Heating Up Simulated Distillation

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The American Society for Testing and Materials (ASTM) has established guidelines for simulated distillation (SimDist) analyses, which include samples that have boiling points in the range of about -44°F to 1139°F. These include ASTM Method D2887 and Method D3710[1]. A new High Temperature Simulated Distillation (HTSD) method is under development that extends the boiling range distribution to final boiling point temperatures upwards of 1300°F to 1380°F.

Data provided from HTSD analysis is currently being utilized to provide valuable information to refiners of heavy crude oils. This information helps improve gas oil yields and minimize vacuum tower residues. The method is precise enough that it can also be used to determine if a crude oil has been adulterated, e.g., by blending pitch (1000°F+) into the crude[2].

Table 1. Boiling points of normal paraffins

Carbon No.	Boiling Point (°F)*	Carbon No.	Boiling Point (°F)*	Carbon No.	Boiling Point (°F)*
2	-127.5	26	774	66	1175
3	-44	28	808	68	1186
4	32	30	840	70	1197
5	97	32	871	72	1207
6	156	34	898	74	1216
7	209	36	925	76	1227
8	259	38	948	78	1238
9	303	40	972	80	1247
10	345	42	993	82	1258
11	385	44	1013	84	1267
12	421	46	1033	86	1276
13	455	48	1051	88	1283
14	489	50	1067	90	1292
15	520	52	1083	92	1299
16	549	54	1098	94	1306
17	576	56	1112	96	1314
18	601	58	1126	98	1321
20	651	60	1139	100	1328
22	696	62	1152	110	1355
24	736	64	1164	120	1382

*Atmospheric Equivalent Boiling Point (AEBP) as described in API Project 44.

Methodology
Typically, capillary GC simulated

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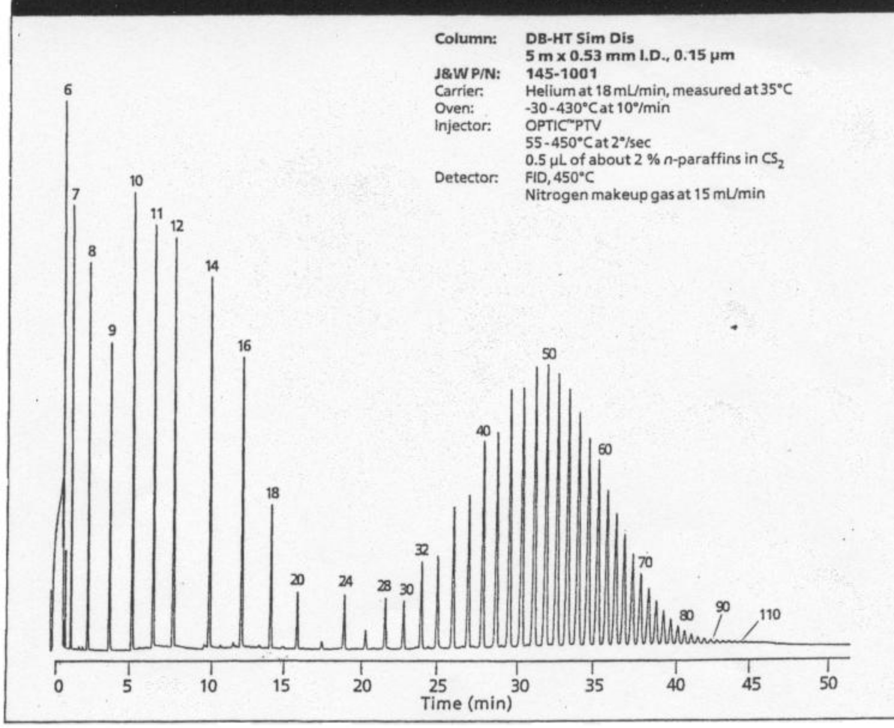
Typically, capillary GC simulated distillation analyses are performed using a bonded methylsilicone stationary phase in 0.53 mm I.D. columns with relatively thick films (>3 microns). The thicker film aids in preventing sample overload of the stationary phase which can affect .the retention times. The thick film also gives adequate retention to the early eluting fractions of the sample and can extend the low end of the boiling point distribution range for the system to n-propane *(n-C_3)* if cryogenic conditions are used.

Thick film columns do have limitations; a thick stationary phase limits the upper end of the distribution curve because of the increased retention of the higher boiling hydrocarbons and interference from stationary phase bleed. ASTM method D2887 has an upper temperature limit for petroleum products with a final boiling point of 1000°F (538°C) at atmospheric pressure.

Figure 1. *n*-Paraffin standard showing distillation range from C_6 to C_{110} on DB-HT Sim Dis



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To extend the boiling point distribution range for analyzing heavy crudes, it is necessary to use a thin film column. With film thicknesses of 0.15 to 0.05 um in a 0.53 mm I.D. column (phase ratio 883 to 2650), it is possible to elute materials equivalent to C_{110} and higher at GC oven temperatures that are 500-600°F below their Atmospheric Equivalent Boiling Point (AEBP) (Table 1). The use of a properly bonded stationary phase can generate a "low bleed" profile, critical for accurate quantitative results at the upper temperature extremes.

The thin stationary phase coating has limited sample capacity. This requires care in the dilution of the standards and samples matrices (about 0.1-2% wt/wt) as well as special sample introduction techniques. Cool oncolumn injection techniques can be used to prevent analyte discrimination, while programmable temperature vaporization (PTV) injectors have a definite advantage with regards to automation, reproducibility, and flexibility.

HTSD is a challenging analytical procedure; extremely high temperatures are used. All of the components of the GC system are pushed to the limits of their capabilities.

To achieve meaningful results it takes care and patience on the part of the analyst operating the instrument. The application demands the use of special column materials because the conventional or even high temperature polyimide coated fused silica column cannot withstand the extreme oven temperatures encountered. Recent advances in surface deactivation[3] have made it possible to utilize capillary dimensioned, stainless steel tubing as the starting point for WCOT columns. The metal tubing does not experience the problems of brittleness and short lifetime encountered with high temperature polyimide coated and aluminum clad fused silica columns.

An n-paraffin standard analysis with an OPTIC temperature programmable injector is shown for DB-HT Sim Dis in Figure 1. This chromatogram is of the "raw" output. That is, the background signal has not been compensated for or subtracted. Figure 2 is the boiling point distribution curve for DB-HT Sim Dis. The polydimethylsiloxane column has an effective distribution range of 156°F (69°C) to 1355°F (735°C).

Analyses of two reference oils with DBHT Sim Dis are shown in Figures 3 and 4.

Both chromatograms show a sharp return to "baseline" at the end of the run for each of the oils indicating the final boiling point of the respective oil.

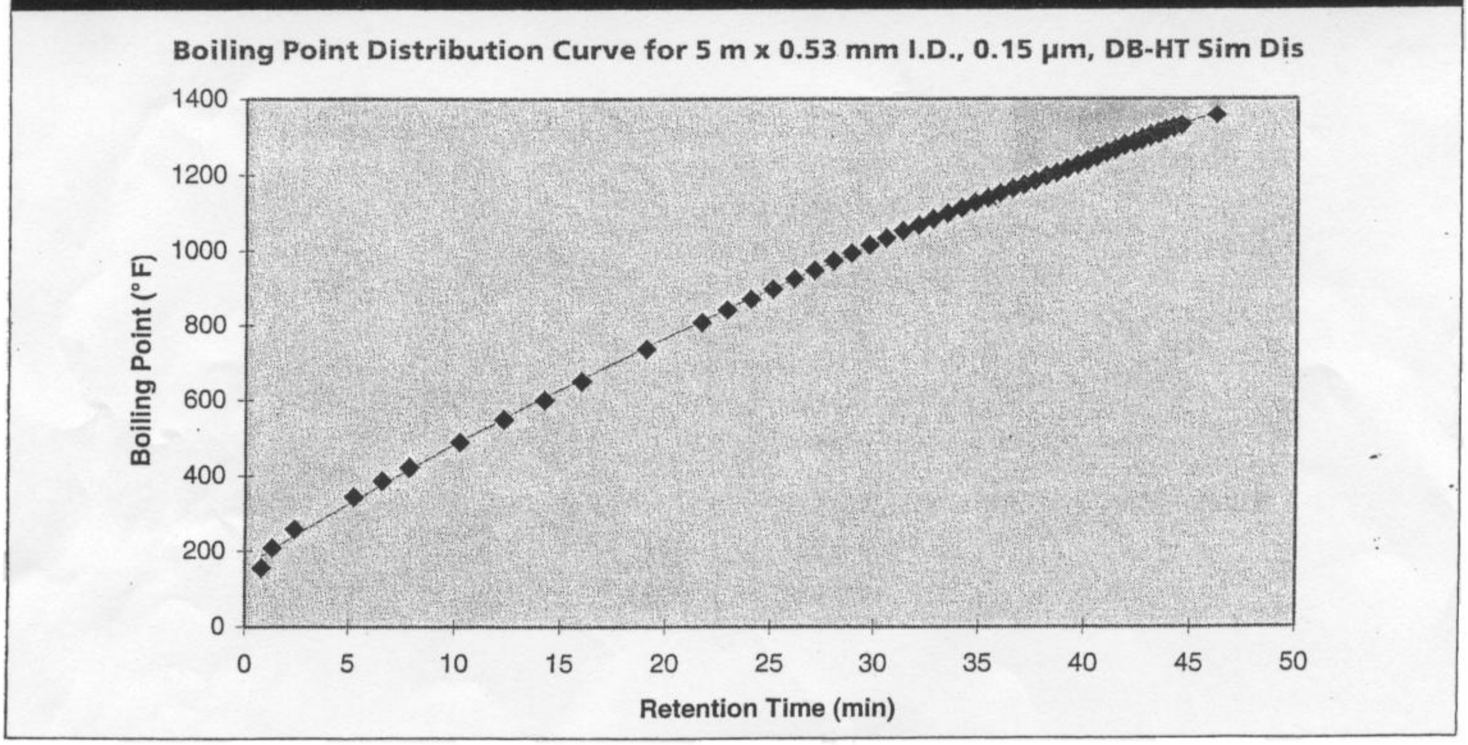
Hot Stuff You Can Do

High temperature simulated distillations of petroleum samples can be performed with a 100% methyl silicone stationary phase. DBHT Sim Dis shows excellent inertness and a low bleed profile at the higher temperatures. The column withstands the extreme temperatures that standard polyimide coated columns cannot and has a 430°C upper temperature limit. The DB-HT Sim Dis column can be used for a boiling point distribution range equivalent of C_5 to C_{110}.

References

1. Annual Books of ASTM Standards. *Vols.* 5.0, 5.02. *and* 5.03, *American Society for Testing and Materials,* 1916 *Race Street, Philadelphia, PA* 19103,1990.
2. *Dan* C. *Villalanti. Personal Communication, Triton Analy tics Corp.,* 16840 *Barker Springs Rd., Suite* 302, *Houston, TX* 77084, 1995.
3. *A.K. Vickers. Mitch Hastings, Dean Rood and Roy Lautamo,* "An Improved Deactivation Process for Meta1 Tubing Used in Capillary Gas Chromatograph y Columns ," *Presented at the Pittsburgh Con ference and Exposition, New Orleans, LA, March* 5-10, 1995.

Figure 2. Boiling point vs. retention time for *n*-paraffins on the DB-HT Sim Dis using the conditions shown in Figure 1.



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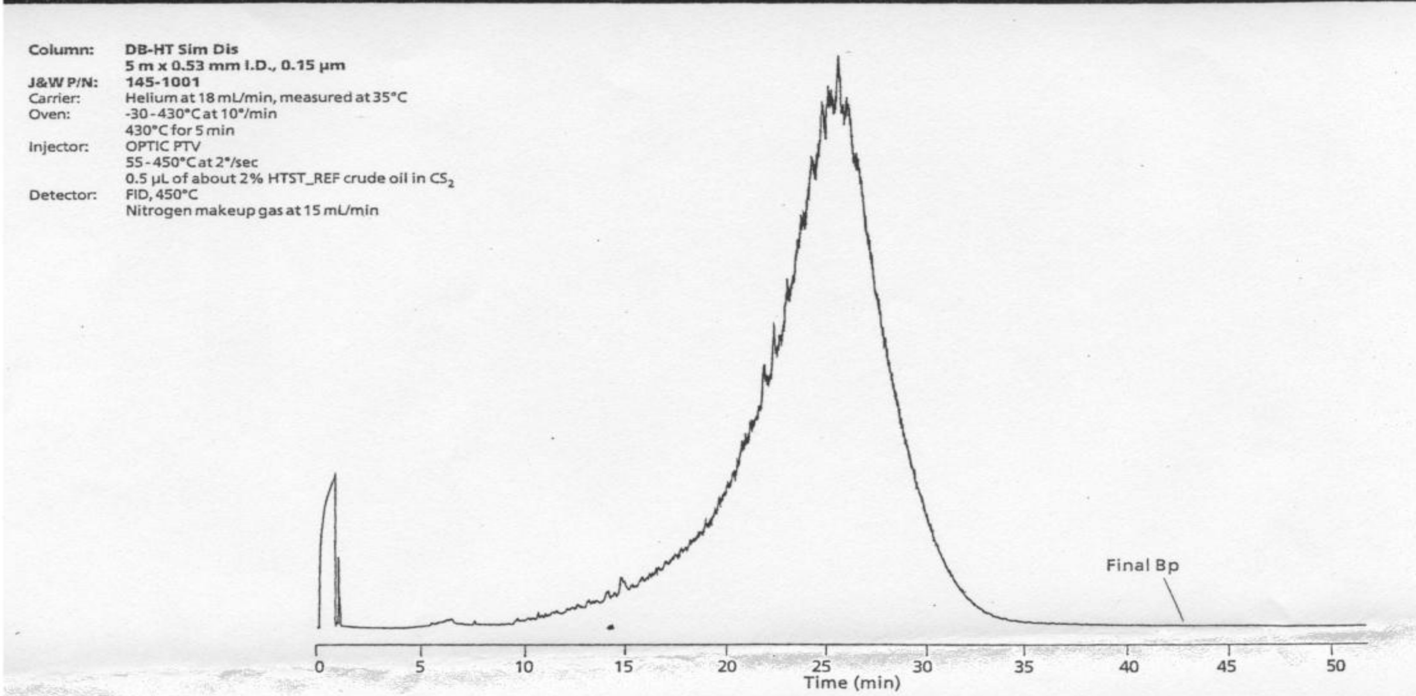

Figure 3. Simulated distillation of a midrange reference crude oil (HTST_REF).

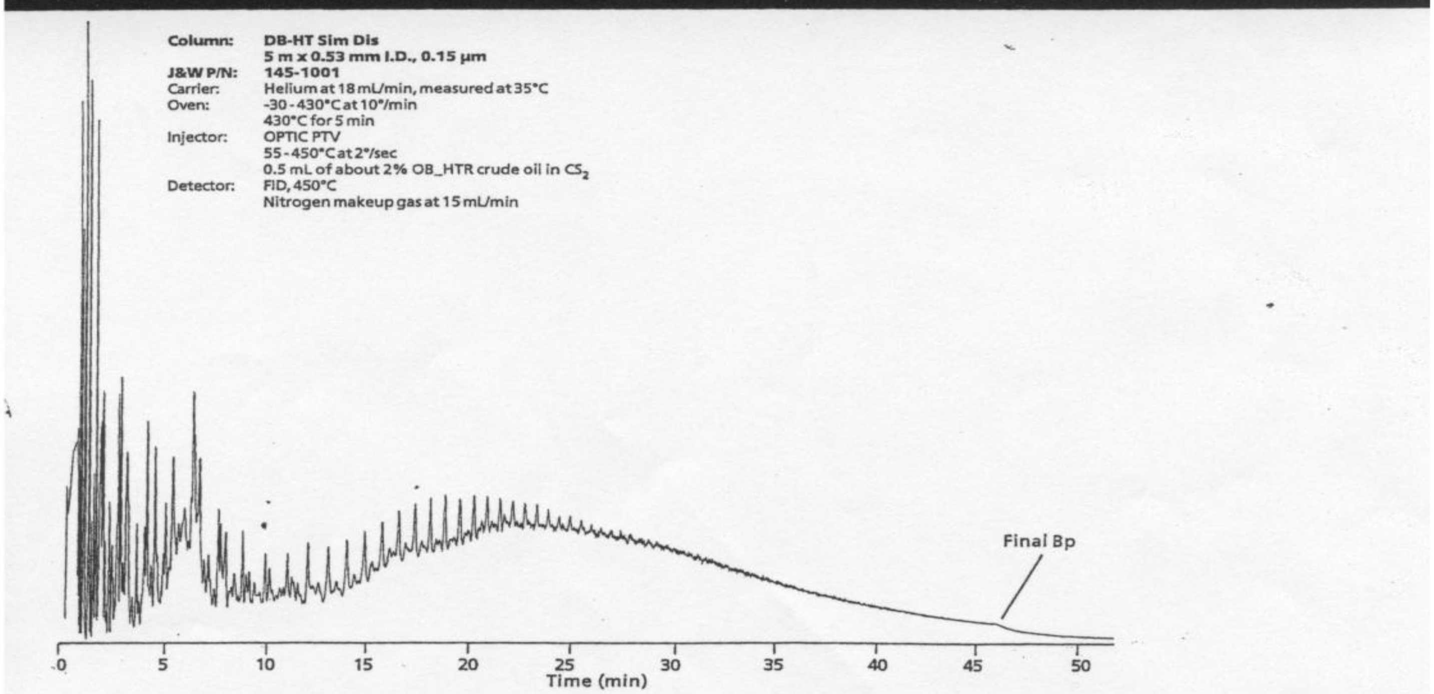

Figure 4. Simulated distillation of a full range reference crude oil (OB_HTR).

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