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Hyphenation of supercritical fluid chromatography and two-dimensional gas chromatography–mass spectrometry for group type separations

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ABSTRACT

The Fischer–Tropsch (FT) process produces a variety of compounds over a wide carbon number range and the synthetic crude oil produced by this process is rich in highly valuable olefins and oxygenates, which crude oil only contains at trace levels. The characterization of these products is very challenging even when using comprehensive two-dimensional gas chromatography coupled to time-of-flight mass spectrometry (GC × GC–TOF-MS). The separation between cyclic paraffins and olefins is especially difficult since they elute in similar positions on the GC × GC chromatogram and since they have identical molecular masses with indistinguishable fragmentation patterns. Previously, a high performance liquid chromatography (HPLC) fractionation procedure was used prior to GC × GC–TOF-MS analysis to distinguish between alkenes and alkanes, both cyclic and non-cyclic, however, there was co-elution of the solvents used in the HPLC fractionation procedure, and the volatile components in the gasoline sample and the dilution introduced by the off-line fractionation procedure made it very difficult to investigate components present at very low concentrations. The hyphenation of supercritical fluid chromatography (SFC) to GC × GC is less complicated and the removal of the supercritical CO_2 can be easily achieved without any loss of the volatile sample components, eliminating the introduction of co-eluting solvents as well as the dilution effect. This paper describes the on-line hyphenation of SFC to a GC × GC system in order to comprehensively characterize the chemical groups (saturates, unsaturates, oxygenates and aromatics) in an FT sample.

1. Introduction

The Fischer–Tropsch (FT) process produces a variety of compounds over a wide carbon number range and involves a series of catalyzed reactions of carbon monoxide and hydrogen. A large variety of synthetic fuels and chemicals are produced during product workup [1] that are practically free of sulphur- and nitrogen-containing compounds–alleviating environmental concerns when compared to crude-derived products. The high temperature FT (HT-FT) products are rich in highly valuable olefins and oxygenates, which crude oil only contains at trace levels. For the HT-FT processes products are spread over gas, oil and water phases with only a small amount of wax being formed. The analysis of any one of these phases is very challenging and typical oil phase samples may contain thousands of compounds. The characterization of these phases is very important for the study of FT selectivity models and their deviations [2]. Previously one-dimensional separation techniques were used for the study of the selectivity models [2–9], however these techniques cannot separate all compounds, even when using high efficiency capillary columns providing peak capacities in the order of ~500–600 [10]. The introduction of comprehensive two-dimensional gas chromatography (GC × GC) provides several advantages for the analysis of these complex oil phase samples. The peak capacities are in the order of tens of thousands and peaks are arranged in highly structured plots where peaks belonging to a homologous series are positioned along straight lines on a retention plane. Another advantage of GC × GC is the increase in sensitivity (up to 10 fold) compared to ^{1}D GC because of the re-concentration of peaks in the modulator and the very fast separation achieved in the second dimension column that minimizes peak broadening and effectively increases the signal-to-noise ratio [11,12]. The application of GC × GC to the analysis of highly complex petrochemical mixtures has been described by a number of authors [12–17]. Even with the huge increase in separation power obtained by comprehensive GC, peak co-elution still occurs when very complex mixtures are analyzed. The separation between cyclic paraffins and olefins

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is especially difficult since they elute in similar positions on the GC × GC chromatogram. Time-of-flight mass spectrometry (TOF-MS) is very powerful in group-type identification but is also not able to distinguish between the cyclic alkane and alkene component classes because of their identical molecular masses and similar fragmentation patterns. One way of improving the GC × GC separation is to apply a fractionation step prior to GC × GC analysis [18–20]. Previously, an HPLC fractionation procedure using a silver-modified column was used prior to GC × GC–TOF-MS analysis to distinguish between alkenes and alkanes, both cyclic and non-cyclic [21,22]. This robust fractionation step before GC × GC was used to separate saturated from unsaturated hydrocarbons since it is known that the silver ions interact with the alkene double bond by formation of a complex. It was shown by Mao et al. [21] that the complexation of silver ions with alkene double bonds occurs with both aromatic and non-aromatic compounds. It was observed that the saturated hydrocarbons were not retained on the silver-modified column and eluted with the non-polar mobile phase, n-hexane, whilst the unsaturated hydrocarbons were retained on the column. The unsaturated hydrocarbons were subsequently released from the column by changing the mobile phase to the more polar acetone. The TOF-MS was then utilized to distinguish between the non-cyclic and cyclic alkanes eluted by the hexane solvent and the non-cyclic and cyclic alkenes eluted by the acetone solvent. Although this approach worked well, there was co-elution of the solvents used in the HPLC fractionation procedure and the volatile components of the gasoline sample [22]. Another drawback of this procedure is that the solvents used in the HPLC method diluted the sample and large amounts of the collected fractions had to be injected in order to detect the smaller peaks by GC × GC. Direct transfer of large volumes of collected fractions requires instrument modifications [24]. Low level components can go undetected without reconcentration of the collected fraction, a process that can lead to severe discrimination against the volatile compounds in the sample. The susceptibility of off-line hyphenated techniques to sample loss and contamination during collection and reconcentration has been described by other groups [23], emphasizing the need for an on-line pre-fractionation step. Supercritical fluid chromatography (SFC) utilizes supercritical CO_2 as mobile phase. The use of SFC for group type separation has been published before and the separation achieved with SFC has proved to be very similar to that obtained by HPLC [25–27]. The hyphenation of SFC to GC × GC is less complicated and has been achieved by other groups merely by decompression of the supercritical fluid through a restrictor into the GC injection port [28–30]. This allows the transfer of an eluting fraction from the supercritical phase to the gas phase with simultaneous loss of only the highly volatile CO_2. Utilizing SFC as pre-fractionation method would eliminate the introduction of co-eluting solvents as well as the dilution stemming from the HPLC fractionation procedure [22]. In order to comprehensively characterize the chemical groups (saturates, unsaturates, oxygenates and aromatics) in a sample, the on-line hyphenation of SFC to a GC × GC system is described. The first part of this paper addresses the development and optimization of the SFC chromatographic conditions to achieve the group type separation whilst the second part deals with the GC × GC method. Subsequently the on-line hyphenation of SFC to the GC × GC and the results obtained from the analysis of an oil sample are also discussed. Some applications are also mentioned at the end of this paper.

2. Experimental

2.1. Chemicals

Analytical gases for both the SFC and the GC × GC were obtained from Afrox (South Africa). The HT-FT Light oil, kerosene and narrow distillation cut samples were obtained from Sasol Synfuels, Secunda, South Africa. Standards of the various chemical groups were obtained from Sigma Aldrich (St Louis, MO, USA).

2.2. SFC group type separation

A Selerity Series 4000 SFC system equipped with SFC pump, autosampler, SFC oven, a pneumatically actuated rotary injection valve and a flame ionization detector operated at a temperature of 400 °C was used for the group type separation on the SFC (Selerity Technologies, Utah, USA). The optimization of the group-type separation (saturates, unsaturates, aromatics and oxygenates) on the SFC was performed using a variety of standards typically found in a HT-FT light oil sample. In order to achieve the group type separation, three analytical columns were used, namely a PVA–silica column (50 mm L × 1.0 mm ID, 5 μm d_p from Selerity Technologies, Utah, USA) that was used to retain the oxygenates whilst the Petrosil column (50 cm L × 1.0 mm ID, 5 μm d_p from Selerity Technologies, Utah, USA) was used to separate the aromatics from the unsaturates. A PetroAG silver-loaded cation exchange column (50 mm L × 1.0 mm ID, 5 μm d_p from Selerity Technologies, Utah, USA) was used to retain all the unsaturates. The SFC oven is also equipped with two six-port two-position switching valves to allow forward and backflushing of the analytical columns. The silver loaded column was operated in a secondary column oven at a temperature of 140 °C throughout to allow faster clearance of the olefins and other unsaturates through the column. The SFC mobile phase (carbon dioxide) was delivered at a constant pressure of 200 atm. The injection volume was 0.1 μl and the analysis temperature of 40 °C was used throughout. An external six-port, two-position switching valve was used to direct the SFC effluent to either the FID on the SFC instrument or the GC × GC instrument. A split connector (Restek, Bellefonte, USA) was installed on the capillary going to the GC × GC in order to control the amount of effluent that is sent to the GC × GC and this amount could be varied using different restrictor combinations. The SFC eluent was introduced into the PTV injector by an integral restrictor [31] inserted through the septum. The combined flow sent through the restrictor and vented by the split matched the flow to the SFC's FID. The SFC columns were set up similar to the method described for the determination of olefin content in denatured ethanol by SFC [32] and once the retention times for each group was determined using the FID, the external valve could be switched on at these respective times to transfer the appropriate SFC fractions to the GC × GC.

2.3. GC × GC method

The GC × GC instrument used was a Pegasus 4D from Leco Corporation (St. Joseph, USA) equipped with a time-of-flight mass spectrometer and a 7683B auto injector system (Agilent Technologies, Little Falls, USA). A programmed temperature vaporization (PTV) injector (Gerstel, Mulheim an der Ruhr, Germany) was used on this system. In previous studies the advantages of a polar × non-polar column set (in contrast to the more common non-polar × polar column set) for the analysis of Fischer–Tropsch oil products were described [16,17]. Hence, in the first dimension a 60 m × 0.25 mm ID, 0.25 μm df StabilWax (Restek, Bellefonte, USA) and in the second dimension a 2 m × 0.1 mm ID, 0.1 μm df RTXi-5 column (Restek, Bellefonte, USA) was used in this study. Helium was the carrier gas at a constant flow rate of 1.2 mL/min. A split ratio of 400:1 and injection volume of 0.5 μL was used for the analysis of the light oil sample whilst for the hyphenation experiments the injector was operated in splitless mode. The first oven was programmed from 40 °C (2.0 min) to 255 °C at 2 °C/min. The secondary oven and modulator followed the first temperature programme but started at 60 and 70 °C, respectively. TOF-MS spectra were collected