Higher-Temperature Simulated Distillation with DB-HT Sim Dis Columns

Application

Hydrocarbon Processing

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Abstract

Improved GC columns have been developed that now permit operation up to 430 °C and can be used to perform simulated distillations covering the range from C_5 to C_{110}. They exhibit excellent inertness and low bleed at high temperatures.

Introduction

Data derived from high-temperature simulated distillation (HTSD) analysis provides valuable information to refiners of heavy crude oils, helping them improve yields and minimize vacuum tower residues. The method is also precise enough to determine if a crude oil was adulterated, for example, by blending pitch (1000 °F+) into the crude [1].

The American Society for Testing and Materials (ASTM) has established guidelines for simulated distillation (SimDist) analyses, which include samples that have atmospheric equivalent boiling points (AEBP) in the range of about –44 to 1139 °F (–42 to 615 °C). These include ASTM Methods D2887 and D3710 [2]. For analysis of heavier samples, such as crude oils, HTSD method D6352 [2] extends the AEBP distribution to temperatures upwards of 1300 to 1380 °F (704 to 749 °C).

HTSD methods require a robust GC column with high upper temperature limits. For this purpose, Agilent Technologies, Inc. provides a metal column, DB-HT Sim Dis, deactivated by a proprietary process, offering excellent performance and exceptional durability.

Method Considerations

Typically, capillary GC SimDist analyses are performed using a bonded 100% dimethylpolysiloxane stationary phase in 0.53-mm id columns with relatively thick films (>3 µm). The thick film aids in preventing sample overload while giving adequate retention to the early-eluting fractions of the sample and extending the low end of the boiling point distribution range down to propane (with cryogenic conditions). However, the increased retention of higher-boiling hydrocarbons and interferences from stationary phase bleeding limit the upper end of the distribution curve achievable with thicker films. ASTM Method D2887 has an upper temperature limit for petroleum products with a final boiling point of 1000 °F (538 °C) at atmospheric pressure.

To extend the boiling point distribution range for analyzing heavy crudes, it is necessary to use a thin film column. With film thicknesses of 0.09 to 0.15 µm in a 0.53-mm id column, it is possible to elute materials equivalent to C_{110} and higher at GC oven temperatures that are 500–600 °F (260–316 °C) below their AEBP.

The polymer bonding and crosslinking processes used to manufacture the DB-HT Sim Dis column (5 m × 0.53 mm id × 0.15 µm film of 100% dimethylpolysiloxane)[1] generate a "low bleed" profile, critical for accurate quantitative results at the upper temperature extremes.

The limited sample capacity of a thin stationary phase coating requires care in the dilution of the standards and sample matrices (about 0.1%–2% wt/wt) as well as special sample introduction techniques. Cool-on-column injection techniques can be used to prevent analyte discrimination, but programmable temperature vaporization (PTV) injectors have a definite advantage with regards to automation, reproducibility, and flexibility, and are generally preferred for this analysis.

The extremely high temperatures used in HTSD make it an especially challenging analytical procedure, pushing the limits of all GC system components including the GC column. Standard fused silica columns cannot withstand the extreme oven temperatures encountered (up to about 430 °C). Advances in surface deactivation [3] have made it possible to use capillary-dimensioned, stainless steel tubing as the starting point for WCOT columns. The metal tubing does not show the problems of brittleness and short lifetime encountered with high-temperature polyimide-coated and aluminum-clad fused silica columns.

The high quality of the proprietary J&W brand deactivation process as well as polymer bonding and crosslinking for DB-HT Sim Dis produces an exceptionally durable column for HTSD.

Results

Users report hundreds of temperature cycles, to 430 °C, with minimal performance degradation caused by phase loss (bleed), making DB-HT Sim Dis the column of choice for this application. For reference, Table 1 shows the atmospheric equivalent boiling points (AEBP) for normal paraffins with carbon numbers from 2 to 120.

[1] Part no. 145-1001

Table 1: AEBP for Normal Paraffins with Carbon Numbers from 2 to 120

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

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

An example of a *n*-paraffin standard analysis using a PTV inlet is shown for a DB-HT Sim Dis column in Figure 1. This chromatogram is of the "raw" output—that is the background signal has not been altered. Figure 2 is a 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).

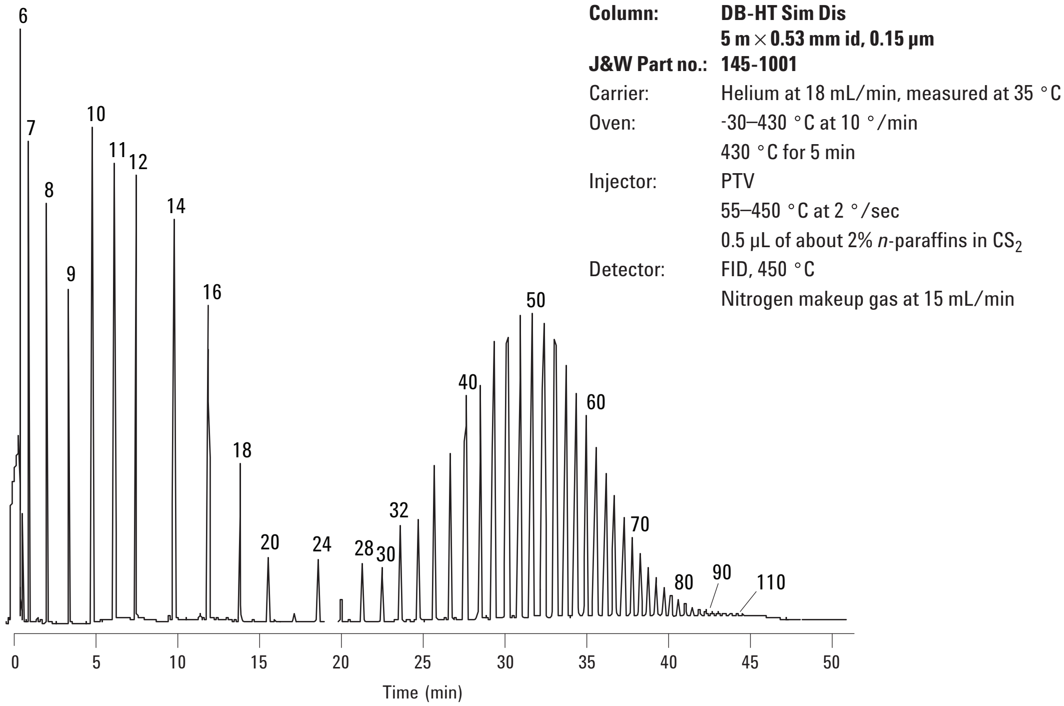

Figure 1. ***n*-paraffin standard showing SimDist results from C_6 to C_{110} on the DB-HT Sim Dis.**

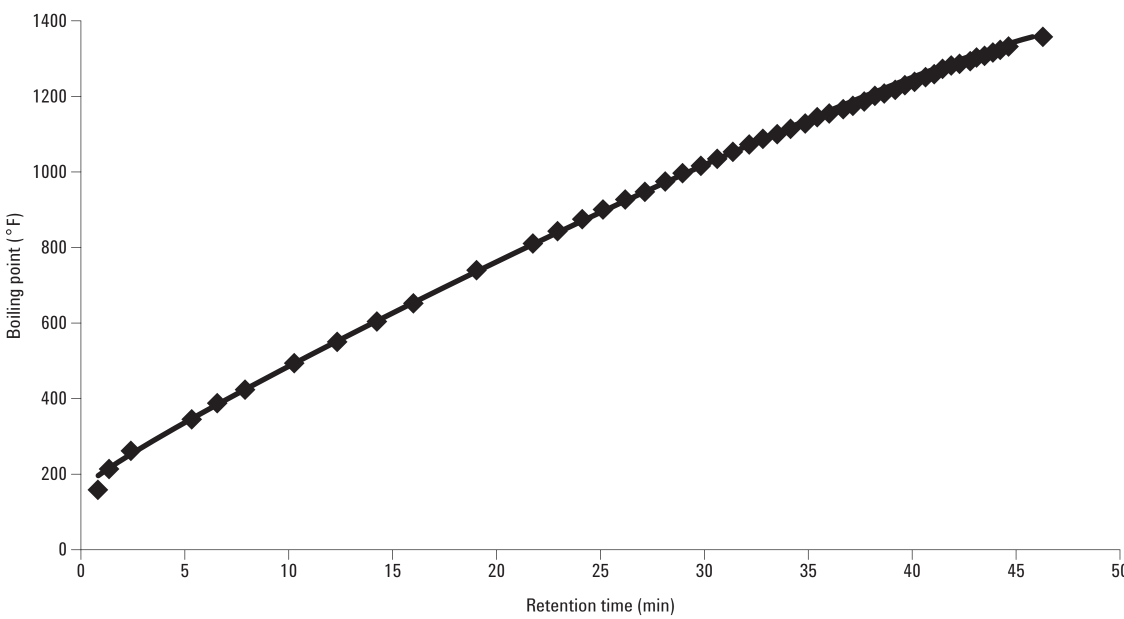

Figure 2. **Boiling point vs. retention time for *n*-paraffins on the DB-HT Sim Dis using the conditions shown in Figure 1.**

Analyses of two reference oils with DB-HT 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.

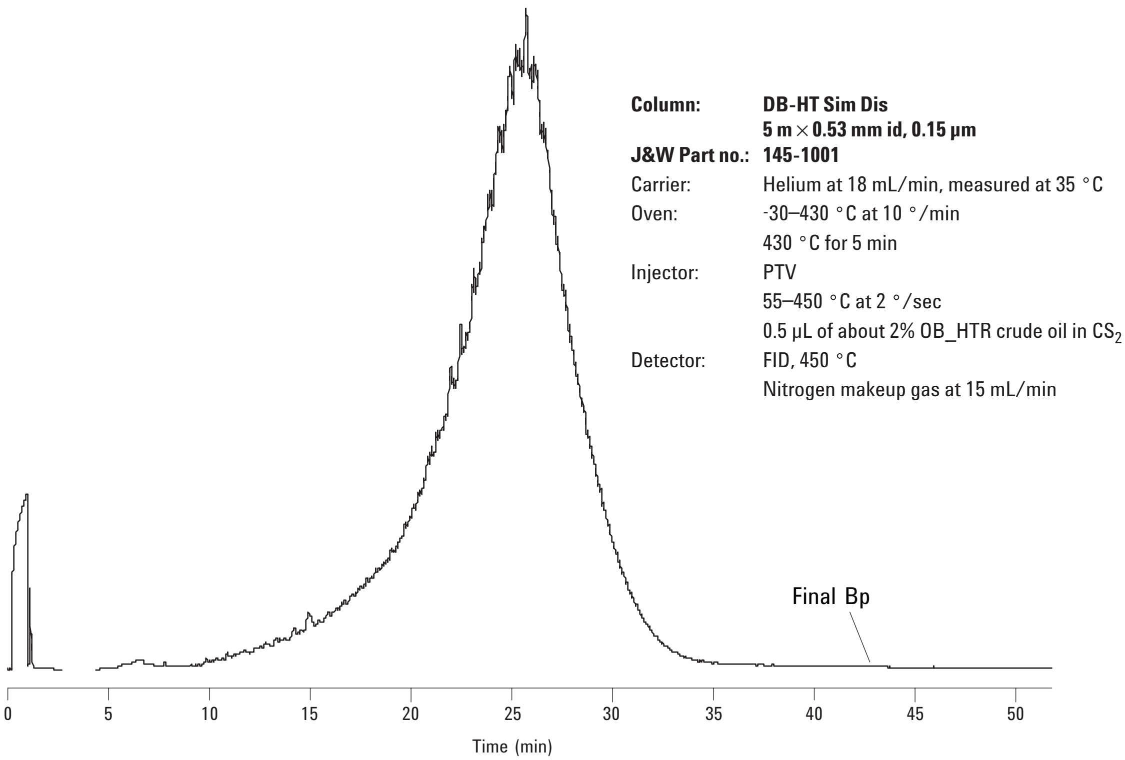

Figure 3. **Simulated distillation of a midrange reference crude oil (HTST_REF).**

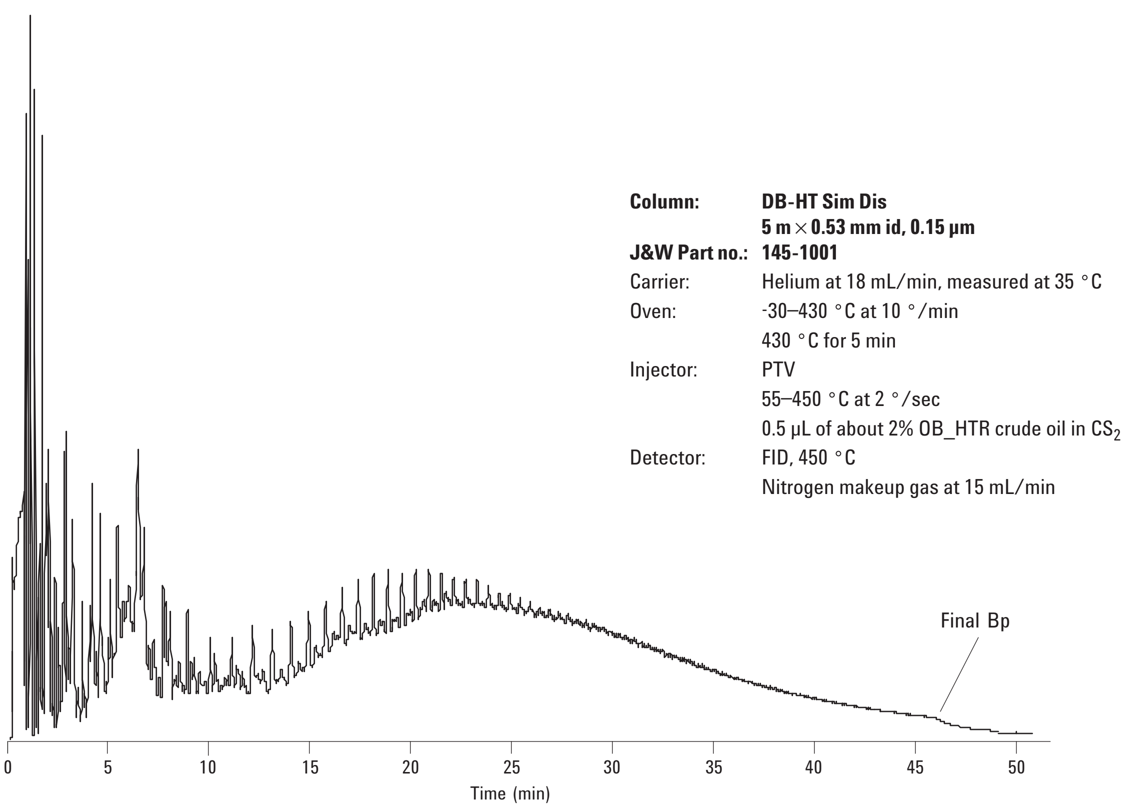

Figure 4. **Simulated distillation of a full range reference crude oil (OB_HTR).**

Superior Performance with the DB-HT Sim Dis—A Customer Example

The DB-HT Sim Dis outperforms and outlasts another manufacturer's metal column (Figure 5).

Figure 5 shows the failure of the Brand R metal column (of equivalent dimensions) while in use at a customer's laboratory (top chromatogram). The Brand R column was installed in an Agilent 6890 GC, and initially performed well. After only 276 injections under harsh analytical conditions (oven temperature cycling from –20 to 425 °C), this column exhibited loss of retention and poor peak shape due to rapid phases degradation. Needing a column to perform their SimDist samples, the customer reinstalled a previously "retired" DB-HT Sim Dis (retired after 376 injections) into the same 6890 GC. With the same samples and temperature conditions, the DB-HT Sim Dis column showed superior performance even after 377 injections (bottom chromatogram). At this point, the DB-HT Sim Dis had outlived the competition's column by 35%. The results of the analysis are shown, not only in the bottom chromatogram of Figure 5, but also for the entire analysis, up to C_{100} at 425 °C, in Figure 6.

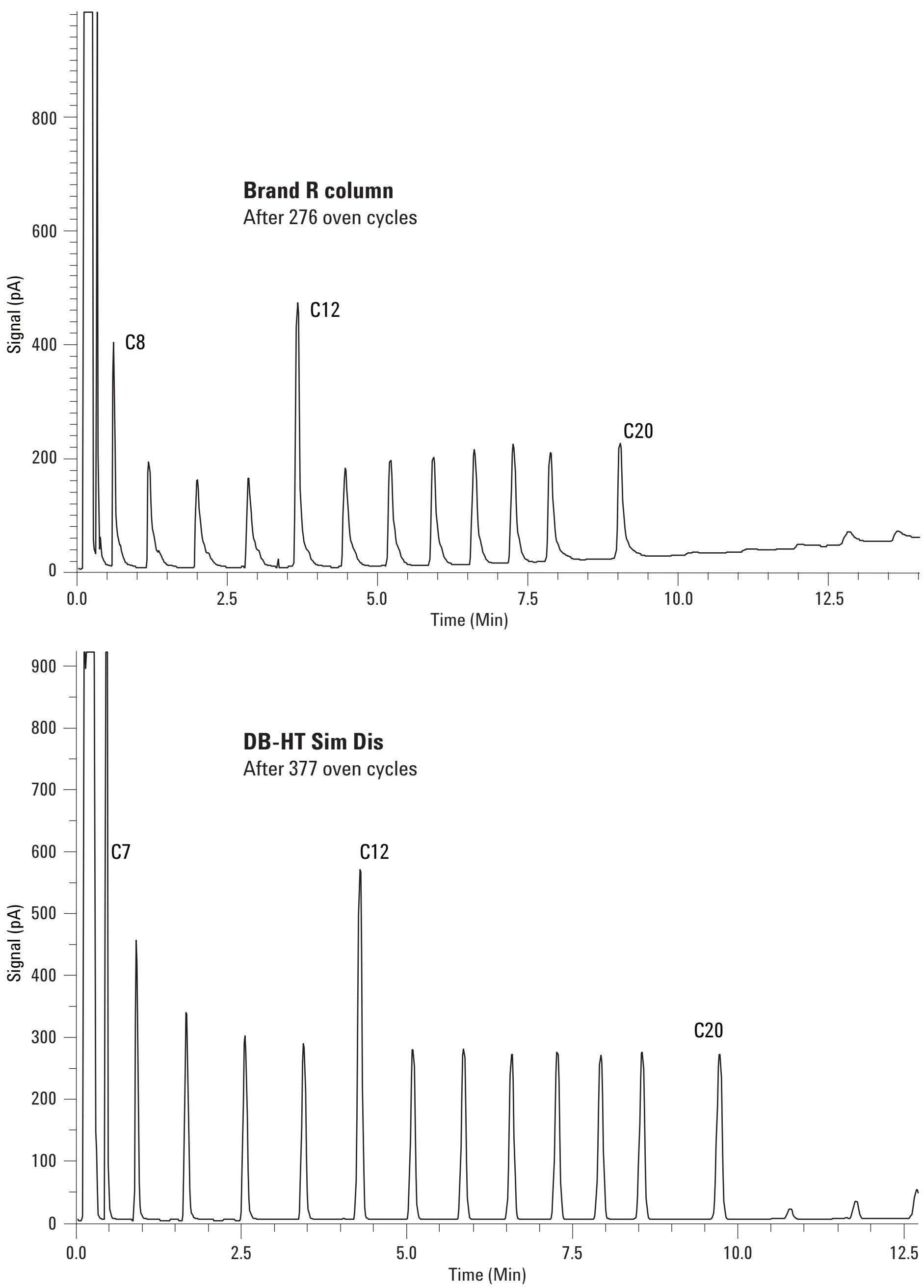

Figure 5. Customer data comparing two high temperature metal columns after injections of *n*-paraffin calibration standards.

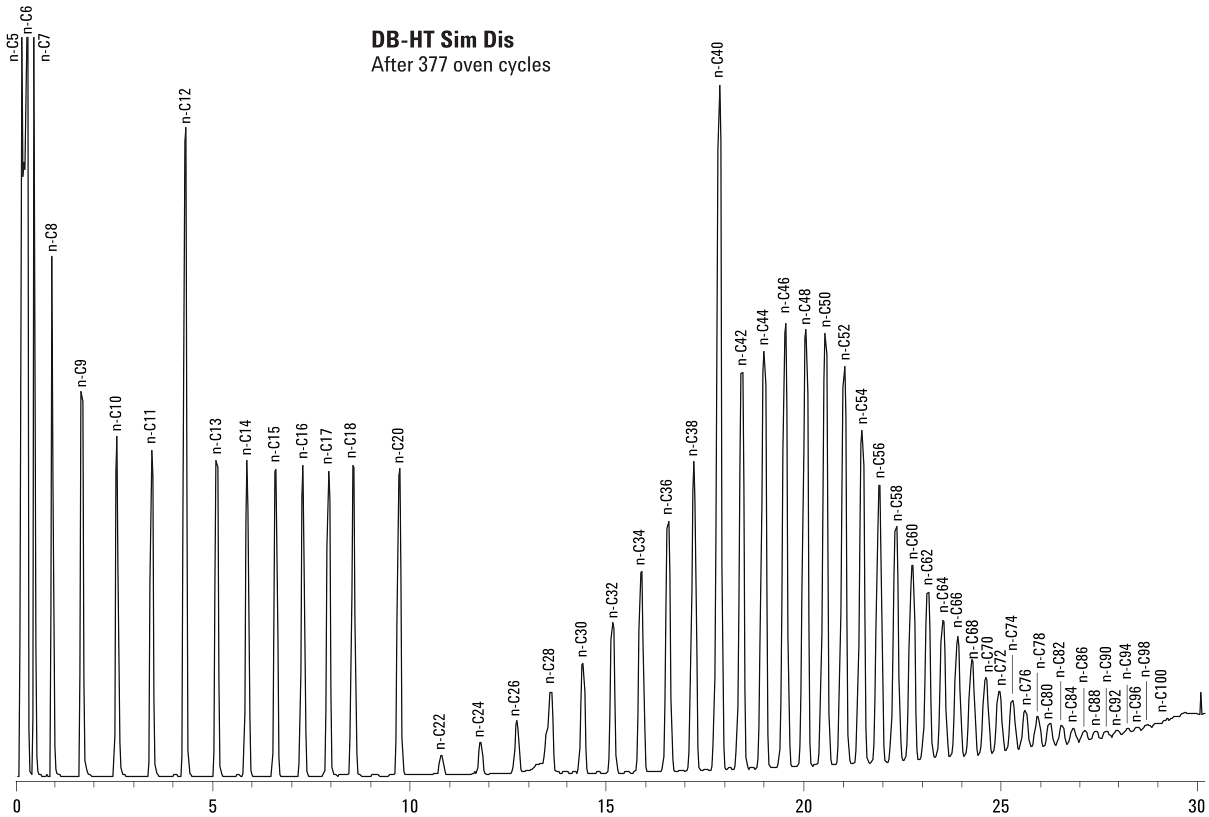

Figure 6. **Customer's full chromatogram for the 377th injection showing performance of the "previously retired" DB-HT Sim Dis column for an extended hydrocarbon mixture up to C_{100}. The front section of this chromatogram is shown in larger format in Figure 5 (bottom).**

Conclusions

The DB-HT Sim Dis column is the column of choice for performing ASTM Method D6352, The Standard Test Method for Boiling Range Distribution of Petroleum Distillates in Boiling Range from 174 to 700 °C by GC.

References

1. D. C. Villalanti, D. Janson, and P. Colle, “Hydrocarbon Characterization by High Temperature Simulated Distillation (HTSD),” Distillation Session, Distillation Column Design and Operation-IV: Advances in Distillation Modeling and Simulation, AIChE1 995 Spring National Meeting, March 19–23, Institute of Chemical Engineers, New York, 1995.
2. American Society for Testing and Materials, 100 Barr Harbor Drive, West Conshohocken, PA 19428-2959; http://www.astm.org
3. A. K. Vickers, Mitch Hastings, Dean Rood, and Roy Lautamo, “An Improved Deactivation Process for Metal Tubing Used in Capillary Gas Chromatographic Columns,” Presented at the Pittsburgh Conference and Exposition, New Orleans, LA, March 5–10, 1995.

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Printed in the USA
October 31, 2002
5988-7929EN