Untangling the Details of North Sea Crude Oil

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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
Geochemical 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 crude which also is evident in the data.

Group-type Analysis
The crude oil samples show typical distributions of saturates and aromatics, with OilS4 having slightly higher content of polar components than the others. The two condensates show a high concentration of light hydrocarbons and monosaccharins, however full SARA distribution was not determined due to lack of method specificity for these type of samples. The oils have low asphaltenic content, and due to the high uncertainty associated with asphaltenine 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 affects the data and interpretation and the values must be used in relation with others and as indications, not absolute facts. Compounds were identified by a combination of deconvolution of high-resolution data and comparison of retention using a reference sample (N250-N50-1) of known composition.

The alkane distribution is noticeable different between OilS1 and the other samples. Maturity parameters indicate that these oils are of similar thermal maturity, and the difference is likely due to slight biodegradation. Ratios of Pr/C27+ and Pr/C25+ add further evidence, as biodegradation affects linear hydrocarbons before branched. OilS2 and OilS3 are the most affected samples. For the condensates, the distribution is shifted towards lighter hydrocarbons as expected. Only very 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>Sample</th>
<th>CPI1</th>
<th>CPI2</th>
<th>CPI3</th>
<th>CPI4</th>
<th>CPI5</th>
</tr>
</thead>
<tbody>
<tr>
<td>OilS1</td>
<td>0.71</td>
<td>0.89</td>
<td>0.72</td>
<td>0.57</td>
<td>0.42</td>
</tr>
<tr>
<td>OilS2</td>
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<td>0.72</td>
<td>0.57</td>
<td>0.42</td>
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<tr>
<td>OilS3</td>
<td>0.71</td>
<td>0.89</td>
<td>0.72</td>
<td>0.57</td>
<td>0.42</td>
</tr>
<tr>
<td>OilS4</td>
<td>0.71</td>
<td>0.89</td>
<td>0.72</td>
<td>0.57</td>
<td>0.42</td>
</tr>
<tr>
<td>OilS5</td>
<td>0.71</td>
<td>0.89</td>
<td>0.72</td>
<td>0.57</td>
<td>0.42</td>
</tr>
</tbody>
</table>

Polyaromatic hydrocarbons in OilS3, where alkylated bicyclic aromatics are the major components. Insert shows region with methylphenanthrene isomers used as maturity indicators.

Experimental Details
Solid Phase Extraction
Crude oils and condensates were first fractionated into saturated and aromatic hydrocarbons using Paramagnetic Bond Elut solid-phase extraction columns. The SPE columns were conditioned with CH2Cl2, and the extracts were washed with a mixture of dichloromethane and acetone, and CH2Cl2. Extracted volumes were chosen based on polarity of samples, and internal standards were added to internal standards. Extract volumes were removed after a gentle spin, and evaporating to dryness in low temperature in order to avoid contamination. Each sample was processed and analyzed in their two replicates.

GC/MS
More quantitative analysis was carried out using an Agilent 7890B gas chromatograph coupled to an Agilent 5975C quadrupole mass spectrometer. Compounds were separated on an HP-5 column (30 m x 0.25 mm, 0.25 μm film thickness). The injection temperature was set at 230°C, and the temperature of the oven was 40°C. The oven temperature was programmed using a 2 min isotherm followed by a linear ramp to 300°C at 10°C min⁻¹. The transfer line was maintained at 320°C. Data were acquired using a 1-2 s full-scan cycle followed by a 12 s full-scan cycle. The data acquisition and processing were performed using Agilent Chemstation software.

Gas chromatograms were calibrated using a mixture of saturated hydrocarbons and polycyclic aromatic hydrocarbons of known concentration. 150 samples were analyzed in triplicate.

Separation, Chromatography & Analysis
SAR Analysis was carried out on a Bruker Optics 300 MALDI-TOF instrument. Separation of saturated and aromatic hydrocarbons was carried out using a Thermo Scientific High-Load HPLC and a Reverse Phase column. Separation of saturates and aromatics were accomplished using a linear gradient elution profile, where samples were heated rapidly to their boiling point. The reaction of interest was then slowed from the column by means of gradient elution using a mixture of dichloromethane and toluene. A Phenomenex P50 column was used to separate aromatics and toluene derivatives for aromatics. For quantification, a standard calibration curve was constructed for the macroparameters, aromatics and polycyclic aromatic hydrocarbons. Macroparameters were determined gravimetrically by dissolving 1% of crude oil in CH2Cl2.

Method (35°C) following addition of 0.1% formic acid to a 1% solution. The resulting solutions were stored at 1% C22 for 2 hours. Any precipitates were collected by filtration, washed with hexane and dried under nitrogen.

Quality Control
Two sets of internal calibration (90.90% and 90.90% 2795) were used as internal quality control during identification and analysis.