Untangling the Details of North Sea Crude Oil

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Publication date: 2018

Document Version
Publisher's PDF, also known as Version of record

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Citation (APA):
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Reservoir Fluid Characterization
A detailed knowledge of the molecular composition of crude oil and reservoir fluids is fundamental to understand its formation, physical properties and macroscopic behavior. Our objective is to study compositional changes that occur during recovery processes, and gain a better understanding of the underlying mechanisms on a molecular level. Additionally, parameters that correlates to maturity, biodegradation and oil genetics are employed to understand migration patterns. The results will provide input for computational models that links laboratory-scale enhanced oil recovery (EOR) experiments to theory, and ultimately field applications.

Sample Set
Chemical parameters were determined for a sample set consisting of 5 oils and 2 condensates from different fields and wells in the Danish North Sea. The condensates are visually distinguishable based on colour, and are lighter than the crudes which also is evident in the data.

Group-type Analysis
The crude oil samples show typical distributions of saturates and aromatics, with OIS4 having slightly higher content of polar components than the others. The two condensates show a high concentration of light hydrocarbons and monomethoxanes, however the SIMA distribution was not determined due to lack of method specificity for these type of samples. The oils have low asphaltene content and due to the high uncertainty associated with asphaltene precipitation at these levels, values are reported as ±0.5% without further specificity. The percentage of resin is back-calculated.

Maturity and Biodegradation
Semi-quantitative parameters used for maturity, biodegradation and oil source correlation are based upon peak area ratios and should be used with care. Issues such as co-elution, and integration parameters affect the data and interpretation and the values must be used in relation with others and as indices, not absolute facts. Compounds were identified by a combination of deconvolution of high-resolution data and comparison of retention using a reference sample (NGS N3-01) of known composition.

The alkane distribution is noticeable different between OIS1 and the other samples. Maturity parameters indicate that these oils are of similar thermal maturity, and the difference is likely due to biodegradation. Rates of Prn+C17 and PhnP+C18 adds further evidence, as biodegradation affects linear hydrocarbons before branched. OIS2 and OIS3 are the most affected samples. For the condensates, the distribution is shifted towards lighter hydrocarbons as expected. Only very low levels of saturated biomarkers were detected in the condensates, which indicates that evaporative fractionation / gas-condensate migration in the source has taken place.

Geochemical Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>CondS1</th>
<th>CondS2</th>
<th>OilS1</th>
<th>OilS2</th>
<th>OilS3</th>
<th>OilS4</th>
<th>OilS5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saturates (%)</td>
<td></td>
<td></td>
<td>59.5%</td>
<td>59.5%</td>
<td>62.3%</td>
<td>57.0%</td>
<td>61.5%</td>
</tr>
<tr>
<td>Resins (%)</td>
<td>7.1%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aromatics (%)</td>
<td>30.7%</td>
<td>25.9%</td>
<td>31.8%</td>
<td>31.9%</td>
<td>31.6%</td>
<td>32.0%</td>
<td>32.0%</td>
</tr>
<tr>
<td>Polycyclic Aromatic Hydrocarbons (PAH)</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
</tr>
</tbody>
</table>

Experimental Details

Solvent Selection
Crude oils and condensates were fractionated into saturated and aromatic hydrocarbons using Parameter's BAX solute phase extraction columns. The API column was conditioned with MeOH and it contains an internal reference of Crude Oil. Initial conditions were maintained with 1% MeOH and internal standards were added below the column. Isocratically eluted fractions were collected and used in the ISDB separation.

GC-MS
More recently, analyses were carried out using an Agilent 6890 gas chromatography coupled to a Varian 3500 GC-MS (field spectrometer). Components were separated on a 30 m (0.25 mm, 0.25 μm) DB-5MS column using a temperature program from 50 °C (3 min) to 300 °C (30 min) at 3 °C/min. The total run time was 30 minutes. Peaks were quantitative using a front detection curve prepared from reference standards measured in 50:50 Mix. Calculated chromatographic retention indices were calculated using representative factors from the gas chromatographic system. Isotopomer fractions were separated using a two-column combination of a 76mm column containing a reference mixture containing 29-30% isotope-labeled compounds and a 30m column containing a mixture of unlabeled hydrocarbons and polyaromatic hydrocarbons of linear and branched hydrocarbon. 150 samples were analyzed and each sample was run in triplicate.

Notes: Analytical Methods & Applications
SIMS Analyses were carried out on a Thermo Finnigan MAT 95 spectrometer ICP AP. Separation of saturated and aromatic hydrocarbons was carried out using a Thermo Scientific High Speed MCH column and a Refractive Index detector. Separations were carried out using a series of two butane-silica columns, each column packed in-house in the first column. Fractions were then eluted from the column by increasing the flow of butane with a mixture of hexane and 1% 2-propanol. A Philips 1000-1000 series was used in combination with a detection column for aromatics. For quantification, a limit dilution was used and decreasing dilution ratios were monitored until the response signal was below 0.5% of the maximum quantified response. The resulting fractions were obtained at 1°C in 24 hours. Aominal purity was achieved by filtration, followed with a trapping and direct injection into the GC-MS.

Quality Control
Two sets of blanks (ISDB and SIMS) were used as internal quality control during fractionation and analysis.