An Overview of Crude Oil/Crude Condensate Vapor Pressure Methodology – Past, Present & Future

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Grabner History

• Dr. Grabner Started Grabner-Instruments in the Mid 1980’s. This Was Largely in Response to The Clean Air Act…Mainly to Address the Vapor Pressure of Hydocarbons and ‘Smogging’.

• Petrolab and Grabner-Instruments (Sister Companies) Were Purchased By Chandler Engineering in 2001

Definitions

• **Vapor Pressure** is the Pressure of a Vapor in Thermodynamic Equilibrium With its Condensed Phase in a Closed System.

• **Reid Vapor Pressure** (RVP) is the Measure of the Absolute Pressure Exerted by a Liquid at 100°F (37.8°C), at a Vapor to Liquid Ratio of 4:1

• **True Vapor Vapor** (TVP), According to the International Maritime Organization, is the Equilibrium Vapor Pressure of a Mixture When the Vapor to Liquid Ratio = 0, e.g., Floating Roof Tanks
ASTM D323 (RVP) – Reid Method

• First Issued in 1930
• Included Sample Preparation (Chilling and Aeration)
• Sample Inserted Into a Test Vessel Possessing a V/L Ratio of 4:1
• Test Vessel (Fitted With Manometer) Immersed Into Water Bath @ 100F, With Periodic ‘Shaking’ of Vessel to ‘Free’ Fixed/Dissolved Gases. Approximate Time of Test = 1 Hour
• Used in a Popular Calculation/Nomograph to Report ‘True Vapor Pressure’
ASTM D6377 - Determination of Vapor Pressure of Crude Oil: VPCRx (Expansion Method)

- Grabner ‘Mini-Method’ using 1 ml of Sample
- Can Measure V/L Ratios Between 0.02:1 and 4:1
- Can Perform Temperature Measurement, T(m), Between 20°C and 70°C
- VPXpert Automatically Performs Internal Shaking of Measurement Cell
- VPXpert Utilizes Grabner ‘Pro Valve’ System – Minimizing Dead Volume
- Performs Measurement in Approximately 7 Minutes

www.ametek.com
EPA Approves ASTM D6377-10 to Report ‘True Vapor Pressure’

• RVP/RVPE Includes Chilling/Aerating of Sample Which, In Turn, ‘Kills’ a Live Sample. This Yields a Much Lower Vapor Pressure Than That of the Pressurized Parent Sample

• This Method Is Applicable to Samples That Exhibit a Vapor Pressure Between 3.62 and 26.1 psi @ 100 Degrees F

• When Performed Properly, Using a Sealed Sample System, this Method Does Not Require Sample Preparation or the Use of Correlations/Nomographs to Estimate TVP (as interpreted in this specification)
Grabner VPXpert w/Crude Package
ASTM D6377-10 (VPCR_x)
ASTM D6377 Correlation Formulas
Reid Vapor Pressure Equivalent (RVPE)

1) RVPE = 0.752 x VPCR$^4$ + 0.88 psi (37.8°C)
   * Average Bias of Different Crude Oils

2) RVPE = 0.834 x VPCR$^4$ (37.8°C)
   * ‘New’ Correlation for ‘Live’ Crudes

3) RVPE = 0.915 x VPCR$^4$ (37.8°C)
   * ‘New’ Correlation for ‘Dead’ Crudes
The Challenge

• Replace Complex Equations With Direct, Automated Measurements to Report True Vapor Pressure Results for Liquid Hydrocarbon Process Applications

• Perform These Measurements In Ten Minutes or Less Using Existing, Industry Proven Online Vapor Pressure Hardware

• Address Fixed And Dissolved Gases Present in Process/Transportation/Storage Settings To Yield TVP Results that Represent the ‘Live’ Sample
WHY?

- Aid in Protecting Expensive Equipment Such as Tankage, Pipelines/Pumps, Transportation Vessels, etc…
- Minimize Evaporative Losses of Product That Results in Lower Profits and Harm to the Environment
- Help Save Human Lives By Reducing Equipment Failure Caused by “Hot” Product
VP of Various Hydrocarbon Mixtures as a Function of V/L Ratio

Vapor Pressure [kPa]

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

Vapor Pressure [kPa]

V/L ratio

Air Saturated
Butane Saturated
Degassed

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Plot of $1/T$ vs. $\ln(P_{vap})$ as Suggested by Clausius-Clapeyron Equation
Difference Between the Measured and Predicted Vapor Pressure as a Function of V/L Ratio

Deviation measured-predicted VP [kPa]

V/L ratio

-1.5
-1
-0.5
0
0.5
1
1.5
2
2.5
3
3.5
4

Neohexane
n-Pentane
Feinbenzin
Benzin
Crude A
Crude B
Now What?

Using This Curve, Created by Applying a Curve-Fit Algorithm (VP vs. Volume Plots) One Can Calculate Two Things:

1) The Vapor Pressure of the Complete (not degassed) Sample at V/L=0

2) The Vapor Pressure of the (numerically) Degassed Sample – Simply by Skipping the \( P_{vap} \) Contribution.
Comparison of Experimental and Calculated Data for Different Hydrocarbon Mixtures and Methods as Introduced in This Paper

<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>
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<tbody>
<tr>
<td>RVP from ASTM D 6377 /2003</td>
<td>5.63</td>
<td>6.98</td>
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<td>RVP from ASTM D5191</td>
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<td>3.51</td>
<td>8.35</td>
<td>15.18</td>
<td>9.72</td>
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<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>
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<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>
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<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>
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<td>3.66</td>
<td>8.81</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>
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Grabner Instruments Vapor Pressure System Online (VPSO) Advancements

• True Vapor Pressure Extrapolation to V/L = 0 In Ten Minutes Or Less. This Proprietary Calculation Uses TVP Results From 3 User Selectable V/L Ratios

• Adjustable Testing Temperature from 20 to 70 Degrees Centigrade. Can Be Automatically Adjusted When Used In a Closed Loop (Modbus RTU) With Sample Temperature Probe

• Repeatability Exceeds ASTM D2889 (Calculation of TVP of Petroleum Distillate Fuels)
Thank You!

QUESTIONS???