Scope of Work For

AQRP Project 17-007
Evaluating Methods for Determining
the Vapor Pressure of Heavy Refinery Liquids

Prepared for

Air Quality Research Program (AQRP)
The University of Texas at Austin

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Approvals

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1.0 Abstract

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), hazardous air pollutants (HAPS) and greenhouse gases (GHGs), 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). State and federal laws require certain facilities to design, install, operate and maintain effective pollution control measures to minimize the emissions of VOCs and HAPs (THSC, 2009, US CFR, 2015a). For example, the federal New Source Performance Standards for Crude Oil and Natural Gas Production (US CFR, 2015b) "requires that new, reconstructed or modified storage vessels with the potential for VOC emissions of equal to or greater than six tons per year reduce VOC emissions by at least 95%." The Texas Commission on Environmental Quality (TCEQ) funded two projects recently (Rosselot, et al, 2014; Rosselot, et al, 2015) to better understand the composition and properties of heavy refinery liquids and the most appropriate method of determining their true vapor pressure (TVP).

The purpose of this research is to improve the estimates of VOC emissions from storage tanks holding heavy refinery liquids. 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 and may explain some of the VOC inventory gap in parts of Texas.

During the course of this project, the most accurate, reliable, convenient, and reasonably priced means of measuring the TVP of heavy refinery liquids stored in tanks will be identified. Identifying an appropriate means of measuring the TVP of these heavy refinery liquids is important because direct measurement of VOC emissions from storage tanks is inherently inexact and expensive, so equations are used to estimate emissions from storage tanks. The value used for the TVP in these equations has a profound impact on the results. The results of this research will facilitate efforts being made by the US EPA, TCEQ, and agencies in other states to better understand, more accurately estimate, and manage emissions from tanks holding heavy refinery liquids.

2.0 Background

Texas, with its storage terminals and petroleum refineries, has a large population of tanks holding heavy refinery liquids. Evidence is mounting that VOC emissions, from tanks holding heavy refinery liquids such as liquid asphalt and fuel oil no. 6, which are typically heated so that their contents can be transferred via pumps, are underreported and are potentially a significant source of VOC emissions. 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). In a presentation to the 4C Environmental Conference in 2015 (Nettles, 2015), Russell Nettles of the Texas Commission on Environmental Quality (TCEQ) noted that several studies have indicated that volatile emissions from heated tanks are potentially underestimated. 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).

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 TVPs 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. Default values are available for only two heavy refinery liquid streams: fuel oil no. 6 and vacuum distillate. In tanks holding fuel oil no. 6, actual emissions have been found to be much larger than emissions estimated using the default vapor pressure values.

To determine the emissions of VOCs, HAPs and GHGs from sources, one must either directly measure these emissions at the source or estimate the potential amount of the liquid source that will evaporate or be released from the liquid and escape to the environment. Direct measurement of emissions from these 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 air flow is blown. The known air flow 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). 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 TVP of a liquid mixture is a property that is critical in estimating emissions from refinery storage tanks and it has a profound impact on the mathematical algorithms and computer programs that have been approved by the US EPA (US EPA, 2006; TCEQ, 2012) to estimate emissions. The TVP is defined in AP-42, Chapter 7, as the equilibrium partial pressure of the volatile organic liquid in the enclosed container (US EPA, 2006). The higher the TVP, the more readily the liquid will form vapor. The TVP is only a function of temperature (Green, 2008). (The term vapor pressure (VP) will be used synonymously with TVP in this work plan.) These equation-based model estimates are strongly dependent on the value that is used for the VP of the stored liquid at a characteristic storage temperature and the accuracy of the emission estimate, in part, depends on the accuracy of the VP used.

The VP 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 VP, the mixture's VP can be estimated using Raoult's Law (US EPA, 2006). Most heavy refinery liquids, however, are complex mixtures of many chemicals whose VPs 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 VP of these liquids is infeasible.

The underreporting of emissions from storage tanks can be due in part to the use of inappropriately low VP values in the equations used to estimate emissions from tanks. The lack of a reliable and convenient method to measure the VP of heavy refinery liquids may be the reason some companies use inappropriate default values in estimating emissions. In a modeling exercise, applying a VP 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 VP 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 VP; in practice, a heavy liquid's VP 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. ***Using inappropriate default values can result in emission estimates that are low by several orders of magnitude (Rosselot and Allen, 2015).*** Being able to accurately, repeatedly, conveniently, and cost-effectively measure the vapor pressure of a sample from or at the storage tank, at the temperature of the liquid surface in the tank, is the goal. This is challenging for heavy liquids with specific gravity near 1 or that are too viscous at room temperature to be pumpable because of the low VPs encountered and the complexities of measuring the VP of complex mixtures of chemical species.

Emissions from asphalt and fuel oil no. 6 storage tanks include greenhouse gases such as methane, HAPs such as benzene, toluene, ethylbenzene, xylene, and n-hexane, and highly reactive VOCs such as propene (Rosselot and Allen, 2015). Hence, not only do these heavy liquids produce emissions that include VOCs and HAPs, but some of these compounds result in the formation of secondary organic aerosols, which contribute to the quantity of aerosol particulate matter in the atmosphere and impact the emission inventory. Hill (2016) noted that emissions from tanks storing liquid asphalt and fuel oil no. 6 also include polyaromatic hydrocarbons and liquid aerosols, and that tanks storing liquid asphalt emit aldehydes (implicated in the production of secondary aerosols) and reduced sulfides (which have toxic effects).

The only default VP 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). It is unknown how these default values were obtained. There is no standard test method whose scope includes the default value for vacuum residual oil, and the only standard test method whose scope explicitly includes the default value for fuel oil no. 6 is ASTM E1719. In spite of this, in many cases (e.g., US EPA, 2006), ASTM D2879 (ASTM, 2010a) is recommended as a method for measuring the VP of organic liquids whose VPs do not appear in the literature or for which default values are not available.

Even though ASTM D2879 is recommended, the appropriateness of applying this method to measure the VP of heavy refinery liquids is questionable. 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 International 2010), so its repeatability, reproducibility, and bias are unknown. An additional weakness of this method is that it involves a degassing step (ASTM International 2010) and because heavy liquids at refineries tend to contain a mixture of substances with highly varying VPs, this degassing step could drive off lighter components of the mixture and provide values for the VP that are lower than the actual VP (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 D-2879 is a labor-intensive method in which heavy, viscous products are the most difficult to test, and dark products that cling to the glass make the test more difficult to perform. In its guidelines for testing the VP of chemicals, the Organisation for Economic Co-operation and Development (OECD, 2006) noted that isoteniscopes are usually not suitable for measuring the VP of multicomponent systems (ASTM D2879 makes use of an isoteniscope).

In the projects recently completed for the TCEQ (Rosselot and Torres, 2014; Rosselot and Allen, 2015) Rosselot found that the range of VPs encountered is critical in determining an appropriate method to determine the appropriate VP to use. In the latter study (Rosselot and Allen, 2015), it was found that for a common heavy refinery liquid, fuel oil no. 6, there is a lack of consistency in reported VPs from one method to the next, along with disagreement with the default value for this material. These discrepancies are not minor. For fuel oil no 6, the methods for determining VP differ by as much as a factor of 92. At 100°F (which is near the temperature of the surface of the liquid in a typical tank holding fuel oil no. 6), the default value is 0.006 psi (API, 2012 with addendum dated 2013). At one tank holding fuel oil no. 6 in Maine, the VP of a sample at 100°F was measured to be 0.0093 psi using ASTM D2879 and the Reid vapor pressure (RVP) was found to be 0.5 psi using ASTM D323. At another tank holding fuel oil no. 6 in Maine, the VP at 100°F was measured to be 0.019 psi using ASTM D2879 and the RVP was found to be 0.55 psi. Note that while the results of ASTM D2879, unlike RVP, are meant to express true vapor pressure and thus exclude the contribution of dissolved gases, such as air in the sample, the difference in the value for ASTM D2879 at 100°F and RVP for heavy refinery liquids is expected to be small. Charts and equations for converting RVP to true vapor pressure show that as the RVP of a crude oil or refined petroleum stock declines, the true vapor pressure and the RVP converge (US EPA, 2006). While there is no default value for the VP of asphalt, there was one asphalt tank whose contents were tested for VP using both ASTM D2879 and RVP; the values were 0.050 psi to .056 psi for ASTM D2879 (depending on whether or not the sample had been dried) and 0.45 psi for RVP, respectively.

3.0   Objectives
The primary objective of this project is to identify the most accurate, reliable, convenient and cost-effective means of measuring the vapor pressure of heavy refinery liquids at temperatures in the range of the typical temperatures of the liquid surface in refinery storage tanks.

4.0 Task Descriptions

The approach to be used on this project is to evaluate three test methods commonly used or prescribed for measurement of the vapor pressure of hydrocarbon liquids. The three test methods that will be evaluated and prescribed for use by the commercial laboratories for this project were selected (shown in Table 1) because their scope is likely to cover the range of VPs of heavy refinery liquids. These methods are ASTM D2879, ASTM E1719, and ASTM D323 Procedure A. The rationale for selection of each method is given in the second row of Table 1. ASTM Method D2879 is the method recommended by the US EPA for measuring the VP of heavy liquids. ASTM Method E1719 was selected because it uses the boiling point at different pressures to determine the VP (ASTM, 2012). This method will not work for liquids that "bump" when they boil or that contain non-condensibles. (A "bump" is when vapor bubbles form suddenly and erupt from the liquid surface at intervals instead of steadily.) ASTM Method D323 Procedure A was selected because it should correlate with ASTM Method D6377 (ASTM, 2015; ASTM 2014), which will be tested using the automated mini-method instrument (Grabner, V 3.02 not dated). Also, the results of ASTM D323 Procedure A should be similar to the results of the other methods at 100°F. In addition to the commercial laboratory tests, an automated mini-method will be used. At this time the only known automated mini-method instrument that is specifically designed to determine the VP of low volatility streams is the Grabner MINIVAP VPXpert-L, and is the instrument that will be used for this project. Table 1 shows that this instrument can perform four methods that are applicable to heavy refinery liquids. These methods are ASTM D6378 and D6377, plus an indirect VOC method and a direct VOC method that should correlate well with ASTM D2879 results.

4.1 Prepare Work Plan

This task includes preparation and delivery of the work plan per the AQRP requirements and concludes with its approval and receipt of an approved start date from the AQRP.

4.2 Project Reporting and Presentation

As specified in Section 7.0 "Deliverables" of this Scope of Work, AQRP requires the regular and timely submission of monthly technical, monthly financial status and quarterly reports as well as an abstract at project initiation and, near the end of the project, submission of the draft final and final reports. Additionally, at least one member of the project team will attend and present at the AQRP data workshop. For each reporting deliverable, one report per project will be submitted (collaborators will not submit separate reports), with the exception of the Financial Status Reports (FSRs). The lead PI (or their designee) will electronically submit each report to both the AQRP and TCEQ liaisons and will follow the State of Texas accessibility requirements as set forth by the Texas State Department of Information Resources. The report templates and accessibility guidelines found on the AQRP website at http://aqrp.ceer.utexas.edu/ will be followed. **Draft copies of any planned presentations (such as at technical conferences) or manuscripts to be submitted for publication resulting from this project will be provided to both the AQRP and TCEQ liaisons per the Publication/Publicity Guidelines included in Attachment G of the subaward.** Finally, our team will prepare and submit our final project data and associated metadata to the AQRP archive.

Table 1. Measurement Methods and Sample Conditions (Temperature or Pressure)

Laboratory Making TVP Measurement	To Be Tested by Several Labs, Preferably Accredited	To Be Tested By At Least One Lab, Preferably Accredited		Automated Mini-Method, Such as Grabner MINIVAP VPXpert-L, Operated By UT Austin		
Method	ASTM D2879*	ASTM E1719**	ASTM D323 Procedure A	ASTM D6378	Direct VOC Method* / Indirect VOC Method*	ASTM D6377
Rationale for selection of method	This is the method recommended by the EPA for measuring the vapor pressure of heavy liquids; it must be performed at as many labs as possible because there is no precision statement for this method so there is no assurance that this method has reasonable repeatability or reproducibility. A couple of these labs (PRI and Saybolt) are not listed in the ASTM directory as performing this test and may not do it any longer.	There is only one lab listed by ASTM that does this test; the rationale for including it is that it measures boiling point at different pressures to determine vapor pressure. Will not work for mixtures that "bump" when they boil or that contain non-condensible gases. It is expected that this method will provide a comparison at typical storage temperatures but not at ambient temperatures.	D323 should correlate with D6377 results using ASTM correlation, and D323 results should be similar to ASTM D2879 results at 100°F.	Automated triple expansion method that the Grabner can run.	Yields results comparable to ASTM D2879 but without any changes in sample composition.	Automated single expansion method that the Grabner can run.
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 (indirect method allows extrapolation from -99°C to 120°C and 120°C to 300°C)	0°C to 100°C (precision statement applies at 37.8°C)
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)	.1 kPa to 100 kPa	<500 kPa (precision statement applies to samples with vapor pressure of 25 kPa to 180 kPa at 37.8°C)
mixture of pure substances***	-14°C to 125°C	1 kPa to 100 kPa	37.8°C	0°C to 100°C	0°C to 120°C with extrapolation from -14°C to 0°C and 120°C to 125°C for the indirect method	0°C to 100°C
Castrol Brayco® Micronic 756	13°C to 150°C	1 kPa to 4 kPa	37.8°C	13°C to 100°C	0°C to 120°C with extrapolation from -54°C to 0°C and 120°C to 150°C for the indirect method	13°C to 100°C
Radco XCELTHERM® SX800	32°C to 154°C	1 kPa to 100 kPa	37.8°C	32°C to 100°C	32°C to 120°C with extrapolations from 120°C to 300°C for the indirect method	32°C to 100°C
No. 6 fuel oil (multiple sources)	4°C to 54°C	1 kPa to the pressure that makes the sample boil at 54°C	37.8°C	4°C to 54°C	4°C to 54°C	4°C to 54°C
Liquid asphalt (multiple sources)	4°C to 38°C and 126°C to 154°C	1 kPa to the pressure that makes the sample boil at 154°C	37.8°C	4°C to 100°C	4°C to 120°C with extrapolations from 120°C to 154°C for the indirect method	4°C to 100°C

*For fuel oil no. 6, typical storage temperature is 120°F (49°C), and for liquid asphalt the typical storage temperature is 300°F (149°C). Where possible, fuel oil no. 6 and liquid asphalt temperature ranges capture expected ambient Texas Gulf Coast temperatures in order the explore the vapor pressure of fluid in tanks that are not being heated as well as the range of surface temperatures expected in heated tanks. Vapor pressure of the contents at the surface is what influences emissions and surface temperatures are expected to be lower than bulk temperatures in heated tanks.

**In the case of ASTM E1719, temperatures are measured as pressure is varied so the values in this column are pressure in kPa.

***This will be a mixture of pure alkane substances whose vapor pressure behavior across temperature is well defined and whose vapor pressures and activity model parameters are available. The vapor pressure of the mixture will be on the order of a tenth of a psi at 120°F. The average molecular weight of the mixture will be as close to the average molecular weight of fuel oil no. 6 as possible (~300 g/mol). For health and safety reasons, an attempt to mimic the naphthenic, aromatic, metals, nitrogen, oxygen, and sulfur content that can be found in fuel oil no. 6 will not be made but the mixture will be chosen so that the potential effects of the size heterogeneity of compounds in fuel oil no. 6 on the nonideality of vapor pressure behavior are represented.

Deliverables: Abstract, monthly technical reports, monthly financial status reports, quarterly reports, draft final report, final report, attendance and presentation at AQRP data workshop, submissions of presentations and manuscripts, project data and associated metadata

Schedule: The schedule for Task 4.2 deliverables is shown in Table 2.

4.3 Purchase Automated Mini-method Instrument Designed to Measure VPs of Low Volatility Liquids

The project will require the purchase of one Grabner MINIVAP VPXpert-L, which will be used to perform VP measurements of the heavy liquids using ASTM methods D6378 and D6377, plus an indirect VOC method and a direct VOC method that should correlate well with ASTM D2879 results. This is the only automated instrument designed to measure the vapor pressure of low volatility liquids, and it has good repeatability and reproducibility. Highlights of the features of the instrument and selected Technical data are provided in Figure 1.

MINIVAP VPXpert / L VAPOR PRESSURE TESTER COMPLIES WITH

- ASTM D5191 (Dry Vapor Pressure Equivalent)
- ASTM D6378 - Vapor Pressure of Gasoline (VP4)
- ASTM D6377 - Vapor Pressure of Crude Oil
- ASTM D6897 - Vapor Pressure of LPG up to 1000 kPa (VPXpert only)
- ASTM D5188 - (V/L-Ratio)
- EN 13016 - 1 (Air Saturated Vapor Pressure)
- EN 13016 - 2 (Absolute Vapor Pressure)
- IP 394 & 409 & 481
- JIS K2258-2, SHT 0769, GOST 52340
- US EPA approved Grabner test method for highest accuracy

Technical Data

Temperature Range	Measured: 0 to 120°C (user programmable) Extrapolated: -99 to +300°C (VPXpert-L only)
Temperature Stability	± 0.01°C
Temperature Profiles	Single temperature, stepped or ramped
Pressure Range	VPXpert: 0 to 1000 kPa (0 to 145 psi) VPXpert-L: 0 to 100 kPa (0 to 14.5 psi)
Pressure Resolution	VPXpert: 0.1 kPa VPXpert-L: 0.01 kPa
Pressure Tolerance	0.1 kPa
Vapor-Liquid Ratio	0.02/1 to 100/1, adjustable per selected method
Power Requirements	90-264 V AC, 45-63Hz, 200W (Switching Power Supply)
Field Application	DC/AC Power Converter 12V / 200W
W x H x D	253 x 368 x 277 mm (10 x 14.5 x 10.9 in)
Weight	9 kg (20 lb)

Precision Data	MINIVAP (37.8°C @ 70 kPa)	ASTM D323 (Wet Reid Bomb)
Repeatability	±0.3 kPa (0.04 psi) ±0.1 kPa (VPXpert-L)	±3.2 kPa (0.46 psi)
Reproducibility	±0.7 kPa (0.10 psi)	±5.2 kPa (0.75 psi)

Figure 1. Highlight of Features and Selected Specifications of the Grabner MINIVAP VPXpert-L

The manufacturer reports that the Grabner MINIVAP VPXpert-L instrument was developed to automate the manual ASTM D2879 Standard Test Method for Vapor Pressure by Isoteniscope used by the chemical industry. It can measure vapor pressures of gasoline, jet fuels, solvents and chemicals with excellent precision with repeatability of better than 0.1 kPa and reproducibility of 0.7 kPa. The principle of operation of the Grabner MINIVAP VPXpert-L is shown in Figure 2. The sample to be measured is contained in a 10 mL syringe (3) or in a sample container for direct sampling. The automatic sample introduction and volume adjustments are made by the action of a piston with an integrated pressure transducer (1). The measuring chamber (2) with a total volume of 5 mL is automatically rinsed and filled with 1 mL of the sample for the measuring process. After closing the valve (4) driven by the valve motor (5), the volume expansion to 5 mL (with the sample under vacuum condition) is obtained by a further stroke of the piston. The temperature of the measuring cell is controlled with a high-power thermoelectric module (6) and measured with a precision platinum RTD sensor (7). After the sample introduction and volume expansion, the test temperature is adjusted. After the equilibrium time, the measurement of the dissolved air is completed. Test results of dry vapor pressure equivalent (DVPE), air saturated vapor pressure (ASVP), pressure of the gas (Pgas), and Pabs are displayed and printed (Grabner, V 3.02).

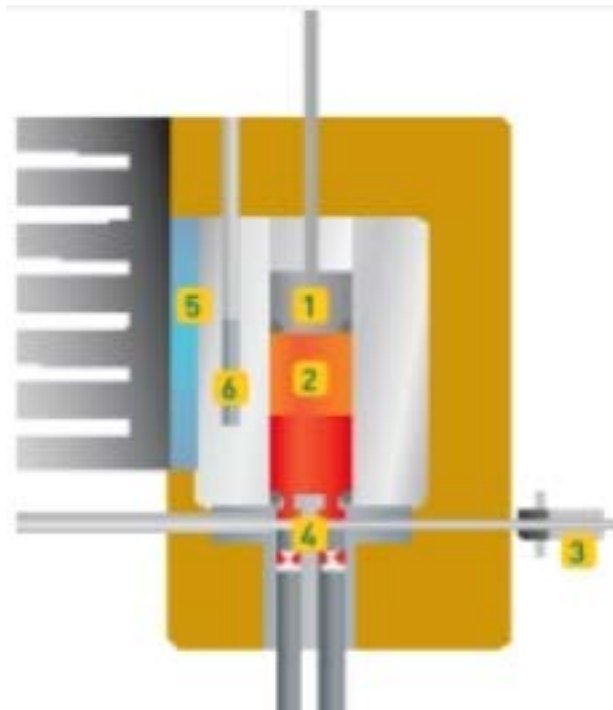Figure 2. Diagram of Grabner MINIVAP VPXpert -L Analyzer Operation (from Grabner, V 3.02)

Deliverables: Purchase and receipt of the Grabner MINIVAP VPXpert-L
Schedule: The schedule for Task 4.3 deliverables is shown in Table 2.

4.4   Identify Labs to Conduct Testing Using ASTM D2879, E1719, and D323, Selecting Accredited Labs Where Possible

It is anticipated that some of the methods are so rarely applied that it will be difficult to find labs that are accredited in those methods. Accredited labs will be identified using the following list of accrediting organizations:

- American Association for Lab Accreditation (A2LA) www.a2la.org
- International Accreditation Service, Inc. (IAS) www.iasonline.org
- Laboratory Accreditation Bureau (L-A-B) www.l-a-b.com
- Perry Johnson Laboratory Accreditation, Inc. (PJLA) www.pjlabs.com
- Laboratory Accreditation Bureau (L-A-B) www.l-a-b.com
- Perry Johnson Laboratory Accreditation, Inc. (PJLA) www.pjlabs.com
- AASHTO Accreditation Program (AAP) www.amrl.net
- National Voluntary Laboratory Accreditation Program (NVLAP) www.nist.gov/nvlap/
- ANSI-ASQ National Accreditation Board (ACLASS & FQS): www.anab-aclass.org

Because there is no precision statement for ASTM D2879, samples will be sent to more than one lab for this test method (up to four different labs).

Deliverables: Selection of the commercial labs to be used and the methods each will be prescribed to perform.
Schedule: The schedule for Task 4.4 deliverable is shown in Table 2.

4.5   Obtain Materials for Testing and Material Safety Data Sheets (MSDSs)

Three materials whose VPs are known (one mixture whose VP can be determined using values in the literature along with an activity model method, i.e., UNIQUAC, for estimating the activity coefficient and the impact of nonideality, and two hydraulic/heat exchanger fluids whose VPs are listed on their MSDSs and whose manufacturers will hopefully be forthcoming about the methods used to produce the vapor pressure values given in the safety data sheets), will be included in the testing. These materials were also chosen because their VPs are anticipated to be in the same range as fuel oil no. 6 and liquid asphalt. Because of the variation found in fuel oil no. 6 and liquid asphalt, multiple samples of these streams will be tested. The composition of the lighter ends of the fuel oil no. 6 and asphalt samples will be determined, probably using a combination of gas chromatography-mass spectrometry (GC-MS) and gas chromatography-flame ionization detection (GC-FID) analysis. ASTM D7845-16 (ASTM 2016), a standard test method for determination of chemical species in marine fuel oil by multidimensional gas chromatography/mass spectrometry, will be applied to the fuel oil no. 6 samples unless it is expected to produce flawed results. This analysis along with Raoult's Law for determining the vapor pressure of the mixture will be used as a quality control measure, if an analysis of the potential nonideality of the behavior of vapor pressure of fuel oils shows that Raoult's Law would be expected to provide reasonable results. The compositional analysis will also give a sense of the variation in composition of the sample heavy refinery liquid streams. At least three times as much material as is needed for tests using each test method will be obtained from each source or prepared in the event that re-tests are required. The mixture will be prepared at UT Austin from analytical grade stock. The hydraulic/heat exchanger fluids will be

purchased, and at least three fuel oil no. 6 and liquid asphalt stocks will be purchased from different vendors.

Deliverables: Receipt by UT Austin of all materials to be used as test samples and their material safety data sheets

Schedule: The schedule for Task 4.5 deliverables is shown in Table 2.

4.6   Remove Identifying and VP Information from MSDSs, Prepare Samples, and Send First Stage Samples with "Sanitized" MSDSs to Labs for Testing

MSDSs must be supplied to the labs testing the materials along with samples of the material but the labs will not be provided with information about the expected VP of each sample. Samples of the fuel oil no. 6 and the asphalt materials will be prepared using applicable guidance from ERG (2013).

Deliverables: Samples of materials to be measured prepared for commercial labs and shipped with sanitized data sheets to labs

Schedule: The schedule for Task 4.6 deliverable is shown in Table 2.

4.7   For the First Stage of Samples, Test Samples Using an Automated Mini-method Designed to Measure the VP of Low Volatility Materials (e.g., the Grabner MINIVAP VPXpert-L); Commercial Labs Conduct their Sample Measurements of First Stage Samples and Report Results

UT Austin will conduct the tests using the automated mini method instrument. ASTM 6377 and ASTM 6378 will be followed when making measurements using these methods. The direct and indirect VOC methods will be done in strict accordance with the procedures outlined by the manufacturer. The tests will be staged so that the model mixture, hydraulic fluids, and any heavy refinery samples that are obtained early on are sent to commercial labs and analyzed on the Grabner MINIVAP VPXpert-L first. The expectation is that the results for the model mixture and the hydraulic fluids will potentially inform areas of further focus and concern.

Deliverables: Completion of VP measurements of samples using the Grabner MINIVAP VPXpert-L by UT Austin, results reported, and confirmation of acceptable measurement results received from the commercial labs

Schedule: The schedule for Task 4.7 deliverable is shown in Table 2.

4.8   Conduct Study of Activity Model Binary Interaction Parameters for Representative Components in Heavy Refinery Liquids

This will be done to determine the applicability of applying Raoult's Law to the composition of the light ends of these streams for estimating the vapor pressure of the liquids.

Deliverables: Prepare summary of the findings and recommendations concerning applicability

Schedule: The schedule for Task 4.8 deliverable is shown in Table 2.

4.9   Analyze and Assess the VP Measurements for First Stage Samples

An analysis of the measurement results for the first stage samples will be conducted to determine if there is a reasonable explanation for any disagreement between methods for the same sample (for example if a choice made by the chemist during sample preparation could have influenced the results of the method). Any areas of focus or concern to consider in the second stage of testing will be identified. If a commercial lab does not produce the expected results for the model mixture or the hydraulic fluids and no reasonable explanation can be found based on the method applied, then consideration will be given to eliminating that lab going forward.

Deliverables: Summary of analysis and assessment of first stage VP measurement results and discrepancies explained

Schedule: The schedule for Task 4.9 deliverable is shown in Table 2.

4.10   Remove Identifying and VP Information from MSDSs, Prepare Samples, and Send Second Stage Samples with "Sanitized" MSDSs to Labs for Testing

MSDSs must be supplied to the labs testing the materials along with samples of the material but the labs will not be provided with information about the expected VP of each sample. Samples of the fuel oil no. 6 and the asphalt materials will be prepared using applicable guidance from ERG (2013).

Deliverables: Samples of materials to be measured prepared for commercial labs and shipped with sanitized data sheets to labs

Schedule: The schedule for Task 4.10 deliverable is shown in Table 2.

4.11   For the Second Stage of Samples, Test Samples Using an Automated Mini-method Designed to Measure the VP of Low Volatility Materials (e.g., the Grabner MINIVAP VPXpert-L); Commercial Labs Conduct their Sample Measurements of First Stage Samples and Report Results

UT Austin will conduct the tests using the automated mini method instrument. ASTM 6377 and ASTM 6378 will be followed when making measurements using these methods. The direct and indirect VOC measurement methods will be performed in strict accordance with the procedures outlined by the manufacturer. Any lessons learned during testing of the first stage of samples will be applied.

Deliverables: Completion of VP measurements of samples using the Grabner MINIVAP VPXpert-L by UT Austin, results reported, and confirmation of acceptable measurement results received from the commercial labs

Schedule: The schedule for Task 4.11 deliverable is shown in Table 2.

4.12   Analyze and Assess the VP Measurements for All Samples

An analysis of the measurement results for the second stage samples will be conducted to determine if there is a reasonable explanation for any disagreement between methods for the same sample (for example if any actions taken by the chemist during sample preparation could have influenced the results of the method). Taking all of the information into consideration, the most likely actual range of values for the VP of the fuel oil no. 6 samples and the liquid asphalt samples will be determined based on the performance of the methods relative to each other and comparison of this value to the default values and other measured values. A summary of the advantages and disadvantages of each method, for example cost, reliability, convenience, and range of vapor pressures within the scope, will also be prepared.

Deliverables: Summary of analysis and assessment of all VP measurement results and discrepancies explained

Schedule: The schedule for Task 4.12 deliverable is shown in Table 2.

5.0   Project Participants and Responsibilities

Vincent M. Torres – Principal Investigator: Mr. Torres will have overall project management responsibility and will have the lead responsibility in preparation of all monthly and quarterly reports. He will have co-responsibility for preparation of the final report. Mr. Torres will also have overall Quality Assurance responsibility.

Kirsten Rosselot – Ms. Rosselot will be the lead person coordinating and obtaining actual refinery samples, when possible, and the other samples to be used by the project and overseeing preparation of any samples to be used by this project. She will have lead responsibility for conducting the assessment of the methods and instruments used to measure VPs. She will also conduct the study of activity model binary interaction parameters to gain insight into the applicability of using light end composition and Raoult's Law to estimate the vapor pressure of heavy refinery liquids. She will collate the measurement results, report them, and provide possible rationales for the variations within the methods and the variations between methods. She will have co-responsibility for preparation of the final report.

Jarett Spinhirne – Mr. Spinhirne will have primary responsibility for preparation and shipping of all samples that will be sent to commercial laboratories and for conducting all measurements and laboratory testing conducted at UT Austin, including VP measurements using the Grabner MINIVAP VPXpert-L.

6.0   Timeline

The timeline for the tasks and deliverables described in Section 4 is shown in Table 2.

Table 2. Project Schedule

Major Tasks/Deliverables	Approximate Dates of Performance
4.1 Prepare and submit Work Plan	0 thru 3 weeks after project kick-off call
4.2 Project reports and presentation	Throughout project period, on or before AQRP due dates shown in Section 7, beginning after approved start date (ASD)
4.3 Purchase and receipt of Automated Mini-method Instrument	0 thru 4 months after ASD
4.4 Identify labs to conduct the ASTM D2879, E1719, and D323 testing	0 thru 4 months after ASD
4.5 Obtain Materials for testing and Material Safety Data Sheets	0 thru 6 months after ASD
4.6 Sanitize safety data sheets, prepare samples and ship first stage of samples to commercial labs	0 thru 2 months after ASD
4.7 For first stage of samples, UT Austin measures VP of materials using Automated Mini-method and reports results; Commercial labs conduct their sample measurements of first stage samples and report results	2 thru 4 months after ASD
4.8 Conduct study of activity model binary interaction parameters to gain insight into the applicability of using light end composition and Raoult's Law to estimate the vapor pressure of heavy refinery liquids	2 thru 6 months after ASD
4.9 Summarize analysis and assessment of VP measurements of first stage samples and provide explanation of any discrepancies	4 thru 6 months after ASD
4.10 Sanitize safety data sheets, prepare samples, and ship second stage of samples to commercial labs	2 thru 6 months after ASD
4.11 For second stage of samples, UT Austin measures VP of materials using Automated Mini-method and reports results; Commercial labs conduct their sample measurements of second stage samples and report results	6 thru 8 months after ASD
4.12 Summarize analysis and assessment of VP measurements of all methods used and provide explanation of any	7 thru 10 months after ASD

discrepancies	

7.0 Deliverables

It is understood that AQRP requires certain reports to be submitted on a timely basis and at regular intervals. A description of the specific reports to be submitted and their due dates are outlined below. The lead PI will submit the reports, unless that responsibility is otherwise delegated with the approval of the Project Manager. All reports will be written in third person and will follow the State of Texas accessibility requirements as set forth by the Texas State Department of Information Resources. Report templates and accessibility guidelines found on the AQRP website at http://aqrp.ceer.utexas.edu/ will be followed.

Abstract: At the beginning of the project, an Abstract will be submitted to the Project Manager for use on the AQRP website. The Abstract will provide a brief description of the planned project activities, and will be written for a non-technical audience.

Abstract Due Date: Wednesday, August 31, 2016

Quarterly Reports: Each Quarterly Report will provide a summary of the project status for each reporting period. It will be submitted to the Project Manager as a Microsoft Word file. It will not exceed 2 pages and will be text only. No cover page is required. This document will be inserted into an AQRP compiled report to the TCEQ.

Quarterly Report Due Dates:

Report	Period Covered	Due Date
Nov2016 Quarterly Report	September, October, November 2016	Wednesday, November 30, 2016
Feb2017 Quarterly Report	December 2016, January & February 2017	Tuesday, February 28, 2017
May2017 Quarterly Report	March, April, May 2017	Friday, May 31, 2017
Aug2017 Quarterly Report	June, July, August 2017	Thursday, August 31, 2017
Nov2017 Quarterly Report	September, October, November 2017	Thursday, November 30, 2017

Monthly Technical Reports (MTRs): Technical Reports will be submitted monthly to the Project Manager and TCEQ Liaison in Microsoft Word format using the AQRP FY16-17 MTR Template found on the AQRP website.

MTR Due Dates:

Report	Period Covered	Due Date

Oct2016 MTR	October 1 - 31, 2016	Tuesday, November 8, 2016
Nov2016 MTR	November 1 - 30 2016	Thursday, December 8, 2016
Dec2016 MTR	December 1 - 31, 2016	Monday, January 9, 2017
Jan2017 MTR	January 1 - 31, 2017	Wednesday, February 8, 2017
Feb2017 MTR	February 1 - 28, 2017	Wednesday, March 8, 2017
Mar2017 MTR	March 1 - 31, 2017	Monday, April 10, 2017
Apr2017 MTR	April 1 - 28, 2017	Monday, May 8, 2017
May2017 MTR	May 1 - 31, 2017	Thursday, June 8, 2017
Jun2017 MTR	June 1 - 30, 2017	Monday, July 10, 2017
Jul2017 MTR	July 1 - 31, 2017	Tuesday, August 8, 2017

Financial Status Reports (FSRs): Financial Status Reports will be submitted monthly to the AQRP Grant Manager (Maria Stanzione) by each institution on the project using the AQRP FY16-17 FSR Template found on the AQRP website.

FSR Due Dates:

Report	Period Covered	Due Date
Oct2016 FSR	October 1 - 31, 2016	Tuesday, November 15, 2016
Nov2016 FSR	November 1 - 30 2016	Thursday, December 15, 2016
Dec2016 FSR	December 1 - 31, 2016	Tuesday, January 17, 2017
Jan2017 FSR	January 1 - 31, 2017	Wednesday, February 15, 2017
Feb2017 FSR	February 1 - 28, 2017	Wednesday, March 15, 2017
Mar2017 FSR	March 1 - 31, 2017	Monday, April 17, 2017
Apr2017 FSR	April 1 - 28, 2017	Monday, May 15, 2017
May2017 FSR	May 1 - 31, 2017	Thursday, June 15, 2017
Jun2017 FSR	June 1 - 30, 2017	Monday, July 17, 2017
Jul2017 FSR	July 1 - 31, 2017	Tuesday, August 15, 2017
Aug2017 FSR	August 1 - 31, 2017	Friday, September 15, 2017
FINAL FSR	Final FSR	Monday, October 16, 2017

Draft Final Report: A Draft Final Report will be submitted to the Project Manager and the TCEQ Liaison. It will include an Executive Summary. It will be written in third person and will follow the State of Texas accessibility requirements as set forth by the Texas State Department of Information Resources. It will also include a report of the QA findings.

Draft Final Report Due Date: Tuesday, August 1, 2017

Final Report: A Final Report incorporating comments from the AQRP and TCEQ review of the Draft Final Report will be submitted to the Project Manager and the TCEQ Liaison. It will be written in third person and will follow the State of Texas accessibility requirements as set forth by the Texas State Department of Information Resources.

Final Report Due Date: Thursday, August 31, 2017

Project Data: All project data including but not limited to QA/QC measurement data, metadata, databases, modeling inputs and outputs, etc., will be submitted to the AQRP Project Manager within 30 days of project completion (September 29, 2017). The data will be submitted in a format that will allow AQRP or TCEQ or other outside parties to utilize the information. It will also include a report of the QA findings.

AQRP Workshop: A representative from the project will present at the AQRP Workshop in the first half of August 2017.

Presentations and Publications/Posters: All data and other information developed under this project which is included in **published papers, symposia, presentations, press releases, websites and/or other publications** shall be submitted to the AQRP Project Manager and the TCEQ Liaison per the Publication/Publicity Guidelines included in Attachment G of the Subaward.

8.0   References

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