Saturated and aromatic biomarker characterization in seven gas oil cuts by comprehensive two-dimensional gas chromatography coupled with time of flight mass spectrometry (GC×GC-TOFMS)

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This paper was selected for presentation by an ALAGO Technical Committee following review of information contained in an abstract submitted by the author(s).

Introduction

The petroleum industry faces increasing demands to convert heavy oil fractions into valuable products. Molecular distillation of vacuum residues from petroleum has been a promising alternative yielding extra heavy gas oil (EHGO) as an important heavy feedstock. The knowledge of the chemical composition of GO samples is crucial for the petrochemical industries, guiding proper treatment and use, as well as actions of environmental concerns1-3. Gas oil (GO) samples are petrochemical products extremely complex with a large number of components, such as saturated hydrocarbons, aromatic and heteroatomic compounds. The geochemical biomarkers are present in the saturated hydrocarbon and aromatic fractions.

Comprehensive two-dimensional gas chromatography coupled with time of flight mass spectrometry (GC×GC-TOFMS) has been recently employed in biomarker characterization1,4-7 allowing better separation of class of molecules, individual identification of compounds and discovery of new molecules.

The aim of this work was to carry out the identification of saturated hydrocarbons and aromatic compounds in seven GO cuts using GC×GC-TOFMS, illustrating the potential of the technique for biomarker characterization.

Materials and Method

Seven GO cuts from the same atmospheric petroleum residuum were obtained by molecular distillation at final temperatures of 490.0, 503.2 (medium gas oils), 522.5, 549.5 (heavy gas oils), 583.7, 622.4 and 662.2 ºC (extra heavy gas oils). The GO samples were fractioned into saturated (n-hexane), aromatic (n-hexane:dichloromethane, 8:2, v:v) and polar compounds (dichloromethane:methanol, 9:1, v:v) by liquid chromatography using activated silica gel.

The GC×GC system used was a Pegasus 4D (Leco, St. Joseph, MI, USA), which uses a GC (Agilent Technologies 6890 GC, Palo Alto, CA, USA) equipped with a secondary oven and a non-moving quad-jet dual-stage modulator. Data acquisition and processing was carried out using ChromaTOF software version 4.21 (Leco Corp., St. Joseph, MI). The GC column set consisted of a DB5 (1D; 30 m, 0.25 mm i.d., 0.25 μm df) and a BPX-50 (2D; 1.5 m, 0.1 mm i.d., 0.1 μm df).

For the GC conditions used to the saturated fraction analysis, the primary oven temperature program was 70 ºC for 1.00 min, ramp at 20 ºC min-1 to 170 ºC, and then ramp at 2 ºC min-1 to 335 ºC. The secondary oven temperature program had a temperature 20 ºC higher than that of the primary one. Helium was used as carrier gas at a flow rate of 1.5 mL min-1. The modulation period was 6 s with 1.5 s hot pulse duration and a 35 ºC modulator temperature offset versus the primary oven temperature. The MS transfer line was held at 280 ºC and the TOFMS was operated in the 70 eV electron ionization mode scanning within the 50-600 m/z range. The ion source temperature was kept at 230 ºC, the detector was operated at 1700 V, the applied electron energy was 70 eV and the acquisition rate was 100 spectra s⁻¹.

Aromatic fractions were analyzed as follow: primary oven temperature program was 70 ºC for 1.00 min, ramp at 20 ºC min⁻¹ to 170 ºC, and then ramp at 2 ºC min⁻¹ to 340 ºC. The secondary oven temperature program had a temperature 20 ºC higher than that of the primary one. Helium was used as the carrier gas at a flow rate of 1.5 mL min⁻¹. The modulation period was 10 s with 2.5 s hot pulse duration and a 30 ºC modulator temperature offset versus the primary oven temperature. The MS transfer line was held at 310 ºC and the TOFMS was operated in the 70 eV electron ionization mode scanning within the 50-700 m/z range. The ion source temperature was 230 ºC, the detector was operated at 1600 V, and the acquisition rate was 100 spectra s⁻¹.

Compound identification was performed by examination and comparison with literature mass spectra, retention time, authentic standards, elution order and Nist Mass Spectral Database (version 2005).

Results and Discussion

Several classes of biomarkers were identified in the saturated fractions, such as tri-, tetra- and pentacyclic terpanes, steranes and secohopanes (Figure 1). Concerning the aromatic fractions, triaromatic steroids were detected in these complex samples (Figure 2).
terpanes, steranes and triaromatic steroids were identified. So, GC×GC-TOFMS is a technique that provides considerable chemical selectivity for the analysis of GO samples and can be used in a broad molecular characterization of these materials.

**Acknowledgments**

The authors thank financial support from ANP, Petrobras, CAPES, CNPq, PROPESQ/UFPE, LAGESE/UFPE, FAPERJ and FUJB.

**References**