Application of High-Temperature Simulated Distillation to the Residuum Oil Supercritical Extraction Process in Petroleum Refining

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Abstract

The gas chromatographic method of high-temperature simulated distillation (HTSD) is described, and the results are presented for the application of HTSD to the characterization of petroleum refinery feed and products from solvent deasphalting operations. Results are presented for refinery residual feed, deasphalted oil, and asphaltene fractions from the residual oil supercritical extraction process. Asphaltene removal from petroleum residuum using solvent deasphalting results in the improved quality and high recovery of deasphalted oil product for use as lube oil, fluid catalytic cracking, or hydrocracker feedstocks. The HTSD procedure presented here proves valuable for characterizing the fractions from the deasphalting process to obtain the percentage yield with boiling point data over the range from approximately 36°C (97°F) to 733°C (1352°F), which covers the boiling range of n-paraffins of carbon number C_5 to C_{108}.

Introduction

In the refining of petroleum, crude oil is processed and converted into commercially valuable products such as transportation fuels, gasoline, turbine (jet) fuels, diesel, light heating oils, lubrication oils, refrigeration oils, transformer oils, and feedstocks for petrochemicals (1). The refining process is typically carried out to achieve high-volume yields of those products with greater economic value, such as the lighter boiling fractions used in transportation and light heating oils.

Crude oil bottoms present challenges to petroleum refiners who need to effectively convert them into useful products of higher economic value. Among the several "bottom of the barrel" processes available, solvent deasphalting is a process that is predominantly used to recover high-value deasphalted gas oil (DAO) from petroleum residuum (resid). DAO is excellent feedstock for lube oil, fluid catalytic cracking (FCC), and hydro-

cracking. The residuum oil supercritical extraction process (ROSE™, licensed by Kellogg Brown & Root) is a solvent extraction process widely used in the industry today (2).

The method of high-temperature simulated distillation (HTSD) is a useful tool for characterizing hydrocarbons using boiling point profiles of fractions from the residuum solvent extraction process. HTSD, which is currently under proposed American Society of Testing and Materials (ASTM) method status, is a method that extends the determination of the boiling range distribution of petroleum hydrocarbons from the 538°C (1000°F) limit of ASTM method D2887 (IP 4060) (3) to a final boiling point of about 750°C (1382°F), as illustrated in Figure 1.

The HTSD method utilizes a capillary gas chromatography (GC) column and stationary phase technologies together with either programmed temperature vaporization (PTV) or on-column injection techniques to achieve adequate separation of n-paraffins from C_5 to approximately C_{120}. HTSD is useful for the boiling point yield characterization of various petroleum
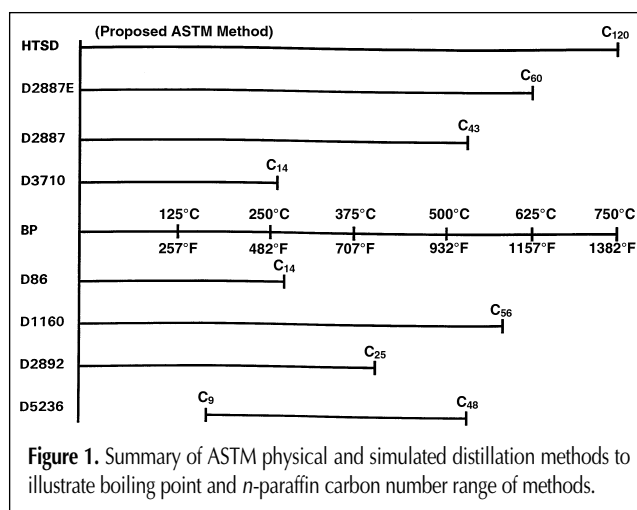

Figure 1. Summary of ASTM physical and simulated distillation methods to illustrate boiling point and n-paraffin carbon number range of methods.

products over a wide range that extends to high-boiling residue-containing materials (4–6). The chromatographic elution of heavy high-boiling materials is accomplished by the use of a thin film of column stationary phase. Film thickness varies from 0.05 to 0.15 μm that, with a 0.53-mm i.d. capillary column, results in a phase ratio (volume of the column versus the volume of the stationary phase) high enough to permit the elution of materials from the column at up to 500–600°F below their atmospheric equivalent boiling point (AEBP). For instance, the elution of C_{110}, which has a boiling point of 735°C (1355°F), occurs at a column temperature of approximately 430°C (806°F).

GC elution (retention) time is calibrated to the AEBP of *n*-paraffins (from boiling point data obtained from API Project 44 (3,7). For HTSD, the analysis of a mixture of hydrogenated poly-olefin wax and *n*-paraffin compounds is used as a calibration reference material for relating chromatographic elution (retention) time with boiling point (Figure 2).
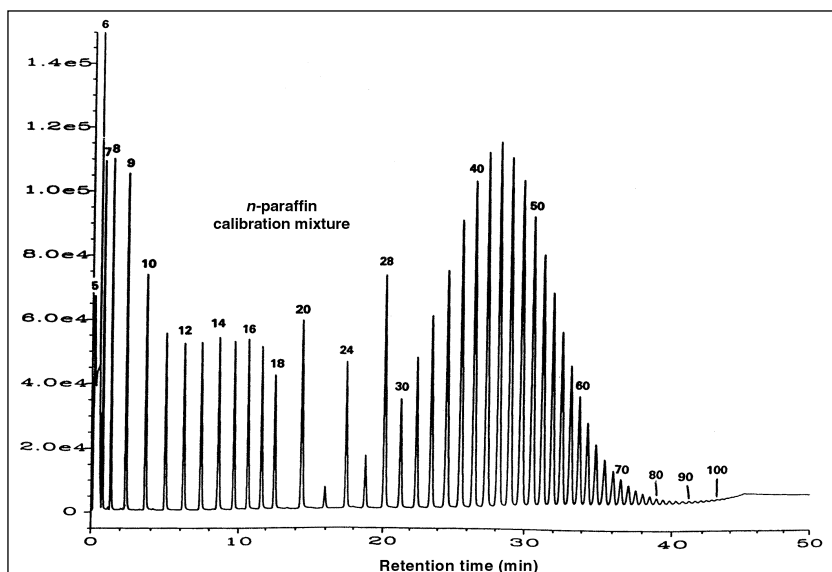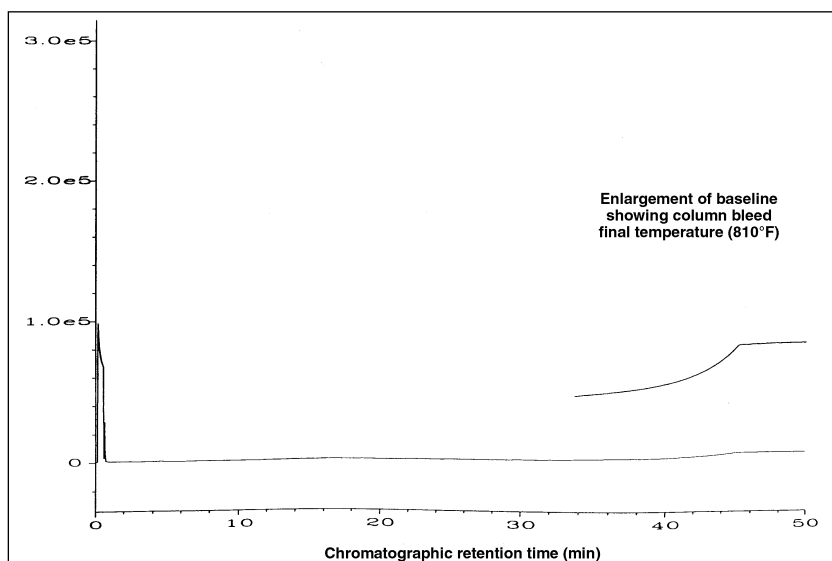
The chromatographic column requirement necessary for HTSD results in a limited capacity of the column because of the small amount of stationary phase. This requires appropriate dilution of the standards and samples (usually in carbon disulfide) for the analysis. Careful operator evaluation of the system performance is a necessity for accurate HTSD data. Performance is affected by variables such as the loss of the stationary phase at high temperatures (i.e., resulting in loss of film thickness and sample capacity) and the unavoidable buildup from residue containing samples of nonvolatile materials such as metals and asphaltenes in the injector and the column. These materials can typically be removed from the system by replacing the injector liner and removing a short piece of the column inlet. The inert conditions of high-purity fused-silica and specially treated metal GC columns, the gentle injection techniques, and the short time at maximum temperature result in little or no evidence of cracking in HTSD.

Because of the column breakdown (bleed) during the final portion of an HTSD analysis and the need to dilute the sample to approximately 1–2 percent mass, a blank GC run using only the solvent is recorded in the data system. This solvent blank is then subtracted from all subsequent GC runs in the analysis sequence of calibration, quality control, and samples (Figure 3). This blank subtraction accomplishes two important goals: it removes the signal produced by the solvent (which would interfere with accurate light end determination), and it compensates for the column bleed. The assumption during this process is that the solvent blank and the column bleed profiles are constant during the calibration and sample analysis. It is the HTSD operator's duty to verify this criteria for statistically meaningful results.

In the ROSE process, readily available light paraffinic solvents such as propane, butane, and pentane are used to extract DAO from petroleum resids (2). Solvents can be chosen based on the desired DAO quality and yield for a given feedstock. The extraction takes place under subcritical conditions, and the solvent separation from the product is achieved at energy efficient supercritical conditions, which provides for significant energy savings. Some conventional deasphalting processes can have substantial energy requirements to vaporize and condense subcritical solvent in the solvent recovery system.

A two-product ROSE unit makes DAO and asphaltene product. The three-product ROSE unit also produces an intermediate resin fraction along with DAO and asphaltene. Depending on the solvent selection, feedstock qualities, and yield levels, the DAO could be an excellent feedstock for lube oil preparation, FCC, and hydrocracking. The DAO is typically lower in sulfur, nitrogen, Conradson carbon residue, and metals than the petroleum resid. The asphaltene frac-

Figure 2. *n*-Paraffin carbon number calibration chromatogram for HTSD.

Figure 3. HTSD chromatogram of a carbon disulfide solvent blank.

tion has been described to be highly condensed aromatic rings with alkyl side chains. The condensed aromatic rings vary from 6 to more than 15 rings. The asphaltenes contain large proportions of hetero atoms such as sulfur, nitrogen, and metals concentrated from the petroleum resid feed, and its typical molecular weights range up to 5,000–10,000. The asphaltenes may be blended to road paving asphalt and fuel oil or pelletized and transported as solid fuel for cement kilns or power generators. The asphaltenes can also be further processed by resid hydrocracking, visbreaking, coking, or partial oxidation to recover additional products. The resins are smaller molecules in comparison with asphaltenes with alkyl chains interspersed with naphthenic and condensed aromatic rings and hetero atoms. The resin fraction is a high-value product and could be used as a peptizing agent to blend with the asphaltene fraction to yield performance grade asphalts. The resins can also be hydrotreated or catalytically or thermally cracked to produce valuable products.

The lighter hydrocarbon solvents such as propane selectively extract saturated hydrocarbons rather than aromatics, resins, and asphaltenes into the DAO. The selectivity increases with an increase in extraction temperature. Thus, the extraction temperature and solvent are the primary variables used to achieve the desired product yield and qualities.

A simplified process flow diagram for a two-product ROSE unit is presented in Figure 4. The feedstock is blended with solvent in certain proportions and charged to the asphaltene separator, where additional solvent is contacted in a counter-current mode at elevated temperature and pressure. The heavy asphaltene fraction drops out of the solution and is withdrawn at the bottom. The solvent dissolved in the asphaltene is separated, recovered, and recycled. The DAO leaves the top of the asphaltene separator with most of the solvent. After heat exchange with the recovered solvent, it is introduced into the DAO separator where DAO separates from solvent at supercritical conditions. The solvent from the DAO separator, after heat recovery, is circulated back to the asphaltene separator. The DAO from the DAO separator is recovered after stripping any contained solvent.

This paper presents results on the application of HTSD for characterizing the boiling point profiles of fractions from the ROSE process. This includes the petroleum resid feed, DAO, and asphaltene fractions in refinery solvent deasphalting operations.
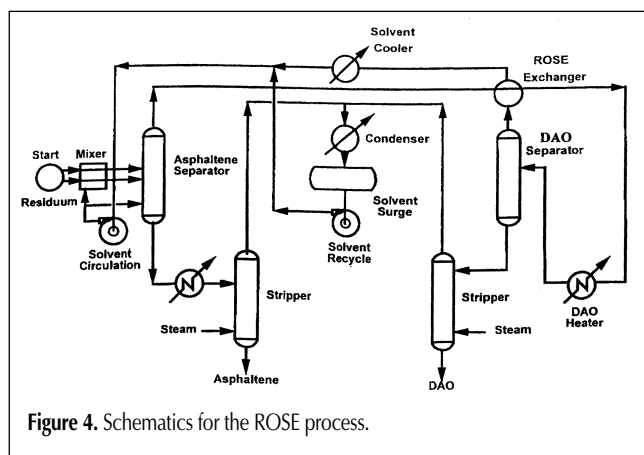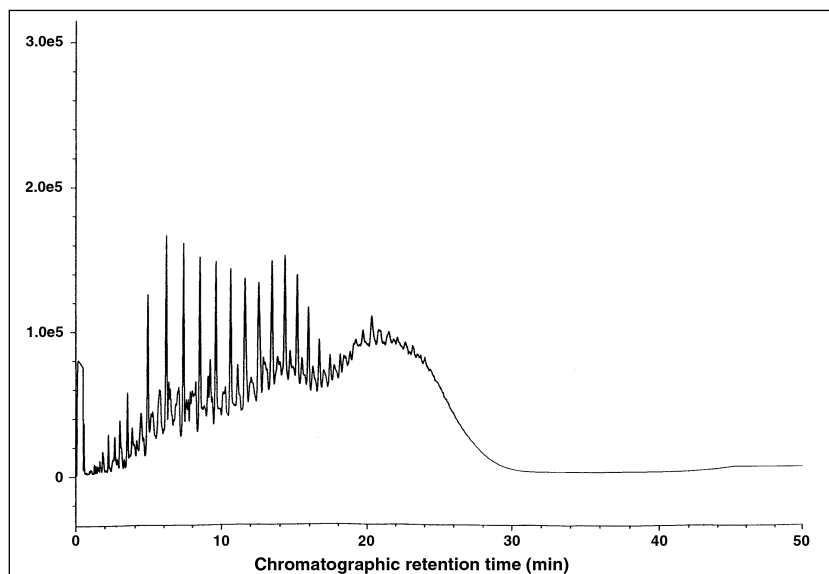

Figure 4. Schematics for the ROSE process.

Experimental

The HTSD method

The HTSD analyses for the work presented in this paper were done using a Hewlett-Packard (HP) 5890 Analytical Controls (AC) GC instrument with an HP 7673 autosampler equipped with a programmed temperature vaporization (PTV) injector and flame ionization detector (FID). The capillary column (5 m × 0.53-mm i.d.) was coated with a polymethylsiloxane phase of 0.05–0.15-µm film thickness. The column oven and injector temperature were at –20°C initially at injection and then raised at 10°C/min to approximately 435°C with a final hold for 5 min. The FID temperature was 440°C. Helium carrier gas was at a column head pressure of 5 psig. Air and hydrogen to the FID were 300 mL/min and 30 mL/min, respectively. The standards and samples were dissolved in carbon disulfide (CS$_2$) at approxiamtely 2% (w), and 1 µL of material was injected for the analysis. Data acquisition and result calculations were obtained with an HP ChemStation and AC SIMDIS software.

The HTSD calibration involved the analysis of a reference oil that had been physically distilled by methods ASTM D2892 and D5236, as shown in Figure 5. This reference oil is used to calibrate the system as an external standard for all sample percent recovery calculations. Detection response factor differences that are observed for aliphatic and aromatic hydrocarbons in other hydrocarbon analysis methods are likewise observed in HTSD. As of yet, there is no consensus among practitioners of HTSD as to the best single calibration protocol that would address all the various types of crude oils and refinery process streams that are

Figure 5. HTSD chromatogram of ASTM D2892 and D5236 physically distilled reference oil.

analyzed by HTSD. In the application presented in this paper, the particular reference oil used for calibration defines the response factor for the analysis.

The HTSD analysis results are compared with the mass distribution data from physical distillation and the statistical error of the difference between HTSD data versus actual boiling point

Table I. HTSD versus ASTM D2892 and ASTM D5236 Results for Reference Oil

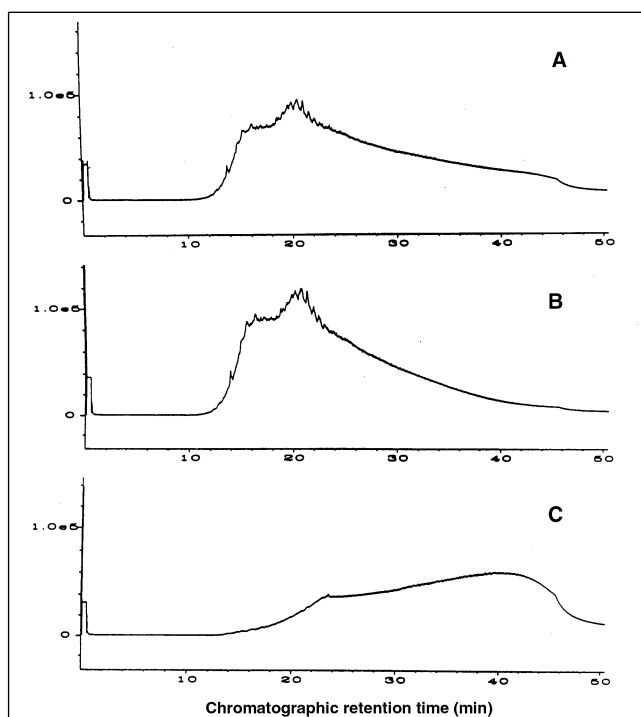| % Area	BP* (°F) referenced (ASTM D2892 and D5236)	BP* (°F) found (HTSD)	Squared difference (maximum acceptance is 139)
10	448	446	4
20	529	526	9
30	603	600	9
40	658	656	4
50	716	715	1
60	777	776	1
70	826	824	4
80	873	871	4
90	923	921	4
			40

* BP, boiling point.

Figure 8. HTSD chromatograms for resid (A), DAO (B), and asphaltene (C) from the ROSE process.
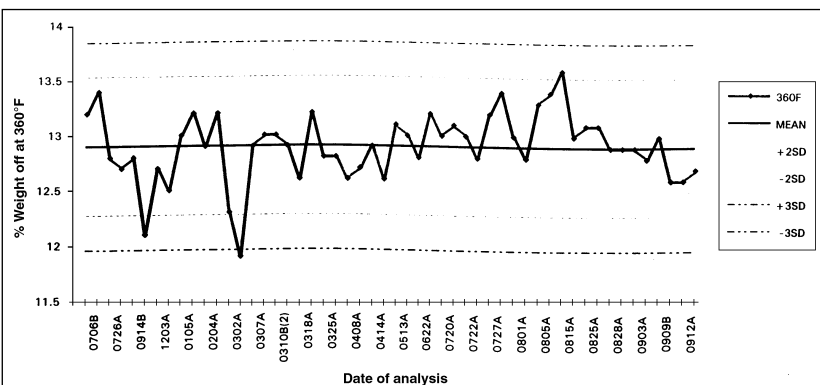

Figure 6. HTSD quality control X-chart for full-range naphtha and residue-containing sample: percent yield at 182°C (360°F).
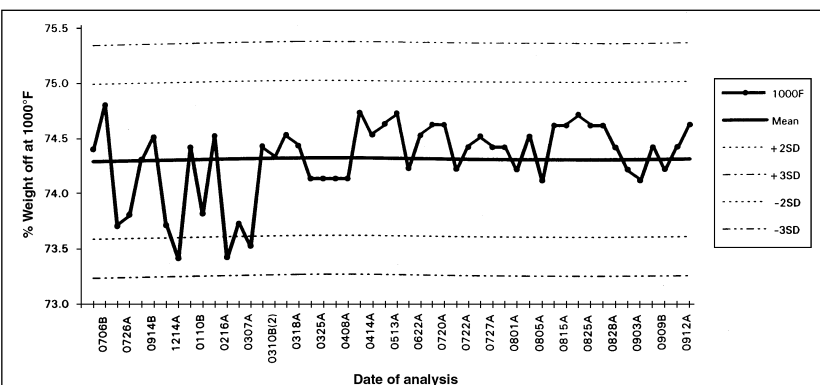

Figure 7. HTSD quality control X-chart for full-range naphtha and residue-containing sample: percent yield at 538°C (1000°F) or pitch yield.

data is reported (Table I). Reference material is currently not available for calibration of the entire higher boiling range of the HTSD analysis. However quality control (QC) samples that contain residue material boiling higher than C_{108} are analyzed as part of the quality assurance for HTSD. Statistical analysis of QC samples is done with materials such as a blend of physically distilled gas oils, lube feed stocks, hydrotreated residue, heavy California crude, or Gulf of Mexico crude.

For each QC sample, the mean and standard deviation of the temperature versus mass percent yield (for example % weight off) are tracked over time. An X-type control chart is useful for recording the QC data, and any excursions beyond ± 2 or 3 standard deviations will signal an out of control range analysis (Figures 6 and 7). Corrective action is taken when required. This may require appropriate maintenance and reanalysis before a sample analysis result is reported.

Results and Discussion

The HTSD results presented in Figure 8 and Table II show the chromatograms and percent mass yield as a function of boiling point (AEBP) for sample fractions from a ROSE process. In this

study, propane was used to extract the deasphalted oil fraction from the petroleum residue. The results show the effect of the asphaltenes being present in the resid feed and then absent in the deasphalted oil fraction product. Removal of the asphaltenes from the resid by extraction produced a deasphalted oil that is richer in lower-boiling material than the resid feed, as shown by the higher cumulative yield at each boiling cut point for the DAO in comparison with the resid feed. The DAO fraction was fully eluted in the HTSD analysis and had a total recovery of 100% mass at 733°C (1351°F). The resid feed was not fully eluted in the HTSD analysis and had a total recovery of 96.4% mass at 733°C. The asphaltene fraction itself was not fully eluting in the HTSD analysis and had a total recovery of 82.6% mass at 733°C.

The asphaltene fraction had a cumulative yield of only approximaately 23% mass at 538°C (1000°F). Nearly 80% mass of the asphaltene fraction boiled above 538°C.

Table III presents data that illustrate typical yields and qualities of DAO products from the ROSE process. The results show data for a petroleum residue from a Middle East source using propane, *n*-butane, and pentane solvents. DAO yields in this example are shown to be 36% mass with propane, 66% mass with *n*-butane, and 77% mass with *n*-pentane. The DAO is lower in sulfur, nitrogen, Conradson carbon residue, and metals than the petroleum resid.

Conclusion

The method of HTSD provides valuable boiling point and percentage yield characterization data over a wide range for products from petroleum refining resid processing operations. HTSD analysis data for fractions obtained from the ROSE solvent deasphalting process were presented in this paper. The results have shown how the method can be used to observe the effects of asphaltene removal from reduced crude and the resultant improved quality and high recovery of the deasphalted oil product for fluid catalytic cracking or hydrocracker feedstocks.

Table II. HTSD Yield (% Mass by Weight) as a Function of Boiling Point for Fractions from the ROSE Process

Sample	IBP* (°C)	371°C (700°F)	482°C (900°F)	538°C (1000°F)	Recovery at 733°C (1351°F)
Resid	317	10.4	46.8	61.6	96.4
DAO	314	13.2	57.9	74.0	100
Asphaltene	361	0.7	11.6	22.6	82.6

* IBP, initial boiling point.

Table III. Typical ROSE Process Estimated Product Yield and Qualities for a Petroleum Residue Using Propane, *n*-Butane, and *n*-Pentane Solvents

Properties	Feed	Deasphalted Oil Propane	*n*-Butane	*n*-Pentane
Yield (% weight of feed)	100	36	66	77
°API gravity	7.0	19.4	13.6	11.5
Nitrogen (%, w)	0.38	0.14	0.21	0.25
Sulfur (%, w)	4.34	2.53	3.3	3.58
Conradson Carbon (%, w)	20.3	2.9	7.7	11.0
Nickel (ppm, w)	25	1	3	6
Vanadium (ppm, w)	116	1	8	23
Viscosity, cst at 99°C (210°F)	1,610	42	141	257
Viscosity, cst at 135°C (275°F)	250	16	40	63

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