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# On-line analysis of complex hydrocarbon mixtures using comprehensive two-dimensional gas chromatography

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ABSTRACT

This paper discusses the first setup for on-line qualitative and quantitative comprehensive two-dimensional gas chromatography (GC × GC) of complex hydrocarbon mixtures. A built-in 4-port 2-way valve allows switching between flame ionization detection (FID) and time-of-flight mass spectrometry (TOF-MS) between runs, without the need to cool down and vent the MS. Proper selection of GC carrier gas flow rates enables maximal agreement between the obtained chromatograms in both configurations. For on-line analysis of reactor effluents, a dedicated sampling system allows automatic sampling of the hot reactor effluent gases and immediate injection of the sample on the GC × GC. To determine a complete effluent composition in a single run of the GC × GC, a subzero oven starting temperature was employed. Modulation is started when the oven temperature reaches 40 °C, thus dividing the chromatogram in a conventional 1D and a comprehensive 2D part. This work illustrates the mature and robust character of GC × GC, extending its capabilities from mere laboratory use to on-line routine analysis for industrial processes in the (petro-)chemical industry.

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## 1. Introduction

Despite the long tradition and vast knowledge base about petrochemical production and petroleum conversion processes there is still room to improve their performance in order to reduce energy consumption, improve selectivity and to better protect the environment. To this end, accurate mathematical simulation models are an indispensable tool and many chemical engineers use simulation software routinely. It is obvious that accurate characterization of petrochemical feeds, intermediates, and products plays a crucial role in predicting their physical and thermodynamic properties and in developing the kinetic models that describe chemical transformations of these streams via the occurring reactions. However, petroleum and the products obtained therefrom contain a vast variety of compounds, mainly but not exclusively hydrocarbons. As the number of carbon atoms increases, the complexity of petroleum fractions and number of components therein increases exponentially. Consequently, chemical engineers often resort to average bulk properties of these mixtures, e.g. average molecular weight, specific density, H/C-ratio, etc. [1]. Several of which may correlate well with certain compositional characteristics and are therefore widely used as fast and inexpensive means to determine those characteristics [2].

More detailed information on chemical composition, obtained by gas or liquid chromatography, makes it possible to confidently and reliably predict mixture properties that are more difficult to determine experimentally, while simultaneously extending our understanding and fundamental knowledge [3]. For the characterization of both petrochemical feeds and products, chromatography is mostly used: (i) to perform group-type classification by multi-column GC, e.g. ASTM D5443, or liquid chromatography–mass spectroscopy (LC–MS), e.g. ASTM D2425, (ii) to determine the boiling point distribution by simulated distillation, e.g. ASTM D2887, or (iii) for trace analysis, often using specific detection methods. However, due to the extreme complexity of most petrochemical samples, conventional chromatographic techniques often lack sufficient peak capacity, which makes detailed analysis of the individual constituents of higher boiling fractions increasingly difficult, if not impossible [4].

Nevertheless, continuous research efforts have lead to more advanced chromatographic techniques that result in a more detailed mixture characterization. In the last decade, the implementation of comprehensive two-dimensional gas chromatography (GC × GC) has proved to be a very powerful tool to unravel the composition of complex mixtures [5–7]. Compared to conventional 1D-GC, the use of GC × GC results in enhanced peak capacity [8,9],

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due to multiple separation dimensions, and high sensitivity, due to analyte compression between separations [10,11]. In particular the ordered retention of structurally related components is exceptionally useful, since it enables a more straightforward classification and identification of components based on their appearance in the two-dimensional separation space.

Many studies underline the benefits of GC × GC, such as for the characterization of naphtha [12,13], gasoline [14–17], kerosene and diesel cuts [18–21] as well as for trace analysis [22–24] and the control of the chemical processes [25,9,26]. The combination of GC × GC with mass spectroscopy has also received much interest over the years, since it permits direct identification of the separated components [27–30]. In all these applications GC × GC is only used for off-line analysis of such complex mixtures, although its superior separation power makes it potentially one of the most suited analytical methods for on-line analysis of product streams in, for example, refineries and steam cracking facilities. After all, better knowledge about feedstock as well as product stream composition can result in a significant improvement of process understanding and consequently process efficiency.

GC × GC is not yet established as an industry-accepted analytical method, but its development has certainly not remained unnoticed [5,31]. Furthermore, the more detailed characterization of petroleum products will bring the implementation of detailed fundamental simulation models even more within reach [32]. Some of the factors which will decide on the further development and use of GC × GC in an industrial production environment are robustness, ease of use, flexibility and instrument portability. A GC × GC should be able to work under severe conditions, giving accurate and reproducible data both off-line and on-line. Moreover it should be possible to mount multiple detectors on the same piece of equipment, saving space and capital cost.

In the following paragraphs, the development of a dedicated GC × GC system, equipped with both a time-of-flight mass spectrometer (TOF-MS) and a flame ionization detector (FID), is presented. To evaluate the capabilities of two-dimensional gas chromatography as an on-line analytical tool, this GC × GC-FID/TOF-MS has been incorporated into the analysis section of the pilot plant for steam cracking operated at the Laboratory for Chemical Technology [33]. Provided the selection of appropriate columns, operating conditions, and modulation settings, GC × GC allows to obtain a highly detailed characterization of steam cracking effluents, i.e. one of the most challenging petrochemical samples consisting of hydrocarbons ranging from methane up to poly-aromatic hydrocarbons (PAHs).

## 2. Experimental

### 2.1. GC × GC-FID/TOF-MS setup

The GC × GC setup used for this work was built from a Thermo Scientific TRACE GC × GC, obtained from Interscience Belgium and fine-tuned at the LCT. The setup, shown schematically in Fig. 1, is equipped with a split/splitless injector. The columns and the modulator, i.e. a two-jet cryogenic modulator (liquid $CO_2$) [34], are positioned together in a single oven. The chosen column combination, i.e. a typical non-polar/polar column set, enables a separation based on differences in component volatility in the first dimension, while in the second dimension the retention is governed by specific polarity based interactions. An overview of the GC × GC settings used in this work is given in Table 1. The setup is equipped with both an FID and a TEMPUS TOF-MS (Thermo Scientific, Interscience). Electron impact (EI) ionization was performed at 70 eV, a detector voltage of 1700 V was applied and the acquisition frequency was set at 30 spectra/s in a mass range of 35–400 amu.

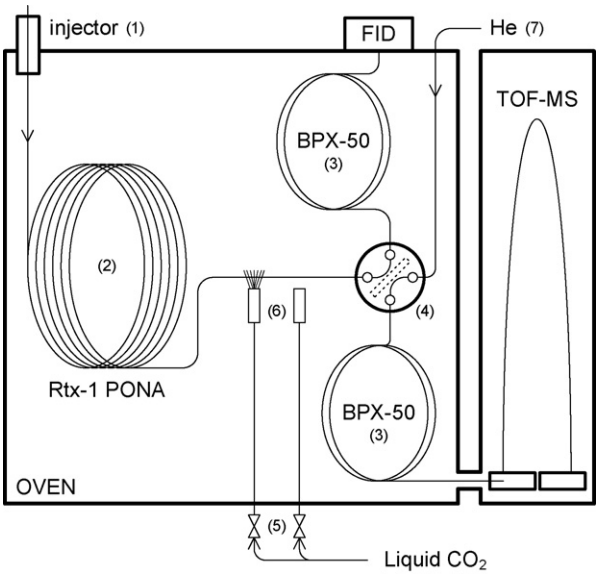


**Fig. 1.** Schematic overview of the GC × GC-FID/TOF-MS setup (1: split/splitless injector, 2: 1st dimension column, 3: 2nd dimension column, 4: manual 4-port 2-way valve, 5: solenoid valves, 6: two-jet cryogenic CO2 modulator, 7: protective helium flow).

A built-in switching system, i.e. a 4-port 2-way valve (VICI AG International, Switzerland), allows to switch between FID and MS without the need to cool down and vent the TOF-MS. In order to avoid eluent build-up after the second dimension column and to ensure a fast second dimension separation, the switch was positioned immediately after the modulator instead of just after the second dimension column.

Fig. 1 shows the columns and the switch in 'FID position'. This way, the analyte is directed towards the FID, while a constant helium flow is maintained through the second dimension column leading to the TOF-MS. The latter prevents degradation of the stationary phase as the oven temperature increases.

Note that the current contribution discusses the combination of an FID and TOF-MS detector. However, the FID could be replaced by any type of detector working at atmospheric pressure, e.g. atomic emission detector (AED) [35,36]. Moreover, the system can be extended to having more than 2 detectors. For example, adding a supplemental chemiluminescence detector, e.g. SCD or NCD, would allow to provide more accurate quantitative measurements of sulfur or nitrogen containing components [37–39].

### 2.2. Pilot plant for steam cracking

The pilot plant, shown schematically in Fig. 2, consists of three sections: the feed section, the furnace/reactor section and the analysis section [33,40,41].

#### 2.2.1. Feed section, furnace and reactor

Several types of hydrocarbon feedstocks can be fed, including gaseous hydrocarbons (e.g. ethane, propane), liquefied gasses (e.g. liquefied butane, $C_4$ cuts), liquid hydrocarbons (e.g. hexane, naphtha, kerosene, gas condensate, gas oil) and solids (e.g. waxes). The inlet flow of water, which is used to produce steam, as well as the hydrocarbons flow is set using computer controlled pumps and/or dedicated mass flow controllers.

The furnace, built of silica/alumina brick (Li23), is 4 m long, 0.7 m wide and 2.6 m high. It is fired by means of 90 premixed gas burners, mounted with automatic fire checks and arranged on the side walls in such a way as to provide a uniform distribution of heat. The fuel supply system comprises a combustion controller

**Table 1**
GC × GC settings for off-line and on-line analysis.

| Detector | FID, 300 °C | TOF-MS, 35–400 amu |
|---|---|---|
| Injection | | |
| Off-line analysis | 0.2 μl, split flow 150 ml/min, 250 °C | |
| On-line analysis | 250 μl (gas), split flow 50 ml/min, 300 °C | |
| Carrier gas | He, constant flow (2.1 ml/min) | He, constant flow (1.6 ml/min) |
| First column | Rtx-1 PONA[a] (50 m × 0.25 mm × 0.5 μm) | |
| Second column | BPX-50[b] (2 m × 0.15 mm × 0.15 μm) | |
| Oven temperature | | |
| Off-line analysis | 50 → 250 °C (3 °C/min) | |
| On-line analysis | −40 (4 min hold) → 40 °C (5 °C/min) → 300 °C (4 °C/min) | |
| Modulation period | | |
| Off-line analysis | 4 s | |
| On-line analysis | 5 s | |

[a] Dimethyl polysiloxane (*Restek*).
[b] 50% phenyl polysilphenylene-siloxane (SGE).

for the regulation of the fuel-to-air ratio. The furnace is divided into seven separate cells that can be heated independently so that any type of temperature profile can be set. Inside the furnace a tubular reactor is mounted, in which the hydrocarbon feedstock is evaporated, mixed with steam and subsequently cracked into a complex and wide boiling mixture, at temperatures ranging from 600 to 900 °C. The cracking coil used for this study is made of Incoloy 800HT. It is 12.8 m long and has an internal diameter of 9 mm. These dimensions are chosen to achieve turbulent flow conditions in the coil with reasonable feed flow rates. The reactor outlet pressure is controlled by a computer regulated restriction valve, as shown in Fig. 2. Twenty-two thermocouples and five pressure transducers are mounted along the coil to measure the temperature and pressure of the reacting gas.

### 2.2.2. On-line effluent analysis

The analysis section of the pilot plant enables on-line qualification and quantification of the entire product stream, i.e. a wide boiling mixture containing $H_2$, CO, $CO_2$ and hydrocarbons ranging from methane to poly-aromatic hydrocarbons (PAHs) such as naphthalene, biphenyl, anthracene, phenanthrene and pyrene, the amounts of which give important information about the coking tendency of the employed feed under the applied process conditions. The enormous boiling range of the product constituents, e.g. −161 °C for methane and 404 °C for pyrene, makes a complete and accurate analysis of such steam cracker effluents a difficult task. The complexity of the effluents calls for several analyzers, including an infrared $CO/CO_2$ gas analyzer (IR-GA) and four gas chromatographs: a permanent gas analyzer (PGA), a refinery gas analyzer (RGA), a detailed hydrocarbon analyzer (DHA) and the GC × GC-FID/TOF-MS described above. The analytical equipment is positioned at different positions on the reactor effluent line, as illustrated in Fig. 2. Their specifications are summarized in Tables 1 and 2.

The pilot plant effluent is sampled on-line, i.e. during pilot plant operation, and at high temperature (400–500 °C). Using a valve-based sampling system [42] and a uniformly heated transfer line,

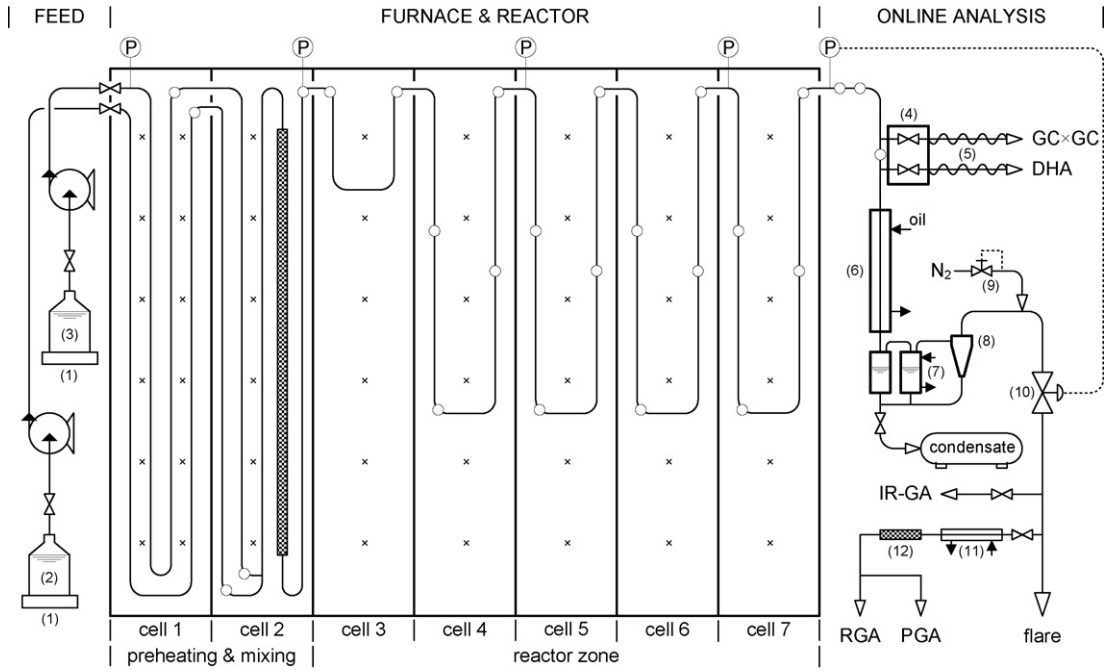


**Fig. 2.** Schematic overview of the pilot plant setup, indicating the most important process gas temperature (◯) and pressure measurements (*P*) (1: electronic balance, 2: demineralized water reservoir, 3: liquid hydrocarbons reservoir, 4: heated sampling oven (300 °C), 5: heated transfer lines (300 °C), 6: oil cooled heat exchanger, 7: water cooled condenser, 8: cyclone, 9: thermal mass flow controller (internal standard addition), 10: outlet pressure regulation valve, 11: water cooled heat exchanger, 12: dehydrator).

**Table 2**
Pilot plant analysis section – GC settings.

| | RGA | | |
|---|---|---|---|
| | Channel 1 | Channel 2 | Channel 3 |
| Injection | 50 μl (gas), 80 °C | 250 μl (gas), 80 °C | 250 μl (gas), 80 °C |
| Carrier gas | He | He | $N_2$ |
| Pre-column | Rtx-1[a] (15 m × 0.53 mm × 3 μm) | Hayesep Q (0.25 m × 1/8″) | Hayesep T (1 m × 1/8″) |
| Analytical column | Rt-Alumina BOND[b] (25 m × 0.53 mm × 15 μm) | Hayesep N (1 m × 1/8″), Molsieve 5A (1 m × 1/8″) | Carbosphere (2 m × 1/8″) |
| Oven temperature | 50 → 120 °C (5 °C/min) | 80 °C | 80 °C |
| Detector | FID, 200 °C | TCD, 160 °C | TCD, 160 °C |

| | PGA | DHA |
|---|---|---|
| Injection | 250 μl (gas), 55 °C | 250 μl (gas), 250 °C |
| Carrier gas | He | He |
| Pre-column | Hayesep N (2 m × 1/8″) | – |
| Analytical column | Carbosphere (1.8 m × 1/8″) | Rtx-1 PONA[a] (50 m × 0.2 mm × 0.55 μm) |
| Oven temperature | 55 °C | −40 → 40 °C (5 °C/min) → 90 °C (3 °C/min) → 250 °C (5°/min) |
| Detector | TCD, 160 °C | FID, 250 °C |

[a] Dimethyl polysiloxane (*Restek*).
[b] $Al_2O_3$/KCl (*Restek*).

as depicted in Fig. 3, a gaseous sample of the reactor effluent is injected onto the DHA and/or the GC × GC. The sampling system consists of two high temperature 6-port 2-way valves (2a and 2b in Fig. 3), kept at 300 °C in the so-called sampling oven to prevent condensation of high molecular weight components. As shown by Van Geem et al. [43], the temperature at which sampling occurs is well above the dew point of the effluent sample. Furthermore, since the reactor effluent is diluted with steam, component partial pressures, and therefore chances of condensation, are reduced. This approach allows analysis of the entire product stream, from methane to PAHs, in a single run of the DHA or GC × GC.

Further downstream the reactor effluent is cooled to approximately 150 °C using an oil cooled heat exchanger. Water and condensed hydrocarbons, i.e. the pyrolysis fuel oil, are removed in a liquid separator, while the remainder of the effluent flows towards the flare, where it is burned. Before reaching the flare, a fixed amount of $N_2$ is continuously added and a fraction of the product stream, uniformly mixed with the added $N_2$, can be withdrawn. After removal of pyrolysis gasoline and all remaining water using a water cooled heat exchanger, this effluent fraction is injected automatically into the PGA and RGA using built-in gas sampling valves. This analysis allows detection of all permanent gasses, such as $N_2$, CO, $CO_2$ and $H_2$, present in the effluent and additional analysis of the lighter hydrocarbons, i.e. methane and $C_2$–$C_4$ hydrocarbons. Since the fixed amount of $N_2$ added to the effluent acts as an internal standard, these analyses permit to determine absolute flow rates of all effluent components, as will be discussed in Section 2.3.2.

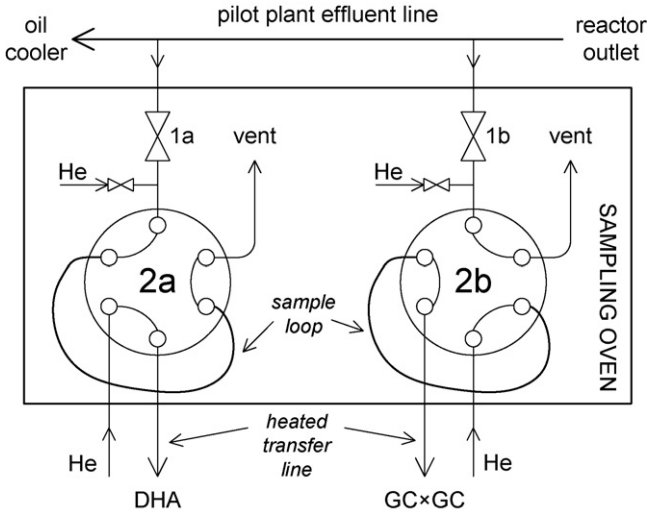


**Fig. 3.** Detailed schematic of the GC × GC and DHA sampling oven and valves. Valve 2a is shown in the purging position, flushing the sample loop with effluent. Valve 2b is shown in injection position: carrier gas (helium) is rerouted to the sampling oven where it is used to transport the effluent sample to the respective GC via a transfer line, i.e. a uniformly heated (300 °C) stainless steel capillary column, pretreated to prevent adsorption of analytes. Between injections, the sample loop can be purged with helium to avoid cross contamination.

### 2.3. Data acquisition and quantification

For all analog detectors, data acquisition and processing was performed using Thermo Scientific's Chrom-Card data system. The data obtained with TOF-MS was acquired using Thermo Scientific's Xcalibur software. The raw GC × GC data files were processed using HyperChrom, i.e. the Chrom-Card extension for GC × GC data handling that enables 3D representation as well as the common color plot representation of the data. HyperChrom also allows automatic 3D peak quantification and identification. The latter is accomplished by cross referencing the measured mass spectra to the spectra in the available MS libraries.

#### 2.3.1. Quantification of off-line analyses

Concerning the off-line GC × GC analysis of complex hydrocarbon mixtures, each peak is assigned a unique name, or is classed into a certain group of components, based on the ordered retention of components and MS confirmation. Only components with identical molecular mass are possibly grouped. To each (grouped) component a weight fraction was assigned by internal normalization [44]:

$$x_i = \frac{f_i \cdot A_i}{\sum_{i=1}^{n} f_i \cdot A_i} \quad (1)$$

where $f_i$ is the relative response factor for component $i$, used to correct the corresponding total peak surface area $A_i$ obtained with FID. It has been demonstrated that various isomeric hydrocarbons, produce only slightly different relative FID responses, so that a fair approximation of the relative response factor may be written as [44]:

$$f_i = \frac{M_i}{N_{C,i}} \cdot \frac{1}{M_{CH_4}} \quad (2)$$

where $M_i$ is the molecular mass of component $i$ with $N_{C,i}$ carbon atoms.

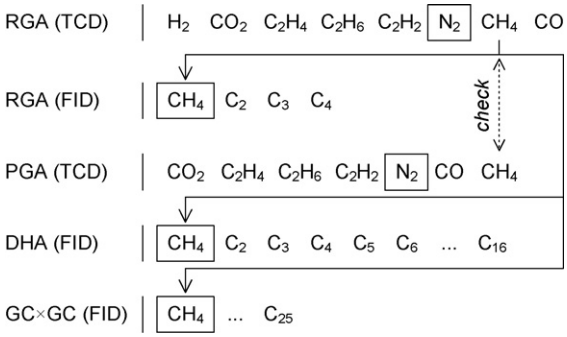


**Fig. 4.** Use of reference components for quantitative on-line effluent analysis.

### 2.3.2. Quantification of on-line analyses

The quantification of all pilot plant effluent components, ranging from $H_2$, CO and methane to PAHs, is done using an internal standard ($N_2$), a fixed amount of which is continuously added to the product stream, as indicated in Fig. 2. The followed quantification approach is based on multiple reference components, as illustrated in Fig. 4, and allows to successfully combine the data from the different instruments. Using the PGA and channel 2 of the RGA, see Table 2, the amount of methane present in the effluent can be determined based on the known mass flow rate of $N_2$.

$$\dot{m}_{CH_4} = \frac{f_{CH_4} \cdot A_{CH_4}}{f_{N_2} \cdot A_{N_2}} \dot{m}_{N_2} \quad (3)$$

The response factor of methane is chosen to be unity ($f_{CH_4} = 1$). The relative response factor for nitrogen is determined by calibration. Subsequently, methane is used as a secondary internal standard for all other quantitative analyses, i.e. the analyses performed on the RGA-FID channel, the DHA and the GC × GC-FID.

$$\dot{m}_i = \frac{f_i \cdot A_i}{f_{CH_4} \cdot A_{CH_4}} \dot{m}_{CH_4} \quad (4)$$

For all major components, the relative response factors $f_i$ on each FID detector were determined by calibration. For the minor products theoretical relative response factors, calculated using Eq. (2), permit to determine their absolute mass flow rates. While, in principle, MS can also be used for quantitative purposes, FID remains the best choice, since different MS instruments and even different tuning parameters are reported to yield substantially different response factors [45]. The GC × GC-TOF-MS is therefore only used for qualitative purposes.

Relating the calculated mass flows to the known flow rate of the hydrocarbon feed, permits to calculate the yields, $x_i$, of all detected components.

$$x_i = \frac{\dot{m}_i}{\dot{m}_{feed}} \quad (5)$$

The resulting sum of yields, which should amount to 100%, therefore acts as an additional control mechanism. Taking into account experimental error, it is clear that the sum of yields will never be exactly equal to 100%. However, if the deviation is small enough, the yields of all components can be confidently scaled, resulting in a sum of yields equal to 100%.

As shown in Fig. 4, this approach requires the separation of methane from all other components on the DHA as well as on the GC × GC. Therefore, the imposed oven temperature of both GC's gradually increases starting from −40 °C. The GC × GC settings for on-line effluent analysis are summarized in Table 1.

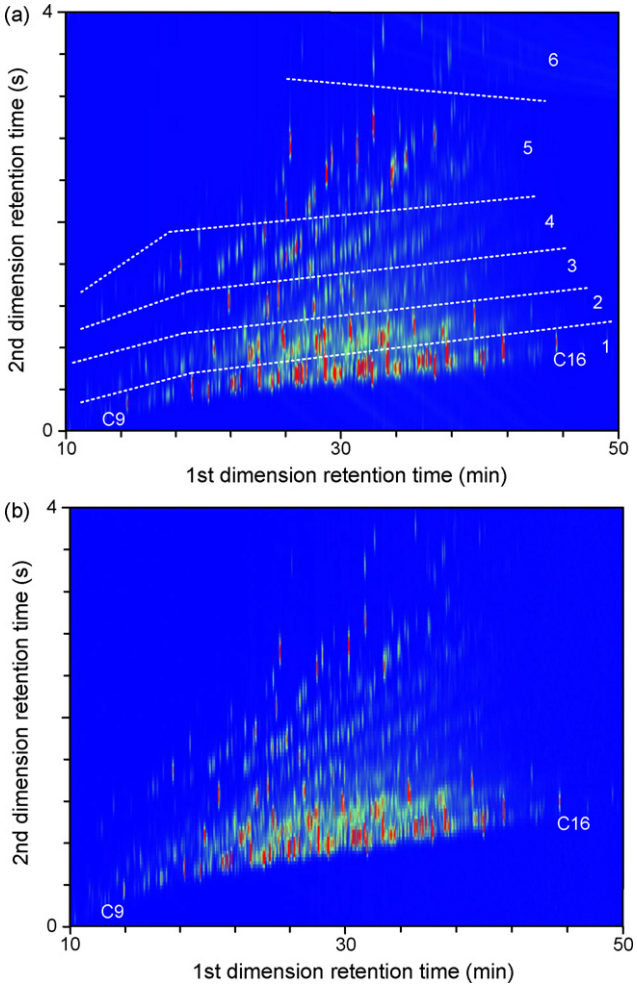


**Fig. 5.** Off-line GC × GC-FID chromatogram of the kerosene (1:paraffins, 2:mono-naphthenes, 3:di-naphthenes, 4:mono-aromatics, 5:naphtheno-aromatics, 6:tri-aromatics); (a) FID and (b) TOF-MS (total ion current).

### 2.4. Chemicals

The hydrotreated kerosene under discussion was provided by Total Petrochemicals Research Feluy (Feluy, Belgium). Analytical gases ($N_2$, He, $CO_2$) were obtained from Air Liquide at a minimum purity of 99.99%. Demineralized water was used for production of steam in the pilot plant.

## 3. Results and discussion

### 3.1. Off-line feedstock analysis

Kerosene is a mixture of aliphatic, naphthenic and aromatic hydrocarbons with a typical boiling point range from 190 to 290 °C. Since such mixtures contain components containing from approximately 10–17 carbon atoms, the total number of components present is enormous. One-dimensional gas chromatography is not able to separate such a huge number of components since, statistically, many overlapping chromatographic peaks will arise [46]. Even hyphenated systems such as HPLC–GC are unable to provide sufficient separation within, for example, the fractions of mono- and dicyclic aromatic components [47].

Using the setup discussed in Section 2.1, a kerosene sample was analyzed. Fig. 5a and b shows the color plot representation of the chromatograms obtained with FID and TOF-MS, respectively. The details of the experimental setup used to acquire this data, are given in Table 1.

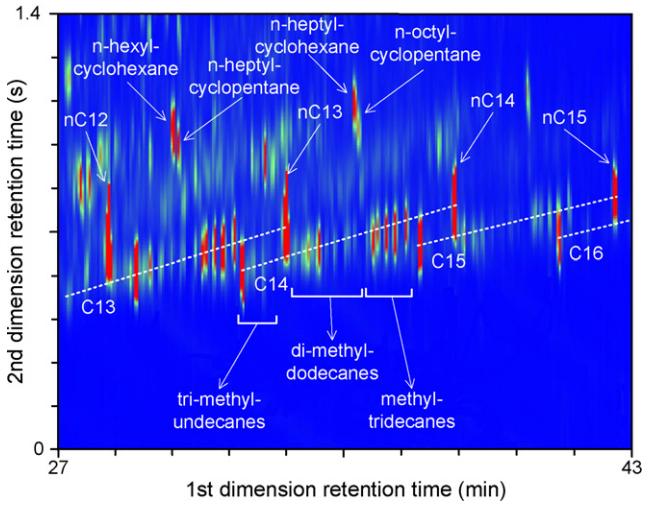


**Fig. 6.** Off-line GC × GC-FID chromatogram of the kerosene – detail of paraffins and naphthenes.

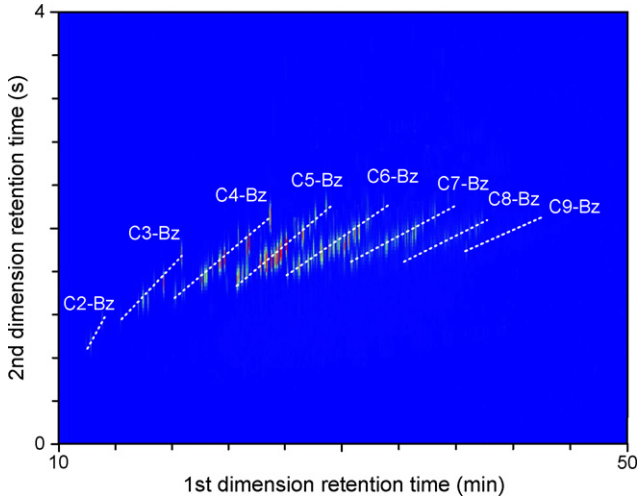


**Fig. 7.** Off-line GC × GC-TOF-MS chromatogram of the kerosene (selected ion traces: 78, 91, 105, 119, 133 and 147).

Despite the significantly higher peak capacity compared to 1D-GC, the overwhelming amount of components makes proper identification and accurate quantification of such complex samples a difficult task. The highly ordered structure of the GC × GC chromatogram aids in a basic group-type classification of the components present in the sample, as indicated in Fig. 5a by the borders that approximately delineate different classes of components [48,18,20]. The pattern of peak placement is in itself informative and makes it possible to, at least, recognize the mixture by simple visual inspection of the chromatogram, even without the need for MS confirmation. Nevertheless, attaching both FID and TOF-MS to the same GC × GC setup, as discussed in Section 2.1, allows a more straightforward qualitative characterization and therefore a more accurate quantification. In order to take full advantage of information obtained with GC × GC–MS analyses, the employed GC × GC settings, shown in Table 1, were determined aiming at maximal agreement between FID and TOF-MS chromatograms. Optimizing the GC × GC procedure is fundamentally more difficult than for 1D-GC [8]. For example, temperature and carrier gas flow will influence the chromatography in both dimensions differently, but not independently. Furthermore, the optimal carrier gas flow rate differs depending on the method of detection, since a TOF-MS operates under vacuum while an FID operates at atmospheric pressure. Optimal flow rates for each detector situation were determined using the Microsoft Excell routine developed by Beens et al. [49]. Fig. 5 shows that the followed approach has lead to highly similar chromatograms using both detection methods, thus enabling a more straightforward conveying of information.

Fig. 6 shows a detailed view of $C_{12}$ up to $C_{15}$ normal and branched paraffins. Since the boiling points of paraffins decrease with increased branching, it is expected that branched paraffins with 14 carbon atoms such as 3-methyl-tridecane elute before *n*-tetradecane [45]. Knowledge of the components boiling point together with MS confirmation allowed to recognize recurring patterns within each carbon number and to identify all normal and branched paraffins, as shown in Fig. 6. Increased branching also leads to a reduced retention in the second dimension, resulting in so-called roof-tiles, i.e. ascending bands of isomeric components, which greatly aids the interpretation of the chromatogram [45,5,6]. In Fig. 7, this effect is also shown for the mono-aromatics in the kerosene (TOF-MS chromatogram, ions extracted at 78, 91, 105, 119, 133 and 147 amu).

Since the kerosene under discussion was hydrotreated, practically no sulfur components, e.g. benzothiophenes, are expected in the sample. This was confirmed by proper ion selection in the TOF-MS chromatogram [27,28]. The detection and quantification of these thiophenes is particularly important for steam cracking feedstocks, because the presence of small levels of sulfur components can have a strong influence on the cracking and coking behavior [50,41].

Although the assignment of all individual peaks in the GC × GC chromatogram is a tedious task, the goal was to determine a truly detailed composition. All individual normal and branched paraffins were identified and quantified, but the same level of detail was not kept throughout the entire chromatogram. With respect to the mono-aromatic components, for example, only the *n*-alkyl benzenes were identified, while the poly-substituted benzenes were grouped according to carbon number based on the roof tile effect and MS confirmation. In total, approximately 300 individual components and component groups were identified and subsequently quantified, as discussed in Section 2.3.1. Table 3 shows a detailed PIONA analysis of the considered kerosene. A distinction is made between normal paraffins, branched paraffins, mono-naphthenes, di-naphthenes, mono-aromatics, naphtheno-aromatics and poly-aromatics.

### 3.2. On-line effluent analysis

The kerosene fraction discussed above was used in a series of steam cracking experiments in the LCT pilot plant over a wide range

**Table 3**
Detailed PIONA of the kerosene [wt%].

| #C | Paraffins | | Naphthenes | | Aromatics | | | Sum |
|---|---|---|---|---|---|---|---|---|
| | *n*- | iso- | mono- | di- | mono- | naphtheno- | di- | |
| 7 | – | – | – | – | 0.01 | – | – | 0.01 |
| 8 | – | 0.04 | 0.03 | – | 0.08 | – | – | 0.16 |
| 9 | 0.16 | 0.10 | 0.31 | 0.02 | 0.39 | – | – | 0.99 |
| 10 | 0.79 | 0.52 | 1.34 | 0.69 | 1.87 | 0.70 | 0.05 | 5.96 |
| 11 | 4.40 | 1.96 | 5.63 | 3.08 | 2.53 | 2.58 | 0.13 | 20.33 |
| 12 | 7.00 | 6.21 | 8.26 | 2.68 | 2.34 | 3.23 | 0.26 | 29.98 |
| 13 | 6.10 | 7.60 | 4.03 | 3.00 | 1.58 | 0.92 | 0.03 | 23.27 |
| 14 | 3.60 | 4.72 | 4.03 | 0.22 | 0.39 | – | – | 12.96 |
| 15 | 1.19 | 3.80 | 0.12 | 0.62 | – | – | – | 5.73 |
| 16 | 0.18 | 0.37 | – | – | – | – | – | 0.56 |
| 17 | 0.03 | 0.03 | – | – | – | – | – | 0.06 |
| 18 | – | 0.01 | – | – | – | – | – | 0.01 |
| Sum | 23.46 | 25.36 | 23.75 | 10.32 | 9.18 | 7.44 | 0.47 | 100 |

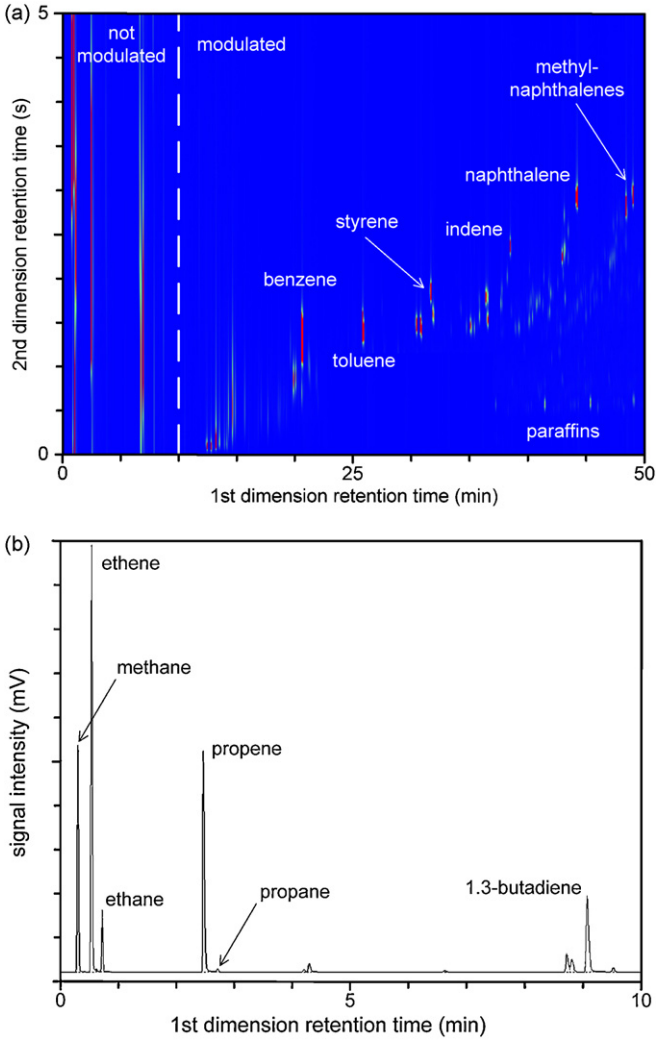


**Fig. 8.** Modulation approach; (a) on-line GC × GC-FID chromatogram (partial) of a pilot plant effluent [$\delta$ = 0.8 kg/kg, COT = 820 °C], (b) 1D visualization of the unmodulated part.

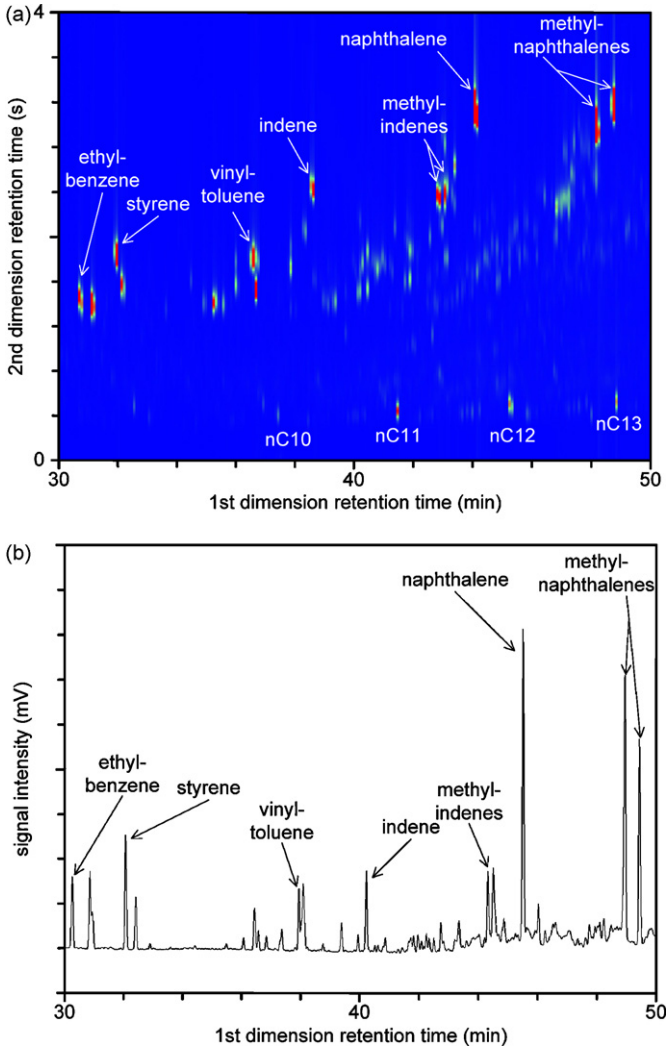


**Fig. 9.** Effect of two-dimensional separation; (a) partial GC × GC-FID chromatogram, (b) partial DHA chromatogram [$\delta$ = 0.6 kg/kg, COT = 800 °C].

of process conditions. The steam dilution ($\delta$) was varied from 0.6 over 0.8 to 1.0 kg steam/kg hydrocarbons, and for each dilution the coil outlet temperature (COT) was varied from 780 to 880 °C. The aim of such experiments is to assess the influence of the imposed process conditions on the product composition. Key components present in a steam cracker effluent are, apart from unreacted feedstock molecules, $H_2$, CO, methane, ethene, propene, 1,3-butadiene, 1,3-cyclopentadiene, benzene, toluene, xylene isomers, styrene, indene, naphthalene and other PAHs.

As explained in Section 2.3.2, yields of all effluent components are determined using a reference component, i.e. methane for on-line GC × GC-FID analysis. In order to separate methane from all other hydrocarbons, the GC × GC oven temperature gradually increases starting from −40 °C. The lower temperatures are accomplished by evaporation of liquid nitrogen inside the GC oven. However, the most volatile components cannot be trapped and refocused by cryogenic modulation using liquid $CO_2$. The modulation is therefore started when the oven temperature reaches 40 °C, thus dividing the resulting chromatogram into a conventional 1D part and a comprehensive 2D part. Since the total area of a GC × GC peak is in fact the sum of all second dimension peak areas belonging to that GC × GC peak, and because of mass conservation in thermal modulation, peak areas obtained in the 1D part and those in the 2D part of a single analysis can be successfully combined.

Fig. 8a shows part of the GC × GC-FID chromatogram obtained when cracking kerosene at a COT of 820 °C and dilution of 0.8 kg/kg. As indicated, the lightest hydrocarbons, i.e. $C_{4-}$ components, elute before modulation was started. In Fig. 8b, this unmodulated part is visualized as a conventional chromatogram. It is obvious that sufficient resolution is available for adequate quantification of these light hydrocarbons, including the reference component methane. As the molecular mass of the eluting components increases, the added value of the second dimension separation becomes evident. Fig. 9a and b shows for the same pilot plant effluent, at a COT of 800 °C and a dilution of 0.6 kg/kg, the chromatograms obtained with GC × GC and DHA, respectively. The ordered retention of components results in a more easily interpretable chromatogram, while simultaneously the enhanced separation power results in reduced peak overlap. The GC × GC analysis therefore allows, for example, a much more accurate quantification of the paraffinic components, as they are visibly separated from the aromatics.

Fig. 10a and b shows the GC × GC-FID chromatograms obtained when cracking kerosene with a dilution of 1.0 kg/kg at a COT of 800 and 840 °C, respectively. In these chromatograms, a distinction can be made between several bands of components, which are indicated roughly by the borders in Fig. 10a and b. These include (unreacted) paraffinic components ($C_{10}$–$C_{14}$), followed by mono-aromatics with increasing alkyl substitution, starting with

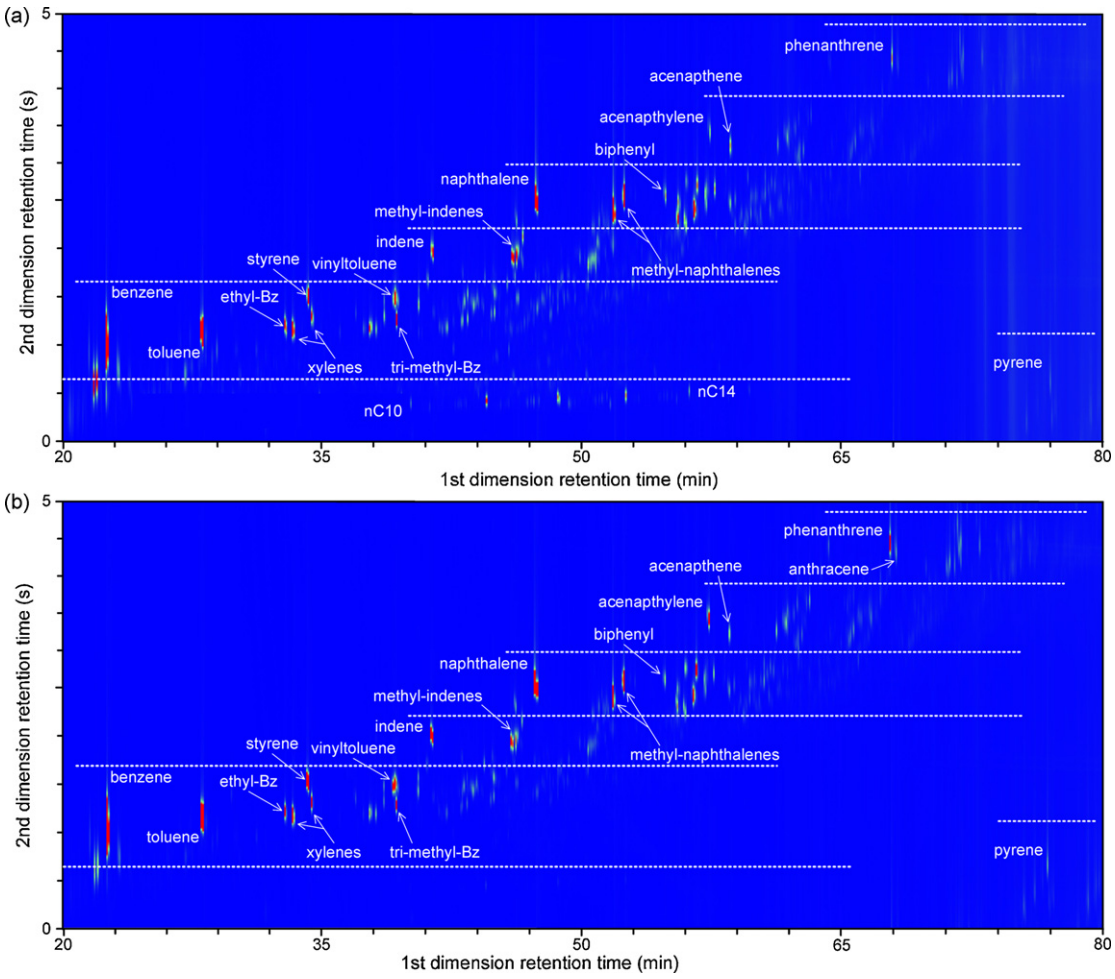


**Fig. 10.** Effect of the coil outlet temperature (COT); (a) on-line GC × GC-FID chromatogram of effluent A [$\delta$ = 1.0 kg/kg, COT = 800 °C], (b) effluent B [$\delta$ = 1.0 kg/kg, COT = 840 °C].

benzene, toluene and ethylbenzene. Naphtheno-aromatics such as indene and alkyl substituted indenes have slightly higher second dimension retention. Di-aromatic components, i.e. naphthalene followed by $C_1$, $C_2$ and $C_3$ alkyl substituted naphthalenes, exhibit even higher second dimension retention. The next bands of components are made up of, respectively, naphtheno-diaromatics such as acenaphthylene, tri-aromatics, such as phenanthrene, and finally tetra-aromatics, such as pyrene. For the heaviest components, some wrap around occurs, but not to the extent that it complicates the chromatogram interpretation, or would make the component quantification impossible.

On-line GC × GC-TOF-MS analysis of the pilot plant effluents made it possible to identify peaks with high confidence. Fig. 11 shows a GC × GC-TOF-MS chromatogram, obtained when cracking the kerosene at high temperature. When comparing this chromatogram with the FID chromatograms discussed above, it

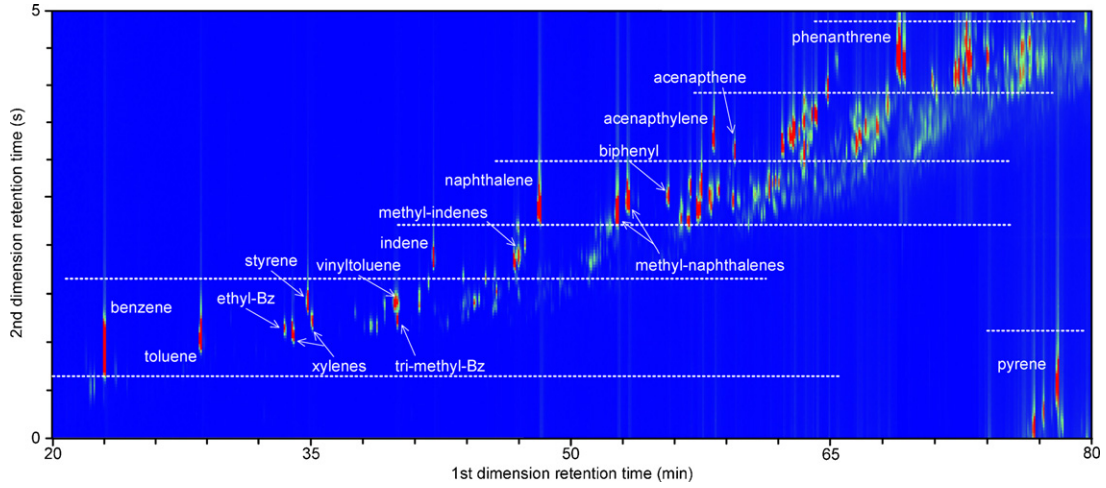


**Fig. 11.** On-line GC × GC-TOF-MS chromatogram (total ion current) [$\delta$ = 0 kg/kg, COT = 800 °C].

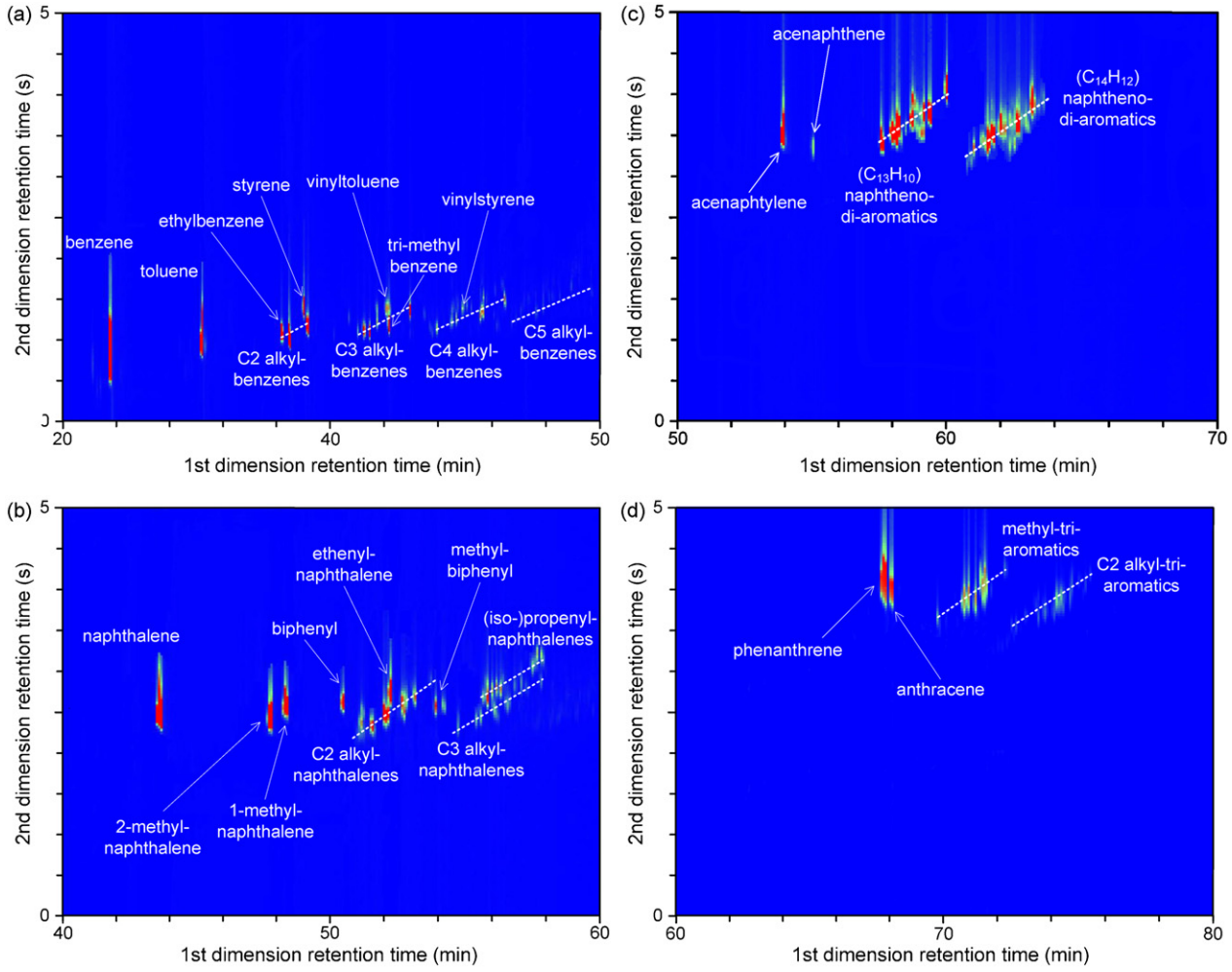


**Fig. 12.** On-line GC × GC-TOF-MS chromatograms (selected ion traces) [$\delta$ = 0 kg/kg, COT = 800 °C]; (a) mono-aromatics (91, 105, 119, 133, 147), (b) di-aromatics (128, 142, 156, 170), (c) naphtheno-di-aromatics (151, 165, 179), (d) tri-aromatics (178, 192, 206).

is clear that the selected GC conditions, see Table 1, resulted in a satisfactory chromatogram similarity between both detection methods. The ability of extracting selected ion traces of interest from the TOF-MS chromatogram, is an interesting and useful tool when identifying peaks [27,28]. Fig. 12a shows mono-aromatic components, visualized by selecting masses 91, 105, 119, 133, 147. As expected, for each carbon number the roof-tile effect is observed, resulting in obvious resolution between benzene, toluene and $C_2$–$C_5$ alkyl substituted benzenes. As shown in Fig. 12a, olefinic aromatics, e.g. styrene, vinyltoluene and vinylstyrene, exhibit slightly higher second dimension retention than the corresponding alkyl substituted aromatics. By selecting masses 128, 142, 156, 170, Fig. 12b focuses on naphthalene and alkyl substituted naphthalenes. Again, olefinic naphthalenes show to have slightly higher second dimension retention. Fig. 12c shows acenaphthylene and acenaphthene as well as $C_{13}H_{10}$ naphtheno-di-aromatics, such as phenalene, benz[e,f]indenes, and methylacenaphthylenes, and $C_{14}H_{12}$ naphtheno-di-aromatics, such as dihydro-phenanthrene and –anthracene, and dimethyl-acenaphthylenes (selected masses: 151, 165, 179) Fig. 12d shows that phenanthrene and anthracene are well separated, and also several methyl- and di-methyl phenanthrenes and anthracenes are detected and visualized by selecting masses 178, 192, 206.

Using MS confirmation, approximately 150 components were identified in these effluents. Based on the quantification approach explained in Section 2.3.2, the FID chromatograms shown in Fig. 10 allowed to obtain a detailed composition of the entire product stream at each of the investigated process conditions. The yields of some key components are given in Table 4.

Fig. 13a and b shows a detail of the respective chromatograms shown in Fig. 10. From Table 4 and these chromatograms, it is clear that higher COT results in increased conversion of saturated components and also a decreased amount of higher alkyl substituted aromatics. The higher conversion mostly leads to higher ethylene yield, but also to increased amounts of mono-aromatics and PAHs such as naphthalene, phenanthrene and pyrene.

While the performance of the proposed methodology, i.e. the combination of cryogenic modulation and oven cooling, has shown to be valid, there are still some practical drawbacks for industrial application. One of them is surely the availability and significant consumption of liquid $CO_2$ and liquid $N_2$, making it more difficult to transport the equipment in the field. One solution for the future might come from the recent improvements of implementing closed cycle cryogenic modulation [51] or valve modulation [52]. Also, application of the recently proposed capillary flow technology could be beneficial [53,54]. Successful application of these modulation concepts would eliminate the need for cryogen, making GC × GC more widely applicable and improving instrument portability. However, the high sensitivity obtained with thermal modulation is an important advantage compared to differential flow modulation.

**Table 4**
Yields [wt%] of selected components for effluents A and B of steam cracking of kerosene (see also Fig. 10) ($\delta$: steam dilution, COT: coil outlet temperature).

| | Effluent A [$\delta$ = 1.0 kg/kg, COT = 800 °C] | Effluent B [$\delta$ = 1.0 kg/kg, COT = 840 °C] |
|---|---|---|
| Methane | 8.74 | 12.72 |
| Ethene | 22.33 | 24.04 |
| Ethane | 2.87 | 2.59 |
| Propene | 13.97 | 11.93 |
| Propane | 0.55 | 0.42 |
| 1.3-Butadiene | 4.66 | 4.52 |
| Benzene | 4.79 | 7.11 |
| Toluene | 3.05 | 3.66 |
| Ethylbenzene | 0.49 | 0.42 |
| Styrene | 0.72 | 1.23 |
| Propylbenzene | 0.07 | 0.02 |
| Indene | 0.49 | 0.80 |
| Naphtalene | 2.52 | 2.96 |
| 1-Methyl-napthalene | 2.40 | 2.13 |
| 2-Methyl-napthalene | 1.92 | 1.67 |
| Biphenyl | 0.22 | 0.20 |
| 1.5-Dimethyl-napthalene | 0.34 | 0.25 |
| 1.6-Dimethyl-napthalene | 0.90 | 0.69 |
| 1.4-Dimethyl-napthalene | 0.40 | 0.33 |
| Phenanthrene | 0.28 | 0.75 |
| Anthracene | 0.08 | 0.21 |
| Methyl-phenanthrene | 0.19 | 0.29 |
| Methyl-anthracene | 0.03 | 0.33 |
| Pyrene | 0.11 | 0.23 |

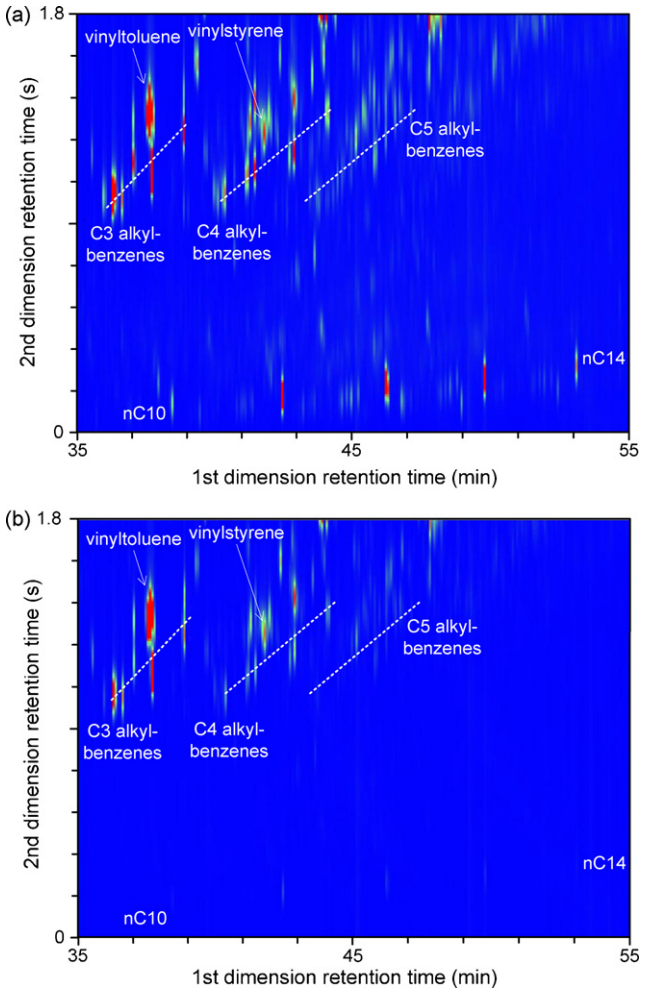


**Fig. 13.** Effect of the coil outlet temperature (COT); (a) detail of on-line GC × GC-FID chromatogram of effluent A [$\delta$ = 1.0 kg/kg, COT = 800 °C], (b) effluent B [$\delta$ = 1.0 kg/kg, COT = 840 °C].

## 4. Conclusions

A dedicated GC × GC-FID/TOF-MS setup that enables both quantitative and qualitative analyses of complex hydrocarbon mixtures using a single apparatus has been evaluated. Using a 4-port 2-way valve it is possible to switch between FID and TOF-MS without the need to cool down and vent the MS. Moreover, proper selection of the carrier gas flow rates in both operation modes, i.e. FID or TOF-MS, results in good agreement between the chromatograms using either of these detectors. This allows to obtain the detailed composition of a petroleum fraction in a straightforward way, as illustrated for a kerosene sample.

To evaluate the capabilities of two-dimensional gas chromatography as an industrial on-line analytical tool, the GC × GC setup was incorporated into the analysis section of a pilot plant for steam cracking. A dedicated sampling system makes it possible to inject all hydrocarbon components in the reactor effluent allowing their analysis from a single GC × GC chromatogram. The latter requires that the oven temperature gradually increases from −40 to 300 °C. The lower temperatures, necessary to separate the most volatile components, are obtained by cooling the GC oven with liquid nitrogen. The two-jet cryogenic modulation with liquid $CO_2$ starts when the oven temperature reaches 40 °C, thus dividing the GC × GC chromatogram into a 1D part and a comprehensive 2D part. This approach enables a complete and exceptionally detailed on-line analysis of steam cracker effluents, both qualitative and quantitative.

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