BIOGRAPHY

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Dr. Heather Dettman received her PhD in Biochemistry from the University of Alberta and held an NSERC Postdoctoral Fellowship at Yale University. In 1990, she joined the Energy, Mines and Resources, now Natural Resources Canada where she began work on developing quantitative nuclear magnetic resonance techniques to describe the chemical changes that occur during heavy oil and bitumen upgrading. Since then, she has developed expertise in characterization of heavy oil and bitumen and has used the knowledge to target specific research objectives to understand the cracking of hydrocarbons in petroleum under thermal conditions, corrosivity of organic acids and sulphur species under refinery conditions, the applicability of biotechnologies to bitumen and heavy oil upgrading, and modeling of diesel fuel combustion. She is currently the Manager of the Bioprocessing Program at CanmetENERGY in Devon.

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Refinery Corrosion: The Influence of Organic Acid and Sulphur Compound Structure on Global Crude Corrosivity

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Since 1920, certain crude oils world-wide have been found to be corrosive in refineries. At temperatures between 220 and 400°C, organic acid and sulphur-containing species are known to be involved. Organic acids, usually referred to as naphthenic acids and described as cycloalkane ring(s) with an attached aliphatic chain having a terminal carboxylic acid group, have been implicated. Elemental sulphur, mercaptan, sulfide and polysulphide species convert to hydrogen sulphide which attacks metal. However, neither total sulphur contents measured by elemental analyses nor total acid contents measured by total acid number (TAN) have been found to correlate well with corrosivity.

A fundamental study of the relationships of molecular structures of organic acid and sulphur compounds to refinery corrosivity has been performed. To understand acid species, the corrosivity of homologous series of organic acids in white oil with respect to temperature and vacuum have been assessed in a test unit that simulates corrosion found in vacuum distillation towers. To understand the corrosion behaviour of sulfur species, two steps were needed. Firstly, thermal decomposition of model sulfur compounds dissolved in white oil was assessed with respect to temperature and residence time in a batch autoclave. The results revealed that the rates of sulfur conversion to hydrogen sulfide were different for different compounds depending on the types of carbon-sulfur bonds present in the molecule. Secondly, the corrosivities of model oil mixtures containing specific organic acid and sulphur compounds in white oil were measured. The type and content of sulfur compound determined whether the presence of the sulfur compound: 1) reduced organic acid corrosion rates by forming a protective film; 2) enhanced organic acid corrosion rates by regenerating the acid species; or, 3) had no influence on organic acid corrosion rates. Corrosivities of global crudes including Athabasca bitumen were measured in the same corrosion test unit. The results for the different crudes will be discussed in terms of their contents of different types of organic acid and sulfur species.
Refinery Corrosion: The Influence of Organic Acid and Sulfur Compound Structure on Global Crude Corrosivity

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Mechanisms of Refinery Corrosion

- Refinery corrosion occurs at temperatures between 220°C and 400°C
  - Organic acids in gas oil reach their boiling points and condense on metal surfaces, eventually causing pits
  - Sulfides decompose to form H₂S, causing general corrosion
- Acids and hydrogen sulfide work together:
  
  \[
  \text{Fe} + 2\text{RCOOH} \rightarrow \text{Fe}(\text{RCOO})_2 + \text{H}_2 \\
  \text{Fe} + \text{H}_2\text{S} \rightarrow \text{FeS} + \text{H}_2 \\
  \text{Fe}(\text{RCOO})_2 + \text{H}_2\text{S} \rightarrow \text{FeS} + 2\text{RCOOH}
  \]
Corrosivity, TAN, and Sulfur

- Corrosivity does not always correlate with total acid number (TAN) (Derungs, 1956; Messer 2004)
  - Are organic acid molecular species in some oils “less active” that those in other oils?
  - Does high sulfide content result in iron sulfide film that protects the plant metallurgy?
  - Another reason?
- This project was conducted to improve the understanding of the contributions of specific structural features of organic acids and sulfur compounds to corrosivity at refinery temperatures
Corrosion Test Unit

Simulates corrosion in vacuum distillation unit

Features:
1. Volume: 250 mL
2. Charge: Any crude or refinery feed blend
3. No. of coupons: 4
4. Operates under vacuum throughout the temperature range

Coupon locations in vapor phase where vapor condenses on metal surface

Coupon location in liquid
Corrosion Unit Commissioning

- Commissioning runs were performed using:
  - White oil (bp 227-512°C)
    - Used to test the mass balance for the unit; obtained > 99% retention of material over 48 hours at atmospheric equivalent temperature (AET) of 350°C (300°C and 225 Torr)
    - Used as the carrier oil for organic acid (model and crude oil-derived) mixtures
  - Commercial naphthenic acids mixture (bp 180-540°C)
Corrosion Unit Performance

- Tests performed using 1018 carbon steel coupons either immersed in liquid phase of commercial naphthenic acids in white oil or suspended in vapor phase with varying TAN and atmospheric equivalent temperatures.
- Corrosion rates in vapor phase increase with TAN and temperature while corrosion rates in liquid increase with TAN (due to increased acid concentration at the coupon locations).
Global Crudes

<table>
<thead>
<tr>
<th>Global Crude</th>
<th>Density (g/mL)</th>
<th>Content (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>ATHB</td>
<td>1.0100</td>
<td>83.07</td>
</tr>
<tr>
<td>Asia1</td>
<td>0.9920</td>
<td>84.81</td>
</tr>
<tr>
<td>SA1</td>
<td>0.9934</td>
<td>86.77</td>
</tr>
<tr>
<td>SA2</td>
<td>1.0090</td>
<td>83.67</td>
</tr>
<tr>
<td>ME1</td>
<td>0.9964</td>
<td>83.33</td>
</tr>
</tbody>
</table>

Notes

1. Geographical sources: Athabasca (ATHB), Asia, South America (SA), and Middle East (ME)
2. Crudes were topped at 204°C (if -204°C fraction present) before corrosion testing except ME1 which was an atmospheric residue (+343°C)
3. Corrosion tests were performed using 1018 carbon steel coupons at an atmospheric equivalent temperature (AET) of 300°C (250°C and 225 Torr)
Corrosion Rates of Carbon Steel Coupons by Global Crudes

TAN (mg KOH/g) 5.00 3.39 0.55 0.60 2.70 0.29

Crude Sources
CMNA – Commercial naphthenic acids in white oil
ATHB – Athabasca
Asia – Asia
SA – South America
ME – Middle East

Corrosivity does NOT correlate with TAN for oils from different sources! Why?
Model Organic Acids

- Model organic acid were chosen to represent the different group of acid species. For example:

- **Aliphatic acids with a straight chain:**
  - \(\text{CH}_3\text{(CH}_2\text{)}_3\text{CH}_2\text{OH}\)
  - \(\text{CH}_3\text{(CH}_2\text{)}_{15}\text{CH}_2\text{OH}\)

- **Aromatic acids with single aromatic ring**

- **Cycloparaffinic acids with single cycloalkane ring**

- **Other acids with multiple rings:**

- Corrosion tests of each model organic acid dissolved in white oil (TAN = 5mg KOH/g) were performed
Corrosivity by Acid Molecular Weight

Corrosion rates of carbon steel coupons immersed in model oils consisting of organic acid compounds in white oil (TAN = 5.0mg KOH/g) at an AET of 300°C
Corrosion rates of carbon steel coupons either immersed in the model oil (●) or suspended in vapor phase (▲) at an AET of 300°C (TAN= 5.0mg KOH/g)
Conclusions for Corrosion due to Organic Acids

- For model oil mixtures with the same TAN (5.0mg KOH/g), different corrosion rates were obtained.
- As molecular weight and number of rings increased, corrosivity decreased.
- Boiling point of the model organic acid determined a threshold temperature for vapor phase corrosion where acid vapors condensed on the coupons.
High temperature simulated distillation results of CMNA and organic acids extracted from Global crude oils
Corrosion Rates of Global Crudes

- Boiling point distribution (and structure) explain the relatively high corrosivity of CMNA in both liquid and vapor phases.
- Differences between the boiling point distributions of the organic acids from these global crudes do not explain corrosivity differences.
  - For these crudes, corrosivity differences are not explained by size (or structure).

### TAN (mg KOH/g)

<table>
<thead>
<tr>
<th>Crude Sources</th>
<th>TAN (mg KOH/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CM – Commercial naphthenic acids in white oil</td>
<td>5.00</td>
</tr>
<tr>
<td>ATHB – Athabasca</td>
<td>3.39</td>
</tr>
<tr>
<td>Asia – Asia</td>
<td>0.55</td>
</tr>
<tr>
<td>SA – South America</td>
<td>0.60</td>
</tr>
<tr>
<td>ME – Middle East</td>
<td>2.70</td>
</tr>
<tr>
<td></td>
<td>0.29</td>
</tr>
</tbody>
</table>

### Diagram:

- **Liquid Phase**
- **Vapour Phase**

<table>
<thead>
<tr>
<th>Crude</th>
<th>Liquid Phase (mm/year)</th>
<th>Vapour Phase (mm/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMNA</td>
<td>2.55</td>
<td>1.0</td>
</tr>
<tr>
<td>ATHB</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Asia1</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>SA1</td>
<td>0.05</td>
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</tr>
</tbody>
</table>
What about Sulfur?

- Sulfur compounds $\text{R-S-R}$
  
  Thermal Cracking

- $\text{H}_2\text{S} + \text{by-products}$

- $\text{FeS}$

- Model sulfur compounds were chosen to represent the different C-S bonds found in petroleum. For example:

- Octyl sulfide

- Dibenzothiophene

- Thermal decomposition studies of nine sulfur compounds dissolved in white oil (1 wt% sulfur) were performed
Sulfur Identification In Liquid

GC-SCD plot of liquid before and after thermal treatment of octyl sulfide
At temperatures as low as 200°C, within 2 hours - CH₂-S- bonds (sulfides) crack and form H₂S.
H₂S Effects on Corrosivity of Organic Acids under Refinery Conditions

Influence of presence (1wt% S) or absence of sulfur compounds on the corrosion rates of commercial naphthenic acids (CMNA) in white oil (TAN = 5.0mg KOH/g) for carbon steel coupons at AET of 300°C

Fe(RCOO)₂ + H₂S → FeS + 2RCOOH

Low H₂S generation
Enhanced corrosion with little film formation

Fe + H₂S → FeS + H₂
High H₂S generation
Inhibited corrosion due to significant film formation

Fe + 2RCOOH → Fe(RCOO)₂ + H₂
No H₂S present
Conclusions for Influence of Sulfur Species on Corrosivity of Organic Acids

- $\text{H}_2\text{S}$ formation from thermolysis of sulfur species depends on their molecular structures: sulfur in ring structures (i.e. thiophenic) are most stable while those in chains (sulfides) are least stable

- Organic acid corrosivity can be inhibited, enhanced, or not affected by the presence of sulfur compounds, depending both on the content and “$\text{H}_2\text{S}$-generating ability” of the sulfur compounds
Identification of Sulfidic Corrosion Influences

- Replace the oil matrix with a sulfur-free medium i.e. white oil
  - Organic acids isolated from each of the Global crudes were dissolved in white oil at TAN values similar or slightly lower than those of the original crude oils tested
  - If the oil matrix has no influence on corrosion, the corrosion rates of the white oil mixtures should be the same as that of the original oil
  - If the oil matrix influences corrosion, the corrosion rates of the white oil mixtures could be either greater or lesser than those of the original oil
Possible Sulfidic Corrosion Influences

Mechanism

1) \( Fe + H_2S \rightarrow FeS + H_2 \)
   - High \( H_2S \) generation
   - Inhibited corrosion due to significant film formation

2) \( Fe(RCOO)_2 + H_2S \rightarrow FeS + 2RCOOH \)
   - Low \( H_2S \) generation
   - Enhanced corrosion with little film formation

3) \( Fe + 2RCOOH \rightarrow Fe(RCOO)_2 + H_2 \)
   - No \( H_2S \) present so corrosion only depends on organic acids (structure and size)

Corrosion Rate Expected

1) Extracted organic acids in white oil will have higher rates than the original oil – no film protection

2) Extracted organic acids in white oil will have lower rates than the original oil – no acid regeneration

3) Extracted organic acids in white oil will have the same rates as the original oil – no matrix effect
Sulfidic Corrosion Influences on Corrosion Rates of Global Crudes

<table>
<thead>
<tr>
<th></th>
<th>CMNA</th>
<th>ATHB</th>
<th>Asia1</th>
<th>SA1</th>
<th>SA2</th>
<th>ME1</th>
</tr>
</thead>
<tbody>
<tr>
<td>TAN (mg KOH/g)</td>
<td>5.00</td>
<td>3.39</td>
<td>0.55</td>
<td>0.60</td>
<td>2.70</td>
<td>0.29</td>
</tr>
<tr>
<td>S content (wt%)</td>
<td>0.00</td>
<td>4.77</td>
<td>0.59</td>
<td>0.94</td>
<td>3.76</td>
<td>4.62</td>
</tr>
</tbody>
</table>

1) Film protection
2) No matrix effect
3) Acid regeneration (or only sulfidic corrosion occurs)

* Corrosion rate difference (Isolated organic acids in white oil – Original oil)
Conclusions

- TAN values of crude oils are not reliable for predicting the corrosivity of crude oils
- Contributions from sulfidic corrosion must be included:
  - Total sulfur content is not reliable for predicting sulfidic corrosion contributions
  - Both rates and total amount of hydrogen sulfide formed under prior/present thermal conditions (in the field or refinery) will be important for understanding the influence of sulfidic corrosion
- “High shear” locations will prevent sulfidic film formation/protection
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