NMR Analysis of Dienes in Model FCC Gasolines

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Abstract: *Detailed analysis of the diene content in FCC gasolines by using 1D and 2D NMR experiments was carried out for a better understandimg of the correlation between the composition and formation of gum. The results show the applicability of 2D NMR to the analysis of complex hydrocarbon mixtures.*

Introduction

Gasoline is a complex hydrocarbonic mixture with more than one hundred compounds divided into paraffins, naphthenes, olefins and aromatics. Small quantities of conjugated dienes are also present in FCC (fluid catalytic cracking)- type gasolines (gasolines type A, from refineries), which are associated with low stability, development of color and loss of transparency of the product. This is caused by "gum" formation (attributed to olefin polymerization initiated by dienes), which leads to low yielding of car motors and also to obstruction of fuel injectors. Some interesting NMR studies involving gasolines using common 1D (^{1}H and ^{13}C) experiments are described in the literature. [1-3]

However, a detailed analysis of the diene content in FCC gasolines focusing on the correlation between the composition and formation of gum has not yet been done. Thus, the objective of the present work was to use usual 2D NMR experiments such as TOCSY and gradient selected (gs) COSY, HMQC and HSQC-TOCSY, combined with ^{1}H NMR database, for the identification of conjugated dienes in olefin rich fractions from FCC gasolines.

Experimental

FCC gasolines (FCC_M) were obtained from Manguinhos Brazilian Refinery (Rio de Janeiro). A sample of *trans*-2-methyl-1,3-pentadiene was used to adjust the ^{1}H pulse width (9.2 μs at 5.0 dB attenuation) and relaxation delay (1.5 sec). Olefin rich fractions were obtained as described elsewhere.[4] All experiments were performed on a Bruker DRX300 spectrometer (300.13 MHz/^{1}H and 75.47 MHz/^{13}C) equipped with 5 mm inverse multinuclear probehead incorporating three axis gradient coils (50G/cm), using the XWinNmr 1.3/9 program for acquisition and processing. Samples were prepared in $CDCl_3$/TMS (0.5% v/v) at concentrations of 30% v/v and measured at 298K. Sweep width of 3000Hz and 12000Hz were used for ^{1}H and ^{13}C nuclei respectively, with 32k and 64k data points for 1D and 8k vs. 256 point matrices for the 2D acquisitions (pulse sequences of TOCSY, gs-HSQC-TOCSY, gs-COSY, gs-HSQC from the XWinNmr 1.3/9 program). Zero filling and/or linear prediction were used in the 2D´s processing. ACD/HNMR program was used as ^{1}H NMR database.

Results and discussion

The first attempt to study the conjugated diene contents in FCC gasoline (FCC_M) with 2D NMR was to analyze it directly by TOCSY and gs-HSQC-TOCSY experiments (Figures 1 and 2). In fact, relatively clear regions can be seen in the spectra (see marked rows/columns). However, due to the complexity of the mixture of olefins with conjugated and non-conjugated dienes, this approach was unsuccessful.

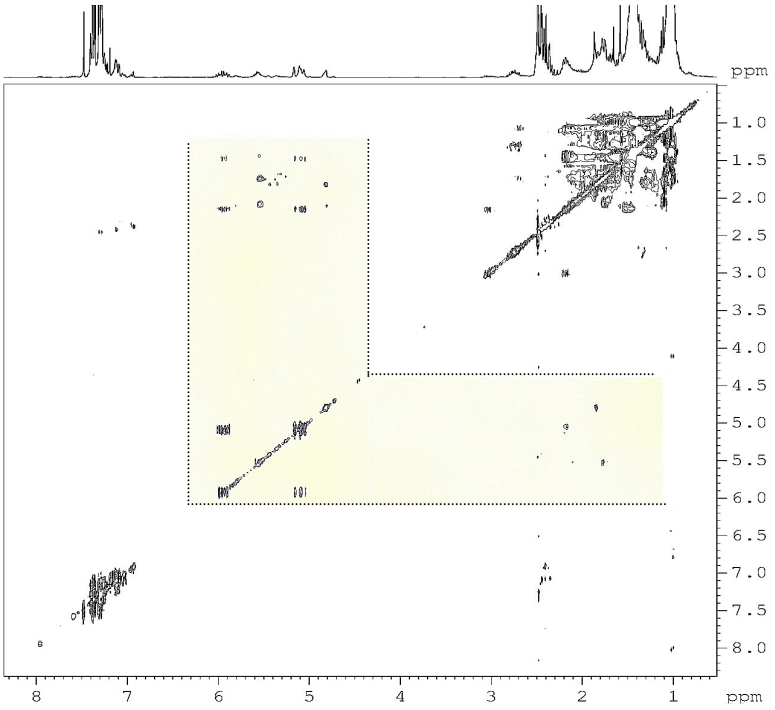

Figure 1. TOCSY spectrum from FCC_M.

This preliminary result shows that the best way to conduct an NMR study of a so complex mixture is to work initially with a model for dienes. This model involves the mixture of some compounds (^{1}H spectra on Figure 3), such as terminal (*trans*-2-methyl-1,3-pentadiene, named A), internal (2,5-dimethy-2,4-hexadiene, named C) and cyclic (1,3-cycloheptadiene, named B) conjugated dienes and a non- conjugated cyclic diene (dicyclopentadiene, named D) as minor component. To obtain a realistic model, the mixture of dienes was added at < 10 % v/v to another mixture containing benzene, toluene, xylene, *iso*-octane and light petroleum ether. The resultant solution, a “synthetic” FCC gasoline, was named FCC_K (Figure 4).

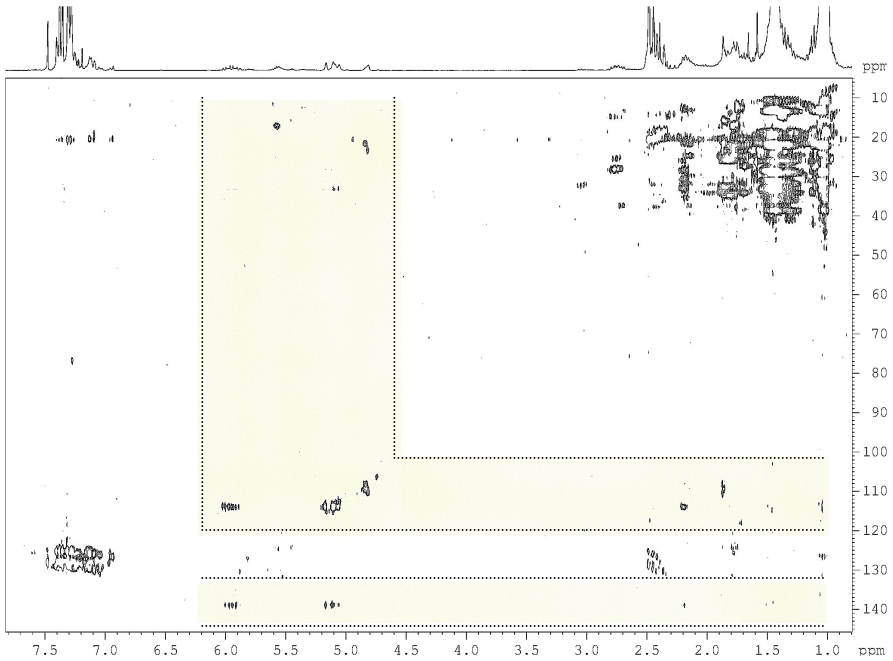

Figure 2. gs-HSQC-TOCSY spectrum from FCC_M.

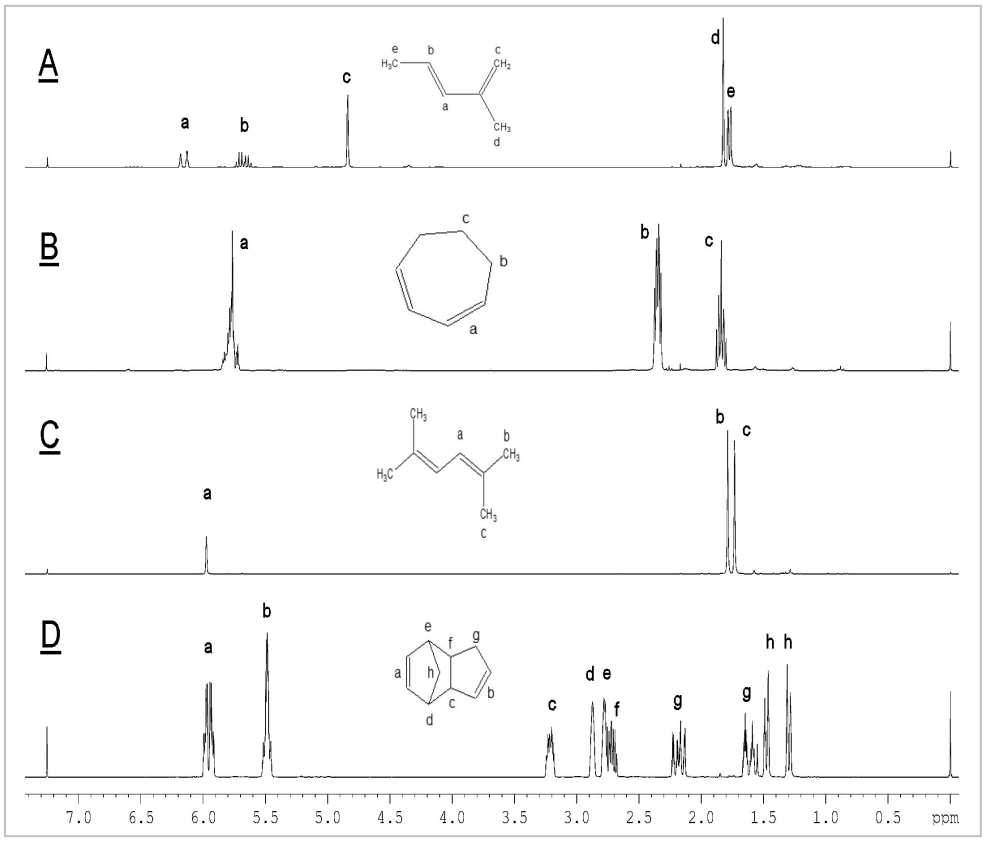

Figure 3. [1]H NMR spectra from *trans*-2-methyl-1,3-pentadiene (A), 1,3-cycloheptadiene (B), 2,5-dimethy-2,4-hexadiene (C) and dicyclopentadiene (D).

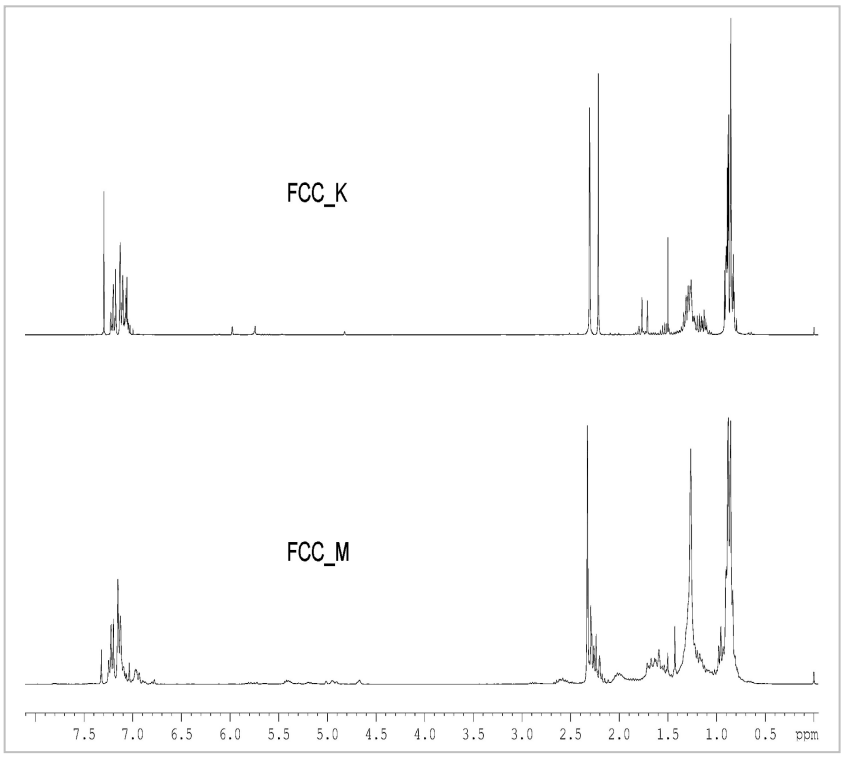

Figure 4. ^{1}H NMR spectra from FCC_M and FCC_K (see text).

The first 2D NMR experiment with the FCC_K sample was a gs-COSY (Figure 5). Extracting high resolution rows from the 2D map made it possible to easily assign the compounds A, B, and C (see projections and marked signals in Figure 5). However, identifying compound D in this experiment was a difficult task due its inherent low concentration level (estimated below 1 % v/v) and high concentration of the other components from the FCC_K mixture. The result of this combination leads to an excessive t_1 noise below 2.3 ppm in which lies 40% of the signals from compound D (mainly the H´s labeled as g and h). This noise also causes the appearance of some non- desirable signals in compound B projections, but they are easily recognized.

With the intent to obtain more spreading of one dimension from a 2D experiment (e.g. ^{13}C chemical shifts) a second analysis on this FCC_K sample was done, a gs-HMQC experiment (Figure 6). The row projections clearly show the hydrogen profile of each diene compound (see marked signals on each row (Figure 7) and without excess of t_1 noise below 2.3 ppm, as is the case of the gs-COSY experiment. As can be seen, with gs-HMQC we can assign the D compound, and both experiments give a good combination to assign such mixture system.

Our results show that two simple 2D experiments were effective to solve the model case, but the analysis of the real gasoline, with several types of olefins present is still complex. Another problem is dilution, e.g., in the FCC_K solution the diene content is close to all olefins in the FCC_M gasoline, and this factor makes gs-COSY and gs-HMQC be time- consuming experiments (4 and 6 hours respectively).

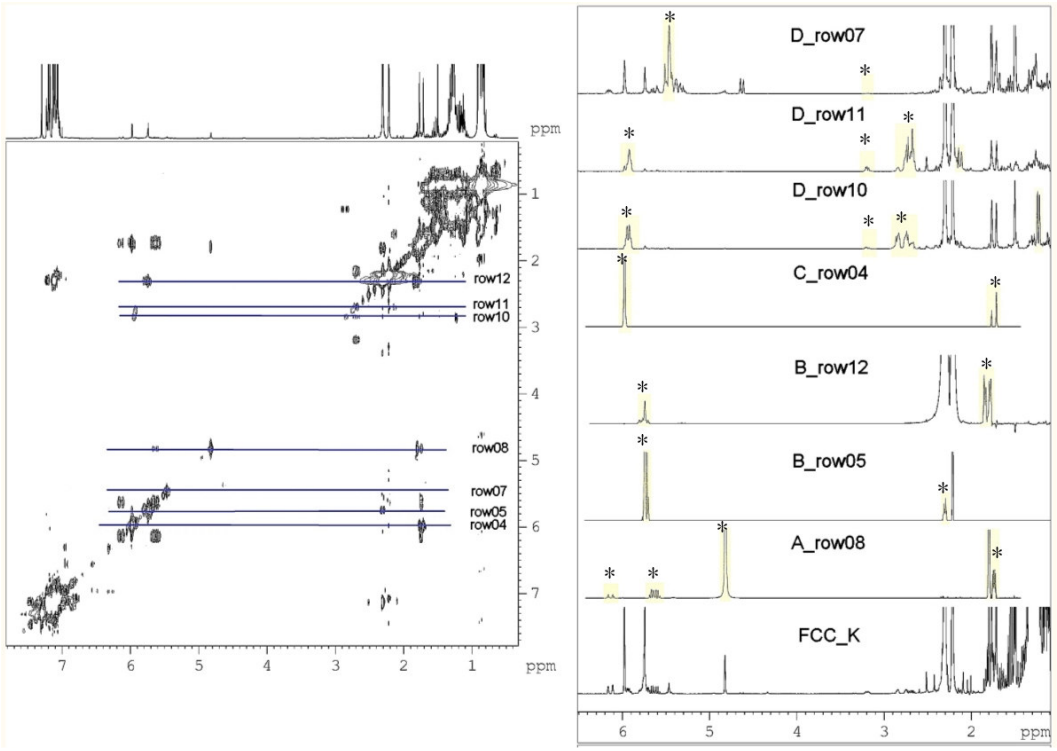

Figure 5. gs-COSY spectrum from FCC_K (selected rows are indicated). In the right side are the projections from the spectrum, identifying dienes A to D (peaks are marked).

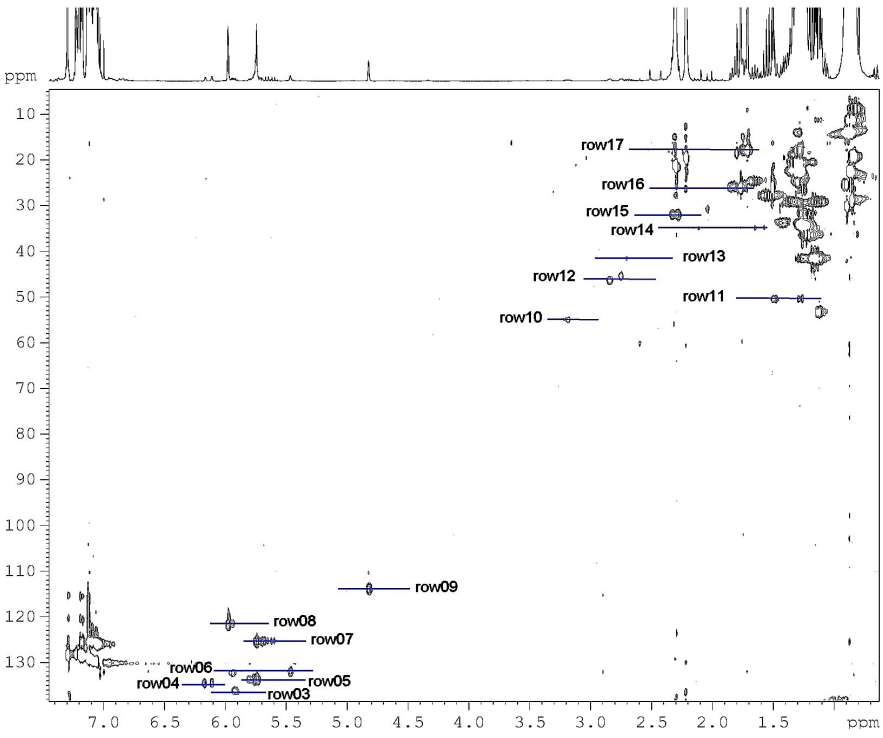

Figure 6. gs-HMQC spectrum from FCC_K (selected rows are indicated).

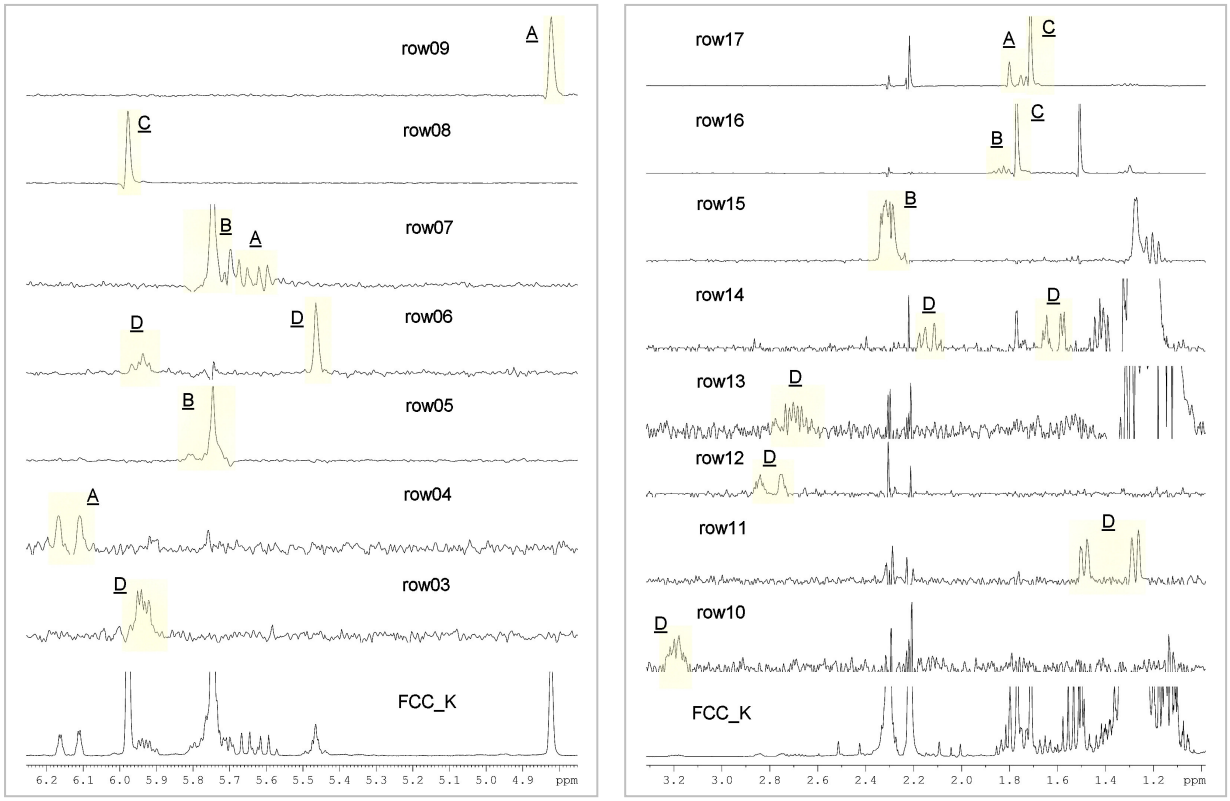

Figure 7. Projections from Fig. 6, identifying dienes A to D.

We tried to obtain a concentrate of olefins, preferably dienes, from FCC gasoline. This was done by eluting a sample of FCC_M through a modified silica gel column with hexane/ethyl acetate. One olefin rich fraction (FCC_F72) from the column was analyzed with a gs-COSY experiment (Figure 8).

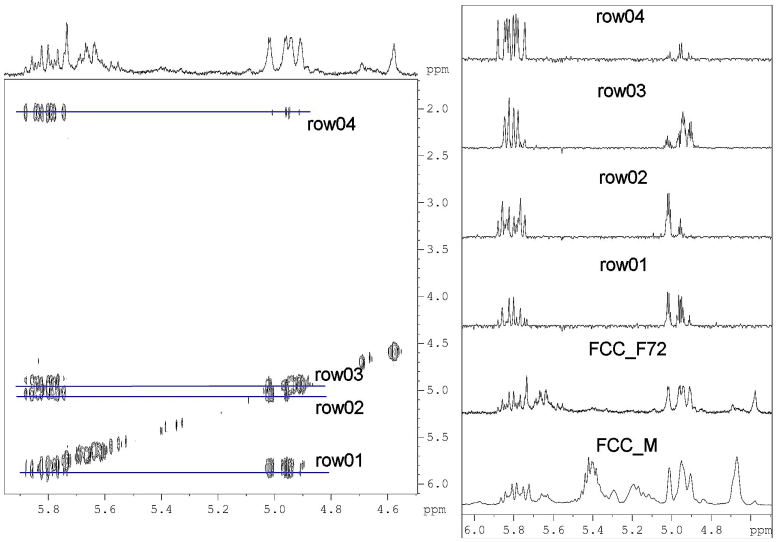

Figure 8. gs-COSY spectrum from FCC_F72 (selected rows are indicated). In the right side are the projections, including the FCC_M for comparison.

Note in Figure 8 by comparison with the original FCC_M, that this fraction is simpler, which is allied to the fact that it does not contain more signals due aromatic H´s (not shown). However, due to the great dilution in hexane/ethyl acetate only the gs-COSY experiment can be performed and only in the limited region shown (severe noise above 3 ppm renders the analysis of this region unpractical). Figs. 8 and 9 suggest the presence of three to five olefin compounds, between substituted *alpha*/internal olefins and/or substituted internal dienes.

Conclusions

The FCC mixture model revealed the viability of using simple 2D experiments to analyze complex systems. Further work are underway in order to obtain an FCC concentrate of olefins by using solvents other than hexane/ethyl acetate so as to make possible the analysis of ^{1}H high field region. 1D selective COSY, TOCSY and HSQC will also be tested in the analysis of olefin rich fractions.

Acknowledgements

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