and vapor volume measurements of the triple expansion).

After it was discovered that the instruments did not perform separate triple expansions at each temperature when operating in “curve” or “multi-point” mode (this is a simplification allowed by ASTM D6378), the single point mode of the low VP method (for the Eralytics instrument) and the single point mode of the VOC method (for the Grabner instrument) was used for conducting the remaining measurements. It was later decided that the “known” recipe would be analyzed first, followed by the fuel oil no. 6 samples, with the fuel oil no. 6 sample that flowed the most easily analyzed first and the sample that flowed the least easily analyzed last. If time remained after the fuel oil no. 6 samples were analyzed, the hydraulic fluid would be analyzed.

Even with modifications designed to accommodate heavy refinery liquids, the primary physical obstacle to using these instruments for analyzing the fuel oil no. 6 samples was the high viscosity of the samples. These instruments were designed for use with much less viscous materials. When processing high viscosity materials, the samples must be preheated prior to introduction into the instrument so that the material will flow easily into the measurement chamber. Even if heat is applied to the sample in preparation for analysis, a syringe must be used to introduce the sample and additional force on the syringe must be applied to help the sample enter the instrument. If multiple injections are expected from a single syringe, an adequately elevated sample temperature must be maintained from the first to the last injection. Observations about designing mini method instruments so that they can be more practically applied to measuring the vapor pressure of heavy refinery liquids are included in Appendix I.

Grabner instruments

Two Grabner instruments were utilized. The first one did not operate properly when it was received in April and was sent for repairs. It was returned in May. It was used to analyze pentane and octane, then stopped operating properly and was sent for repairs. It was returned in June and operated until June 27. The ASTM D6378 multi-point method was used to analyze hydraulic fluid three times and the “known” recipe twice, in addition to analyses of pentane for operation checks. At which time it stopped operating properly. A second instrument was received in August. This instrument was used to analyze five single point measurements of the “known” recipe in VOC mode, in addition to analyzing pentane and nonane as operation checks. After that, the second instrument stopped operating properly.

An opportunity to analyze the fuel oil no. 6 samples using a Grabner instrument never arose. Suggestions for making the instrument more viable for analyzing the vapor pressure of heavy refinery liquids are given in Appendix I.

The Grabner instruments did not have an option for including the first and second expansion pressures with the results. Without this, quality checks that could be performed for the Eralytics machine could not be made. For example, the instrument’s algorithm for calculating pGas (and therefore pAbs) could not be verified. In addition, the equilibrium constant could not be estimated and the number of moles of air in the vapor phase at each expansion could not be estimated. The three vapor volumes after correcting for dead space and other affects would also need to be made available by the instrument manufacturer in order to best conduct quality control checks of the results and analyze sensitivities. These quality control checks and sensitivities are discussed in Appendix H.

Eralytics instrument

The Eravap instrument from Eralytics was able to process all of the samples that were analyzed in this project. All errors on sample injections were due to the instrument failing to expel the spent flush injection. These errors resulted in the loss of limited sample volume and the loss of operator time. Although this instrument was rugged enough to process fuel oil no. 6 samples, there are improvements that could make it a more viable for option routine analysis. Suggested improvements are given in Appendix I.

The Eralytics instrument was received in June. At first, along with operational checks and practice runs on pentane, hydraulic fluid and the “known” recipe were analyzed using the ASTM D6378 curve method. Starting at the end of June and throughout July, the low VP curve method was used to analyze all five of the study materials. In late July, three of six readings of the BT fuel oil no. 6 material using the low VP curve method returned negative vapor pressure results at 60°F. This material had been analyzed the day before using the same temperatures, same instrument, and same technique without returning negative vapor pressure results at 60°F. The following day, five of six readings of MB fuel oil no. 6 returned a negative value for vapor pressure and one of six readings at 80°F.

This ushered in an intensive investigation of the formulas used by the instrument to calculate vapor pressure. One result of this investigation was that in August, results from previously conducted curve methods were abandoned and the low VP single point method was used to analyze the “known” recipe and the three fuel oil no. 6 samples.

It was discovered that the “known” recipe samples could not be directly expelled from the instrument when analyzed using the single point method at temperatures below 100°F. This is because the expulsion temperature of sample material from the chamber depends on the temperature of the vapor pressure reading and the “known” recipe is a solid below 100°F. Therefore, going forward, the fuel oil no. 6 samples were tested at 120°F, 140°F and 160°F instead of 60°F, 80°F, 100°F, 120°F, and 140°F, and the “known” recipe was tested at 100°F, 120°F, and 140°F instead of 60°F, 80°F, 100°F, 120°F, and 140°F. Fewer temperatures were tested in the hopes that each syringe could result in three pairs of readings, one pair at each temperature.

The results using the low VP single point method were not always sensible or repeatable, raising further questions and areas for exploration. However, further analysis was halted so that remaining project resources could be devoted to studying the data that had already been obtained and preparing this report.

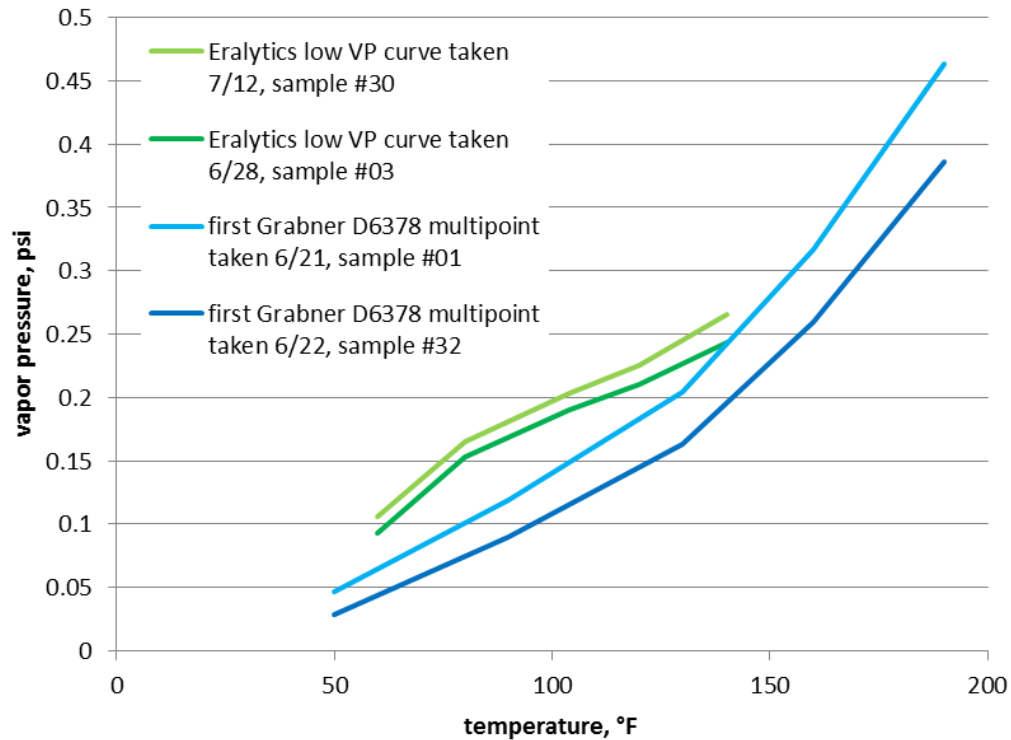
The manufacturer of this instrument was very helpful and forthcoming about addressing the issues that arose around the results.

Sample uniformity

Vapor pressure results from samples dispensed at the beginning and end of the dispensing regimen were used to understand the effect of any volatiles lost during the process of separating the sample into smaller containers. There are only a few opportunities to make these comparisons because of breakdowns in the case of the Grabner instrument and revised measurement methods in the case of the Eralytics instrument. All of the opportunities were for measurements taken using curve methods. As described earlier, these methods rely on one triple expansion to determine the partial pressure of gas in the vapor chamber and then apply the ideal gas law to find the partial pressure at all the temperatures in the curve. This introduces an unknown level of uncertainty in the curve results, and curve method vapor pressures are presented here only to show the potential effect of dispensing order on measured vapor pressures.

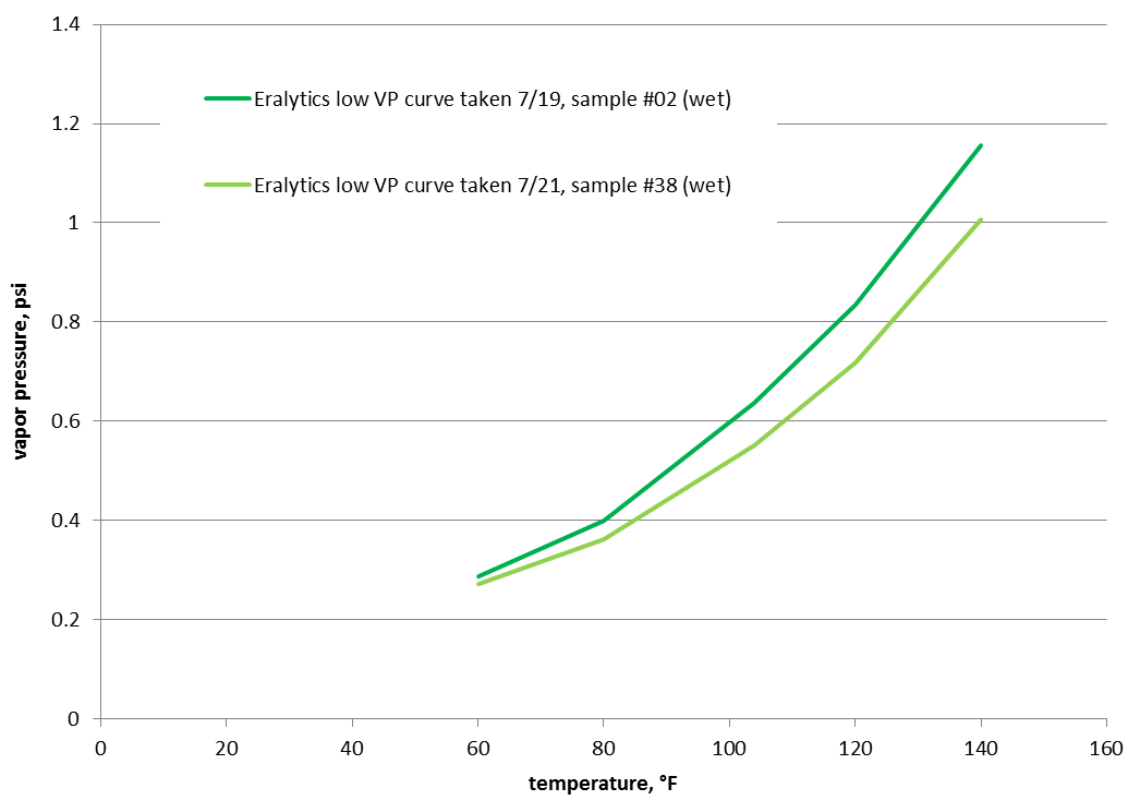
Figure 42 and Figure 43 show that in one case, the samples dispensed early in the dispensing process had slightly higher vapor pressures than the ones dispensed later, while in another case it was reversed. Figure 44 shows that samples that were dispensed adjacent to each other do not produce identical vapor pressure results. This provides reassurance that any loss of volatiles that might have occurred during the dispensing process was not substantial.

Figures



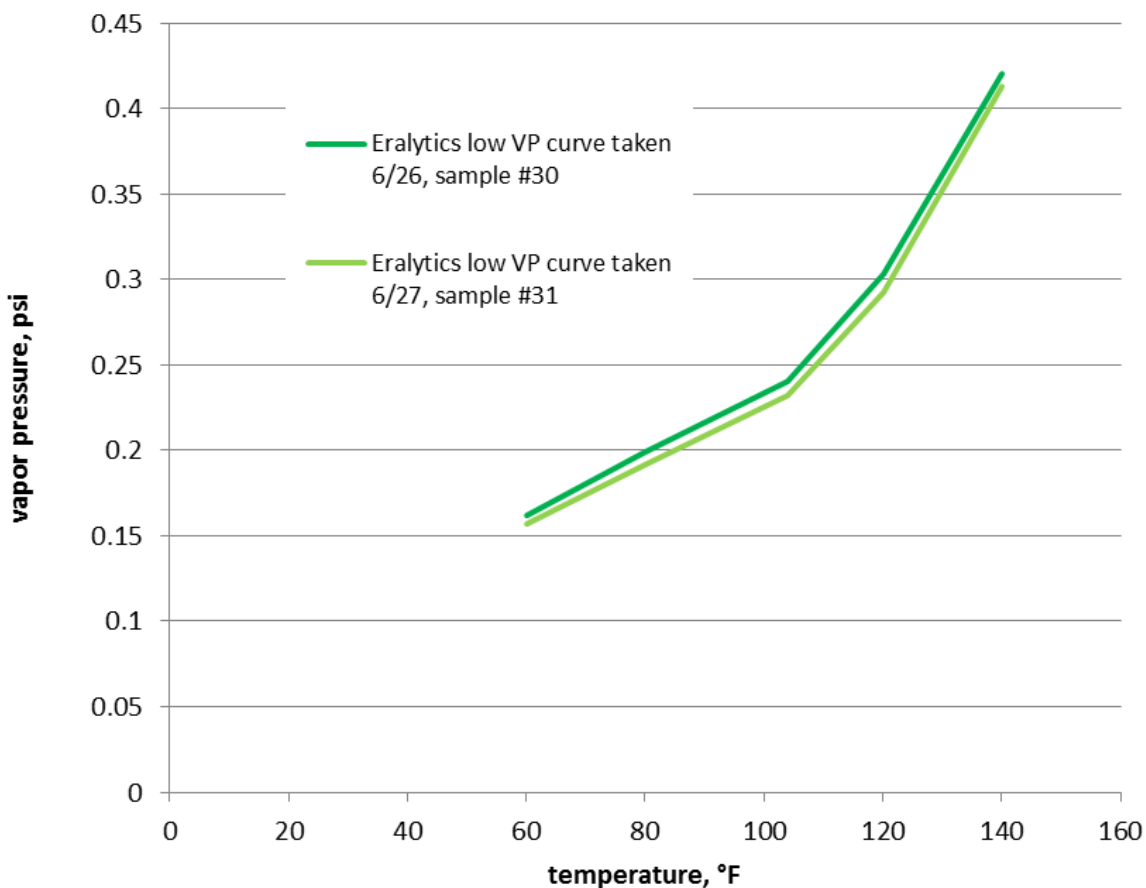
HY3

Figure 42. Vapor pressure of hydraulic fluid samples dispensed early and late in the dispensing scheme. The values presented are the average after omitting the first injection of each syringe.



MM3

Figure 43. Vapor pressure of MM fuel oil no. 6 samples dispensed early and late in the dispensing scheme. The values presented are the average after omitting the first injection of each syringe.



KR6

Figure 44. Vapor pressure of the “known” recipe dispensed from adjacent samples. The values presented are the average after omitting the first injection of each syringe.

Sample degradation

The potential for sample degradation over time could not be assessed based on mini method results because none of the methods were run over the entire course of the study. However, the D2879 runs at Lab 3 were done much later than the ones at Lab 1 and Lab 2 and they returned higher vapor pressure results. This suggests that sample degradation was not an overwhelming factor over the course of the study.

Effect of water on vapor pressure

The potential effect of water on vapor pressure was examined using process simulation software and the boiling point distributions for a sample of fuel oil no. 6 and a sample of a lighter marine fuel oil.

The pure component data manager feature of ChemSep LITE (Kooijman and Taylor 2016) can be used to create hypothetical compounds based on boiling point distribution and specific gravity. Once these hypothetical compounds are created, they can be selected as mixture components for a flash simulation in order to estimate the vapor pressure of the mixture. Water was added to the mixture of hypotheticals as a means of determining the effect of additional water on the vapor pressure of the mixture.

For one set of ChemSep LITE runs, the boiling point distribution for a fuel oil no. 6 sample originating from Imperial Oil Ltd. in Nova Scotia, Canada in 2002 (US EPA 2003) was used. The density of this material is given as 0.9888 g/ml at 15°C and its water content is given as 0.1 vol %. Its boiling point distribution is given in Table 17.

The specific gravity for each cut was calculated by assuming that the Watson characterization factor for this fuel oil no. 6 is constant across the distillation fractions. This assumption probably does not introduce a great deal of uncertainty because the cutter stock and the residual streams that are combined to make fuel oil no. 6 must have somewhat similar Watson characterization factors or solvency problems will be encountered when the streams are mixed (the asphaltenes will settle out). A Watson characterization factor greater than 12.5 indicates a material that is largely paraffinic, while a Watson characterization factor less than 10 indicates a material that is highly aromatic. Fuel oil no. 6 generally has a density between 0.89 and 1. The Watson characterization factor was calculated as follows.

$$K_W = \frac{T_B^{1/3}}{\gamma_0}$$

In this equation, K_W is the Watson characterization factor for the sample, T_B is the average boiling point of the sample in Rankine, and γ_0 is the specific gravity of the sample.

In order to get the specific gravity for the boiling point distribution cuts, the equation was rearranged.

$$\gamma_{0'} = \frac{T_{B'}^{1/3}}{K_W}$$

In this equation, K_W is as before, $\gamma_{0'}$ is the specific gravity of the boiling point distribution cut and $T_{B'}$ is the average boiling point of the boiling point distribution cut.

The average temperature for each cut was used to determine the average boiling point for the fuel oil no. 6 sample and that was used to calculate the Watson characterization factor of the sample as a whole, which was 11.24. The specific gravities calculated for each cut

along with the average boiling point temperature of each cut was input into the pseudo component generator. These values are given in Table 18.

Figure 45 is a screenshot of the pseudo component generation form from the pure component data manager of ChemSep LITE. This figure shows which models were chosen for generating the properties of the pseudo components. These models are the same models chosen for the multicomponent distillation tutorial for ChemSep (Kooijman and Taylor, not dated).

To estimate the vapor pressure, a simulation of flash distillation was conducted with the K-value based on Raoult's law and the Lee-Kesler or Riedel vapor pressure models. The developers of ChemSep recommend Lee-Kesler and Riedel vapor pressure models for hydrocarbon mixtures (Kooijman and Taylor 1998). No other thermodynamic selections affect the results of this exercise. The option to use default models to determine physical properties was selected. The temperature and pressure option for the feed stream state was selected; the pressure and temperature of the feed stream do not affect the vapor pressure estimate. The flash type was set to temperature and vapor flow, with a vapor flow of zero and the temperature set at either 100°F, 120°F, or 140°F.

When pure water was modeled by itself using these simulation settings, the values were within 94% of literature values for the Riedel vapor pressure model and within 90% for the Lee-Kesler vapor pressure model.

The original sample contained 0.1 vol % water (note that for this sample, that is 0.1 mass % water), and simulations were run on the original sample and at additional water increments of 0.05, 0.1, 0.2, 0.4, 0.5, 0.8, 1.0, 1.6, and 2 mass % (for a total of 0.1, 0.15, 0.2, 0.3, 0.5, 0.6, 0.9, 1.1, 1.7, and 2.1 mass % water). Results are given in Table 19 and Figure 46. Table 19 gives the values simulated using the Lee-Kesler vapor pressure model alongside the values simulated using the Riedel vapor pressure model. The two models provide very similar results, with Lee-Kesler values 94% to 97% of Riedel values, and greatest agreement found at higher temperatures and higher water contents. Figure 46 shows Riedel results only.

Figure 46 shows that the modeled values for vapor pressure for the Imperial fuel oil no. 6 sample have a consistent pattern throughout the range of water content; the simulated vapor pressures at additional increments of water bear a relationship to each other that is the same as their relationship to the simulated vapor pressure of the original sample, which contained water. If this had not been the case, it would signal that these simulations of a mixture of water and a fuel oil no. 6 sample whose boiling point distribution is known would not produce reliable results. That they are consistent with each other does not prove that the results are reliable, but they are not definitively unreliable based on inconsistency between simulated entrained water and simulated mixtures of water with the fuel oil no. 6 in this case.

Figure 46 shows that the vapor pressure curves over the range the simulation was conducted fit a quadratic equation very well. However, all of the curves have a negative y-

axis intercept value, which could only happen in a case where the material had a negative vapor pressure unless there was some water in it. This shows that the vapor pressure of a fuel oil no. 6 sample cannot be predicted by using a traditional boiling point distribution and these simulations. However, the purpose of this exercise is not to come up with a predicted vapor pressure for the material as a whole, but the predicted contribution in vapor pressure due to the presence of water. Figure 47 shows the simulated incremental contribution to vapor pressure for various additions of water. As expected, each of the curves is a good fit to a quadratic equation. These equations all have a non-zero intercept, but it is small. Figure 47 gives curves constructed using the Lee-Kesler vapor pressure model as well as the curves constructed using the Riedel vapor pressure model. The curve fit equations in Figure 47 are for the simulated vapor pressures that were produced using the Riedel vapor pressure model.

In order to see whether the simulated contribution of vapor pressure is the same for different fuel oil no. 6 samples, the method was applied to another heavy fuel oil whose boiling point distribution was available. It was difficult to locate even one sample of fuel oil no. 6 for which a boiling point distribution was available. The comparison material is for a lighter fuel oil than fuel oil no. 6 whose boiling point distribution is represented by the yellow curve in figure 6 in CONCAWE (2016). This material will be referred to as the yellow fuel oil sample. Figure 48 shows the boiling point distributions for both the yellow fuel oil and the Imperial fuel oil no. 6.

The boiling point distribution data in CONCAWE (2016) is presented in a figure, and Engauge Digitizer (Winchen et al 2002) was used to produce tabulated values from the figure. These tabulated values are given in Table 20, along with other values needed for modeling that were determined by a curve fit. The initial boiling point (IBP) and final boiling point (FBP) of the stream was determined by fitting the curve to a 6th order polynomial. These values were needed in order to generate the hypothetical compounds. Also, the first cut identified for this material was 4.8 wt %, but the vapor pressure is sensitive to hypothetical components near the IBP. The curve fit equation was used to estimate boiling points at 0.05, 0.1, 0.2, 0.4, 0.8, 1.6, and 3.2 wt %.

The water content of this HFO is not given in the documentation. It is assumed that hypothetical compounds based on a boiling point distribution that includes the effects of entrained water would produce simulated vapor pressures that are consistent with simulated vapor pressures produced from a mixture of the hypothetical compounds and water, because that was demonstrated in the case of the Imperial fuel oil no. 6 sample. The specific gravity of this sample is not provided either, and two sets of simulations were conducted, one assuming a specific gravity of 0.89 and the other a specific gravity of 1, because the range of specific gravities encountered for HFO is expected to fall within that range.

The model setup was the same as for the Imperial fuel oil no. 6, except that only the Riedel vapor pressure model was applied, as simulations using the Imperial fuel oil no. 6 sample showed that the Lee-Kesler model would not produce meaningfully different results.

Figure 49 gives the simulated contribution of vapor pressure due to incremental additions of water for both the high- and low-density cases for the yellow fuel oil. The high- and low-density cases have similar values, with the high-density case values being lower at 89% to 91% of the low-density case values.

Using the process simulation approach, the high-density case for the yellow six oil and the Imperial fuel oil no. 6 represent the lowest and highest simulated contributions to vapor pressure due to addition of water, respectively. In spite of the differences in the two materials that were simulated, the simulated incremental contribution of vapor pressure due to addition of water are of similar magnitude; the values for the high-density yellow fuel oil are 76% to 82% of the values for the Imperial fuel oil no. 6. A low-density fuel oil no. 6 sample would be expected to have higher simulated incremental contributions to vapor pressure due to addition of water than the Imperial fuel oil no. 6 material.

The researchers of this study are unaware of any similar attempts to assess the contribution of water to the vapor pressure of heavy refinery liquids. If a reliable means of determining vapor pressures for heavy refinery liquids was available, it could be used to test the validity of these simulated contributions. It may be that boiling point distributions, no matter how carefully conducted, cannot be used to produce accurate estimates of incremental contributions to vapor pressure of these materials in combination with water. Also, this simulation approach was limited to using Raoult's law for estimating the vapor pressure of a mixture, and Raoult's law only applies to ideal mixtures where there are no interactions between the molecules in the mixture. Mixtures of water and fuel oil no. 6 are not ideal; the water molecules are held by polar forces such as those created by the presence of sulfur and oxygen atoms trapped in the matrix of the fuel oil no. 6 molecules, but most of the functional groups in the fuel oil no. 6 are less polar than water and are attracted to each other more than to water.

Application to the fuel oil no. 6 samples of this study

As shown in Table 15 and Figure 18, the BT fuel oil no. 6 sample of this study was analyzed using ASTM D95 (water by distillation) to have 0.1 (Petrolubricant's result) to 0.2 (Inspectorate's result) vol % water, while the other two fuel oil no. 6 samples (MM and MB) were found to contain 0.00 vol % water. Inspectorate measured the density of the BT fuel oil no. 6 sample using ASTM D4052 (density by digital density meter) and found it to be 990.3 kg/m³. Thus, the BT fuel oil no. 6 sample is similar in density to the Imperial fuel oil no. 6 sample and the high-density case for yellow fuel oil.

Table 21 gives the potential contribution of water to vapor pressure for the BT fuel oil no. 6 sample for the two different water contents at 100, 120, and 140°F, based on the simulation exercise for the two fuel oils described here. This table also shows the comparison of these contributions to vapor pressure values measured using the Eralytics mini method instrument and measured by the commercial labs along with the percent of the measured and curve fit values that are contributed by water in the sample, using this method of estimating the contribution of water.

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Pseudo Component Generation

☒ Tb+SG ☐ Tb+API ☐ Reverse order

Tb (K)	SG

Tc: Cavett 1962
 Pc: Cavett 1962
 Vc: Riazi-Daubert 1980
 w: Kesler-Lee 1976
 Mw: Riazi-Daubert 1980

Name: T[Tb] [C]
 [Tb][SG][Mw][API][K] [C][H][S][NN][AA]

CplG: Riazi-Daubert 1980
 ViscL: Twu 1984
 kL: Riazi-Faghri 1985

☒ CAS# 999TTT-NN-C

Methods selection:

Figure 45. Screenshot showing the model selections for generating pseudo components in the pure component data manager feature of ChemSep LITE 7.15.

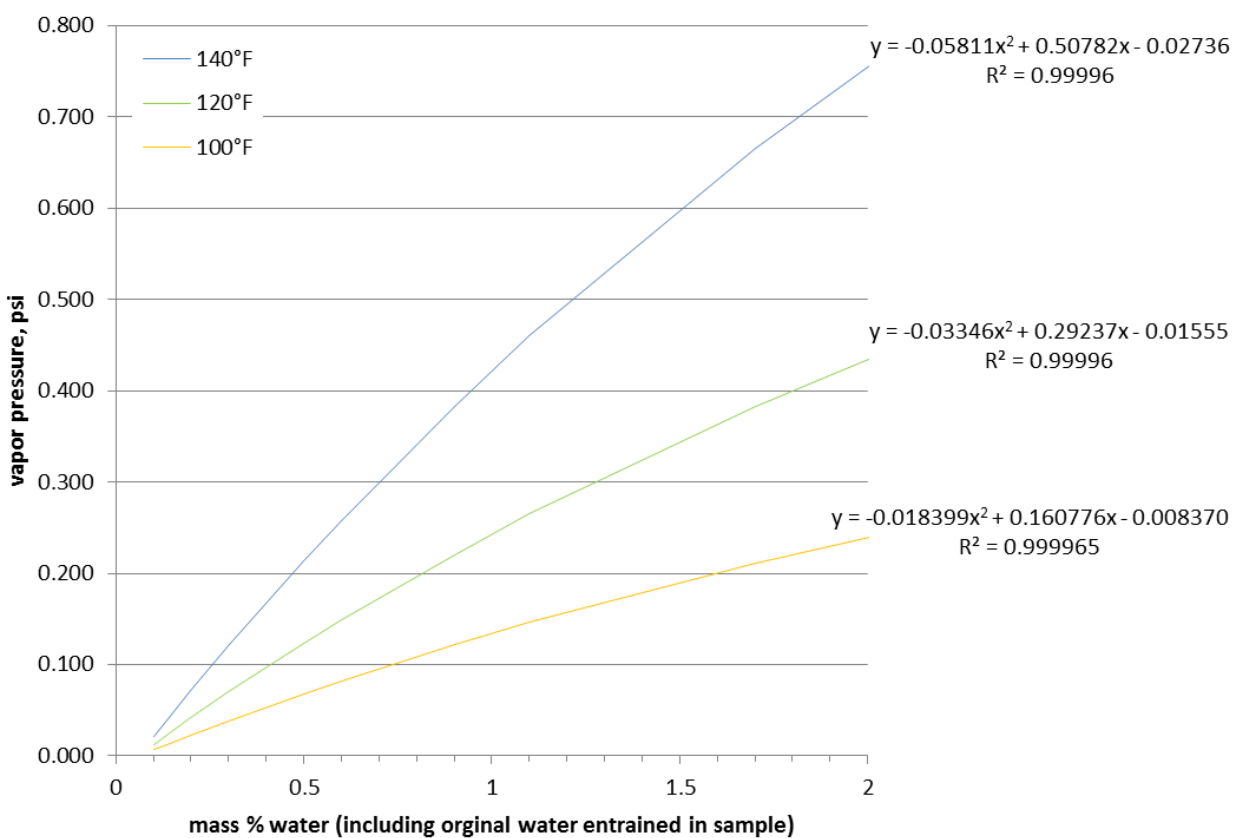


Figure 46. Simulated vapor pressure for mixtures of water and hypothetical compounds developed for the Imperial fuel oil no. 6 sample using the Riedel vapor pressure model. The endpoint of each curve at the left, at 0.1 mass % water, is based on hypothetical compounds developed from the boiling point distribution of the Imperial fuel oil no. 6 sample, which contained 0.1 wt % water.

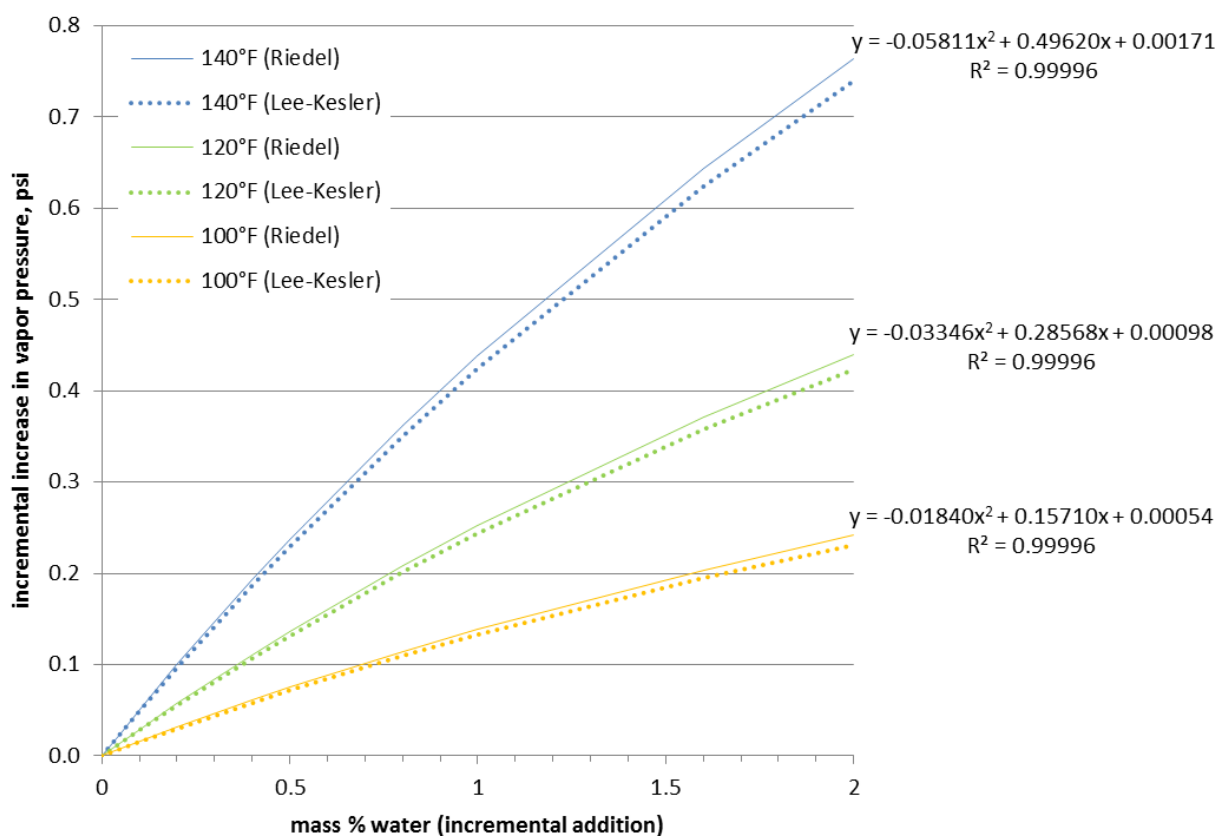


Figure 47. Simulated contribution of water to vapor pressure for mixtures of water and hypothetical compounds developed for the Imperial fuel oil no. 6 sample. Curve fit equations are for the simulations conducted using the Riedel model for vapor pressure.

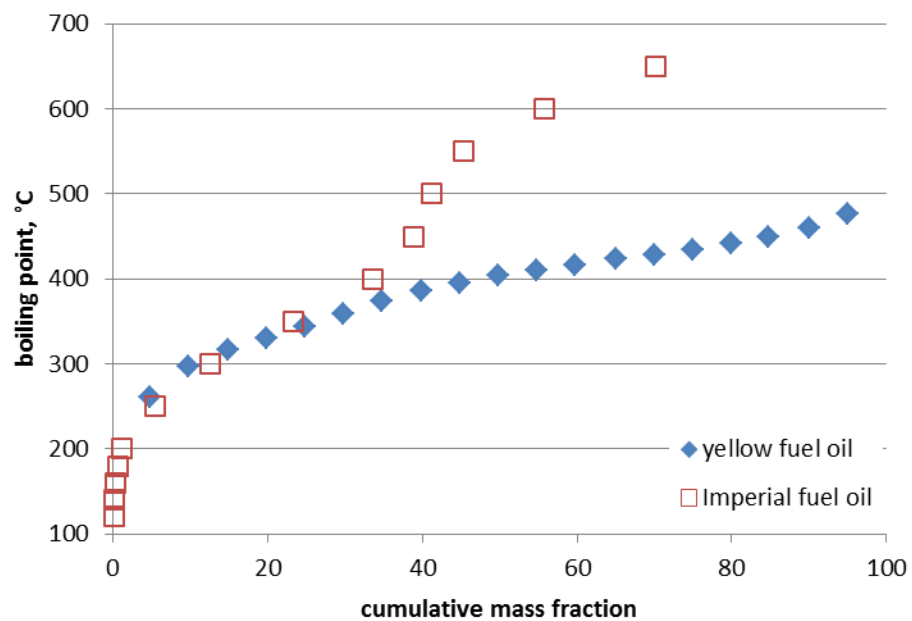


Figure 48. Boiling point distribution for yellow fuel oil (CONCAWE 2016) and Imperial fuel oil no. 6 (US EPA 2003).

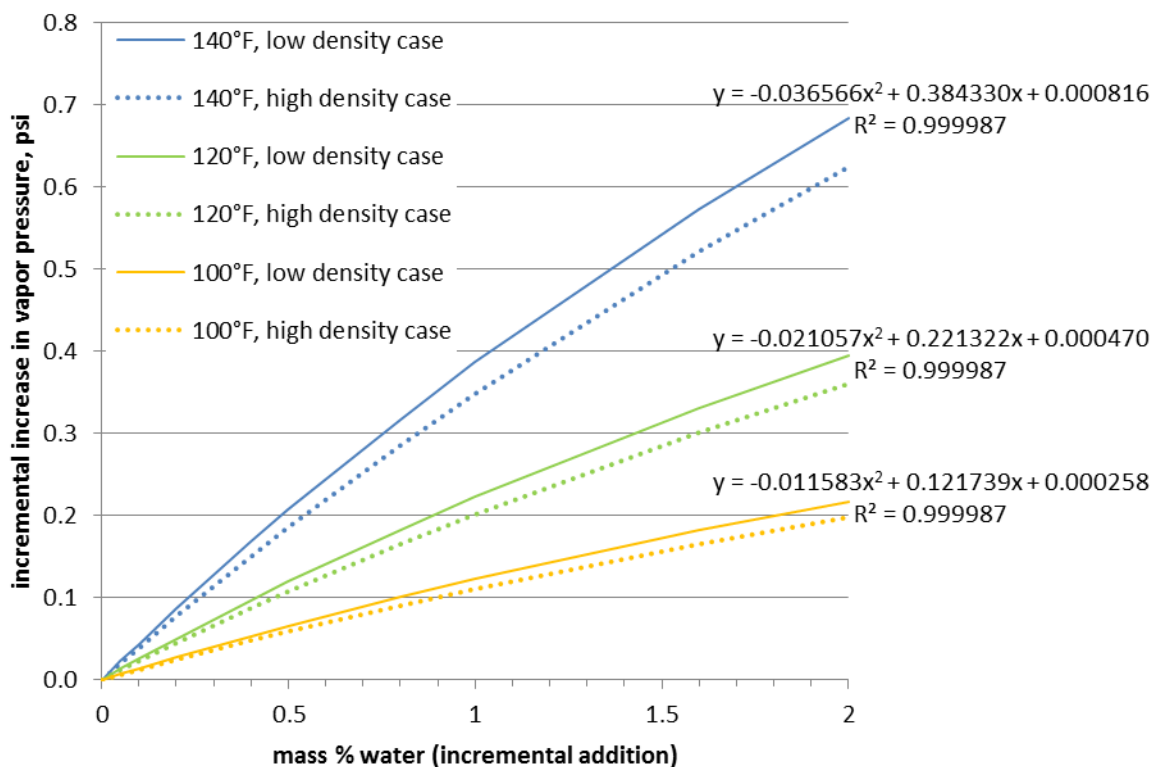


Figure 49. Simulated contribution of vapor pressure due to incremental additions of water to hypothetical compounds generated using the high-density and low-density cases for yellow fuel oil. Equations for curve fits are for the high-density case.

Table 17. Boiling point distribution for fuel oil no. 6 from Imperial Oil Ltd.

Cumulative wt %	Temperature, °C
0	100 ^a
0.05	110 ^a
0.1	120
0.2	140
0.3	160
0.6	180
1.2	200
2.4 ^b	216
3.9 ^b	234
5.5	250
12.5	300
23.3	350
33.5	400
38.8	450
41.2	500
45.3	550
55.7	600
70.1	650
100	773 ^c

^aValues at 0 and 0.05 wt % estimated based on linear trend at 0.1, 0.2, and 0.3 wt %.

^bBased on 2nd degree polynomial fit of curve from 180°C to 300°C

^cValue at 100 wt % set equal to final boiling point of fuel oil no. 6 as given in table 1 of US EPA (2012).

Table 18. Average boiling point temperature and specific gravity for each Imperial fuel oil no. 6 cut.

Average boiling point, K	Specific gravity
378	0.783
388	0.790
403	0.800
423	0.813
443	0.825
463	0.838
481	0.848
498	0.858
515	0.868
548	0.886
598	0.912
648	0.937
698	0.960
748	0.983
798	1.004
848	1.025
898	1.045
960	1.068

Table 19. Simulated vapor pressures for a mixture of hypothetical compounds based on the Imperial fuel oil no. 6 sample and for mixtures of water and the hypothetical compounds based on Imperial fuel oil no. 6 sample, psi.

Total water, mass %	Water added to hypothetical compounds, mass %	100°F		120°F		140°F	
		Riedel vapor pressure model	Lee-Kesler vapor pressure model	Riedel vapor pressure model	Lee-Kesler vapor pressure model	Riedel vapor pressure model	Lee-Kesler vapor pressure model
0.1*	0	0.0070	0.0066	0.012	0.012	0.021	0.020
0.15	0.05	0.0151	0.0143	0.027	0.026	0.047	0.045
0.2	0.1	0.023	0.022	0.042	0.040	0.072	0.069
0.3	0.2	0.039	0.037	0.070	0.067	0.12	0.12
0.5	0.4	0.068	0.065	0.12	0.12	0.21	0.21
0.6	0.5	0.082	0.079	0.15	0.14	0.26	0.25
0.9	0.8	0.121	0.116	0.22	0.21	0.38	0.37
1.1	1	0.15	0.14	0.26	0.26	0.46	0.45
1.7	1.6	0.21	0.20	0.38	0.37	0.67	0.64
2.1	2	0.25	0.24	0.45	0.44	0.78	0.76

*This is the water content of the original Imperial fuel oil no. 6 sample.

Table 20. Tabulated values for boiling point distribution based on digitization of yellow HFO in figure 6 of CONCAWE (2016).

Cumulative wt %	Temperature, °C
0	216*
0.05	216*
0.1	217*
0.2	218*
0.4	220*
0.8	225*
1.6	233*
3.2	249*
4.8	261
9.8	297
14.8	316
19.8	331
24.8	344
29.7	360
34.8	373
39.8	386
44.8	395
49.8	403
54.8	410
59.8	416
65	423
70	428
75	434
79.9	442
84.8	450
90	460
95	477
100	488*

*From 6th order polynomial curve fit of digitized data points.

Table 21. Potential effect on vapor pressure results of the BT fuel oil no. 6 sample due to the presence of water.

		Type	Temperature, °F		
			100	120	140
Contribution of vapor pressure due to presence of water, psi					
0.1 vol % ≈ 0.1 mass %	Imperial fuel oil no. 6 sample correlation		0.02	0.03	0.05
	yellow fuel oil correlation		0.01	0.02	0.04
0.2 vol % ≈ 0.2 mass %	Imperial fuel oil no. 6 sample correlation		0.03	0.06	0.10
	yellow fuel oil correlation		0.02	0.04	0.08
Uncorrected vapor pressure measurements/curve fits, psi (contribution of water, %)					
Eralytics (two measurements each using low VP single point method)				0.5 (4-11%)	0.4 (9-22%)
				0.7 (3-8%)	0.01 (>100%)
default value from EPA (2006)			0.006 (>100%)	0.01 (>100%)	0.02 (>100%)
ASTM E1719, calculated			0.09 (14-35%)	0.1 (18-46%)	0.2 (23-59%)
ASTM D2879	Lab 1	measured	0.07 (17-42%)	0.09 (25-63%)	0.1 (37-94%)
		curve fit	0.02 (79->100%)	0.03 (89->100%)	0.04 (99->100%)
	Lab 3	measured			0.7 (5-14%)
		curve fit	0.2 (7-19%)	0.2 (9-23%)	0.3 (11-29%)

7. Conclusions

Measuring the vapor pressure of heavy refinery liquids is difficult not just because the vapor pressure is low, but also because the materials are viscous, sticky, and opaque. This project demonstrated that mini method instruments can process samples of heavy refinery liquids and that there is often an order of magnitude agreement in measured vapor pressures of heavy refinery liquids using mini method instruments and the commercial lab results of this study. For both ASTM D2879 (vapor pressure by isoteniscope) and the mini method instruments, it appears that accounting for or removing dissolved air in the material being analyzed is a major hurdle. Opportunities for overcoming that hurdle were identified in this project.

ASTM D2879 (vapor pressure by isoteniscope) results from different commercial labs disagreed by more than an order of magnitude in some cases in this project. It is likely that the conditions of the degassing step in this method are a primary cause of disagreement in results at different labs. The only lab accredited for this method produced measurements very near the modeled vapor pressure of a mixture containing a volatile compound and a nonvolatile compound (the “known” recipe), indicating that this method may be appropriate for heavy refinery liquids if the conditions of the degassing step are carefully controlled. None of the measured values of the “known” recipe that were taken using this method by any of the commercial labs were larger than the estimated vapor pressure, indicating that perhaps the measured values taken using this method represent a lower bound on vapor pressure.

The measured results for ASTM E1719 (vapor pressure by ebulliometry) were taken at temperatures higher than the temperatures of interest for estimating emissions from heated storage tanks. The measured results of this method were in agreement with the estimated vapor pressure of the “known” recipe. This method generates calculated values for vapor pressure across a range of temperatures from measurements taken in a fairly tight band of temperature and the curves that were generated from these calculated values had a flatter slope than any other method’s results for all five study materials.

Results from ASTM D323 (Reid vapor pressure) (<0.2 psi for all five study materials) were generally in agreement with all of the other methods. The only method that returned a higher result than ASTM D323 was the calculated values for ASTM E1719 for the “known” recipe. ASTM D323 measures the air- and water-saturated vapor pressure of a material at 100°F and is expected to represent an upper bound of actual vapor pressure because the study materials were not air- and water-saturated.

This project showed that the mini method instruments tested in this study show great promise as tools for measuring the vapor pressure heavy refinery fuel oils. However, great care and understanding of the operation of the instrument and factors affecting the vapor pressure measurement of these fluids must be exercised when conducting these measurements. The results of the fuel oil no. 6 samples were very sensitive to the values

for pressure and volume that were obtained at each of the expansions conducted by the instruments.

At 100°F and above (which would include typical storage temperatures) the single point mini method results using methods intended for heavy refinery fluids were in every case near the estimated results for the “known” recipe. Except for one measurement at 140°F for the BT fuel oil no. 6 sample, the vapor pressures of the fuel oil no. 6 samples taken using the Eralytics instrument were between 0.1 and 1 psi. In addition, at least some of the Eralytics mini method results were within an order of magnitude of measured results from at least one commercial lab for each of the study’s fuel oil no. 6 materials.

One of the three fuel oil no. 6 materials used in the study was identified as containing water at 0.1 or 0.2 vol %. The contribution of water to the vapor pressure of this material was estimated by applying the results from simulation of mixtures of water and hypothetical compounds that were developed based on boiling point distribution and specific gravity of heavy fuel oils. Using this method, the estimated contribution of water at these concentrations to the vapor pressure of a fuel oil no. 6 with the density of this sample ranges from 0.01 to 0.03 psi at 100°F, from 0.02 to 0.06 psi at 120°F, and from 0.04 to 0.10 psi at 140°F. The contribution of water to the measured vapor pressures obtained during this study for this material (including all methods) were 17 to 42% at 100°F, 3 to 63% at 120°F, and 9 to >100% at 140°F.

8. Recommendations

Further research and analysis is necessary to identify a practical method or methods that can be relied upon to produce acceptable results for the vapor pressure of heavy refinery liquids. Potential areas of interest include:

- Contract with Dr. Tom Bruno's group at NIST to apply their advanced distillation curve techniques for assessing the vapor-liquid equilibrium of mixtures to heavy refinery liquids that are also analyzed using the methods that showed the most promise in this study. While too expensive to be practical for routine analysis, advanced distillation curve techniques could be used to produce reliable vapor pressure measurements for comparison with results from commercial laboratories and mini method instruments.
- Make refinements to ASTM D2879 (vapor pressure by isoteniscope) to determine whether this method can be adapted for use in determining the vapor pressure of heavy refinery fluids. For example, seeding the boil might make degassing possible under gentler conditions, and conditions for the pressure/temperature of the degassing step could be set. Perhaps the manometer could be constructed of a material or coated with a material that heavy refinery liquids will be less inclined to cling to, which would facilitate sighting of the menisci.
- Use the Eralytics instrument to get low VP single point readings of fuel oil no. 6 samples at higher temperatures (e.g., 160°F, 180°F, and 200°F). It is reasonable to hypothesize that readings at higher temperatures will be of better quality than those taken at lower temperatures, and if higher temperature readings pass the quality checks described in Appendix H, they could be used to construct a curve so that vapor pressure at typical storage conditions can be determined.
- Investigate whether ASTM E1719 could be easily modified to obtain vapor pressure measurements at typical storage temperatures instead of higher temperatures.
- Test whether methods that are proving effective for fuel oil no. 6 can be applied to liquid asphalt as well.
- Assess the contribution of water content on vapor pressure by testing the effect on vapor pressure of additional aliquots of water to fuel oil no. 6 samples whose initial water concentration is known.
- Determine sampling (e.g., floating piston cylinders) and instrument operation practices for use in the field.
- Assess whether typically available properties (density, flash point, viscosity, pour point, etc.) can be used to develop ranges of vapor pressure of heavy refinery liquids.
- Assess the potential for developing ranges of vapor pressure that coincide with speciation information (up to C20) and Raoult's law.

APPENDICES

Appendix A. Procedures for Dispensing Samples

Appendix B: Safety data sheets for study materials

Appendix C: Quality assurance and audits of data quality

Appendix D: Vapor Pressure Analysis Using Minivap Method Standard Operating Procedure

Appendix E: Grabner mini method instrument application study

Appendix F: Eralytics' recommendations for analyzing heavy refinery liquids

Appendix G: Photos of the mini method instruments

Appendix H: Factors to consider when using a triple expansion method to measure the vapor pressure of heavy refinery liquids

Appendix I: Observations on the design of automated mini method instruments