

Improving Accuracy and Precision in Crude Oil Boiling Point Distribution Analysis

Abstract

High Temperature Simulated Distillation (High Temp SIMDIS) is one of the most frequently used techniques to determine the boiling point range of an entire crude oil range. Accuracy of data for this analysis play a key role in determining crude oil value and it is an excellent tool for decision-making during the refining process in order to improve yields and also enhance the quality of the final product. High Temp SIMDIS is a very good fit for estimating and quantifying the amount of these products present in crudes due to being a robust Chromatography technique that requires minimum operator involvement and a very small sample amount compared to other techniques for boiling point distribution determination. These together with other reasons, like high precision, good repeatability of results, and automation, make High Temp SIMDIS an easy alternative for refineries, independent testing labs, transportation companies, and pipelines to analyze and obtain an accurate and precise assessment of their crudes boiling range. However, High Temp SIMDIS on its own, presents a challenge due to the broad range of its analysis. The challenge is the identification in the front part of the chromatogram, where the light portion resides. As dilution of Crude samples with CS₂ is needed, this creates a “Quenching” effect in the CS₂ region, causing an unreliable boiling point data around the CS₂ peak. In order to overcome this light-end analysis hurdle, a technique known as DHA Front-End is used to better evaluate the components and boiling point curve in this region. Analysis between just High Ttemp SIMDIS versus High Temp SIMDIS/DHA-FE will be compared in order to visualize the differences and show the value that the merged analysis has to offer to the Oil Refining Industry.

Introduction

It is not a secret that the most valuable cuts of the crudes are present in the lighter part of them, where primarily gasoline, kerosene, diesel and jet fuel are obtained. These “essential” products play a vital role in the worldwide economy, where the cost involved in producing them can vary greatly depending on the crude source.

Accurate analysis of crude oil samples is always a challenge due to:

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

Background Information

Back in the 1960's, SIMDIS was known as a gas chromatography (GC) technique capable of simulating the lengthy and timely consuming physical distillation TBP technique. In 1973, the SIMDIS technique capable to analyze streams between Hydrocarbons of C₅ and C₄₄ (jet and diesel range) was born. It became an ASTM standard method known as D2887. Later, High Temp SIMDIS made its appearance making it possible to analyze heavier streams, like crude oil, covering a boiling range from C₅ to C₁₂₀. Many laboratories around the world were using it successfully and back then it was simply known as High Temp SIMDIS. It eventually (in 2005) became ASTM method D7169.

The implementation and introduction of a dedicated inlet, like the PTV (Programmable Temperature Vaporizer), has been crucial for the accuracy of data and integrity of analysis as using other inlets with split injection caused severe problems by discriminating sample.

Comparison of Analysis between HighTemp SIMDIS and DHA-FE merge

Simulated Distillation (SIMDIS) analysis provides the true boiling point (TBP) distribution of petroleum streams. The SIMDIS analyzer used is based on packed or capillary gas chromatography hardware with an additional dedicated SIMDIS mode kit. In this case, the boiling point range provides sample distribution information in the range from ambient to 720°C (C₅-C₁₀₀). This analysis report can be found on Fig 2.

When performing SIMDIS analysis, a sample is introduced into a GC column that separates hydrocarbons in boiling point order. The column temperature is raised at a reproducible rate, and the area under the chromatogram is recorded throughout the run. 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.

DHA-FE is a technique where the entire crude is injected into a GC with a pre-fractionator. The roll of the pre-fractionator is to retain the heavies and allow the light compounds to pass through and be subsequently analyzed into a 50 mt. long capillary column, where all the light components are separated and individually identified/quantified using a Flame Ionization Detector. Column with different dimensions can be used, especially when running similar DHA-Combi systems that are equipped with a pre-fractionator.

Baseline Compensation, Calibration & Validation

To meet the performance requirements of the application, a baseline compensation analysis, a boiling point calibration, and validation must be performed.

A baseline compensation analysis, or baseline blank, is performed under the same operation conditions as an analysis. Performing a blank analysis is necessary due to the usual occurrence of chromatographic baseline instability (column bleeding).

A calibration mixture containing a series of known n-Alkanes and, in some cases, aromatics must be used to establish the correlation between retention time and distillation temperature. The calibration mixture must cover the complete boiling range of the sample to be analyzed and must contain at least one component boiling below and one boiling above the range of the sample. N-Alkanes which are not found will be interpolated or extrapolated with the exception of n-Alkanes with a boiling point before the first found n-Alkane component. The extrapolated times are only valid for Alkanes eluting in the temperature programmed area of the analysis. A boiling point calibration curve is plotted in the report.

To verify both the chromatographic and calculation processes involved, a reference sample analysis should be performed. The results of this analysis must comply with specified target values. The boiling point distribution data provided for the reference samples have been generated by validating the data through an interlaboratory study.

The gravimetric blend sample is used for a detector response check. This blend consists of a lower boiling fraction and a higher boiling fraction with a baseline in between. Both fractions should have a similar height and the ratio between the fractions must be constant. Together with the resolution and peak skew, this is a diagnostic tool when the system does not meet the reference oil specification.

The crude assay analyzer uses a combination of a SIMDIS High Temperature analysis from C9-C100 (D7169) and DHA Front-End analysis for C1-C9 ((D7900)). The boiling point results are merged in the SIMDIS software creating the most accurate recovery calculation for the crude oil samples.

Report of High Temp SIMDIS

The report shown below has been generated by a High Temp SIMDIS analyzer, starting at ambient temperature.

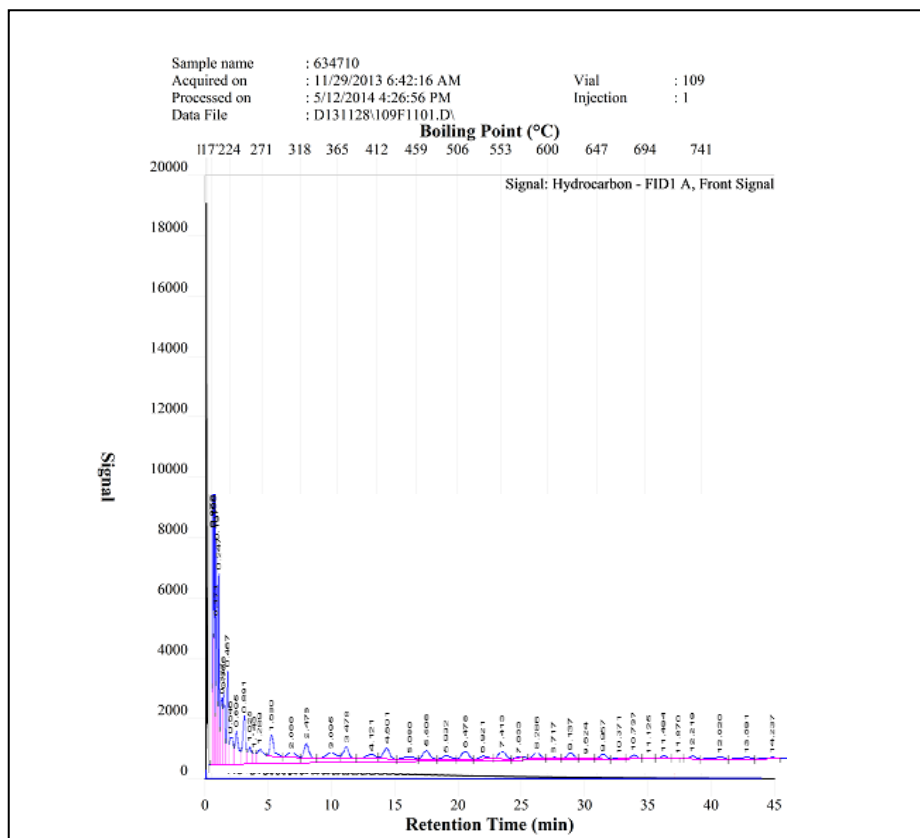


Figure 1 - Crude Oil Chromatogram

BP Distribution table - Percent

Recovered mass%	BP °C	Recovered mass%	BP °C	Recovered mass%	BP °C	Recovered mass%	BP °C
4.5	36.0	28.0	179.8	52.0	298.8	76.0	436.4
5.0	59.0	29.0	185.4	53.0	302.8	77.0	443.2
6.0	59.0	30.0	191.0	54.0	308.4	78.0	450.4
7.0	75.0	31.0	196.2	55.0	313.8	79.0	458.0
8.0	89.0	32.0	199.0	56.0	317.4	80.0	465.8
9.0	89.0	33.0	204.4	57.0	323.4	81.0	473.8
10.0	89.0	34.0	209.8	58.0	329.2	82.0	482.0
11.0	100.2	35.0	216.0	59.0	333.2	83.0	490.6
12.0	106.0	36.0	218.4	60.0	339.6	84.0	499.8
13.0	111.8	37.0	224.4	61.0	344.6	85.0	509.4
14.0	117.4	38.0	229.0	62.0	350.2	86.0	519.6
15.0	123.2	39.0	234.8	63.0	356.0	87.0	530.4
16.0	127.2	40.0	238.0	64.0	361.4	88.0	541.8
17.0	131.4	41.0	245.0	65.0	367.6	89.0	554.4
18.0	138.0	42.0	249.4	66.0	373.0	90.0	567.4
19.0	140.2	43.0	254.0	67.0	379.4	91.0	582.2
20.0	144.4	44.0	257.8	68.0	385.2	92.0	597.8
21.0	151.0	45.0	264.0	69.0	391.6	93.0	615.8
22.0	153.6	46.0	269.0	70.0	397.8	94.0	637.4
23.0	159.0	47.0	272.0	71.0	403.8	95.0	664.2
24.0	163.4	48.0	278.0	72.0	410.4	96.0	703.4
25.0	167.0	49.0	283.6	73.0	416.6	96.3	719.6
26.0	173.2	50.0	287.8	74.0	423.0		
27.0	175.4	51.0	293.4	75.0	429.8		

Table 1 - HT Simdis Boiling Point Table

From the report we can clearly see that the sample has an initial boiling point of 36°, which is the boiling point of the first N-Paraffin calibrating the system. It also determines a recovery of 96.3%, which indicates there is still material

eluting above the last calibrated point, in this case 720°. At the same time, in the front portion of the Chromatogram, it appears to be some sample eluting below C5, but it is hard to analyze with just High Temp SIMDIS.

Report of DHA-FE

The same sample was analyzed by using the DHA-FE technique. This analysis will report the boiling point distribution table (Figure 3). DHA-FE also generates a composite report with group type and carbon number information better known as a PIONA report.

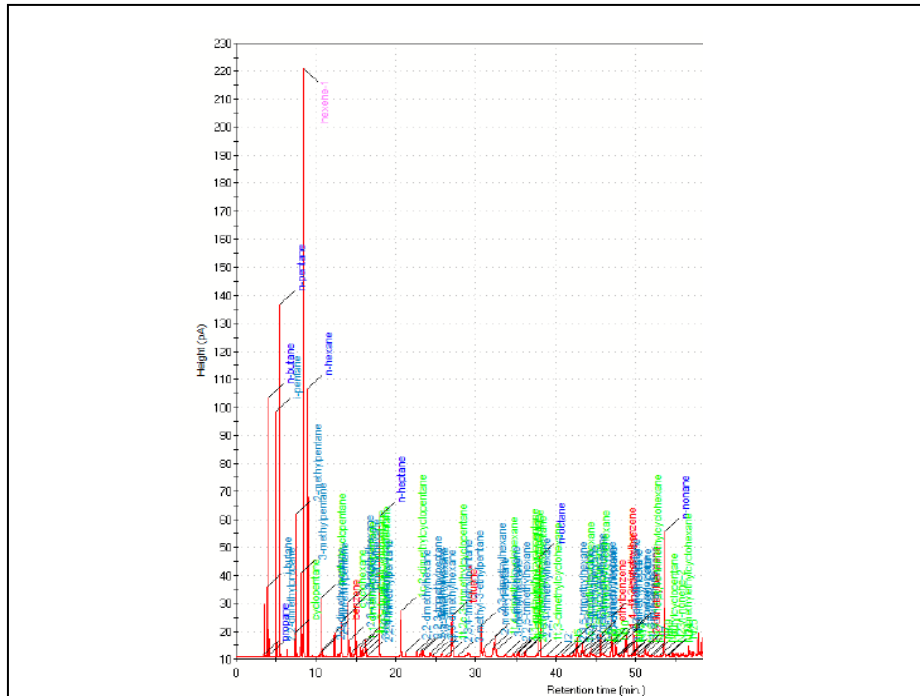


Figure 2 - Chromatogram with peaks identification on DHA-FE

AC Analytical Controls		DHA Front End	
Data File	: C:\CHEM32\3\DATA\D131128A\106F0201.D	Seq. Line #	: 2
Used Calibration	: C:\CHEM32\3\DATA\D131127C\102F0501.D	Vial #	: 106
Sample name	: 634710	Inj	: 1
Date injection	:	Inj vol µl	: 0.1
Date report	:	Peaks #	: -
Sample Type	: Crude	Sample wt	: 1.006
Sequence name	: C:\CHEM32\3\SEQUENCE\S131128.A.S	ISTD wt	: 0.0361
Operator	: Admin	Density	: 0
Method	: DHA-FE		

Boiling point Distribution Table					
Perc	BP°C (m%)	Perc	BP°C (m%)	Perc	BP°C (m%)
0.5	-0.5	10.0	98.4	20.0	144.2
1.0	-0.5	11.0	98.4	21.0	146.6
2.0	27.8	12.0	99.5	22.0	150.8
3.0	36.1	13.0	110.6	22.7	151.8
4.0	60.3	14.0	115.6		
5.0	63.3	15.0	117.7		
6.0	68.7	16.0	125.7		
7.0	68.7	17.0	125.7		
8.0	80.7	18.0	136.0		
9.0	90.8	19.0	139.1		

Figure 3 - DHA-FE Boiling point report

Report with Merge

The next step after obtaining the report in DHA-FE is merging the results from the High Temp SIMDIS chromatogram in Figure. 1 with the data shown in Figure 4. The combined report is as follows:

BP Distribution table - Percent							
Recovered mass%	BP °C	Recovered mass%	BP °C	Recovered mass%	BP °C	Recovered mass%	BP °C
IBP	-0.5	25.0	162.6	50.0	282.4	75.0	421.9
1.0	-0.5	26.0	166.1	51.0	287.4	76.0	428.5
2.0	27.8	27.0	172.4	52.0	292.2	77.0	435.0
3.0	36.1	28.0	174.9	53.0	297.6	78.0	441.8
4.0	60.3	29.0	178.9	54.0	302.4	79.0	449.1
5.0	63.3	30.0	184.9	55.0	307.3	80.0	456.6
6.0	68.7	31.0	189.7	56.0	312.7	81.0	464.4
7.0	68.7	32.0	195.8	57.0	317.0	82.0	472.3
8.0	80.7	33.0	198.1	58.0	322.3	83.0	480.5
9.0	90.8	34.0	203.2	59.0	328.2	84.0	489.0
10.0	98.4	35.0	208.9	60.0	332.1	85.0	498.2
11.0	98.4	36.0	215.2	61.0	338.4	86.0	507.6
12.0	99.5	37.0	217.6	62.0	344.0	87.0	517.7
13.0	110.6	38.0	223.4	63.0	349.1	88.0	528.4
14.0	115.6	39.0	228.2	64.0	355.2	89.0	539.8
15.0	117.7	40.0	234.2	65.0	360.0	90.0	552.1
16.0	125.7	41.0	236.8	66.0	366.5	91.0	565.1
17.0	125.7	42.0	244.0	67.0	371.6	92.0	579.2
18.0	136.0	43.0	248.6	68.0	378.4	93.0	594.8
19.0	139.1	44.0	253.5	69.0	384.0	94.0	612.5
20.0	144.2	45.0	256.6	70.0	390.6	95.0	633.2
21.0	146.6	46.0	263.2	71.0	396.5	96.0	658.7
22.0	150.9	47.0	267.8	72.0	402.6	97.0	695.7
23.0	152.8	48.0	271.5	73.0	409.4	97.5	720.0
24.0	158.1	49.0	276.6	74.0	415.3		

Table 2 - High Temp SIMDIS & DHA-FE Merged Results

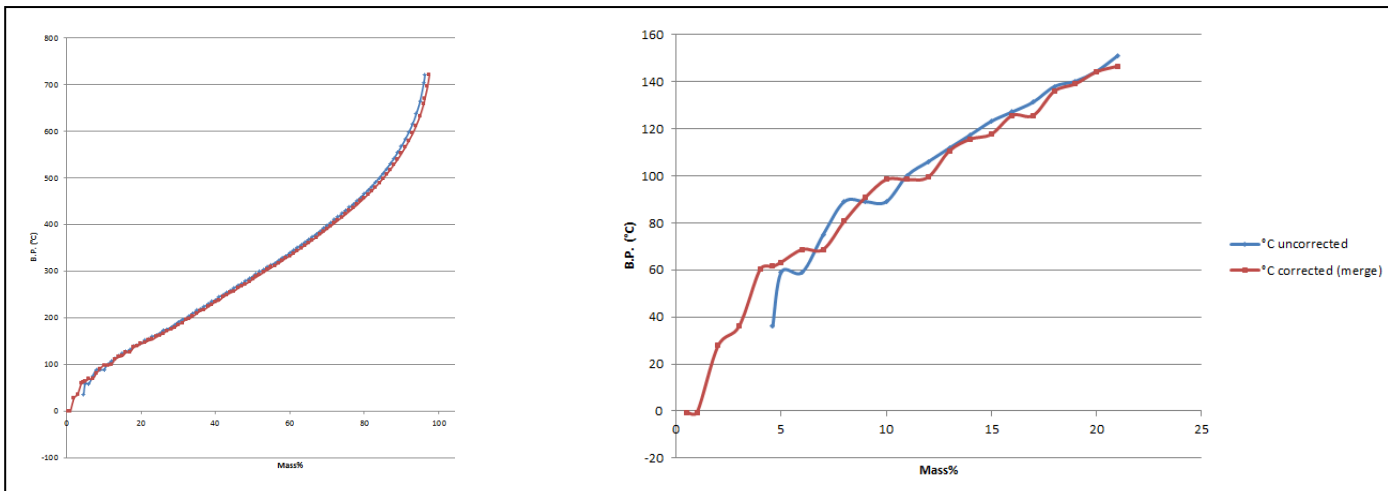


Figure 4 - Corrected vs Uncorrected Plots

Conclusion

Evidently the data merged data in Table 2 shows that there is a significant amount of light hydrocarbons present in the sample below C9, giving an IBP of -0.5°C versus 36°C shown in Table 1. This data of lower boiling feed becomes very valuable for refineries as it directly impacts the yield and therefore can alter decisions on final products. In this specific case, about 22% of the total crude is eluting below C9, which would roughly translate in an average 200,000 barrel per day refinery to about 44,000 barrels per day. If more specific data is needed, the DHA-FE analysis data can be used to quantify directly the amounts of specific components, such as methane, propane, n-Butane, Iso-Butane, pentane, benzene, and higher.

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