Devils Tower (GOM) Crude

A Case Study in TAN Determination
• History of Devils Tower TAN

• Uses and Misuses of ASTM D664 TAN Test

• Potential Errors in D664 TAN Measurements
  - Devils Tower Examples
  - Sampling, Preparation and Testing

• Addressing Refinery Corrosion Problems

• Enhancing Value of High TAN Crude Oils
In June 2006, Williams Pipeline reported to Dominion that the Total Acid Number (TAN) of Devils Tower crude was 2.4 mg KOH/g. In July, a Gulf Coast refiner heard that it was 3.1.

Refiners purchasing South Louisiana Intermediate (SLI) began to do so at an increased discount to HLS. Some of the discount was associated with reduced gravity and increased sulfur content.

DEPI began a process to determine whether TAN readings were accurate and whether SLI crude was deserving of such a large discount.

Test results of combined crude and of individual wells at multiple labs created concerns about testing methodology due to repeatability and accuracy issues.
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History of Devils Tower TAN

- Quality control analysis found that labs were using different versions of ASTM D664 and that the sample preparation procedures were inconsistent or lacking.
- A consistent sample prep procedure was developed to reduce repeatability and reproducibility errors.
- Testing evolved to obtaining naphthenic acid measurements (Horvath-Gumulka and Carboxylic Acid Number) to directly measure the naphthenic acid content.
- Comprehensive crude assays were obtained for Devils Tower and South Louisiana Intermediate.
Intended Use of D664 TAN Test

Per ASTM D664-06 TAN is “the quantity of base, expressed in milligrams of potassium hydroxide per gram of sample, required to titrate a sample in a specified solvent to a specified end point”.

- 1.1 TAN test is intended for Petroleum Products and Lube Oils.
- 1.2 TAN used to indicate RELATIVE changes that occur under oxidizing conditions.
- 5.1 TAN used as a guide in quality control of lubricating oil formulations and a measure of lubricant degradation in service.
Refineries concerned about Naphthenic Acids that cause corrosion of carbon steel (at temperatures 450°-850°F).

- ASTM D664 test is used as a proxy for Naphthenic Acid test.
- Naphthenic Acid is generic name for organic acids in crude.
- TAN test measures all “mobile protons” in the oil
  - Some are very problematic (Naphthenic Acids)
  - Some are not as problematic
    - Esters
    - Phenolic compounds
    - Lactones
    - Resins
    - Agents such as inhibitors and detergents
Per ASTM D664-06

- 1.2 No general relationship known between bearing corrosion and acid number.

- 5.2 The test method cannot be used to predict corrosiveness of oil under service conditions.

- 5.2 No general correlation is known between acid number and the corrosive tendency of oil towards metals.
ASTM D664 is the industry standard (inexpensive test and puts burden of proof of its inaccuracy on the producer).

ASTM D664 TAN should be used as a screening test.
- Low TAN – No problems.
- High TAN – May or may not have problems.
  – Additional testing necessary.

Per SET Website
Crude oils with a TAN higher than 0.5 are considered to be POTENTIALLY corrosive between the temperatures of 450° to 750° F. However, there are many cases including high velocity, high TAN and others where this rule of thumb breaks down and correlating the TAN to corrosivity is still far from being reached.
Potential Errors in TAN Measurement

- Various Labs used different tests for TAN
  - ASTM D664-04
  - ASTM D664-01 (significantly different)
  - Titrilube Test Kit (never tested on crude oil)

- ASTM D664-06 is available (minor modification from –04)

- Other, less common test methods are ASTM D974, UOP565 and UOP587
Variation in ASTM D664 TAN Tests

Devils Tower XX Well

Different labs, different sampling, different preparation methods
Potential Errors in ASTM D664
Sampling & Preparation

- Samples should be taken free of additives if possible
  - Defoamer and other Detergents
  - Low Density Hydrate Inhibitor (LDHI)
  - Paraffin Inhibitors et cetera

- Samples should be adequately prepared
  - Water wash to remove solubles
  - Remove all water possible (heat, demulsifier, centrifuge)
  - Small amounts of impurities can dramatically affect TAN
ASTM D664 and 2 other acid tests were run on each sample.

ASTM D664 tests on assay samples indicated TAN between 1.0 and 3.5 mg KOH/g in all cuts from 450º to 850º F.

- **Horvath-Gumulka Test (Naphthenic Acid Number)**
  - Shell Global Solutions proprietary method of measuring crude acidity.
  - Devils Tower crude tested ~8000 ppm, of which 45% was free acid. This corresponds to an acid equivalent of 1.44 mg KOH/g.

- **Carboxylic Acid Number Test (CAN)**
  - Devils Tower crude corresponds to acid equivalent of 1.45 mg KOH/g.
Appropriate Use of TAN Test

No Problems

Screening test OK?

Appropriate screening test procedures?

Detail test OK?

WELL TEST OIL

Yes

Yes – run detail test

Retest

Address Issues

No
Protecting against corrosion from naphthenic acids requires either the use of corrosion resistant alloy materials in the overhead still columns or injection of a high temperature corrosion inhibitor.

- Measure Naphthenic Acid specifically using:
  - Horvath-Gumulka (SGS Proprietary Test)
  - Naphthenic Acid Titration (Baker Petrolite Test)

- While performing Crude Assay, at various cuts:
  - Measure TAN at each temperature
  - Assume ratio of Nap-acid to total TAN is constant
Two industry majors provided current information on acid discounts that are applied to high TAN crudes - based on refinery processing costs and market perception.

- **Technical Discounts**: $0.50 - $0.55/bbl per 1 TAN
  - Treating: $0.20/bbl
  - Segregation/Blending: $0.15 - $0.20/bbl
  - Metallurgy Investment: $0.15/bbl

- **Market Discounts**: $1.00 - $2.00/bbl per 1 TAN
  - Market Entry: $0.50/bbl
  - Hurdle Discount: $0.50/bbl

- **Expected Total Discount**: $1.00 - $2.55/bbl per 1 TAN
Obtain sufficient test oil for assays and follow-up testing.

Confirm that a high TAN is caused by Naphthenic Acid.

Work Closely with Refiners.

- Provide testing results before and after well completion.
- Convey value of crude (complete assay and comparison).
- Propose cost sharing for injection of corrosion inhibitors.
- Consider process changes to reduce charge rate & temp.
- Evaluate blending and lease of refining capacity.
- Consider cost sharing for upgrading construction materials (last resort).
Conclusions

● Retain large quantity of test oil from new wells
  - Add TAN testing process map to standard quality tests.
  - Insure comprehensive assays include TAN values in each cut.

● ASTM D664 TAN test is best used as a screening tool.
  - Controlled sampling, preparation and test procedures necessary.
  - High TAN from D664 does not always mean high corrosivity.
  - Precise Naphthenic Acid content not determined by ASTM D664.

● Work Closely with Refiners to maximize value of high TAN crudes.
Devils Tower TAN – A Case Study

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