

Improve the Boiling Point Characterization of Crude Oil using the DVLS PetroReporter to merge the SimDist and DHA Data

Introduction

Reporting accurate Simulated Distillation (SimDist) data on the light hydrocarbons in crude oil is a challenge due to the quenching effects of the crude oil solvent. The solution to these effects is merging the Detailed Hydrocarbon Data (DHA) data with the SimDist results as standardized in the test method IP 601. This application note describes the merge of the DHA and SimDist data using the DVLS PetroReporter software.

Application Note

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Accurate Crude Oil Analysis

One of the most widely used SimDist methods to determine boiling point data in crude oil is ASTM method D7169; a High Temperature SimDist method applied to atmospheric and vacuum residues in refineries. A common issue of the D7169 method is the presence of Carbon Disulfide (CS₂) in the chromatogram and its quenching effects on C5-C6 hydrocarbons. As the high concentration of CS₂ reduces the detector sensitivity for hydrocarbons, the mass recovery data for the light-end of the crude oil will be inaccurate.

Some quantification software packages use a quenching factor to correct for the signal loss, however this factor strongly depends on the type of the crude oil. A better approach is to calculate the light-end boiling point curve of the crude oil based on a capillary GC analysis as described in the standard method IP 601. This method uses a DHA technique to calculate a boiling point curve for the naphtha fraction of the crude.

To automate the merge of the original SimDist boiling point data with the DHA light-end hydrocarbon analysis Da Vinci Laboratory Solutions (DVLS) developed the PetroReporter software. The software will implement the light-end data of the naphtha fraction into the Boiling Point curve of the crude oil and will generate a complete Boiling Point distribution report based on 2 different analyses, the DHA analysis and the SimDist analysis.

Application Description

To determine the DHA data for the light-end of crude oil Da Vinci Laboratory offers a dedicated DHA kit that complies with IP 601: a gas chromatography method for determination of light hydrocarbons in stabilised crude oil.

To characterize the boiling points of a crude oil DVLS composed the SimDist D7169 kit dedicated to High Temperature Gas Chromatography.

DHA Light-End IP 601 Kit	High Temp SimDist D7169 Kit		
 50-100 meter Capillary GC column fused silica 0.25 id Pre-column 	 Programmable on-column inlet Liners (0.53 mm) incl. flat seal Septa 9.5 mm Adapter-column 0.45-0.53mm ID columns 100% Graphite FID High Temp SimDist jet SR-AG-0.63/0.47 ul Syringe High Temp SimDist column 5 m x 0.53 id x 0.09 um 		
 Calibration samples: PIANO-1 Standard PIANO-P, PIANO Paraffins 	 Calibration samples: Light and heavy calibration samples: Stock SimDist Paraffin Solution C5-C28 Polywax 655 D7169 Reference oil samples 5010 		
PetroReporter Software	PetroReporter Software		

Table One: Content of DHA and SimDist Kits

Boosting Laboratory Efficiency

The PetroReporter uses predefined sample settings, component databases and formulas to provide a correct identification. On-screen editing enables analysts to customize the settings, for example drag and drop the calibration peaks in the on-screen chromatogram to optimize the n-alkane calibration. This will automatically update the analysis.

By clicking the analysis data in the on-screen property grid and correcting the parameters, the chromatogram displays both the uncorrected and corrected signal including the BP curve.

The PetroReporter sofware offers extensive options to report the petrochemical properties for the SimDist and DHA applications. Table Two lists the range of report options of the DVLS PetroReporter software.

The DVLS PetroReporter is compatible with all chromatographic data systems (CDS) of major suppliers including:

- Agilent EZChrom Elite 3.2, 3.3, 3.3.1 and 3.3.2
- OpenLab EZChrom A01.00
- Agilent ChemStation 04.01, 04.02, 04.03
- **OpenLab ChemStation A01.00**
- Other CDS systems on request •

Figure One: Chromatrogram of SimDist D7169 analysis of an Arab Light Crude Oil

DHA	A Report Options	SimDist Report Options		
	Individual components list PIONA report in wt %, vol% and mol% TBP Report in °C or °F in 5°C steps from IBP up to FBP Chromatogram plot of the peak labels over a user selectable time interval Properties summary: - Reid Vapor Pressure in psi at 100°F - Specific Gravity at 60/60°F - RON and MON - Gross and Nett Heat of Combustion of liquid in Btu/lb at 77°F (25°C) - Bromine Number Export of TBP data to merge SimDist results and improve the front-end analysis of crude oil Export to CSV, XLS or PDF	 TBP Distillation Percent report TBP Distillation Boiling Point report Alkane Profile report Volume Correlation report for (customizable) ASTM D86, ASTM D86/STI 577 or ASTM D1160 Chromatogram Flash Point report MOV report Noack Evaporation repor Export to CSV, XLS or PDF 		

iable Two: Report Options

SimDist ASTM D7169:

The SimDist application is based on a gas chromatographic method. A representative crude oil sample is introduced in to a GC that is configured with an temperature programmed controlled inlet and capillary column. A flame ionization detector converts mass to an electrical signal. The software accumulates the signal in slice mode.



A calibration mixture is used to develop a retention time versus boiling point curve. A reference oil is used to determine the detector response factor. The solvents signal is subtracted from the sample chromatogram to calculate the amount of sample recovered. After converting the retention times of the sample slices to temperature, the boiling point distribution can be calculated up to the recovered amount.

DHA IP 601:

A representative crude oil sample is introduced into the gas chromatograph (GC) equipped with a capillary column and a pre-column. The light hydrocarbon part up to n-Nonane is introduced into the capillary column, the pre-column backflushes the higher boiling components to vent. The carrier gas transports the vaporized light-end sample through the column, in which it is separated into the individual components.

At the end of the column the components are detected by a flame ionization detector (FID). Each peak is identified using the Kovats Retention Indices (RI). The RI of unknown peaks are calculated from:

- the retention time of the unknown peak
- the retention time of the n-paraffin eluting before and after the unknown peak.

The calculated RI is matched against a database in the software to identify the component. The concentration of each component in mass % is determined by normalization of the peak areas after correction with detector response factors. Unknown components are reported as a total unknown mass %.

Analytical Results

The first two minutes of the SimDist D7169 analysis (as shown in Figure One) are used for the DHA IP 601 analysis to identify the individual components up to n-Nonane (displayed in Figure Four).

The individual components are identified using a reference sample and a database of hydrocarbons. The boiling point up to and including n-Nonane is calculated.

The Simdist-DHA merge point can be chosen at the common used n-Nonane elution time or different using the PetroReporter software. The merged report will list both the SimDist, DHA and combined recoveries.

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Total Recovery Jsed Recovery Distribution Rec Mass% 1.0 2.0 3.0 4.0 5.0 6.0 7.0 6.0 7.0 6.0 7.0 8.0 9.0 10.0 11.0 12.0 11.0 12.0 11.0 11.0 11	v 94, v 94, on Report TBP °C -26,6 -9,2 -2,2 2,2 31,5 34,4 52,1 60,7 63,8 52,4 52,1 60,7 63,8 65,6 67,5 70,6 82,3 92,8 94,9 97,0 98,5 98,5	Rec Mass % 24.0 25.0 26.0 29.0 30.0 31.0 32.0 33.0 34.0 35.0 36.0 35.0 36.0 39.0 40.0 40.0 41.0	TBP °C 119,7 121,7 123,8 126,5 137,8 149,2 157,9 172,5 176,4 181,2 187,7 193,0 203,6 214,5 220,4 214,5 220,4 221,7 233,5	Rec Ma55% 48.0 49.0 50.0 51.0 52.0 53.0 55.0 55.0 55.0 57.0 58.0 57.0 58.0 57.0 58.0 60.0 61.0 61.0 62.0 63.0 64.0 65.0 65.0 65.0 65.0 60.0 61.0 65.0 60.0 61.0 65.0 60.0 61.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 60.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0 80.0	TBP °C 285.8 293.0 300.4 306.8 314.4 320.5 328.2 334.9 349.6 356.7 365.1 372.5 380.1 372.5 380.1 388.8 396.4 404.4 412.3	Rec Moss% 72.0 73.0 74.0 75.0 76.0 77.0 80.0 81.0 82.0 83.0 84.0 85.0 86.0 85.0 86.0 87.0 88.0 89.0 90.0	TBP °C 472,7 492,4 502,8 514,2 526,3 538,8 548,9 558,5 568,3 578,4 558,5 568,3 578,4 588,7 599,6 610,9 622,6 634,8 647,3 660,8 647,3
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Figure Two: Report of the Merged SimDist and DHA analyses of an Arab Light Crude Oil

Figure Three: PetroReporter provides direct Access to Merge point and Data File information

maysis	C. VChemoz Normalist D / 165 VChadewerge VCalib.D
✓ Carbon	
Total Area	2511029.75
Recovery Style	DHA Merge
Response standard	C:\Chem32\Simdist D7169\CrudeMerge\Ref.D
Response Factor	1.66036693E-06
Found Recovery	94.26639
Used Recovery	94.26639
Start Search	ASTM / IP / ISO / EN
Start	0.21667
End Search	ASTM / IP / ISO / EN
End	39.29833
Blank	C:\Chem32\Simdist D7169\CrudeMerge\Solvent.D
⊿ DHA Merge	
Analysis	C:\Chem32\DHA D6730\CrudeMerge\CrudeMerge 1.D
Merge Point	151
Merge recovery	29.2223225
Sample Preset	
Name	CrudeMerge
Туре	Sample
Peak Response	None
✓ Solvent	
Start Time of Solvent	0
End Time of Solvent	0



Figure Four Chromatogram of the DHA Analysis of the light hydrocarbons in an Arab Light Crude Oil

The DVLS PetroReporter software enables analysts to improve the boiling point characterization of crude oils through a merge of the High Temp SimDist and a capillary GC (DHA) analyses. As a result refiners have a better control of the naphtha yield for any crude oil source. The universal software setup, the predefined settings and extensive report options automate the data processing of the SimDist and DHA applications.

References:

ASTM D7169 – 05: Standard Test Method for Boiling Point Distribution of Samples with Residues Such as Crude Oils and Atmospheric and Vacuum Residues by High Temperature Gas Chromatography1

IP 601-12: Determination of light hydrocarbons in stabilized crude oils - gas chromatography method

ASTM D5134 - 98(2008)e1: Standard Test Method for Detailed Analysis of Petroleum Naphthas through n-Nonane by Capillary Gas Chromatography

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