Review of Participant Funded Projects

– Condensate Quality
– Emulsion Characterization
– Phosphorus in Crude
– Tan
– Organic Chlorides
– Dilbit Blending Viscosity
CONDENSATE QUALITY
Condensate Quality Project Participants

- AITF – in kind
- Keyera
- Pembina
- Canmet – in kind
- Cenovus
- Pall – in kind
- Intertek – in kind
- MEG Energy
- Total
- Marathon
- Shell Canada
- Imperial Oil
- ADOE
- Phillips 66
- Suncor
- Maxxam – in kind
- Devon
- Enbridge
- Husky
- Nexen
Condensate Quality

• **Key Activities**
  – Supplying CRW committee with project developed test methods for measuring filterable solids and organic particulates in condensates.
  – Assessing suitability of Mercury test methods for crude oil. ASTM D7842 deemed to be suitable.

• **Future Activities**
  – Assist CRW committee with spec review/upgrade
EMULSION CHARACTERIZATION
<table>
<thead>
<tr>
<th>Participants</th>
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<td>Baker Hughes – WIK</td>
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<td>Chevron</td>
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<td>Flint Hills</td>
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<td>Suncor</td>
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Emulsion Characterization

• **Key Activities**
  – Compiling data on emulsion properties
  – Developing a protocol for analyzing emulsions
  – Assessing impact of brine quality on effluent treatment/fish toxicity

• **Future Activities**
  – Assess the impact of vacuum condensate on emulsion stability/brine quality
  – Explore options for alternate handling/disposal of VTOH
    • Mechanical filtration/separation
PHOSPHORUS IN CRUDE
Phosphorus in Crude
Participants

BP
- Chevron Canada
- Phillips 66
- Enerchem
- Imperial Oil Limited
- Newalta
- Marathon Petroleum
- Tesoro
- Intertek Caleb Brett
- Valero
- Husky
- Pembina
- Shell

Tervita
- Gibsons
- Flint Hills
- Halliburton
- Maxxam Analytics
- Suncor
- Baker Hughes
- Citgo
- XOS
- Total
- Irving Oil
- AITF
Phosphorus in Crude

• **Key Activities**
  – Establishing & monitoring baseline data for phosphorus in Canadian crude
  – Prepared a plant incident summary report

• **Future Activities**
  – Continue monitoring P levels in Canadian crude.
    • Levels have subsided/dropped in the last 2 years
  – Collect US plant data
    • Evidence that phosphorus is becoming more prevalent in US domestic crudes
## Project Participants

<table>
<thead>
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<th>Company</th>
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<tbody>
<tr>
<td>Suncor Energy</td>
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<td>Phillips 66</td>
<td>Shell</td>
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<td>Cenovus</td>
<td>Canmet Energy – WIK</td>
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<td>Alberta Department of Energy</td>
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<tr>
<td>Chevron – WIK</td>
<td>Petrobras</td>
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<tr>
<td>Flint Hills Resources</td>
<td>Nexen</td>
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<td>Statoil</td>
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</tbody>
</table>
• **Key Activities**
  – Testing of targeted streams nearly complete
  – Compiling all results to date and preparing a summary report

• **Future Activities**
  – Were applicable collect plant data/operating history to compare/validate test results
  – Enlist interested participants and some 3rd party experts to provide a technical review of project results and conclusions
ORGANIC CHLORIDES
Project Participants

- BP
- TCPL
- Calumet Specialties
- Plains Midstream
- Marathon Petroleum
- Flint Hills
- Shell
- Suncor
- Imperial Oil

- Enbridge
- United Refining
- Kinder Morgan
- CITGO
- Nalco Champion
- Gibsons
- Cenovus
- Irving
- Husky

Work in kind
- Maxxam
- PAC
- AGAT
- Phillips 66

- Exova
- Intertek
- AITF
Organic Chlorides

• **Key Activities**
  – Published four documents on CCQTA website dealing with test method review, impact of volatile phosphorus, recommendations on laboratory testing and a protocol for dealing with future incidents
  – Letter to ASTM D4929 D02.03 committee members requesting a method addendum/appendix re the practice of crude water washing

• **Future Activities**
  – Explore the option of developing a TOX method for distillates and gas oils
BITUMEN BLEND

Viscosity
Bitumen Blend Viscosity

- This project is a continuation/extension of the Bitumen Dewatering and Volume Correction Project
- Participants list is still being established
Bitumen Blend Viscosity

• **Key Activities**
  – Development of a procedure for bitumen dewatering and solids removal
  – Development of an improved model for blend predictions
  – Both methods published in a report on the CCQTA website

• **Future Activities**
  – Follow up with API re blend prediction model
  – Complete viscosity blend model
End of Review of Participant Funded Projects...Questions??

- Condensate Quality
- Emulsion Characterization
- Phosphorus in Crude
- Tan
- Organic Chlorides
- Dilbit Blending Viscosity
Review of CCQTA Funded Projects

- TVP/RVP
- H₂S PVT
- Crude Oil Flammability
- Manual Piston Cylinder
- VLE Method
- Crude Oil Compatibility
TVP/RVP
TVP/RVP

- **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 D323 results and D6377 results for volatile crude oils.
  - Widespread adoption of D6377 for accurate vapor pressure measurement.
  - ASTM D7975 published Jan 2015 *(Field VP Tester)*
  - ASTM D8003 published June 2015 *(HPLIS Method)*
  - ASTM D8009 published Dec 2015 *(MPC Practice)*
• **Temperature Correction for Field VP Measurement**
  - Correlations developed based on:
    - 19 different commodities
    - Density Range — 800 kg/m$^3$ to 935 kg/m$^3$
    - Temperature Range — 25°C, 37.8°C, 50°C and 65°C
    - 5000+ samples
  - Two data sets selected to develop regression curves
    - Light Crude (<878 kg/m$^3$)
      - Conventional and shale oil (~1000 samples)
    - Heavy Crude (>878 kg/m$^3$)
      - Heavy crude and diluted bitumen (~4000 samples)
  - Regression data used to calculate coefficients of the Clausius-Clapeyron equation between 41 kPa and 100 kPa.
• Temperature Correction for Field VP Measurement
  – Development of How To Guide (CCQTA website)
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.

- **Estimated project completion Sept 2016**
H$_2$S PVT
H$_2$S PVT

• **Progress to Date**
  – Originally set out to build a standardized predictive tool to estimate H$_2$S in the vapor phase based on liquid phase measurements.
  – Predictive modeling based on liquid phase was not feasible.
  – Updated objectives to develop a field measurement tool that can be used to assess H$_2$S evolution risk.
  – Developed prototype field tester
    • Single phase sampling protocol
    • Sealed vapor expansion chamber
  – Initial prototype too large and complex for field deployment.
  – Initiated development of a miniaturized version of field prototype.
• Field Tester Requirements
  – Replacement for ASTM D5705 for use specifically with crude oils/condensates.
  – Measure H₂S under different conditions (V/L ratio, temperature).
  – Must be portable and easy to use (12VDC-Tailgate).
  – Must have a wide operating range.
    • 1ppm to 2%
  – Must be robust for field operability.
  – Must be simplistic in design to minimize cost.
H$_2$S PVT

• **Field Tester Uses**
  – Provide standardized method for transportation regulators, EHS, 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 H$_2$S evolution with V/L ratio
    • Test H$_2$S at multiple V/L ratios to develop evolution curve with outage conditions.
Field Tester Development

- **Sample Expansion/Gas Evolution**
  - Fully Automated
    - Sample introduction
    - Fill/Purge cycles
    - Heating/Agitation
    - V/L ratios

- **Operator Controls**
  - “Push button get banana”
Field Tester Development

- **Field Tester Timeline**

  - **6 Months**  
    (Mar 2016)  
    - Evaluation of separation and detection technologies and success potential.  
    - 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.
CRUDE OIL

FLAMMABILITY
Crude Oil Flammability

Project Scope

• An in-depth study to provide a more defensible and definitive answer on the concerns of crude oil flammability. Objective is to provide the industry with empirical data to the questions regarding various crude types and their flammability characteristics.
  ▪ Ignition vs. sustained combustion.
  ▪ Ignition and self-extinguish.
  ▪ Ignition energy.

• Review current and possibly develop new sampling and testing methods to properly determine crude oil flammability.

• Test flammability of a variety of North American crudes.

• Project work should concentrate on transported crudes. (e.g. Dilbits, Bakken, Condensate, Cardium, etc…)

• Investigation of ignition versus sustained combustibility of various crude types to determine if some crudes may ignite but self-extinguish or if they ignite and continue to burn.
Crude Oil Flammability

• Phase I Summary
  – IBP was misrepresented by ASTM D86 by as much as 50°C in the 7 studied crudes (679 kg/m³ to 946 kg/m³).
  – Flashpoints showed little difference from dilbits to condensates. (All results < -20°C [-4°F])
  – All crudes tested would be identified as Class 3 PG I.
  – Composition profiles illustrated variations in crudes that could be used in an ERAP.
  – D92 Flash vs. Fire points did not provide differentiation between ignition and sustained combustion.
  – D7094 results compared reasonably well with D93. Dual peak results provide preliminary evidence of ignition/self-extinguish phenomenon.
Crude Oil Flammability

• Phase II - Two studies proposed:
  – Comparative Dilbit Blend Flammability
    • Flashpoint versus Diluent Content (Threshold)
    • Sustained Combustion
  – Jet (Torch) Fire Characteristics
    • Simulation
    • Spray Type Evaluation
    • Ignitability
Dilbit Blend Flammability

• **Flashpoint versus Diluent Content (Stage 1)**
  – Suncor Hot Bit + Diluents (SLD, CFT, CRW, CPM)
  – 5 blends of each diluent. Target 0.5%, 1%, 3%, 5%, 10% (railbit).
  – Blends prepared and stored in sealed cylinders.
  – Analyze each blend for composition, density & viscosity.
  – Perform flashpoint measurements of each blend using the D7094 method (sealed).
  – Compare flashpoint with blend EOS TVP and composition.
Dilbit Blend Flammability

• **Sustained Combustion (Stage 2)**
  – Theory that a fraction of the bitumen will not combust in a fire and is therefore lower risk.
  – Consider that burning diluent and lower boiling bitumen components may be exhausted before the “resid” reaches the vaporization temperature.
  – Study allows material to burn until it is completely consumed or self-extinguishes.
    • Remaining residue characterized.
    • Density, C/H ratio, etc…
Dilbit Blend Flammability
Jet or Torch Fire Characteristics

Jet (Torch) Fire
Jet (Torch) Fire Characteristics

• **Questions to consider**
  – How fast is the crude exiting the railcar?
    • What is driving the material out?
    • How readily will the crude exit given a fixed orifice, puncture or breach?
  – What form is the crude in when it exits?
    • Ultra-fine droplet spray (atomized)?
    • Fine droplet spray (aerosol)?
    • Continuous stream(s)?
  – How do the exit form(s) effect the ignition and sustained combustion?
Current Project Status

• **Dilbit Blend (Stages 1 & 2)**
  – Blending in Progress
  – Flammability Testing to Follow
  – Data should be available in September 2016

• **Jet (Torch) Fire Characteristics**
  – Pending results of Dilbit Blend Flammability
  – Will revisit in June 2016
MANUAL PISTON CYLINDER METHOD
Manual Piston Cylinder

• Initiated from TVP/RVP project in 2014
  – Initially recommended the VP Field tester as 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.
  – Concurrrently 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
VLE GAS COMPOSITION SCREENING METHOD
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 September/October 2016
CRUDE OIL COMPATIBILITY METHOD
Crude Oil Compatibility Method

• **Background**
  - Following the termination of the Heavy Oil Compatibility Project, some members requested the development of a standardized CCQTA method for compatibility testing.
    - Heavy Oil Compatibility project had determined that ASTM D7060, ASTM D6703, ASTM D7112, Wiehe Method, Chevron Method, Microscopy, were equally effective in predicting incompatibility
    - The project also found evidence that ALCOR testing combined with SARA Analysis (CII) was capable of assessing plant fouling issues not predicted by the methods in above.
  - CCQTA method is intended to be a modification of existing methods.
    - CCQTA method will be a manual method, (e.g. employ microscopy) in order to permit the identification of various contributing sources (asphaltenes, solids, TIOM, waxes)
Crude Oil Compatibility Method

• **Status**
  
  - Preliminary method has been developed and is being testing/validated in a commercial lab
  
  - Some CCQTA members have volunteered to act as a technical resource/method reviewers prior to method publication
  
  - Target completion date – December 2016