SIMULTANEOUS SIMULATED DISTILLATION (CNS-SIMDIS) IN CRUDE OILS USING GAS CHROMATOGRAPHY

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Outline

- Why CNS-SIMDIS?
- Overview
- Scope & Performance
- Technical Information
- Benefits
  - Laboratory Personnel
  - Refinery Personnel
- Examples
- Q&A
Why CNS-SIMDIS Analysis?

Crude distillation optimization, it is about the dollars.

<table>
<thead>
<tr>
<th>Product</th>
<th>Price $/mt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphtha</td>
<td>423</td>
</tr>
<tr>
<td>Jet</td>
<td>464</td>
</tr>
<tr>
<td>Diesel</td>
<td>439</td>
</tr>
<tr>
<td>Gas oil</td>
<td>431</td>
</tr>
</tbody>
</table>

Temperature, Deg F

Liquid volume percent of crude
Why CNS-SIMDIS Analysis?

<table>
<thead>
<tr>
<th>Differentiator</th>
<th>Δ</th>
<th>Price effect*</th>
</tr>
</thead>
<tbody>
<tr>
<td>API</td>
<td>+1°</td>
<td>0.007 US$/$ Brent</td>
</tr>
<tr>
<td>Sulphur</td>
<td>+1%</td>
<td>-0.056 US$/$ Brent</td>
</tr>
<tr>
<td>TAN</td>
<td>+1 unit</td>
<td>-0.051 US$/$ Brent</td>
</tr>
</tbody>
</table>

Example:

1 barrel Crude
Brent price level = 50US$/barrel
+1% Sulphur
(All other parameters identical)

Expected price difference
-2.80 US$
→ 47.2 US$

* Crude Oil Price Differentials and Differences in Oil Qualities: A Statistical Analysis. ESMAP Technical paper October 2005

Quality (API & Sulfur) and production location define the price of a crude
Why CNS-SIMDIS Analysis?

- Regulations (Sulfur)
- Catalyst poisoning (Sulfur)
- FCC unit catalyst deactivation (Nitrogen)
- Salt formation (Nitrogen) - heat exchanger fouling or filter blockage

Negative impact on:
- Up-time
- Profit
- Process control
- Product value
Why CNS-SIMDIS Analysis?

- CNS provides key data
  - Fast quantified information on sulfur and nitrogen versus boiling point
  - Better understanding on input crude quality
  - Allows improved modelling and blending

- Improve production rates (lowering down-times)
- Decrease Cost of Labor
- Improve Refinery Profit
- Optimize value within specification (product giveaway)
Overview

• Gas Chromatography solution based on Simulated Distillation / Chemiluminescence Technology (SCD & NCD)
• Compares to ASTM D2887, D6352, D7500 and D7169
• Provides detailed Sulfur, Nitrogen and Carbon speciation boiling point information comparable to traditional Crude Assay information
  – Can provide a distribution of the components in various boiling point ranges, that total sulfur or nitrogen analyzers cannot do
• Analysis time <30 minutes for crude and crude final products
• Optional DHA FE Merge for <C9 information (151°C)
## Scope & Performance

<table>
<thead>
<tr>
<th>Analysis Scope</th>
<th>LOW TEMP CNS SIMDIS</th>
<th>HIGH TEMP CNS SIMDIS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comparable to</td>
<td>ASTM D2887, D3710, D7096, D7807, ISO3924, IP406</td>
<td>ASTM D6352, D7500, D6417, D7213, D7398 and D7169, EN15199-3, IP545 (DHA FE)</td>
</tr>
<tr>
<td>Sample Type / Range</td>
<td>Jet Fuel, Diesel</td>
<td>Distillates, Base Oils, Lube base Stocks</td>
</tr>
<tr>
<td>Carbon Number Range</td>
<td>C5-C44</td>
<td>C9-C90*</td>
</tr>
<tr>
<td>Boiling Point Range</td>
<td>FBP &lt; 538°C (1000°F)</td>
<td>IBP &gt; 151°C (304°F)</td>
</tr>
<tr>
<td></td>
<td>FBP &lt; 700°C (1292°F)</td>
<td></td>
</tr>
<tr>
<td>Sample Injection</td>
<td>Neat</td>
<td>1-2% dilution</td>
</tr>
</tbody>
</table>

### Analysis Performance

<table>
<thead>
<tr>
<th></th>
<th>LOW TEMP CNS SIMDIS</th>
<th>HIGH TEMP CNS SIMDIS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>S</td>
<td>N</td>
</tr>
<tr>
<td>Application Range**</td>
<td>50-10000 (ppmS wt)</td>
<td>100-10000 (ppmS wt)</td>
</tr>
<tr>
<td>Repeatability</td>
<td>&lt;10% RSD</td>
<td>&lt;10% RSD</td>
</tr>
<tr>
<td>Equimolarity</td>
<td>&lt;10%</td>
<td>&lt;10%</td>
</tr>
<tr>
<td>Selectivity</td>
<td>S/C: 5E7</td>
<td>S/C: 5E7</td>
</tr>
<tr>
<td></td>
<td>N/C: 2E7</td>
<td>N/C: 2E7</td>
</tr>
</tbody>
</table>

* With DHA FE addition (option)
** Depending on distribution / recovery of a sample

www.paclp.com
Technical Information

- **Simulated Distillation**
  - Cool on Column (COC) injection
  - A nonpolar (DB-1) gas chromatographic capillary column with 100% polydimethylsiloxane
  - Flame Ionization Detector (FID)
  - Sample preparation - 1-2% dilution solvent
  - DHA Front End Option for <C9 Merge (Separate GC)
  - Specialized reference standards and reference oils

- **Sulfur & Nitrogen Chemiluminescence Detector (NCD & SCD)**
  - Microfluidic splitter with constant split ratio to detectors
  - Post column vent

\[ R-S + O \rightarrow SO + \text{other products} \]
\[ SO + O_3 \rightarrow SO_2^* \rightarrow SO_2 + O_2 + h\nu \text{ (around 350 nm)} \]
\[ R-N + O_2 \rightarrow NO + CO_2 + H_2O \]
\[ NO + O_3 \rightarrow NO_2^* \rightarrow NO_2 + O_2 + h\nu \]
3 Channels Run Simultaneous from 1 injection

- Hydrocarbon
- Sulfur: 327 ppm S
- Nitrogen: 199 ppm N
Benefits - Refinery Personnel

• Unique, accurate and precise method to <10% RSD
  – Blending and process accuracy
• Less sample required
• Real time decision making <30 minutes analysis
• Accurate sulfur and nitrogen data for each carbon number or range
• Easy to read report with export functions for use with models and calculations
Benefits - Laboratory Personnel

- Minimal technician/chemist training
  - Sample preparation 1-2% dilution only with solvent
  - Prepared standards for purchase
  - Software does the rest
  - Software used for regular SIMDIS is used
- <30 minutes analysis time. Time saver!
- Easy to calibrate all-in-one
- Smaller laboratory footprint
- Less expensive
- Safety!
  - Smaller sample amount required
  - Dilution of sample is cyclohexane, isooctane or toluene, not CS$_2$