

DATA FOR DESIGN OF VAPOR RECOVERY UNITS FOR CRUDE OIL STOCK TANK EMISSIONS

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Title: Data for Design of Vapor Recovery Units for Crude Oil Stock Tank Emissions

Investigators:

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Research Category: Pollution Prevention

This report covers the period of January 27, 2003 to April 27, 2003 and summarizes the current activities which include the selection of the field sites, the purchase of the equipment and supplies, the initiation of the development of laboratory protocols, and the initiation of the development of a thermodynamic model for estimating cumulative emission from stock tanks.

Progress Summary/Accomplishments:

Field Study

Site Selections:

The selection of the field study sites was accomplished by considering five sites proposed by the industrial collaborators. The five sites were narrowed to three after site visits by the principle investigator accompanied by representatives of the industrial collaborators. Two selected were in central/west central Oklahoma and one in southern Arkansas. The sites selected and the reasons for their selection are as follows:

South Arkansas Site – Shuler Drilling Co. Exxon Vastar # 1

This site is reasonably accessible being approximately 45 minutes east of El Dorado, Ar. The well was put online about one year ago with production averaging approximately 30 BPD. Oil is approximately 50 API gravity and “live”. Lease setup is relatively simple with one well, a heater/treater with minimum or no heat input, and a 30 psia pressure swing flash to the stock tank. Thief hatch holds a back pressure of 2 oz.

and vent gas is composed of high percent methane and ethane. Lease personnel are competent and cooperative. Cell phones are out of service in the area but a hard wire phone is installed on nearby lease available for use. Only disadvantage is no lease electricity but weather station and other equipment to be used during field data collection can be battery operated.

Central Oklahoma Site – Marathon Oil –

This site is very accessible just off the boundaries of the Will Rogers International Airport in Oklahoma City. It is a complicated lease set-up with 26 wells online flowing into two tandem sets of 4 stock tanks each. A heater/treater is inline as well as a vapor recovery unit. Daily production rate is approximately 800 BPD of 40 API gravity oil that is relatively nonvolatile. Thief hatch holds 2 oz backpressure and vent gas is highly dependent upon oil temperature. Lease personnel are competent and cooperative. Lease site has electricity and cell phone have service in the area. Operating flexibility on this lease site is a definite advantage.

Central Oklahoma Site # 2 – ENOGEX – Wellston Stabilizer Facility

This site is equally accessible being just south of the Wellston off-exit of Interstate Highway 44 east of Oklahoma City and reasonably close to the Marathon site listed above. It also has complicated upstream processing of condensate gas yielding a very high gravity (60 to 80 API) condensate oil feeding three 300 stock tanks with production of 600-700 BPD. This site will provide the opportunity to study the impact on the model of multiple tank emptying events during a single 36 hour monitoring period. The site has power and strict safety measures. Training of all persons entering the lease site is required and available. This site will provide important training of the three students to be involved in lease site monitoring. ENOGEX field personnel will cooperate fully and for safety reasons will be present at all times during the lease site monitoring periods and perform all necessary activities related to rigging up and rigging down of field monitoring equipment.

Criteria for the selection process of these field sites included the following considerations:

- a. Lease site accessibility to project personnel
- b. Relative volatility of the sales crude oil so that a range of methane solubility as a function of temperature can be studied.
- c. Type and layout of lease site processing equipment available for project use. This consideration will influence the relative ease of setting up on the lease site to collect the data. The layout of the lease will not influence the model.
- d. Amount of physical property data available on lease sales oil
- e. Lease's potential for an economically feasible vapor recovery project.
- f. Lease potential for vapor control environmental significance.
- g. Assessment of the lease's ability to be representative of typical leases in the area.

- h. Relative consistency of lease site production practices. This consideration will be evaluated using production data from sales records to quantify the expected throughput in the stock tank during the year long study of the lease site.
- i. Tank integrity (thief hatch seals, corrosion pit holes, etc.)
- j. Accessibility of sales oil sample ports and tank vents.
- k. Exclude H₂S for first year contract.
- l. At least one lease site in Arkansas and one in Oklahoma all other things being equal.

Most necessary field equipment and supplies have been ordered and received. Field protocols have been developed with the intent they will be modified as appropriate after each field trial.

Spring Field Trials

Exxon Vastar # 1 – Shuler Drilling; March 2-4, 2003

The first field trial to the south Arkansas site of the Exxon Vastar #1 served the purpose of testing field protocols but failed to yield any vapor emissions from the stock tanks. This was because the stock tank oil stayed at a temperature below the saturation temperature of the produced oil and due to the fact that the well ceased to produce shortly after the research team moved on location and rigged up. Valid crude oil samples for oil characterization analyses were obtained and results will be reported in the next quarterly report. The Exxon Vastar # 1 site is being re-evaluated and other sites are being considered as an alternative or as an additional site for the summer field trials in south Arkansas.

Oklahoma Airport Site- Marathon Oil; March 31 – April 2, 2003

The spring field trial at this site provided both crude oil samples and vapor emission samples for analysis. The vapor recovery unit was not operating during this field trial. This is the normal operating procedure for the lease site during the winter/spring season. Analysis of the data collected on this site is in progress.

Oklahoma Wellston Site – Enogex; April 1- April 2, 2003

The spring field trial at this site also provided crude oil samples and vapor emission samples and continuous cumulative vapor rates. Analysis of the data collected is in progress. This field trial was conducted in tandem with the airport site and the logistical experience gained by the research team in conducting simultaneous field trials will aid in planning of future Oklahoma field trials.

Laboratory Analysis

The necessary laboratory equipment has been acquired and protocols have been developed for the following tasks:

1. ASTM D-86 Crude Oil Boiling Point Distribution Curve analysis
2. Gas meter calibration
3. Pressure gauge and thermometer calibration
4. Weather station data retrieval

5. GC standards and calibration curves
6. Emission sampling canisters and sampling protocols

Full gas chromatography analysis procedures are in progress. These procedures will be reported in the next quarterly report.

Solubility Parameter Model Development

This project proposes a model to approximate the emissions from crude oil storage tanks based on the variations in solubility due to changes in temperature and pressure between feed and ambient weather conditions at a site. Values will be estimated for year round operation using normalized weather conditions and taking into account production and unloading cycles.

The crude oil will be characterized using a simulated distillation (Boiling point curve -ASTM D86) and specific gravity (API gravity). These two parameters are commonly available for lease sites and will be correlated in order to determine solubility parameters for light gases for the crude oil.

The following concepts and equations are the basis for the proposed model. They will be used to define the different parameters that will be taken into account in the prediction of tank emissions.

Solubility Parameter Calculations

The calculation of solubility parameters will be done using the Scatchard-Hildebrand equation taking into account the considerations presented by Prausnitz and Shair for gases far from their critical point in a mixed solvent:

$$X_i = \frac{f^G}{f^{L_i}} \exp\left(\frac{-v_i^L (\delta_i - \overline{\delta_{oil}})^2}{R \times T}\right)$$

δ = the Hildebrand solubility parameter.

f^G = the fugacity of the gaseous solute at the initial state.

f_i^L = the fugacity of the solute (hypothetical) as a pure liquid at the defined temperature.

X_i = solubility of gas i expressed as mole fraction in the solvent
Subscript "i" refers to the gas.

In this equation the liquid fugacity and volume of the solute are hypothetical values taking into account the fact that vapor emissions are well above the critical point. These values will be obtained from a figure and a table presented by Prausnitz and Shair.

The crude oil solubility parameter $\bar{\delta}_{oil}$ will be calculated using a volume-fraction weighted average in which volume fractions Φ_i of distillation cuts of the ASTM-D-86 curve will be multiplied by the solubility parameter of that fraction. The solubility parameter of the various fractions will be calculated using the energy of vaporization and the molar specific volume of the fraction.

$$\delta_i = \sqrt{\frac{\Delta U_i^{vap}}{v_i^L}}$$

The energy of vaporization ΔU_i^{vap} is equal to $\Delta H_i^{vap} - P\Delta V$. Since at low pressures it is possible to assume ideality of the vapor in equilibrium with the liquid (5) $P\Delta V$ is replaced with RT . The final expression for solubility becomes:

$$\delta_i = \sqrt{\frac{\Delta H_i^{vap} - RT}{v_i^L}}$$

Where T is the temperature at which the value of solubility is being estimated. The molar volume will be calculated using the following expression:

$$v_i^L = \frac{Mw_i}{\rho_i}$$

Density of the different weight fractions will be measured during the D-86 analysis. The molecular weight will be estimated using the correlations presented by Twu. The heat of vaporization is another factor necessary to determine the solubility parameter of the oil fractions. This variable will be calculated using procedures documented in the literature which calculates liquid and gas enthalpies for petroleum fractions.

The heating degree day concept has been proposed as an indicator of the amount of time an area is above certain pre established temperature. It has been used by ecologists to measure or predict the effect of temperature on biological processes and by engineers as an index of heating fuel requirements.

The latter application defines the heating degree day as the difference between the mean of the high and low temperatures for one day minus 65 F , which is normally the temperature limit for a building to require heating to maintain an inside temperature of 70 F. The ecological definition is more complex and approximates better the behavior of ambient temperature through out a normal day. The calculations are based on the area under the diurnal temperature curve and between the predefined thresholds. The various methods used to evaluate degree days are being investigated to determine the one most appropriate for application to vapor emissions. The expression given below for gas solubility will be used in conjunction with a gas mass balance to yield the yearly cumulative vent gas emissions.

$$R_s = 60.34 \times \left(\frac{\rho_{oil}}{Mw_{oil}} \right) \times \left(\frac{f^G}{f_{pure}^L} \right) \times \exp \left(\frac{-v^L (\delta - \bar{\delta})^2}{R \times T} \right)$$

Where R_s is the solubility of one of the vent gas components in Scf / bbl.

ρ_{oil} is the density for the stored crude oil in kg/m^3 .

Mw_{oil} is the molecular weight of the crude oil

f^G is the fugacity of the gaseous solute at the initial state.

f_{pure}^L is the fugacity of the solute (hypothetical) as a pure liquid at the defined temperature.

v^L is the hypothetical molar liquid volume of the solute.

δ is the solubility parameter of the gaseous solute

$\bar{\delta}$ is the solubility parameter for the crude oil at the established temperature
 R is the universal gas constant
 T is absolute temperature.
 60.34 is a unit conversion constant.

The fugacity parameter of the gas at the initial state f^G is considered to be equal to the product of the gas fraction and the total pressure of the system. So the equation becomes,

$$Rs = 60.34 \times \left(\frac{\rho_{oil}}{Mw_{oil}} \right) \times \left(\frac{y_i P}{f_{pure}^L} \right) \times \exp \left(\frac{-v^L (\delta - \bar{\delta})^2}{R \times T} \right)$$

The vapor emissions will be analyzed using gas chromatography to determine the compounds and their different proportions in the emissions. This fraction composition will also be included in the model through the Rs factor. Thus, the weighted volume solubility will be calculated as follows:

$$Rs_T = \sum \psi_i \cdot Rs_i$$

Where:

Rs_T is the total emissions in Scf / bbl
 ψ_i is the volume fraction of i.
 Rs_i is the solubility of i in Scf / bbl.

Publications/Presentations

No publications or presentations on this project have occurred.

Future Activities

The first field trials have identified modifications to field protocols and may require alternative or additional field sites to be selected. The solubility model will be refined and the appropriate degree day model calculation selected. Development of chromatography protocols is continuing.

Supplemental Keywords:

Degree days, solubility parameter, fugacity

Relevant Web Sites:

IPEC: www.ipec.utulsa.edu