



CROATICA CHEMICA ACTA  
CCACAA, ISSN 0011-1643, e-ISSN 1334-417X  
*Croat. Chem. Acta* **84** (4) (2011) 537–541.  
CCA-3510

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# The Use of $^{13}\text{C}$ NMR Spectroscopy and Comprehensive Two-dimensional Gas Chromatography, GC $\times$ GC, for Identification of Compounds Involved in Diesel Fuel Oxidative Behavior

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RECEIVED MARCH 8, 2011; REVISED JUNE 1, 2011; ACCEPTED JUNE 1, 2011

**Abstract.** An approach has been proposed combining one dimensional inverse gated  $^{13}\text{C}$  NMR spectroscopy and a comprehensive two dimensional gas chromatography (GC $\times$ GC) to analyze diesel fuels prior and after oxidation under the standard conditions. Classes of hydrocarbons present before and after oxidation have been identified and quantified. A decrease in aromatic iso- and n-paraffinic hydrocarbons and an increase in the total saturated hydrocarbons have been observed after oxidation. In that respect NMR spectroscopy has potential to be used as standard method for determination of oxidation stability. Furthermore, GC $\times$ GC has been applied to identify compounds involved in the formation of sediments during oxidation. Obtained results have shown that hydrocarbon composition, especially the normal paraffin content play a role in the formation of sediments in these distillate fuels. This is important since sediments may influence the quality of diesel fuels. (doi: [10.5562/cca1874](https://doi.org/10.5562/cca1874))

**Keywords:** diesel fuel,  $^{13}\text{C}$  NMR, GC $\times$ GC, oxidation stability, sediments, normal paraffins

## INTRODUCTION

Diesel fuel properties are dependent primarily on the composition of diesel fuels, which consist of hundreds of individual components belonging to aromatic, paraffinic, olefinic and polar hydrocarbon classes. Oxidation degradation is the most important limiting factor for diesel fuel stability which determines the amount of insoluble sediments formed during oxidation. These can lead to engine operating difficulties. Some of the problems include efficiency of engine ignition, reduced fuel spray quality, engine noise, excessive smoke, loss of power, poor fuel degraded emissions *etc.* The formation of sediments during the oxidation is a complex process in which many compounds of stocks are involved. Components that influence fuel stability have been reported in the recent literature and those included hydrocarbons (usually olefins and polycyclic aromatic hydrocarbons) sulphur, nitrogen and some metals (Fe and Cu). However, the composition of sediments that are usually formed has been less investigated. Hence, it is the aim of this paper to analyze several commercial diesel fuel samples with respect to changes in hydrocarbon composition during the process of oxidation espe-

cially to composition of sediments. Although NMR spectroscopy has been used in fuel analysis<sup>2,3</sup> we believe that a combination of  $^{13}\text{C}$  NMR and comprehensive GC $\times$ GC experiments can provide more details for better understanding of the relationships between chemical composition of diesel fuels before and after oxidation under conditions described in the standard ISO 12205 procedure.<sup>1</sup>

Chemical composition of diesel fuels is meant in terms of the percentage of different types of hydrocarbons present. NMR spectroscopy has proven useful to determine total carbon to proton ratio and to characterize fuels providing information on naphthenic, normal and isoparaffin as well as mono and poliaromatic compound contents.<sup>2–8</sup> Average chain lengths of normal and isoparaffins can be obtained too.<sup>9,10</sup>

Comprehensive two dimensional GC $\times$ GC is an analytical technique which provides powerful multidimensional separation and detection of low concentrations of normal paraffins in insoluble sediments.<sup>11–14</sup> This can help in determining reaction pathways and chemical mechanisms involved in oxidative degradation of diesel fuels.

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**Table 1.** The percentage of different carbons in the samples 1–4<sup>(a)</sup>

$^{13}\text{C}$ NMR Structural Parameters	Sample 1		Sample 2		Sample 3		Sample 4	
	unoxidized	oxidized	unoxidized	oxidized	unoxidized	oxidized	unoxidized	oxidized
Saturated carbons (Csat)	87.80	88.30	91.65	93.14	87.60	88.80	87.24	88.72
Aromatic carbons (Car)	12.20	11.70	8.35	6.86	12.40	11.20	12.76	11.28
Naphtenic carbons (Cn)	35.61	37.28	35.35	38.72	33.37	36.41	31.38	40.8
Paraffinic carbons (Cp)	52.19	51.02	56.3	54.42	54.23	52.39	55.86	47.87
Normal paraffins (Cnp)	34.15	33.74	40.18	39.75	41.37	39.54	41.83	33.98
n-paraffinic $\alpha$ -carbon (Cnp $\alpha$ )	5.26	5.98	5.39	6.92	5.80	6.83	6.38	6.66
n-paraffinic $\beta$ -carbon (Cnp $\beta$ )	4.90	4.92	5.60	5.28	6.20	6.27	5.99	5.42
n-paraffinic $\gamma$ -carbon (Cnp $\gamma$ )	4.65	4.20	5.59	5.21	5.57	3.93	5.61	4.74
n-paraffinic $\delta$ -carbon or higher (Cnp $\delta$ )	19.34	18.64	23.06	22.34	23.80	22.51	23.85	17.16
Iso paraffins (Cip)	18.07	17.28	16.12	15.70	12.90	12.85	14.03	13.89
ACL <sup>(b)</sup>	12.98	11.28	13.55	11.48	13.36	11.58	13.11	10.20
C/H ratio	0.532	0.530	0.522	0.518	0.533	0.529	0.534	0.529

<sup>(a)</sup> Standard deviation was better than 0.04 for all samples.

<sup>(b)</sup> ACL = 2Cnp/Cnp $\alpha$ .

## EXPERIMENTAL

### Samples

All the diesel fuel samples used in this study were of commercial grades obtained in a refinery in the boiling point range from 180 °C to 350 °C at the atmospheric pressure. Samples have been treated using the procedures described in the standards HRN EN ISO 3170<sup>15</sup> and HRN EN ISO 590<sup>16</sup> which defined the requirements for diesel fuel quality.

### Aging Procedure

Oxidation stability of the samples has been obtained by the use of standard method for determination of the oxidation stability of middle-distillate fuels under accelerated oxidizing conditions, ISO 12205.<sup>1</sup>

A test portion of a filtered middle-distillate fuel was left at 95 °C for 16 h while bubbling oxygen through the sample. After aging, the sample was cooled to approximately room temperature before filtering to obtain the quantity of filterable insolubles. The filtration was performed by using the standard procedure as describe in ISO 12205.<sup>1</sup> Adherent insolubles were then removed from the oxidation cell and associated glassware with trisolvent (TAM), a solution of equal volumes of acetone, toluene and methanol. The trisolvent was evaporated to obtain the quantity of adherent insolubles. The sum of the filterable and adherent insolubles is expressed as g m<sup>-3</sup> and must be less than 25 g m<sup>-3</sup>. The following results were obtained; 10, 8, 5; and 20 g m<sup>-3</sup> for samples 1, 2, 3, and 4, respectively.

### NMR Spectroscopy

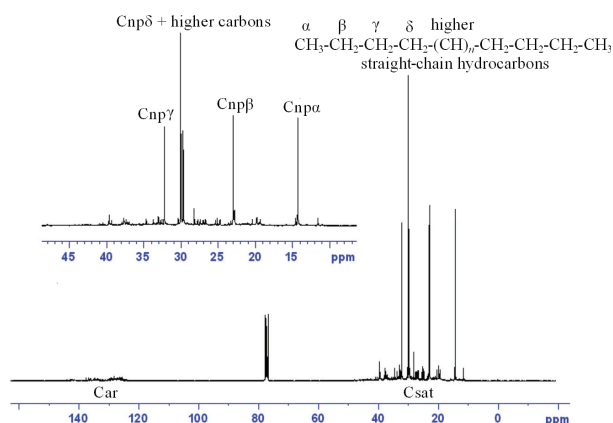
All the  $^{13}\text{C}$  NMR spectra were recorded on a Bruker Avance 300 NMR spectrometer operating at 300 MHz for  $^1\text{H}$  and 75 MHz for  $^{13}\text{C}$  using a C/H dual 5 mm probe. The experiments were performed at room temperature. Chemical shifts were reported relative to tetramethylsilane (TMS) used as an internal standard.

For  $^{13}\text{C}$  NMR experiments an inverse gated decoupling sequence was used to suppress unwanted nuclear Overhauser enhancement (NOE). Sample solution was prepared (w = 50 %) in deuterated chloroform (99.8 % D) containing approx. 0.1 mol dm<sup>-3</sup> chromium(III) acetylacetonate as a relaxation agent to induce the spin-lattice relaxation time.<sup>2,3</sup>

The measuring conditions for quantitative  $^{13}\text{C}$  NMR experiments were: 18 kHz sweep width; 8.70  $\mu\text{s}$  pulse width; 10 s relaxation delay; 1024 scans. The phase and base line of the resulting spectra were manually adjusted. The percentages of different hydrocarbon classes were determined from the integrated carbon peak areas and are given in Table 1.

### Comprehensive GC×GC

The GC×GC system is built on a gas chromatograph HP 7890A (Agilent Technologies, Wilmington, DE and SRA Instruments Italy) platform. The separation was carried out at the helium constant flow of 0.83 cm<sup>3</sup> min<sup>-1</sup>. A flame ionization detector (FID) system set at 250 °C and operating at 500 Hz was used for detection. Hydrogen, air and nitrogen (make up) flows were set to 25, 250 and 25 cm<sup>3</sup> min<sup>-1</sup>, respectively. The GC×GC modulation was obtained with dual-stage thermal modulator KT-2004 ZOEX (Zoex Corporation,



**Figure 1.**  $^{13}\text{C}$  NMR spectrum of the sample 1. A narrow region shows n-paraffinic carbons.

Lincoln, NE) using liquid nitrogen as a cryo-medium for the cold jet. Modulation period was set to 6 s, modulation duration to 500 ms and hot jet temperature to 280 °C. Oven temperature started at 35 °C and after 1 min was increased to 340 °C at a rate of 3 °C min<sup>-1</sup>. 1 μL of the sample was injected manually in the split mode with split ratio 1:200. PTV injector was programmed from 50 °C to 220 °C at a rate of 500 °C min<sup>-1</sup>.

GC×GC system consisted of two columns which were connected to GC oven by a 2 m of deactivated fused silica column (RESTEK), 0.18 mm I.D. as a modulator tube. A column in the first dimension was HP-5 (Agilent Technologies), stationary phase polydimethylpolysiloxane, 30 m × 0.32 mm I.D. and 0.25 μm film thickness and column in second dimension was BPX-50 (SGE), stationary phase polyethylene glycol, 2 m × 0.1 mm and I.D. 0.1 μm. The GC-Image software ver. 1.8b6 ZOEX (Zoex Corporation, Lincoln, NE) was used for GC×GC data processing.

## RESULT AND DISCUSSION

Most of what is known about mineral oil chemistry today results from the use of highly sophisticated instrumental methods. Quantitative estimation of the carbon content by  $^{13}\text{C}$  NMR methods can provide an average structure representation of the mineral oils and also give detailed information on  $\text{CH}_n$  type and nature of branching of paraffin molecules and on average chain length (ACL).<sup>2,3,6</sup> The mineral oil NMR spectra are difficult to analyze owing to severe peak overlapping and only information on different classes of hydrocarbons can be obtained. As mineral oil is a complex mixture, it is difficult to identify specific reaction pathways that may occur. The number of reactive compounds is large and the chemical mechanism by which they are converted into insoluble products has not yet been established in spite of many years of investigations. Some

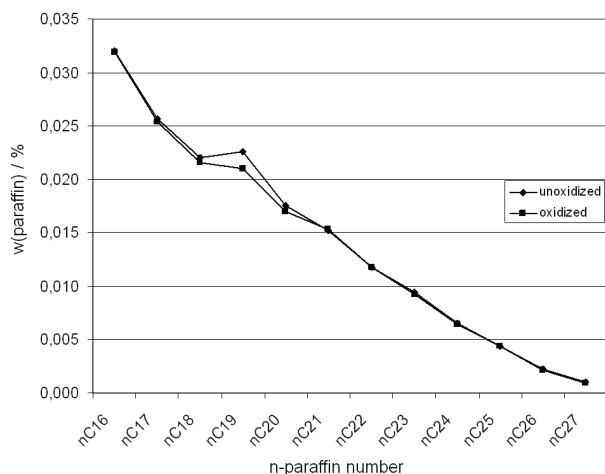
authors<sup>17</sup> suggested that the sediment precursor compounds may be formed by the condensation of phenalenes with indoles. Others reported on significant molecular transformation during oxidation of base oils, resulting in the formation of naphthenes and alkyl benzenes with shorter chain length via polar intermediates.<sup>10</sup> Similar results were reported for marine diesel fuels.<sup>18</sup>

In order to estimate the content of paraffins and aromatic compounds present in four commercial diesel fuels, (samples 1–4), the inverse gated  $^{13}\text{C}$  NMR spectra were recorded and analyzed. The inverse gated  $^{13}\text{C}$  NMR spectroscopy has been shown to be a powerful tool for providing information about differences in composition of un-oxidized and oxidized diesel fuels. The samples studied in this work originated from various refinery commercial diesel fuel blends obtained by different processes<sup>9</sup> without additives.

A typical  $^{13}\text{C}$  NMR spectrum is displayed in the Figure 1 for the sample 1 showing aromatic (Car) and saturated hydrocarbon (Csat) regions.

The signals in the inverse-gated spectra can be integrated and used to provide quantitative information on the aromatic and saturated carbon contents present in diesel fuel samples. The signals of aromatic carbons are found in the region between 100 ppm and 160 ppm while those of paraffinic are in the region 5–65 ppm relative to tetramethylsilane.<sup>4</sup> Saturated hydrocarbons can be divided into two subgroups, e.g. cyclic or naphthenic and paraffinic, each of them with different impact on the oxidation stability. The naphthenic carbons can be identified by a broad hump in the 24–60 ppm paraffin region and can be quantified by a manual baseline spectral correction.<sup>2,3</sup> The paraffinic carbons can be divided into normal paraffinic and iso-paraffinic carbons. Normal or n-paraffins are of special interest since they might precipitate and give sediments after oxidation which could block fuel filters and lead to engine stopping. Fortunately, they can easily be identified and differentiated from iso-paraffins in the  $^{13}\text{C}$  NMR spectrum, as seen in the Figure 1. For n-paraffins  $\alpha$ -carbon observed at 14.1 ppm is assigned as Cnp $\alpha$ ,  $\beta$ -carbon at 22.7 ppm as Cnp $\beta$ ,  $\gamma$ -carbon at 32.0 ppm as Cnp $\gamma$ , and  $\delta$ -carbon at 29.4 ppm as Cnp $\delta$ . Higher n-paraffinic carbons are observed at 29.7 ppm and correspond to the number of  $(\text{CH}_2)_n$  groups present in the molecule.<sup>5,6,9</sup> The iso-paraffinic carbons can then be calculated as the difference between the total and normal paraffinic carbons.

As mentioned, the area under the peaks can be integrated giving a relative ratio between various hydrocarbons present in the samples prior and after aging, as seen in the Table 1, which can further be exploited to calculate their total amounts. A close inspection of data presented in Table 1 reveals that a percentage of aromatic carbons decrease during oxidation in favor of the

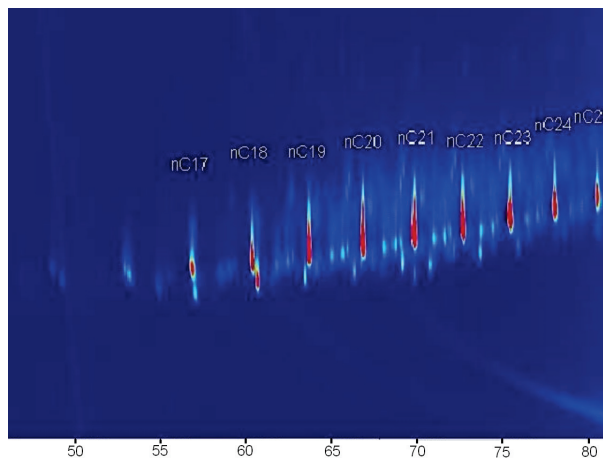


**Figure 2.** The percentage of nC16–nC27 hydrocarbons in the sample **3** prior and after oxidation process.

increase in the total saturated carbons. The naphthenic carbons increase, while n-paraffin and iso-paraffin carbons decrease. It has already been reported that more branching in alkyl chains lead to lower oxidation stability.<sup>3</sup> Only the integrals of  $\text{C}_{n\text{p}\alpha}$  increases as a consequence of forming smaller normal and isoparaffin chains. This is in accordance with the calculated average chain length,  $\text{ACL} = 2\text{C}_{n\text{p}}/\text{C}_{n\text{p}\alpha}$  (Table 1). The average chain length represents the number of carbons in normal and iso-paraffin chains and also the side chains attached to aromatic and naphthenic rings.<sup>2,3</sup> At this point we can only speculate on possible mechanisms of degradation due to complexity of the system but degradation pathways may be similar to those mentioned above.<sup>10,16,17</sup> Additional experiments using other techniques are needed to gain further insight into this matter. However, the potential of NMR spectroscopy lies in the fact that it can give accurate data on percentage of different hydrocarbons present before and after oxidation and hence can further be exploited to become a standard method for determination of the oxidation stability.

The total carbon to hydrogen ratio C/H and total n-paraffinic content were also determined from NMR data (Table 1).<sup>7</sup> These parameters can also be affected by the oxidation process as seen in the Table 1.

In order to further characterize both oxidized and unoxidized diesel fuel samples **1–4** and their insoluble sediments the comprehensive two dimensional gas chromatography (GC×GC) was used. By applying GC×GC it was possible to separate, identify by retention times and determine the amounts of different n-paraffins present in samples **1–4** prior and after oxidation process. The results presented in Figure 2 for sample **3** show that only portions of n-paraffin nC19, and some portions of nC18 and nC20 have decreased in the fuel during oxidation while all others seem to remain constant.



**Figure 3.** The two dimensional GC×GC chromatogram of insoluble sediments in the sample **3**.

However, n-paraffins nC17–nC25 have also been detected in the chromatogram of the sediment as a consequence of oxidation process. Similar findings were obtained for other samples. GC×GC chromatogram of the precipitates formed after 16 hours in the stream of oxygen is shown in Figure 3. Data obtained by GC×GC is in accordance with NMR data which showed that average chain length has decreased during oxidation. Hence, the two dimensional chromatogram of insoluble sediments provides a complete picture of compounds involved in the formation of sediment during aging of diesel fuels.

## CONCLUSION

In conclusion, it was demonstrated that a combination of the inverse gated  $^{13}\text{C}$  NMR spectroscopy and two dimensional GC×GC provided useful information about changes in diesel fuel composition during the process of oxidation. The data from  $^{13}\text{C}$  NMR spectra showed a decrease in aromatic, n- and iso-paraffinic hydrocarbons and an increase in the total saturated and naphthenic hydrocarbons. An average chain length has been shown to decrease too. The results obtained by GC×GC method are in good agreement with this. Furthermore, GC×GC analysis of insoluble sediments formed during oxidation process has shown that n-paraffins nC17–nC25 have precipitated.

*Acknowledgements.* We thank the Ministry of Science, Education and Sports of the Republic of Croatia (Project No. 119-1191342-1083) for the financial support.

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