Crude Oil/Crude Condensate Vapor Pressure Methodology & Practices – Continued

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COQA – Feb. 2014 Summary

• Informal Industry advisory on discontinuation practice of ASTM D323 and its use in the API Calculation/Nomograph for reporting TVP of Crude Oil

• U.S. EPA approval to accept ASTM D6377-10 (VPCR_x @ 37.8°C – Expansion Method) as a broadly applicable alternative test method to determine TVP of Crude Oil

• Identified inherent problems with adopting this Method (as currently written) to directly report TVP. Also, ambiguity surrounding practice

• Introduced new (not really) On-Line technology for direct physical measurement of Crude Oil TVP

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As The ‘Experts’...

Take responsibility to ensure that the appropriate Methods and their respective Correlations are properly selected and practiced in the field (according to application) to protect:
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1) The Health and Safety of all Personnel and Residents within the immediate area and vicinity of the ‘process’
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3) $$$ - minimizing ‘give away’ with more sophisticated process control and/or ‘enhancement’ without violating regulations and contracts
TVP/BPP Definitions

- **Title 40 CFR (AP-42)** - True vapor pressure is the equilibrium partial pressure exerted by a volatile organic liquid, as defined by ASTM D2879 or as obtained from standard reference texts.

- **International Maritime Organization (IMO)** – The TVP or bubble-point vapour pressure is the equilibrium vapour pressure of a mixture when the gas/liquid ratio is effectively zero. It is the highest vapour pressure, which is possible at any specified temperature.

- **Maritime Transportation Guidelines (ISGOTT)** – The true vapour pressure exerted by the gas produced by evaporation from a liquid when gas and liquid are in equilibrium at the prevailing temperature and the gas liquid ratio is effectively zero.

- **Sandia National Laboratories** – refers to the BPP as the vapor pressure at V/L = 0.

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Why TVP/BPP vs. RVP(E)?

→ True Vapor Pressure and/or Bubble Point Pressure best identify the Sample’s worst case Vapor Pressure potential during transportation and storage

Remember:

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TVP Methods (40 CFR)

• ASTM D323 result used in API Nomograph
  — V/L = 4:1; 80% ullage
  — Sample ‘prep’ causes loss of light ends
  — Calculation based on a single, weathered Crude (1950)

• ASTM D2879 (Isoteniscope)
  — V/L = 2:3; 40% ullage
  — excludes partial pressure exerted by fixed gases (air)

• ASTM D6377 (VPCRₓ @ 37.8°C)
  — V/L = .02:1 – 4:1; ~2% - 80% ullage
  — No Standard for V/L, Tmeas set @ 100°F

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Grabner VPXpert w/ Crude Package

- Performs ASTM D6377 (among many other Methods)
- 1 ml sample/measurement
- Excellent Repeatability and Reproducibility
- Temp. Measuring range 0°C to 120°C
- V/L ratios from 0.02/1 to 100/1, adjustable per selected method
- Pressure range - 0 to 1000 kPa (0 to 145 psi)
Grabner Instruments FPC-250

Technical Data

- Maximum working pressure: 7000 kPa (1000 psi)
- Sample volume: 250 mL
- Connector for sample and back pressure: Swagelok Series QM
- Material of piston and cylinder: stainless steel
- Material of valves: stainless steel and PVDF
- Material of O-rings: Viton (Kalrez on request)
- Physical dimensions:
  - D x L = 48 x 415 mm
  - D x L = 1.9” x 16.3”
- Weight: approx. 2.5 kp (5.5 pounds)

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Why, you ask? So do we!

Why use this... …for correlation to this?
ASTM D6377 Correlation Formulas
Reid Vapor Pressure Equivalent (RVPE – Eq X1.1)

1) \( RVPE = 0.752 \times VPCR_4 + 0.88 \text{ psi (37.8°C)} \)
   
   * Average Bias of Different Crude Oils

2) \( RVPE = 0.834 \times VPCR_4 (37.8°C) \)
   
   * Samples in Pressurized FPC’s

3) \( RVPE = 0.915 \times VPCR_4 (37.8°C) \)
   
   * Samples in Non Pressurized 1-L Containers

Note: Emperically, ‘most’ stabilized crude condensate reflects a Vapor Pressure delta somewhere between .5 and 1 psia (pressurized vs. non-pressurized), however, why is the slope < 1?
ASTM D6377-14 Summary of Changes (10/1/14)

• Updated definitions and discussions for *live* and *dead* crude oils as well as the definition for *RVPE*. Also, clarified “$P_{tot}$” reference used in D5191 is equivalent to D6377 VPCR$_4$ (37.8°C)

• **3.2.3.1 (New)** – Equation X1.1 for estimating RVPE is not universally applicable to all crude oils. It is recommended that VPCR$_4$ (38.7°C) is used to report results for crude oil samples
ASTM D6377-14 Summary of Changes (10/1/14)

- **X1.2 (Updated)** – a statistically significant relative bias was observed for crude oil in a limited 2005 ILS involving VPCR₄ (38.7°C) results by this test method and results obtained using Test Method D323 (7 Laboratories and 6 crude oil samples). For the 6 crude oils evaluated, results can be predicted by Eq X1.1, however, it is recommended to report VPCR₄ (38.7°C) for **all** crude oils. If Eq X1.1 is used to estimate RVPE, confirm its validity by comparing results from both D323 and D6377 for the same sample. In any case, Eq X1.1 only applies to dead crude oil samples (since live ones can’t be compared using D323).
ASTM D6377-14 (VPCR_x) limitation for V/L = 0
VP of Various Hydrocarbon Mixtures as a Function of V/L Ratio

- Neohexane
- n-Pentane
- Feinbenzin
- Benzin
- Crude A
- Crude B
Influence of Amount and Type of Dissolved Gas in a Hydrocarbon Sample as a Function of V/L Ratio
On-Line TVP Measurement

- Same Hardware as Industry proven Grabner Mini-Method based Laboratory Analyzers
- Proprietary extrapolation found in Grabner On-Line Analyzer (VPSO) based on research work of Dr. Thomas Hinkebein and Sandia National Laboratories
- Extrapolation assumes and considers the presence of three components: ‘very light’ (e.g., methane, nitrogen or air), intermediate volatility (e.g., C2 and higher) and a non-volatile fraction
- Highly accurate model, successfully demonstrated on a large number of crude oil samples at the US Strategic Petroleum Reserve

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Comparison of Experimental and Calculated Data for Different Hydrocarbon Mixtures and Methods

<table>
<thead>
<tr>
<th>Vapor pressures in psi</th>
<th>Crude B</th>
<th>Crude A</th>
<th>Gasoline w/o Aromatics</th>
<th>Commercial Gasoline</th>
<th>n-Pentane</th>
<th>Neohexane</th>
</tr>
</thead>
<tbody>
<tr>
<td>RVP from ASTM D 6377 /2003</td>
<td>5.63</td>
<td>6.98</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RVP from ASTM D5191</td>
<td></td>
<td></td>
<td>3.51</td>
<td>8.35</td>
<td>15.18</td>
<td>9.72</td>
</tr>
<tr>
<td>TVP from Online</td>
<td>14.60</td>
<td>18.20</td>
<td>15.50</td>
<td>18.50</td>
<td>21.02</td>
<td>17.95</td>
</tr>
<tr>
<td>TVP from extrapolation to zero using 28 measured points</td>
<td>14.54</td>
<td>18.58</td>
<td>15.77</td>
<td>18.88</td>
<td>21.05</td>
<td>18.50</td>
</tr>
<tr>
<td>TVP from API 19 for crude oils</td>
<td>6.88</td>
<td>8.89</td>
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<tr>
<td>TVP From API 19 for refined products</td>
<td></td>
<td></td>
<td>3.66</td>
<td>8.81</td>
<td>16.12</td>
<td>10.27</td>
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<tr>
<td>TVP assuming proper degassing (28 points)</td>
<td>6.70</td>
<td>8.85</td>
<td>3.34</td>
<td>9.60</td>
<td>15.84</td>
<td>10.72</td>
</tr>
</tbody>
</table>
RVPE/TVP On-Line Analyzer ROI Example (For Fun)

- Stabilizer Site wishes to receive Grab/Catch Sample VP results once every hour
- Field Hand takes ~ 20 Min. to capture sample and record/report result
- ~$10 x 24 hours x 365 days = $87.6k/Year using a $20k+ Lab Analyzer
- On-Line Analyzers do not require employment benefits and Operator is free to perform critical functions on site
- Additionally, Measuring Interval as low as 7 minutes
‘Suggested’ Do’s and Don’ts of TVP Testing

• Don’t use an open bottle to transport and test the Crude Oil Sample. A properly prepared, pressurized container will prevent Parent Sample decomposition.

• If V/L ratio and testing temperature is not clearly defined for testing (e.g., Methods, Regulations, Contracts), do use the lowest V/L ratio that equipment allows or a V/L ratio that simulates the filling level and temp of the Stock in the transportation/storage medium.

• If not restricted to reporting RVPE (A x VPCR₄ @ 37.8°C), do report TVP as VPCRₓ, t (ASTM D6377-14), P or NP — where x = .02 to 4 (V/L ratio between 0.02:1 & 4:1) and t = 0 to 120°C
Thank You!

QUESTIONS???