OIL AND GAS

APPLICATION NOTE

Chromatec GC SimDist analyzers by test methods ASTM 6352, 7169, 7213

Overview

Determination of fractional composition of medium and heavy distillates and crude oil is essential for refinery and monitoring of final product parameters.

The techniques used to determine light distillates are widely spread, while determination of heavy distillates offer the opportunity of seeing the big picture of oil fractional composition.

Short capillary column with thin film of stationary liquid phase (0.1 μm) enables the elution of hydrocarbons up to C100.

Analysis method ASTMD6352 is suitable for oil distillates with boiling range from 174 °C to 700 °C (from C10 to C90) and involves plotting the boiling curve based on high temperature gas chromatography analysis.

Analysis method ASTMD7169 is suitable for oil and its residues after atmospheric (residual fuel oil) and vacuum distillation (oil tar) with boiling temperature up to 720 °C (C100).

Analysis method ASTMD 7213 is suitable for oil distillates with boiling range from 100 °C to 600 °C and involves plotting the boiling curve based on gas chromatography method.

Analysis methods

1. ASTM D 7169-11. 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
2. ASTM 6352-12. Standard Test Method for Boiling Point Distribution of Petroleum Distillates in Boiling Range from 174 to 700 °C by Gas Chromatography
3. ASTM D7213-2015. Standard Test Method for Boiling Range Distribution of Petroleum Distillates in the Boiling Range from 100 °C to 615 °C by Gas Chromatography.

Instrument configuration

- Gas chromatograph Chromatec-Crystal 9000
- Capillary column CRmx-1HT SimDist Column, 5*0.53*0,1 #388-140224 or similar (D7169)
- FID detector
- Programmable inlet (“fan cooling”), cryogenic cooling is available by request
- LCO2 or LN2 oven cryogenic cooling option* (**)
- Autosampler AS-2M (P/N 400-0202) incorporating syringes with 51mm needle length. For better sample storage, Autosampler AS-2M (3D) (P/N 400-0501) with optional Cooling/heating tray (P/N 400-0594) and a chiller recommended.
- Chromatec Analytic software and Chromatec SimDist application software

*required for ASTM 7169-11 method only.

** Liquid CO2 as cryo-agent required for operation (see recommendations below).

Operating mode

(referred to D7169 test method)

Chromatograph			
Analysis time		40 min	
Column			
Carrier-gas flow		20 ml/min	
injection type		Cool on-column	
Column temperature		0 min	15 °C/min
Isotherm 1	20 °C	5 min	
Isotherm 2			
425 °C			
Inlet			
Inlet temperature			
Isotherm 1	50 °C	0 °C	15 °C/min
Isotherm 2			
425 °C			
FID detector			
Hydrogen flow rate		25 ml/min	
Air flow rate		250 ml/min	
Detector temperature		425 °C	
Syringe			
Capacity		10 µL (540-1152)	
Needle length		51 mm	
Sample size		0.2 uL	

Experiment

All SimDist methods involve cool on-column injection with programmable heating of the inlet. Such a method provides an accurate injection of the sample avoiding discrimination of components. The column oven and the inlet are programmed linearly at the same speed.

Polywax 655 or Polywax 1000, the mixture of normal paraffin hydrocarbons C5-C100 or up to C120 respectively, it is used for retention time calibration, linking the peaks to time-boiling temperature curve. See chromatogram on Figure 1.

Carbon Disulfide (CS2) used for sample dilution following test methods procedures.

Thanks to high performance of Unitary Electronic Pneumatic Control (UEPC) incorporated into GC, high accuracy in setting flow and pressure keeps excellent stability in retention time repeatability. Figure 2 shows fragment of 8 overlaid repeatable injections of Polywax 655 sample.

Capillary column separation performance is observed by evaluation of separation C50 – C52 normal paraffins. The resolution value shall be between 1.8 and 4.0 (see Figure 2).

Typical blank run is demonstrated on Figure 4. This displays baseline drift subtracted from standard reference Oil 5010 standard.

The external standard Reference Oil 5010 is used to determine the non-distilled residue oil residue according to ASTM D7169. The standard chromatogram is shown on Figure 5. Absolute detector response factor is defined basing on overall standard peak area. The amount of non-distilled oil residue is defined by comparing the concentration of prepared solution with the calculated concentration.

All procedures automatically processed in Chromatec Analytic and Chromatec SimDist software.

Typical chromatogram of crude oil sample is shown on Figure 6.

Chromatec SimDist software report includes the following tables: Boiling point distribution (yield at temperature and Temperature at yield), distillation curve and non-distilled residue (%), Group and Fractional composition, Components composition by normal Paraffins (Figures 7 – 10). Chromatec SimDist software calculations and report comply with a range of SimDist GC test methods: ASTM D2887, D5307, D6352, D7213, D7169.

Conclusion

Knowledge of composition of residual fuel oils, oil lubricants and other heavy petroleum products is critical when defining the output of light hydrocarbons, optimizing refinery processing and testing products quality. GC Simdist analyzers suggest simple and automated analysis procedure in a short time with a good run-to-run repeatability and comprehensive report; it is a good advantage comparatively to traditional labor methods D86, D1160.

Chromatograms

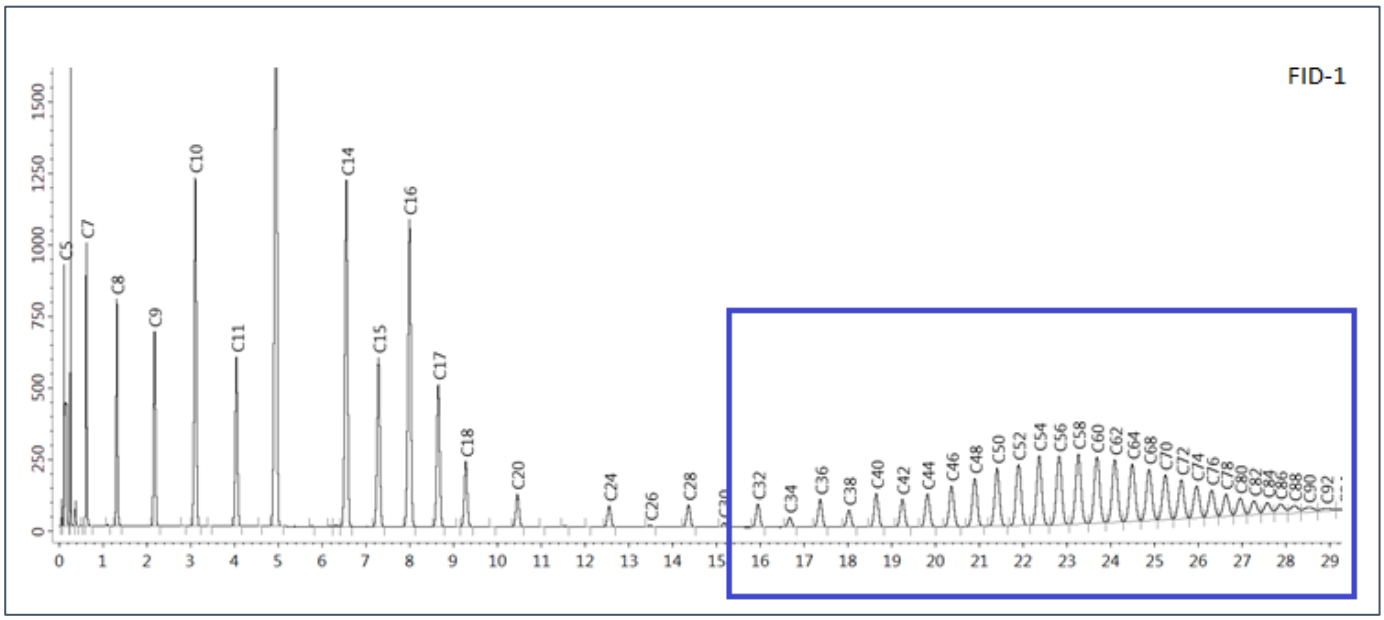

Figure 1. Polywax 655 retention time calibration mix

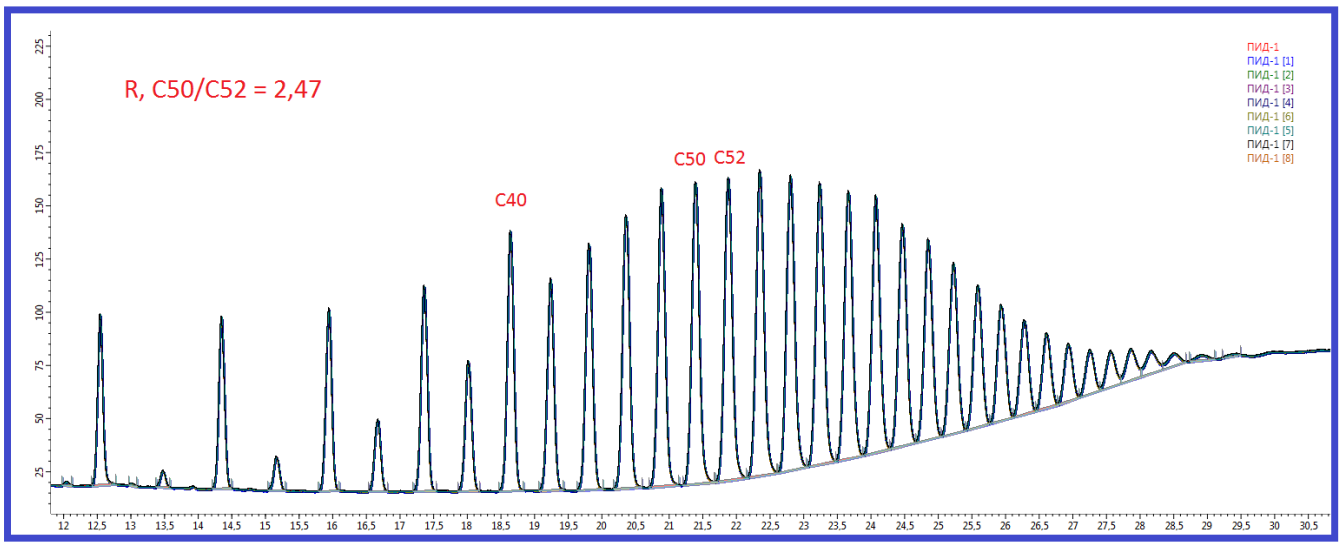

Figure 2. Retention time stability and separation of C50/C52 peaks

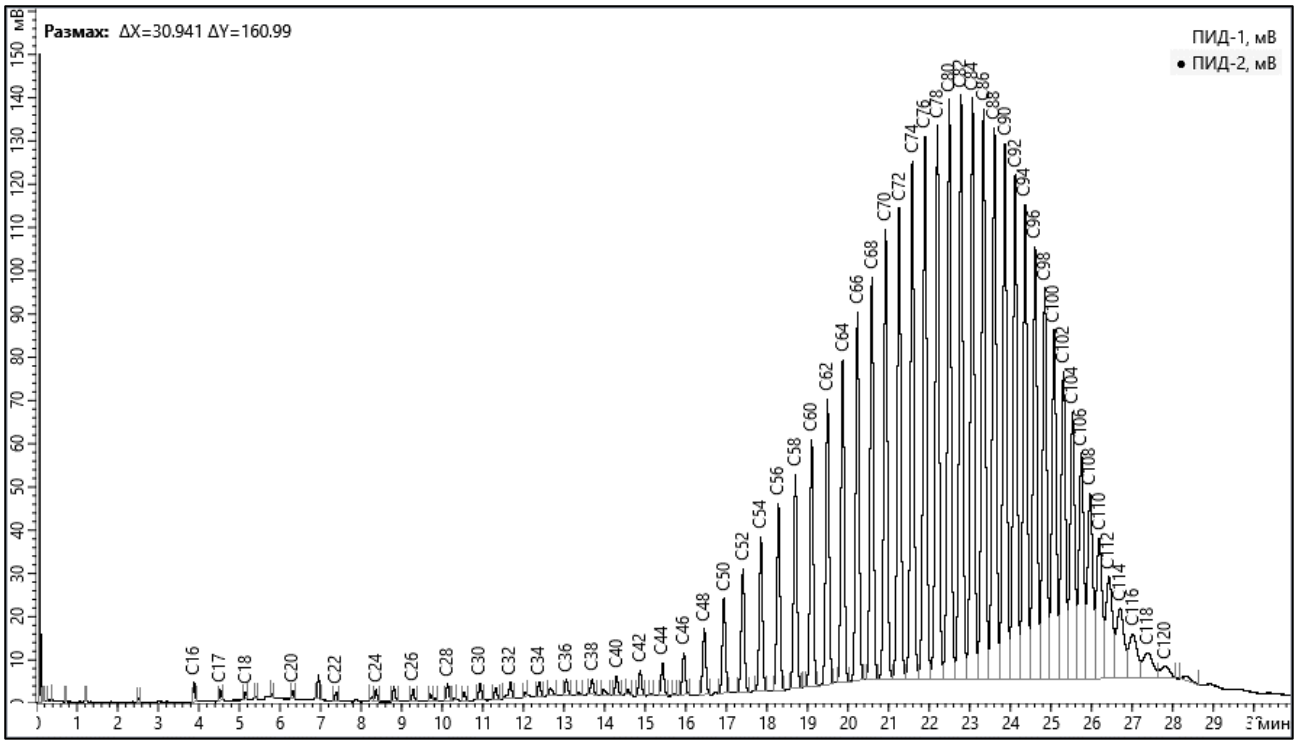

Figure 3. Polywax 1000 retention time calibration mix

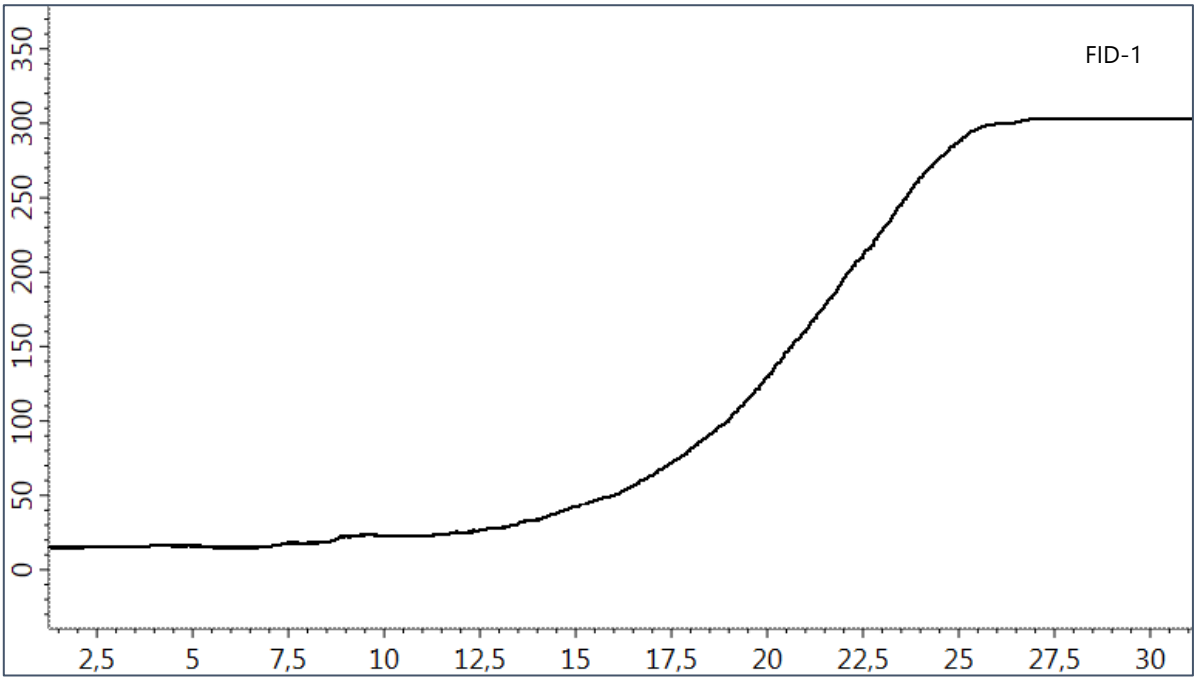

Figure 4. Blank run chromatogram

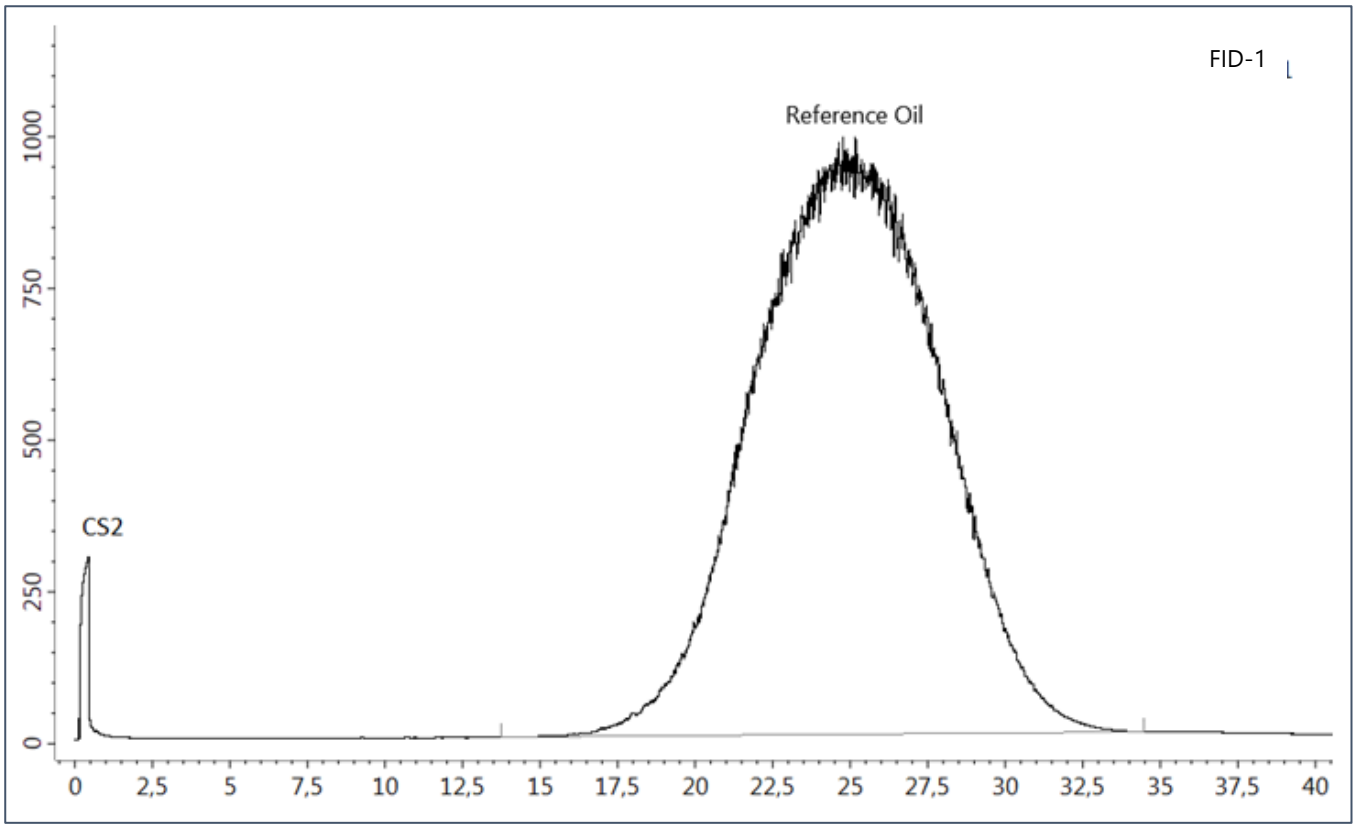

Figure 5. Reference Oil 5010 standard chromatogram

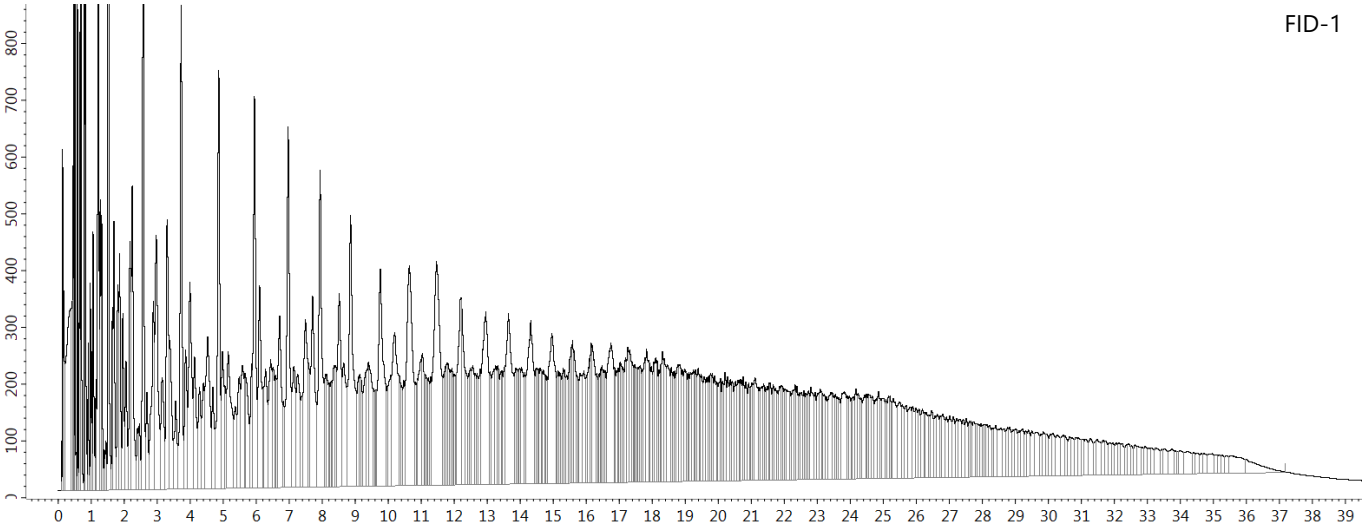

Figure 6. Typical crude oil chromatogram after subtraction baseline

Yield at temperature

Temperature, °C	% OFF
0.0	0.000
40.0	0.248
80.0	2.455
120.0	6.810
160.0	13.139
200.0	20.085
240.0	27.485
280.0	35.190
320.0	43.573
360.0	51.206
400.0	58.610
440.0	66.107
480.0	72.997
520.0	79.517
560.0	85.474
600.0	90.168
640.0	93.493
680.0	95.787
720.0	96.837

Temperature at yield

% OFF	Temperature, °C
0.0	34.51
0.5	46.17
20.0	199.45
40.0	303.10
60.0	407.46
80.0	522.77
96.8	710.16

Residue: 3.16265

Figure 7. Reports examples: Boiling point distribution table

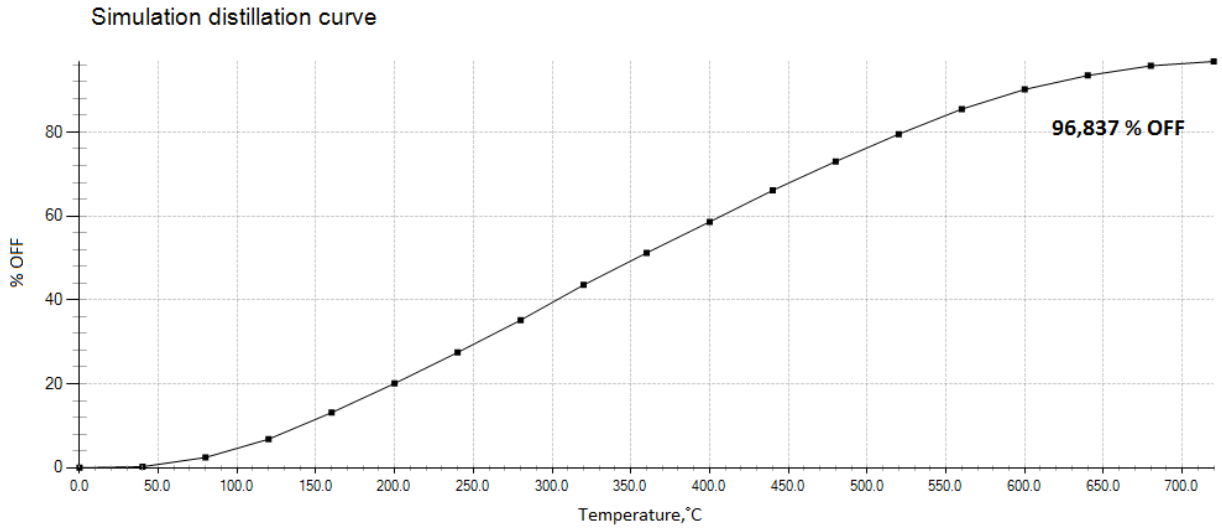

Figure 8. Reports examples: Distillation curve

Group composition of the high-boiling fractions

Group	Mass %
C5	0.0812
C6	1.9356
C7	2.0649
C8	3.7091
C9	4.0121
C10	4.0395
C11	3.7684
C12	3.6360
C13	3.7910
C14	3.6299
C15	3.5577
C16	3.0008
C17	3.1561
C76	0.3698
C78	0.2963
C80	0.1850
C82	0.2083
C84	0.3226
C86	0.1067
C88	0.1118
C90	0.4395

Fractional composition

Temperature, °C	Mass %
0.0 - 40.0	0.2480
40.0 - 80.0	2.2065
80.0 - 120.0	4.3560
120.0 - 160.0	6.3281
160.0 - 200.0	6.9467
200.0 - 240.0	7.3999
240.0 - 280.0	7.7047
280.0 - 320.0	8.3836
320.0 - 360.0	7.6326
360.0 - 400.0	7.4041
400.0 - 440.0	7.4964
440.0 - 480.0	6.8907
480.0 - 520.0	6.5199
520.0 - 560.0	5.9568
560.0 - 600.0	4.6941
600.0 - 640.0	3.3245
640.0 - 680.0	2.2940
680.0 - 720.0	1.0508

Figure 9. Reports examples: Fractional and Group composition

Components

Component Name	Mass %
C5	0.0812
C6	0.3217
C7	0.6489
C8	0.8623
C9	0.9622
C10	0.9818
C11	0.9601
C12	0.9349
C13	1.0763
C14	1.0725
C15	1.2149
C16	1.1623
C17	1.3494
C84	0.1170
C86	0.0490
C88	0.0567
C90	0.2080

Figure 10. Reports examples: Individual components composition

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