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Comprehensive two-dimensional gas chromatography for basic and neutral nitrogen speciation in middle distillates

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ABSTRACT

The molecular knowledge of nitrogen compounds in diesel feedstocks has become a key issue in the development of hydrotreatment processes, especially for ultra-low sulfur diesel production. Indeed, nitrogen species have a strong impact on the hydrodesulfurization (HDS) pathway, since basic nitrogen is known to poison acidic sites of HDS catalysts.

Since conventional methods only allow a poor degree of information, the increased separation power of comprehensive two-dimensional gas chromatography (GC × GC-NCD) was used in this study to obtain a detailed overview of nitrogen compounds by type (basic/neutral), by family and by carbon breakdown in diesel and liquefied coal samples. Partially hydrogenated compounds such as tetrahydrocarbazole and tetrahydroquinoline derivatives could even be detected in liquefied coal samples as well as diesel from ebullated bed conversion units. Comparison of GC-NCD with GC × GC-NCD for quantitative determination of nitrogen compounds by family was achieved in a first step. These results demonstrate the superiority of GC × GC to allow for a comprehensive characterization of nitrogen compounds in diesel and related samples in one injection. Furthermore, nitrogen speciation by GC × GC-NCD technique allows identifying most nitrogen species in conventional diesel or liquefied coal samples, with no use of mass spectrometry.

GC × GC-NCD was also applied to a wide range of diesel feedstocks obtained from distillation, cokefaction, FCC, ebullated bed hydroconversion units to correlate nitrogen species to the origin of the feedstocks or distillation end points, giving interesting indications on reaction mechanisms involved in the processes.

1. Introduction

Clean fuel legislation in Europe, America and Asia is driving the demand for ultra-low sulfur diesel (ULSD) fuel: in the US, the total sulfur content of on-road diesel is lower than 15 ppm since June 2006, whereas in Europe it is still limited to 50 ppm and is expected to decrease to 10 ppm by 2009 [1]. The increasing demand of transportation fuels and worldwide dieselization (there is a 2.2% increase per year of worldwide demand for diesel fuel) lead refiners to produce ever cleaner middle distillates from heavier feedstocks containing a growing quantity of impurities such as sulfur, nitrogen but also metals such as vanadium and nickel. Nowadays, supply of transportation fuels mainly relies on conversion units such as hydrocrackers for diesel; thus, hydrotreatment of higher fractions of light cycle oil (LCO) from fluid catalytic cracking (FCC) unit is expected from hydrotreatment units.

The improvement of hydrocrackers and diesel hydrotreating performances implies better catalysts and even more accurate kinetic models. Key obstacles to deep hydrodesulfurization have been reported: very low reactivity of refractory compounds such as alkyldibenzothiophenes and inhibition of reaction by nitrogen compounds, especially basic nitrogen compounds (six membered ring heterocycle compounds, Fig. 1) [2]. Furthermore, catalyst deactivation by coking is increased in the presence of basic nitrogen compounds. In the hydroprocessing of heavier feedstocks, hydrodenitrogenation (HDN) becomes even more important because the concentration of nitrogen compounds in the heavier feedstocks is much higher than in the straight-run distillates, and the acidic catalysts used in catalytic conversion are poisoned by basic nitrogen compounds.

Because nitrogen compounds impact HDS and catalyst stability, catalyst design as well as kinetic models used for design, operation

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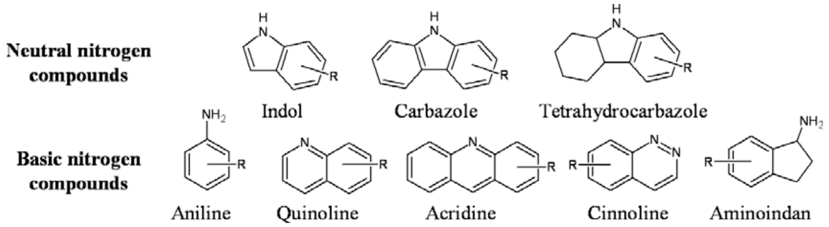

Fig. 1. Typical basic and neutral nitrogen compounds present in middle distillates.

and monitoring of ULSD units, more efficient processes clearly require taking these compounds into account.

Global nitrogen as well as total basic nitrogen contents, which do not provide any molecular information, is not sufficient [3]. As for hydrocarbons [4], the complexity of nitrogen compounds increases dramatically with increasing boiling point; therefore their identification by class of compound and by carbon number in middle distillates represents an important analytical challenge. For detailed molecular analysis of nitrogen compounds in diesel samples, a separation is required prior to the detection step. In this respect, gas chromatography (GC) hyphenated to various nitrogen specific detectors has been extensively used during the past decades: atomic emission detector (AED) [5–10], nitrogen chemiluminescence detector (NCD) [11–13] and mass spectrometer (MS) [14–17]. However, the complexity of nitrogen compounds and the limited peak capacity of GC appear as a limitation to the identification of these compounds: indoles are coeluted with quinolines and carbazoles with acridines, leading to a low degree of information. Thus, in order to resolve these strong coelutions, lots of energy has been devoted to the extraction and concentration of nitrogen compounds into two basic and neutral fractions, either by liquid/liquid extraction (LLE) [18,19] or liquid/solid extraction (LSE) [16,20]. However, it turned out that these procedures are time consuming and neither selective nor quantitative.

Therefore, comprehensive two-dimensional gas chromatography (GC × GC) is a promising alternative to the limited resolution of conventional separation techniques. GC × GC associates by mean of a modulator two columns having different selectivities, which theoretically offers an increased peak capacity, estimated as the product of the peak capacities of each separation column [21,22] as well as a ca. 5–10 times higher sensitivity [23]. Such a technique has already been successfully applied to unravel the hydrocarbon [21,24,25], sulfur [26] and biodiesel [27] compositions in diesel samples. In the past decade, a first attempt [28] using GC × GC hyphenated to a NCD detector lead to the partial determination of nitrogen compounds in middle distillates.

Recently, the optimization of separation and detection conditions of nitrogen compounds in diesel samples using comprehensive two-dimensional gas chromatography has been described [29]. It appeared that among available detectors for nitrogen speciation using GC × GC, nitrogen chemiluminescence detectors offer decisive advantages in terms of selectivity, sensitivity, linearity and equimolarity [29].

Therefore, the aim of this paper is to compare GC × GC-NCD results to reference methods in order to demonstrate the advantages of this technique to achieve a comprehensive characterization of nitrogen compounds in various diesels and related samples, in one single injection. The first part of this work is devoted to the identification of nitrogen compounds present in various diesels and related samples using comprehensive two-dimensional gas chromatography. For that purpose a LLE procedure has been evaluated and synergetically used with a GC × GC-Time of Flight Mass Spectrometry (TOF-MS) system to ascertain the identification of nitrogen compounds. The second part of this study is dedicated to the quantification of nitrogen compounds by class and by carbon number. Additionally, a comparison of GC × GC-NCD results with GC-NCD reference method is proposed. The last part of this paper is devoted to the application of the GC × GC-NCD method to a wider range of diesel samples to derive general trends in nitrogen distribution according to various parameters such as the origin of the crude oil, the process or even the distillation range.

2. Experimental

2.1. GC × GC setup

The GC × GC system consists in a modified HP6890 chromatograph (Agilent Technologies, Massy, France). The CO_2 dual jets modulator was built in-house as described by Beens et al. [30] and was installed inside the GC oven for GC×GC experiments. Modulation occurred at the beginning of the second column and was set at 10 s. In order to prevent boiling points discrimination during injection, 0.5 μl sample analyzes were carried out with a direct on-column injector (Agilent Technologies, Massy, France) which was programmed from 90 to 260 °C with a 70 °C/min temperature rate. Column association consisted in a non polar first column (SPB5, Supelco, St Quentin-Fallavier, France, 30 m × 0.25 mm I.D. × 1.0 μm film thickness) and a polar (Solgel Wax, SGE, Courtaboeuf, France, 1.6 m × 0.1 mm I.D. × 0.2 μm film thickness) second dimension. All experiments were carried out at a constant flow of 1.4 mL/min. GC × GC was operated with a NCD detector (255 Dual Plasma, Sievers, Boulder, CO, USA) according to manufacturer's recommendations. Acquisition frequency was set at 100 Hz.

2.2. GC×GC-TOF-MS setup

The GC × GC-TOF-MS system consists in a 6890N (Agilent Technologies, Massy, France) gas chromatograph and a Pegasus IV time of flight mass spectrometer (LECO, St. Joseph, MI, USA). The separation was conducted at a constant flow of 1.4 mL/min. Electron impact (EI) ionization was performed at 70 eV, the acquisition frequency was 100 Hz in a mass range of 35 to 600 amu and a multi plate voltage of −1400 V was applied. Identification of compounds was achieved by comparison of acquired mass spectra with NIST 2.0 (2002) library.

2.3. GC-NCD set up

GC-NCD analysis was achieved using a 6890 (Agilent Technologies, Massy, France) gas chromatograph equipped with an on-column injector which was programmed from 90 to 280 °C at a rate of 70 °C/min. An OV1 capillary column (30 m × 0.32 mm I.D × 3 μm film thickness) was installed in the oven programmed from 60 to 240 °C at a rate of 5 °C/min. The Helium (carrier gas) flow rate was set at 1.5 mL/min. In this work, detection was performed with a 7090N NCD equipped with a ceramic flameless burner (Antek Instrument, Houston, TX, USA).