

Physical and Chemical Characterization of Petroleum Products by GC-MS

A. Mendez*, R. Meneghini, and J. Lubkowitz

SEPARATION SYSTEMS Inc., 100 Nightingale Lane, Gulf Breeze, FL 32561

Abstract

There is a need for reliable and fast means of monitoring refining, conversion, and upgrading processes aiming to increase the yield of light distillates, and thus, reducing the oil barrel bottoms. By simultaneously utilizing the FID and mass selective detectors while splitting the column effluent in a controlled way, it is possible to obtain identical gas chromatograms and total ion chromatograms from a single run. This means that besides the intensity vs. time graphs, the intensity vs. mass and boiling point can also be obtained. As a result, physical and chemical characterization can be performed in a simple and rapid manner. Experimental results on middle, heavy distillates, and crude oil fractions show clearly the effect of upgrading processes on the chemical composition and yields of diesel, jet fuels, and high vacuum gasoil fractions. The methodology is fully compliant with ASTM D-2887, D-7213, D-6352, and D7169 for simulated distillation and the previously mentioned mass spectrometry standards. The group type analysis correlated satisfactorily with high-performance liquid chromatography data.

Introduction

The world economy is currently facing a major threat due to the sudden rise of oil prices. In general, industrialized countries are not oil-producing countries. This fact creates a complex dependence on the source of energy and carries a great deal of consequence for the world economy in terms of increasing the cost of technological products and operations. It is evident, in a general overview of the situation, how directly and negatively this impacts the industry's profitability, and, consequently, the industrial growth and pay balance of industrialized countries.

As a direct consequence of high oil prices, the spot market is continuously provided with tempting offers about a wide variety of crude oils at attractive prices. Many of them are of unknown origins and physicochemical properties.

The refiners need to have a fast and reliable means of assaying these crude oils, to help with the decision to buy and process

them. The same analytical tool will also be very useful in planning the optimum processing route based on the chemical information gathered. Conventionally, a crude oil assay evaluation of the properties and qualities, which involves conventional glass distillation, takes several days (if not weeks) to be accomplished.

The main objective of this work is to develop an analytical system to rapidly evaluate a crude oil for its potential yield of highly praised refining products like distillates and lubricant base stocks, as well as the quality in its chemical composition.

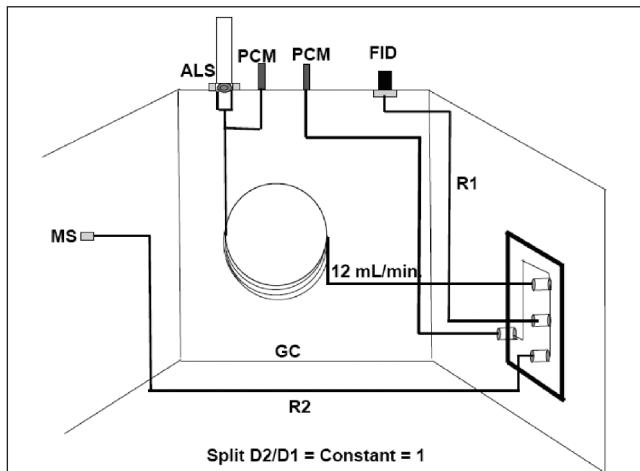


Figure 1. Split configuration via the two-way microfluidic splitter.

Table I. Experimental Conditions for ASTM D-7213

| | |
|-----------------------|---|
| Inlet | Separation Systems Temperature Programmable near column injection |
| Injection Technique | oven-track mode |
| Injection Temperature | capillary 5 m × 0.53 mm i.d. × 0.1 µm |
| Column | FID 390°C |
| Detector | Helium UHP at 12 mL/min, constant flow |
| Flow Conditions | 40°C to 380°C @ 10°C/min hold 12 min, equilibration time 2 min |
| Oven Program | 0.2 µL |
| Sample Size | 2% in CS ₂ |
| Sample Dilution | |

* Author to whom correspondence should be addressed: email AMendez@separationsystems.com.

As energy prices continue to escalate, the optimum performance and high efficiency of all oil processing plants becomes of critical importance. In many cases, performance evaluations are quite difficult, due to the extremely complex nature of the materials involved and the lack of convenient analytical procedures. This statement is particularly true in hydrocarbon upgrading processes, where quality control can be both problematic and lengthy.

Starting in boiling point ascending order, for a conventional crude oil, there are detailed gas chromatography (GC) compositional analyses only for compressed liquids (LPG) and the naphtha. This constitutes only a small fraction of the total material yield. For heavier samples up to high vacuum gasoil, the amount of chemical compounds are such that it is mainly mass spectrometry, liquid chromatography, and nuclear magnetic resonance that provide useful chemical information on the chemical composition in terms of hydrocarbon types. This information is presented in a wide variety of forms. The more detailed information is provided by mass spectrometry. ASTM D-2425, D2786, and D-3239 standard methods require the separation of saturates and aromatic prior to the analysis, to deal with

overlapping isobaric species (1).

To avoid the chromatographic separation step to reduce the sources of errors, especially in the solvent strip stage, several authors have developed a high mass resolution algorithms (2,3),

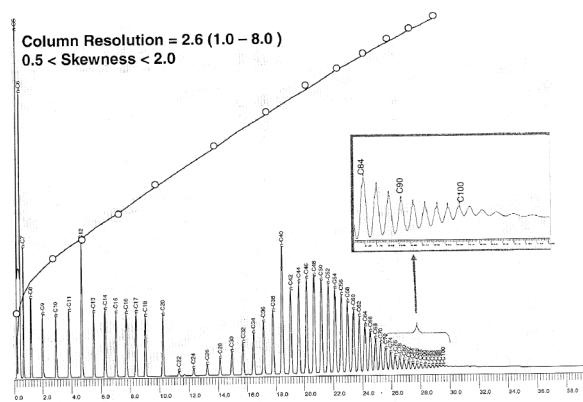


Figure 3. FID signal for boiling point calibration curve.

Table II. Experimental Conditions for ASTM D-7169

| | |
|-----------------------|---|
| Inlet | Separation Systems Temperature Programmable near column injection |
| Injection Technique | oven-track mode |
| Injection Temperature | capillary 5 m × 0.53 mm i.d. × 0.1 µm |
| Column | FID 450°C |
| Detector | Helium UHP at 20 mL/min, constant flow |
| Flow Conditions | 10°C/min @ 40°C to 430°C hold 12 min, equilibration time 2 min |
| Oven Program | 0.2 µL |
| Sample Size | 2% in CS ₂ |
| Sample Dilution | |

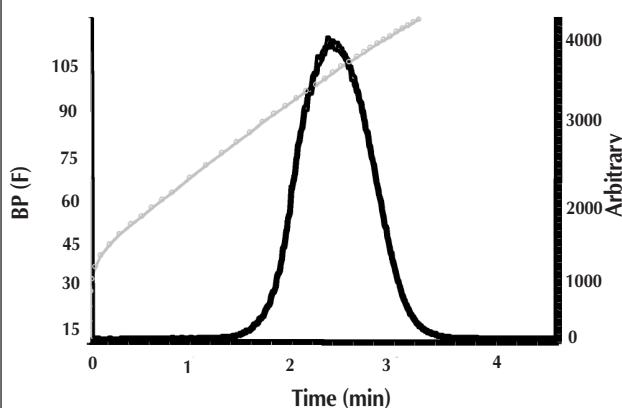


Figure 4. FID signal for the 5010 high temperature reference oil.

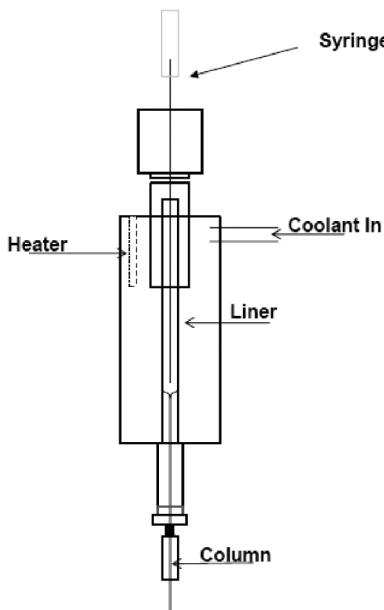


Figure 2. Temperature programmable inlet.

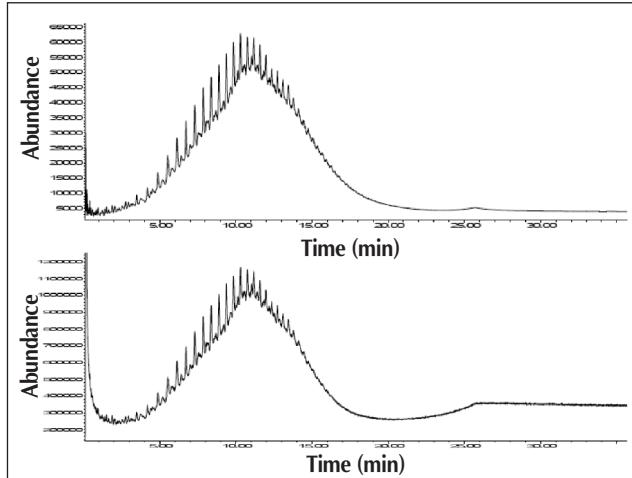


Figure 5. Hydrocracking product sample.

to cite only a few. The main disadvantage of this solution lies in the complexity and high cost of the instrumentation required.

Dzidic et al. (4) and Wadsworth and Villalanti (5) extended to jet fuels and kerosene samples the detailed compositional group

type analysis, allowing for sub-grouping of paraffins, olefins, naphthenes, and aromatic compounds. They utilized a nitric oxide Townsend discharge source. The hydrocarbon group types react differently with the chemical reagent NO₊, allowing complete separation of the groups.

Roussis and Fitzgerald (6) presented a method that combines gas chromatography (GC) and low-resolution mass spectrometry (MS) to obtain physical as well as chemical information of crude oils. However, the column dimensions and other experimental conditions were not identical to the ASTM high-temperature D-7169 standard method.

In this work, the development of a GC-MS system is presented that simultaneously acquires both flame ionization detector (FID) and mass selective detector (MSD) signals by means of a controlled splitting device. By splitting the column flow, the problem associated with the vacuum conditions needed for a satisfactory performance of the MSD detector is greatly reduced, while maintaining the integrity of the sample. This integrity can be observed from the similar signals obtained from the two detectors, as well as the results on standard reference materials with FID and MSD detection.

Results when compared with the ASTM QC samples were in total observance of the maximum deviation limits allowed, proving that there are no observable discrimination effects. The method was tested for a wide variety of hydrocarbon fractions and crude oils with equal satisfactory results.

Experimental

Experiments were performed on an Agilent 5975 XL EI/CI Inert MSD coupled with a 6890 GC (Agilent, Palo Alto, CA). The GC was also equipped with a FID in the front detector position. The analytical column was connected to both detectors, MSD and FID, via an Agilent two-way microfluidic splitter G3180B, with makeup gas to split the flow to both detectors in a controlled manner. Figure 1 shows a schematic representation of the split arrangement.

A Separation Systems temperature programmable inlet (7), illustrated in Figure 2, was installed in the back inlet position (Separation Systems, Inc., Gulf Breeze, FL). This inlet performs "near column" injections in which the sample is deposited approximately 1 mm above the column. A temperature programmable inlet is preferable and

Table III. Experimental Results vs. Tuning Conditions

| Mass | Tune 1 (%) | Tune 2 (%) | Tune 3 (%) | Mean Value | Standard Deviation |
|-----------------------------------|------------|------------|------------|------------|--------------------|
| 69 | 100 | 100 | 100 | | |
| 131 | 39 | 55 | 42 | | |
| 219 | 35 | 45 | 53 | | |
| 5 02 | 5 | 2.5 | 2.5 | | |
| Sample A | | | | | |
| Total Saturates (Volume %) | 77.3 | 78.3 | 70.2 | 75.3 | 4.4 |
| Paraffins | 48.4 | 53.2 | 40.5 | 47.4 | 6.4 |
| Monocycloparaffins | 13.1 | 12.4 | 13.9 | 13.1 | 0.8 |
| Dicycloparaffins | 8.2 | 7.5 | 9.4 | 8.4 | 1.0 |
| Tricycloparaffins + | 7.7 | 5.2 | 6.4 | 6.4 | 1.3 |
| Total Aromatics (Volume %) | 22.7 | 21.7 | 29.8 | 24.7 | 4.4 |
| Monoaromatics | 18.5 | 15.3 | 20.9 | 18.2 | 2.8 |
| Benzenes | 7.2 | 5.3 | 7.3 | 6.6 | 1.1 |
| Naphthalenebenzenes | 7.7 | 7.1 | 10.2 | 8.3 | 1.6 |
| Dinaphthalenebenzenes | 3.7 | 2.9 | 3.4 | 3.3 | 0.4 |
| Di aromatics | 4 | 5.9 | 8.2 | 6.0 | 2.1 |
| Naphthalenes | 3.2 | 3.8 | 5.6 | 4.2 | 1.2 |
| Acenaphthenes | 0.3 | 1 | 1.5 | 0.9 | 0.6 |
| Fluorenes | 0.5 | 1.1 | 1.1 | 0.9 | 0.3 |
| Tri aromatics | 0.2 | 0.2 | 0.3 | 0.2 | 0.1 |
| Phenanthrenes | 0.2 | 0.2 | 0.3 | 0.2 | 0.1 |
| Naphthenophenanthrenes | 0 | 0 | 0 | 0.0 | 0.0 |
| Thiopheno aromatics | 0 | 0.3 | 0.5 | 0.3 | 0.3 |
| Benzothiophenes | 0 | 0.3 | 0.5 | 0.3 | 0.3 |
| Dibenzothiophenes | 0 | 0 | 0 | 0.0 | 0.0 |
| Naphtobenzothiophenes | 0 | 0 | 0 | 0.0 | 0.0 |
| Sample B | | | | | |
| Total Saturates (Volume %) | 83.3 | 79.1 | 75.3 | 79.2 | 4.0 |
| Paraffins | 60.8 | 59.5 | 51.3 | 57.2 | 5.2 |
| Monocycloparaffins | 10.6 | 10 | 11.6 | 10.7 | 0.8 |
| Dicycloparaffins | 6 | 5.5 | 7 | 6.2 | 0.8 |
| Tricycloparaffins + | 6 | 4.1 | 5.3 | 5.1 | 1.0 |
| Total Aromatics (Volume %) | 16.7 | 20.9 | 24.7 | 20.8 | 4.0 |
| Monoaromatics | 9.4 | 7.9 | 9.9 | 9.1 | 1.0 |
| Benzenes | 3.4 | 2.6 | 3.3 | 3.1 | 0.4 |
| Naphthalenebenzenes | 3.4 | 3.2 | 3.9 | 3.5 | 0.4 |
| Dinaphthalenebenzenes | 2.7 | 2.1 | 2.6 | 2.5 | 0.3 |
| Di aromatics | 6.9 | 12.2 | 13.8 | 11.0 | 3.6 |
| Naphthalenes | 6.3 | 10.1 | 11.3 | 9.2 | 2.6 |
| Acenaphthenes | 0 | 0.5 | 0.9 | 0.5 | 0.5 |
| Fluorenes | 0.6 | 1.6 | 1.6 | 1.3 | 0.6 |
| Tri aromatics | 0.1 | 0.1 | 0.1 | 0.1 | 0.0 |
| Phenanthrenes | 0.1 | 0.1 | 0.1 | 0.1 | 0.0 |
| Naphthenophenanthrenes | 0 | 0 | 0 | 0.0 | 0.0 |
| Thiopheno aromatics | 0.3 | 0.7 | 0.9 | 0.6 | 0.3 |
| Benzothiophenes | 0.3 | 0.7 | 0.9 | 0.6 | 0.3 |
| Dibenzothiophenes | 0 | 0 | 0 | 0.0 | 0.0 |
| Naphtobenzothiophenes | 0 | 0 | 0 | 0.0 | 0.0 |

widely used to avoid sample discrimination (i.e., needle discrimination), which occurs in hot inlets for wide boiling range samples. Both inlet and column were programmed in the "oven track" mode.

Two ASTM methods for Simulated Distillation D-7213 (8) and the High Temperature Method for Crude Oils D-7169 (8) were

tested. The chromatographic conditions used are listed in Tables I and II for both methods, respectively.

The mass spectrometer was set to scan at 70 eV, continuously over the entire mass range from 29 to 1050 Da. Tuning was performed using the conventional "autotune" procedure.

Samples were prepared in carbon disulfide according to the

Sample preparation section of both simulated distillation methods (8).

To explore the effect of the tuning conditions on the quantitative results, a preliminary evaluation was made on four low-sulfur middle distillates and reported in Table III.

The main purpose of this experiment is to explore how different tuning conditions might impact the reproducibility of the method in an interlaboratory round robin study. Table III shows that there are some tuning parameters that should be avoided, as in the case shown in conditions under the column TUNE 3, which presents the highest deviations. These conditions are very dependable on the source cleanliness, background pressure, source temperature, etc.

The experimental error can also be substantially reduced by running a QC sample, similar in viscosity or average molecular weight to the samples being analyzed. An appropriate QC sample can be a hydrocarbon fraction of known chemical composition, preferably obtained by different methodologies.

The boiling point calibration curve shown in Figure 3 was obtained by injecting 0.2 μ L of the retention time standard SS-3E-06, a paraffin, and Polywax blend spiked with C5-C20 and C40 (manufactured by Separation Systems Inc.).

The dimensions of the restrictors R1 and R2 (Figure 1) were calculated using the calculator spread sheet shown in Table IV. A split ratio of 1:1 for the two detectors was considered to give satisfactory results, with no appreciable time shift between the two signals. Deactivated fused-silica tubing of 0.25 mm i.d. was used as restrictors.

The FID signal was used to determine the yield, boiling point distribution (8), and average molecular weight of the sample. The software uses an average molecular weight, which corresponds to an average carbon number equal to the *n*-paraffin at T₅₀ (i.e., the carbon number in the calibration curve shown in Figures 3 and 4), at the temperature when 50% yield is obtained. The simulated distillation calculations were accomplished by means of the special software Simdist Expert version 8 (Separation Systems).

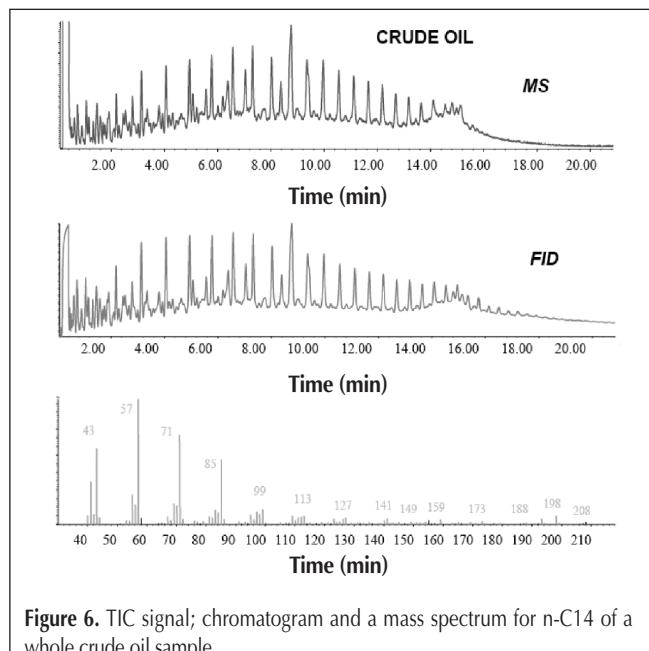
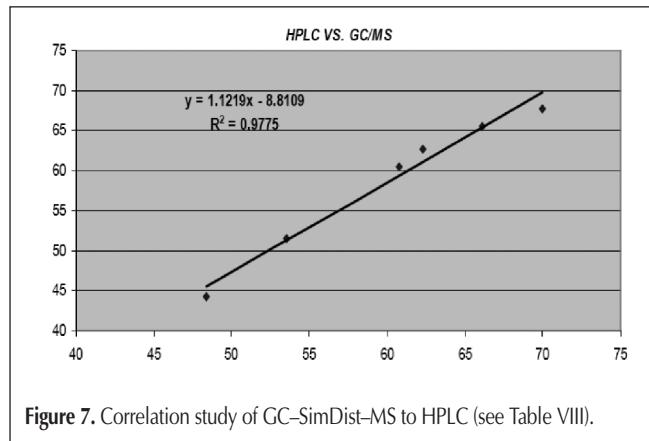
The MSD signal was used to obtain the Group Type quantitative report in volume %

Table III. (Continued) Experimental Results vs. Tuning Conditions

| Mass | Tune 1 (%) | Tune 2 (%) | Tune 3 (%) | Mean | Standard Deviation |
|-----------------------------------|------------|------------|------------|------|--------------------|
| 69 | 100 | 100 | 100 | | |
| 131 | 39 | 55 | 42 | | |
| 219 | 35 | 45 | 53 | | |
| 502 | 5 | 2.5 | 2.5 | | |
| Sample C | | | | | |
| Total Saturates (Volume %) | 90.7 | 91.4 | 92.4 | 91.5 | 0.9 |
| <i>Paraffins</i> | 41.8 | 39.5 | 40.9 | 40.7 | 1.2 |
| Monocycloparaffins | 17.6 | 17.6 | 17.8 | 17.7 | 0.1 |
| Dicycloparaffins | 15 | 17 | 17 | 16.3 | 1.2 |
| Tricycloparaffins + | 16.2 | 17.3 | 16.7 | 16.7 | 0.6 |
| Total Aromatics (Volume %) | 9.3 | 8.6 | 7.6 | 8.5 | 0.9 |
| <i>Monoaromatics</i> | 9.2 | 6.6 | 5.6 | 7.1 | 1.9 |
| Benzenes | 5.8 | 5.9 | 5 | 5.6 | 0.5 |
| Naphthenebenzenes | 1.5 | 0.3 | 0.2 | 0.7 | 0.7 |
| Dinaphthenebenzenes | 1.9 | 0.4 | 0.3 | 0.9 | 0.9 |
| <i>Diaromatics</i> | 0 | 1.9 | 1.9 | 1.3 | 1.1 |
| Naphthalenes | 0 | 0.9 | 1 | 0.6 | 0.6 |
| Acenaphthenes | 0 | 0 | 0 | 0.0 | 0.0 |
| Fluorenes | 0 | 1 | 0.9 | 0.6 | 0.6 |
| <i>Triaromatics</i> | 0 | 0 | 0 | 0.0 | 0.0 |
| Phenanthrenes | 0 | 0 | 0 | 0.0 | 0.0 |
| Naphthophenanthrenes | 0 | 0 | 0 | 0.0 | 0.0 |
| <i>Thiopheno aromatics</i> | 0 | 0.1 | 0.1 | 0.1 | 0.1 |
| Benzothiophenes | 0 | 0.1 | 0.1 | 0.1 | 0.1 |
| Dibenzothiophenes | 0 | 0 | 0 | 0.0 | 0.0 |
| Naphtobenzothiophenes | 0 | 0 | 0 | 0.0 | 0.0 |
| Sample D | | | | | |
| Total Saturates (Volume %) | 95.5 | 96.7 | 97.6 | 96.6 | 1.1 |
| <i>Paraffins</i> | 44 | 41.3 | 41.8 | 42.4 | 1.4 |
| Monocycloparaffins | 18.4 | 18.7 | 19.3 | 18.8 | 0.5 |
| Dicycloparaffins | 16 | 18.1 | 18.4 | 17.5 | 1.3 |
| Tricycloparaffins + | 17.1 | 18.7 | 18.2 | 18.0 | 0.8 |
| Total Aromatics (Volume %) | 4.5 | 3.3 | 2.4 | 3.4 | 1.1 |
| <i>Monoaromatics</i> | 4.1 | 1 | 0.9 | 2.0 | 1.8 |
| Benzenes | 0.9 | 0 | 0 | 0.3 | 0.5 |
| Naphthenebenzenes | 1.4 | 0.4 | 0.4 | 0.7 | 0.6 |
| Dinaphthenebenzenes | 1.8 | 0.6 | 0.5 | 1.0 | 0.7 |
| <i>Diaromatics</i> | 0 | 1.7 | 1.4 | 1.0 | 0.9 |
| Naphthalenes | 0 | 0.4 | 0.4 | 0.3 | 0.2 |
| Acenaphthenes | 0 | 0 | 0 | 0.0 | 0.0 |
| Fluorenes | 0 | 1.3 | 1 | 0.8 | 0.7 |
| <i>Triaromatics</i> | 0 | 0.4 | 0 | 0.1 | 0.2 |
| Phenanthrenes | 0 | 0.4 | 0 | 0.1 | 0.2 |
| Naphthophenanthrenes | 0 | 0 | 0 | 0.0 | 0.0 |
| <i>Thiopheno aromatics</i> | 0.4 | 0.2 | 0 | 0.2 | 0.2 |
| Benzothiophenes | 0.4 | 0.2 | 0 | 0.2 | 0.2 |
| Dibenzothiophenes | 0 | 0 | 0 | 0.0 | 0.0 |
| Naphtobenzothiophenes | 0 | 0 | 0 | 0.0 | 0.0 |

Table IV. Restrictor Lengths Calculation Step [Agilent Technologies Effluent Splitter Calculator (with Makeup)]

| Inputs | | | | | | | |
|---|---------|---------|---------|---------|---------|---------|--------|
| Initial Column Flow (mL/min) | | | | | | | 20 |
| Initial Oven Temp (C) | | | | | | | 35 |
| Carrier Gas (Helium, Hydrogen, Nitrogen, Argon) | | | | | | | Helium |
| Column Outlet Pressure (psig) | | | | | | | 4 |
| Detector 1 Operating Pressure (psia) | | | | | | | 14.696 |
| Detector 1 Desired Flow (mL/min) | | | | | | | 7.5 |
| Detector 2 Operating Pressure (psia) | | | | | | | 0 |
| Flow Ratio of Det 2 to Det 1 | | | | | | | 1 |
| Results | | | | | | | |
| 0.10 | 0.18 | 0.20 | 0.25 | 0.32 | 0.45 | 0.53 | |
| mm i.d. | mm i.d. | mm i.d. | mm i.d. | mm i.d. | mm i.d. | mm i.d. | |
| Length Det 1 Tube (m) | 0.029 | 0.309 | 0.471 | 1.149 | 3.084 | 12.059 | 23.204 |
| Holdup Time Det 1 (min) | 0.000 | 0.001 | 0.002 | 0.008 | 0.0037 | 0.282 | 0.754 |
| Length Det 2 Tube (m) | 0.077 | 0.808 | 1.231 | 3.006 | 8.070 | 31.558 | 60.723 |
| Flow Det 2 (mL/min) | 7.5000 | 7.5000 | 7.5000 | 7.5000 | 7.5000 | 7.5000 | 7.5000 |
| Holdup Time Det 2 (min) | 0.000 | 0.002 | 0.004 | 0.016 | 0.071 | 0.549 | 1.466 |
| Makeup Flow (mL/min) | 3 | | | | | | |

**Figure 6.** TIC signal; chromatogram and a mass spectrum for n-C14 of a whole crude oil sample.**Figure 7.** Correlation study of GC-SimDist-MS to HPLC (see Table VIII).

as well as in weight %, shown in Table VII. For this particular application, an Aromatic & Saturate Analysis (Separation Systems Inc., ASA software) was applied. This software was developed based on a previous method published by C.J. Robinson (9). The procedure determines 4 saturated hydrocarbons and 21 aromatic types. Saturated compounds are classified as paraffins, noncondensed cycloparaffins, 2-ring condensed cycloparaffins, and 3-ring and greater condensed cycloparaffins, which are denominated in the reports as "Tricycloparaffins +" compounds.

Results and Discussions

The described GC-FID-simulated distillation-MS system was tested to determine possible sample discrimination of either the detectors or the splitting of the column effluent.

The fact that the retention time standard allowed the system to be calibrated by boiling points of normal paraffins up to C100, and the fact that the reference oil samples produced a boiling point distribution within the ASTM consensus values (as can be seen in Figures 3 and 4 and Table V), proves that the sample was not affected in any way. Therefore, the experimental conditions for column resolution, skewness of peaks, and boiling point distribution for the quality control (QC) samples of the standard methods were rigorously maintained. The conditions met in

Table V. External Standard for Response Factor Calibration

| % Off | BP (C) | QC (C) | (-) | Limit |
|-------|--------|--------|------|-------|
| IBP | 429.0 | 427.2 | 1.7 | 8.9 |
| 5.00 | 476.2 | 477.2 | -1.0 | 2.8 |
| 10.00 | 491.3 | 492.2 | -0.9 | 2.8 |
| 15.00 | 500.9 | 502.2 | -1.3 | 2.8 |
| 20.00 | 508.4 | 510.0 | -1.6 | 3.3 |
| 25.00 | 515.7 | 517.2 | -1.5 | 3.3 |
| 30.00 | 522.4 | 523.9 | -1.5 | 3.9 |
| 35.00 | 528.9 | 530.6 | -1.7 | 3.9 |
| 40.00 | 535.0 | 536.7 | -1.6 | 4.4 |
| 45.00 | 540.8 | 542.2 | -1.4 | 4.4 |
| 50.00 | 546.7 | 548.3 | -1.6 | 4.4 |
| 55.00 | 552.8 | 554.4 | -1.6 | 4.4 |
| 60.00 | 559.9 | 560.0 | -1.0 | 4.4 |
| 65.00 | 565.1 | 566.1 | -1.0 | 4.4 |
| 70.00 | 571.0 | 572.2 | -1.2 | 4.4 |
| 75.00 | 577.4 | 578.3 | -0.9 | 5.0 |
| 80.00 | 584.6 | 585.6 | -0.9 | 4.4 |
| 85.00 | 592.6 | 592.8 | -0.1 | 3.9 |
| 90.00 | 602.3 | 602.2 | 0.1 | 4.4 |
| 95.00 | 616.9 | 615.6 | 1.4 | 3.9 |
| FBP | 659.5 | 656.1 | 3.4 | 17.8 |

Table V are an assurance of appropriate instrument performance. In this table, "QC (C)" represents the boiling point consensus values in °C for the quality control material, column "(–)" represents the difference between experimental reference oil runs [column "BP(C)"] and the boiling point distribution consensus values [column "QC(C)"]. This variation should not be greater than the limit values.

The similarity of both traces, the MSD total ion chromatogram (TIC), and the FID chromatogram also confirm the sample integrity.

There are, however, some differences in the two signals. These differences can be explained by the intrinsic properties of the two detectors. The FID responds weakly to the carbon disulfide, whereas in the MS its signal is very high. Another aspect that merits consideration is the background level and column bleeding response being higher in the mass spectrum, as can be seen from Figure 5. These differences reflect the need to record inter-sample blank runs. These blanks have to be subtracted from the corresponding previous sample signals.

The simultaneous system was tested on samples of different nature: crude oils, diesel, lube fractions, and products of various conversion processes. Figure 5 is a typical representation of the simultaneous acquisition of both MSD and FID detectors. The upper trace in Figure 5 represents the FID signal, whereas the lower trace corresponds to the MSD signal conventionally known as TIC. This signal corresponds to a high vacuum gasoil charge and product of hydrocracking, as identified in the Sample ID of Table VII.

The algorithm was tested on different tuning conditions, as shown in Table III. From these data, it can be concluded that by performing an instrumental autotune, procedure results can be repeatable. Based on the results of Table III, even after manually altering the tuning conditions, the standard deviations were pre-

Table VI. Simulated Distillation Repeatability Study

| % Off | BP (C)(1) | BP (C)(2) | BP (C)(3) | Average | STD Dev |
|-------|-----------|-----------|-----------|---------|---------|
| IBP | 337.8 | 337.5 | 337.6 | 337.6 | 0.0 |
| 5.00 | 355.6 | 355.6 | 355.7 | 355.6 | 0.0 |
| 10.00 | 362.8 | 362.9 | 362.9 | 362.9 | 0.0 |
| 15.00 | 367.9 | 367.9 | 367.9 | 367.9 | 0.0 |
| 20.00 | 371.2 | 371.2 | 371.2 | 371.2 | 0.0 |
| 25.00 | 374.6 | 374.6 | 374.7 | 374.6 | 0.0 |
| 30.00 | 377.6 | 377.6 | 377.7 | 377.7 | 0.0 |
| 35.00 | 380.6 | 380.6 | 380.6 | 380.6 | 0.0 |
| 40.00 | 382.7 | 382.7 | 382.7 | 382.7 | 0.0 |
| 45.00 | 385.2 | 385.2 | 385.2 | 385.2 | 0.0 |
| 50.00 | 387.7 | 387.7 | 387.7 | 387.7 | 0.0 |
| 55.00 | 390.3 | 390.3 | 390.3 | 390.3 | 0.0 |
| 60.00 | 392.9 | 392.9 | 392.9 | 392.9 | 0.0 |
| 65.00 | 395.0 | 394.9 | 394.9 | 394.9 | 0.0 |
| 70.00 | 397.9 | 397.9 | 397.9 | 397.9 | 0.0 |
| 75.00 | 401.1 | 401.1 | 401.1 | 401.1 | 0.0 |
| 80.00 | 404.2 | 404.2 | 404.2 | 404.2 | 0.0 |
| 85.00 | 408.6 | 408.7 | 408.6 | 408.6 | 0.0 |
| 90.00 | 413.9 | 413.9 | 413.8 | 413.9 | 0.0 |
| 95.00 | 422.7 | 423.0 | 422.7 | 422.8 | 0.0 |
| FBP | 456.0 | 457.9 | 456.1 | 456.7 | 0.2 |

dominantly below 1% with a few exceptions, with 6.4 being the maximum deviations which correspond to the paraffin content of Sample A.

This analytical procedure allows the feed and product of a process to be compared under the same analytical and processing conditions, to study the changes undergone during the upgrading process (10,11). Table VII is an example of the chem-

Table VII. Group-Type Analysis of Feed and (Product) of Hydrocracking [Sample ID: HVGO Chg & (Product) and Average Molecular Weight: 436 & (408)]

| | Aromatic and Saturate Analysis by Mass Spectrometry | |
|---------------------------------|---|---------------|
| | % Volume | % Weight |
| Saturates | 47.12 (49.66) | 44.16 (47.62) |
| Paraffins | 12.47 (12.00) | 11.14 (10.90) |
| Monocycloparaffins | 12.60 (12.16) | 11.54 (11.32) |
| Dicycloparaffins | 12.07 (13.90) | 11.58 (13.58) |
| Tricycloparaffins+ | 9.98 (11.60) | 9.90 (11.84) |
| Aromatics | 52.88 (50.34) | 55.84 (52.38) |
| <i>Monoaromatics</i> | 21.96 (33.06) | 21.31 (32.68) |
| Benzenes | 8.54 (12.24) | 8.01 (11.67) |
| Naphthalenebenzenes | 6.71(10.93) | 6.65 (11.03) |
| Dinaphthalenebenzenes | 6.71 (9.89) | 6.65 (11.03) |
| <i>Di aromatics</i> | 10.39 (6.98) | 10.82 (7.39) |
| Naphthalenes | 1.97 (1.26) | 2.00 (1.30) |
| Acenaphthenes and Dibenzofurans | 3.70 (2.65) | 3.84 (2.79) |
| Fluorenes | 4.72 (3.07) | 4.99 (3.30) |
| <i>Tri aromatics</i> | 5.51 (3.48) | 6.03 (3.90) |
| Phenanthrenes | 2.92 (2.07) | 3.12 (2.28) |
| Naphthalophenanthrenes | 2.59 (1.40) | 2.91 (1.62) |
| Tetraaromatics | 3.77 (1.60) | 4.36 (1.91) |
| Pyrenes | 2.60 (0.94) | 2.98 (1.11) |
| Chrysenes | 1.16 (0.66) | 1.37 (0.80) |
| <i>Pentaaromatics</i> | 0.65 (0.41) | 0.84 (0.56) |
| Perylenes | 0.64 (0.41) | 0.82 (0.56) |
| Dibenzanthracenes | 0.02 (0.00) | 0.02 (0.00) |
| <i>Thiopheno Aromatics</i> | 8.99 (2.85) | 10.40 (3.41) |
| Benzothiophenes | 5.03 (1.34) | 5.55 (1.51) |
| Dibenzothiophenes | 3.02 (1.36) | 3.67 (1.69) |
| Naphthobenzothiophenes | 0.93 (0.16) | 1.18 (0.20) |
| <i>Unidentified Aromatics</i> | 1.62 (1.89) | 2.08 (2.54) |
| Class II | 0.00 (0.00) | 0.00 (0.01) |
| Class III | 0.02 (0.06) | 0.02 (0.09) |

Table VIII. Correlation Study of GC-SimDist-MS vs. HPLC

| | GC-SimDist-MS (%w) | | HPLC (%w) | | Diff. |
|----------|--------------------|-----------|-----------|-----------|-------|
| | Saturates | Aromatics | Saturates | Aromatics | |
| Sample 1 | 62.73 | 37.27 | 62.3 | 37.7 | 0.43 |
| Sample 2 | 69.48 | 30.52 | 70.0 | 30.0 | -0.52 |
| Sample 3 | 71.4 | 28.6 | 66.1 | 33.9 | 5.3 |
| Sample 4 | 56.99 | 43.01 | 53.5 | 46.5 | 3.49 |
| Sample 5 | 60.43 | 39.57 | 60.8 | 39.2 | -0.37 |
| Sample 6 | 44.2 | 55.8 | 48.4 | 51.6 | -4.2 |

ical changes of a feed stock (left column) during hydrocracking (right column in brackets).

From Table VII, it can be determined how, for instance, the total sulfur compound content was reduced by a third. It has to be considered that the reduction in the thiophenic content is independent of the yield of the fractions. This information is available from the simulated distillation data.

There are several changes in composition that can be explained from the nature of the refining process. This process catalytically introduces hydrogen in the sample; therefore, the reduction of polycyclic aromatics and the increase of monoaromatics (benzenes, naphthalenebenzenes, and dinaphthalenebenzenes) can be expected. The polycyclic aromatics evidently decreased and the triaromatics resulted to be the more reactive species.

Although it is difficult to correlate these values with other techniques, some attempts were made in this direction. A comparison study was performed with liquid chromatography (LC), which separates the compounds differently: the thiophenics are distributed in the aromatics according to their aromaticity and the polars are reported as a separate fraction. This evidently gives the study no other option but to compare them at the total saturate and total aromatic level. Table VIII and FIGURE 6 is the result of such a comparison.

Whole crude oils were also considered. As it has been presented elsewhere (12), Figure 7 presents traces of a high paraffinic crude oil. As can be seen, the time axis can be calibrated in terms of number of carbons, boiling point, and chemical composition. Therefore, it is possible to perform a group type analysis on a particular time slot corresponding to a fraction of interest to get the primary chemical composition, without having to obtain the cuts by conventional glass distillation.

Conclusions

The availability of a fast and reliable procedure that provides the physical and chemical information of crude oils and their fractions is very useful for the oil industry. The developed analytical method is fast, repeatable, and can serve as an excellent screening technique to study changes in the refining and upgrading processes. Its low-resolution mode demands simple hardware; therefore, high costs and highly resolving multidimensional chromatographic techniques are not required.

The controlled split of column elution for the simultaneous data acquisition from two detectors has been proved with no discrimination of either light or heavy components in the hydrocarbon mixtures tested. This no-discrimination effect can be shown by constructing a boiling point calibration curve with the use of *n*-paraffin standards up to C100 and the proper temperature of transfer lines synchronized with the oven temperature.

Additionally, the QC samples rendered identical traces for both mass and FID detectors. The boiling point distribution was always within the allowed deviation limits.

Because no changes in either the software or experimental conditions have been introduced, it can be concluded that the procedure is fully compliant with existing ASTM methods for simulated distillation.

Because crude oil samples can be directly analyzed, it is possible to obtain chemical information on any particular fraction across the boiling range without the need for glass distillation methods that demand time and a large amount of samples.

References

1. Annual Book of ASTM Standards. Vol 05.01 and 05.02. American Society for Testing and Materials, West Conshohocken, PA, 2002.
2. E.J. Gallegos, J.W. Green, L.P. Lideman, R.L. Le Torneau, and R.M. Teeter. Petroleum group-type analysis by high-resolution mass spectrometry. *Anal. Chem.* **39**: 1833–1838 (1967).
3. A. Fafet, J. Bonnard, and F. Prigent. New developments in mass spectrometry for group-type analysis of petroleum cuts: development and validation of a new inlet system for heavy cuts. *Oil & Gas Science and Technology Rev. IFP* **54(4)**: 453–462 (1999).
4. I. Dzidic, H. Petersen, P.A. Wadsworth, and H.V. Hart. Townsend discharge nitric oxide chemical ionization gas chromatography–mass spectrometry for hydrocarbon analysis of the middle distillates. *Anal. Chem.* **64**: 2227–2232 (1992).
5. P.A. Wadsworth and D.C. Villalanti. Pinpoint hydrocarbon types. *Hydrocarbon Process.* **71**: 109–112 (1992).
6. S.G. Roussis and W.P. Fitzgerald. Gas chromatographic simulated distillation–mass spectrometry for the determination of the boiling point distributions of crude oils. *Anal. Chem.* **72(7)**: 1400–1409 (2000).
7. J. Lubkowitz and R. Meneghini. Determination of the boiling-point distribution by simulated distillation from *n*-pentane through *n*-tetratetracontane in 70 to 80 seconds. *J. Chromatogr. Sci.* **40(5)**: 269–275 (2002).
8. Annual Book of ASTM Standards. Vol. 05.04.
9. C.J. Robinson. Low-resolution mass spectrometric determination of aromatics and saturates in petroleum fractions. *Anal. Chem.* **43**: 1425–1434 (1971).
10. A. Mendez, R. Meneghini, and J.A. Lubkowitz. “GC/MS serving to screen changes in chemical composition & yields of hydrocarbon fractions undergoing conversion & upgrading processes”, presented at Pittcon. Chicago, IL, February, 2007.
11. A. Mendez, R. Meneghini, S. Elliott, and J.A. Lubkowitz. “Group Type Analysis of Middle Distillates by GC/MS”, presented at Pittcon. Orlando, FL, February, 2006.
12. A. Mendez, R. Meneghini, and J.A. Lubkowitz. “Physical and Chemical Characterization of Petroleum Fractions by GC-SIMDIST-MS”, presented at Gulf Coast Conference. Galveston TX, October, 2006.

Manuscript received May 31, 2007
revision received July 12, 2007.