Agenda

CCQTA

• background for newcomers
• contacts and next meetings
• project list

Project briefing (2)

• Organic Chlorides (brief)
• TVP RVP workshop summary (expanded)
CCQTA Background

The Canadian Crude Quality Technical Association membership consists of companies from multiple segments of the Canadian oil industry.

The Association is established with the following educational and scientific objectives:

- To facilitate communications among industry stakeholders
- To provide a forum for the presentation and consideration of proposals for industry projects related to any aspect of crude oil quality.
- To improve industry knowledge and awareness of crude oil quality through the cooperative exchange of technical information among industry sectors.
CCQTA Background

• CCQTA does not typically fund projects, but acts as a facilitator for projects
  – Provides meeting venues, phone and web-conferencing support, and third party
    accounting to project groups

• CCQTA currently has 74 member companies from across the globe
# CCQTA Contacts

Website > [www.ccqta.com](http://www.ccqta.com) (public and private access)

Prime Contact > Secretary - Andre Lemieux (Omnicon)

E-mail: [secretary@ccqta.com](mailto:secretary@ccqta.com)

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<thead>
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<tbody>
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</tr>
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</table>
Next CCQTA meeting (Calgary)

Tuesday April 2nd
- 9:00 am - 12:00 pm  Tan Phase 4 - Project Manager - Randy Segato
- 1:30 pm - 4:30 pm  Heavy Oil Compatibility - Project Manager - Cecile Siewe

Wednesday April 3rd
- 8:30 am - 11:30 am  Condensate Quality - Project Manager - Bob Falkiner
- 12:00 pm - 1:30 pm  Executive Meeting
- 1:30 pm - 4:30 pm  Phosphorus - Project Manager - James Graham

Thursday April 4th
- 9:00 am - 12:00 pm  Emulsion Characterization - Project Manager - Martin Flatley
- 1:00 pm - 3:00 pm  TVP/RVP - Project Manager - Cameron Konecnik
- 3:00 pm - 5:00 pm  Bitumen Dewatering & Volume Correction - Project Manager - Bill Lywood

Note that these meetings are for project participants only. If you are not a project participant and wish to attend as a guest, please contact the respective project manager or CCQTA secretary. Agendas, including an outlook web-conferencing meeting notice, will be distributed to participants prior to the meeting.

The OSBP and Organic Chloride projects will communicate via web-conferencing at the end of March. The H2S PVT web meeting will be held in mid or late April. (Project participants will be notified of the timing in coming weeks.)
CCQTA Active Projects

- Tan – Phase IV
- Oilsands Bitumen Processability – Phase III
- Heavy Oil Compatibility – Phase II
- Condensate Quality – Phase II
- Tan Method Testing – Phase II
- Emulsion Characterization
- Crude Quality Tutorial
- Phosphorus
- Bitumen Dewatering and Volume Discrepancy
- H₂S PVT – Phase II
- Organic Chlorides
- TVP/RVP
CCQTA Active Projects

Organic Chlorides ... a few interim highlights

- both ASTM D 4929 A/B and ASTM D 7536 M found to be effective if properly followed
- results suggests that organic chloride material tested in recent “hits” is **Dry Cleaning Fluid** tetrachloro ethylene (from two different sources; now confirming with two others)
- in addition, false positives causing concern and unnecessary work
- assessing use of Owlstone FAIMS technology (Field Asymmetric Ion Mobilization Spectrometry) for at line/site testing
CCQTA Active Projects

TVP/RVP

- TCPL (Cameron) was project manager and providing key source of funding to date
- Two day CCQTA sponsored workshop held an AITF Edmonton in February
- New Vapor Pressure project proceeding with Bob and Cameron Leading
  - CCQTA agrees to provide seed funding ($10K) to project

....lets review this important workshop’s findings...

Thanks ahead of time to the workshop panel specifically Harry Giles, Cameron Konecnik, Bob Falkiner and CCQTA for providing presentations I will be referencing.
CCQTA TVP/RVP WORKSHOP
Edmonton February 5 & 6, 2013

CCQTA TVP /RVP WORKSHOP
A New TVP Field Method

Proposal for an Improved Method of Crude Oil Vapor Pressure Determination

R.J. (Bob) Falkiner
Imperial Oil
Engineering Service Canada

VAPOR PRESSURE
Observations on Sampling, Analysis, & Data Comparisons

Harry N. Giles, PetroStorTech LLC

CCQTA NEW PROJECTS REVIEW
TVP and V/L of High Vapour Pressure Crude Oil

R.J. (Bob) Falkiner
Imperial Oil
Engineering Service Canada
Dec 5, 2012
Rev 1 Feb 5, 2013
What are some concerns driving improved light ends measurement?

Environmental and Loss Control
“Regulatory agencies require TVP for estimation of evaporative emissions”

Safety
“high vapor pressure causing bubbling crude “

Equalization and Standards
“Light ends penalties being applied require accurate data”
“For light crude oils such as condensates, some recommend use of refined petroleum stocks nomograph”

Logistics
Rail/Truck Transport Safety (leaks, un/loading safety)
Tank Design (floating roofs vs vapor recovery)
Pump Design (cavitation)

Participants
CCQTA
COQA
ASTM
API

Omnicon Consultants Inc.
Crude Quality Inc.
Alberta Innovates – Technology Futures
Parkes Scientific
Stanhope-Seta
AGAT Laboratories

TransCanada Pipelines Ltd
Enbridge Pipelines Inc.

Eralytics
Ironedge Resources
Torq Transloading
TGB Partnership
Simba/FLLL
Transcendent

Exxon Mobil, Imperial Oil, CNRL
Marathon, Suncor, Magellan
Mobil, Gibsons, Phillips 66
To address this decades old issue, we need alignment across industry sectors. Wide consultation is needed for a new Standard to be adopted by Industry.

**COQA** along with **CCQTA** alliance has the ability to bring together the technical, regulatory and engineering resources to get this done.
Rational 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

...Railcar concerns...  

Tank cars are of two types:
- General Purpose (GP) are designed for 100 psig with 75 psig Safety Valves (vapor tight at 60 psig).
- Pressure cars are higher pressure: sealed containers, no coils, no bottom outlet valves.

Crude Oil Fleet:
The current tank construction is carbon steel/no special metals.

Recent Industry Reports:
- Crude cars with solids settling in the car, corrosion in the bottom of the car; corrosion in the top of the car; and high vapor pressure causing bubbling crude (potentially a mix of methane, ethane, propane, H2S and more).

Rail Regulations specify that the shipper shall have no leaks during transportation:
- Both Transport Canada and Federal Railroad Administration work through AAR: Association of American Railroads.

- As long as the car moves without leaking, there are no other pressure requirements.
- If conditions exist that cause bubbling crude, there may be safety and environmental issues at the destination.
- A large shipper set a standard that C5 and lighter products have to ship in pressure cars.
- This translates to a general rule that products with a vapor pressure over 15 psia at 110F (or over 5 psia at 60F) must ship in a pressure car.
- Basis was the Lab Heads network that set standards for samples in bottles vs. sample cylinders—circa 1988.
Rational for Vapor Pressure Project

...Tankage TVP Requirements

• Very important that contents of a large fuel tank not spontaneously start to Boil

• Large amount of vapour can split the tank, sink the roof and emit flammable gas cloud

• Very Serious – If 4:1 Vapor volumes evolved, a 100,000 bbl tank will generate 400,000 bbl vapour

• TVP is used to ensure contents remain below bubble point and no vapor is generated

• Think of the TVP as the pressure at the start of boiling, while RVP is the pressure after about 2-5 vol% of the contents has boiled/vaporized
  • Like the difference between initial boiling point and T05 in a distillation after 5% of sample has been distilled
  • Actual value depends upon light ends distribution
Rational for Vapor Pressure Project

*Tankage TVP Requirements*

- The TVP requirement for tanks is conservatively below atmospheric pressure, generally 13.0 to 13.5 psi
- Intent is that if hurricane/storm low pressure or heat wave suddenly appears, then tank will not spontaneously start to boil
- The TVP is measured at a reference temperature DEPENDENT ON THE DELIVERY POINT AMBIENT TEMPERATURE
  - Southern Canada: 13.0 TVP at 28C (82F)
  - Southern USA: 13.0 TVP at 40C (104F)
- The reference temperature changes throughout the year, following seasonal temperature variation
- Similar to rail car “Outage” calculation that leaves more vapour space to accommodate thermal expansion if shipping to hotter climate
Definitions

• Reid vapor pressure (RVP). Resultant total pressure reading of a specific empirical test method for measuring the vapor pressure of volatile products (ASTM D323)
  – at 100F, 4:1 V/L

• Total vapor pressure (TVP). The observed pressure ... that is the sum of the partial pressure of the sample and the partial pressure of the dissolved air (ASTM D5191)
  – Definition does not account for presence of water
  – Not Well Defined, basically bubble point, VP at V/L =~ 0.0
ASTM Sampling Practices

- **D3700 Obtaining LPG Samples Using a Floating Piston Cylinder**
  - Covers equipment and procedures for obtaining a sample of LPG.
  - With modification, applicable to collecting single phase samples of volatile crude oil
- **D4057 Manual Sampling of Petroleum and Petroleum Products**
  - Covers procedures for manually obtaining samples whose vapor pressure at ambient conditions is <101 kPa (<14.6 psi)
- **D5842 Sampling and Handling of Fuels for Volatility Measurement**
  - Covers procedures and equipment for obtaining, mixing, and handling samples of volatile fuels in range 13 to 105 kPa (2 to 15 psi)
  - Primarily for motor fuels; some guidance applicable to crude oils
Floating Piston Cylinder
Standard Test Methods – 1

• D323 *Vapor Pressure of Petroleum Products (Reid Method)*
  – Covers procedures for the determination of vapor pressure of volatile crude oil and other volatile petroleum products
  – “The Reid vapor pressure differs from the *true* vapor pressure of the sample due to *some small sample vaporization* and the *presence of water vapor and air* in the confined space”
  – Precision of the method for crude oil has not been determined since the early 1950s.

  – 8.1 “The extreme sensitivity of vapor pressure measurements to losses through evaporation ... requires meticulous care”
  – 8.3 “… sample containers ... shall be 70 to 80% filled ....”
  – 8.5 “… cool the sample container and contents to 0 to 1° C before the container is opened”
Standard Test Methods – 2

- D5191 *Vapor Pressure of Petroleum Products (Mini Method)*
  - Covers the use of automated vapor pressure instruments to determine the total vapor pressure exerted in vacuum by air-containing, volatile petroleum. Suitable for testing samples with boiling points >0°C that exert a vapor pressure between 7 and 130 kPa (1 and 19 psi)
  - No account made for dissolved water in the sample.
  - Interlaboratory studies to determine precision of the method did not include any crude oil in the sample set.
Standard Test Methods – 3

• D6377 *Determination of Vapor Pressure of Crude Oil: VPCR*$_{x}$ (*Expansion Method*)
  – Covers the use of automated vapor pressure instruments to determine the vapor pressure exerted in vacuum of crude oils
  – Method suitable for samples that exert a vapor pressure between 25 and 180 kPa (3.6 and 26 psi) at 37.8°C at vapor-liquid ratios from 4:1 to 0.02:1 ($X= 4$ to 0.02)
## D323, D5191, or D6377

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<tr>
<td><strong>Range, kPa</strong></td>
<td>Up to 180</td>
<td>7 – 130</td>
<td>25 – 180</td>
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<tr>
<td><strong>Sample size, mL</strong></td>
<td>100</td>
<td>~10</td>
<td>~10</td>
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<tr>
<td><strong>R, kPa</strong></td>
<td>0.05 @ 21 kPa</td>
<td>0.04 @ 21 kPa</td>
<td>0.76</td>
</tr>
<tr>
<td></td>
<td>0.1 @ 70 kPa</td>
<td>0.05 @ 70 kPa</td>
<td></td>
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<tr>
<td><strong>Issues:</strong></td>
<td></td>
<td>Not scoped for crude oils</td>
<td>Samples must be chilled to 0 - 1°C</td>
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RVP – TVP Relationship

• Regulatory agencies require reporting of TVP for estimation of evaporative emissions

• Currently, accomplished by
  – First, measuring RVP; *(need good sample first!)*
  – Then, TVP determined from API MPMS Chapter 19.2 nomograph, and as published in EPA AP42
    • Nomograph developed in 1950s using a single artificially weathered mid-continent U.S. crude oil
    • Nomograph not applicable to many of today’s crude oils
  – For light crude oils such as condensates, some recommend use of refined petroleum stocks nomograph
Rational for Vapor Pressure Project

Synopsis of Currently Accepted Vapor Pressure Methods

• RVP through ASTM D323A: most widely accepted method for crude oil vapor pressure measurement and tariff enforcement.

• Crude Oil TVP calculated from RVP using the approach dictated by API Bulletin 2517 (API MPMS Ch. 19.2 or AP-42).

...likely to produce highly erroneous results due to:
1) The Reid method (ASTM D323) allows high potential for light end loss through the atmospheric sample collection and air saturation steps stipulated within the procedure.
2) The nomograph and regressed equations relating RVP to TVP are thought to be originally developed on weathered crude oil (unlike the live crude oil which is of concern today) with little to no reference surrounding the logic behind the correlation.

Furthermore, it may be found questionable as to how a TVP vs. temperature relationship for a range of different crude oils can be regressed from one single point (one measure of RVP). (equivalent for naphthas/gasoline have several curves to use)

http://www.epa.gov/ttn/chief/ap42/ch07/final/c07s01.pdf
Vapor Pressure vs. V/L

From: Pichler & Hense, PTQ Q1 2013
Project Initial Charter

Development of an Improved Method for Determination of Volatile Crude Oil True Vapor Pressure

Background

Through consultation and discussion with many industry experts and from review of experimental data gathered thus far, the current consensus held by the CCQTA Vapor Pressure Project Team is that crude oil TVP may be estimated directly through slight modification \(^2\) of the existing ASTM D6377 procedure.

Furthermore, it is thought that a field method for crude oil TVP determination may be possible which will allow a reasonably accurate vapor pressure determination at the field level.

\(^2\) Modification of the V/L ratio from 4.0 to a value closer to zero (representative of conditions found within a storage tank, rail car or tanker ship). As well, implement instrument software changes to modify valve sequencing during sample introduction and heating. This will eliminate pressure contributions from thermal expansion effects at the low V/L ratios when there is significant delta between sample introduction temperature and equilibrium temperature.
Continued Project Scope and Direction

Below is an overview of initiatives currently being perused by the CCQTA Vapor Pressure Project Team:

1) Sampling and testing of various live crudes utilizing constant pressure piston cylinders for:
   a. **Derivation of ASTM D6377 VPCR’s over a range of V/L ratios** (0.05 to 4.0) and temperatures (20oC to 60oC) to best approximate the crude TVP.
   b. Comparison of the D6377 VPCR vs. Temperature curves to the thermodynamically derived TVP found through Gas Chromatography (Antoine’s Equation with Rault’s Law or EOS software packages).

2) Development of a device and procedure for field level TVP measurements:
   a. **Development of the simple operation low cost device and procedure.**
   b. Working with ASTM for approval.
   c. Comparison of field measurements with those derived through D6377.

3) Development of a light end SIMDIST method for high vapor pressure crudes:
   b. Working with Alberta Innovates Technology Futures to perfect device and procedure.
Interim Recommendations

While further experimentation and data collection continues to take place it is recommended that the following methods are utilized when estimating the True Vapor Pressure of volatile crude oils:

1) Collect all samples utilizing constant pressure piston cylinders such that the potential flashing of light ends is eliminated and the sample can be connected directly to the testing apparatus without atmospheric subjection.

2) Generate ASTM D6377 VPCR’s over a range of temperatures for development of a pressure vs. temperature curve that is specific to the crude type. A low V/L ratio should be used to best mimic conditions experienced within a storage tank, rail car or tanker ship. At this time it is believed that a V/L of 0.2 may give a good approximation to the bubble point pressures while avoiding the complications arising from liquid thermal expansion at low V/L ratios.

For inquiries regarding involvement with the CCQTA Vapor Pressure Project contact:
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Bob Falkiner, M.Sc., P.Eng  416-806-3776  bob.j.falkiner@esso.ca
Add Field method to D6377

- ExxonMobil, Imperial Oil making this public knowledge
  - No IP or patent implications
  - Ensures freedom of use by CCQTA, COQA, ASTM etc.

- Cost is low (< $300 per test unit)
  - Valves, swage fittings is majority of cost
  - $25 for aluminum cylinder, $75 for stainless
  - Widely available multiple manufacturers (125, 250 psig typ)
  - Need only specify bore, stroke, pressure rating and seal material

- Wide range of cylinder sizes avail, but ~1” dia x ~10” stroke “best”
  - Hydraulic force low enough for up to ~ 100 psig sample point pressure
  - 100 ml internal volume for Method A with 500 ml cylinder
  - One stroke = 80% full for TDG transport

- ASTM process will take 6-24 months

- CCQTA could publish as interim measure
  - Available for industry use under contract spec
  - Available for Regulatory use by Authorities having Jurisdiction
CCQTA TVP /RVP WORKSHOP

- Additional detail was provided in terms of practical field testing equipment trials and learning's emphasizing low cost and fit for purpose.

- Also this field equipment can be/should be integrated with vapor tight HPLIS systems to obtain improved accuracy of light ends (say for EQ). There was considerable detail on accuracy improvements potentials to real world high vapor pressure crude handling by these instruments.

....contact project members for updates and more info!

Thank You
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