A Unique Approach to Estimating Emissions of HRVOCs
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Why are we here?

LDEQ Data Request → Incorrect Sampling Method → Results into Title V Permit → Corrected Emission Factor
Why should you care about Placid’s factors?

Facilities outside of the BR Non-Attainment Area
- Upcoming lower ozone standards
- New regulations will have engineering and administrative costs
- LDEQ data requests and ERIC

Facilities inside of the BR Non-Attainment Area
- Experience in additional VOC and NOx regulations
- Continuously looking for ways to better estimate emissions
- Our factors can affect you
Background – HRVOCs and Non-Attainment

2003 LDEQ Memo:
- “Rapid, excessive ozone formation led to ozone peaks not seen by the Area in a decade.”

2004: LDEQ issued Administrative Orders for facilities in Baton Rouge Non-Attainment Area to audit for HRVOCs
- 1,3-butadiene, butenes, ethylene, propylene, toluene, and xylenes
- HRVOCs associated with elevated ozone
- Placid sampled liquid streams
Background – Permitting

Expansion permit (2008)
- 50% capacity increase
- Could have been held up by over-estimating emissions

Iterative calculation process
- Discovered a emission estimation problem with HRVOCs (low VPs)
- Error carried through all calculations
- Detection limit

Liquid weight % results incorporated into the Title V Permit
- Conservatively high values were chosen for 1,3-butadiene, propylene, and butenes
Liquid Vs. Vapor Concentrations

Liquid samples give liquid weight concentrations

- Appropriate for species that are liquid at standard conditions
- 1,3-butadiene, propylene, and butenes are not liquid at standard conditions

Vapor weight concentrations best for emission calculations

- Convert from liquid to vapor weight concentrations
- Either manually convert or use a method that incorporates a conversion (i.e. TANKS 4.09d)
Typical Conversion Methodology

- Raoult's Law
- Dalton's Law of Partial Pressures
- AP-42 Section 7.1 Equation 4-4
- AP-42 Section 7.1 Equation 4-6

Final conversion:

\[
\text{Vapor Wt Conc.}_{\text{species}} = \frac{\text{Liquid Wt Conc.}_{\text{species}} \times MW_{\text{liquid stock}} \times VP_{\text{species}}}{MW_{\text{vapor stock}} \times VP_{\text{liquid stock}}}
\]
Conversion Example

1,3-Butadiene (species) in Jet Fuel (product)

\[
V_{\text{apor Wt Conc.}}^{\text{species}} = \frac{V_{\text{apor Wt Conc.}}^{\text{species}} \times MW_{\text{liquid stock}} \times VP_{\text{species}}}{MW_{\text{vapor stock}} \times VP_{\text{liquid stock}}}
\]

\[
V_{\text{apor Wt Conc.}}^{\text{species}} = \frac{267 \text{ ppmw} \times 120 \text{ lb/lbmole} \times 36.3 \text{ psia}}{99 \text{ lb/lbmole} \times 0.029 \text{ psia}}
\]

\[
V_{\text{apor Wt Conc.}}^{\text{species}} = 405,103 \text{ ppmw} = 40.5\%
\]

Obviously, 40% 1,3-Butadiene in Jet Fuel is incorrect!
Interim Estimation Methodology

Expansion Permit – “Use What We Have”

- Needed to get application submitted in order to maintain planned construction schedule
- Knowingly chose overly-conservative values
  - Estimated as the highest liquid concentration of any other species present in that product
  - Allowed increases less than the MERs

Renewal (2 years after expansion) – “Fix It Later”

- Develop new *representative* factors
Revised Methodology – Bagging Study

Took preliminary samples at two heights in two tanks to ensure that results were conservative and repeatable, within reason

- 5 feet above the liquid surface (most conservative)
- 5 feet below the tank roof
Revised Methodology – Bagging Study

Sampled tank vapor spaces of representative tanks across the refinery

- Chose to not sample external floating roof tanks (no vapor space) and any tanks which could have posed a safety hazard

Used resulting concentrations to develop speciations for 1,3-butadiene, propylene, and butenes

- For each capped product group, the highest concentration is conservatively used
Photos
Results

Bagging study data is closer to expected values

- Previous methodology: 40% 1,3-butadiene
- Bagging study: ~0.0001% 1,3-butadiene (below detection limit)

Developed factors were used across the refinery

- Tanks
- Loading
- Fugitives
Results (continued)

Resulting reductions were significant

- Permit to Permit
  - 2.4 tpy of 1,3-butadiene (93% reduction)
  - 9 tpy total of the three species (97% reduction)

- Actuals (more difficult to quantify due to the number of variables)

Reduced risk

- Future projects will have more accurate estimations
- Saves effort on any potential modeling
- Lower cost of compliance (ERIC, modeling)
Results (continued)

Lower emissions profile for upcoming rules, etc.

- Accurate emissions assist LDEQ in developing accurate models
- Lower chance of being affected by new standards
- Data requests can always resurface (new NAAQS, model refinement)

Bagging study was easy and inexpensive

- Some coordination between the Environmental, Operations, Safety, and the contractor
- Cost was less than that of a complex 3 1-hour run stack test
Take Away Points

Using industry standard factors may be overly conservative

- How many data points went into those standard factors?
- How similar was the process used in the factors to what happens at your facility?
- Downstream effect can be significant

Majority of permit applications have errors and conservative estimations

- This example was clearly known, quantifiable, and self-inflicted
- Keep a ranked, evergreen list of such issues
  - Error
  - Cost
Take Away (continued)

Permit applications provide an opportunity to develop a better estimation

- Focus on the highest ranked items
- Conduct a “mini-study” to determine if correcting an issue is cost-, time-, and emission-effective
  - Used the sampling height data to calculate estimated permit reductions

Smaller facilities can easily develop a site-specific factor

- Use your ranked list to get the most “bang for your buck”
- Choose a manageable study size
Questions?

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