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*Presented at the
Symposium on Separation
Science and Technology for
Fuel Applications,
224th ACS Meeting,
August 18–22, 2002,
Boston, Massachusetts,
USA*

Determination of conjugated dienes in petroleum products by supercritical fluid chromatography and ultraviolet detection

A method for determining total conjugated dienes in petroleum products, such as catalytic or thermal cracking fractions, using supercritical fluid chromatography (SFC) is presented. The separation is carried out in one or two silica columns and with CO₂ as mobile phase. The conditions of analysis are the same as used in group-type analysis of diesel fuels by SFC (ASTM D 5186 standard method), except that UV detection at 240 nm is used. Hydrocarbons with two conjugated double bonds are the only substances eluting in the retention time range of the non-aromatics that appreciably absorb UV radiation at this wavelength. This was confirmed by analyzing standards of olefins, isolated diolefins, and conjugated diolefins. Results are reported in mol L⁻¹ of 1,3-pentadiene. Several samples of different natures, such as fluid catalytic cracking liquid products and hydrotreated cracking naphthas, were successfully analyzed. The results correlate quite well with the respective diene values as determined by UOP method 326, although the slope and intercept were specific for each type of product.

Key Words: Supercritical fluid chromatography; Conjugated dienes; Petroleum products

Received: September 20, 2002; revised: January 22, 2003; accepted: March 25, 2003

DOI 10.1002/jssc.200301469

1 Introduction

Aliphatic unsaturated hydrocarbons such as olefins and diolefins are formed during thermal or catalytic cracking of heavy petroleum fractions. Among these compounds, conjugated dienes are particularly reactive for polymerization and are known to contribute significantly to the instability of the resulting fuels. Nevertheless, the participation of cracking fractions in fuel blends is tending to grow, as the world feedstocks of light petroleum diminish. To attain stable fuels the cracking conditions should be optimized in order to minimize the formation of conjugated dienes. Afterwards, the conjugated dienes should be removed, usually by hydrogenation. To support the investigation of both cracking and hydrotreatment operational parameters, a fast and precise analytical method for quantification of this hydrocarbon family is desirable.

Although gas chromatography is usually used for compositional analysis of light distillates, this technique is not well suited for the determination of conjugated dienes. Problems inherent to the complexity of the matrix, such as coelution or lack of chromatographic standards, and the low concentration of conjugated dienes make the unequivocal identification of the conjugated dienes, specially the heavy ones, by GC-MS very difficult. As a consequence,

quantification by GC with flame ionization detection (FID) is also troublesome.

UOP method 326 is generally used to measure the total content of conjugated dienes in petroleum products [1]. In this method, a fuel sample is refluxed with maleic anhydride, leading to Diels-Alder reactions with the conjugated diolefins. Unreacted maleic anhydride is then hydrolyzed to maleic acid, which in turn is quantified by titration against a strong base. Consumed maleic anhydride is taken as a measure of the content of conjugated dienes present in the fuel. The result is reported as diene value, defined as the number of grams of I₂ equivalent to the amount of maleic anhydride, on a 1:1 molar basis, that reacts with 100 g of sample. The determination is rather empirical, since some diolefins may not react completely, while certain compounds like vinyl aromatics or anthracene and its homologues may react as if they were conjugated diolefins. The method is cumbersome and requires too much manipulation. In addition, it takes more than three hours and its automation is impossible. It is not suitable, for instance, for analyzing a large number of samples in a short period of time.

Supercritical fluid chromatography with flame ionization detection (SFC-FID) has been successfully used for determining total aromatics and aromatics by ring number in samples ranging from light fractions up to vacuum distillates and residues [2–5]. Non-aromatics, which include

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saturated hydrocarbons, olefins, dienes, and alkyl-sulfur compounds, are separated from aromatics on one or more silica columns using CO₂ as mobile phase. This system may also be modified to allow the analysis of olefins, by adding a silver-containing column and two backflush valves to the flow path [6]. Olefin content is normally much higher than diene content, and since neither chromatographic system separates them, a more selective way of detecting conjugated dienes, like UV detection, is needed.

2 Experimental

A supercritical fluid chromatograph from Berger Instruments (Newark, DE, USA) was used, which included an autosampler, a high-pressure pump, a column oven, and a flame ionization detector. An Agilent UV diode-array detector, model 1100, with a high-pressure analytical cell, provided detection (Agilent Technologies, Wilmington, DE, USA). Carbon dioxide 99.95% pure (Praxair, Duque de Caxias, RJ, Brazil) was used as mobile phase. The outlet pressure of CO₂ was set at 216 bar. The oven temperature was set at 35°C, resulting in a density of CO₂ of 0.880 g mL⁻¹. An internal loop of 0.5 µL was used for injection. Chromatographic separation was performed on one or two silica columns (HP Group Separation, 250 mm × 2.0 mm ID, Agilent Technologies), depending on the required resolution. Chromatograms for quantification of conjugated dienes were obtained at 240 nm. Samples were injected as received or diluted five times with toluene (HPLC grade), depending on the content of the conjugated dienes. The conditions of analysis can be the same as those used for determination of aromatics in diesel fuel [7], except that UV detection is used instead of FID.

Pure olefins and isolated and conjugated diolefins were of chromatographic grade and were purchased from several sources. The standards were diluted in hexane (HPLC grade) and were injected under the mentioned conditions. Calibration curves were constructed with piperylene (1,3-pentadiene, mixture of isomers, Aldrich, St. Louis, MO, USA) and the concentration of conjugated dienes was reported in mol L⁻¹. The SFC method was tested with several samples, including fluid catalytic cracking (FCC) liquid products, FCC naphthas, and respective hydrotreating products and hydrotreated delayed coking naphthas. Diene values given by UOP standard method 326 were also obtained for all these samples.

3 Results and discussion

Absorption data for some non-aromatic, unsaturated hydrocarbons are reported in **Table 1**. While the absorbance of both olefins and isolated dienes extinguishes at around 225–240 nm, the UV absorption of the conjugated dienes remains up to 250 nm. Alkyl-sulfur compounds,

Table 1. Retention time and absorption data of selected non-aromatic, unsaturated hydrocarbons (conditions: see Section 2. Experimental).

| Hydrocarbon | Retention time [min] | $\lambda_{\varepsilon = \max^a}$ [nm] | $\lambda_{\varepsilon \approx 0^b}$ [nm] |
|-------------------------|----------------------|---------------------------------------|--|
| <i>cis</i> -Cyclohexene | 1.38 | 192 | 192 |
| 2- <i>cis</i> -Octene | 1.37 | 200 | 226 |
| 1-Docosene | 1.38 | 200 | 226 |
| 2-Methyl-1,5-hexadiene | 1.43 | 196 | 240 |
| 1,7-Octadiene | 1.36 | 200 | 226 |
| 2,4-Hexadiene | 1.45 | 220 | 258 |
| 1,3-Pentadiene | 1.40 | 206 | 250 |

a) Wavelength of maximum absorptivity.

b) Lower transparency limit (absorbance ≤ 10 mAU).

like thiols, alkyl-sulfides or alkyl-disulfides, can be considered weak UV-absorbing substances in this wavelength range, since their absorption around 240 nm is normally 10 times smaller than that of conjugated dienes [8]. This offers the possibility of selectively detecting aliphatic hydrocarbons with conjugated double bonds in petroleum fractions. Since aromatic and non-aromatic hydrocarbons are easily separated under these chromatographic conditions, the only interfering substances that could possibly exist are trienes or polyenes, which also cause instability in gasoline-range products and also react with maleic anhydride in method 326.

Retention times of the hydrocarbons tested are shown in Table 1. The reproducibility (standard deviation) of the retention times was always smaller than 0.01 min. These compounds are non-aromatic hydrocarbons and elute very close to each other, which means that conjugated dienes are expected to elute as a single peak in the chromatogram. This is confirmed by the chromatogram recorded at 240 nm, which is shown in **Figure 1**.

The chromatogram of a standard solution of 1,3-pentadiene in toluene (0.4 mol L⁻¹) is shown in **Figure 2**. Two

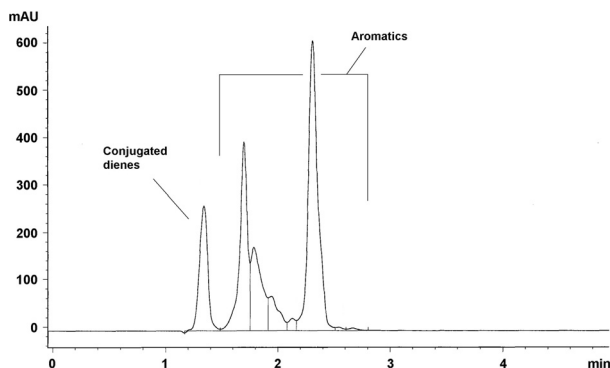


Figure 1. Chromatogram of a hydrotreated FCC naphtha (one silica column; remaining conditions of analysis, see Section 2. Experimental).

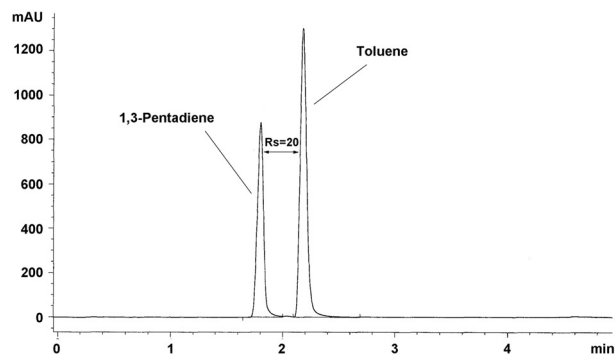


Figure 2. Chromatogram of a solution of 1,3-pentadiene (0.4 mol L^{-1}) in toluene (two silica columns; remaining conditions of analysis, Section 2. Experimental).

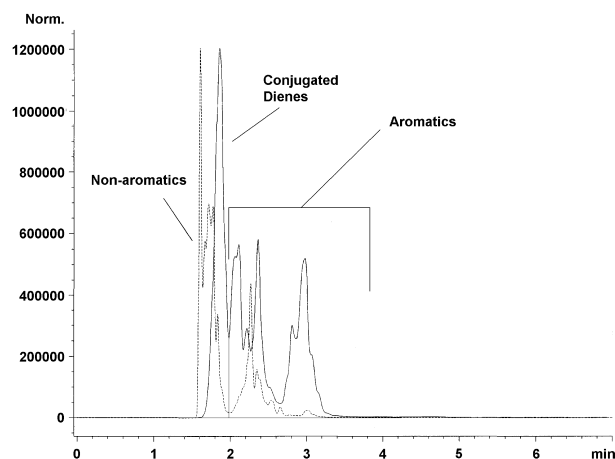


Figure 3. Overlaid chromatogram of a FCC naphtha: UV detection @ 240 nm (solid line) and FID (dotted line) (two silica columns; remaining conditions of analysis, see Section 2. Experimental).

silica columns were used this time and a resolution (R_s) between the conjugated diene and the aromatic hydrocarbon of 20 was obtained. This value by far exceeds the minimum resolution between aromatics and non-aromatics compounds required in ASTM method D 5186 ($R_s = 4$). Nevertheless, resolutions are usually not so good when analyzing some samples. This situation is illustrated in **Figure 3**, in which UV at 240 nm (solid line) and FID (dotted line) chromatograms of a FCC naphtha are presented. Although non-aromatics and aromatics are quite well separated in the FID chromatogram, the same does not occur in the UV chromatogram, in which a peak partially coelutes with one of conjugated dienes. This interfering peak is absent from the FID chromatogram, which indicates that their components strongly absorb UV radiation at 240 nm. Although this peak elutes in the retention time range of the aromatic compounds, the UV spectrum taken at its apex (not shown) is quite different from that of a typical alkyl-benzene: there is only one transition with maximum around 240 nm and the absorption gradu-

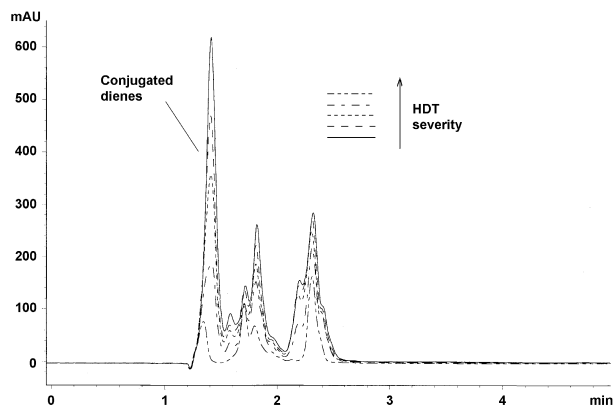


Figure 4. Overlaid chromatograms of FCC naphthas hydro-treated at different severities (one silica column; remaining conditions of analysis, see Section 2. Experimental).

ally finishes around 275 nm. Hence, this coeluting peak is possibly due to conjugated and non-conjugated trienes or polyenes.

FCC naphthas hydrotreated to different degrees were also analyzed by the SFC-UV method. The resulting chromatograms are shown in **Figure 4**. Clearly, the peak attributed to the conjugated dienes diminishes as the severity of hydrotreatment increases. As mild hydrogenation conditions were used, reduction of total sulfur content or olefin content was not observed (results not shown).

Several samples of petroleum products were analyzed both by the SFC and by the UOP 326 method, in order to test the suitability of the SFC method for measuring the content of conjugated dienes. The results are plotted in **Figure 5** and are split into four groups, each of them representing samples generated from a given feed processed under different pilot-plant conditions. For example, square symbols in Figure 5 represent a set of samples produced from the same FCC naphtha, under different hydrotreatment conditions. The results for samples belonging to the same set are well fitted by straight lines,

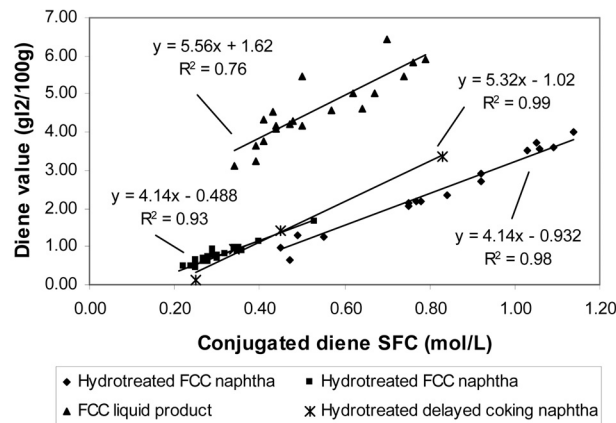


Figure 5. Correlation plots for samples with different origins.

whose slopes are similar considering that each sample has a particular distribution of conjugated dienes. Therefore, the hypothesis of a constant average absorption, which is implicit in the proposed method, seems reasonable from these results. On the other hand, negative intercepts were obtained for all types of samples, except for the sample set "FCC liquid product". In these cases, the determination of conjugated dienes by SFC-UV could be subject to interfering substances, such as some UV-absorbing alkyl-sulfur compounds (i.e. vinyl-sulfur compounds). Negative intercepts may also suggest that the reaction between conjugated dienes and maleic anhydride is not stoichiometric, at least during the reflux time specified in UOP method 326.

A positive intercept indicates that substances other than conjugated dienes, such as vinyl-arenes or anthracene and its homologues, reacted with maleic anhydride. Among the sample sets investigated, "FCC liquid product" is the only one whose equation has a positive intercept. The whole FCC stream is included in these samples, so they are the only ones where substantial contents of these interfering substances are expected to exist.

4 Concluding remarks

A method for determination of total conjugated dienes in petroleum products by supercritical fluid chromatography

and UV detection is presented. The method is accurate and faster (10 min) than the diene value method (UOP method 326). Samples of both catalytic and thermal cracking naphthas were examined by both methods, with well-correlated results.

Acknowledgements

The author is grateful to Petrobras for allowing this research work to be published.

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