Exploring the variability between methods for characterizing flash gas emissions from oil storage tanks

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Flash gas emissions from storage tanks represent one of the largest single point sources of fugitive emissions to the atmosphere from the oil and gas industry. Accurate measurement of these flashing emissions is critical to government agencies tasked with monitoring and regulating air quality, yet emissions from the industry are thought to be grossly underestimated.

Traditional methods of estimating flash emissions rely on complex equation sets to simulate these vapors after measuring the composition of a hydrocarbon product via a Gas Chromatograph. New methods that directly measure the flash emissions, either on site or in a laboratory, have been established; however, their performance relative to process simulators has not been evaluated directly. To test the performance, this work directly measured Gas-to-Oil ratios (GOR) using a laboratory flash liberation technique against the results of GOR flash emissions calculated using VMG process simulation software across three types of pressurized liquid hydrocarbon test-standard: a light, mid, and heavy grade condensate. GOR values obtained from the process simulation software underestimate the flashing emissions by 10-50% when compared to the GOR's measured from the flash liberation technique for the same sample. The GOR variability from process simulators may be attributed to the challenges of measuring light-end hydrocarbon components (C1-C4) due to early vaporization within the heated GC environment, which can lead to larger standard deviations per component between repeat GC injections. In addition, compositional variability can produce considerable discrepancy in GOR data from process simulators depending on how each simulator is modeled to represent the pseudo-components of long-chained hydrocarbons. While the application of PIONA modeling helped bring process simulator GORs closer to those obtained from flash liberation, continued research on the appropriate technique to measure stock tank flashing emissions are required.

Stock Tank Emissions

The advent of hydraulic fracking eventually led the oil and gas industry to a new generation of onshore E&P. This expansion of onshore E&P and associated increase in air emissions is often cited as one of the many contributors of increasing levels of greenhouse gas (GHG) and volatile organic carbons (VOC) to the atmosphere. For decades, the Oil and Gas industry was exempt from common regulations aimed at limiting air pollution1. However, studies have demonstrated that emissions from onshore oil and gas operations can contribute to higher ozone locally2, contribute to global warming, and can have potentially negative effects on human health1,3. As strict local, state and federal environmental regulations are now being passed aimed at curbing oil and gas emissions, accurate measurement and estimation of emissions is critical. Arguably one of the largest sources of onshore GHG and VOC emissions comes from hydrocarbon storage tanks. These tanks typically receive processed liquid hydrocarbon product to hold prior to transportation.

There are three main types of vapors that contribute to storage tank emissions (figure 1(4)). First, breathing losses which result from the evaporation of liquid inside the tank usually in response to temperature fluctuations. Second, working losses are typically caused by movement of the liquid inside the tank during fill/empty cycles. Third and final, flash emissions are considered to be volumetrically the most significant contributor to stock tank emissions. Flash emissions occur when the pressurized product containing dissolved gases enters the zero pressure environment of the storage tanks, which allows the dissolved gas to escape the liquid product. This process is similar to that of cracking open a can of soda and the resulting carbonation to "fizz" off. The resulting vapors in the storage tanks must be dealt with in an appropriate manner. In some circumstances this may mean the vapors are sent to flare or vented to the atmosphere, in other cases this high BTU gas maybe routed back into a sales line. Regardless, producers looking to register their tanks must permit based on the amount of emissions the tank puts off, typically by estimating the Gas-to-Oil (GOR) ratio. In addition to permitting, accurate determination of the volume of flash emissions is applicable to other applications such as EHS and equipment sizing.
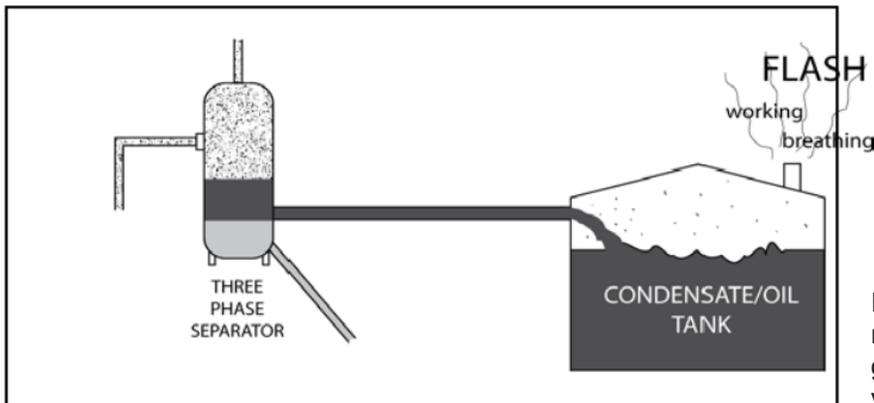
Figure 1: Schematic from TCEQ Air Permit reference Guide APDG 5942 illustrating the general set up of onshore stock tanks and vapor sources.

Measurement Methods

Presently, a number of methods can be used to estimate tank emissions, but method acceptance for permitting varies from state to state. Therefore, if permitting the available methods for use depends on acceptance from the regulatory agency.

Measurement methods can be characterized into two main groups: simulation and physical measurement. Simulation methods include simple equations sets like the Vasquez-Beggs equation, to complex computer models like process simulators that utilize the equations of state. Many simulation-based methods, still require information about the physical properties of the hydrocarbon product from a qualified laboratory to characterize the liquid and optimize the simulation. Examples of physical measurement methods range from direct measurement of tank emissions using light detection and ranging (LIDAR) technology, to laboratory based GOR determination via flash liberation. Each of the aforementioned methods vary in applicability and cost depending on the application one wishes to use it for. Additionally, some methods will characterize all three types of vapors emitted from stock tanks while others only estimate the flashing portion. Therefore, when choosing a tank emission method to follow careful consideration must be given to the application (and if permitting, agency acceptance), cost and accuracy requirements. While the first two should be relatively straight forward, the accuracy of each method relative to one another has rarely been explored.

This paper will focus on two of the most common methods for emission determination: process simulators and laboratory-based flash liberation. Both methods have comparable cost, are accepted by most permitting agencies, are thought to produce reliable results and only capture flash emissions (since flash emissions are the dominant source of emissions from tanks this alone is sufficient for estimating tank emission GORs). Process simulators use manipulations of the equations of state, paired with laboratory analysis of the physical properties of the product (density, vapor pressure, composition), to simulate the expected GOR for that tank. A variety of simulators exist, including VMG and Promax, each with their own proprietary set up of equations aimed at obtaining the most accurate simulation possible. Alternatively, flash liberation is a laboratory based, direct measurement of the GOR where a known volume of pressurized liquid hydrocarbon is depressurized and allowed to flash. A GOR can be calculated after the flash gas is collected and measured, along with the known volumes of the pressurized and dead product.

Currently there is no industry standard (GPA or ASTM) that governs the set up and procedure of the flash analysis, presenting a critical challenge moving forward. Some permitting agencies including the California Air Resources Board and Colorado Department on Public Health and Environment5 have loosely defined a flash liberation procedure, yet many laboratory companies' standard operating procedure (SOP) for flash liberation are different as the labs make their own proprietary improvements to the experimental design. This has been thought to cause variations in GOR for the same sample between two independent labs depending on variations of SOP. A thorough vetting of the laboratory and demonstration of flash liberation SOP should be conducted prior to contracting with a lab company.

GOR Performance Evaluation

To evaluate the measurement performance of process simulators relative to flash liberation three gravimetrically blended test-standards of known composition were used (Table 1). As illustrated in table 1, the composition of the test-standards were chosen to reflect variations of typical onshore condensate: mainly a "light", "mid" and "heavy" composition. A Shimadzu 2014 series Gas Chromatograph (GC) was recalibrated using independent sets of blended standards prior to measuring the composition of each test-standard. The blended standards for calibration were unique from, while remaining representative of, the test-standards used in this study for GOR determination. Each test-standard injected for GOR determination was introduced to the GC three consecutive times to obtain three compositions to evaluate GOR reproducibility.

Next, the data collected from the GC test-standards were entered into the VMG process simulator. To establish a baseline GOR for each test-standard, the certified blended composition on the sample tag was entered into the VMG program. Then, each of the test-standard runs were applied to the VMG software to calculate GORs for each run. With this, the inter-run and sample tag difference to the GOR was evaluated. It is important to note that the test-standard data from the GC was processed according to GPA 2186(M) for which no precision statement currently exists to evaluate inter-run repeatability and reproducibility.

Gravimetrically Blended Certified Standard Compositions	Light	Mid	Heavy
Component	Wt %	Wt %	Wt %
Nitrogen	0.044	0.078	0.018
Methane	2.430	1.787	0.097
Carbon Dioxide	1.616	0.612	0.106
Ethane	4.595	2.262	0.716
Propane	6.103	3.091	1.564
Isobutane	6.200	8.281	2.060
n-Butane	6.220	8.146	2.059
Isopentane	5.510	2.022	3.841
n-Pentane	5.510	2.022	3.821
C6+	61.770	71.295	84.464

Table 1: Compositions of the customized gravimetrically blended standards used for GOR evaluation in this study.

To evaluate the flash liberation process, each test-standard was then sent to the lab for the physical GOR determination. Prior to test-standard introduction the flash station was cleaned to remove any potential biases from contamination. A minimum of 25mL of test-standard was introduced to the flash chamber to depressurize and equilibrate.

For each test-standard, a minimum of three flash liberation analyses were performed. The relative difference was reviewed and compared to the GOR data from the VMG process simulator. Table 2 displays the GOR data for flash liberation. GOR measurements made with the flash liberation technique produced values with very little variability for all three of the test- standard compositions. The lightest composition evaluated produced the highest GOR measurements with little variation.

The average GOR was 882 SCF/bbl with only a 2% different between minimum and maximum GOR values. The "mid" composition averaged a GOR of 515 SCF/bbl also with a 2% difference between minimum and maximum measured values while the "heavy" standard averaged 76.7 SCF/bbl with a slightly higher measurement variability of 2.5%. The reproducibility of the data regardless of composition indicates a sound methodology and experimental design. Compositional bias does not appear to influence GORs using this method.

Table 2: GOR data from flash liberation.

Flash Liberation GOR Data (in SCF/bbl)				
		Measurement		
Standard	Average GOR	#1	#2	#3
Light	882	901	880	893
Mid	515	525	503	516
Heavy	76.7	77.5	75.1	76.6

To establish a baseline GOR for the process simulator, certified tag compositions were input into the process simulator. The baseline GORs were 800, 437 and 26 for the light, mid and heavy compositions, respectively (table 3). The data from the GC runs were then used to calculate the GOR with the VMG program. Interestingly, the average GOR from the GC for each test-standard differed substantially from the baseline tag composition (table 3) and flash liberation (table 2). Notably, a very high percent difference, ranging from 12-25%, exists between the test-standard on the GC versus the tag composition. Large variations in GOR from the GC runs of the same composition was also observed, and is concerning because unlike flash liberation where the analysis is easily and quickly repeated to ensure measurement fidelity, repeated analyses is not usually extended to process simulators due to time and cost restraints.

This means the analysis and subsequent GOR must be as accurate and reliable as possible. Since there is no industry standard to evaluate reproducibility for GPA 2186 currently relative to the known composition, we instead looked at the standard deviations of each individual component for all runs of each standard. The largest standard deviations of inter-run compositional values were seen in the lighter components C1-C4. A possible explanation for this may lie in the GC design, where the sample introduction system must also be kept at high temperatures to prevent heavy-end fallout prior to the column. This in turn may cause early vaporization of the light-end hydrocarbons prior to sample injection and makes these components more difficult to characterize in these types of GCs. This concept is being explored further with non-heated sample injection GC configurations. However, it is interesting to note that the largest discrepancy between average GOR values of both methods came on the "heavy" composition standard rather than the "light" standard used.

Table 3: GOR data from the VMG process simulator.

Process Simulator GOR Data (in SCF/bbl)				
	GOR from Tag	Avg GOR from GC	GOR from Tag w/ PIONA	Avg GOR w/ PIONA
Light	800	754	867	846
Mid	437	505	499	571
Heavy	26	29	31	34.4

For each composition, each method produced significantly different average GOR values. Which is right? The answer to this isn't straightforward since there is not a certified GOR value for the standards that can be used in comparison. On one hand, the reproducibility of the flash liberation measurements remains high. On the other hand, the process simulators also have tight measurement constraints and wide acceptance in the industry. A key variable not yet discussed is the role of liquid characterization in process simulators. Whereas, the flash liberation analysis is a direct measurement of the liquid, process simulators require laboratory-derived variables of the product in order best characterize the behavior of the hydrocarbon product in the simulator. These variables include composition, plus fraction properties, and/or a combination of both. However, there is no industry best practice that exists defining the laboratory inputs required to best optimize simulator output. As a result, there are varying schools of thought surrounding the level of hydrocarbon component characterization and physical properties needed. Component characterization is critical particularly for compositionally heavy products. Pseudo- components are molecules that share the same number of carbons as the parent group but are arranged differently and behave differently. For example, Benzene can be considered a pseudo-component of the Hexanes (6 carbon) group. Most simulators allow the user to define the level of detail and characterization to define their product.

A common practice is to set the model up by component groups that assign the same characteristics to all pseudo-components of the carbon chain group. For lighter hydrocarbon product with lesser amounts of total C6+ components such as LPG and light condensate this approach is acceptable. However, the heavier the condensate, the more pseudo-components there are and the more "generalized" the product becomes in this type of model6. The process simulator used in this study, VMG, allows the user to define the level of characterization using a PIONA modeling.

This PIONA model uses a predefined list of compounds to span the desired carbon number range that can be easily applied to predict chemical characteristics and chemical behavior of an oil feed beyond what it was analyzed for6. Using the VMG PIONA modeling option pseudo-components of heavy-end carbon chains, C7-C15, were simulated using the test-standard's existing data set, molecular weight and density. When applied, the GOR values for each tag composition shifted toward the flash liberation average values.

In the case of the "light" and "heavy" compositions the average GORs from the GC runs also shifted closer to the flash liberation values (table 3, above). Although the GOR increase for the heavy composition was only 5 SCF/bbl the application of the PIONA model to the process simulator tag data increased the tag composition GORs by 8%, 13% and 17% for the light, mid and heavy compositions respectively. While the GOR simulated for the heavy test standard still differs significantly from the flash liberation value, the significant percent increase in GOR when the PIONA model was applied supports the idea that the heavier the hydrocarbon composition, the more important it is to fully characterize the pseudo-component properties.

A limitation to this analysis is that the synthetically based test-standards used in this study only contain hydrocarbon chains going out to roughly C11 with limited pseudo-components to characterize. This limits the extent to which the effectiveness of the PIONA modeling can be evaluated to have on simulated GORs. New standards made from real oil are currently being prepared for analysis out through C31 to evaluate if this level of characterization necessary. The influence of physical properties was not explored yet. These parameters include plus fraction molecular weight, plus fraction specific gravity, vapor pressure and other measurable or calculable parameters.

Conclusion

Gas-to-Oil ratios using process simulators and flash liberation were obtained using 3 compositionally different test standards to test relative performance. GOR values differed significantly between the two methods until a PIONA model was applied to the process simulator. Yet considerable differences still exist between the methods.

To address these differences considerable work is still to be completed to fully characterize the measurement performance of both methods. First, a different process simulator will be used to calculate GORs using the same data to see how these programs compare with each other as well as the flash liberation data. Secondly, partner labs will be engaged to perform their own flash liberation on the samples for additional comparison. And lastly, new test standards made with real oil and not synthetic representations will be used to evaluate the influence of extended pseudo- component modeling on process simulators.

The results presented here are considered preliminary and are not intended to deter or encourage users from one method or another. Rather, the ideas discussed here are intended to stimulate conversation within the oil and gas community that encourages innovation in the area of air emissions measurement from oil and gas operations.

Environmental stewardship is a key piece of public relations the industry must continue to invest in to ensure the trust of those of the communities in which we operate.

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