Unconventional Crude Oils Briefing

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Acknowledgments

• RDML Brown, CG-5R
• CAPT Gelzer, CG-MER
• LT Sara Booth, CG-MER
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• Mr. Steve Lehmann, NOAA SSC, Region 1
• ENS Cathy Durand, CGA
Unconventional Crude Oils

• Issue Statement
  • New production in North America

• Crude oil Composition and Properties
  • What is crude oil?
  • How do we measure/characterize?
  • Specifics for Light Crude Oils & Dilbit

• CG Implications
  • Facilitated discussion / Q&A
“In 2012, America’s total oil production averaged 6.5 million barrels a day, according to government estimates. This year, U.S. oil production is expected to set new records, rising over 30 percent to 8.53 million barrels per day.”

“Since 2007, U.S. crude reserves have risen by over 40% and are now at a 36 year high.”

North America’s New Source of Abundance

America’s Energy Revolution, API, 2014
Issue – Part A

Derailment & explosion – Lac Mégantic

Paul Chiasson/CP
Issue – Part B

“The Canadian oil sands contain the world’s third-largest oil reserves after Saudi Arabia and Venezuela…. Increased exports of oil sands products have been proposed by industry, involving pipeline, rail and marine tanker transport.”

<table>
<thead>
<tr>
<th></th>
<th>2013</th>
<th>2015</th>
<th>2020</th>
<th>2025</th>
<th>2030</th>
</tr>
</thead>
<tbody>
<tr>
<td>Western Canada</td>
<td>3.2</td>
<td>3.7</td>
<td>4.6</td>
<td>5.6</td>
<td>6.4</td>
</tr>
<tr>
<td>Conventional</td>
<td>1.3</td>
<td>1.4</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Oil Sands</td>
<td>1.9</td>
<td>2.3</td>
<td>3.2</td>
<td>4.1</td>
<td>4.8</td>
</tr>
<tr>
<td>Eastern Canada</td>
<td>0.2</td>
<td>0.2</td>
<td>0.3</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>Total *</td>
<td>3.5</td>
<td>3.9</td>
<td>4.9</td>
<td>5.7</td>
<td>6.4</td>
</tr>
</tbody>
</table>

*Totals may not add due to rounding
Issue – Part B

Enbridge Pipeline Spill

http://www.epa.gov/enbridgespill
Oil and Water

Monthly crude shipments by barge and tanker from Midwest and Canadian oilfields to the Gulf Coast

5.5 million barrels

5.0

4.5

4.0

3.5

3.0

2.5

2.0

1.5

1.0

0.5

0

Source: U.S. Energy Information Administration

The Wall Street Journal
Crude Composition
Organic Chemistry Review  “HCs”

alkane
Organic Chemistry Review  “HCs”

aromatic
Petroleum – The Molecules

alkanes (15-20%)

branched alkanes (15-20%)

paraffins

“C8”

cycloalkanes (30-40%)

aromatics (20-45%)
Petroleum – The Molecules

- Alkanes (15-20%)
- Branched alkanes (15-20%)
- Cycloalkanes (30-40%)
- Aromatics (10-45%)
  - Bakken (9.3%)
  - Dilbit (5-11%)

At least 1 report for Bakken that the aromatic fraction is a little high in small PAH.
Aromatics – PAH
Polycyclic Aromatic Hydrocarbons

- Naphthalene
- Phenanthrene
- Pyrene
- Benzo[a]pyrene
# Asphaltenes & Resins

<table>
<thead>
<tr>
<th>Campana Asphaltene</th>
<th>Mid-Continent U. S. Asphaltene</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Chemical Structure" /></td>
<td><img src="image2" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>San Joaquin Valley Asphaltene</td>
<td>Loydminster W. Asphaltene</td>
</tr>
<tr>
<td><img src="image3" alt="Chemical Structure" /></td>
<td><img src="image4" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>Maya Asphaltene</td>
<td>Heavy Canadian</td>
</tr>
<tr>
<td><img src="image5" alt="Chemical Structure" /></td>
<td><img src="image6" alt="Chemical Structure" /></td>
</tr>
</tbody>
</table>

**Fig. 16**

Structures of asphaltene and resin from Khafji crude oil.
### Petroleum – Isomers

<table>
<thead>
<tr>
<th>C12</th>
<th>355 isomers</th>
</tr>
</thead>
<tbody>
<tr>
<td>C40</td>
<td>$6.2 \times 10^{13}$ isomers</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Pentane</th>
<th>Hexane</th>
<th>Heptane</th>
<th>Octane-decane</th>
<th>Undecane-Pentadecane</th>
<th>Hexadecane and higher</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Methylpentane</td>
<td>3-Methylpentane</td>
<td>2-Methylhexane</td>
<td>3-Methylhexane</td>
<td>2-Methylheptane</td>
<td>3-Methylheptane</td>
</tr>
<tr>
<td>2-Methyloctane</td>
<td>3-Methyloctane</td>
<td>2-Methylnonane</td>
<td>3-Methylnonane</td>
<td>4-Methylnonane</td>
<td>Pristane (isoprenoid)</td>
</tr>
<tr>
<td>Cyclopentane</td>
<td>Methylcyclopentane</td>
<td>Cyclohexane</td>
<td>Ethylcyclopentane</td>
<td>Methylcyclohexane</td>
<td>1,1-Dimethylcyclopentane</td>
</tr>
<tr>
<td>1-trans-2-Dimethylcyclopentane</td>
<td>1-cis-3-Dimethylcyclopentane</td>
<td>1-trans-3-Dimethylcyclopentane</td>
<td>Propylcyclopentane</td>
<td>Ethylcyclohexane</td>
<td>1-trans-2-Dimethylcyclohexane</td>
</tr>
<tr>
<td>1-cis-3-Dimethylcyclohexane</td>
<td>1,1,3-Trimethylcyclopentane</td>
<td>1-trans-2-cis-3-Trimethylcyclopentane</td>
<td>1-trans-2-cis-4-Trimethylcyclopentane</td>
<td>1,1,2-Trimethylcyclopentane</td>
<td>1,1,3-Trimethylcyclohexane</td>
</tr>
<tr>
<td>1-trans-2-trans-4-Trimethylcyclohexane</td>
<td>Methanethiol</td>
<td>Ethanethiol</td>
<td>2-Thiapropane</td>
<td>2-Propanethiol</td>
<td>2-Methyl-2-propanethiol</td>
</tr>
<tr>
<td>2-Thiabutane</td>
<td>1-Propanethiol</td>
<td>3-Methyl-2-thiabutane</td>
<td>2-Butanethiol</td>
<td>2-Methyl-1-propanethiol</td>
<td>3-Thiapentane</td>
</tr>
<tr>
<td>2-Thiapentane</td>
<td>1-Butanethiol</td>
<td>2-Methyl-2-butane</td>
<td>3,3-Dimethyl-2-thiabutane</td>
<td>2-Methyl-3-thiapentane</td>
<td>2-Methyl-2-butanol</td>
</tr>
<tr>
<td>2-Pentanethiol</td>
<td>3-Pentanethiol</td>
<td>3-Thiachexane</td>
<td>2,4-Dimethyl-3-thiapentane</td>
<td>2,2-Dimethyl-3-thiapentane</td>
<td>Thiacyclopentane</td>
</tr>
<tr>
<td>2-Thiachexane</td>
<td>2-Methyl-3-thiahexane</td>
<td>Cyclopentanethiol</td>
<td>2-Methylthiacyclopentane</td>
<td>4-Methyl-3-thiahexane</td>
<td>3-Methylthiacyclopentane</td>
</tr>
<tr>
<td>2-Hexanethiol</td>
<td>Thiacyclohexane</td>
<td>trans-2,5-Dimethylthiacyclopentane</td>
<td>cis-2,5-Dimethylthiacyclopentane</td>
<td>3-Thiachexane</td>
<td>2-Methylthiacyclohexane</td>
</tr>
<tr>
<td>3-Methylthiacyclohexane</td>
<td>4-Methylthiacyclohexane</td>
<td>Cyclohexanethiol</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Petroleum – Minor Components of Major Importance

Sulfur (0.1-0.6%)  

Polycyclic Aromatic Hydrocarbons (~ 1%)  

Benzo[a]pyrene  

Natural Gas (widely varies)  

H – C – C – H  

Ethane  

H – C – H  

Methane
Petrogenesis

Fig. 11-5  Details of a saturated pool
Oil Sands

bitumen
Products

"fractions"
Products

Crude Oil Refining

1. Atmospheric distillation uses heat to separate crude oil into naphtha, light oils, and heavy oils.

2. Atmospheric residue is further distilled to extract oils under vacuum conditions.

3. Heavy oils are cracked into usable products, using several processes.

4. Blending creates final products.
Typical Composition of Fuel Oils

- **Gasoline**
  - C4 to C12
  - Rich in straight and branched alkanes (paraffins), cycloalkanes (naphthenes), alkenes (olefins), and aromatics

- **Kerosene (some jet fuels)**
  - C12 to C20
  - Rich in straight and branched alkanes (paraffins), and cycloalkanes (naphthenes)

- **Diesel (Fuel Oil No.2)**
  - C12 to C20
  - Rich in straight and branched alkanes (paraffins), cycloalkanes (naphthenes), aromatics

- **IFOs (Fuel Oil No.6)**
  - Blend of low boiling products and residuum
  - Alkanes, Aromatics, PAHs, NSOs
Chromatography – Charting the Crudes
Gas Chromatography (GC)

- Gas mobile phase (helium or hydrogen)
- Injector
- Oven
- Column with liquid polymer (polydimethylsiloxane)
- Stationary phase
- Detector
- Chromatogram

(amount vs. time)
South Louisiana Crude

lighter
low bp

heavier
high bp

Carbon Number

Time
Gasoline

- Carbon Number
- Time

(lighter) ——— (heavier)
South Louisiana Crude

Carbon Number

Time

lighter

heavier
Diesel Fuel

![Diagram of Diesel Fuel Analysis]

- Carbon Number
- Time

Lighter to heavier carbon numbers along the time axis.
South Louisiana Crude

Carbon Number

Time

lighter

heavier
Exxon Valdez Cargo Oil

[Graph showing carbon number and time with lighter and heavier labels]
Bakken Crude

Carbon Number

Time

lighter

heavier
South Louisiana Crude

Carbon Number

Time

lighter

heavier
Kalamazoo River, Michigan 2010 (diluted bitumen “Dilbit”)

Carbon Number

Time

lighter

heavier

10  15  20  25  30  35  40  45  50

5  10  15  20  25  30  35  40  45  50
South Louisiana Crude

lighter

heavier

Carbon Number
Mayflower, Arkansas 2013 (diluted bitumen)

- 

- Carbon Number

- Time

lighter

heavier
Operational Measurements
Physical Measurements - Solubility

• How much solute can water hold
• It is not a measure of dissolution rate, but related to it
• Solubility of benzene -> 1800 mg/liter
• Solubility of hexane -> 10 mg/liter
Lehr, B., S. Bristol, and A. Possolo. "Oil budget calculator—deepwater horizon, federal interagency solutions group, oil budget calculator science and engineering team, pp. A2. 1 – A2. 10 (2010)."

Figure 6: Solubility per carbon number for hydrocarbon molecules, (Modified from MoAuliffe, 1987 IOSC - proc. Pp 275-288)
Physical Measurements - Density

- Density (δ) is mass per unit volume e.g. g/mL.

- Specific gravity (SG) is the ratio of density of oil to the density of freshwater.

- API Gravity = (141.5/SG@60F) - 131.5
Density

Specific Gravity vs. °API

Table 4-1. Gravities of military fuels (60°F)

<table>
<thead>
<tr>
<th>Fuel</th>
<th>From</th>
<th>To</th>
<th>Average</th>
<th>Specific Gravity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diesel</td>
<td>24.3</td>
<td>27.4</td>
<td>26.3</td>
<td>0.8927</td>
</tr>
<tr>
<td>Gasoline</td>
<td>55.1</td>
<td>61.4</td>
<td>58.4</td>
<td>0.7451</td>
</tr>
<tr>
<td>JP4</td>
<td>45.0</td>
<td>57.0</td>
<td>51.0</td>
<td>0.7753</td>
</tr>
<tr>
<td>JP5</td>
<td>36.0</td>
<td>48.0</td>
<td>42.0</td>
<td>0.8165</td>
</tr>
<tr>
<td>JP6</td>
<td>46.0</td>
<td>50.0</td>
<td>48.7</td>
<td>0.7852</td>
</tr>
<tr>
<td>JP8</td>
<td>37.0</td>
<td>51.0</td>
<td>44.0</td>
<td>0.8075</td>
</tr>
<tr>
<td>Kerosene</td>
<td>39.0</td>
<td>46.0</td>
<td>42.0</td>
<td>0.8156</td>
</tr>
</tbody>
</table>

API Gravity = (141.5/SG@60°F) - 131.5 °API
Physical Measurements - Viscosity

- A measure of a fluid's resistance to flow and spreading.
- Usually reported in centipoise (cP) or centistokes (cSt) ranging from 1 to 100,000.
- Correlates imperfectly with density.
- Viscosity is sensitive to temperature.
- Viscosity increases with weathering.
Viscosity

<table>
<thead>
<tr>
<th>Viscosity (cP)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Dilbit</td>
<td>~150</td>
</tr>
<tr>
<td>North Slope, AK</td>
<td>11.5</td>
</tr>
<tr>
<td>Brent</td>
<td>~6</td>
</tr>
<tr>
<td>South Louisiana Crude (MC 807)</td>
<td>4.8</td>
</tr>
<tr>
<td>Bakken Crude</td>
<td>3.3</td>
</tr>
<tr>
<td>Diesel</td>
<td>~2</td>
</tr>
</tbody>
</table>

“[Bakken] Looks like two-stroke oil mixed with gasoline.”
Physical Measurements – Vapor Pressure

- How much vapor will be present in the space above its liquid form.
- Temperature dependent
- Not technically correct for mixtures, but a good guide.
- A liquid with a vapor pressure of 1 atm or 1 bar is boiling.
- “VOCs”
Volatilety - Flashpoint

- A word about flashpoint.
  - Part of the determination of Packing Group within Hazard Class 3 (Flammable Liquids) 49 CFR 171-180
  - Several studies including DOT and NDPC agree that fresh Bakken is below detection.

- Packing group is then determined by Initial Boiling Point. IBP cut off for Group I (Great Danger) is 95 °F. Significant #s of samples from this play test lower (in Group 1)
  - It is location and time dependent.
  - Those that test higher are very close.
The North Dakota Petroleum Council Study on Bakken Crude Properties

Volatility
Volutility – Notes from responses

• Bakken
  • Recoverable oil may only persist 4-8 hours.
  • Air monitoring important for safety
Volatility – DOT Operation Safe Delivery - Bakken

“Prior to the launch of our sampling and analysis, FRA identified that most crude oil loading facilities were basing classification solely on a generic Safety Data Sheet (SDS), formerly known as Material Safety Data Sheets (MSDS). “ … “PHMSA observed that SDSs for crude oil were out-of-date with unverified information and provide ranges of chemical and physical property values instead of specific measured values. “

“Based upon the results obtained from sampling and testing of the 135 samples from August 2013 to May 2014, the majority of crude oil analyzed from the Bakken region displayed characteristics consistent with those of a Class 3 flammable liquid, PG I or II, with a predominance to PG I, the most dangerous class of Class 3 flammable liquids. “
## Dissolved Gasses? - Bakken

<table>
<thead>
<tr>
<th>Crude</th>
<th>% C2- C5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Louisiana Light Sweet</td>
<td>3.0</td>
</tr>
<tr>
<td>Brent</td>
<td>5.3</td>
</tr>
<tr>
<td>Bakken</td>
<td>7.2</td>
</tr>
<tr>
<td>Eagle Ford</td>
<td>8.3</td>
</tr>
</tbody>
</table>
# Lab Result Summary (Bakken)

<table>
<thead>
<tr>
<th>Sample Date Range Total (152 Samples)</th>
<th>3/25 to 4/24/2014</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Avg</td>
</tr>
<tr>
<td>Ambient Temp (°F)*</td>
<td>34</td>
</tr>
<tr>
<td>API Gravity</td>
<td>41.0</td>
</tr>
<tr>
<td>Vapor Pressure (PSI)</td>
<td>11.7</td>
</tr>
<tr>
<td>D86 IBP (°F)</td>
<td>99.5 (PG II)</td>
</tr>
<tr>
<td>Light Ends (C2-C4s)</td>
<td>5.48</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Rail (49 Samples)</th>
<th>Avg</th>
<th>Min</th>
<th>Max</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ambient Temp (°F)*</td>
<td>29</td>
<td>10</td>
<td>47</td>
</tr>
<tr>
<td>API Gravity</td>
<td>41.7</td>
<td>39.2</td>
<td>44.0</td>
</tr>
<tr>
<td>Vapor Pressure (PSI)</td>
<td>11.5</td>
<td>9.6</td>
<td>12.9</td>
</tr>
<tr>
<td>D86 IBP (°F)</td>
<td>100.3 (PG II)</td>
<td>96.7 (PG II)</td>
<td>104.1 (PG II)</td>
</tr>
<tr>
<td>Light Ends (C2-C4s)</td>
<td>4.95</td>
<td>3.91</td>
<td>6.44</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Well (103 Samples)</th>
<th>Avg</th>
<th>Min</th>
<th>Max</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ambient Temp (°F)*</td>
<td>36</td>
<td>11</td>
<td>65</td>
</tr>
<tr>
<td>API Gravity</td>
<td>40.6</td>
<td>36.7</td>
<td>46.3</td>
</tr>
<tr>
<td>Vapor Pressure (PSI)</td>
<td>11.8</td>
<td>8.9</td>
<td>14.4</td>
</tr>
<tr>
<td>D86 IBP (°F)</td>
<td>99.1 (PG II)</td>
<td>91.9 (PG I)</td>
<td>106.8 (PG II)</td>
</tr>
<tr>
<td>Light Ends (C2-C4s)</td>
<td>5.76</td>
<td>3.52</td>
<td>9.30</td>
</tr>
</tbody>
</table>

*Some later samples missing Ambient Temp readings, may skew results colder*
Volatility – Notes from responses

- Dilbit
  - Evaporates more than other heavy oils.
  - Air monitoring also important
  - What is left may sink.
Oil Weathering Processes

Figure 3: Processes acting on spilled oil.

ITOPF Technical Information Paper No.2, Fate of Marine Oil Spills (http://www.itopf.com)
Corrosive?

AK Dept of Environmental Conservation
Summary

• Bakken and others from new shale plays are very light crudes.
  • Could contain dissolved natural gas in transport.
  • Bakken may not even be the lightest.

• Dilbit from oil sands and other bitumen products are mixtures of heavy petroleum and lighter diluents.
  • This mixture will act differently from other heavy crudes.

• While it is claimed that both are within the range of other crudes, they do push the limits and/or redefine their categories.

• Neither is fundamentally different from other products that are shipped, but they challenge our intuition of the characteristics of a “crude”. 
Implications
Implications - Response

- Know the product spilled.
- Air monitoring may be indicated more often.
- Increasing diversity of crudes.

www.darrp.noaa.gov
Implications - Transport

- Geographic and modal specifics are dynamic.
- Are the regulations/testing specific enough?
- Are they aligned well with DOT?

Table 1 – Grade Classification per 46 CFR 30.10

<table>
<thead>
<tr>
<th>Grade</th>
<th>Flashpoint (°F)</th>
<th>RVP (psia)</th>
<th>Venting</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>&lt;80</td>
<td>&gt;14</td>
<td>P/V</td>
</tr>
<tr>
<td>B</td>
<td>&lt;80</td>
<td>8 to 14</td>
<td>P/V</td>
</tr>
<tr>
<td>C</td>
<td>&lt;80</td>
<td>&lt;8</td>
<td>P/V</td>
</tr>
<tr>
<td>D</td>
<td>80 to 150</td>
<td>N/A</td>
<td>Open</td>
</tr>
<tr>
<td>E</td>
<td>&gt;150</td>
<td>N/A</td>
<td>Open</td>
</tr>
</tbody>
</table>

“The Coast Guard’s design, construction and operating standards for Grade A and Grade B cargos are identical for cargoes with RVP below 25 psia.”
Implications – Information?

- Where is this information coming from?
Questions?

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