Tan Phase IV Project Update
“A Journey to a Corrosivity Index”

CCQTA/COQA Meeting
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New Orleans

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TAN Phase IV
Project Update

- Past CCQTA Tan Projects (I,II,III)
- Project Scope (IV)
- Cost Breakdown
- Participants and Sample Proposals
Recall...Naphthenic Acids

Typical world wide high TAN Crudes ►
...acidic species exist throughout gasoil range

◄ Refinery and Upgrader corrosion concerns ...tend to focus on heavy distillate through vacuum circuits
Project History
Phase I (Q4 2003 - Q4 2004)

- Phase I of the TAN Project was initiated given concerns regarding crude oil marketing of growing volumes of high TAN Canadian Crude.

- Analytical methodology was undertaken for:
  - measurement of acid concentration (total TAN\(_{D664}\) & naphthenic N\(A\)N\(_{UOP565}\))
  - their repeatability
  - the acid content distribution in crude oil fractions of Western Canadian heavy crude oils and Oil Sands Bitumens
Project History

Phase II (Q4 2004 – Q2 2006)

• Phase II immediately continued examining then delivering modifications to the existing D664* method for high density/viscosity crudes
• Given improved standards for TAN measurement, gasoil benchmark corrosivity comparisons were undertaken with Canadian (&Global) heavy crude oils/bitumens
• Phase II developed a pressurized, non flow through, autoclave system to align the improved TAN measurement to a Corrosivity Index

(ie seeking the development of an improved lab based corrosion rig for industry)

*ASTM is now working on adding these modifications to D664, or a new method for heavy crude oils
Project History
Phase III (Q2 2006 – Q3 2009)

• Phase III continued with corrosivity studies of gas-oil fractions from Western Canadian heavy crudes and Oil Sands bitumens, including some foreign high TAN samples.
• Now using an improved corrosivity apparatus developed to allow testing under continuous sample flow through, while under vacuum.
• Analysis of fundamental corrosion principles was undertaken given the controlled conditions.
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Tan Phase IV
Project Description (Q4 2009 – ?)

Scope:

1. Continue *corrosivity* studies of gas-oils derived from Canadian Oil Sands bitumens and heavy crudes and internationally marketed bitumens/crude oils
   - Testing will be done using a *vacuum, continuous flow* through autoclave similar to Phase III *(diagram on next slide)*
   - Testing will be done at *higher shear rates* to model normal piping and heat exchanger flows around the vacuum tower circuits
   - *Smaller volume* apparatus to reduce sample requirements
(Phase III) Vacuum autoclave block flow diagram
(Phase III) Vacuum autoclave process rack
Phase III
Large volume autoclave
TAN Phase IV
Proposed small volume autoclave
TAN Phase IV
Proposed small volume autoclave

- Note only two rings in topmost and bottommost sets of rings,
- Three rings in intermediate sets of rings
- One ring slotted to hold insulators, second solid to provide support

- Same ring design to be used for bottom ring and for top ring
- Middle rings will have slotted rings on either side of the unslotted ring

Each layer of coupons consists of two rings such as this, one below and one on top.
- Slots are to be equidistant for balance
- Slots are oriented parallel to tangent of ring at middle of slot
Tan Phase IV
Project Description (Q4 2009 – ?)

Scope (continued):

2. Naphthenic acid and sulfur speciation to be conducted to identify the classes/concentrations present
   • Preference/consideration will be given to refinery sourced gas-oil samples, to avoid costly laboratory distillations

3. Possibility of testing the impact of crude blending for corrosivity synergy/inhibition as well as corrosion inhibitor additives usage
   • surface passivation physical phenomena
Scope (continued):

4. Blanks to be run for each sample to quantify thermal degradation impact on decarboxylation
   • Sample residence times will be reduced to less than one hour to minimize decarboxylation

General Decarboxylation Reaction
\[ R-\text{CH}_2\text{-COOH} + \Delta \rightarrow R-\text{CH}_3 + \text{CO}_2 \]

5. The degradation/decarboxylation products will investigated to understand their potential role in corrosion

6. More internationally sourced gas-oils will be included in the testing
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# TAN Phase IV Costs/Sample Preliminary Projections

<table>
<thead>
<tr>
<th>TEST PARAMATER</th>
<th>WITH DISTILLATION</th>
<th>WITHOUT DISTILLATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distillation</td>
<td>$18K</td>
<td></td>
</tr>
<tr>
<td>Autoclave Testing</td>
<td>$6K</td>
<td>$6K</td>
</tr>
<tr>
<td>SEM Coupon Testing</td>
<td>$2K</td>
<td>$2K</td>
</tr>
<tr>
<td>Speciation – S (3 options)</td>
<td>$1.0 - 1.5K</td>
<td>$1.0 - 1.5K</td>
</tr>
<tr>
<td>Speciation – Nap acid</td>
<td>$4K</td>
<td>$4K</td>
</tr>
<tr>
<td>Decarboxylation</td>
<td>$3K</td>
<td>$3K</td>
</tr>
<tr>
<td>Corrosion Impact</td>
<td>(Test ½ of samples)</td>
<td>(Test ½ of samples)</td>
</tr>
<tr>
<td>Decarboxylation By-Product Analysis</td>
<td>$2K</td>
<td>$2K</td>
</tr>
<tr>
<td>(Test ½ of samples)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Data compilation, Reporting Consulting</td>
<td>$6K</td>
<td>$6K</td>
</tr>
<tr>
<td>Miscellaneous</td>
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<td></td>
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<tr>
<td>TOTAL</td>
<td>$42K</td>
<td>$26K</td>
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</table>

Costs
Phase IV TAN Project
Nap Acid Speciation Options

Option N1.

C\textsuperscript{13}-NMR, FTIR, SimDist, and CHNOS elemental analysis $3160/smp

– Dettman proposal

Option N2.

FT-ICR-MS analysis $5000/smp

– U of F HMFL cost
Phase IV TAN Project
Sulfur Speciation Options

Option S1.

**Two(2) Dimensional GC**  $1K/sample

- Good speciation & detection limits at lower temps
- Likely just sulfur types at higher temps

Option S2.

**H2S Generation model**  $1.5K/sample

- Results not temperature (product range) specific
- Requires acceptance of the corrosion theory

Option S3.

**Synchrotron X-Ray**  $1.5K/sample

- Potential to speciate fully in any stream/solid
- Detection limits ~ 100 ppm
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Participants and Sample Proposals
TAN Phase IV
Participants List

Confirmed
✓ Suncor (merged with Petro-Canada)
✓ Petrobras
✓ BP
✓ NCUT

Interested
😊 Total
😊 Conoco Philips
😊 Chevron
😊 Cenovus (legacy Encana)
😊 MEG Energy
😊 ...add your name here
TAN Phase IV
Sample Proposals

• **Samples to be tested**
  – A function of number of participants
  – Seeking minimum of 6 commercial bitumens
  – Number of samples to be scaled according to available project funding (especially globals)
  – Increased corrosivity testing if suitable gasoil feed provided by participants

• **Share cost = $20K CAN (proposed)**

*Scope historically expanded should more participants join after project begins however direction setting established at start.*
TAN Phase IV
Sample Proposals

(Potential_candidate_samples)

1. Seal
2. Wabasca
3. Athabasca Bitumen (Suncor neat gasoil)
4. Christina Lake
5. Cold Lake
6. Western Canadian Select (WCS)

(Sulfur and blending dilution candidates)

- sweet synthetics (OSA/SYN)
- conventionals (MSW, USGC sours/heavies)
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....Questions?

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