CCQTA Update for COQA
Houston Meeting

October 13, 2016

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CCQTA

“The New Direction”

1. Have completed change from a volunteer board to a governance model.
2. Increased membership fees ($5K) to permit more shared CCQTA funded projects (open projects; broadly shared learnings).
3. Option to have outside sources (Gov’t, regulators, other Associations, etc..) commission CCQTA work.
4. Members continue to have the option to sponsor/promote member funded (closed) projects.
5. Some historical participant funded projects converted to CCQTA funded projects
CCQTA PROJECTS LIST

Participant Funded
1. Condensate Quality
2. Organic Chlorides/Halides
3. Phosphorus (Legacy)
4. TAN (Phase 4)
5. Emulsion Characterization
6. Pipeline Corrosion
7. Sour Service

CCQTA Funded
1. Bitumen Dewatering
2. Bitumen Blend Viscosity
3. TVP/RVP
4. H2S PVT
5. Crude Oil Flammability
6. Compatibility Test Method
7. Single Phase Sampling Program
8. VLE Method Development
9. Analysis of TIOM
10. Properties of Thermally Processed Material

(Today's update focus)
1. Bitumen Dewatering and Volume Correction

- Project details provided at March 2016 COQA joint San Antonio meeting.
- Project work led to the
  - development of a standard dewatering and solids removal procedure to prepare bitumen for analysis
  - development of arithmetic **correction factors to API 12.3** for improved accuracy of blend volume calculations for Alberta bitumen and diluent
- Work initially funded by 6 members. CCQTA provided additional funding
- Report published on public side of CCQTA website
  - Results made available to industry at large
2. Bitumen Blend Viscosity

• Project work
  – Development of an improved viscosity model for blend predictions for bitumens and diluents

• Work initially funded by members of the Bitumen Dewatering project. CCQTA has agreed to provide additional funding

• Report to be published on private side of CCQTA website (members only)
  – Report to include an open source model based on all data
  – Some members funding additional internal optimized fitting of their own data
3. TVP/RVP
(True/Total Vapor Pressure, Reid Vapor Pressure)

Progress to Date

- Dataset showing bias in vapor pressure test results based on sampling methods.
  Conventional bottle vs.
  Evacuated cylinder vs.
  Floating piston cylinder

- Dataset showing bias between Legacy D323 results and D6377 results for volatile crude oils.

- Widespread adoption of D6377 for accurate vapor pressure measurement. Diluent pending.

- ASTM D7975 published Jan 2015 (“Field” VP Tester)
- ASTM D8003 published June 2015 (HPLIS Method)
- ASTM D8009 published Dec 2015 (MPC Practice)
TVP/RVP

Work pending

– Development of D7975 operating FAQ
– AITF drafting paper on EOS vapor pressure based on HPLIS (D8003) vs. D6377 measurements.
– Draft “Best Practice” white paper to summarize findings and recommendations. Useful for Equalization, New Contracts, Referee methods/Arbitration, Technical Studies

Estimated project completion Dec 2016
4. **H₂S PVT**

*Hydrogen Sulfide Pressure Vapor Temperature (Relationship)*

**Progress to Date**

- Originally set out to build a standardized predictive tool to estimate H₂S in the vapor phase based on known accurate liquid phase measurements. Predictive modeling based on liquid phase was not feasible.

- Updated objectives to develop a **field measurement tester** that can be used *to assess H₂S evolution risk.*
  - Developed prototype field tester. Initial prototype too large and complex for field deployment.
    - (Single phase sampling protocol, sealed vapor expansion chamber)
  - Initiated development of a miniaturized version of field prototype.
Field Tester Requirements

- Targeting a replacement for ASTM D5705 for use specifically with crude oils/condensates.
- Direct Measure H₂S in vapor space under different conditions (V/L ratio, temperature).
- Must be portable and easy to use (12VDC-Tailgate).
- Must have a wide operating range.
  - 1 to 20000 ppm (2%)
- Must be robust for field operability.
- Must be simplistic in design to minimize cost.
Field Tester Uses

- Provide standardized method for transportation regulators (TC), EH&S, etc...
  - Ability to clearly define test conditions with fit for purpose test.
- Evaluation of scavenger dosing requirements
  - Direct scavenger injection and vapor testing
  - Test, dose, retest...
- Generation of H₂S evolution with V/L ratio
  - Test H₂S at multiple V/L ratios to develop evolution curve with car/truck/tank outage conditions.
  - Two version (field and lab)
H$_2$S PVT

Field Tester Development
Sample Expansion/Gas Evolution to be Fully Automated

• Sample introduction
• Fill/Purge cycles
• Heating/Agitation
• V/L ratios

Operator Goal is to have the now famous Dave-ism of “Push button get banana”
Proposed Analysis System

- Sample bottle (300-500 mL liquid sample)
- Air intake
- Heated gas line
- Piezo transducer for U-S mixing
- Thermo-couple
- Consumable
- Heated sample syringe (40-50 mL)
- Air Pump
- MOF Filtre
- H2S Scvgr
- Exhaust
- Det. 1
- Det. 2
- Non-consumable waste container (>200 mL)
- Level Sensor
H2S Vapor Field Tester

Milestones

               ✔ Short list of two technologies.

12 Months  (Sept 2016)  ✔ Progress evaluation and decision on project continuation.

18 Months  (Mar 2017)  ▪ Final decisions on technologies, functions and layout.

24 Months  (Sept 2017)  ▪ Complete 5 prototype units for field evaluation.
                         ▪ Draft ASTM Method.
5. Crude Oil Flammability

Phase 1:
- Evaluate suitable test methods using a small subset of samples ranging from light condensate to “railbit”

Phase 2:
- gain a better understanding of flammable behaviours of diluted bitumen.

Part 1: Evaluate the ignition potential of various diluent/bitumen blends to identify a potential threshold for diluent blend volumes as it applies to the flammability of the dilbit.

Part 2: Investigate immediate ignition (flash) versus sustained combustion
Phase 2

Part 1: Flashpoint vs. Diluent Content

– 5 blends of each of 4 commonly used diluents with raw undiluted bitumen
– Identify potential threshold for diluent blend volumes as applied to flammability of dilbit

Part 2: Sustained Combustion

– Evaluate the self-extinguish and/or self combustion properties of dilbit blends in a static pool fire scenario.
– 2 diluents
– 3 blend concentrations at 4 temperatures
# SLD(light diluent)/Bitumen Blend Properties

<table>
<thead>
<tr>
<th>Blend</th>
<th>0.5 Mass%</th>
<th>1 Mass%</th>
<th>3 Mass%</th>
<th>5 Mass%</th>
<th>10 Mass%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass % Diluent</td>
<td>0.61</td>
<td>1.09</td>
<td>3.01</td>
<td>5.01</td>
<td>10.01</td>
</tr>
<tr>
<td>Density @ 15°C (kg/m³)</td>
<td>1010</td>
<td>1008</td>
<td>998.8</td>
<td>990.0</td>
<td>967.5</td>
</tr>
<tr>
<td>Viscosity @ 20°C (cSt)</td>
<td>338930</td>
<td>321248</td>
<td>88553</td>
<td>28854</td>
<td>3651</td>
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<tr>
<td>IBP (°C) - GC merge</td>
<td>95.5</td>
<td>37</td>
<td>23.5</td>
<td>22.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Flashpoint (°C)</td>
<td>106</td>
<td>62</td>
<td>39</td>
<td>27</td>
<td>2</td>
</tr>
</tbody>
</table>
## CPM(heavy diluent)/Bitumen Blend Properties

<table>
<thead>
<tr>
<th>Blend</th>
<th>0.5 Mass%</th>
<th>1 Mass%</th>
<th>3 Mass%</th>
<th>5 Mass%</th>
<th>10 Mass%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass % Diluent</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.56</td>
<td>0.99</td>
<td>3.00</td>
<td>5.04</td>
<td>10.01</td>
<td></td>
</tr>
<tr>
<td>Density @ 15° C (kg/m³)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1011</td>
<td>1009</td>
<td>1003</td>
<td>997.2</td>
<td>982.4</td>
<td></td>
</tr>
<tr>
<td>Viscosity @ 20° C (mm²/s (cSt))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>444989</td>
<td>324129</td>
<td>141478</td>
<td>66352</td>
<td>11309</td>
<td></td>
</tr>
<tr>
<td>IBP (° C) - GC merge</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Flashpoint (° C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>&gt;120</td>
<td>97</td>
<td>66</td>
<td>46</td>
<td>26</td>
<td></td>
</tr>
</tbody>
</table>
Flash Points

Threshold for classification as a flammable liquid: flash point ≤ 60°C

Mass % diluent required to cross threshold for a Class 3, PG III flammable liquid…

SLD: between 1-3 mass%
CPM: between 3-5 mass%
Burn Pan (at AITF)
# SLD/Bitumen Blend Properties

<table>
<thead>
<tr>
<th>Blend</th>
<th>10 Vol.%</th>
<th>20 Vol.%</th>
<th>30 Vol.%</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Density @ 15° C (kg/m³)</strong></td>
<td>981.5</td>
<td>949.4</td>
<td>916.1</td>
</tr>
<tr>
<td><strong>Flashpoint (° C)</strong></td>
<td>22</td>
<td>-11</td>
<td>&lt;-37</td>
</tr>
<tr>
<td><strong>Carbon (mass%)</strong></td>
<td>83.00</td>
<td>82.58</td>
<td>81.37</td>
</tr>
<tr>
<td><strong>Hydrogen (mass%)</strong></td>
<td>11.92</td>
<td>12.19</td>
<td>12.29</td>
</tr>
<tr>
<td><strong>C/H ratio</strong></td>
<td>6.96</td>
<td>6.77</td>
<td>6.62</td>
</tr>
</tbody>
</table>
SLD/Bitumen Blend Flash Points Part 1 & 2

Flammable Liquid

Flash Point (°C)

Mass % Diluent
10 Vol.% SLD/Bitumen Blend Video
30 Vol.% SLD Blend Video
6. Crude Oil Compatibility Method

**Bases of Development of the New (industry shared) Method Petroleum containing asphaltenes**

- Deliberately precipitate asphaltenes by having excess non-solvent oil in a mixture of Aromatic + Paraffinic

- Adjusting the amount of solvent oil in the mixture of Aromatic + Paraffinic solvents to dissolve asphaltenes
Crude Oil Compatibility Method
(example observations)

WCS as received

1g WCS + (9mL H + 4.3mL T)

1g WCS + (9mL H + 1mL T)

1g WCS + (9mL H + 4.4mL T)
Crude Oil Compatibility Method

Status

– Preliminary method has been developed and is being testing/validated in at Maxxam Analytics

– 42 members! participated in the project meeting on Tuesday.

Target completion date – December 2016
Crude Oil Compatibility Method

Path forward

• Firm up the procedures A and B (repeatability (WCS, LA 10 X)
• Firm up SOP for posting on CCQTA website
• Apply the methodology to crudes with asphaltenes:
  – different crudes with different properties (10 crudes)
  – Heavy oils/bitumen
  – Waxy crudes
  – Processed samples – Partially upgraded
• Initiate Round Robin (CanmetENERGY, AITF, U of A)
• Apply the method to crudes with no/little asphaltenes
  – Crudes with asphaltenes < 1wt%
  – Processed stream, Condensate/diluents
7. Single Phase Sampling Program

“Manual Piston Cylinder”

Initiated from TVP/RVP project in 2014

• Initially recommended the VP Field tester as simply a means to capture a single-phase sample and transport it to the laboratory for D6377 or D8003.

• Found too many dead legs (gauges, lines, etc…) that could trap previous sample material and contaminate the composition of the next sample.

• Needed a simplified version that was functionally equivalent to the D3700 Floating Piston Cylinder and suitable for D6377 and D8003.
Manual Piston Cylinder

Road to a Published Standard

- Drafted as an annex to D3700 in February 2015
- Balloted in ASTM SC D02.H in March 2015 (1 negative)
- Ballot withdrawn and the practice was revised as a standalone.
- Concurrently balloted SC D02.H and D02 Main (9 negatives (jurisdiction issues between D02.H and D02.02)
- Ballot withdrawn and jurisdiction transferred to D02.02 which is also joint with API COMQ.
- ASTM/API working group formed and revised the practice to ensure it is technically sound.
- Passed concurrent SC D02.02 and D02 Main ballot in October 2015.

Published December 2015
8. VLE Gas Composition Screening Method

Synopsis

− Utilizes the **MPC** as an expansion chamber to create a known vapor-liquid-equilibrium condition.
− Equilibrium vapor is transferred isobarically to a **standard refinery gas analyzer** and the composition determined.
− **Provides hydrocarbon and fixed gas** (CO, CO₂, H₂, H₂S, N₂, O₂) composition of the vapor phase.
− Intended for use in screening the bulk of gaseous components present in the vapor that may contribute to vapor pressure, **but not identified by D8003**.
− Gases may originate from production, or may be the result of pad gas, or other gas addition during handling or transport.
VLE Gas Composition Screening Method

Status

– ASTM Standard Practice has been drafted.
– Intended to submit to both D02.08 and D02.02 (API COMQ) for review and comment prior to submitting for ballot.
– Potential for ballot in 2016/2017
9. Analysis of TIOM

(Toluene Insoluble Organic Material)

Synopsis

– TIOM’s have been identified as an issue in the CCQTA since 2005.
– First detected in NGL Fractionator reboilers and subsequently reported in condensate deposits and refinery exchangers.
– High molecular weight carbon based material, often mistaken for asphaltenes.
– TIOM’s have little/no functional chemistry and are not toluene soluble.
– Previous work on TIOM with 4 CCQTA projects led to the development of a Deposit Analysis Protocol
– Recently acquired some TIOM materials from a gas plant which are to be analyzed
  • Sample believed to be closer to source!
10. Properties of Thermally Processed Material

Synopsis

- AI-EES and Canmet Energy have received funding for studying quality issue associated with partially upgraded bitumens.
- Step 1 is to review the role of olefins/di olefins on refinery fouling
- Additional work will look at the impact of olefins on product quality/plant operation.
- CCQTA’s role is to function as technical resource (particularly a liaison for refiners) for this work.
  - CCQTA is not asked to provide any funding for this work.
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