Crude oil boiling point distribution by HT SIMDIS

- Accurate and reliable boiling distribution analysis of crude oil
- Crude oil analysis according ASTM D7169 & D7900 and EN15199 part 3 & 4
- Merge HT Simdis and DHA Front-end distillation results
- IRIS Simdis^{xlnc} & DHA^{xlnc} integrated software package

Keywords: Crude Oil, High-Temperature Simdis, DHA Front-End, Merge

Crude oil analysis:

Routine distillation tests are widely used to determine the boiling ranges of crude oils and their products. For crude oils, distillation curves are mostly determined using a combination of ASTM methods D2892 and D5239. ASTM D2892 determines the boiling point curve of stabilized crude oils up to 400 °C (752 °F). It uses a fractionation column with 14 – 18 theoretical plates, operating under a 5:1 reflux ratio. The residue obtained from this test may be further distilled using ASTM D5239, a vacuum Potstill method, which can determine the distillation curve for heavy hydrocarbon mixtures up to approximately 565 °C (1050 °F).

By using High-Temperature Simulated Distillation (HT Simdis, a gas chromatography-based method), a complete determination of the TBP (true boiling point) curve can be performed in considerably less time than a conventional true boiling point distillation and requires minimal operator involvement.

The accurate boiling point distribution analysis of a crude oil sample is a challenge due to:

1. Samples generally having a very wide boiling point range (<100°C to >750 °C)
2. API gravity ranges from light to heavy
3. Viscosity of sample

The main challenge is to get accurate results from the light fraction of the crude oil, due to the relatively high concentration of low boiling components and the quenching effect of the solvent to be used. This can be overcome by analyzing the crude oil not only on a HT Simdis (simulated high temperature distillation), but also on a detailed hydrocarbon analyzer known as a DHA front end analysis. On the DHA Front-end (DHA-FE), the light fraction of the crude oil (up to C9) is separated into its individual components, which are identified and quantified, and based on this result, the boiling point distribution is calculated. This result is merged with the Simdis data, resulting in an accurate and reliable boiling point distribution.

Standardization

Standardization committees such as ASTM, IP, and CEN have developed specific methods for crude to allow the merging of data from a separate DHA analyzer (the front end of a crude oil up to C9), with data from a High-Temperature SIMDIS analyzer, allowing improved accuracy for determining cut point intervals for the whole crude oil.

ASTM D7169: *"Standard Test Method for Boiling Point Distribution of Samples with Residues Such as Crude Oils and Atmospheric and Vacuum Residues by High Temperature Gas Chromatography"*

Paragraph 1.3 of the scope of the method highlights the recommendation for combining HT Simdis and DHA FE data:

> *"...in addition, quenching of the response of the detector employed to hydrocarbons eluting during carbon disulfide elution, results in unreliable quantitative analysis of the boiling distribution in the C4-C8 region. Since the detector does not quantitatively measure the carbon disulfide, its subtraction from the sample using a solvent-only injection and corrections to this region via quenching factors, results in an approximate determination of the net chromatographic area. A separate, higher resolution gas chromatograph (GC) analysis of the light end portion of the sample may be necessary in order to obtain a more accurate description of the boiling point curve in the interval in question as described in Test Method D7900...."*

EN 15199 part 3: *"Determination of boiling range distribution by gas chromatography method - Part 3: Crude oil"*

The scope of the method describes two procedures, with procedure B for combining High-Temperature Simdis with DHA Front-End data:

> *"Procedure B (or Dual analysis mode) combines procedure A with the boiling point distribution from C1 up to C9 using the Detailed Hydrocarbon Analysis (DHA) according EN 15199-4. The results of both analyses are merged into one boiling point distribution."*

Merge Principle

The AC Crude oil analyzer combines the results of DHA Front End (DHA FE) and High-Temp (HT) Simdis analyzers into one total true boiling point (TBP) report for the best performance in crude oil analysis.

A: HIGH TEMPERATURE SIMULATED DISTILLATION (ASTM D7169 & EN 15199 PART 3)

The technique of simulated distillation is based upon the assumption that individual components of a sample elute from a gas chromatographic (GC) column in order of their boiling point. The sample is introduced into a GC column that separates hydrocarbons based on their boiling point properties. The column temperature is raised at a reproducible rate, and the area under the chromatogram is recorded throughout the run.

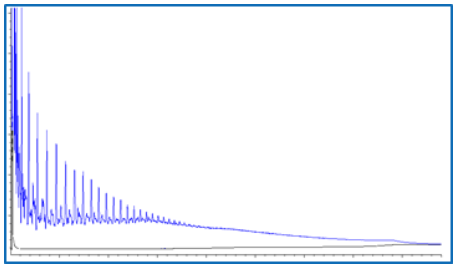
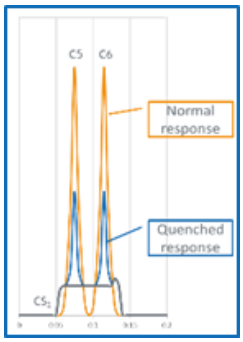


Fig 1: HT Simdis Crude oil chromatogram

Boiling temperatures are assigned to the time axis from a calibration curve obtained under the same conditions by running a known mixture of hydrocarbons covering the boiling range expected in the sample. From these data, the boiling range distribution is obtained.

The AC Simdis analyzers are configured with the AC Temperature Programmable Inlet (TPI), designed dedicated to Simdis. Use of the TPI results in a longer column lifetime as the TPI liner catch the residuals (like asphaltenes) that might be present in the sample which otherwise may deteriorate the column. The TPI is configured with a septum purge (to eliminate memory or carry-over) and does not show sample discrimination. The TPI in combination with the AC light-solvent optimized autosampler ensures excellent performance of the analyzer.

Figure 2: AC TPI



In High Temperature Simdis, the CS2 used as a sample diluent quenches the FID signal of the relatively volatile part of the sample (Figure x). As a result, data obtained from High Temperature Simdis has a slightly lower recovery in the initial fractions of the sample than may have been expected. Although it can be partially corrected for, the quenching also affects precision.

Figure 3: Quenching

B: DHA FRONT END ANALYZER (ASTM D7900 & EN 15199 PART 4)

Detailed Hydrocarbon Analysis (DHA) uses single column technology to determine the individual components in petroleum streams. Typically, a DHA is equipped with a split/splitless injector, sometimes a polar pre-column, a dimethyl silicone-coated capillary column and a flame ionization detector (FID). The long capillary column separates sample constituents, after which peak identification is performed by the DHAxlnc software. The identification is performed by comparing the calculated Kovats index for each peak in the chromatogram with the Kovats indexes in a large component database.

For crude oils, a DHA Front End is available which is with PTV inlet. The PTV inlet allows the light end of crude oils to be analyzed (up to C9), whilst the heavy end is backflushed thereby protecting the analytical system. The unique AC Front End solution is designed for robustness and prevents crude oils contaminating inlet tubing or EPC valves.

Quantification is based on an internal standard added to the crude sample before injection.

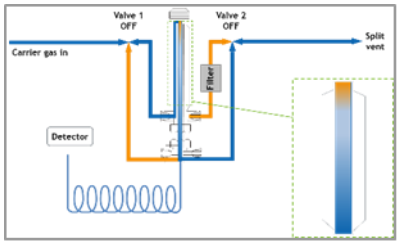


Figure 4a: DHA- FE injection

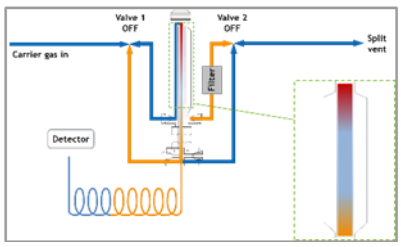


Figure 4b: DHA-FE separation

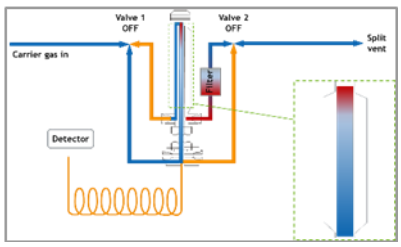
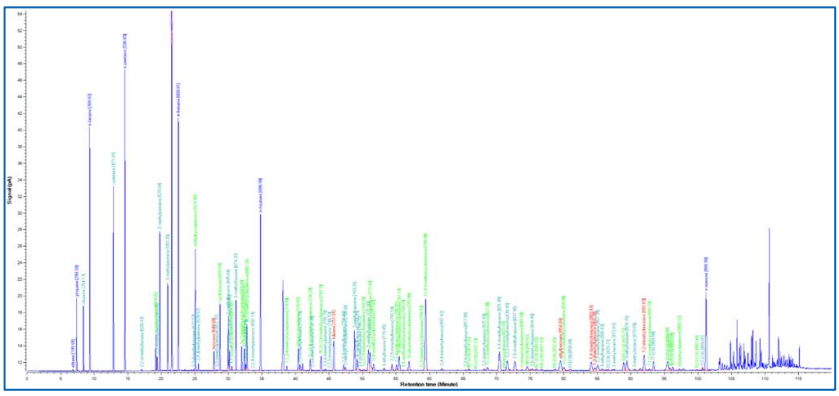


Figure 4c: DHA-FE backflush



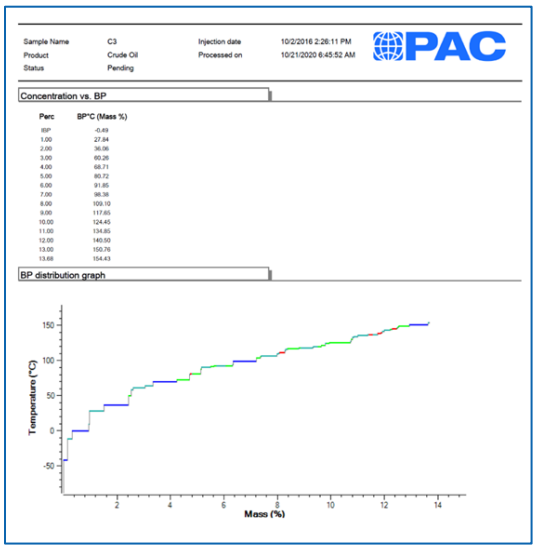


Figure 5: DHA-FE crude oil analysis chromatogram & report

MERGE SIMDIS & DHA DATA

The crude oil is analyzed on the HT Simdis and boiling point distribution and recovery are calculated by the SIMDISXLNC software from the pre-defined merge point (often C9 - 151 °C / 304 °F) onwards till either end-of-elution point or the last final calibration point (according the methods C100 - 720°C / 1328 °F).

In addition, the crude oil is analyzed on the DHA Front-End application. Components are identified and quantified (based on an internal standard calculation) by the DHAXLNC software, using this composition the boiling point distribution data is calculated up to and including the pre-defined merge point.

The DHAXLNC software makes this data automatically available for the SIMDISXLNC where the user can select the DHA boiling point data into the Simdis data. The software then calculates the merged data by first taking the light fraction boiling point curve (from the DHA) and then extends the curve by adding the Simdis boiling point data.

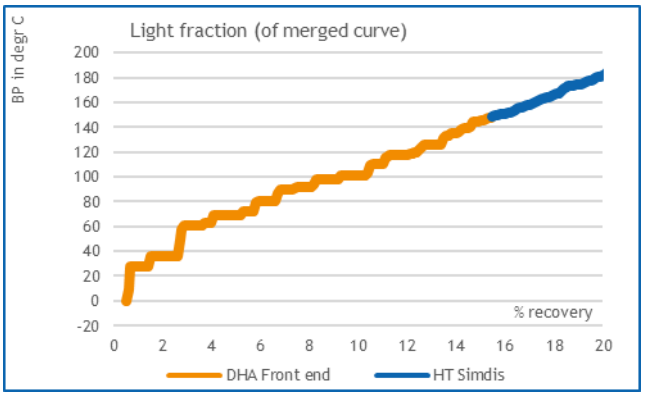


Figure 6a: Final boiling point curve after merge

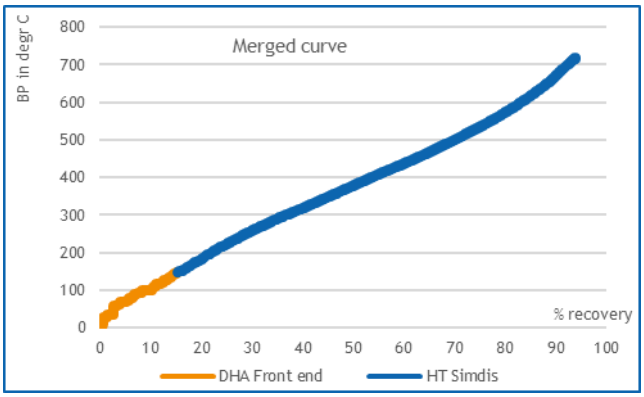


Figure 6b: Final boiling point curve after merge

Recovery is calculation by summing the DHA and Simdis recovery:

Total amount recovered = w1 + w2

Where:

- w1=fraction up to and including merge point (C9)
- w2=fraction from merge point (C9) till C100

Figure 7 shows the first part of a HT Simdis chromatogram with the DHA data merged. Indicated are:

- the IBP as calculated from the DHA data
- the merge point, the SIMDIS data is used from this point onwards
- in red the merged boiling point curve

In addition, the chromatogram demonstrates the used blank and normal paraffin calibration for the Simdis analysis.

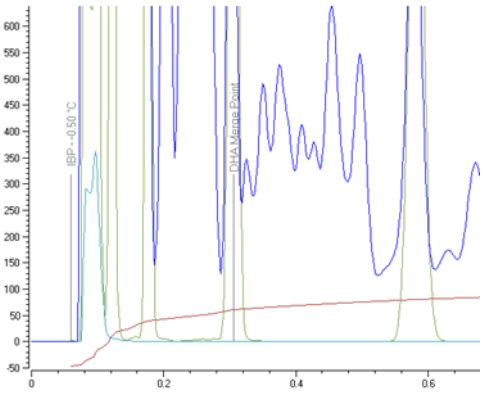
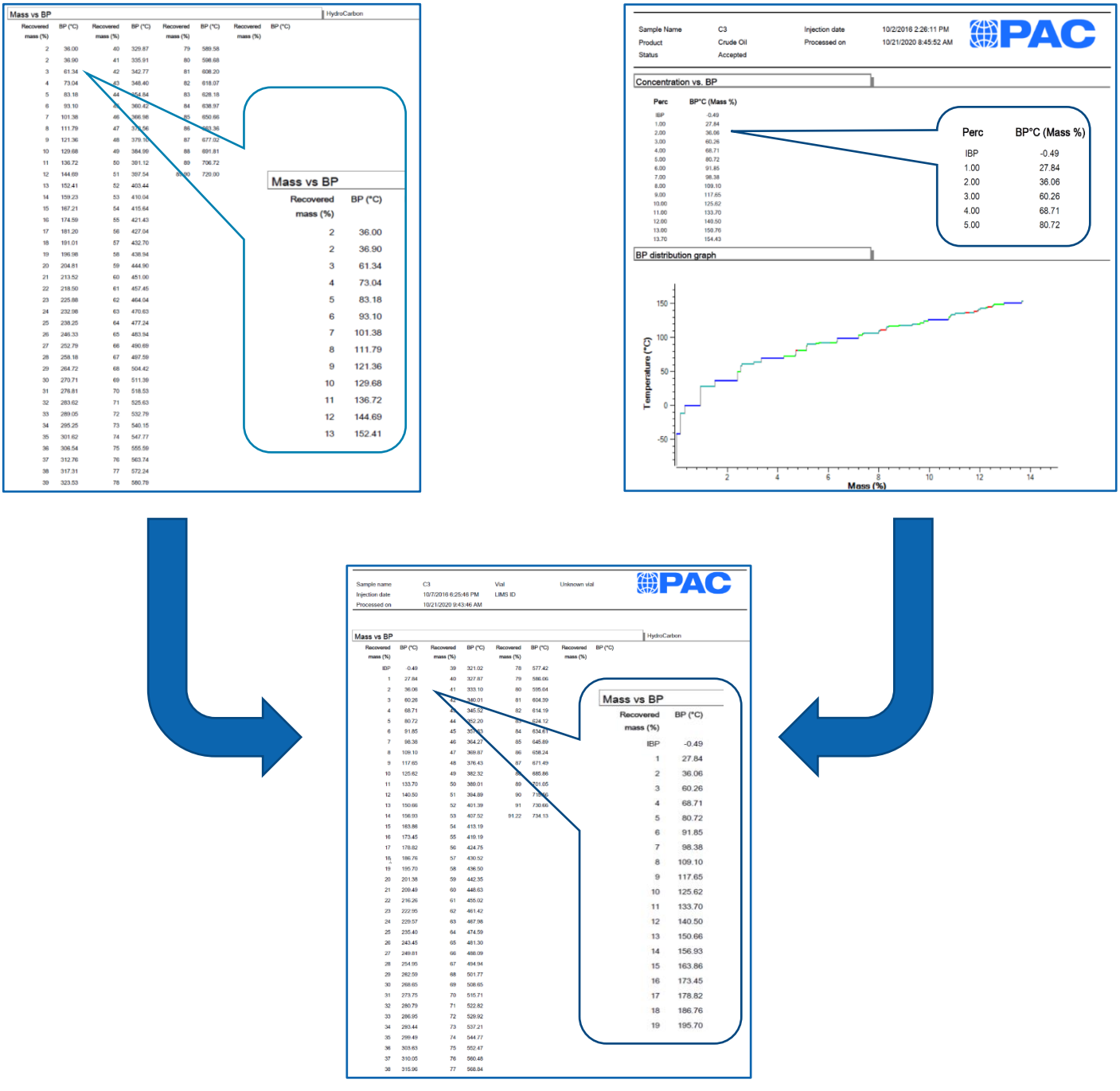


Figure 7: Merged Simdis chromatogram



Conclusion

Determining characteristics of the whole crude oil using an AC Crude Oil Analyzer improves accuracy and precision of data, reduces product giveaway, and creates models of the final product that are closer to the desired specification, while still meeting stringent product requirements. Using the merge option not only improves accuracy of the data, but also offers the user additional detailed information about the light fraction of the crude.

Determining characteristics of the whole crude oil using an AC Crude Oil Analyzer improves accuracy and precision of data, allowing for modelling final product closer to specs desired and ultimately less product giveaway, while still meeting stringent product specifications.

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