Upstream Oil and Gas Storage Tank Project
Flash Emissions Models Evaluation

Final Report

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Executive Summary

This document reports the results of a six month study to determine the VOC emissions from oil and condensate storage facilities. The flow measurements represent the volumetric flow rate over a twenty four hour cycle. These flow measurements were conducted at each test site to determine the total vented tank emission rate. VOC content was determined from the stock tank gas composition and metered flow rate. The site locations were not pre-selected and were completely random; the locations were tested with production rates of 10 to 1,979 barrels per day. Total flow measurements were made at thirty six production sites. Twenty-three of the sites were in West Texas and thirteen sites were taken in the North Texas. The study was conducted in these areas during July – September 2008. Six of the locations have been excluded from the test due to analysis data. These samples would not provide sufficient data inputs for the models and methods used in this study.

The Vasquez-Beggs Correlation could not estimate emissions for 90 percent of the sites due to site operating parameters outside of the correlation constraints. Low separator pressures are the single biggest contributing factor. However, for comparison purposes, the method results were calculated and compared to measured VOC emissions. For the 27 sites that had operating parameters outside of the Vasquez-Beggs Correlation constraints, Vasquez-Beggs underestimated VOC emissions for 85 percent of these sites.

The laboratory GOR method with the addition of Tanks 4.09 resulted in underestimating VOC emissions for 76.6 percent of the thirty sites. Gas-oil ratios for condensates systems were significantly greater than those from crude oil systems. Measurement error and lack of a standard laboratory procedure introduce uncertainty for emissions factors based on a laboratory determined gas-oil ratio.

GRI-HAPCalc uses the Vasquez-Beggs Correlation to estimate flash emissions and modified AP-42 methods to calculate working and breathing losses. The program restricts usage to sites within the Vasquez-Beggs constraints. As a result, only three sites have results.
Lack of substantive results precludes any analysis and assessment of overall performance.

While researching the EC/R Equation, it was discovered that the method is not applicable to VOC flash emissions. The EC/R is primarily intended for BTEX emissions: benzene, toluene, ethylbenzene, and isomers of xylene. The EC/R equation is not meant to estimate paraffin VOC emissions in higher proportion than in the default composition. The liquid compositions encountered deviate substantially from the composition used to derive the equation. The EC/R Equation is outside the project scope and as a result, the EC/R Equation was not used to estimate emissions.

The Valko-McCain Correlation was evaluated in place of the EC/R Equation. The correlation is empirically based and calculates VOC flash emissions from a calculated gas-oil ratio. The Valko-McCain Correlation resulted in better agreement with measured emissions than the laboratory determined GOR and the Vasquez-Beggs Correlation. However, the correlation underestimated VOC emissions for 70 percent of the sites.

E&P tank provides different options for estimating VOC flash, working, and breathing emissions. Three options were used: 1) Low Pressure Oil Input & AP-42, 2) Low Pressure Oil Input & RVP distillation column, 3) sites from geographical data base. The first option overestimated VOC emissions for 85.7 percent of the sites. Working and standing losses were not computed because the sites failed to meet the RVP pressure specification for the program. Option 2- Low Pressure Oil and RVP Distillation Column can model the working and breathing losses as a distillation column as an alternative to AP-42 methods. If the column does not meet the specified RVP , then it computes a more conservative estimate of the working and breathing losses. The results obtained from sites where the column fails to meet these criteria do not realistically represent working and breathing losses. This option overestimated VOC emissions for 82.1 percent of the sites.

The Hysys process simulator model was also evaluated for accuracy in calculating VOC flash emissions for each site. Hysys was found to over predict VOC emissions for 64.3 percent of the facilities tested. The results may indicate the difficulty of extending results to a 24 hour time period from instantaneous measurements of temperature, pressure, and composition.

The summary tables demonstrate how well each emissions estimation method correlates to the direct measurement method. The emission model results are grouped according to the accuracy of VOC emissions estimates for each location. This table also shows the percentage of samples whose emissions were either over or under-estimated when compared to direct measurement. The "out of range" column denotes the number of sites whose operating or related parameters fell outside of that model's constraints or minimum requirements.

EMISSION METHODS	Under Estimated	Percent Under Estimated	Over Estimated	Percent Over Estimated	Out of Range	Failed to Estimate VOC
Tank 4.09	24	100.00%	0.00	0.00%	**6.00**	**20.00%**
Vasquez-Beggs + Tanks 4.09	2	66.67%	1.00	33.33%	**27.00**	**90.00%**
GOR + Tanks 4.09	23	76.67%	7.00	23.33%	**0.00**	**0.00%**
Valko-McCagn + Tanks 4.09	14.00	66.67%	8.00	38.10%	**9.00**	**30.00%**
Hysis VOCs	10	35.71%	18.00	64.29%	**2.00**	**6.67%**
E&P Tank - RVP VOCs	4	14.29%	24.00	85.71%	**2.00**	**6.67%**
E&P Tank -GEO/RVP VOCs	20	66.67%	10.00	33.33%	**0.00**	**0.00%**
AP-42 LPO VOCs	4.00	14.29%	24.00	85.71%	**2.00**	**6.67%**
GRI-HAPCalc VOCs	2.00	66.67%	1.00	33.33%	**27.00**	**90.00%**

Table ES- 1 Emission Model 1s Comparison to Direct Measurement

The "Failed to Estimate" column in Table ES-1 represents the percentage of the thirty sample sites for which the model could not estimate the VOC emissions. This data can provide some guidance in the model selection process. In conclusion, each model reviewed has limitations and shortcomings. No one model resulted in the extremely strong correlation to measured data. The measurement must be over a full twenty four hour time span – and during a 24 hour period that is representative of the normal operation of the tanks. The emission rate can be extrapolated monthly or annually with a much smaller percentage of error.

Introduction

This document reports the results of a six month study to determine the VOC emissions from oil and condensate storage facilities. The flow measurements represent the volumetric flow rate over a twenty four hour cycle. These flow measurements were conducted at each test site to determine the total vented tank emission rate. VOC content was determined from the stock tank gas composition and metered flow rate, derived from a field sample of gas collected from the tanks. The site locations were not pre-selected and were completely random; the locations were tested with production rates of 10 to 1,979 barrels per day. Total flow measurements were made at thirty-six production sites. Twenty-three of the sites were in West Texas and thirteen sites were taken in the North Texas. The study was conducted in these areas during July – September 2008. Six of the locations have been excluded from the test due to analysis data. These samples would not provide sufficient data inputs for the models and methods used in this study.

The input data required for each of the modeling techniques was collected for evaluation and comparison with the current acceptable methods and models for estimating emissions from storage tank batteries servicing oil and gas wells. As part of the study, the GasFindIR camera was used to visually document emission sources venting to atmosphere at each of the sites. The leak sources were evaluated and addressed prior to placement of the metering equipment. Each leak source was documented and recorded from various distances to provide a reference to future tank emissions evaluations. The process consisted of gathering sufficient operational and measurement data from a minimum of thirty tank batteries. The samples were collected and processed at an accredited laboratory. The operational and sampling data was then used in each of the approved methods and model evaluations to determine the most accurate methods for comparison to the measured VOC emissions. These methods include a Hysys process simulator model; the American Petroleum Institute's E&P Tank model; and the Vasquez-Beggs equation; the Oil and Gas ratio method; GRI-HAP Calc; and Tanks 4.09. Each model output was then compared to a direct measurement of total vent gas flow and chemical composition from the field measurement.

It should be noted that the project encountered significant industry reluctance to provide optimum test sites, despite the assurance that all data would be confidential, and no company

names or locations would be provided in the final data set. As a result, the survey team sampled sites which had very low production volumes, and resultant low volumes of vent gas. As participation was completely voluntary and confidential, the concern over use of the results resulted in a survey site pool of locations with relatively low vent volumes. Some of the models evaluated in this study may produce somewhat different aggregated results when modeling sites with larger vent volumes.

Project Objectives

The objective of this study was to use the information and data gathered at each of the test sites to estimate the VOC emissions using a variety of conventional emissions estimation methods. The estimated emission values would then be compared to the actual measured VOC loss emissions from the battery.

1) Quantify the flashing, working, and standing loss emissions at each of the production sites. The flow rate is a total emissions flow measurement; it is impossible to speciated these in a field setting. Gas samples were collected and laboratory analysis performed to provide the speciation of the gas constituents. This was the data used to convert the measured volume to measured VOC emissions.
2) Compare measured VOC emissions to the VOC emissions determined by conventional estimation methods. Analyze the conventional emissions methods by comparing the predicted emissions to the direct measure results.
3) Draw conclusions about how accurately each method or model will predict the emission flow rate.

Background Information

Oil and condensate storage tank emissions at wellhead and gathering sites are composed of working losses, standing losses, and flashing losses. Working losses are vapors that are displaced from a tank during the filling/unloading cycle and standing losses are vapors that are produced in response to the daily temperature change. Flashing losses are vapors that are released when a liquid with entrained gases experiences a pressure drop, as during the transfer liquid hydrocarbons from a wellhead or separator to a storage tank that is vented to atmosphere.

There are several methods to calculate emissions from the storage tanks, but most models only focus on one or two of the vent gas streams. In an actual storage tank, these tank emissions are mixed together and often occur simultaneously. Each vent stream can be estimated by several methods. For example, the U.S. Environmental Protection Agency (EPA) TANKS model only calculates working and standing emissions whereas the Vasquez-Beggs equation only calculates flash emissions. For comparison, the models will be combined to determine a total emissions rate. Several other methods are available for estimating flash emissions from oil and condensate storage tanks, which will also need to be combined with other methods to calculate working and standing losses for a total VOC emissions inventory.

These methods include: process simulator models such as HYSIM; the American Petroleum Institute's E&P Tank model; and the Vasquez-Beggs equation. These emissions estimating tools are described in the TCEQ's *2007 Emissions Inventory Guidelines*. Direct measurement of vent gas flow and chemical composition results in a gas volume which is a total of each three vent sources. The TCEQ considers the direct measurement approach to be the most accurate for estimating oil and condensate storage tank emissions at wellhead and gathering sites; however, other, less accurate, approaches appear to be much more commonly used.

Technical Approach

This section describes the technical approach that was used in the site selection process and the measurement process; the lab data collected and the procedures used to obtain a quality sample; and the operational data collected to estimate emission factors for each of the models.

It should also be noted that the one major variable that was not directly measured on site was the volume of oil produced through the tanks during the 24 hour test period. All possible efforts were made to get accurate production data, requesting actual volumes from the daily production report for the time period the flow measurement was taken. This data was provided by the participating company and is preferable to estimated volumes or average production rates for a location. It should be noted that these volumes are critically important variables in the modeling software outputs, and were provided by the participating companies and will be used as factual production data.

Site Selection

The sites were not predetermined and TCEQ made efforts to obtain voluntary participation in the study by operating companies. The participation would include providing sites with a specified minimum production rates. Unfortunately, some of the operating companies were not comfortable with participating in this type of study. Canvassing local contacts yielded several test site opportunities. The data gathered from the study would be provided to the customer at no charge, and the operating company was assured the company name or identity would not be included in the data. However, most of the sites volunteered did not meet the original minimum threshold of oil/condensate throughput. After consultation with TCEQ, it was decided the minimum production rate threshold could not be achieved and to proceed with the data collection. It should be noted that due to the process of the site selection, very few sites with medium or large emission sources were included in the survey.

One of the key factors for each of the estimating methods is the production rates of the battery. These rates are a critical part of the process and could not be directly measured from most of the sites. This information was provided to the survey team by the operating company, and must be assumed as correct and valid for the study.

Measurement Approach

Storage tank losses, including flash losses, from representative tank batteries and separators were metered through a Daniel's turbine meter mounted in the thief hatch for a period of 24 hours to obtain the total daily flow rate. This rate is representative of the total flow rate of working, standing and flash losses over a complete daily heat cycle.

Figure 1 Example Metering Equipment Installed on Thief Hatch

The majority of the sites had multiple storage tanks which were connected through a common vent line or header system. The common vent system allowed metering of the gas from the entire battery using a single thief hatch. This stainless steel turbine meter is lightweight, versatile and has a high repeatability factor with high resolution and rangeability and is commonly used in custody transfer applications. The totalizer is a battery powered digital display capable of accepting magnetic pickup inputs. The flow totalizer rate was recorded in units of cubic feet per hour. The meter also has an instantaneous flow measurement display.

The GasFindIR camera was used to quickly identify and document each source of gas leaking at the facility. Each emission source was recorded at varying ranges to allow for an alternate perspective. An overview of the entire location was documented and recorded. Mid-range and close-up videos were recorded of each of the emission sources. Once the turbine meter was installed the emission sources were then reviewed using the GasFindIR camera to ensure total metering of the tank emissions. Leaking components were then addressed and repairs made to ensure total capture of the tank emissions through the meter.

Figure 2 Example Thief Hatch Emissions Prior to Measurement

Laboratory Data Analysis

Sampling for compositional analysis was performed using 300 CC stainless steel evacuated canisters. A pressurized gas sample from both the storage tanks and separator were collected. To obtain a pressurized sample from the storage tanks a flexible hose was inserted into the storage tank approximately one foot above the liquid level and connected to a vacuum pump; the sample canister was connected directly to the vacuum pump, after purging the sample line and the collection cylinder the sample was pressurized to 60 psi. This pressurized sample provided the lab with a sufficient volume to perform the chemical composition of gas mixtures using gas chromatography. The pressurized separator gas sample was taken directly off the gas line from the separator. An accredited lab was used to analyze the samples off-site for methane, individual C2 through C12 alkanes, benzene, toluene, and ethylbenzene, isomers of xylenes, nitrogen, hydrogen sulfide, and oxygen using Gas Processors Association (GPA) Method 2286. Liquid samples from the storage tanks and the separators were collected for analysis to determine the Reid Vapor Pressure (RVP). These samples were kept below 50 degrees Fahrenheit to

prevent flashing prior to the RVP lab test being performed off-site. The liquid samples were drawn into a graduated cylinder and the API gravity measurement was taken using hydrometers. The API gravity was recorded along with the temperature of the liquid so that temperature corrected API gravity could be determined. The samples were collected and processed at Caprock laboratories; the data was used to run each of the approved methods and model evaluations to determine the most accurate methods for comparison to the measured volumes. These methods include a Hysys process simulator model; E&P Tank 2.0; the Vasquez-Beggs Correlation; the Gas-Oil Ratio Method; -HAPCalc 3.0; the Valko-McCain Correlation, Tanks 4.09; all of which were compared to a direct measurement of vent gas flow and chemical composition

Operational Data Collected

The collected process and operational data from the test sites were recorded the day of the test along with any required data needed to perform modeling estimations. Operational data was collected from the site operator and the input data required for each of the modeling techniques was collected in the form of direct measurements and liquid and gas samples which were taken for laboratory analysis. This process consisted of gathering sufficient data from both the operational and direct measurement data to provide adequate information to complete the data modeling.

The following tables illustrate the data collected during each site visit. A site designation was given to each of the sites denoting Region, State, Battery #. The measured volume is the total flow rate for the twenty four hour test period. Production rate is the produced (barrels of oil per day) during the test period. This production information was provided by the operating company and represents the production rate for the day of the test. Separator operating data was collected the day of the site test. Operating pressure and temperature of the separator were also recorded. API gravity tests were obtained on a liquid sample taken from the separator and also the stock tank liquid sample. Liquid temperatures were recorded during this test to obtain a temperature corrected API gravity values for each of the samples collected. Additionally data was collected which is shown in the table. This data consists of the tank size and dimensional data along with the shell and roof characteristics, number of tanks and paint color for each test sites. Wind speed and ambient temperature were also documented the day of the test.

North Texas Batteries 1 thru 8									
Survey Site:		NTB #1	NTB #2	NTB #3	NTB #4	NTB #5	NTB #6	NTB #7	NTB #8
Survey Date		7/29/2008	7/29/2008	7/31/2008	8/26/2008	7/29/2008	9/22/2008	9/22/2008	9/22/2008
County		Ochiltree	Hansford	Hansford	Sherman	Ochiltree	Denton	Wise	Wise
Hours sampled		24	24	24	24	24	24	24	24
Measured Volume	mcfd	3.32	1.1	0.87	0.668	10.1	1.99	3.821	7.77
Well Type (Oil/Gas)		Oil	Oil	Oil	Oil	Oil	Gas	Gas	Gas
Ambient Temperature	°F	82	82	75	65	71	73	77.4	84
Daily Production Rate	bbl/day	69	74	98	41	50	13	14	34
Separator Temp	°F	72	162	125	145	69	76	77	60
Separator Pressure	psig	47.7	34	26	16.7	30	144	147	125
API Separator	°API	45	45	43	43	49	57	61	61
Separator Liquid Temp	°F	78	80	54	76	68	74	77	72
API Separator Corrected	°API	43.5	43.3	43.5	41.7	48.3	55.5	59	59.6
API Stock Tank	°API	46	46	42	43	48	57	61	61
Stock Tank Liquid Temp	°F	74	68	56	64	66	74	80	78
API Stock Tank Corrected	°API	44.8	45.3	42.3	42.7	47.5	55.5	58.7	58.9
Number of Product Tanks		4	4	4	2	4	1	2	2
Tank Capacity	barrels	300	300	300	300	300	300	300	300
Tank Color		Tan	Tan	Tan	Tan	Tan	Brown	Brown	Brown
Tank type		Welded	Welded	Welded	Welded	Welded	Welded	Welded	Welded

Table MA- 1 Field data collected during North Texas site visit

North Texas Batteries 9 thru 13						
Survey Site:		NTB #9	NTB #10	NTB #11	NTB #12	NTB #13
Survey Date		9/22/2008	9/23/2008	9/23/2008	9/23/2008	9/23/2008
County		Wise	Wise	Wise	Wise	Wise
Hours sampled		24	24	24	24	24
Measured Volume	mcfd	3.08	0.74	7.47	1.24	3.07
Well Type (Oil/Gas)		Gas	Gas	Gas	Gas	Gas
Ambient Temperature	°F	85	85	84	86	85
Daily Production Rate	bbl/day	16	12	12	5	62
Separator Temp	°F	79	82	98	86	77
Separator Pressure	psig	153	45	231	225	125
API Separator	°API	71	59	65	64	57
Separator Liquid Temp	°F	38	75	76	76	60
API Separator Corrected	°API	N/A	57.3	63	62.1	57
API Stock Tank	°API	59	60	66	66	58
Stock Tank Liquid Temp	°F	82	79	78	78	76
API Stock Tank Corrected	°API	82.2	57.8	63.7	63.7	56.2
Number of Product Tanks		1	1	1	1	1
Tank Capacity	barrels	300	300	300	300	300
Tank Color		Brown	Brown	Brown	Brown	Brown
Tank type		Welded	Welded	Welded	Welded	Welded

Table MA- 2 Field data collected during North Texas site visits

West Texas Batteries 1 thru 8									
Survey Site:		WTB #1	WTB #2	WTB #3	WTB #4	WTB #5	WTB #6	WTB #7	W
Survey Date		7/22/2008	7/24/2008	8/4/2008	8/6/2008	8/7/2008	8/11/2008	8/13/2008	8/
County		Ector	Irion	Ward	Terrel	Terrel	Pecos	Crane	
Hours sampled		24	24	24	24	24	24	24	
Measured Volume	mcfd	84.1	59.2	1.86	0.862	3.755	13.32	0.0197	
Well Type (Oil/Gas)		Oil	Oil	Oil	Oil	Oil	Oil	Oil	
Ambient Temperature	◦F	92	93	94	90	85	79	78	
Daily Production Rate	bbl/day	976	450	16	34	18	176	7	
Separator Temp	◦F	107	92	90	100	86	80	82	
Separator Pressure	psig	70	25	28	75	90	46	19	
API Separator	◦API	44	41	40	50	50	38	33	
Separator Liquid Temp	◦F	64	89	86	70	76	68	85	
API Separator Corrected	◦API	43.7	38.7	38	49.1	48.5	37.4	31.3	
API Stock Tank	◦API	43	40	38	50	50	38	34	
Stock Tank Liquid Temp	◦F	64	79	76	71	78	72	74	
API Stock Tank Corrected	◦API	43.7	38.2	36.8	50	48.3	37.1	33	
Number of Product Tanks		3	4	4	1	1	4	2	
Tank Capacity	barrels	500	500	500	500	500	500	500	
Tank Color		Tan	White	Tan	Tan	Tan	White	Tan	
Tank type		Welded	Welded	Welded	Welded	Welded	Welded	Welded	W

Table MA- 3 Field data collected during West Texas site visits

West Texas Batteries 9 thru 16								
Survey Site:		WTB #9	WTB #10	WTB #11	WTB #12	WTB #13	WTB #14	WTB
Survey Date		8/19/2008	8/20/2008	8/20/2008	8/21/2008	8/22/2008	9/16/2008	9/25/
County		Ector	Crane	Crane	Crane	Crane	Winkler	Mar
Hours sampled		24	24	24	24	24	24	24
Measured Volume	mcfd	75.12	86.67	6.22	4.32	5.56	61.7	8.
Well Type (Oil/Gas)		Scrubber	Oil	Oil	Oil	Oil	Oil	O
Ambient Temperature	◦F	64.8	84	85	82	85	73	7
Daily Production Rate	bbl/day	n/a	350	250	45	94	137	33
Separator Temp	◦F	70	70	80	70	70	75	6
Separator Pressure	psig	10	15	20	23	23	24	1
API Separator	◦API	34	38	46	28	32	40	4
Separator Liquid Temp	◦F	70	96	94	90	90	61	7
API Separator Corrected	◦API	33.3	35.6	43.1	26.1	30	39.9	40
API Stock Tank	◦API	32	36	45	31	31	39	4
Stock Tank Liquid Temp	◦F	68	86	86	88	88	72	7
API Stock Tank Corrected	◦API	31.5	34.1	42.8	29.1	29.1	38.1	40
Number of Product Tanks		1	2	2	3	3	2	3
Tank Capacity	barrels	500	1000	1000	500	500	300	50
Tank Color		Lt Grey	Tan	Tan	Tan	Tan	White	Bro
Tank type		Welded	Welded	Welded	Welded	Welded	Welded	Wel

Table MA- 4 Field data collected during West Texas site visits

West Texas Batteries 17 thru 23								
Survey Site:		WTB #17	WTB #18	WTB #19	WTB #20	WTB #21	WTB #22	WTB #23
Survey Date		9/25/2008	9/25/2008	9/29/2008	9/29/2008	9/30/2008	9/30/2008	9/30/2008
County		Martin	Martin	Ector	Ector	Ector	Ector	Andrews
Hours sampled		24	24	24	24	24	24	24
Measured Volume	mcfd	1.14	0.86	149.95	6.97	5.97	11.49	10.24
Well Type (Oil/Gas)		Oil	Oil	Oil	Oil	Oil	Oil	Oil
Ambient Temperature	◦F	83	88	72	77	71	81	81
Daily Production Rate	bbl/day	166	28	1979	119	232	85	327
Separator Temp	◦F	80	80	100	68	74	85	88
Separator Pressure	psig	22	25	60	40	40	40	40
API Separator	◦API	42	42	45	37	37	40	46
Separator Liquid Temp	◦F	82	80	78	76	74	78	88
API Separator Corrected	◦API	40.2	40.4	43.5	35.8	36	38.1	43.6
API Stock Tank	◦API	43	41	44	39	39	41	45
Stock Tank Liquid Temp	◦F	80	78	745	76	78	78	80
API Stock Tank Corrected	◦API	41.4	39.6	42.8	37.8	37.6	39.6	43.3
Number of Product Tanks		2	2	4	3	2	4	4
Tank Capacity	barrels	500	500	500	500	400	500	300
Tank Color		Brown	Brown	Brown	Primer	Green	White	Lt Grey
Tank type		Welded	Welded	Welded	Welded	Welded	Welded	Welded

Table MA- 5 Field data collected during West Texas site visits

Direct Measurement Method

The measurement equipment use for this field study provides the measurement data in actual cubic feet per day. To correct the volumes from actual to standard conditions for comparison the procedure is as follows:

Actual to Standard Volume Correction

Standard conditions provide a common reference for variables measured or calculated at actual conditions.

The standard conditions for the project are

- Pstd = 14.65 psia
- Tstd = 60°F (520°R)

The standard conditions provide a common reference to correct variables measured or calculated at actual conditions. The tank emissions were estimated in actual cubic feet per day (acfd). The following relation corrects the measured volume to scfd.

$$V_{std} = (P_{amb}/P_{STD})*(T_{STD}/T_{AVG})*V_{acfd}$$

where

V_{std} = corrected measured volume, scfd

P_{std} = standard pressure, 14.65 psia

P_{amb} = site ambient pressure, psia

T_{avg} = average annual temperature, °R

T_{std} = standard temperature, 520°R

V_{acfd} = actual measured volume, acfd

To correct the volumes from actual to standard conditions, different ambient pressure and average temperature were used. The West Texas batteries used Midland/Odessa as a base for ambient pressure and average annual temperature. The North Texas Batteries are based on conditions from Dallas/Ft. Worth. The following table summarizes the base conditions.

Base Conditions	Midland/Odessa	Pamb1	13.28	psia	Tavg1	80	°F
	Dallas/Ft. Worth	Pamb2	14.44	psia	Tavg2	80	°F
	Standard Conditions	Pstd	14.65	psia	Tstd	60	°F

Table DM- 1 Summary Base Conditions

Before calculating VOC emissions, the standard volumes are converted to a mass flow rate. The following equation computes total emissions.

$$E_{TOT} = \left(V_{STD}\frac{scf}{day}\right)\times\left(\frac{1}{380.8}\frac{lb-mole}{scf}\right)\times\left(MW_{TV}\frac{lb}{lb-mole}\right)\times\left(\frac{1ton}{2000lb}\right)\times\left(\frac{365days}{1year}\right)$$

Where

E_{TOT} = (*) total measured emissions, ton/year

V_{STD} = measured volume corrected to standard conditions, scf/day

MW_{TV} = tank vapor molecular weight, lb/lb-mole

(*) Note, E_{TOT} includes Non-VOC and VOC components.

The next equation calculates VOC emissions in tons per year.

$$E_{VOC} = E_{TOT} \times X_{VOC}$$

Where

E_{VOC} = measured VOC emissions, ton/yr

X_{VOC} = tank vapor VOC weight or mass fraction, dimensionless

Measurement Results

Table DM-2 lists the measured VOC emissions. The measured emissions will be compared with the following models:

- E&P Tank 2.0
- AspenTech Hysys 2006.5
- Vasquez-Beggs Correlation
- Gas-Oil Ratio Method
- GRI-HapCalc 3.0
- Environmental Consultants Research (EC/R) Algorithm
- Valko-McCain Correlation

		V_{ACT}	V_{STD}	MW_{TV}	E_{tot}	X_{VOC}	E_{voc}
		[ACFD]	[MSCFD]	[lb/lb-mole]	[ton/yr]	[lb/lb]	[ton/yr]
1	*WTB# 1*	84100	73.40	41.90	1473.90	0.770	1134.90
2	*WTB# 2*	59230	51.70	39.70	983.70	0.674	663.00
3	*WTB# 3*	1860	1.60	28.40	21.80	0.403	8.80
4	*WTB# 4*	862	0.80	42.60	16.30	0.771	12.60
5	*WTB# 5*	3755	3.30	42.10	66.60	0.796	53.00
6	*WTB# 6*	13320	11.60	30.50	169.60	0.510	86.50
7	*WTB# 8*	3870	3.40	35.50	57.80	0.571	33.00
8	*WTB# 10*	86670	75.70	34.70	1258.90	0.544	684.80
9	*WTB# 11*	6220	5.40	40.20	104.00	0.692	72.00
10	*WTB# 12*	4320	3.80	36.20	65.90	0.333	21.90
11	*WTB# 13*	5560	4.90	42.10	98.90	0.565	55.90
12	*WTB# 14*	61700	53.90	28.90	746.50	0.340	253.80
13	*WTB# 15*	8800	7.70	38.00	140.20	0.705	98.80
14	*WTB# 17*	1140	1.00	40.50	19.40	0.677	13.10
15	*WTB# 18*	860	0.80	37.60	14.40	0.535	7.70
16	*WTB# 19*	149950	130.90	39.30	2465.50	0.726	1790.00
17	*WTB# 20*	6970	6.10	32.40	94.70	0.539	51.00
18	*WTB# 22*	11490	10.00	37.60	180.20	0.687	123.80
19	*WTB# 23*	10240	8.90	35.40	151.00	0.619	93.50
20	*NTB# 1*	3320	3.20	37.50	57.50	0.638	36.70
21	*NTB# 2*	1100	1.00	31.20	15.00	0.551	8.30
22	*NTB# 3*	870	0.80	32.90	12.60	0.547	6.90
23	*NTB# 5*	10100	9.60	42.80	196.90	0.786	154.80
24	*NTB# 6*	1990	1.90	35.60	32.40	0.597	19.30
25	*NTB# 7*	3820	3.60	36.00	62.10	0.614	38.10
26	*NTB# 8*	7770	7.40	39.80	141.10	0.711	100.30
27	*NTB# 9*	3080	2.90	39.50	54.90	0.703	38.60
28	*NTB# 11*	7470	7.10	35.00	119.10	0.600	71.50
29	*NTB# 12*	1240	1.20	38.10	21.90	0.675	14.80
30	*NTB# 13*	3070	2.90	41.30	57.40	0.684	39.30

Table Measured Flow Rates

Table DM- 2 Direct Measurement Results to VOC Emissions

Tanks 4.09

The Tanks 4.09 model estimates evaporative or non-flash emissions from fixed roof storage tanks. Changes in ambient temperature are the primary cause of standing losses while working losses occur while the tank is filled or emptied. The program uses AP-42 methodologies and equations. Table 4 illustrates the inputs used in this project.

Assumptions

- The tank is stable, i.e., no flashing losses occur concurrently
- The tanks have a fixed roof
- The tank average liquid height is half of the shell height
- Midland/Odessa meteorological data approximates average conditions for West Texas Batteries
- Dallas/Fort Worth meteorological data approximates average conditions for North Texas Batteries
- The stock tank oil is best approximated by RVP, MW, Ideal liquid density, and tank vapor MW

Note: The program gives the user four options to specify how the stock tank liquid vapor-liquid equilibrium will be computed. This input is then used to predict the true oil vapor pressure at the liquid surface temperature. The options consist of:

- Option 1-speciate the individual components of the liquid
    - (requires data from options 2-4)
- Option 2-specify the RVP of the liquid
- Option 3- specify the liquid vapor pressure for various temperatures
- Option 4-specify vapor pressure coefficients for the Antoine Equation

Neither Antoine coefficients nor the range of vapor pressure data are available for the C12+ fraction of the stock tank liquid. Options 1, 3, and 4 are primarily meant for single component liquids. Option-2 provides the best method to calculate the liquid's vapor pressure for a multi-component hydrocarbon liquid.

The ideal liquid density, another input parameter, is calculated by converting the measured API gravity to units of lb/gal. The following relation illustrates the unit conversion.

$$\rho_o = \left(\frac{141.5}{131.5 + API} \right) * 8.34$$

Where

ρ_o	=	ideal liquid density at standard conditions, lb/gal
API	=	measured API gravity of stock tank oil, °API
8.34	=	density of water at 60F, lb/gal

Table 4 displays the meteorological data used.

Volumetric Data	Tank Capacity gal Production Rate [gal/yr]
Tank & Shell Info	Shell Diameter (ft) Shell Height (ft) Roof Height (ft) Cone Roof/Slope Shell Avg Liquid Height (ft) Breather Pressure (psi) Vacuum (psi) Shell and Roof Paint Color Paint Condition
STOCK TANK LIQUID PROPERTIES	Liq Density @ 60F (lb/gal) Stock Tank Liquid MW Tank Vapor MW Stock Tank Oil RVP [psia]

Table T- 1 Tanks 4.09 Input Parameters

			Paint Factor (α)	
	Tank Paint Color	**Tank Paint Shade or Type**	**Good**	**Poor**
Tank Color Paint Factors	Aluminum	Specular	0.39	0.49
	Aluminum	Diffuse	0.60	0.68
	Gray	Light	0.54	0.63
	Gray	Medium	0.68	0.74
	Red	Primer	0.89	0.91
	White	NA	0.17	0.34
	Aluminum	Mill finish, unpainted	0.1	0.15
	Beige/Cream		0.35	0.49
	Brown		0.58	0.67
	Green	Dark	0.89	0.91
	Rust	Red iron oxide	0.38	0.5
	Tan		0.43	0.55

Table T- 2 Paint Condition Factors

All of the listed paint factors above were not available for selection in the program. For colors not available for selection, a tank color approximating the paint condition α was selected. Table 6 shows what color is used to approximate the actual tank color.

	Tank Paint Color	Tank Paint Shade or Type	Modeled As
Colors not Available in Tanks	Aluminum	Mill finish, unpainted	White
	Beige/Cream		Aluminum Specular
	Brown		Gray/Light
	Green	Dark	Red Primer
	Rust	Red iron oxide	Aluminum Specular
	Tan		Aluminum Specular

Table T- 3 Tank Paint Factor Cross-reference

The stock tank vent gas rate for the sites was measured during the months of July, August, and September. Consequently, the program was run for these months and the results were averaged. The results of the program will be added the other methods which do not account for breathing and working losses.

Reid Vapor Pressure Requirement

Tanks 4.09 indirectly restricts the input values for Reid Vapor Pressure (RVP). The program uses a -correlation to calculate True Vapor Pressure (TVP) from a RVP. If the TVP is greater than the atmospheric pressure, the program will fail.

Summary

The Tanks 4.09 program estimates working and breathing losses according to AP-42 equations. Twenty-four out of the thirty sites met the RVP requirements. The results of Tanks are not meant for comparison with the measured emissions. The results are added to programs that only calculate flash losses.

Vasquez-Beggs Correlation

Introduction

The Vasquez-Beggs (VB) Solution Gas-oil Ratio Equation (VBE) is one of three empirical correlations proposed in "*Correlations for Fluid Physical Properties Prediction*". The objective of the study was to "use a large base of laboratory measured PVT data to develop improved empirical correlations to replace those commonly in use "[3]. Vasquez and Beggs developed correlations from 600 laboratory PVT analyses which included 5,008 measurements of gas solubility [8]. The correlation enables petroleum engineers to calculate the crude oil's transport and physical properties in lieu of PVT data. The VBE utilizes a separator gas gravity corrected to simulate a separator operating at 100 psig. Vasquez and Beggs improved the accuracy of their correlation by using two sets of empirical constants based on API gravity.

Application to Flash Emissions

The VBE was originally designed to calculate a solution gas-oil ratio at the reservoir bubble point pressure and temperature. The bubble point pressure is the "*pressure at which the first bubble of gas evolves as the pressure on the oil is decreased. It is frequently called saturation pressure; the oil will absorb no more gas below that pressure*" [4]. *Chapter 22 Oil System Correlation* provides guidance for application of the GOR correlations below bubblepoint conditions. The author states "*any pressure below the bubblepoint pressure is also a bubblepoint pressure since the oil is saturated with gas at this pressure, therefore GOR correlations can be used to find a value of Rs below the reservoir bubblepoint pressure* " [4]. The objective of the VB correlation (applied to flash emissions) is to calculate the solution gas-oil ratio, Rs. The gas-oil ratio quantifies the amount of gas remaining in solution with oil before the separator pressure is reduced to atmospheric conditions. The Vasquez-Beggs Correlation alone does not calculate a mass flow rate necessary to compute VOC emissions in tons per year. The correlation computes emissions in standard cubic feet per barrel of oil produced. To determine the emission factors in tons per year, the gas-oil ratio must be converted into a mass flow rate.

Required Data

- stock tank gas composition
- stock tank oil relative density
- separator pressure and temperature
- separator gas composition

VASQUEZ-BEGGS STOCK TANK FLASH EMISSIONS

INPUT PARAMETERS

Variable	Symbol	Value	Range & Units
Stock Tank Liquid Relative Density	*API*		(16-58)°API
Separator Pressure	*Ps*		(50-5250) psia
Separator Temperature	*Ts*		(70-295)°F
Separator Gas SG @ P_S, T_S	SG_S		(0.56-1.18)
Production Barrel of Oils per day	*Q*		bbl/d
Stock Tank Gas Molecular Weight	MW_{TV}		lb/lb-mole
Mass Fraction VOC (C3+) of Stock Tank Gas	*Xvoc*		lb_{VOC}/lb

Empirical Constants

Coefficient	API<=30	API >30
C1	0.0362	0.0178
C2	1.0937	1.187
C3	25.724	23.931

OUTPUT PARAMETERS

Variable	Symbol	Value	Range & Units
Separator Gas Gravity Corrected to Separator Pressure of 100 psig	*SGc*		N/A
Solution Gas Oil Ratio (GOR)	*Rs*		(20-2070)scf/bbl
Volume	V_{VB}		MSCFD
Total Flash Emissions	E_{TOT}		ton/year
VOC Flash Emissions	E_{VOC}		ton/year

Figure VB- 1 Vasquez-Beggs Input and Output Parameters

**Note: Some Vasquez-Beggs Guidance documents restrict the vent stream molecular weight to 18-180 lb/mole. The VB technical documents do not include this restriction. Additionally, GRI-HapCalc places not restriction on the MW.

Assumptions

- variable inputs are within the allowable ranges
- separator gas does not behave as an ideal gas
- stock tank crude oil contains no solution gas (i.e. R_S=0 scf/bbl @ Ambient Pressure)

Vasquez-Beggs (Spreadsheet) Flash Calculation Procedure

Separator gas specific gravity at operating conditions was not measured. However, the separator gas composition is available and the specific gravity can be computed. The separator specific gravity required by the VB correlation is not the ratio of separator gas MW to the MW of air. The SG of the separator gas is the ratio of the density of the separator gas to air. The compressibility of the separator gas cannot be assumed to be 1.0. Step 1 in the procedure below is used to compute the separator gas compressibility and then SGs.

The following is a procedure used to calculate the separator gas specific gravity at Ps, Ts.

Calculate the following parameters:

Step-1 calculate the separator gas specific gravity at actual conditions

a. pseudocritical temperature and pressure

b. pseudoreduced temperature and pressure –Law of Corresponding States

c .separator gas compressibility -Hall-Yarborough Correlation

d. separator gas specific gravity at actual conditions

Step- 2 VOC weight/mass fraction of the solution gas

Step– 3 Solution gas-oil ratios, Rs

Step– 4 Corrected separator gas specific gravity

Step- 5 VOC tank emissions

Step -1a

Utilizing Kay's Mixing Rule, the pseudo critical temperature and pressure are determined by

$$P_c' = \sum y_i P_{ci} \quad \text{and} \quad T_c' = \sum y_i T_{ci}$$

where

y_i = mole fraction of each component in the mixture

P_{ci} = critical pressure for component i, psia

T_{ci} = critical temperature for component i, $^\circ$R

P_c' = separator gas mixture pseudocritical pressure, psia

T_c' = separator gas mixture pseudocritical temperature, °R

Step -1b

The pseudoreduced temperature and pressures are found by the equation shown below.

$$P_r = P_s/P_c'$$

and

$$T_r = T_s/T_c'$$

Where

P_r = separator gas mixture pseudoreduced pressure, dimensionless

T_r = separator gas mixture pseudoreduced temperature, dimensionless

Step – 1c

The Hall-Yarborough Equation is an empirical correlation that directly calculates compressibility. *The Petroleum Engineering Handbook* lists the method as "one of the best" methods for direct calculation of natural gas compressibility. The correlation consists of two equations, one of which is non-linear and requires Newton-Raphson iteration.

$$Z = \frac{0.06125 P_r t \exp\left(-1.2(1-t^2)\right)}{y} \quad \text{(Eq-1)}$$

Where

Z_s = separator gas compressibility, dimensionless

P_r = pseudoreduced pressure, dimensionless

t = the reciprocal of the pseudoreduced temperature 1/Tr, dimensionless

y = the reduced density, dimensionless

$$f(y) = 0.06125 P_r t \exp\left(-1.2(1-t^2)\right) + \frac{y + y^2 + y^3 - y^4}{(1-y)^2} -$$

$$(14.76t - 9.76t^2 + 4.58t^2)y^2 + (90.7t - 24.2t^2 + 42.4t^3)y^{(2.18+2.82t)} = 0$$

The Newton-Raphson iteration listed below is used to solve for f(y) = 0. The minimum tolerance to determine convergence is 1 x 10^{-15}.

$$y_{n+1} = y_n + \frac{f(y_n)}{f'(y_n)}$$

n = number of iterations

y_n = value of y at iteration n

y_{n+1} = the value of y computed from iteration n

$f(y_n)$ = result from then 2nd equation at iteration n

$f'(y_n)$ = the derivative of the 2nd equation with respect to y given by the equation

$$\frac{y^4 - 4y^3 + 4y^2 + 4y + 1}{(y-1)^4} - (14.76t - 9.76t^2 + 4.58t^2)(2y) + (2.18 + 2.82t)y^{(1.18+2.82t)}(90.7t - 242.2t^2 + 42.4t^3)$$

The Newton-Raphson efficiently converges if the initial iteration is close to the final value. The numerator of equation 1 provides an excellent initial guess. The initial iteration value of y is described by the relation below.

$$f(y_1) = 0.06125 P_r t \exp\left(-1.2(1-t^2)\right)$$

Once the separator gas compressibility Z is known the following relation will calculate the separator gas specific gravity at operating conditions.

$$SG_S = \frac{\rho_{SP}}{\rho_{air}} = \left(\frac{MW_{SP} / Z_{SP}}{MW_{AIR} / Z_{AIR}} \right)$$

Where

MW_{SP} = molecular weight of the separator gas, lb/lb-mole

Z_{SP} = separator gas compressibility, dimensionless

MW_{AIR} = molecular weight of air, 28.97 lb/lb-mole

Z_{AIR} = compressibility of air

Compressibility factors for air are listed in the *Flow Measurement Engineering Handbook.* For temperatures and pressures ranging from -10 to 170°F and 14.5 to 290 psia the resulting compressibility range is 0.9992 to 1.0004. Therefore, the compressibility of air is assumed to be 1.0 and the equation reduces to the equation below.

$$SG_S = \frac{\rho_{SP}}{\rho_{air}} = \left(\frac{MW_{SP} / Z_{SP}}{28.97} \right)$$

Step - 2

Calculate weight fraction of VOC from stock tank gas from composition. From the tank vapor extended composition, add the weight fraction (WT Fract) of the VOC components.

Step - 3

Calculate corrected separator gas specific gravity

$$SGc = SGs\left[1.0 + (5.912\times10^{-5}(API)(Ts)\log\left(\frac{Ps}{114.7}\right)\right]$$

where

SG_c = separator gas specific gravity corrected to a separator pressure of 100 psig

SG_s = separator gas specific gravity at separator actual conditions

P_s = separator operating pressure, psia

T_s = separator operating temperature, °F

API = stock tank oil gravity, °API

Step - 4

Calculate solution gas-oil ratio, Rs

$$R_s = (C_1)(SGc)(P_S^{\,C_2})e^{\left(\frac{(C_3)(API)}{T_S+460}\right)}$$

where

R_s = solution gas-oil ratio, scf/STB

C_1 = empirically derived constant, see VB-1

C_2 = empirically derived constant, see VB-1

C_3 = empirically derived constant, see VB-1

Step – 5

With solution gas-oil ratio known, the following equation calculates total flash emissions.

$$E_{TOT} = (Q)(R_s)(MW_{TV})\left(\frac{lb-mole}{380.8scf}\right)\left(\frac{365days}{year}\right)\left(\frac{1ton}{2000lb}\right)$$

Where:

E_{TOT} = total stock tank emissions, ton/year

Q = oil production, bbl/day

MW_{TV} = stock tank gas molecular weight, lb/lb-mole

380.8 = molar volume of an ideal gas at 14.65 psia and 60°F, scf/lb-mole

The next equation solves for VOC flash emissions in tons per year.

$$E_{VOC} = E_{TOT} \times X_{VOC}$$

Where

E_{VOC} = VOC flash emissions, ton/year

X_{voc} = weight or mass fraction of VOC in stock tank gas, lb_{voc}/lb

The Vasquez-Beggs Correlation was calculated on an Excel spreadsheet. Table VB-1 lists the input parameters. The values listed in red denote the variable is out of range.

INPUT PARAMETERS					
Site	Stock Tank Oil Relative Density	Separator Pressure	Separator Temperature	Separator Gas Specific Gravity	Oil Production
	API	Ps	Ts	SGs	Q
	◦API	psia	˚F	-	bbl/d
	(16-58)	(50-5250)	(70-295)	(0.56-1.18)	-
WTB# 1	43.7	83.82	**64**	0.83	976
WTB# 2	38.5	**38.82**	89	1.15	450
WTB# 3	36.8	**41.82**	86	0.99	16
WTB# 4	50.0	88.82	70	1.01	34
WTB# 5	48.3	103.82	76	0.99	18
WTB# 6	37.1	59.82	**68**	0.73	176
WTB# 8	38.8	**30.82**	74	0.98	7
WTB# 10	34.1	**28.82**	96	0.98	350
WTB# 11	42.8	**33.82**	94	1.01	250
WTB# 12	29.1	**36.82**	90	1.13	45
WTB# 13	29.1	**36.82**	90	**1.20**	94
WTB# 14	38.1	**37.82**	**61**	1.04	137
WTB# 15	40.6	**30.82**	70	0.81	332
WTB# 17	41.4	**35.82**	82	1.01	166
WTB# 18	39.6	**38.82**	80	0.99	28
WTB# 19	42.8	73.82	78	0.83	1979
WTB# 20	37.8	53.82	76	0.76	119
WTB# 22	39.6	53.82	85	0.80	85
WTB# 23	43.3	53.82	88	0.93	327
NTB# 1	44.8	62.14	78	0.93	69
NTB# 2	45.3	**48.44**	80	0.75	74
NTB# 3	42.3	**40.44**	**54**	0.79	98
NTB# 5	**67.5**	**44.44**	**68**	0.77	50
NTB# 6	55.7	158.44	74	0.76	13
NTB# 7	**58.6**	161.44	77	0.74	34
NTB# 8	**58.9**	139.44	72	0.75	16
NTB# 9	55.2	167.44	**38**	0.74	12
NTB# 11	**63.7**	245.44	76	0.78	5
NTB# 12	**63.7**	239.44	76	0.77	14
NTB# 13	56.2	139.44	**60**	0.79	62

Table VB- 1 Vasquez-Beggs Inputs

OUTPUT PARAMETERS								
Corrected Separator Gas Specific Gravity	Solution Gas Oil Ratio	Emissions Volume	Tank Vapor MW	VOC Mass Fraction	Total Flash Emissions	Total VOC Flash Emissions	Measured VOC Emissions	Site
SGc	Rs	V_{VB}	MW_{TV}	X_{VOC}	E_{TOT}	E_{VOC}		
-	scf/bbl	MSCFD	lb/lb-mole	lb_{VOC}/lb	ton/year	ton/year	ton/year	
-	(20-2070)		-	-				
0.81	20.4	19.9	41.9	0.770	399.8	**307.8**	1134.90	*WTB# 1*
1.04	**7.6**	3.4	39.7	0.674	65.1	**43.9**	663.00	*WTB# 2*
0.91	**6.8**	0.1	28.4	0.403	1.5	**0.6**	8.80	*WTB# 3*
0.99	34.6	1.2	42.6	0.771	24.0	**18.5**	12.60	*WTB# 4*
0.98	37.3	0.7	42.1	0.796	13.5	**10.7**	53.00	*WTB# 5*
0.70	**8.6**	1.5	30.5	0.510	22.1	**11.3**	86.50	*WTB# 6*
0.89	**5.3**	0.0	35.5	0.571	0.6	**0.3**	33.00	*WTB# 8*
0.87	**3.6**	1.3	34.7	0.544	21.0	**11.4**	684.80	*WTB# 10*
0.88	**6.5**	1.6	40.2	0.692	31.3	**21.7**	72.00	*WTB# 11*
1.04	**7.6**	0.3	36.2	0.333	5.9	**2.0**	21.90	*WTB# 12*
1.11	**8.1**	0.8	42.1	0.565	15.4	**8.7**	55.90	*WTB# 13*
0.97	**7.4**	1.0	28.9	0.340	14.0	**4.8**	253.80	*WTB# 14*
0.73	**4.8**	1.6	38.0	0.705	29.0	**20.4**	98.80	*WTB# 15*
0.91	**7.0**	1.2	40.5	0.677	22.6	**15.3**	13.10	*WTB# 17*
0.90	**7.1**	0.2	37.6	0.535	3.6	**1.9**	7.70	*WTB# 18*
0.80	**15.8**	31.3	39.3	0.726	588.9	**427.5**	1790.00	*WTB# 19*
0.72	**7.9**	0.9	32.4	0.539	14.6	**7.9**	51.00	*WTB# 20*
0.75	**8.6**	0.7	37.6	0.687	13.2	**9.1**	123.80	*WTB# 22*
0.86	**11.5**	3.8	35.4	0.619	63.8	**39.5**	93.50	*WTB# 23*
0.88	**15.5**	1.1	37.5	0.638	19.2	**12.2**	36.70	*NTB# 1*
0.69	**9.2**	0.7	31.2	0.551	10.2	**5.6**	8.30	*NTB# 2*
0.74	**7.6**	0.7	32.9	0.547	11.7	**6.4**	6.90	*NTB# 3*
0.68	23.3	1.2	42.8	0.786	23.9	**18.8**	154.80	*NTB# 5*
0.79	69.7	0.9	35.6	0.597	15.5	**9.3**	19.30	*NTB# 6*
0.77	78.0	2.7	36.0	0.614	45.8	**28.1**	38.10	*NTB# 7*
0.77	68.1	1.1	39.8	0.711	20.8	**14.8**	100.30	*NTB# 8*
0.76	83.7	1.0	39.5	0.703	19.0	**13.4**	38.60	*NTB# 9*
0.85	178.6	0.9	35.0	0.600	15.0	**9.0**	71.50	*NTB# 11*
0.84	171.4	2.4	38.1	0.675	43.8	**29.6**	14.80	*NTB# 12*
0.80	66.4	4.1	41.3	0.684	81.5	**55.7**	39.30	*NTB# 13*

Table VB- 2 Vasquez-Beggs Outputs

Results

The Vasquez-Beggs Correlation alone does not estimate VOC emissions. Before an assessment of VOC emissions is made, a discussion of the resulting gas-oil ratio must be performed. Only

three sites are within the Vasquez-Beggs Correlation Range: WTB#4, WTB#5, and NTB#6. The following is a summary of the variables causing the VB to be out of range:

1. Ps <50 psia - 14 sites
2. API >58 - 5 sites
3. Ts<70°F - 7 sites
4. SGs - 1 site
5. Rs<20 scf/bbl - 20 sites

Low separator pressure is the single greatest cause for the majority of the sites not meeting the VB variable restraints. Furthermore, each site with a separator pressure below 50 psia calculated a solution gas-oil ratio (Rs) below the required 20 scf/bbl. The correlation is most sensitive to separator pressure and API gravity. Relatively high separator pressure and API gravity enabled the three sites mentioned above to be within the correlation's range.

To assess VOC emissions calculated using the Vasquez-Beggs Correlation, the results of Tanks 4.09 are added to the results. Table VB-2 shows the results of the calculated emissions compared to the measured VOC emissions. VB plus Tanks 4.09 over-estimated VOC emissions for twenty-five out of thirty sites. Of the three sites that met the Vasquez-Beggs restraints, WTB#4 overestimated by a factor of two.

Sites Outside Vasquez-Beggs Variable Restraints Range

Twenty-seven sites did not meet the variable restraints of the Vasquez-Beggs Correlation. The correlation plus Tanks 4.09 overestimated VOC emissions for four of these sites and underestimated emissions for the remaining twenty-three sites. VB plus Tanks 4.09 underestimated VOC emissions for eighty-five percent of the sites not within the VBC constraints. The Vasquez-Beggs Correlation should not be applied outside of its intended scope. The results of the Vasquez-Beggs outside of its intended range is important because there are several variations of the correlation on state websites with default values outside the allowable variable ranges.

Sites within Vasquez-Beggs Variable Restraints Range

Only three sites are within the variable restraints range. A recent publication entitled ”*Correlation of Black Oil Properties at Pressures Below Bubblepoint Pressure-A New Approach*” indicates gas-oil correlations applied below bubble point pressures results in considerable error when compared to application above the reservoir bubble point. The study used an independent data from 541 PVT reports/4103 data sets to assess Vasquez-Beggs, Standing, Petrosky-Farshad, and the Kartoatmodjo-Schmid correlation for performance below bubble point pressures. The Vasquez-Beggs resulted in an average error of -19.8 percent. This translates into under-estimating GOR by an average of 20 percent.

GAS-OIL RATIO (GOR) METHOD

The GOR method uses a laboratory measured gas-oil ratio (GOR) as the basis to estimate flash emissions. The GOR method is equally suitable for crude oil and condensate systems. The GOR method is similar to the Vasquez-Beggs and Valko-McCain Correlation; however it has not constraints on separator operating conditions.

There is no standard test method to determine a gas oil-ratio from a pressurized oil/condensate sample. A flash liberation process was used to determine the solution gas-oil ratio from the pressurized liquid samples. Below are the steps that were used to determine the solution gas-oil ratio in the laboratory.

Step 1. The fluid sample is charged to a PVT cell.
Step 2. The cell pressure is elevated at a pressure higher than the saturation pressure by injecting mercury
Step 3. Pressure is lowered in small increments until the PVT cell is at atmospheric pressure.
Step 4. The resulting volume of solution gas and oil remaining are measured and corrected to conditions of 60°F and 14.65 psia.

The application of the GOR method is straightforward. The method assumes the dissolved gas will flash from the oil as pressure is lowered atmospheric conditions.

Required Data:

- laboratory measured GOR from a pressurized oil/condensate sample taken downstream of the separator liquid outlet and upstream the pressure reducing valve
- stock tank composition
- VOC mass or weight fraction of the tank vapors
- oil production rate

The following equation calculates total flash emissions, E_{TOT}. The total flash emissions includes Non-VOC and VOC components.

$$E_{TOT} = (Q)(R_s)(MW_{TV})\left(\frac{lb-mole}{380.8scf}\right)\left(\frac{365days}{year}\right)\left(\frac{1ton}{2000lb}\right)$$

Where:

E_{TOT}	=	total stock tank flash emissions, ton/year
R_S	=	measured gas-oil ratio, scf/bbl
Q	=	oil production, bbl/day
MW_{TV}	=	stock tank gas molecular weight, lb/lb-mole
X_{voc}	=	weight fraction of VOC in stock tank gas

Given total emissions, E_{TOT}, the following equation calculates VOC emissions.

$$E_{VOC} = E_{TOT} \; x \; X_{VO}$$

Where:

E_{VOC} = VOC flash emissions, ton/year

Inputs Parameters					Output Parameters			
	Lab Measured Gas Oil Ratio	Oil Production	MW Tank Vapors	Tank Vapor VOC Mass Fraction	Volume [SCFD]	Total Flash Emissions	VOC Flash Emissions	
	Rs	Q	MWtv	Xvoc	Vgor	E_{TOT}	E_{VOC}	
SITE	scf/bbl	bbl/d	lb/lb-mole	-	MSCFD	ton/yr	ton/yr	SITE
WTB# 1	21.1	976	41.9	0.770	20.60	413.5	318.4	WTB#1
WTB# 2	26.8	450	39.7	0.674	12.10	229.5	154.7	WTB#2
WTB# 3	7.1	16	28.4	0.403	0.10	1.5	0.6	WTB#3
WTB# 4	91.8	34	42.6	0.771	3.10	63.7	49.1	WTB#4
WTB# 5	50.6	18	42.1	0.796	0.90	18.4	14.6	WTB#5
WTB# 6	1.9	176	30.5	0.510	0.30	4.9	2.5	WTB#6
WTB# 8	3.6	7	35.5	0.571	0.03	0.4	0.2	WTB#8
WTB# 10	7.6	350	34.7	0.544	2.70	44.2	24.0	WTB#10
WTB# 11	0.8	250	40.2	0.692	0.20	3.9	2.7	WTB#11
WTB# 12	4.1	45	36.2	0.333	0.20	3.2	1.1	WTB#12
WTB# 13	0.8	94	42.1	0.565	0.10	1.5	0.8	WTB#13
WTB# 14	5.3	137	28.9	0.340	0.70	10.1	3.4	WTB#14
WTB# 15	4.2	332	38.0	0.705	1.40	25.4	17.9	WTB#15
WTB# 17	7.9	166	40.5	0.677	1.30	25.5	17.3	WTB#17
WTB# 18	3.3	28	37.6	0.535	0.10	1.7	0.9	WTB#18
WTB# 19	58.5	1979	39.3	0.726	115.80	2180.5	1583.0	WTB#19
WTB# 20	40.3	119	32.4	0.539	4.80	74.5	40.2	WTB#20
WTB# 22	2.2	85	37.6	0.687	0.20	3.4	2.3	WTB#22
WTB# 23	27.6	327	35.4	0.619	9.00	153.1	94.8	WTB#23
NTB# 1	16.4	69	37.5	0.638	1.10	20.3	13.0	NTB#1
NTB# 2	5.1	74	31.2	0.551	0.40	5.6	3.1	NTB#2
NTB# 3	26.9	98	32.9	0.547	2.60	41.6	22.8	NTB#3
NTB# 5	146.5	50	42.8	0.786	7.30	150.3	118.1	NTB#5
NTB# 6	21.5	13	35.6	0.597	0.30	4.8	2.9	NTB#6
NTB# 7	12.2	34	36.0	0.614	0.40	7.2	4.4	NTB#7
NTB# 8	30.2	16	39.8	0.711	0.50	9.2	6.5	NTB#8
NTB# 9	358.9	12	39.5	0.703	4.30	81.5	57.3	NTB#9
NTB# 11	37.5	5	35.0	0.600	0.20	3.1	1.9	NTB#11
NTB# 12	112.8	14	38.1	0.675	1.60	28.8	19.4	NTB#12
NTB# 13	100.9	62	41.3	0.684	6.30	123.8	84.7	NTB#13

Table G- 1 VOC Flash Emissions Calculations: Laboratory Gas Oil Ratio

Results

For comparison with measured VOC emissions, the results of Tanks 4.09 were added to the calculated VOC flash emissions. The GOR method with the addition of Tanks 4.09 underestimated emissions for 76.67 percent of the sites and overestimated emissions for 23.33 percent of the sites.

Site	GOR VOC Flash Emissions	Tank 4.09	GOR+Tanks	Measured VOCs
	ton/year	ton/year	ton/year	ton/'yr
WTB# 1	318.40	36.90	355.30	1134.90
WTB# 2	154.70	17.60	172.30	663.00
WTB# 3	0.60	1.30	1.90	8.80
WTB# 4	49.10	7.70	56.80	12.60
WTB# 5	14.60	5.20	19.80	53.00
WTB# 6	2.50	6.40	8.90	86.50
WTB# 8	0.20	2.00	2.20	33.00
WTB# 10	24.00	11.80	35.80	684.80
WTB# 11	2.70	19.20	21.90	72.00
WTB# 12	1.10	3.30	4.40	21.90
WTB# 13	0.80	7.90	8.70	55.90
WTB# 14	3.40	2.70	6.10	253.80
WTB# 15	17.90	19.20	37.10	98.80
WTB# 17	17.30	8.90	26.20	13.10
WTB# 18	0.90	5.10	6.00	7.70
WTB# 19	1583.00	44.80	1627.80	1790.00
WTB# 20	40.20	7.30	47.50	51.00
WTB# 22	2.30	10.90	13.20	123.80
WTB# 23	94.80	12.00	106.80	93.50
NTB# 1	13.00	2.50	15.50	33.20
NTB# 2	3.10	1.20	4.30	8.30
NTB# 3	22.80	5.70	28.50	6.90
NTB# 5	118.10	6.30	124.40	141.90
NTB# 6	2.90	3.60	6.50	17.30
NTB# 7	4.40	4.50	8.90	34.90
NTB# 8	6.50	6.00	12.50	92.20
NTB# 9	57.30	1.90	59.20	35.90
NTB# 11	1.90	2.30	4.20	65.40
NTB# 12	19.40	3.60	23.00	13.60
NTB# 13	84.70	7.50	92.20	36.50

Table G- 2 GOR Method: Comparison of Calculated and Measured VOC Emissions

The gas-oil ratio is directly proportional to separator pressure and stock tank API gravity. The results indicate this trend. Below is a summary of the gas-oil ratio, Rs for gas-oil ratios below and above 10 scf/bbl.

Comparison Table	**Units**	**Rs < 10 scf/bbl**	**Rs > 10 scf/bbl**
Average gas-oil ratio	scf/bbl	4	69
Average separator pressure	psig	26	97
Average stock tank gravity	API°	38	51

Table G- 3 Results Breakdown

Overall, the laboratory GOR method underestimated emissions for 23 out of the 30 sites. The laboratory measurement represents an instantaneous measurement reflective of a single separator pressure, temperature, and composition. Process conditions fluctuate substantially and consequently, VOC emissions will fluctuate as well. The laboratory results are indicative of a steady state system. Additionally, there are difficulties of capturing a pressurized sample and preventing flashing of the sample. Furthermore, there is no current laboratory procedure or guidance from TCEQ on how to perform the single stage flash. Hy-Bon recommends the development of a standard procedure for measuring the gas-oil ratio.

Environmental Consultants Research Algorithm (EC/R)

The Environmental Consultants Research (EC/R) Algorithm estimates flash emissions from hydrocarbon condensate storage tanks. While researching the EC/R algorithm, Hy-Bon Engineering discovered inconsistencies between the EC/R spreadsheet and the EC/R source document. For clarification, Hy-Bon contacted the original authors of the EC/R algorithm. The authors could not produce the original spreadsheet, but offered some guidance. The EC/R algorithm is primarily intended to estimating BTEX emissions:

- Benzene
- Toluene
- Ethylbenzene
- Isomers of Xylene

A default composition was used to develop the basis for the algorithm shown in the following relationship

$$Yv = 0.0523(Pv-1.636)$$

Where

Yv = the mole fraction of vapor flashed, lb-mole$_v$/lb-mole$_l$

Pv = the total vapor pressure of the of the condensate stream entering the tank

The authors noted the equation is suitable as long as the composition does not deviate significantly from the assumed composition. Unfortunately, the compositions used in this report deviate substantially from the assumed composition. Table 13 illustrates the differences between EC/R's default composition and the average pressurized composition for all of the sites. The C9+ plus fractions differs by an average of 25 percent. The C9+ difference constitutes a major deviation from the default composition. The heavy fractions of the liquid composition dominate the phase envelope of hydrocarbons. As a result, the EC/R equation is outside of the project scope and will not be investigated.

Summary for the EC/R Equation Exclusion

While researching the EC/R Equation, Hy-Bon discovered the method is not applicable to this project. The EC/R equation is not meant to estimate other paraffin VOC emissions in higher proportion than in the default composition. Next, the method is unsuitable because the liquid

compositions encountered deviate substantially from the composition used to derive the equation.

1.) The EC/R is primarily intended for benzene, toluene, ethylbenzene, and isomers of xylene
2.) The EC/R equation is not meant to estimate other paraffin VOC in higher proportion than in the default composition.
3.) Condensate compositions deviate substantially from composition used to develop the estimation method.

Component	EC/R Default Composition mole fraction	Average Liquid Sample Composition mole fraction
X_{N2}	0	0
X_{CO2}	0.001	0.001
X_{C1}	0.024	0.024
X_{C2}	0.019	0.03
X_{C3}	0.055	0.081
X_{nC4}	0.045	0.111
X_{iC4}	0.015	0.026
X_{nC5}	0.038	*0.115*
X_{iC5}	0.034	*0.066*
X_{C6}	0.081	0.081
X_{C7}	0.229	0.063
X_{C8}	0.287	0.044
X_{C9+}	**0.07**	**0.326**
$X_{Benzene}$	0.003	0.003
$X_{Toluene}$	0.028	0.005
$X_{EthylBenzene}$	0	0.002
X_{Xylene}	0.032	0.004
$X_{n\text{-}Hexane}$	0.035	0.02
Total	*1*	1
% Difference X_{C9+}	***25.6***	

Table ECR- 1 Comparison of EC/R default composition with average composition

Valko and McCain - Stock Tank Gas-Oil Ratio

Valko and McCain developed an empirical correlation to determine stock tank gas-oil ratio. To develop the correlation, Valko and McCain used 881 reservoir fluid studies from samples taken worldwide. Accurate determination of the gas-oil ratio at reservoir bubblepoint pressures necessitates knowledge of the stock tank gas-oil ratio. Table VC-1 lists the correlation's data set range. The correlation should only be applied within the limits of Table VC-1.

Parameter	Variable	Range and Units
Separator Pressure	P_S	(12-950) psig
Separator Temperature	T_S	(35-194)°F
Stock Tank Oil Gravity	API	(6-56.8)◦API
Separator Gas-oil Ratio	R_{SP}	(8-1817)scf/STB
Stock Tank Gas - Oil Ratio	R_{ST}	(2-527)scf/STB
Separator Gas Specific Gravity	SGs	(0.566-1.292)
Stock Tank Gas Specific Gravity	SG_{ST}	(0.581-1.598)

Table VC- 1 Correlation Data Set

The separator gas-oil ratio is not a required input; however, Valko & McCain developed the correlation using the range of separator gas-oil ratios listed in Table VC-1.

Note: *The separator gas-oil ratio was not recorded, but for the purposes of this study, the separator gas-oil ratio is assumed to be within the allowable range.*

Table VC-2 summarizes the Valko-McCain inputs, equations, and outputs.

Valko-McCain Summary			
INPUT PARAMETERS			
Input Parameters	**Variable**	**Value**	**Range & Units**
Stock Tank API Gravity	*API*		(6 - 56.8)°API
Separator Pressure	P_S		(12 - 950) psig
Separator Temperture	T_S		(35 -194)°F
Oil Production Rate	Q		(N/A) bbl/d
Stock Tank Gas Molecular Weight	MW_{TV}		(16.83 - 46.29) lb/lb-mole
Mass Fraction VOC (C3+) of Stock Tank Gas	X_{VOC}		(N/A) dimensionless

EQUATIONS

$$\ln R_{ST} = 3.955 + 0.83Z - 0.024Z^2 + 0.075Z^3$$

$$Z = \sum_{n=1}^{3} Z_n$$

$$Z_n = C0_n + C1_n VAR_n + C2_n VAR_n^2$$

CORRELATION CONSTANTS

n	VAR	C0	C1	C2
1	lnP_s	-8.005	2.7	-0.161
2	lnT_s	1.224	-0.5	0
3	*API*	-1.587	0.0441	-2.29E-05

OUTPUTS

Parameter	Variable	Value	Range & Units
Stock Tank Gas-Oil Ratio	R_{ST}		(2-527)scf/bbl
Total VOC Flash Emissions	E_{TOT}		(N/A) ton/year
VOC Flash Emissions	E_{VOC}		(N/A) ton/year

Table VC- 2 Correlation Summary

Example Calculation

Given:

stock tank API Gravity, *API* = 40 °API

separator pressure, P_S = 100 psig

separator temperature, T_S = 80°F

Find:

Stock tank gas-oil ratio, R_{ST}

Step 1- Solve for Zn

$Z_1 = -8.005 + 2.7(\ln P_s) - 0.161(\ln P_s)^2$

$Z_2 = 1.224 - 0.5(\ln T_s) + 0$

$Z_3 = -1.587 + 0.0441(API) - 2.29 \times 10^{-5}(API)^2$

$Z_1 = -8.005 + 2.7(\ln(100psig)) - 0.161(\ln(100psig))^2 = 1.01$

Z_2	=	$1.224 - 0.5(\ln(80^\circ F) + 0$	=	-0.967
Z_3	=	$-1.587 + 0.0441(40^\circ API) - 2.29 \times 10^{-5}(40^\circ API)^2$	=	0.140
Z	=	$Z_1 + Z_2 + Z_3$	=	0.188

Step 2 – Find R_{ST}
The next relation will solve for the stock tank gas-oil ratio, R_{ST}.

$$R_{ST} = \exp(3.955 + 0.83Z - 0.024Z^2 + 0.075Z^3)$$

$$R_{ST} = 61 \text{ scf/bbl}$$

With Rst known, the vent gas rate in tons per year can be computed. Refer to the GOR section for the formula. The following charts represent the Valko-McCain Correlation variable relationships.

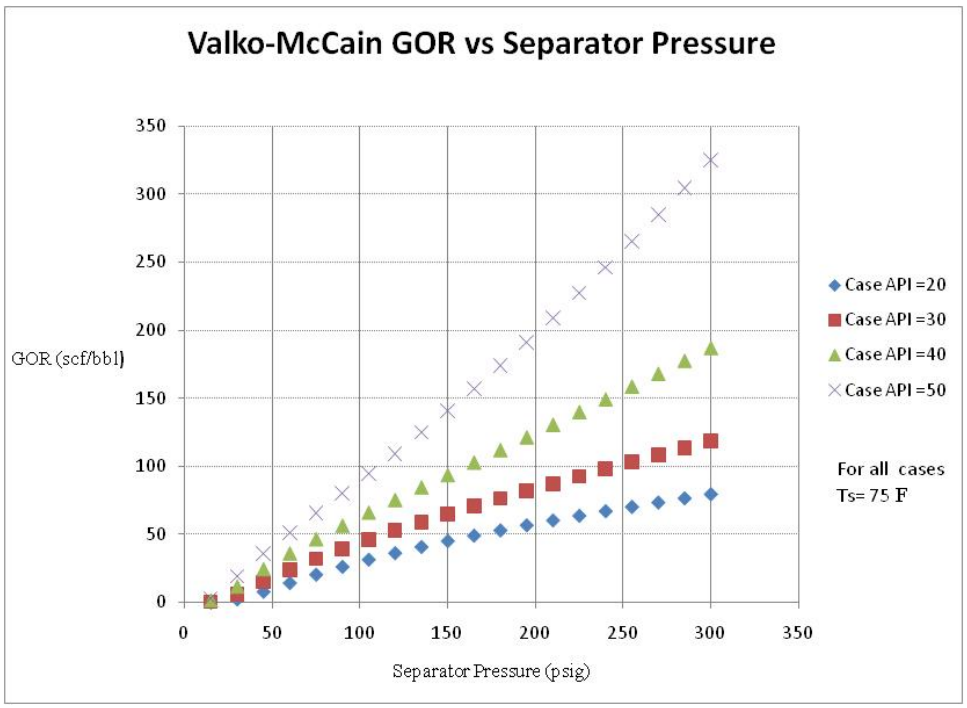

Chart VC- 1 Valko-McCain Gas-Oil Ratio vs. Separator Pressure

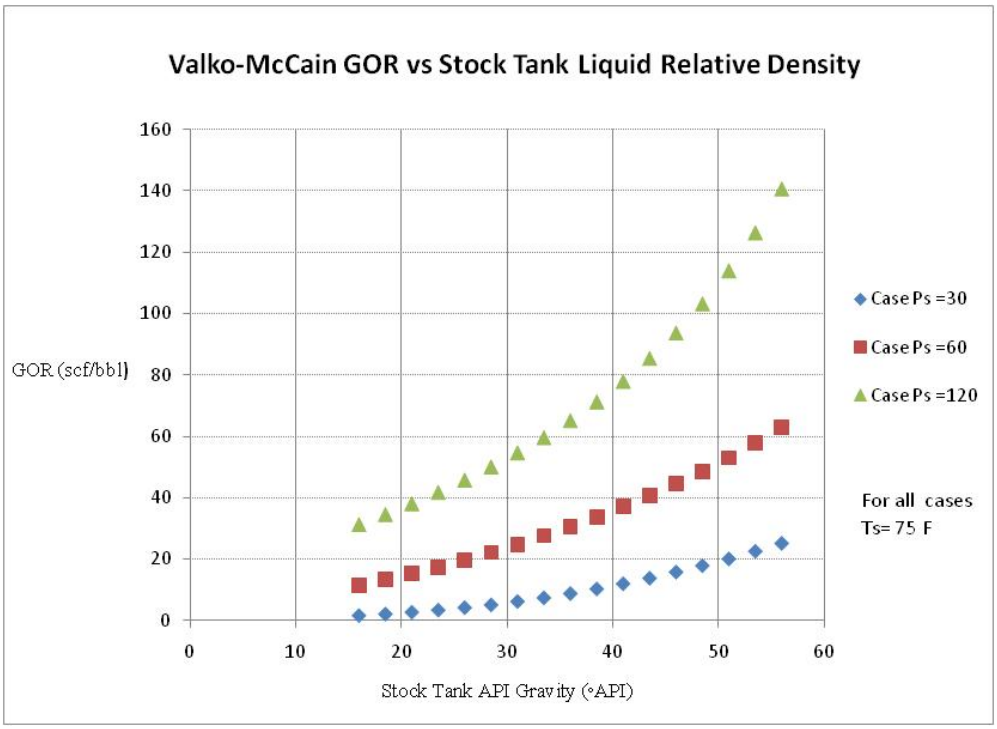

Chart VC- 2 Valko-McCain Gas-oil Ratios vs. Stock Tank API Gravity

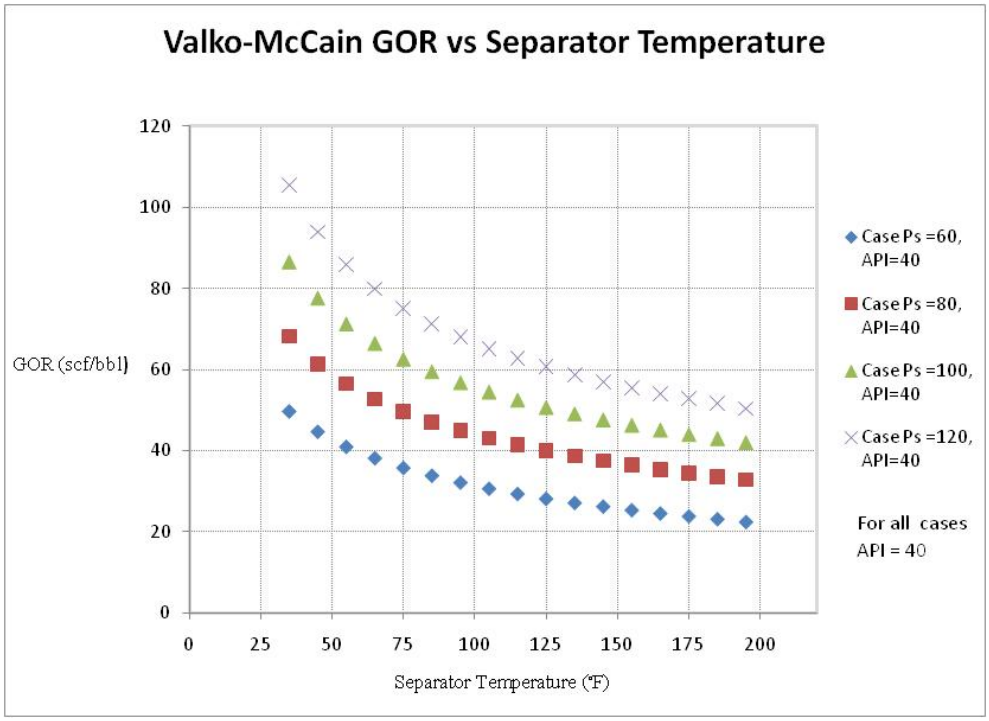

Chart VC- 3 Valko-McCain Gas-oil Ratios vs. Separator Temperature

Separator pressure and API Gravity are directly proportional to the gas-oil ratio. However, the gas-oil ratio will decreases as separator temperature increases. VOC emissions will follow the same functional relationships.

RESULTS

The next tables present the results of the Valko-McCain Correlation used to estimate VOC flashing emissions.

Site	Input Parameters					
	Stock Tank Oil Relative Density	Separator Pressure	Separator Temperature	Oil Production	Tank Vapor Mol. Weight	Tank Vapor VOC (C3+) Mass Fraction
	API	Ps	Ts	Q	MW_{TV}	X_{VOC}
	◦API	psig	°F	bbl/d	lb/lb-mole	lb_{VOC}/lb
	(6-56.8)	(12-950)	(35-194)	-	-	-
WTB# 1	43.7	70.0	64.0	976.0	41.9	0.770
WTB# 2	38.5	25.0	89.0	450.0	39.7	0.674
WTB# 3	36.8	28.0	86.0	16.0	28.4	0.403
WTB# 4	50.0	75.0	70.0	34.0	42.6	0.771
WTB# 5	48.3	90.0	76.0	18.0	42.1	0.796
WTB# 6	37.1	46.0	68.0	176.0	30.5	0.510
WTB# 8	38.8	17.0	74.0	7.0	35.5	0.571
WTB# 10	34.1	15.0	96.0	350.0	34.7	0.544
WTB# 11	42.8	20.0	94.0	250.0	40.2	0.692
WTB# 12	29.1	23.0	90.0	45.0	36.2	0.333
WTB# 13	29.1	23.0	90.0	94.0	42.1	0.565
WTB# 14	38.1	24.0	61.0	137.0	28.9	0.340
WTB# 15	40.6	17.0	70.0	332.0	38.0	0.705
WTB# 17	41.4	22.0	82.0	166.0	40.5	0.677
WTB# 18	39.6	25.0	80.0	28.0	37.6	0.535
WTB# 19	42.8	60.0	78.0	1979.0	39.3	0.726
WTB# 20	37.8	40.0	76.0	119.0	32.4	0.539
WTB# 22	39.6	40.0	85.0	85.0	37.6	0.687
WTB# 23	43.3	40.0	88.0	327.0	35.4	0.619
NTB# 1	44.8	47.7	78.0	69.0	37.5	0.638
NTB# 2	45.3	34.0	80.0	74.0	31.2	0.551
NTB# 3	42.3	26.0	54.0	98.0	32.9	0.547
NTB# 5	67.5	30.0	68.0	50.0	42.8	0.786
NTB# 6	55.7	144.0	74.0	13.0	35.6	0.597
NTB# 7	58.6	147.0	77.0	34.0	36.0	0.614
NTB# 8	58.9	125.0	72.0	16.0	39.8	0.711
NTB# 9	55.2	153.0	38.0	12.0	39.5	0.703
NTB# 11	63.7	231.0	76.0	5.0	35.0	0.600
NTB# 12	63.7	225.0	76.0	14.0	38.1	0.675
NTB# 13	56.2	125.0	60.0	62.0	41.3	0.684

Table VC- 3 Valko-McCain Calculations: Input Parameters

Output Parameters										
Site	Z_1	Z_2	Z_3	$Z = Z_1+Z_2+Z_3$	X	Solution Gas Oil Ratio	Emissions Volume Basis	Total Flash Emissions	Total VOC Flash Emissions	Within Range
						Rs	V_{VB}	E_{TOT}	E_{VOC}	
						scf/bbl	MSCFD	ton/year	ton/year	
						(5-527)				
WTB# 1	0.560	-0.855	0.296	0.001	3.956	52.2	50.9	1023.1	787.8	TRUE
WTB# 2	-0.982	-1.020	0.077	-1.926	1.732	5.7	2.6	48.8	32.9	TRUE
WTB# 3	-0.796	-1.003	0.005	-1.794	1.956	7.1	0.1	1.5	0.6	TRUE
WTB# 4	0.651	-0.900	0.561	0.312	4.214	67.6	2.3	46.9	36.2	TRUE
WTB# 5	0.885	-0.941	0.490	0.433	4.316	74.9	1.3	27.2	21.7	TRUE
WTB# 6	-0.028	-0.886	0.018	-0.896	3.138	23.1	4.1	59.4	30.3	TRUE
WTB# 8	-1.648	-0.928	0.090	-2.486	0.591	1.8	0.0	0.2	0.1	out of range
WTB# 10	-1.874	-1.058	-0.110	-3.042	-0.903	0.4	0.1	2.3	1.3	out of range
WTB# 11	-1.361	-1.048	0.259	-2.151	1.313	3.7	0.9	17.8	12.3	TRUE
WTB# 12	-1.122	-1.026	-0.323	-2.471	0.626	1.9	0.1	1.5	0.5	out of range
WTB# 13	-1.122	-1.026	-0.323	-2.471	0.626	1.9	0.2	3.6	2.0	out of range
WTB# 14	-1.050	-0.831	0.060	-1.822	1.910	6.8	0.9	12.9	4.4	TRUE
WTB# 15	-1.648	-0.900	0.166	-2.382	0.828	2.3	0.8	13.9	9.8	TRUE
WTB# 17	-1.197	-0.979	0.199	-1.977	1.640	5.2	0.9	16.8	11.4	TRUE
WTB# 18	-0.982	-0.967	0.123	-1.826	1.903	6.7	0.2	3.4	1.8	TRUE
WTB# 19	0.351	-0.954	0.259	-0.345	3.663	39.0	77.2	1453.7	1055.4	TRUE
WTB# 20	-0.236	-0.941	0.047	-1.130	2.878	17.8	2.1	32.9	17.7	TRUE
WTB# 22	-0.236	-0.997	0.123	-1.110	2.902	18.2	1.5	27.9	19.2	TRUE
WTB# 23	-0.236	-1.015	0.280	-0.971	3.058	21.3	7.0	118.2	73.2	TRUE

Table VC- 4 Valko-McCain Results 1 of 2

Output Parameters										
Site	Z_1	Z_2	Z_3	$Z = Z_1+Z_2+Z_3$	X	Solution Gas Oil Ratio	Emissions Volume Basis	Total Flash Emissions	Total VOC Flash Emissions	Within Range
						Rs	V_{VB}	E_{TOT}	E_{VOC}	
						scf/bbl	MSCFD	ton/year	ton/year	
						(5-527)				
NTB# 1	0.025	-0.954	0.343	-0.586	3.445	31.3	2.2	38.8	24.8	TRUE
NTB# 2	-0.486	-0.967	0.364	-1.089	2.926	18.6	1.4	20.6	11.4	TRUE
NTB# 3	-0.917	-0.770	0.237	-1.450	2.472	11.8	1.2	18.2	10.0	TRUE
NTB# 5	-0.684	-0.886	1.285	-0.285	3.715	41.1	2.1	42.2	33.2	out of range
NTB# 6	1.437	-0.928	0.798	1.307	5.167	175.3	2.3	38.9	23.2	TRUE
NTB# 7	1.460	-0.948	0.919	1.430	5.312	202.9	6.9	119.0	73.1	out of range
NTB# 8	1.278	-0.914	0.931	1.295	5.152	172.8	2.8	52.7	37.5	out of range
NTB# 9	1.503	-0.595	0.778	1.686	5.645	283.0	3.4	64.3	45.2	TRUE
NTB# 11	1.921	-0.941	1.129	2.109	6.302	545.4	2.7	45.7	27.4	out of range
NTB# 12	1.896	-0.941	1.129	2.084	6.259	522.5	7.3	133.6	90.2	out of range
NTB# 13	1.278	-0.823	0.819	1.274	5.129	168.8	10.5	207.1	141.7	TRUE

Table VC- 5 Valko-McCain Results 2 of 2

Table VC-6 shows Valko-McCain results when paired with Tanks 4.09. The product of the two models was compared to the direct measured VOC emissions. 70 percent of the sites were under-estimated by Valko-McCain and 30 percent were over-estimated.

Sgte	Valko-McCain VOC Flash Emissions	Tanks 4.09 W&B Emissions	Valko-McCain + Tanks 4.09	Measured VOC Emissions
	ton/year	ton/year	ton/year	ton/year
WTB# 1	787.80	36.90	824.70	1134.90
WTB# 2	32.90	17.60	50.50	663.00
WTB# 3	0.60	1.30	1.90	8.80
WTB# 4	36.20	7.70	43.90	12.60
WTB# 5	21.70	5.20	26.90	53.00
WTB# 6	30.30	6.40	36.70	86.50
WTB# 8	0.10	2.00	2.10	33.00
WTB# 10	1.30	11.80	13.10	684.80
WTB# 11	12.30	19.20	31.50	72.00
WTB# 12	0.50	3.30	3.80	21.90
WTB# 13	2.00	7.90	9.90	55.90
WTB# 14	4.40	2.70	7.10	253.80
WTB# 15	9.80	19.20	29.00	98.80
WTB# 17	11.40	8.90	20.30	13.10
WTB# 18	1.80	5.10	6.90	7.70
WTB# 19	1055.40	44.80	1100.20	1790.00
WTB# 20	17.70	7.30	25.00	51.00
WTB# 22	19.20	10.90	30.10	123.80
WTB# 23	73.20	12.00	85.20	93.50
NTB# 1	24.80	2.50	27.30	33.20
NTB# 2	11.40	1.20	12.60	8.30
NTB# 3	10.00	5.70	15.70	6.90
NTB# 5	33.20	6.30	39.50	141.90
NTB# 6	23.20	3.60	26.80	17.30
NTB# 7	73.10	4.50	77.60	34.90
NTB# 8	37.50	6.00	43.50	92.20
NTB# 9	45.20	1.90	47.10	35.90
NTB# 11	27.40	2.30	29.70	65.40
NTB# 12	90.20	3.60	93.80	13.60
NTB# 13	141.70	7.50	149.20	36.50

Table VC- 6 Valko-McCain Comparison of Measured vs. Calculated

Gas Research Institute (GRI)-HAPCalc 3.0

GRI-HAPCalc estimates flash, working, and breathing emissions from hydrocarbon storage tanks. The program uses the Vasquez-Beggs Correlation to compute flash emissions and modified AP-42 equations to estimate working and standing losses.

Inputs

Table GRI-1 lists the necessary inputs to GRI-HAPCalc. Please note that GRI-HAPCalc has the same input restraints as the Vasquez-Beggs spreadsheet. If the user attempts to input a variable outside the appropriate range, the program will prevent the user from running the program. Therefore, only sites with parameters within the allowable ranges have results.

Operating Conditions & Tank Parameters	Annual Throughput [bbl/year]
	Tank Capacity [bbl]
	Vertical or Horizontal Tank
	Separator Temp. [°F]
	Separator Gas Specific Gravity
	Separator Pressure [psia]
	Stock Tank Gravity [°API]
Composition Mole %	Methane
	Ethane
	Propane
	Butane
	Pentane
	C6+
	n-Hexane
	Benzene
	Toluene
	Ethylbenzene
	Xylenes (m,o,p)
	2,2,4-Trimethylpentane
	Nitrogen
	Oxygen

Table GRI- 1 HAPCalc Inputs

GRI-HAPCalc restricts the composition to the components in Table GRI-1. Table GRI-2 shows how the C1-C12+ composition is transformed into the C1-C6+ composition.

HapCalc Composition	Tank Vapor Composition
Nitrogen	Nitrogen
Oxygen	Oxygen
Methane	Methane
Ethane	Ethane
Propane	Propane
I-Butane	Butane
N-Butane	Butane
Pentane	I-Pentane N-Pentane Cyclopentane
N-Hexane	n-Hexane
C6+	2,2 Dimethyl Butane 2-Methylpentane 3-Methylpentane Methylcyclopentanes Cyclohexane 2-Methylhexane 3-Methylhexane Dimethylcyclopentanes N-Heptane Methylcyclohexane N-Octane N-Nonane N-Decane N-Undecane Dodecane Plus
Benzene	Benzene
Toluene	Toluene
Ethylbenzene	Ethylbenzene
Xylenes (m,o,p)	P-M-Xylene
	O-Xylene

Table GRI- 2 HapCalc Composition

Working & Standing Losses Calculation

To calculate working and breathing losses, HapCalc makes the following assumptions**:**

- Vertical Tanks have dome-roof construction
- The dome-roof radius is two times the tanks shell radius
- The ratio of tank height to diameter is 2:1
- The surface coating of the tank is white paint in good condition
- The maximum liquid volume is 50 percent of the total shell volume
- The daily max., min., and avg. temperatures are 76°F, 54°F, and 67°F
- The pressure in the tank is 14.7 psia

- Tank breather vent settings are 0.03 psig and 0.03 psig vacuum
- The vapor-liquid equilibrium inside the tank can be modeled by simplified Raoult's Law: an ideal gas in equilibrium with an ideal solution.

Flash Losses Calculation

GRI-HAPCalc computes flash emissions with the Vasquez-Beggs Correlation. Please refer to that section for the model description and equations.

Outputs

Table GRI-3 lists the resultant flash, working, and standing losses in ton/year.

Outputs	Speciated Emissions ton/yr
	Benzene
	Toluene
	Ethylbenzene
	Xylenes(m,p,o)
	n-Hexane
	Methane
	Ethane
	Propane
	Butane
	Pentane
	C6+
	Total Stream VOC Emissions
	[ton/year]

Table GRI- 3 HAPCalc Outputs

			WTB#4	WTB#5	NTB#6
Inputs	Operating Conditions & Tank Parameters	*Annual Throughput [bbl/yr]*	34	18	13
		Annual Throughput [bbl/yr]	12410	6570	4745
		Tank Capacity [bbl]	500	500	500
		Tank Type	Vertical	Vertical	Vertical
		Separator Temp. [°F]	70	76	74
		Separator Gas Specific Gravity	1.01	0.99	0.76
		Separator Pressure [psia]	88.28	103.28	158.44
		Stock Tank Gravity [°API]	50	48	55
	Tank Vapor Composition	*COMPONENT*			
		Tank Vapor Composition	Mole%	Mole%	Mole%
		Methane	14.3478	17.4136	27.4
		Ethane	15.0336	17.6687	21.3
		Propane	29.1193	34.0387	20.2
		Butane	22.0703	21.5467	13
		Pentane	7.3577	6.2246	4.55
		C6+	1.6723	1.3344	1.912
		n-Hexane	0.2559	0.2022	0.16
		Benzene	0.0394	0.0311	0.025
		Toluene	0.0245	0.0198	0.024
		Ethylbenzene	0.0086	0.0069	0.0084
		Xylenes (m,o,p)	0.0232	0.0187	0.0217
		2,2,4-Trimethylpentane	0	0	0
		Nitrogen	8.2321	1.1458	9.55
		Oxygen	1.4259	0.0149	1.48
Outputs	Results	*Calculated Emissions*	ton/year	ton/year	ton/year
		Methane	1.44052445	0.9015143	2.092778
		Ethane	2.82961517	1.7148167	3.04987
		Propane	8.03804581	4.8449715	4.241879
		Butane	20.49948697	32.648497	7.312823
		Pentane	8.48374413	11.70859	3.177341
		C6+	2.30319034	2.9981223	1.602823
		n-Hexane	0.3524406	0.4543018	0.133457
		Benzene	0.04918266	0.0633321	0.0189
		Toluene	0.03607642	0.0475631	0.021403
		Ethylbenzene	0.01459182	0.0190989	0.008632
		Xylenes(m,p,o)	0.03936398	0.0517607	0.022299
		VOC Emissions			
		[ton/year]	39.8	52.8	16.5

Table GRI- 4 HAPCalc: Inputs and Calculated Emissions

Summary

Only three sites are within the Vasquez-Beggs allowable range: WTB#4, WTB#5, and NTB#6. The lack of results precludes any assessment of the program's overall performance.

E&P Tank 2.0

E&P Tank was developed in an effort to estimate working, breathing and flash components of hydrocarbon production tanks. The program is based on the Peng-Robinson (PR) equation of state. An equation of state (EOS) is a mathematical equation that specifies the relationships between thermodynamic variables such as pressure, temperature and volume of a specific material in thermodynamic equilibrium. E&P Tank was run using three program options. The three options include RVP Low Pressure Oil, AP-42 Low Pressure Oil, and RVP Geographical Database. AP-42 Geographical Database was not used because it requires detailed meteorological and tank data which may not be available to users. Each option requires slight differences in the data inputs. Minimum input parameters are required for E&P Tank and are listed below:

Minimum Inputs

- Separator Oil Composition, Temperature, and Pressure
- Sales Oil API Gravity and Production Rate
- Reid Vapor Pressure
- Ambient Air Temp and Pressure

Note: E&P Tank provides two methods to determine working and breathing losses: AP-42 Equations and a fractional distillation column. The AP-42 method is a modified version of the AP-42 from the Environmental Protection Agency. E&P Tank utilizes rigorous thermodynamics and a material balance approach to achieve working and breathing losses. The drawback is that the program may artificially change input parameters to match the AP-42 parameters inputted by the user. A fractional distillation column provides the second option for estimating working and breathing losses. AP-42 methods are typically limited to RVP below 12.0 psia. The distillation column is meant to overcome this deficiency. First, the program attempts a four tray distillation column to estimate working and breathing losses. If convergence is not achieved a more conservative (higher emissions) single tray column is performed at 90 percent saturation pressure.

Hy-Bon collected the necessary inputs to each model though direct measurement and laboratory samples. The following procedures and program selections were made to determine emissions at each site.

E&P Tank requires the temperature of the gas/oil mixture entering the tank. The program indicates if this temperature is not known, to either use the separator temperature or ambient temperature. Tank emissions were measured in July, August, and September at sites in West and North Texas. As a result, the average ambient conditions are used for this project. The average ambient conditions for all of the sites is listed below:

Daily Minimum Ambient Temperature – 69°F Daily Maximum Ambient Temperature - 93°F
Daily Average Ambient Temperature – 81°F Sales Oil bulk liquid temperature - 65°F

Flowsheet Selection	Known Separator Information	Model Selection for W&S Losses	Required Information	Calculated Emissions
Tank with Separator	Low Pressure Oil	RVP Distillation	Separator Pressure and Temperature Lab Analysis Data Input Production Rates Days of Operation API Gravity Reid Vapor Pressure	

Table EP- 1 Option 1: RVP-Low Pressure Oil Inputs

Flowsheet Selection	Known Separator Information	Model Selection for W&S Losses	Required Information	Calculated Emissions
Tank with Separator	Low Pressure Oil	AP-42	Separator Pressure and Temperature Lab Analysis Data Input Tank & Shell Information Production Rates Days of Operation API Gravity Reid Vapor Pressure	

Table EP- 2 Option 2: AP-42 – Low Pressure Oil Inputs

Flowsheet Selection	Known Separator Information	Model Selection for W&S Losses	Required Information	Calculated Emissions
Tank with Separator	Geological	RVP Geological Database	Separator Pressure and Temperature Southwest Region Production Rates Days of Operation API Gravity Reid Vapor Pressure	

Table EP- 3 Option 3: Geographical Database

Site	Ps [psig]	T_S separator. [°F]	Q_{ACT} [BOPD]	E&P Tank RVP-GEO Volume [MSCFD]
WTB# 1	70	64	976	35.69
WTB# 2	25	89	450	19.47
WTB# 3	28	86	16	0.39
WTB# 4	75	70	34	1.24
WTB# 5	90	76	18	1.44
WTB# 6	46	68	176	2.98
WTB# 8	17	74	7	0.33
WTB# 10	15	96	350	16.50
WTB# 11	20	94	250	6.57
WTB# 12	23	90	45	1.95
WTB# 13	23	90	94	4.07
WTB# 14	24	61	137	4.45
WTB# 15	17	70	332	15.65
WTB# 17	22	82	166	7.18
WTB# 18	25	80	28	0.69
WTB# 19	60	78	1979	74.40
WTB# 20	40	76	119	2.01
WTB# 22	40	85	85	1.44
WTB# 23	40	88	327	5.53
NTB# 1	47.7	78	69	6.69
NTB# 2	34	80	74	1.81
NTB# 3	26	54	98	3.18
NTB# 5	30	68	50	1.22
NTB# 6	144	74	13	0.70
NTB# 7	147	77	34	1.83
NTB# 8	125	72	16	0.82
NTB# 9	153	38	12	0.65
NTB# 11	231	76	5	0.27
NTB# 12	225	76	14	0.75
NTB# 13	125	60	62	3.18

Table EP- 4 E&P Tank Results: Geographical Database

Table EP-4 represents the results of the E&P Tank GEOGRAPHICAL Option. Working and Breathing losses are calculated via the RVP fractional distillation option. Sites were selected from the southwest region based on separator pressure and temperature. The only other parameter that was changed was oil production rate. API Gravity and RVP were NOT altered.

Summary Option 1- Low Pressure Oil and RVP Distillation Column

E&P Tank Option 1- Low Pressure Oil and RVP Distillation Column models working and breathing losses as a distillation column as an alternative to AP-42 methods. If the four-tray column does not converge, it computes a more conservative single-tray column to model evaporative emissions. The results obtained from sites where the column fails to meet these criteria do not realistically VOC emissions. This option overestimated emissions volumes in 64.3 percent and VOC emissions in 82.1 percent of the sites.

Summary Option 2- Low Pressure Oil and AP-42

E&P Tank Option 2- Low Pressure Oil and AP-42 over-predicted emission volumes for 78.6 percent of sites. Additionally, the option over-estimated VOC emissions for 85.7 percent of the sites. Working and standing losses were not computed because the sites failed to meet the RVP pressure specification for the program.

Option 1 and 2 overestimated the emissions and were highly sensitive to the input value of designated stock tank operating temperature.

Summary Option 3- GEO-RVP

The GEO-RVP option underestimated stock tank volumes for 73.3 percent and VOC emissions 70 percent of the sites tested. Sites were selected from the southwest region based on separator pressure. The gas-oil ratio is proportional to separator pressure; gas-oil ratio increases with separator pressure.. RVP is selected to model working and breathing losses because it does not require detailed meteorological and tank data.

AspenTech HYSYS 2006.5

Equation of State Selection

Hysys allows the user to select the appropriate Equation of State (EOS) for the system model. TCEQ's technical supplement 6 references the Peng-Robinson EOS; however, no EOS is suitable for all systems. Many factors require consideration before an appropriate EOS is utilized in any process simulation software such as data available, temperature and pressure range, and type of mixtures-encountered. In this case, the components are multi-phase hydrocarbon mixtures. Equations of State were initially developed for single or pure component systems. However, the early forms of Equations of State did not match measured liquid densities. As a result, binary interaction coefficients, additional mixing rules, and empirical relations have been added to extend the range of EOS to predict hydrocarbon phase behavior. Furthermore, proprietary enhancements to EOSs by software vendors further increase the range of applicability and accuracy. For example, the API Technical Data Book uses a modified version of the Soave-Redlich-Kwong (SRK) EOS. For the system being modeled, the Hysys SRK EOS will give comparable results to the Hysys Peng-Robinson (P-R) EOS. However, Hysys technical reference manuals indicate the Hysys P-R gives better overall performance and has a greater range of applicability than the Hysys SRK EOS. Consequently, the Hysys P-R EOS was selected for this project.

HYSYS performs a rigorous heat and material balance to predict the vapor-liquid equilibrium behavior necessary to find the speciated emissions.

Required Data

- Extended Pressurized Separator Compositional Analysis
- Separator Pressure, psia
- Separator Temperature, °F
- Oil Production, bbl/day

Assumptions

- Only flash emissions are calculated
- Adiabatic Flash *
- The process is steady state
- Stock tank operates at ambient pressure

  West Texas Batteries - 13.28 psia

  North Texas Batteries - 14.44 psia

*"*SPE Paper 26588 API Tank Vapor Project*" indicates that an adiabatic flash (pressure reduction without heat gain or loss) best approximates process of gas flashing as the oil is reduced to atmospheric pressure. Additionally, the assumption of adiabatic flash was validated by Core Lab in the laboratory.

Emissions Calculation Procedure

The HYSYS calculation procedure consists of specifying the separator liquid composition, temperature, pressure, and production rate. A pressure control valve (PCV) and a stock tank are utilized to model the process. The pressure control valve reduces the separator pressure to ambient pressure. The stock tank will then separate the 2-phase gas-oil mixture.

A process flow diagram shown below summarizes the system.

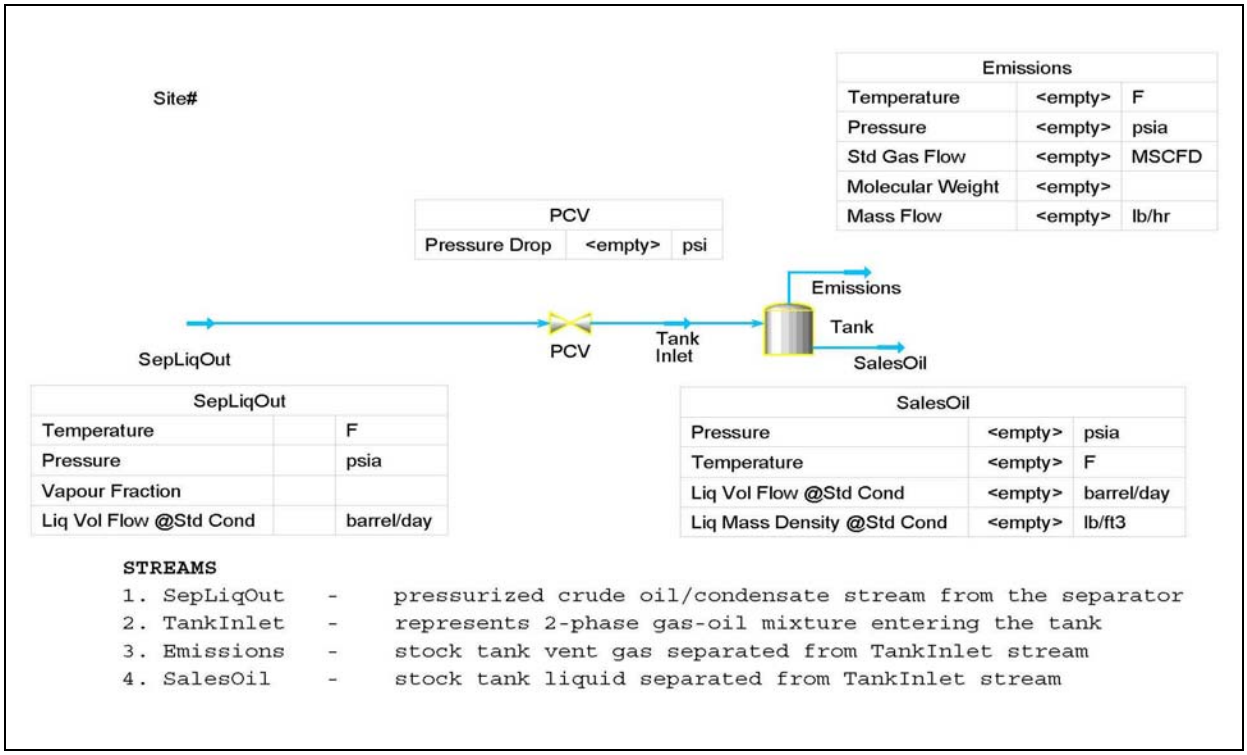

Figure 3 HYSY Process Flow Diagram

Program Inputs

1. Liquid Exiting the Separator
   - Pressure
   - Temperature
   - Composition-extended analysis
2. Pressure Control Valve Data
   - ΔP pressure difference between separator and atmospheric conditions, psi
3. Stock Tank
   - Oil production flow rate, bbl/day

.

Program Outputs

The compositions and mass flow rates for all streams listed on the PFD are provided. The emissions output will consist of:

- mole fraction composition
- mass flow (lb/hr) for each component in the composition
- molecular weight

- gas density (lb/ft^3) and gas volume flow rate (MSCFD)corrected to standard conditions of 14.7 psia & 60°F

VOC emissions in ton/year are found by summing the VOC components and converting to tons/year. The conversion from VOC in lb per year to tons per year is

$$E_{VOC}(ton/yr) = \frac{1lb}{hr} \times \frac{1ton}{2000lb} \times \frac{24hr}{1day} \times \frac{365day}{1yr}$$

$$E_{VOC}(ton/yr) = 4.38 \times 1lb/hr$$

Summary

The Hysys process simulator model was also evaluated for accuracy in calculating estimated volumes of emissions at each site. Hysys over predicted VOC emissions on 64.3 percent of the facilities tested. The results may indicate the difficulty of extending results to a 24 hour time period from instantaneous measurements of composition, pressure, and temperature.

Results

The flow measurements represent the volumetric flow rate over a twenty four hour cycle. These flow measurements were conducted at each test site to quantify tank emissions. VOC content was determined from the gas composition and a metered flow rate. The site locations were not pre-selected and were completely random; the locations were tested with production rates of 10 to 1,979 barrels per day. Total flow measurements were made at thirty six production sites. Twenty-three of the sites were in West Texas and thirteen sites were taken in the North Texas. The study was conducted in these areas during July – September 2008. Six of the locations have been excluded from the test due to analysis data. These samples would not provide sufficient data inputs for the models and methods used in this study.

The Tanks 4.09 program estimates working and breathing losses according to AP-42 equations. Twenty-four out of the thirty sites met the RVP requirements of Tanks 4.09. The results of Tanks are not meant for direct comparison with the measured volumes. The results are added to those programs which do not estimate working and breathing losses.

The results of the study provided some interesting, and at times surprising results. Overall, four methods underestimated emissions for a majority of sites. These four included Laboratory GOR, Valko-McCain, E&P Tank GEO/RVP, and Vasquez-Beggs. Three of the modeling methods resulted in the VOC emissions being overestimated. These include Hysys, E&P Tank AP42 LPO, and E&P Tank – RVP LPO. The variable constraints of the Vasquez-Beggs equation made it inapplicable on 27 of the 30 sites, suggesting this equation may not be a viable option for estimating vent volumes in many vent tank applications.

The GOR method uses a field-collected sample of oil to develop a laboratory determined gas-oil ratio. The GOR method with the addition of Tanks 4.09 resulted in underestimating emissions for 76.67 percent and overestimating 23.33 percent of the sites.

GRI-HAP Calc uses the Vasquez-Beggs Correlation to estimate flash emissions and uses AP-42 equations to estimate working and breathing losses. As a result, the program was only run for the same three sites as the Vasquez-Beggs Correlation.

One of the more commonly used industry emission modeling approaches, using the geographic database in the American Petroleum Institute's E&P Tank, was found to underestimate tank VOC emission in 70.0 percent of the facilities tested.

In contrast, using the E&P Tank model; Option 1- Low Pressure Oil and AP-42 resulted in an over prediction of VOC emissions in 85.7 percent of the sites tested. Working and standing losses were not computed because the sites failed to meet the RVP pressure specification for the program. Option 2- Low Pressure Oil and RVP Distillation Column can model the working and breathing losses as a distillation column as an alternative to AP-42 methods. If the column does not meet the RVP given, then it computes a more conservative form to account for the working and breathing losses. The results obtained from sites where the column fails to meet these criteria do not realistically represent working and breathing losses. This option overestimated VOC emissions in 82.1 percent of the sites. Both of the models that overestimated these emissions were highly sensitive to the input value of designated stock tank operating temperature. This value was obtained from sampling the oil tank, but it is generally not an available variable when this modeling software is used – and is therefore estimated

The Hysys process simulator model was also evaluated for accuracy in calculating estimated volumes of emissions at each site. Hysys was found to over predict the VOC emissions on 64.3 percent of the facilities tested. The results indicate the difficulty of extending results to a 24 hour time period from an instantaneous measurements.

The summary tables show the correlation and deviation from measured values. The emission model results are grouped according to their ability to predict the volume of vented gas and the quantity of VOC emissions for each location.

Estimation Methods - Over-Estimated

	HYSYS	E&P Tank - AP42 LPO	E&P Tank - RVP LPO
valid sites	28	28	28
sites over	18	23	24
Percentage	64.30%	82.10%	85.70%

Estimation Methods -Under-Estimated

	Laboratory GOR	Valko-McCain	E&P Tank GEO/RVP	Tanks 4.09
valid sites	30	21	30	24
sites under	23	14	21	24
Percentage	76.70%	66.67%	70.00%	100.00%

The following table illustrates the comparison between the Direct Measurement Method and the Equations of State which calculate flash emissions. To make a valid comparison VOC emissions estimated calculated using Tanks 4.09, which estimates working and breathing losses, were added to the equations of state. Six of the sites did not meet the requirements for the Tanks 4.09 and an assumed value for Reid Vapor Pressure of nine was used to validate these for comparison purposes.

Results Table-1

Site	Total VOC Measurement	Working & Breathing	Equations of State for Flash Emissions		
	Direct Measure Method VOCs	Tank 4.09	Vasquez-Beggs + Tanks 4.09	GOR + Tanks 4.09	Valko-McCagn + Tanks 4.09
	ton/'yr	ton/year	ton/year	ton/year	ton/year
WTB# 1	1134.90	36.90	344.70	1479.60	824.70
WTB# 2	663.00	17.60	61.50	724.50	50.50
WTB# 3	8.80	1.30	1.90	10.70	1.90
WTB# 4	12.60	7.70	26.20	38.80	43.90
WTB# 5	53.00	5.20	15.90	68.90	26.90
WTB# 6	86.50	6.40	17.70	104.20	36.70
WTB# 8	33.00	2.00	2.30	35.30	2.10
WTB# 10	684.80	11.80	23.20	708.00	13.10
WTB# 11	72.00	19.20	40.90	112.90	31.50
WTB# 12	21.90	3.30	5.30	27.20	3.80
WTB# 13	55.90	7.90	16.60	72.50	9.90
WTB# 14	253.80	2.70	7.50	261.30	7.10
WTB# 15	98.80	19.20	39.60	138.40	29.00
WTB# 17	13.10	8.90	24.20	37.30	20.30
WTB# 18	7.70	5.10	7.00	14.70	6.90
WTB# 19	1790.00	44.80	472.30	2262.30	1100.20
WTB# 20	51.00	7.30	15.20	66.20	25.00
WTB# 22	123.80	10.90	20.00	143.80	30.10
WTB# 23	93.50	12.00	51.50	145.00	85.20
NTB# 1	33.20	2.50	14.70	47.90	27.30
NTB# 2	8.30	1.20	6.80	15.10	12.60
NTB# 3	6.90	5.70	12.10	19.00	15.70
NTB# 5	141.90	6.30	25.10	167.00	39.50
NTB# 6	17.30	3.60	12.90	30.20	26.80
NTB# 7	34.90	4.50	32.60	67.50	77.60
NTB# 8	92.20	6.00	20.80	113.00	43.50
NTB# 9	35.90	1.90	15.30	51.20	47.10
NTB# 11	65.40	2.30	11.30	76.70	29.70
NTB# 12	13.60	3.60	33.20	46.80	93.80
NTB# 13	36.50	7.50	63.20	99.70	149.20

Under Estimated		24.00	2.00	23.00	14.00
Percent Under Estimated		100.00%	66.67%	76.67%	66.67%

Over Estimated		0.00	1.00	7.00	8.00
Percent Over Estimated		0.00%	33.33%	23.33%	38.10%

Out of Range	0.00	6.00	28.00	7.00	16.00
Failed to Estimate VOC	0.00%	20.00%	93.33%	23.33%	53.33%

The Results Table also shows the number of times the data was outside of range of the specified methods' constraints.

Results Table-2

Site	Direct Measure Method VOCs	Hysis VOCs	E&P Tank - RVP VOCs	E&P Tank - GEO/RVP VOCs	AP-42 LPO VOCs	GRI-HAPCalc VOCs
	ton/'yr	[ton/year]	ton/'yr	ton/'yr	ton/'yr	ton/year
WTB# 1	**1134.90**	2390.80	6663.00	309.10	4395.00	Out of Range
WTB# 2	**663.00**	1904.90	2955.00	394.00	2156.00	Out of Range
WTB# 3	**8.80**	22.60	57.00	4.30	28.00	Out of Range
WTB# 4	**12.60**	54.00	111.00	10.80	92.00	39.80
WTB# 5	**53.00**	26.80	48.00	14.20	41.00	52.80
WTB# 6	**86.50**	174.40	685.00	31.60	347.00	Out of Range
WTB# 8	**33.00**	9.70	32.00	6.80	17.00	Out of Range
WTB# 10	**684.80**	1038.60	1872.00	338.50	1035.00	Out of Range
WTB# 11	**72.00**	409.40	897.00	126.50	406.00	Out of Range
WTB# 12	**21.90**	Out of Range	Out of Range	39.40	Out of Range	Out of Range
WTB# 13	**55.90**	Out of Range	Out of Range	82.30	Out of Range	Out of Range
WTB# 14	**253.80**	182.00	810.00	56.40	411.00	Out of Range
WTB# 15	**98.80**	416.70	1095.00	321.10	790.00	Out of Range
WTB# 17	**13.10**	476.30	1071.00	145.30	629.00	Out of Range
WTB# 18	**7.70**	55.60	173.00	7.60	78.00	Out of Range
WTB# 19	**1790.00**	8193.80	19959.00	717.50	11024.00	Out of Range
WTB# 20	**51.00**	586.10	818.00	21.40	755.00	Out of Range
WTB# 22	**123.80**	165.50	338.50	15.30	206.00	Out of Range
WTB# 23	**93.50**	2532.90	3311.00	58.70	2781.00	Out of Range
NTB# 1	**33.20**	150.00	329.00	103.50	122.00	Out of Range
NTB# 2	**8.30**	98.00	242.00	20.10	131.00	Out of Range
NTB# 3	**6.90**	89.00	474.00	40.30	224.00	Out of Range
NTB# 5	**141.90**	43.00	546.00	13.50	491.00	Out of Range
NTB# 6	**17.30**	30.00	57.00	3.30	32.00	16.50
NTB# 7	**34.90**	11.00	109.00	8.60	51.00	Out of Range
NTB# 8	**92.20**	11.00	77.00	5.60	44.00	Out of Range
NTB# 9	**35.90**	10.00	159.00	3.00	82.00	Out of Range
NTB# 11	**65.40**	8.00	16.00	1.30	11.50	Out of Range
NTB# 12	**13.60**	7.00	62.00	3.50	48.00	Out of Range
NTB# 13	**36.50**	6.00	346.00	21.70	294.00	Out of Range

Under Estimated		10.00	4.00	20.00	4.00	2.00
Percent Under Estimated		35.71%	14.29%	66.67%	14.29%	66.67%

Over Estimated		18.00	24.00	10.00	24.00	1.00
Percent Over Estimated		64.29%	85.71%	33.33%	85.71%	33.33%

Out of Range	**0.00**	**2.00**	**2.00**	**0.00**	**2.00**	**27.00**
Failed to Estimate VOC	**0.00%**	**6.67%**	**6.67%**	**0.00%**	**6.67%**	**90.00%**

The Results Table -3 also shows the comparison between measured and the estimated volumes of each method. The results changed slightly. Overall, the measured volume results and VOC results are very similar in the comparison of each model

Results Table-3

	Producer Info	Measured Volume Data		VOLUME EMISSION ESTIMATION MODELS OVERESTIMATED		
SITE	Production Rate	Measured Volumes (MCFD)	Tank Vapor Heating Value	HYSYS	E&P Tank AP-42 - LPO	E&P Tank RVP LPO
				57.10%	64.30%	78.60%
	[BBL]	[MCFD]	[Btu/ft^3]	[MSCFD]	[MSCFD]	[MSCFD]
WTB 1	976	84.1	2369.5	118.8	196	284
WTB 2	450	59.23	2015.5	90.4	102	133
WTB 3	16	1.86	1275.9	1.2	1.5	2.5
WTB 4	34	0.86	2253	2.7	4.12	4.9
WTB 5	18	3.76	2370.8	1.3	1.81	2.1
WTB 6	176	13.32	1532.7	9.8	16.4	29
WTB 8	7	3.87	1670.1	0.5	0.743	1.3
WTB 10	350	86.67	1638.7	47.3	49	78
WTB 11	250	6.22	2039.3	16.5	17	34
WTB 12	45	4.32	813.1	0	0	0
WTB 13	94	5.56	1639.2	0	0	0
WTB 14	137	61.7	1131	10.5	19.3	33
WTB 15	332	8.8	1683.3	21.7	36	47
WTB 17	166	1.14	1910.5	21.7	27.5	43
WTB 18	28	0.86	1395.8	2.6	3.5	6.6
WTB 19	1979	149.95	2239.4	409.7	523	855
WTB 20	119	6.97	1765.7	40.8	48	50.6
WTB 22	85	11.49	2063.1	7.5	9.03	14
WTB 23	327	10.24	1976.9	148.8	162	182
NTB 1	69	3.32	1535.7	7.7	10.2	14.8
NTB 2	74	1.1	1696.5	2.9	6	10.5
NTB 3	98	0.87	1528.6	3.6	9.9	19
NTB 5	50	10.1	2408.6	20.9	26	28
NTB 6	13	1.99	1843	1.1	1.5	2.5
NTB 7	34	3.82	1907.6	1.9	2.5	4.6
NTB 8	16	7.77	2248.8	1.4	2	3.23
NTB 9	12	3.08	2111.8	2.9	5	7.9
NTB 11	5	7.47	1328.7	0.5	0.568	0.757
NTB 12	14	1.24	2087.3	2.4	2.7	3.28
NTB 13	62	3.07	1957.7	11.6	16.4	18.7

Results Table-4

	Producer Info	Measured Volume Data		VOLUME EMISSION ESTIMATION MODELS UNDERESTIMATED			
SITE	Production Rate	Measured Volumes (MCFD)	Tank Vapor Heating Value	Valko-McCain	Laboratory GOR	E&P Tank GEO LPO	Tanks 4.09
				68.20%	80.00%	73.30%	100.00%
	[BBL]	[MCFD]	[Btu/ft^3]	[MSCFD]	[MSCFD]	[MSCFD]	[MSCFD]
WTB 1	976	84.1	2369.5	50.982	20.56	35.69	1.99
WTB 2	450	59.23	2015.5	1.537	12.05	19.47	0.95
WTB 3	16	1.86	1275.9	0.113	0.11	0.391	0.07
WTB 4	34	0.86	2253	2.298	3.12	1.24	N/A
WTB 5	18	3.76	2370.8	1.348	0.91	1.44	N/A
WTB 6	176	13.32	1532.7	4.059	0.33	2.98	0.35
WTB 8	7	3.87	1670.1	N/A	0.02	0.329	0.11
WTB 10	350	86.67	1638.7	N/A	2.65	16.5	0.64
WTB 11	250	6.22	2039.3	0.929	0.21	6.57	1.04
WTB 12	45	4.32	813.1	N/A	0.19	1.95	0.18
WTB 13	94	5.56	1639.2	N/A	0.08	4.07	0.42
WTB 14	137	61.7	1131	0.925	0.73	4.45	0.15
WTB 15	332	8.8	1683.3	0.76	1.4	15.65	1.04
WTB 17	166	1.14	1910.5	0.856	1.31	7.18	0.48
WTB 18	28	0.86	1395.8	0.188	0.09	0.685	0.28
WTB 19	1979	149.95	2239.4	77.113	115.82	74.4	2.41
WTB 20	119	6.97	1765.7	2.116	4.79	2.01	0.39
WTB 22	85	11.49	2063.1	1.548	0.18	1.44	0.59
WTB 23	327	10.24	1976.9	6.959	9.03	5.53	0.65
NTB 1	69	3.32	1535.7	2.163	1.13	6.69	N/A
NTB 2	74	1.1	1696.5	1.38	0.37	1.81	N/A
NTB 3	98	0.87	1528.6	1.161	2.64	3.18	N/A
NTB 5	50	10.1	2408.6	N/A	7.33	1.22	N/A
NTB 6	13	1.99	1843	2.279	0.28	0.698	0.19
NTB 7	34	3.82	1907.6	6.897	0.41	1.83	0.24
NTB 8	16	7.77	2248.8	N/A	0.48	0.821	0.31
NTB 9	12	3.08	2111.8	3.395	4.31	0.645	0.1
NTB 11	5	7.47	1328.7	N/A	0.19	0.269	0.12
NTB 12	14	1.24	2087.3	N/A	1.58	0.752	N/A
NTB 13	62	3.07	1957.7	10.464	6.26	3.18	N/A

In conclusion, each model reviewed has limitations and shortcomings. No one model resulted in the extremely strong correlation to the measured data. Continuous monitoring or multiple sampling may provide the user with better and more consistent input data when using these

methods or models. The direct measurement method is more representative of the actual emissions. The measurement must be over a full twenty four hour time span – and during a 24 hour period that is representative of the normal operation of the tanks. The emission rate can be extrapolated monthly or annually with a much smaller percentage of error.

Appendix A ---------- References

Appendix B ---------- Nomenclature

Appendix C (CD Format) ---------- Field Data Sheets & Laboratory Results

Appendix D (DVD Format) ---------- Field IR Videos

Appendix E (CD Format) ---------- Model Calculation Results

Appendix A References

1. *2007 Emissions Inventory Guidelines,* RG-360A/07, January 2008

2. "VOC Emissions from Oil and Condensate Storage Tanks: Final Report," Houston Advanced Research Center (HARC) Project H051C

3. Vasquez, M. and Beggs, H.D., *Correlations for Fluid Physical Property Predictions*, Journal of Petroleum Technology, June: 968-970, 1980

4. Beggs, D. H. 1987. Petroleum Engineering Handbook, Chapter 22. Oil System Correlations

5. *Lyons,W.C., and Plisga,G.J,.* Standard Handbook of Petroleum & Natural Gas Engineering, Gulf Publishing, Burlington, MA, 2005

6. Miller, R.W., *Flow Measurement Engineering Handbook,* McGraw-Hill Book Company, New York, 1983.

7. Campbell, J.M., *Gas Conditioning and Processing Vol. 1: The Basic Principles,* John M. Campbell & Company, Norman, OK, 2001.

8. Ahmed, T.H., *Hydrocarbon Phase Behavior,* Gulf Publishing Company, Houston, TX, 1989.

9. Whitson, C.H. and Brule, M.R., *Phase Behavior SPE Monograph Volume 20*, Society of Petroleum Engineering Monograph Series, Richardson, TX, 2001.

10. Valko, P.P, McCain, W.D., Reservoir Oil Bubble point Pressures Revisited; Solution Gas-Oil Ratios and Surface Gas Specific Gravities, Journal of Petroleum Engineering and Science, 37 (2003), PP-153-169.

11. Choi, M., *API Tank Vapors Project,* Paper (SPE 26588) presented at the meeting of 68th Annual Technical Conference and Exhibition of the Society of Petroleum Engineers. Houston, Texas: October 3-6, 1993

12. Radian International LLC, *Evaluation of a Petroleum Production Tank Emission Model*, API Publication No. 4662 American Petroleum Institute, Washington, D.C.,

13. Akin, T., and Battye, W.H., *Memorandum to Martha E. Smith: Recommendation of an Algorithm to Estimate Flash Emissions from Process Vessels in the Oil and Gas Industry,* Environmental Protection Agency, 1994

14. *Emission Factors, Volume I: Stationary Point and Area Sources (AP-42), Section 7.1, Organic Liquid Storage Tanks.*

References (cont)

15. Lesair Environmental, Inc., 2002. Flashing VOC Emissions Study for E&P Facilities in Colorado. Prepared for Colorado Oil & Gas Association, August 2002

16. ASTM D 323, "*Standard Test Method for Vapor Pressure of Petroleum Products",*

17. McCain, W.H., The Properties of Petroleum Fluids, Penn Well Publishing Company, Tulsa, Oklahoma, 1990.

Appendix B

Nomenclature

T_s	=	separator temperature, °F or °R
P_s	=	separator pressure, psig or psia
Q	=	oil production rate, BOPD
API	=	stock tank oil/condensate relative density, °API
ρ_o	=	ideal liquid density at standard conditions
MW_{tv}	=	stock tank vapors molecular weight, lb/lb-mole
P_{std}	=	standard pressure, 14.65 psia
T_{std}	=	standard temperature, 60°F (520°R)
P_{amb}	=	site referenced ambient pressure, psia
V_{acfd}	=	actual measured volume, acfd
V_{std}	=	corrected measured volume, scfd
ρ_{air}	=	density of air at standard conditions, 0.076 lb_m/ft^3
X_{voc}	=	mass or weight fraction of VOCs, lb_{voc}/lb
Z	=	compressibility factor, dimensionless
R_s	=	solution gas-oil ratio, SCF/STB
$\bar{v}$	=	molar volume of any gas at standard conditions, SCF/lb-mole
P_c'(mix)	=	pseudocritical mixture pressure, psia
T_c'(mix)	=	pseudocritical mixture temperature, °R
P_r	=	pseudoreduced mixture pressure, dimensionless
T_r	=	pseudoreduced mixture pressure, dimensionless
y_i	=	mole fraction of component i
R	=	universal gas constant, 1545 ($ft \cdot lb_f / lb \cdot °R$)
SG_c	=	separator gas specific gravity corrected to a separator pressure of 100 psig

Appendix C

Field Data Sheets Laboratory Results	CD – Field Data

Appendix D

Field IR Videos	DVD 1 – IR Videos DVD 2 – IR Videos DVD 3 – IR Videos DVD 4 – IR Videos DVD 5 – IR Videos

Appendix E

Model Calculation Results	CD – Model Results