Tight oil: An opportunity or a challenge?
Quality Variations, Contaminants, Incompatibility, and Look-Alike Blends

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U.S. Refinery Capabilities

- c. 1974 – 2008, large percentage of complex refinery capacity configured for heavy crude oils
  - Numerous revamps, e.g., cokers, completed to process an average stream growing heavier, and higher in sulfur, metals, and other contaminants

- Since 2008, supplies of tight oils have risen steadily straining refinery capability to efficiently process them¹
  - Changes needed to handle increasing volumes of light ends, yet keep heavy oil units, e.g., cokers, operating

¹Superscript numbers are to references provided on slide 44.
What is Tight Oil?

- AKA, “unconventional crude”, “light tight oil (LTO)
- Produced by hydraulic fracturing (fracking) of shale deposits
- In U.S., commonly refers to production from the Bakken, Eagle Ford, and Permian Basin
- Quality typically varies over production region
  - All streams a kaleidoscopic blend
  - “Buyers are wary of grades such as Eagle Ford….”

^2
Some Characteristics

- Wide range in API gravity (45° to > 60°), and substantive batch-to-batch variation
- High naphtha and distillate; low VGO and resid. yields
- Low sulfur and nitrogen, & heavy metals (Ni, V)
- Vapor pressure and H₂S often high
- Alkali (Ca, Mg) & other metals (As, Ba) may be high
- Paraffin (wax) and WAT commonly high
- Water, filterable solids and microfines generally high
- Problematic production chemicals (e.g. P) may be present
Quality Variation Example

* Data for 83 barge shipments of a tight oil from West Texas to a Louisiana terminal.

<table>
<thead>
<tr>
<th>Property</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>API Gravity, °</td>
<td>40.8 – 46.7</td>
</tr>
<tr>
<td>Sulfur, mass %</td>
<td>0.11 – 0.48</td>
</tr>
<tr>
<td>Ni, ppm</td>
<td>0.1 – 3.2</td>
</tr>
<tr>
<td>V, ppm</td>
<td>0.1 – 11.0</td>
</tr>
</tbody>
</table>
Same Week Deliveries to One Refinery

- API varied from 44.6 to 55.0°
- Filterable solids ranged from 176 to 295 ptb
- Appreciable waxy sludge present

Courtesy Baker Hughes
Comparative Distillation Yields

![Graph showing distillation yields for different crude types.](image)
Hydraulic Fracturing Chemicals

- Recent report identified 750 chemicals and other compounds, including ones containing B, Cr, P, Sb, Ti, and Zn. Most common is MeOH, but in low concentration\(^5\)
- Used as proppants, gels, biocides, H\(_2\)S scavengers, scale control additives, etc.
Their Impact?

- Problematic in many instances
  - Phosphorus a notable exception
- Some seem relatively innocuous; long-term impact mostly unknown
- Spikes may have undesirable / unexpected consequences
Tight Oil Quality Issues - 1

- Increased levels of biological activity and presence of H$_2$S often observed
- Vapor pressure can exceed atmospheric pressure
- Large volumes of water and solids impact transportation, and ultimately require environmentally-acceptable and potentially costly disposal

More …
Tight Oil Quality Issues - 2

- Generally, highly paraffinic chemical character ($K \geq 12.0$)
- Frequently contain appreciable wax; WAT of 93°C reported\textsuperscript{6}
- Naphtha fraction commonly has low N+2A indicating poor reformer feedstock quality and need for higher conversion severity

Courtesy K. Nabi

More …
Tight Oil Quality Issues - 3

- To optimize feed, tight oil frequently blended with heavier, more asphaltic crude oils or VGO which can result in incompatibility & …
  - Sludge buildup in tanks, emulsion formation in desalters, and fouling in cold and hot trains.

More …
Some Metals Pose Further Issues

- Catalyst poisons such as As & Ba often present at elevated levels
- Fe, as naphthenate, deactivates catalysts
- Alkali metals (Na, Ca) stabilize emulsions impacting WWTP operations
- Ca & Mg salts increase potential for formation of HCl
Where Can Issues Occur?

- Production and transportation
- Terminals and interim storage
- Refineries
- Finished products
Production & Transportation

- Wax and asphaltenes buildup …
  - In pipelines, barges, trucks, rail tank cars reduces throughput, and increases transportation costs
  - In LACT units and meter provers, affects their operation and measurements
  - Remediation and environmentally-acceptable disposal can be problematic and costly

- $\text{H}_2\text{S}$ induces corrosion
- High vapor pressure poses S & H risks
Terminals & Interim Storage

- Asphaltenes agglomeration contributes to sludge buildup and loss of storage capacity
- Measurement and blending errors can occur
- Again, remediation and environmentally-acceptable disposal can be problematic and costly

Courtesy Gibson Energy
Refineries

- Storage tanks: Incompatibility & sludge buildup
- Desalters: Excessive mud loads and emulsion formation
- Cold and hot trains: Fouling
- CDUs: Corrosion, fouling, and bumping
  - Latter can damage towers
- Feedstock imbalances result in less than optimum runs
  - Too much light ends; too little VGO and residuum
Refinery Process Feedstocks

- Naphtha reformer: Low octane products
- Vacuum tower: Low yields
- FCCU: Low octane products
- Coker: Low yields and MCR
Wastewater Treatment Plants

- Upsets from increased loads of solids, sulfides, and heavy metals. E.g. …
  - Fracking surfactants and microfines stabilize emulsions
  - Amine-based H$_2$S scavengers pose risk to biota
- As a consequence, environmental excursions can occur and excessive solids loads could require costly disposal\textsuperscript{7}
Finished Products

- Poor workmanship and failure to meet specifications, resulting from …
  - Excessive solids and water
  - Increased corrosion
  - Poor conductivity
  - Low lubricity
  - High cold flow temperatures, i.e. cloud and pour points
  - Decrease in water separation tendency of ATF
Some Problems!
API Gravity / Density

- Variations can adversely affect crude tank level measurements
- This, in turn, can impact accountability and achieving blend predictions
Total Sulfur & H₂S

- Low total sulfur contributes to poor lubricity and conductivity, especially of ATF
- H₂S a corrosive and noxious gas
- Appreciable H₂S can necessitate use of scavengers
  - These can produce tramp amines that partition into oil and water phases in desalters
  - In CDUs, amines can form salts which can be corrosive and also foul process units
  - In WWTPs, these can also pose issues
Vapor Pressure

- Numerous fiery accidents in crude-by-rail shipments, e.g.
  - Lac Megantic, QC
  - Casselton, ND
  - Lynchburg, VA

- Excessive light ends can impact CDU handling capacity
Phosphorus

- Presence commonly results from oilfield fracking chemicals
- Phosphorus esters\(^8\)
  - Thermally decompose and form precipitate that fouls CDU tower trays
  - Deposit on catalysts blocking active sites
  - Contribute to inferior distillate fuel quality
  - Hydrolyze to form corrosive acids
Phosphate Fouled CDU Tray

Courtesy KBW Process Engineers
Water

- Substantial volumes co-produced with tight oil …
  - Often contaminated with a myriad of organic and inorganic substances
  - Supports microbial activity
  - Impacts rail tank car winter deliveries
  - Contributes to desalter and WWTP overloads
  - In CDUs, can cause bumping and damage
  - Contributes to inferior product quality

Courtesy B. Lines
Solids

- Filterable solids …
  - Increase desalter mud wash loads
  - Foul heat trains, CDUs, & other units
  - Stabilize emulsions and cause WWTP upsets

- Microfines …
  - Stabilize emulsions and contribute to WWTP excursions
  - Foul process units
  - Contaminate products
Olefins

- One report indicates “some samples of Eagle Ford have been shown to contain olefins and carbonyls…. ”\(^9\)
  - The presence of olefins has not, however, been substantiated by other reports.
- If present, these fouling precursors can adversely impact processing and product quality
Catalyst Poisons

- Fe naphthenates form eutectics that coat particles blocking active sites
- Other metals such as As & Ba mobilized from production deposits exhibit similar behavior
Asphaltenes Precipitation

- Decreases throughput & energy efficiency
- Increases operating cost & maintenance

Fouled HEX

Courtesy Dr. A. Mansoori, UIC
Wax Crystallization

- Fouls pipelines, meter provers, *etc.*, and contributes to tank sludge

Production Tubing

Scrapper Trap

Courtesy DynMcDermott
Case Study: Meter Prover Fouling

- Wax buildup prevented proper operation
- Prover shutdown and wax buildup removed – mechanically & with chemicals
  - Costly, time-consuming operation impacting throughput and potentially contaminating subsequent throughput
**H₂S Scavengers**

- Amine-based scavengers widely used
- Treatment may be at production, during transportation, or at terminals
- Refiners often unaware of type and concentration
- Amine salts can be corrosive and can foul process units\(^{10}\)
- Detection not trivial; no standard test method
Look-Alike Blends

- Tight oil blended with heavier crude oils to replicate other streams. *E.g.* …
  - Bakken + WCS ≈ ANS & WTI look-alikes
  - Eagle Ford + WCS ≈ Mars look-alike

- API gravity and total S mimic stream replaced; other properties can vary significantly
  - Yields may be “dumbbell”
  - Acid number, MCR, and Ni & V often elevated
  - Compatibility frequently an issue

- Some Permian Basin producers now marketing a blend named “WTI Light”
  - API gravity differs from WTI (45 - 50° vs. 38 - 42°)
  - Blend component(s) not identified
Yields: Typical (L); “Dumbbell” (R)

% Yield on Crude

Boiling Point Temperature →
Case Study: Egregious Blending - 1

- Barge terminal operator purchased vacuum tower bottoms from refiner
- At terminal, these blended with tight oil, then sold back to refiner as “virgin” crude oil
  - Deliveries mirrored API gravity and total S of locally produced crude oil
- Refiner experienced “dumbbell” yields, other issues
  - Testing of archive samples revealed a mixture
Case Study: Egregious Blending - 2

- Trader, using computer blend model, devised a look-alike mixture approximating WTI
- In October, direction given to merchant storage terminal operator to prepare 600,000 bbl of mixture by in-tank blending for future sale
- Before batch could be sold, ambient temperature dropped ~40°F, making it too viscous to pump
- Mixture sat in tank for six months costing trader large sum
New CME / NYMEX WTI Specs

› To deter egregious blending, and “preserve the ‘quality and integrity’ of WTI in light of rising volumes of light oil….”\(^\text{11}\), new specs take effect January 2019

◦ Existing specs include limits on mass % sulfur, API gravity, S&W, viscosity, RVP, and pour point

◦ To be added are limits on MCR, TAN, and Ni & V, and HTSD yields

› Changes based on recommendations by COQA dating to 2010, and other studies\(^\text{12}\).

› Domestic sweet quality data tracked on www.crudemonitor.us
Some Tight Oil-by-Rail Issues

Courtesy G. Weimer, Irving Oil
Tight Oil Opportunities

- Abundant and secure U.S. resource
  - Production continues to rise
  - In 2017, 53% of lower 48 production had API gravity >40°
- High naphtha and distillate yields
- Low sulfur, nitrogen, asphaltenes, acid number, and metals (Ni & V)
Tight Oil Challenges

- High vapor pressure
- High naphtha & distillate, but low VGO & resid yields pose CDU, FCCU, and coker issues
- Problematic production chemicals, *e.g.* P
- Highly variable quality
- High \( \text{H}_2\text{S} \), and possible presence of amines
- High solids (filterable & microfines), water, alkali (Ca & Mg) and heavy (As, Ba, & Fe) metals
- Wax fouling
- Blend incompatibility; dumbbell distillation yields
Closing Words

- “…the unique challenges associated with processing tight oils can be overcome with a combination of baseline and ongoing monitoring, defining and implementing new operating envelopes, and utilizing multi-functional chemical treatment programs….”

- “Because their properties are so variable, an old-style crude assay does not make sense. Hence, the need is for real-time analysis to provide the data for *ad hoc* blending of crude supplies and intelligent process control”
References

Thank you for your attention!

Questions?