Proposal for an Improved Method of Crude Oil Vapor Pressure Determination

Canadian Crude Quality Technical Association

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Presentation Outline

- Rationale for Vapor Pressure Project Initiation
- Conclusions from Early Study
- Vapor Pressure Project Results – Phase 1
- Phase 1 Project Highlights and Learnings
- Project Objectives and Go-Forward – Phase 2

Rationale for Vapor Pressure Project

Examination of Currently Accepted Industry Methods for Measurement of Crude Oil Vapor Pressure

- Design related vapor pressure constraints (equipment cavitation, CSA/ASME limits for low vapor pressure pipelines, pipeline tariffs, etc).
- Compliance with regulatory and environmental standards (EPA Title 40, CCME PN 1180, etc).
- Familiarization with current vapor pressure standards D323, D6377, D5191, D2879, etc. to ensure accurate measurement and ultimate safety.
- Relationships between field measurements of vapor pressure and True Vapor Pressure.

Rational for Vapor Pressure Project

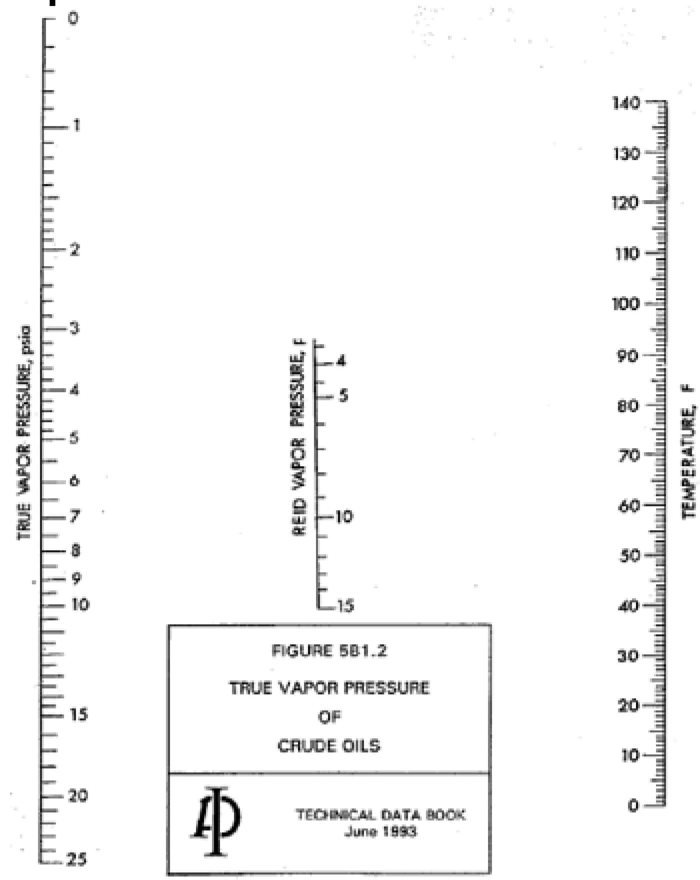
Synopsis of Currently Accepted Vapor Pressure Methods

- Reid Vapor Pressure through ASTM D323A is the most widely accepted method for crude oil vapor pressure measurement and tariff enforcement.
- Crude Oil True Vapor Pressure calculated from Reid Vapor Pressures using the approach dictated by API Bulletin 2517 (API MPMS Ch. 19.2 or AP-42).

$$P = \exp\left(A - \left(\frac{B}{T_s + 459.6}\right)\right)$$

$$A = 12.82 - 0.9672 \ln(RVP)$$

$$B = 7261 - 1216 \ln(RVP)$$



Conclusions from Early Study

Reid Vapor Pressure through D323

- ASTM D323A is specified for petroleum products with vapor pressure < 26psi.
- Sampling specifications dictate use of 1 Liter containers filled 70% - 80%.
- D323 procedure includes an air saturation step whereby the sample container is opened to atmosphere, closed and shaken vigorously (performed 3 times).

The Issues with D323 for Vapor Pressure Measurement

- Collecting crudes into atmospheric containers from a high pressure source such as a pipeline may allow the flashing of volatile light end components.
- When collecting samples into containers with a headspace there will be a certain amount of light end volatile components lost from the liquid (which is to be sampled) into the vapor when equilibrium is reached.
- The air saturation step may allow further flashing of volatile components.
- "The precision for crude oil has not been determined since the early 1950's."

Conclusions from Early Study

True Vapor Pressure from RVP and API Bulletin 2517

- True vapor pressure at a certain temperature is derived via nomograph from a given RVP.
- True vapor pressure can also be calculated via equations regressed from the nomograph.

The Issues with TVP from RVP and API Bulletin 2517

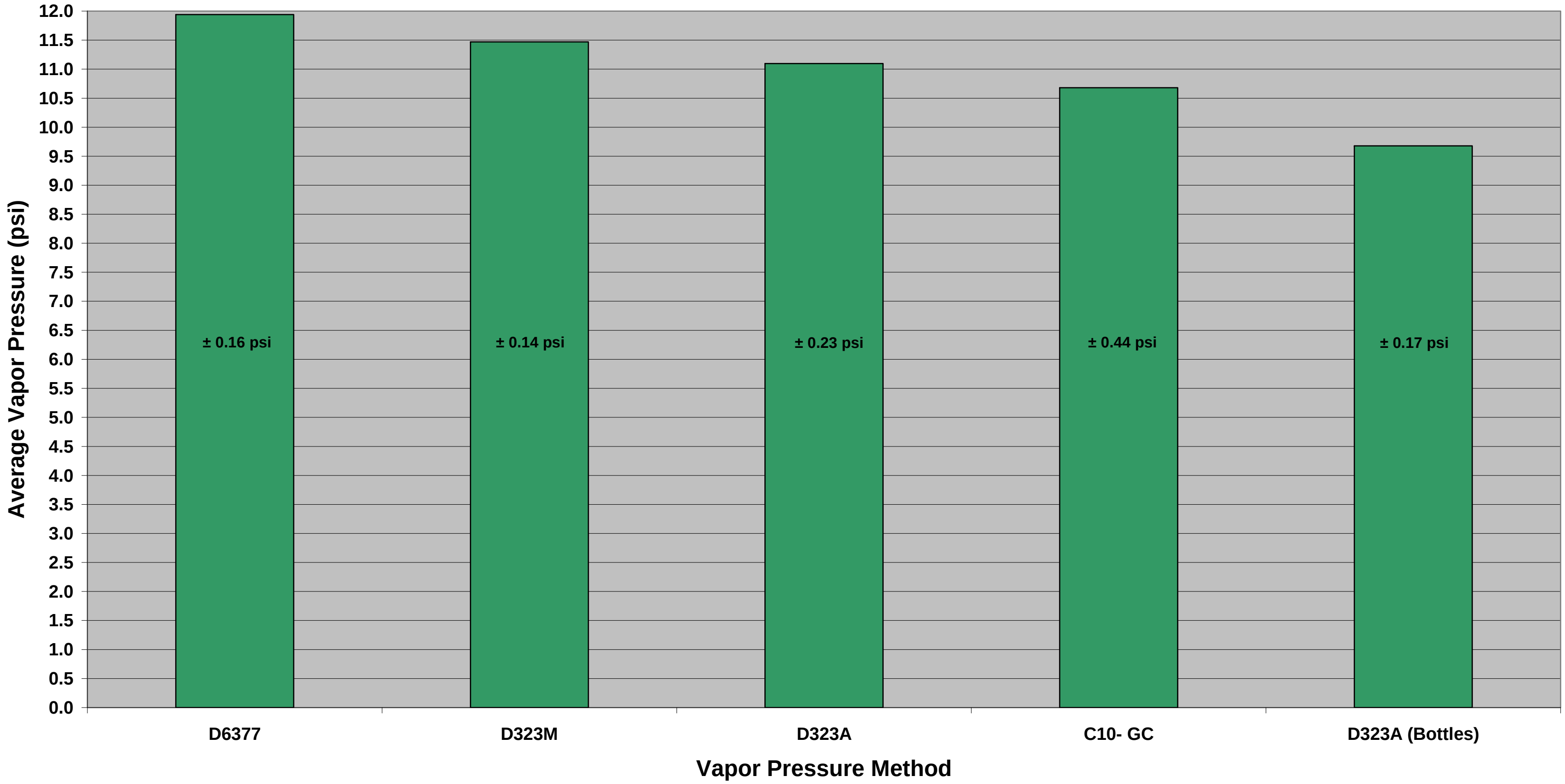
- Correlation dates back from the 50’s or 60’s with little documented reference as to how data was analyzed and correlations made.
- Based on “weathered crude” and therefore there has questionable applicability for today’s stabilized crudes vs. those in which the correlation was derived.
- Uncertainty as to whether certain stabilized crudes would better fit the Refined Products nomograph or the Crude Oil nomograph.

Vapor Pressure Project Phase 1

Project Initiated in Q1 2012 to Determine Best Sampling Method to Minimize/Eliminate Loss of Light Ends

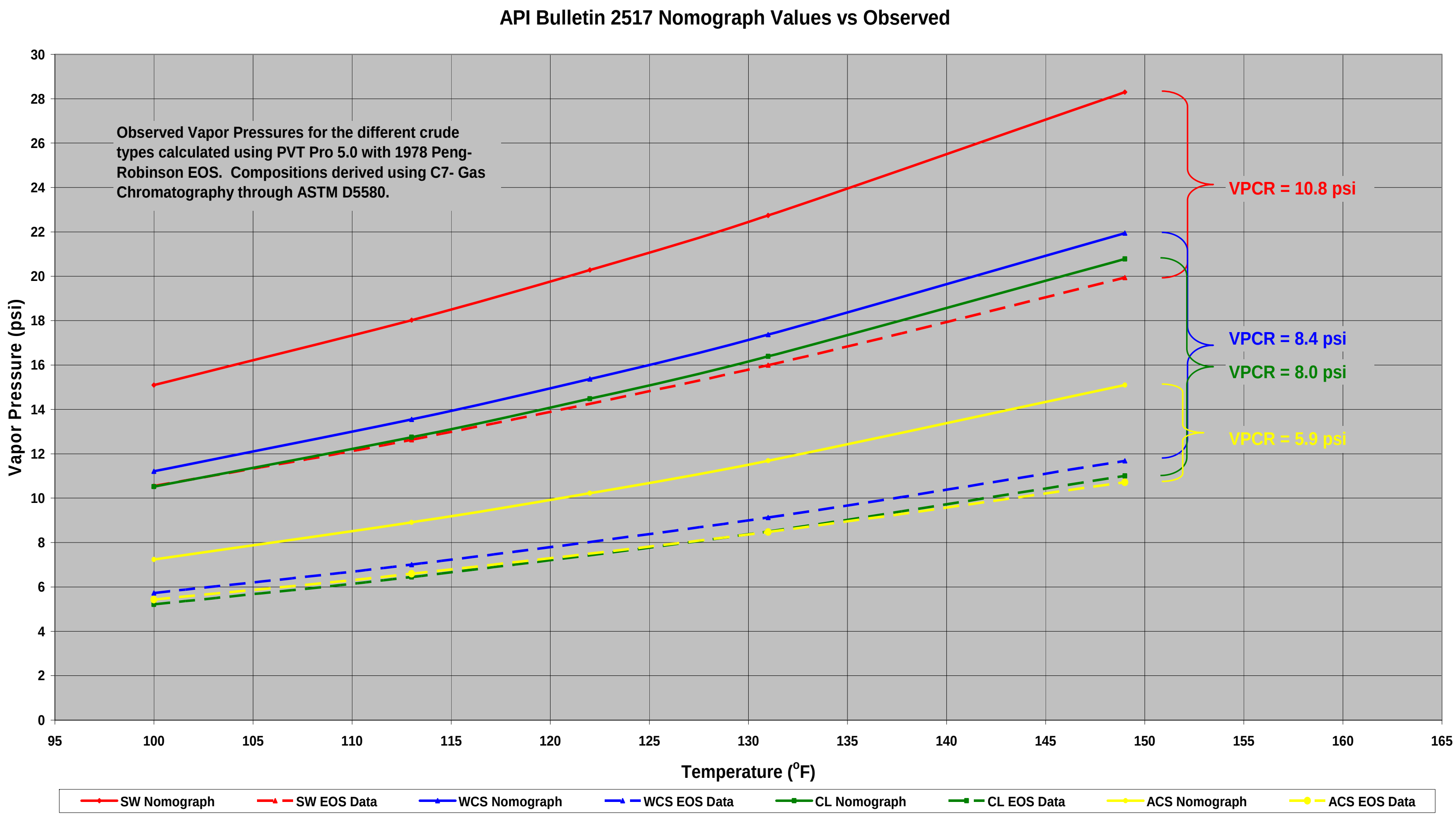
- Contracted a reputable ISO 17025 certified laboratory to conduct sample acquisition and analysis.
- Study conducted with 200+ samples of a relatively high VP commodity.
- All testing conducted utilizing the constant volume evacuated cylinders.
- Examined liquid displacement, flow through and non-atmospheric subjection methods.
- D323A, D323A (80% bottles), D323M, D6377 and C10- gas chromatography were the vapor pressure methods tested.

Vapor Pressure Project Results – P1



- Resulting vapor pressure of the samples were insignificantly affected by the sample collection methods.

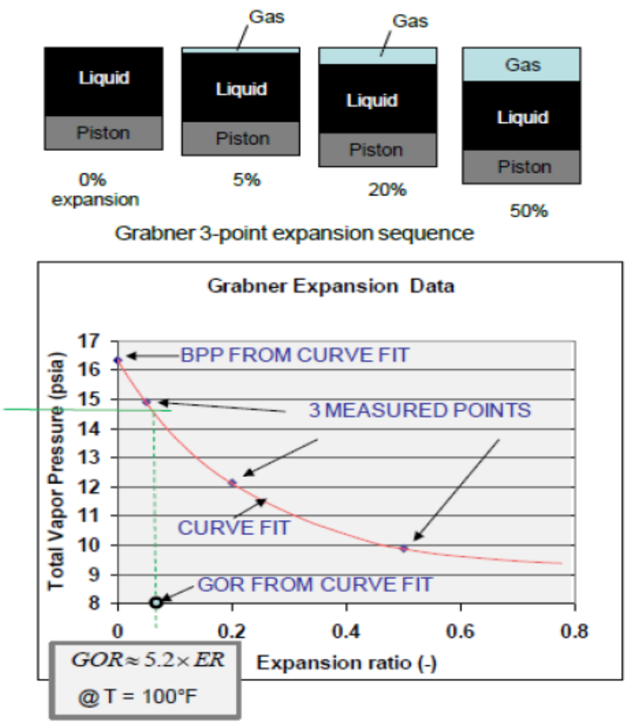
Vapor Pressure Project Results – P1

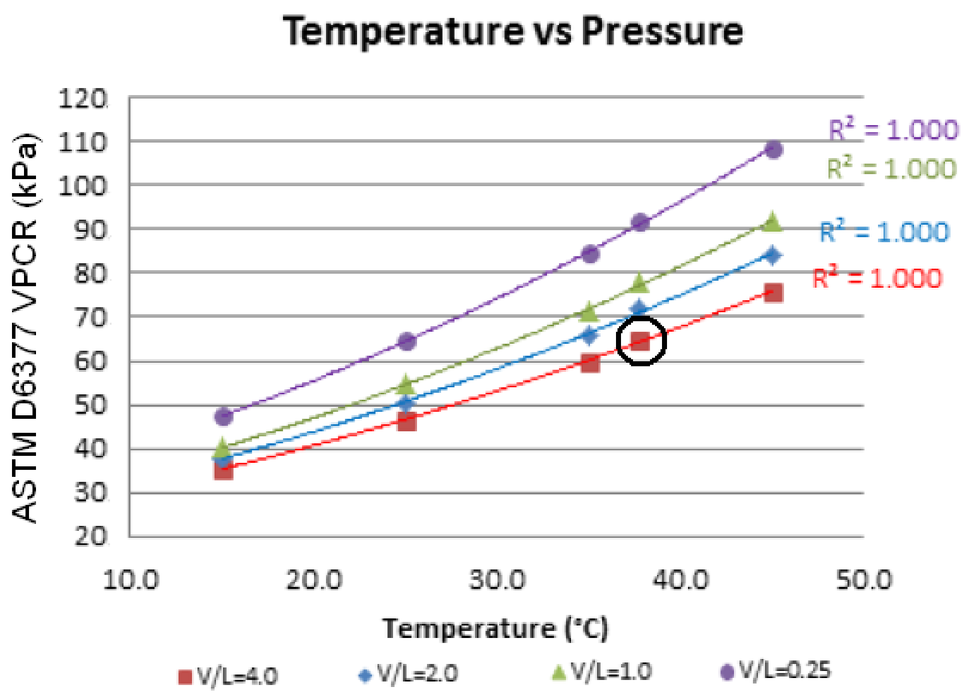


Vapor Pressure Project Results – P1

Effect of Varying V/L Ratio

- Differing V/L ratios show larger differences for more volatile crudes.
- V/L's closer to 0 approach the sample bubble point (True Vapor Pressure).





Phase 1 Project Highlights

A New Standard is Required for Vapor Pressure Testing

- D323 not suitable for crudes with significant light end components.
- There is little to no documentation to support the validity of the nomographs published in API Bulletin 2517.

ASTM D6377 is Most Suited for Crudes with Light Ends

- Allows for the capture of samples from pressurized sources without phase separation.
- Allows for sample transfer between the source and testing apparatus without atmospheric subjection and light end component loss.
- D6377 may be used for vapor pressure determination over a range of temperatures and V/L ratios.

Phase 2 Project Direction

Current Conviction

- The CCQTA Vapor Pressure Project team believes that D6377 at a low V/L ratio will produce results representative of the True Vapor Pressure for crude oil.

Rationale

- Samples can be gathered under pressure and injected into the apparatus test cell without subjection to atmosphere. This instills confidence that the samples obtained are 100% representative to the crude at the terminal.
- D6377 can be performed at very low V/L ratios. By definition the bubble point is when the first bubble of vapor is formed at a V/L ratio of 0.
- Tests conducted over a range of temperatures will result in a vapor pressure vs. temperature curve. This is preferred to extrapolating vapor pressures over a range of temperatures from a singe point.

Phase 2 Project Scope

- Collect transport quality crude samples from various sources using constant pressure piston cylinders as dictated for live crude oil within ASTM D6377.

- For each sample:

  a. Collect D6377 VPCR's at a specified V/L ratio over 4 different temperatures: 25^{o}C, 37.8^{o}C, 50^{o}C and 65^{o}C.
  b. Perform Step a. for 5 different V/L ratios: 0.2, 0.5, 1.0, 2.0 and 4.0
  c. Conduct an HPLIS Gas Chromatography analysis for each of the collected samples.
  d. Use both Antoine's Equation with Rault's Law and Equation of State software to calculate the samples theoretical True Vapor Pressure over the same range of temperatures using results from the light end GC analysis.
  e. For each sample determine the V/L ratio which most closely mimics the theoretical True Vapor curve as determined in Step d.
  f. Compile results and formulate conclusions.

Phase 2 Project Scope

- Develop a field test method for on-site TVP determination. This portion of the project should run parallel to the above scope as it will determine the feasibility of low cost on-site TVP spot testing.
    a. Field apparatus has been designed

    b. Draft sampling and testing procedure has been written
- Explore development of a vapor tight GC method using HPLIS to obtain reliable detailed analysis of light ends from the same sample that is utilized for D6377 analysis.

Field TVP Procedure Summary VPCRFx

- Flush hydraulic cylinder several times with sample. Hold backpressure during final fill.
- Close sample source, confirm liquid full with compression test.
- Open sample source, force sample out to 80% full mark (0.2 V/L), or to 20% full mark (4:1 V/L), close sample source. Draw cylinder back to 100% mark.
- Adjust temperature with bath if required. Rock cylinder to equilibrate phases. Read resulting pressure.
- Obtain local barometric pressure and add to reading. Use 14.7 PSI if unknown. Report result as VP in PSIA.

Status Update

- EPA has now accepted the use of ASTM D6377 for measurement of true vapor pressure.
- API MPMS is currently being updated to incorporate D6377 as an acceptable alternate TVP determination method for crude oil. The updated document is forecasted to be published before August 2013.
- Ten prototype field instruments have been built and will be distributed to key stakeholders for field testing
- Field test to be submitted to ASTM in June 2013 as a companion method to D6377.
- TransCanada Keystone is now fully commissioned for batch vapor pressure testing utilizing ASTM D6377 with Welker type floating piston cylinders.

Questions

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