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 understanding 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 correlate to maturity, biodegradation and oil genetics are employed to understand migration patterns. The results will provide input for computational models that link 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 crudes 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 monoaromatics, however full SARA 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 affects the data and interpretation and the values must be used in relation with others and as indications, not absolute links. Compounds were identified by a combination of deconvolution of high-resolution mass spectra and comparison of retention using a reference sample (NIST N30-1) of known composition.

The alkane distribution is noticeable different between OES1 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/nPr and Ph/Pr show 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 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>Sample</th>
<th>Pr/Ph</th>
<th>Ph/n</th>
<th>-C18</th>
<th>a-C18</th>
<th>n-C18</th>
<th>Pr/nPr</th>
<th>Ph/nPr</th>
<th>Pr</th>
<th>Ph</th>
<th>Ts/(Ts/Tm)</th>
<th>STY/TeX</th>
<th>Aromatics</th>
<th>Lower and Upper</th>
<th>OilS2</th>
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<tbody>
<tr>
<td>OilS1</td>
<td>0.64</td>
<td>0.62</td>
<td>0.72</td>
<td>0.57</td>
<td>0.97</td>
<td>0.95</td>
<td>0.92</td>
<td>0.9</td>
<td>0.40</td>
<td>(0.71)</td>
<td>0.9</td>
<td>25.9%</td>
<td>12% 14%</td>
<td></td>
</tr>
<tr>
<td>OilS2</td>
<td>0.64</td>
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<td>0.95</td>
<td>0.92</td>
<td>0.9</td>
<td>0.40</td>
<td>(0.71)</td>
<td>0.9</td>
<td>25.9%</td>
<td>12% 14%</td>
<td></td>
</tr>
<tr>
<td>OilS3</td>
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<td>0.62</td>
<td>0.72</td>
<td>0.57</td>
<td>0.97</td>
<td>0.95</td>
<td>0.92</td>
<td>0.9</td>
<td>0.40</td>
<td>(0.71)</td>
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<td>25.9%</td>
<td>12% 14%</td>
<td></td>
</tr>
<tr>
<td>CondS1</td>
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<td>0.97</td>
<td>0.95</td>
<td>0.92</td>
<td>0.9</td>
<td>0.40</td>
<td>(0.71)</td>
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<td>12% 14%</td>
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<tr>
<td>CondS2</td>
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<td>0.97</td>
<td>0.95</td>
<td>0.92</td>
<td>0.9</td>
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<td>12% 14%</td>
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</table>

**Experimental Details**

**Solid Phase Extraction**

Crude oils and condensates were fractionated into saturated and aromatic hydrocarbons using Paramagnetic Bond Elut solid phase extraction columns. The SPE columns were conditioned with CHCl3, and 1 ml hexane, afterwards aliquots of crude or condensate were conditioned with neutral standards and loaded on the columns. Columns were washed with 1 ml of hexane following aliquots of standards using CHCl3. Extracted solvents were volatilised under a gentle stream of N2, avoiding evaporation in dryness to increase the yield of the extract. Each sample was processed and analysed in triplicate.

**GC/MS**

More recently, a fraction of the sample was used in an Agilent 7890B gas chromatograph coupled to a 5977B MSD (E/I) (110 eV) mass spectrometer. Compounds were separated on a 60 m, 0.25 mm, 0.25 μm film thickness column using a temperature gradient from 60°C (1 min) to 300°C (20 min) with a 10°C/min ramp from the zero min at 19°C. PAHs were quantified using a 5-point calibration curve prepared from reference standards measured in 5977B mode. Concentrations of alkylated biomarkers were indicated using response factors of the parent undecylated compound. Linear hydrocarbons were quantified using a 5-point calibration curve prepared from reference standards measured in 7890B mode. Concentration factors were measured at 4.177, 0.263, 2.097, 2.097, 2.097 and 0.263 nmol sample corresponding to a mixture of saturated hydrocarbons and polyaromatic hydrocarbons of linear hydrocarbons and saturated hydrocarbons over 100 nmol sample is more instrumental peak area.

**Separation, Determination, Formula & Apolarities**

MS/MS Analyses were carried out on a Sciex 5500 QTRAP with preparation EPI stage. Separation of saturated and aromatic hydrocarbons was carried out using a Thermo Scientific Hypercarb column and a Reverse Phase column connected in tandem. Separation and detection were operated by an ion of 6 minutes elution profile, where samples were heated in the first column. Result was then removed from the ion by reverse flow gradient station using a mixture of elution and 2.5% of added a mixture for 2 minutes. A photodiode array detector was used to detect saturated and 0.5% of the solvents is a mixture. The resulting fractions were eluted at 1°C for 2 hours. All the prepared samples were collected by filtration, neutral eluent, and sheet and copper-plate.

**Quality Control**

Two crude oils of known composition (DBS 101 and EOR Crude Oil) were used as internal quality control during identification and analysis.