GETTING BETTER VALUE FROM PETROLEUM PRODUCTS USING SIMULATED DISTILLATION GAS CHROMATOGRAPHY

Boiling point distribution determination for petroleum products, feedstocks and other petroleum fractions is of vital importance to the industry for several reasons. Obviously, for most final products it is mandatory as part of certification. For crude oil, boiling point data is essential as an input for blending & modelling processes, maximizing uptime, production capacity and product output value and profit.

There are many models describing key price differentiators for Crude. Key parameters are API gravity and Sulphur content. Each extra degree of API gravity (relative to another crude) raises the relative crude price for the product. Similarly, each percent point of sulphur lowers the price. Hence, having sufficient boiling point data as early in the process as possible allows for maximizing profits and uptime during refining processes.

Typically, D86 is mandatory as a method for certifying final product. In many regions however, Simulated Distillation by Gas Chromatography (SIMDIST) may be used instead. Gas Chromatography has significant advantages over physical distillation justifying this choice: it covers wider scope, requires less sample, and omits the inherent safety concerns that come with doing a physical distillation in the lab. Furthermore, analysis by GC typically has better precision, higher throughput, less hands-on time resulting in lower operational cost. Since correlations between SIMDIST and physical methods are also well understood, both methods are often used in conjunction.

The list of standardized SIMDIST methods is very extensive and covers a very wide boiling point range, from gasoline to residuals and even biodiesels. Most common are the methods covering diesel/jet fuel range (ASTM D2887) and crude (ASTM D7169). Whist our portfolio can meet any SIMDIST method listed, our solutions for D2887 and D7169 methods are highlighted below.

ASTM D2887-B

Quite recently, D2887 has undergone some significant changes: Whereas the classical D2887 method remains as procedure A, a second method (procedure B) has been added, allowing for an 'accelerated' method, using faster temperature programming of the GC oven. This offers a 3-4 times faster result in under 10 minutes. Procedure B has a wider scope; It still covers boiling point range from 36°C to 545°C but has been validated also for biodiesels. Results for the fast method B 'may be considered to be practically equivalent' to those produced by method A, providing samples fall in scope of the collaborative study that was used to produce the individual Bias and Precision statements as listed for these respective methods.

Table 1: Analytical conditions ASTM D2887-B

Injector	Cold-on-Column w. air cooling
Column	SIMDIST 5m x 0.53mm x 2.65µm w. Retention gap
Oven Program	Start @ 40°C, 35°C/min to 350°C, hold 1 min.
Carrier	Helium @ 35ml/min
Detector	FID @ 350°C with ceramic HT flame tip
Inj. Volume	0.1µl neat
Software	Compass CDS w. SIMDIST module

The SCION SIMDIST analyser used for this, comprises of a small footprint 436-GC, configured with cool on column (COC) injector, a 5m x 0.53mm x 2.65µm SIMDIST column, and a Flame Ionization Detector (FID) with ceramic High Temp Flame tip. A 8400

A qualitative mixture of normal paraffins covering the range from C5 up to C44 (1% wt. each in CS2) was used to determine the relationship of boiling point (BP) versus retention times (RT).

Figures 1 and 2 show a chromatogram of the normal paraffins calibration standard and the resulting RT vs BP calibration curve as used for this analysis.

Reference Gasoil No. 2 was analysed to check that the requirements of ASTM D2887 are met using this configuration. Figure 3 shows a chromatogram of this Reference Gasoil, with table 2 showing the analytical results set out against the reference values and maximum allowable deviations. Table 3 demonstrates repeatability (n=11) and estimated reproducibility obtained for the method. All results obtained via this method, using this configuration fall within the allowed limits for ASTM D2887.

Table 2: Results, reference values and allowable difference for Reference Gasoil 2 in D2887B

% Off	°C	Allowable Difference (°C)	Result °C
IBP	106	7	105,2
10	196	4,4	194,7
20	233	5	230,1
30	267	4,8	263,6
40	298	4,3	295,3
50	321	4,3	319,5
60	342	4,3	341,5
70	358	4,3	359,0
80	378	4,3	378,8
90	406	4,3	407,8
FBP	496	11,8	499,6

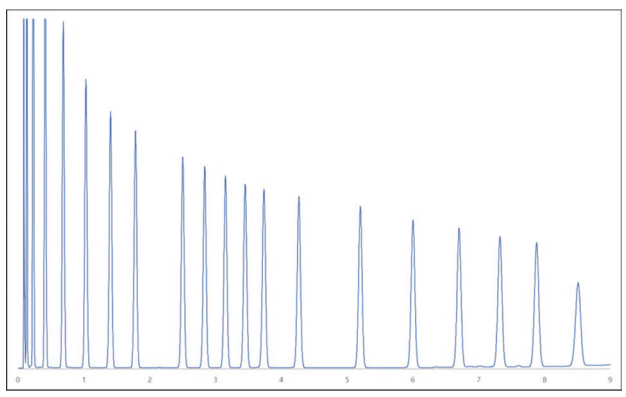

Figure 1: D2887B Cal. STD (C5-C44)

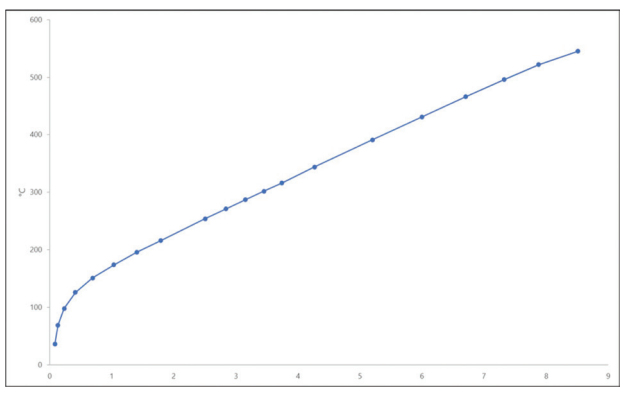

Figure 2: RT (min) vs. BP (°C)

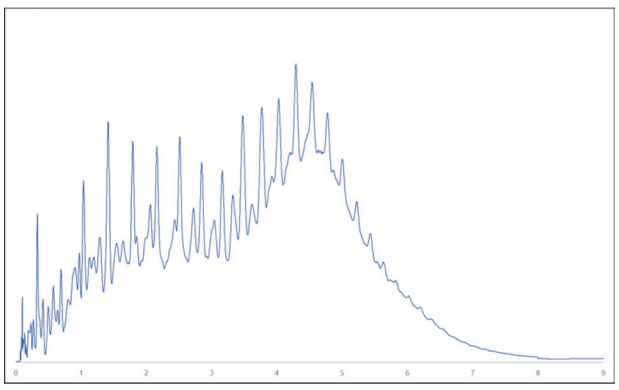

Figure 3: D2887B Reference Gasoil No. 2

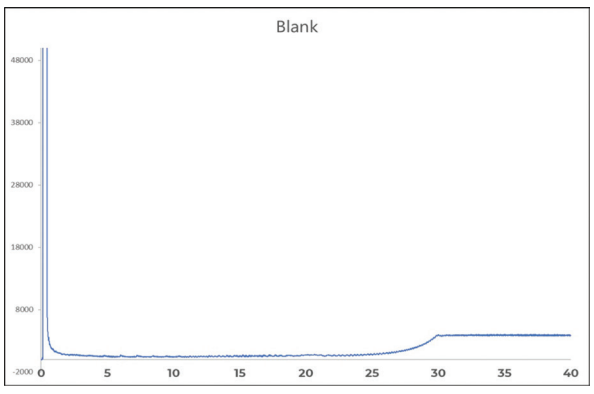

Figure 4: D7169 Blank CS2

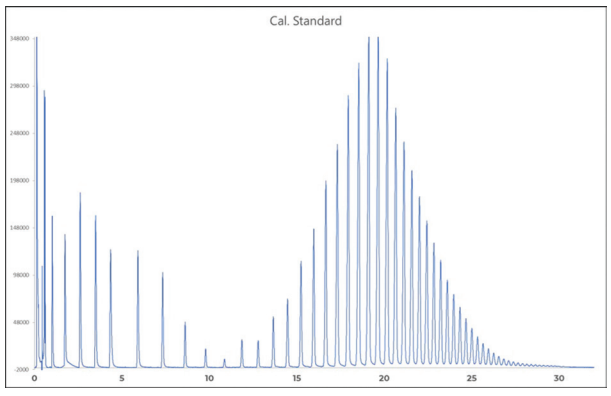

Figure 5: D7169 Cal. STD (C8-C100)

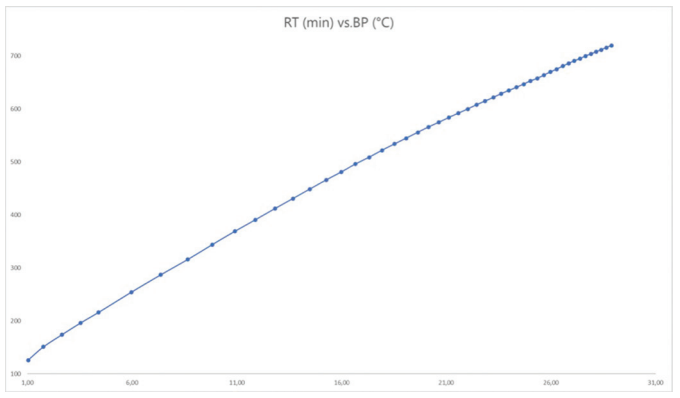

Figure 6: RT (min) vs. BP (°C)

Table 3. Obtained Precision for Gasoil 2 in D2887B

% Off	r (°C)	R (°C)
IBP	0,14	0,47
10	0,25	0,63
20	0,28	0,78
30	0,43	1,10
40	0,31	0,94
50	0,21	0,79
60	0,16	0,47
70	0,15	0,47
80	0,10	0,31
90	0,12	0,31
FBP	0,23	0,63

Table 5: Results, reference values and allowable difference for Reference oil 5010 in D7169

% Off	Consensus Value (°C)	Allowable Difference (°C)	Result (°C)	CoA Result (°C)
IBP	428	9	426,3	427,4
10	493	3	492,4	493,3
20	510	3	509,7	510,5
30	524	4	523,3	524,5
40	537	4	535,3	537,1
50	548	4	546,8	548,7
60	560	4	558,4	560,4
70	572	4	570,1	572
80	585	4	583,2	585,1
90	602	4	600,5	602,1
FBP	655	18	648,7	656,3

ASTM D7169

ASTM Method D7169 describes determination of cut point intervals and boiling point distribution of (crude) samples up to 720°C (n-C100). This method can also be used for the simulated distillation of other samples that do not fully elute, such as atmospheric and vacuum residues.

Table 4: Analytical conditions ASTM D7169

Injector	Cold-on-Column w. Air cooling
Column	SIMDIST 5m x 0.53mm x 0.09µm w/ Ret. Gap
Oven Program	Start @ -20°C, 15°C/min to 430°C, hold 10 min.
Carrier	Helium @ 20ml/min
Detector	FID, @ 435°C w. HT Flame tip
Inj. Volume	0,5µl
Software	Compass CDS w. SIMDIST module

A typical challenge in D7169 is sample cross contamination, which can be negated with proper cleaning of syringes in the sampling. Other challenges are mostly injection related: high-boiling components may deposit, especially in low flow situations, which may be observed as "memory effects" in subsequent runs. Additionally, any cold spots in the injection flow path can result in similar "memory effects". Solvent backflash into carrier, purge & vent lines especially when injecting a very volatile solvent is another possible contributor to what we observe as a poor blank. Hence special care is to be taken for injection, and sampling cleaning cycles.

The SCION SIMDIST analyser used for this, comprises of a small footprint 436-GC, configured with a temperature programmable cool on column (COC) injector with air cooling, a 5m x 0.53mm x 0.09µm SIMDIST column, and a Flame Ionization Detector (FID) with ceramic HT flame tip. This special flame tip with larger bore ID lowers maintenance frequency, adds sensitivity and improved linearity. The GC oven was equipped with LCO2 coolant to facilitate oven starting at -20°C. A CP-8400 Autosampler was used in Standard On-Column mode.

Standards were prepared in CS2 and used to determine system performance. N-paraffin Retention times and response factors were determined. A qualitative mixture of normal paraffins covering the range from C8 up to C100 (1% wt. each in CS2) was used to determine the relationship of boiling point (BP) versus retention times (RT). CS2 blanks were run and evaluated for cleanliness of the blank, for blank subtraction. All samples were dissolved in CS2 (2% m/m) before analysis.

Figure 4 shows a stable, clean blank injection run, free of any hydrocarbon interferences. Figures 5 and 6 represents the paraffins calibration standard and the resulting RT vs BP calibration curve obtained from it.

Reference Oil "5010" was analysed to verify that requirements of ASTM D7169 are met using this configuration. Table 5 clearly shows the analytical results obtained for this reference material passes criteria for acceptance. To demonstrate repeatability of injections, the hydrocarbon response factor was calculated for 2 successive injections of this reference oil: the difference was 1.73%, which passes criteria set forth by the method.

Conclusion

Simulated distillation can provide a very suitable alternative for conventional distillation methods. They typically provide a much more robust, economical, safe, automatable, and easy solution for obtaining accurate boiling point and cut point data for petroleum products, feedstocks and other petroleum fractions as specified in these different methods.

In this study, SCION Instruments SIMDIST analysers for D2887B and D7169 were demonstrated to pass all criteria set forth in the referenced methods with relative ease, providing a compliant solution platform for Simulated Distillation.

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