Unconventional Crude Processing
Part 2: Heteroatoms

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DRIVING EXCELLENCE

Agenda

- Strategic Rationale
- Basis/Assumptions
- Unconventional Crude Oil Qualities
- Heteroatoms
- Decision Criteria

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- **Strategic Rationale**
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Strategic Rationale

- This is a continuation in a presentation series aimed at understand unconventional crudes processing costs
- Metals were discussed in the presentation in Opportunity Crudes Conference in April 2008
  - Metals are being observed in lower boiling range cuts than conventional heavy crudes
  - Impact catalytic unit run lengths or usage
- Current presentation focus: Heteroatoms
  - Heteroatoms are any atoms that are not hydrogen and carbon
    - Sulfur, oxygen and nitrogen along with the analogs
  - Higher metals and heteroatoms increase operating costs by corrosion, fouling and catalyst usage

Strategic Rationale

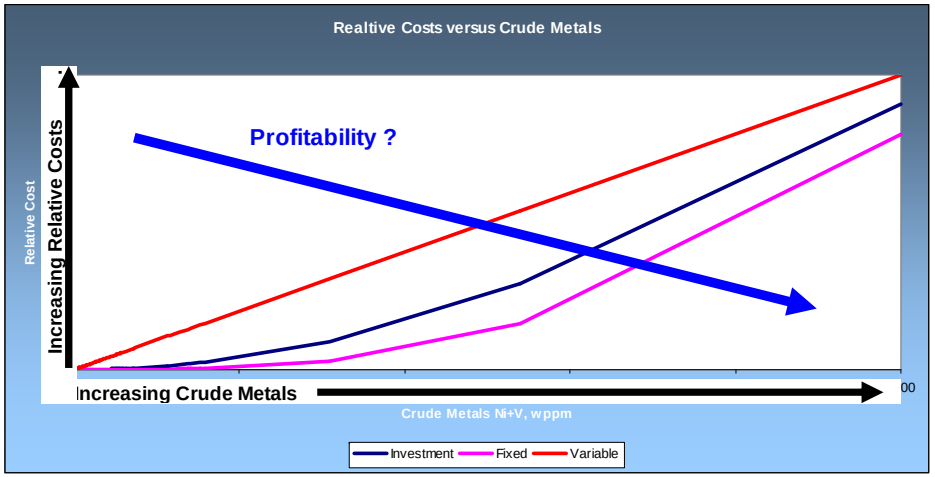
- Unconventional crudes are tar sands bitumen, coal liquids, shale oil and bio-oils
- These have several competitive advantages over conventional crude……
  - Favorable Margin (lower price)
  - Available in rate-able quantities
  - Deposit locations and quantities are known
  - Produce equivalent clean products
  - Potential to tailor upgrader to downstream refinery optimizing overall performance

Strategic Rationale

- And disadvantages….
  - Metals (April 2008)
  - TAN
  - Aromatics
  - Asphaltenes
  - Lack of hydrogen
  - Sulfur (this presentation)
  - Nitrogen (this presentation)
  - Oxygen (this presentation)
- These lead to higher
  - Fixed costs
  - Variable costs
  - Investment

Strategic Rationale

- Key Questions….
  - Will operating and investment costs exceed the crude margin thereby reducing profitability?



  - What drives operating costs?
    - One Factor →Crude Heteroatoms

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Basis/Assumptions

Point of view is from the refinery receiving the unconventional crude

- Crude Heteroatoms impact the following….
  - Variable operating costs:
    - Catalyst replacement
    - Chemical consumption
    - Energy usage
    - Hydrogen consumption
    - Waste disposal
  - Fixed costs:
    - Higher staffing needs
    - Increased maintenance repair costs
  - Higher investment costs:
    - Specialized upgrading units
    - Higher metallurgy
    - Increases in existing unit complexity

KBC
Next Gen Performance

Basis/Assumptions

- Heavy conventional crudes currently processed in refineries are used for comparison, such as:
  - Maya
  - BCF-17
  - Oriente
- Unconventional crudes may require upgrading before processing in refineries.
  - Current Production
    - Western Canada Athabasca Tar Sands Bitumen
    - Venezuela Orinoco
    - Bio-products
  - Future Production
    - Coal Liquids
    - Shale Liquids

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Unconventional Crude Oil Qualities

- Unconventional Crude Quality Observations
  - For all fractions:
    - Higher densities
    - Directionally higher sulfur and nitrogen
    - May have increased asphaltenes and aromatics
    - Organic acids are higher
    - Metals distributions are different and typically higher
    - Hydrogen deficient
  - This leads to:
    - Addition of hydrogen or removal of carbon
    - Increased processing complexity
    - Requirement to understand the crude quality implications
  - Following discusses the implications of one crude quality aspect, metals.

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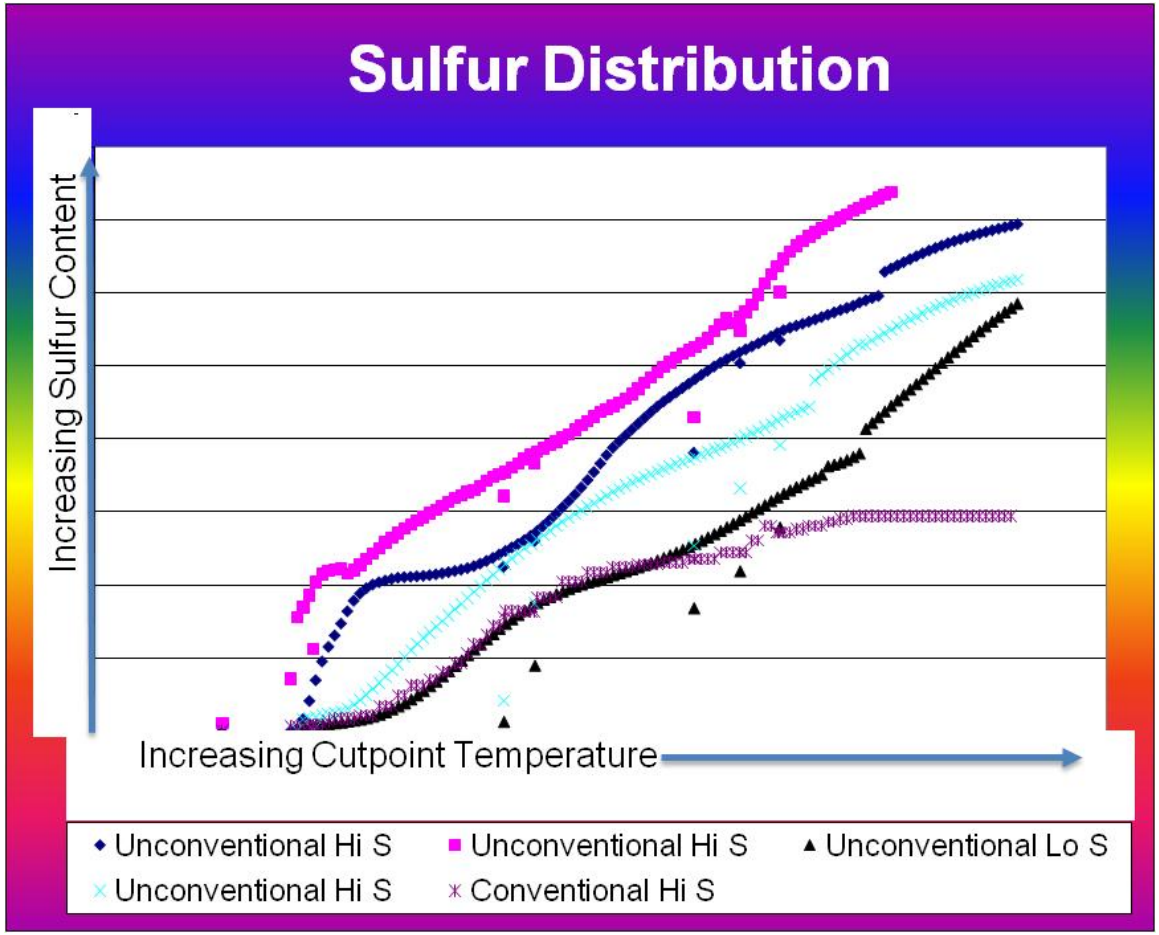
Heteroatoms Atoms

- Unconventional Crude Heteroatoms may not behave the same as in conventional crudes
  - Increased frequency
    - Found more often at higher levels
  - Distributions are different
    - Higher concentrations in lower boiling ranges
  - Chemical hydrogen compositions may be different
    - Typically more aromatic but does not always seem to be the case

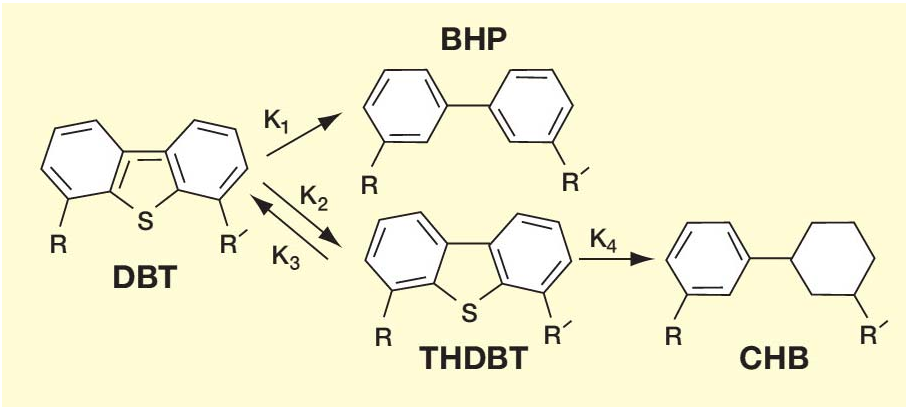
Sulfur Distribution

- Unconventional Crudes sulfur is higher



Easy, Hard or Very Hard Sulfur?

- The impact on hydrotreater cycle length is summarized below:
- Easy sulfurs convert first:
  - Sulfides, mercaptans, thiophenes and benzothiophenes
- Difficult sulfur are converted next:
  - Dibenzothiophenes without substituent at the 4 and 6 positions



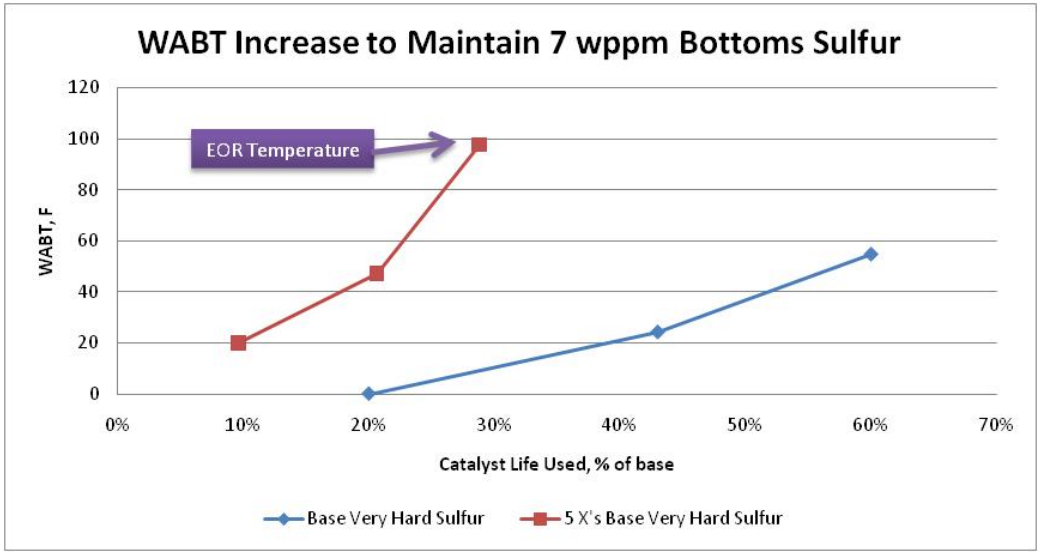
- Very difficult sulfur limits hydrotreater catalyst cycle length:
  - Dibenzothiophene isomers substituted at the 4 and 6 positions
  - Opportunity crudes may have higher levels of very difficult sulfurs

Case Study: Feedstock Very Hard Sulfur Effect on ULSD

- Prior reported work, KBC has demonstrated the usefulness of our DHTR-SIM model to predict the effect of very hard sulfur (Sayles, et al, "Solutions to Common Problems in Scoping Designs, Implementing, and Operating ULSD Units," NPRA Ann Mtg (March 2006) AM 06-07)
- The results of this work demonstrated ULSD unit response to feedstock very hard sulfur changes
- KBC's DHTR-SIM model was used to study the effect of very hard sulfur in the feed on ULSD WABT
- A conventional multi-bed single reactor ULSD design was used as the basis for the study

Case Study: Feedstock Very Hard Sulfur Effect on ULSD

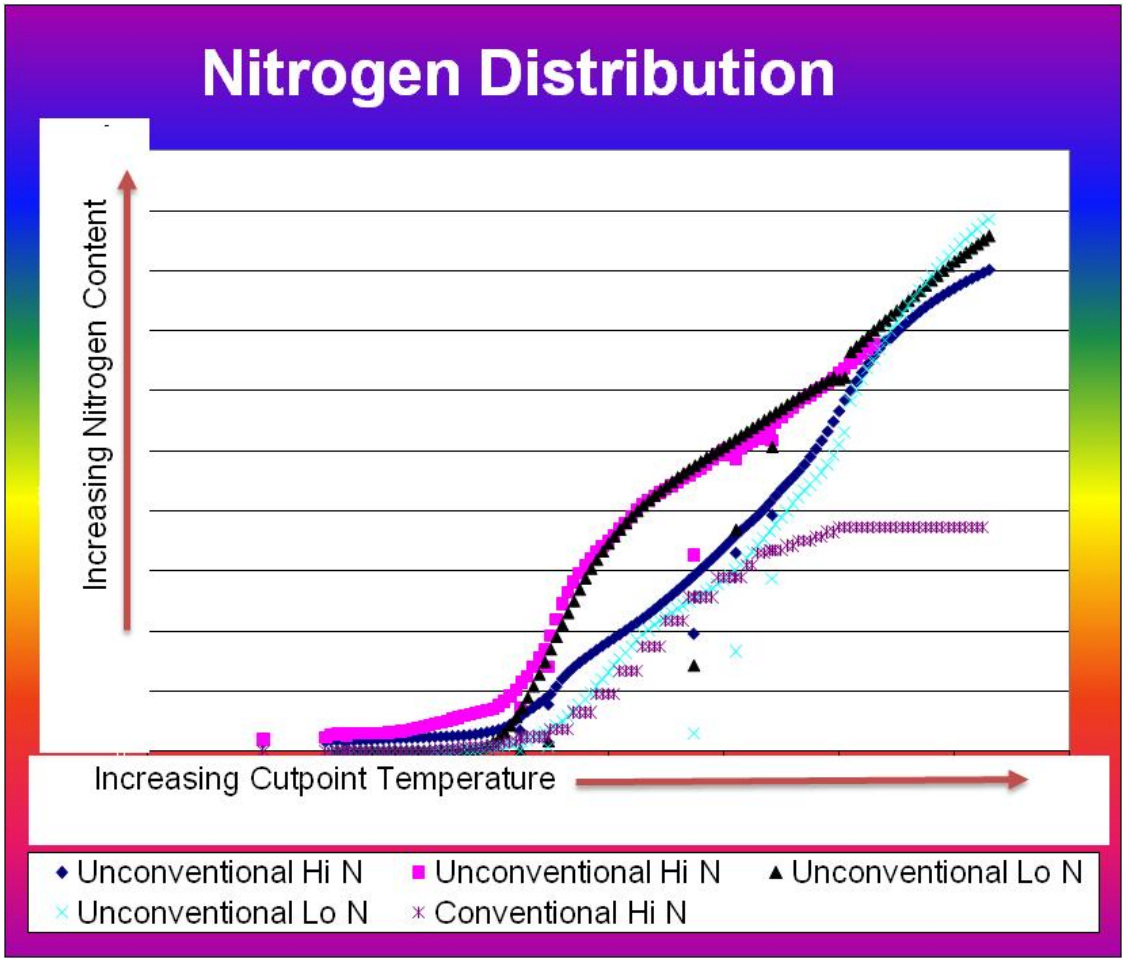
- Very hard sulfur was increased by a factor of 5 from the base
- Other feed quality and operating conditions other than WABT remained constant
- Catalyst life to reach EOR temperature at very hard sulfur of 5 times the base was 30% of the base run



- Two additional catalyst replacements would be needed for the same base feed very hard sulfur cycle length
- Operational costs including catalyst change increased by a factor of 2.5 times the base

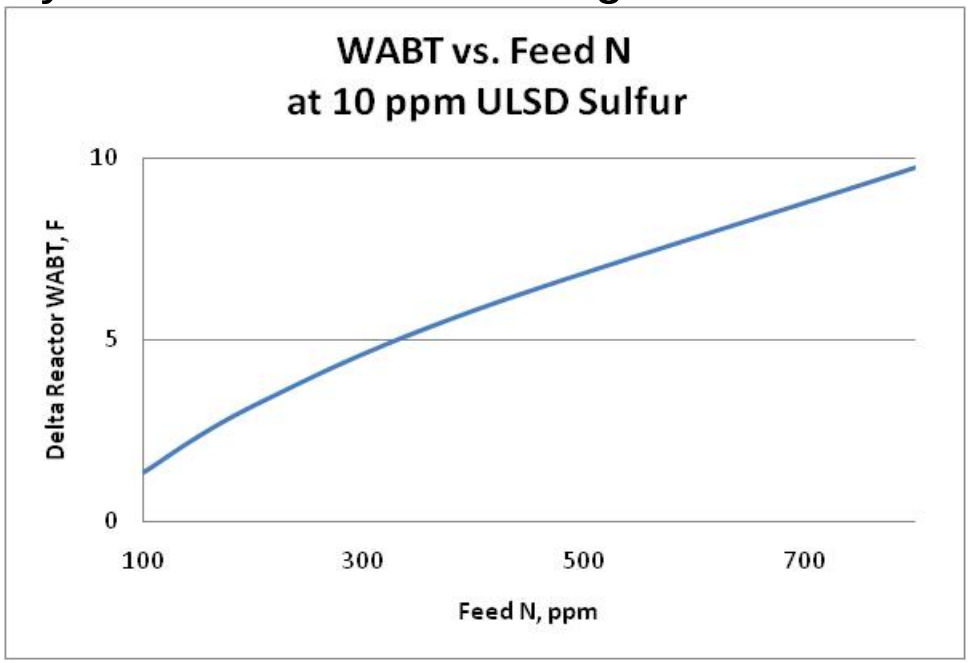
Nitrogen

- Unconventional Crudes have higher nitrogen



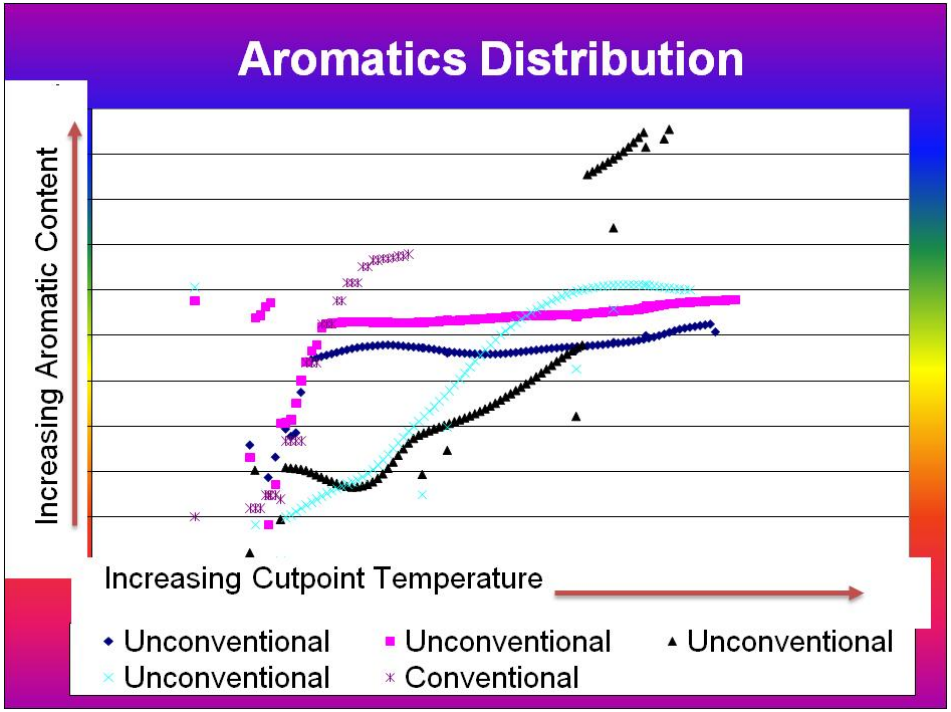
Nitrogen Inhibits Hydrogenation and Cracking Reactions

- Nitrogen content reduces the acid sites on the catalyst
- Basic nitrogen is more likely to reduce the acidity but total nitrogen trends towards lower activity
- FCC catalyst has a downward conversion shift as nitrogen increases
- New ULSD catalyst formulations are sensitive to nitrogen levels and care during catalyst selection and loading is needed to address feed nitrogen



Aromatics

- Unconventional Crudes may have higher aromatics but some are lower than conventional crudes
  - Challenges idea that unconventional=higher aromatics
- Testing may be influencing the data



Aromatics

- Aromatics limit conversion in FCCU and increase severity requirements to produce ULSD
  - FCCU conversion decreases as aromatics increase
  - ULSD severity increases as aromatics increase
- Saturation of aromatics also has a high heat release requiring multi-bed reactors with quench
  - Increases investment costs
  - Increases operating costs (hydrogen, energy)
- Aromatics to the FCC do not crack although side chains will
  - LCO in the diesel boiling range is very aromatic
  - Adds to ULSD hydrotreating load

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Decision Criteria: Heteroatoms Management

- Goal is reduced fixed and variable costs
- Establish a crude management plan
  - Refiner gains proactive control of contaminants
  - Unit operations engineer leads effort
- Clean fuels requires sulfur removal:
  - Sterically Hindered Sulfur Species requires higher severity
  - Nitrogen is removed at a lower rate requiring larger reactors
  - Nitrogen inhibits reactions and contributes to fouling
- Aromatics require more hydrogen

Decision Criteria: Heteroatoms Management (Cond't)

- Tools
  - Comprehensively analyze data
  - KBC Unit Health Check tool provides:
    - Integration of process data and lab data
    - Identifies and alert the engineer to technical anomalies
    - Suggested courses of action are included
- Technical Advancement
  - Catalyst choice determines removal capability
  - Understand the impact of coking

Thank You for Your Attention

Questions?