TWO - DIMENSIONAL GAS CHROMATOGRPHY-ONLINE HYDROGENATION FOR IMPROVED CHARACTERIZATION OF PETROCHEMICAL SAMPLES

H. Potgieter[1], R. Bekker[1], A. Govender[1] , E. Rohwer[2]

[1] Operations and Analytics Department, Group Technology R&T, Sasolburg, 1947, South Africa.

[2] Department of Chemistry, University of Pretoria, Hatfield, Pretoria, 0002, South Africa

Corresponding author: johann.potgieter@sasol.com,

tel: +27169602478, cell: +27822004373, fax: +27112193768

ABSTRACT

The Fischer-Tropsch (FT) process produces a variety of hydrocarbons over a wide carbon number range and during subsequent product workup a large variety of synthetic fuels and chemicals are produced. The complexity of the product slate obtained from this process is well documented and the high temperature FT (HT-FT) process products are spread over gas, oil and water phases. The characterization of these phases is very challenging even when using comprehensive two-dimensional gas chromatography time-of-flight mass spectrometry (GC×GC-TOF-MS). Despite the increase in separation power, peak co-elution still occurs when samples containing isomeric compounds are analysed by comprehensive two dimensional GC. The separation of cyclic and double bond containing compounds and combinations thereof is especially difficult since these compounds elute in a similar position on the GC×GC chromatogram and have identical molecular masses and similar fragmentation patterns. Pre-separation of alkenes and alkanes with HPLC prior to the GC×GC-TOF-MS analysis was used to distinguish between the cyclic and non-cyclic isomers of both these compounds. Subsequently, a method utilizing supercritical fluid chromatography (SFC) as an on-line pre-fractionation step was also developed. These pre-fractionation methods cannot be used to distinguish between classes like dienes and cyclic olefins since both contain alkene double bonds that will form adducts with the silver ions in these methods. On-line hydrogenation after GC×GC separation is a possible way to distinguish between these compounds since the number of rings and alkene double bonds can be determined from the mass spectra of the compounds before and after hydrogenation. This paper describes development of a GC×GC method with post column hydrogenation for the determination of the backbone of cyclic/olefinic structures enabling

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us to differentiate between classes like dienes and cyclic olefins in complex petrochemical streams.

1 <u>INTRODUCTION</u>

The complexity of the product slate obtained from the Fischer-Tropsch (FT) process is well documented in literature [1]. A series of catalysed reactions of carbon monoxide and hydrogen produces a variety of hydrocarbons over a wide carbon number range and during subsequent product workup a large variety of synthetic fuels and chemicals are produced. Contrary to crude-derived products, these FT products are practically free of sulphur- and nitrogen-containing compounds making them more environmentally friendly. The high temperature FT (HT-FT) process products are spread over gas, oil and water phases with only a small amount of wax being formed. These products are rich in highly valuable olefins and oxygenates, which crude oil only contains at trace levels.

The characterization of these phases is very important for better understanding, control and optimization of conversion processes. The characterization of any one of these phases is very challenging and a typical oil phase sample may contain thousands of compounds. All these components cannot be separated by one-dimensional separation techniques, even when high efficiency capillary columns are used [2]. The introduction of comprehensive two-dimensional gas chromatography (GC×GC) provides several advantages for the analysis of these complex oil samples. The peak capacities are in the order of tens of thousands and peaks are arranged in highly structured contour plots where peaks of a homologous series are positioned along lines on a retention plane. Increased sensitivity of up to 10 fold is also obtained by GC×GC when compared to ^{1}D GC. This is due to the re-concentration of peaks in the modulator as well as the very fast separation achieved in the second dimension that minimizes peak broadening and effectively increases the signal-to-noise ratio [3, 4].

The application of GC×GC to the analysis of highly complex petrochemical mixtures has been described by a number of authors [3-9]. However, despite the increase in separation power, peak co-elution still occurs when samples containing isomeric compounds are

analysed by comprehensive two dimensional GC. The separation of cyclic and double bond containing compounds and combinations thereof is especially difficult since these compounds elute in a similar position on the GCxGC chromatogram [10]. By using time-of-flight mass spectrometry (TOF-MS), group-type identification can be achieved to a large extent, but this technique is also not able to distinguish between compounds with identical molecular masses and similar fragmentation patterns e.g. cyclic alkane and alkene pairs, and between dienes and cyclic alkenes. One way of addressing this problem is to apply a fractionation step prior to GCxGC analysis [11-13]. Pre-separation of alkenes and alkanes with HPLC prior to the GCxGC-TOF-MS analysis was used to distinguish between the cyclic and non-cyclic isomers of both these compounds [14, 15]. Although this approach worked well, the large dilution of the sample as well as the co-elution of the HPLC solvents with the volatile components in the gasoline sample were disadvantages associated with this method [15]. Subsequently, methods utilizing supercritical fluid chromatography (SFC) as an on-line pre-fractionation step were developed [16-17]. The hyphenation of SFC to GCxGC is less complicated and the removal of the supercritical CO_2 can be easily achieved without any loss of the volatile sample components or the introduction of co-eluting solvents and their dilution effect. The SFC method [17] separates the sample into four groups, namely (cyclic and non-cyclic) alkanes, (cyclic and non-cyclic) alkenes, aromatics and oxygenates. These groups were transferred separately to the GCxGC-TOF-MS in an on-line mode. As in the case of the HPLC fractionation, the separation of cyclic paraffins and olefins was achieved using a silver-modified column whereby the silver ions interact with the alkene double bond by formation of a complex. This approach cannot be used to distinguish between classes like dienes and cyclic olefins since both contain alkene double bonds that will form adducts with silver ions and therefore both will be retained on the silver modified column. On-line hydrogenation after GCxGC separation is a possible way to distinguish between these compounds since the number of rings and alkene double bonds in the compound structure can be determined from the mass spectra of the compounds before and after hydrogenation. Hydrogenation of compounds after their separation, but before their entry into the mass spectrometer was proposed Lindeman in 1962 [18]. Other groups have used hydrogenation after one dimensional gas chromatographic separation to characterise complex samples [19-22] where hydrogenation was achieved using a capillary fused silica tube coated with either platinum or palladium using hydrogen as carrier gas. Delmonte et al. [23] developed a GCxGC method utilizing columns of the same polarity in the first and second dimensions and used

on-line hydrogenation between the first and second dimension columns to change the chemical structure of the analytes before separation on the second dimension column as a means of introducing orthogonality to the separation in the two dimensional space.

The aim of this study was the development of a GC×GC method with post column hydrogenation by which the analytes undergo hydrogenation after the second dimension separation, before their entry into the mass spectrometer. Capillary hydrogenation after GC×GC separation will allow for the determination of the backbone of these cyclic/olefinic structures and hence enable us to differentiate between classes like dienes and cyclic olefins in complex petrochemical streams.

2 EXPERIMENTAL

2.1 Chemicals

Analytical gases for the GC×GC were obtained from Afrox (South Africa). Standards of the various chemical groups were obtained from Sigma Aldrich (St Louis, MO, USA).

2.2 Capillary Reactor Preparation

The coated capillaries were prepared by static coating according to the procedure described by Schomburg [19] whereby Pt or Pd acetyl-acetonate salt is loaded on a capillary tube and dried on the inner surface of the tube before decomposition into metallic Pt or Pd. Precious metals are highly active hydrogenation catalysts [25] and platinum was selected as the catalyst in this application. One hundred milligrams of Pt acetyl acetonate was weighed into a 10 ml volumetric flask and dissolved in dichloromethane. A deactivated fused silica capillary column (3 m) was filled with the solution using a 1 ml syringe. After filling the column, one end was plugged and the other end evacuated to enable static coating of the capillary for 24 hours before subsequent decomposition of the Pt acetyl-acetonate salt under a mild hydrogen flow for 2 hours at 340°C. The coating procedure was repeated 5 times to increase the amount and dispersion of Pt metal inside the capillary and hence to increase the hydrogenation efficiency of the reactor.

2.3 <u>GC×GC method.</u>

The GC×GC instrument used was a Pegasus 4D from Leco Corporation (St. Joseph, USA) equipped with a time-of-flight mass spectrometer. A split/splitless injector and 7683B auto injector (Agilent Technologies, Little Falls, USA) was used on this system. The first dimension column was a 30 m × 0.25 mm ID, 0.25 µm df StabilWax column (Restek, Bellefonte, USA) and in the second dimension a 1.5 m × 0.1 mm ID, 0.1 µm df RTXi-5 column (Restek, Bellefonte, USA) was used. Helium was used as a carrier gas at a constant flow rate of 1.2 mL/min. A split ratio of 200:1 and injection volume of 0.5 µL was used for all analysis. 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 program but started at 60 °C and 70 °C, respectively. TOF-MS spectra were collected between 35 and 500 m/z at 100 spectra/s.

2.4 <u>Installation of hydrogenation reactor</u>

The capillary hydrogenation reactors used in previous studies [19-20, 22] were typically between 30 and 60 cm in length and ranged from 0.15 to 0.35 mm in diameter. All of these reactors were heated inside the GC oven along with the analytical column or by means of a separate oven. For this study, the aim was to install a capillary reactor in the transfer line of the TOF-MS. This would allow for independent heating of the capillary reactor without the installation of an additional oven or any other instrument modifications. However, installing the capillary reactor in the transfer line only allows for a reactor length of 21 cm and therefore high efficiency capillary reactors are required to ensure complete hydrogenation. For the hydrogenation experiments, a capillary reactor (21 cm) was installed in the TOF-MS transfer line and operated at 250°C. The capillary was connected to the 2nd dimension column by means of a universal presstight connector (Restek, Bellefonte, USA) and hydrogen was used as a carrier gas at a constant flow rate of 1.5 mL/min.

3   **RESULTS AND DISCUSSION**

3.1 <u>Optimization of the coating procedure.</u>

After coating with the Pt, the capillary was inspected under a light microscope to investigate the salt dispersion within the capillary. Inconsistent deposition was

observed with large crystals of Pt acetyl-acetonate salt randomly distributed throughout the capillary. The influence of vacuum as well as temperature control on the coating efficiency was therefore investigated in order to optimize the coating procedure. For the purpose of investigating the influence of vacuum on the coating efficiency, the same capillary was coated at pressures between 40 and 70 kPa below atmosphere and inspected under the light microscope after each coating. The influence of temperature control on the coating efficiency was also investigated and the capillary was again coated at different pressures whilst dispersed in water at 20°C. Dispersion of the capillary in water maintained a constant temperature throughout the evaporation process and prevented the formation of cold spots within the capillary due to solvent evaporation. The capillary was again inspected after each coating. A pressure of 66 kPa below atmosphere combined with constant column temperature (20°C) were found to yield the most uniform coating throughout the column. The Pt acetyl-acetonate salt was subsequently decomposed under a mild hydrogen flow for 2 hours at 340°C to deposit platinum inside the column [24]. Small uncoated areas were still observed throughout the capillary after coating and therefore the coating procedure was repeated an additional 4 times to increase the amount of Pt metal inside the capillary. After the capillary was coated five times, no uncoated areas could be observed through the light microscope and the capillary appeared grey and non-transparent throughout. The metal dispersion within the capillary reactor was investigated by means of a Scanning Electron Microscope and Energy Dispersive X-Ray Spectrometer (SEM-EDS) to ensure that high efficiency reactors were prepared successfully. Figure 1 show two SEM images of the inside of the capillary.
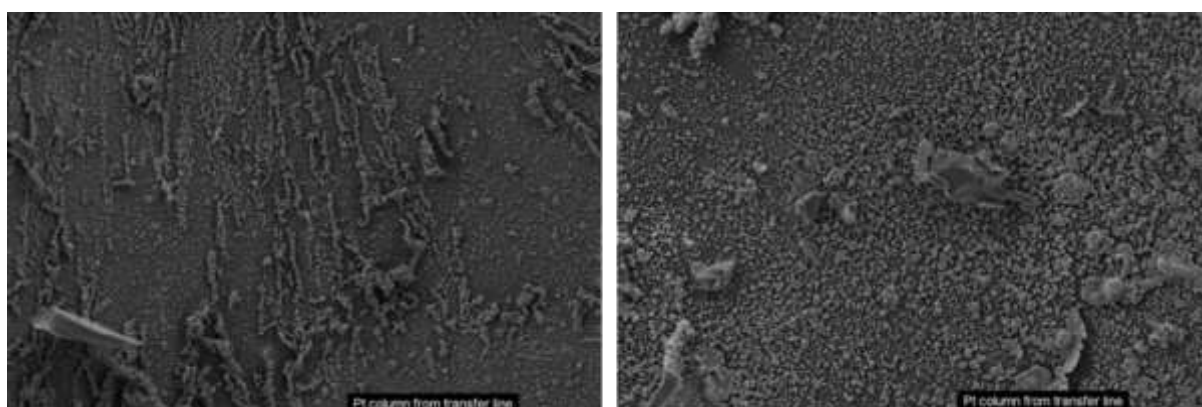

Figure 1. SEM images of the inside of the Pt coated capillary.

Figure 1 indicates that high dispersion of particles was obtained within the capillary. The presence of platinum was confirmed with EDS mapping of the SEM images. Figure 2A shows a SEM image of the inside wall of the capillary whilst Figure 2B shows the EDS platinum map of Figure 2A.
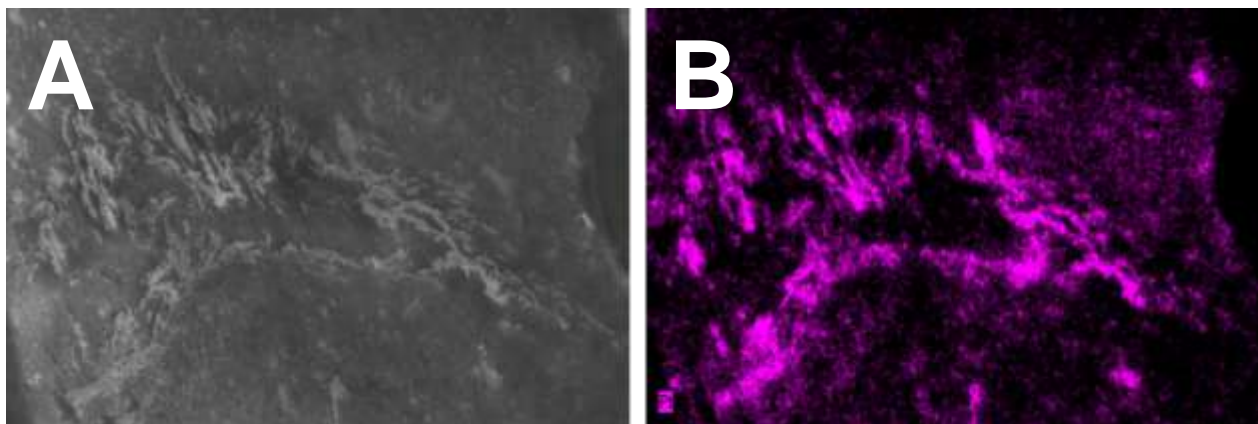

Figure 2. A) SEM image of the inside wall of the capillary. B) EDS platinum map of the same area in A.

The observed platinum matches the pattern of observed particles exactly (Figure 2) and therefore confirms the high dispersion of platinum within the capillary.

3.2 Optimization of capillary reactor diameter

A mixture of standards was prepared in hexane to optimize the GC×GC-TOF method with post column hydrogenation. This standard included 1-butanol; 1-octene; 1-octanol; 3-octyne; 1,3-octadiene; 1,7-octadiene; 1,3-cyclooctadiene; toluene and cyclooctane. Figure 3 shows the GC×GC-TOF contour plot of the standard mixture without a capillary reactor installed and the observed molecular masses of all the compounds are indicated on the chromatogram.
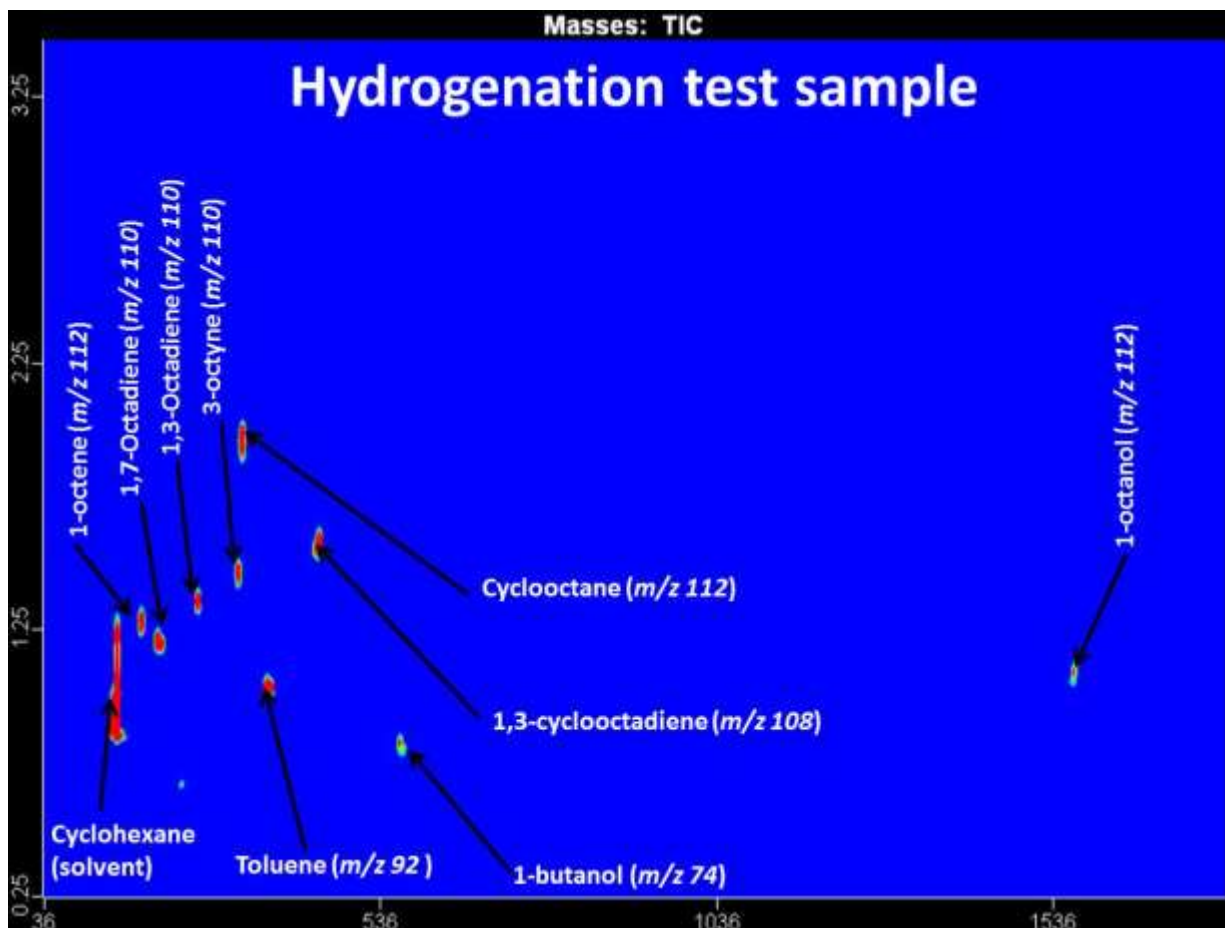
Figure 3. GC × GC-TOFMS contour plot of the standard mixture without a capillary reactor installed.

All the compounds within the mixture are well separated and good peak shapes were obtained throughout. Molecular masses for all the compounds were observed in the mass spectra except for 1-octanol where the molecular ion with a loss of water was observed (m/z 112).

Temperature, pressure, residence time and catalyst loading influence the rate of hydrogenation [25]. In order to optimize the residence time of compounds within the hydrogenation reactor, the flow through the reactor was optimized. In GC×GC, the carrier gas flow rate is set to the optimum flow rate of the 1st dimension column. Since the 1st and 2nd dimension columns are connected in series, but have different internal diameters, the carrier gas linear flow rate through the 2nd dimension column is dependent on the diameter of that column. The same is also true for the capillary reactor since it is installed in series after the 2nd dimension. The optimum residence time of compounds within the hydrogenation reactor was optimized by evaluating the extent of hydrogenation achieved using capillary reactors with different diameters. For

the purpose of this study, capillary reactor with diameters of 0.10, 0.15 and 0.18 mm were evaluated. Figure 4 shows the GC×GC-hydrogenation-TOF-MS chromatogram utilising a 0.10 mm diameter capillary reactor in series after the 0.10 mm 2nd dimension column. Once again the observed molecular masses of all the compounds are indicated on the chromatogram.
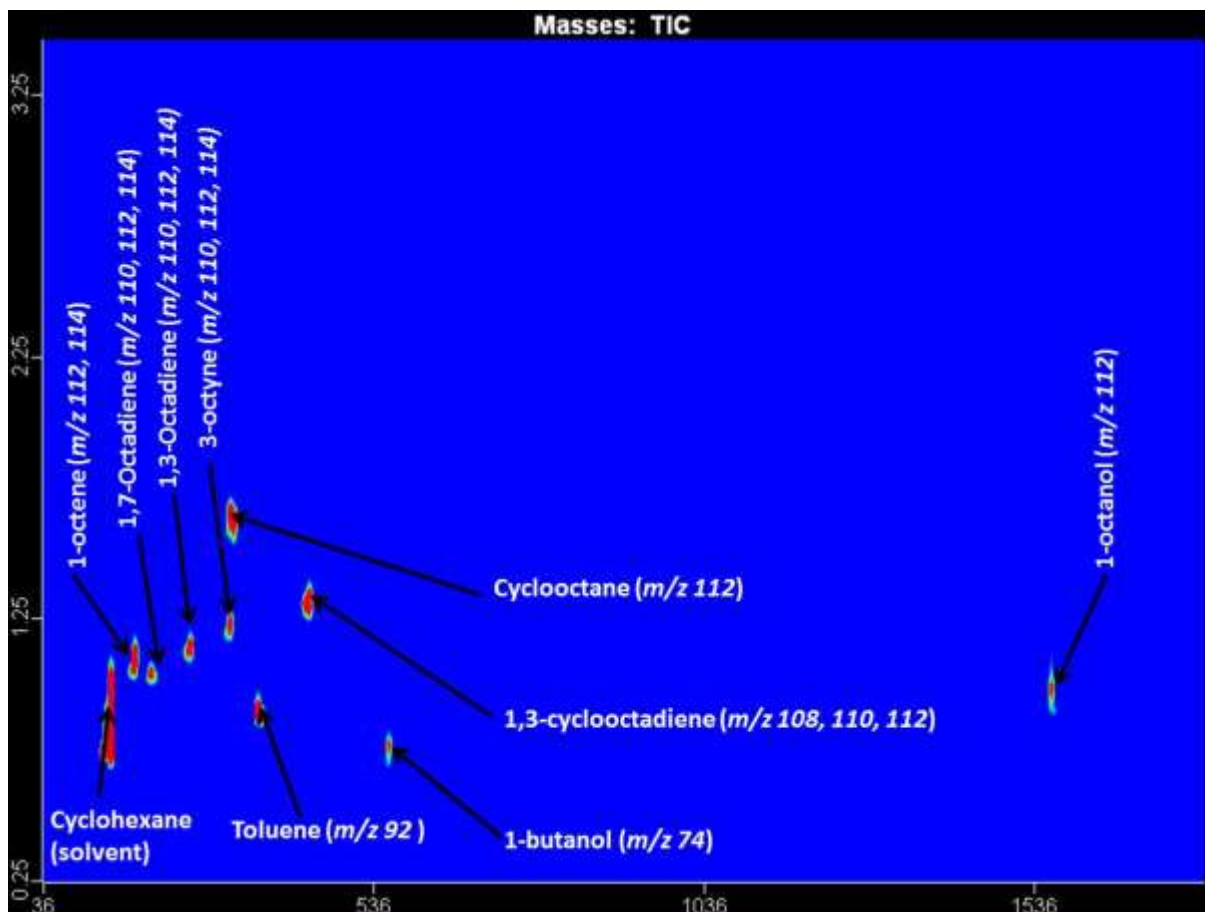

Figure 4 GC × GC-hydrogenation-TOFMS chromatogram utilising the 0.10 mm capillary reactor in combination with a 0.10 mm 2nd dimension column showing that the capillary reactor did not influence the separation or the peak shapes previously achieved without a capillary reactor.

The use of a capillary reactor after the 2nd dimension column did not influence the separation or the peak shapes previously achieved without a capillary reactor (compare figures 3 and 4). However, inspection of the mass spectra of all the compounds showed that only partial hydrogenation was achieved with the 0.10 mm capillary reactor and the molecular masses of the un-hydrogenated compounds were still observed in the mass spectrum. No hydrogenation was achieved for butanol, octanol and toluene.

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Figure 5A, 5B and 5C shows the molecular ion region of the 1-octene mass spectrum obtained with 0.10, 0.15 and 0.18 mm capillary reactors, respectively.
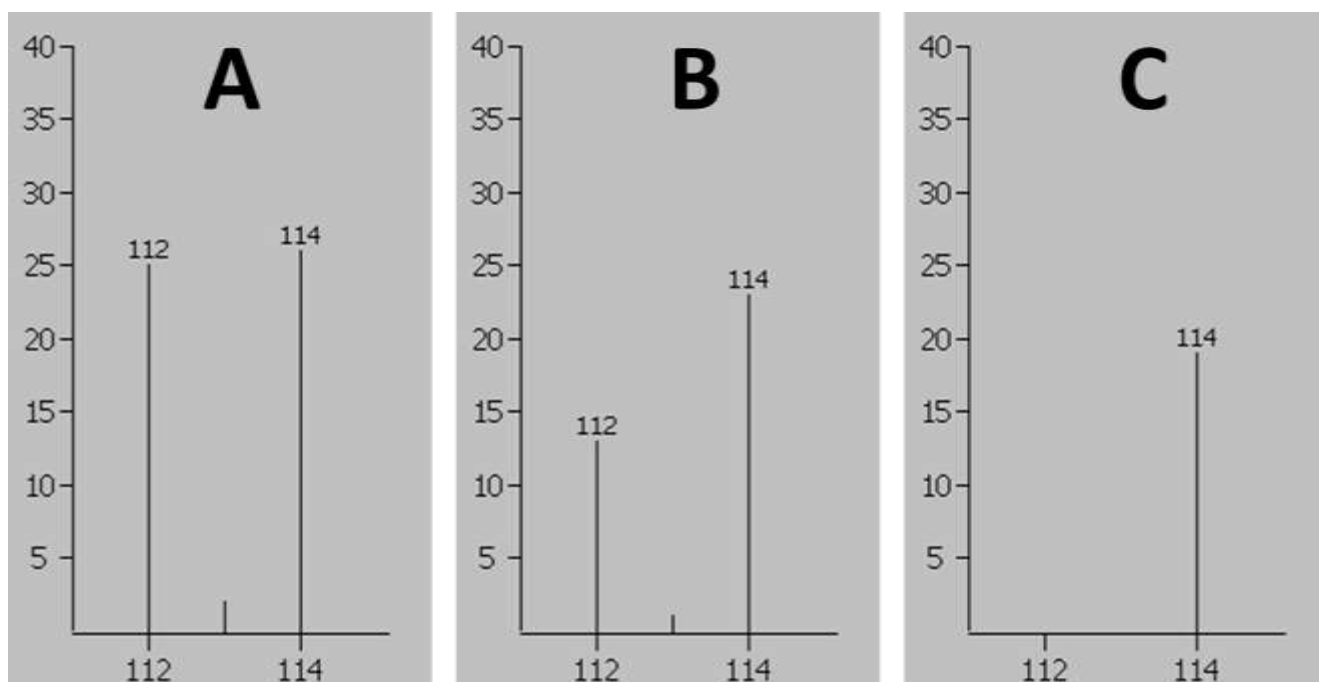

Figure 5 The molecular ion region of the 1-octene mass spectrum observed with the A) 0.10 mm, B) 0.15 mm and C) 0.18 mm capillary reactors showing that hydrogenation improves with an increase in the diameter of the capillary reactor.

It is clear that hydrogenation improves with an increase in the diameter of the capillary reactor and that complete hydrogenation was achieved with the 0.18 mm capillary reactor. This was also true for the other olefinic compounds. Heptane was the primary product obtained after hydrogenation of 1-octanol with the 0.18 mm capillary reactor whilst propane was the primary product obtained after hydrogenation of 1-butanol. Other studies [26, 27] on Pt catalysts with C3 alcohols have shown that these undergo an initial dehydrogenation to form an aldehyde, which can then undergo decarbonylation to produce ethane and CO. No hydrogenation was achieved for toluene with the use of these capillary reactors. This is expected since hydrogenation of these compounds is generally more difficult to achieve compared to olefinic compounds [26].

The low degree of hydrogenation with the 0.10 and 0.15 mm reactor might be ascribed to two factors. Firstly, the higher linear flow rates achieved with the smaller diameter reactors results in insufficient residence times and subsequently, incomplete hydrogenation. Secondly, the lack of hydrogenation might be due to the difference in

the mass of platinum present in the different reactors. The coating procedure requires that a column is coated 5 times using a 1% platinum salt solution. The volume of solution present in these reactors before evaporation is higher for the 0.18 mm reactor than for the other two reactors, resulting in different masses of platinum deposited within the reactors. In order to investigate the possibility of the different platinum loadings in these reactors being responsible for incomplete hydrogenation, a 0.18 mm reactor with only two coatings was prepared. This resulted in the 0.18 mm reactor containing a mass of platinum similar to the 0.10 mm reactor. The different platinum loadings in the different reactors is Illustrated in Table 1.

Table 1. Mass of platinum deposited in each reactor.

Reactor Diameter (mm)	Reactor Volume (mm^2)	Number of coats	Mass Platinum (μg)
0.10	1.649	5	56
0.15	3.711	5	125
0.18	5.344	5	181
0.18	5.344	2	72

Figure 6 shows the GC×GC-hydrogenation-TOF-MS chromatogram utilising the 0.18 mm capillary reactor coated only two times. The molecular ion region of the 1-octene mass spectrum is shown in the chromatogram, while the observed molecular masses of all the other standards are also indicated on the chromatogram.
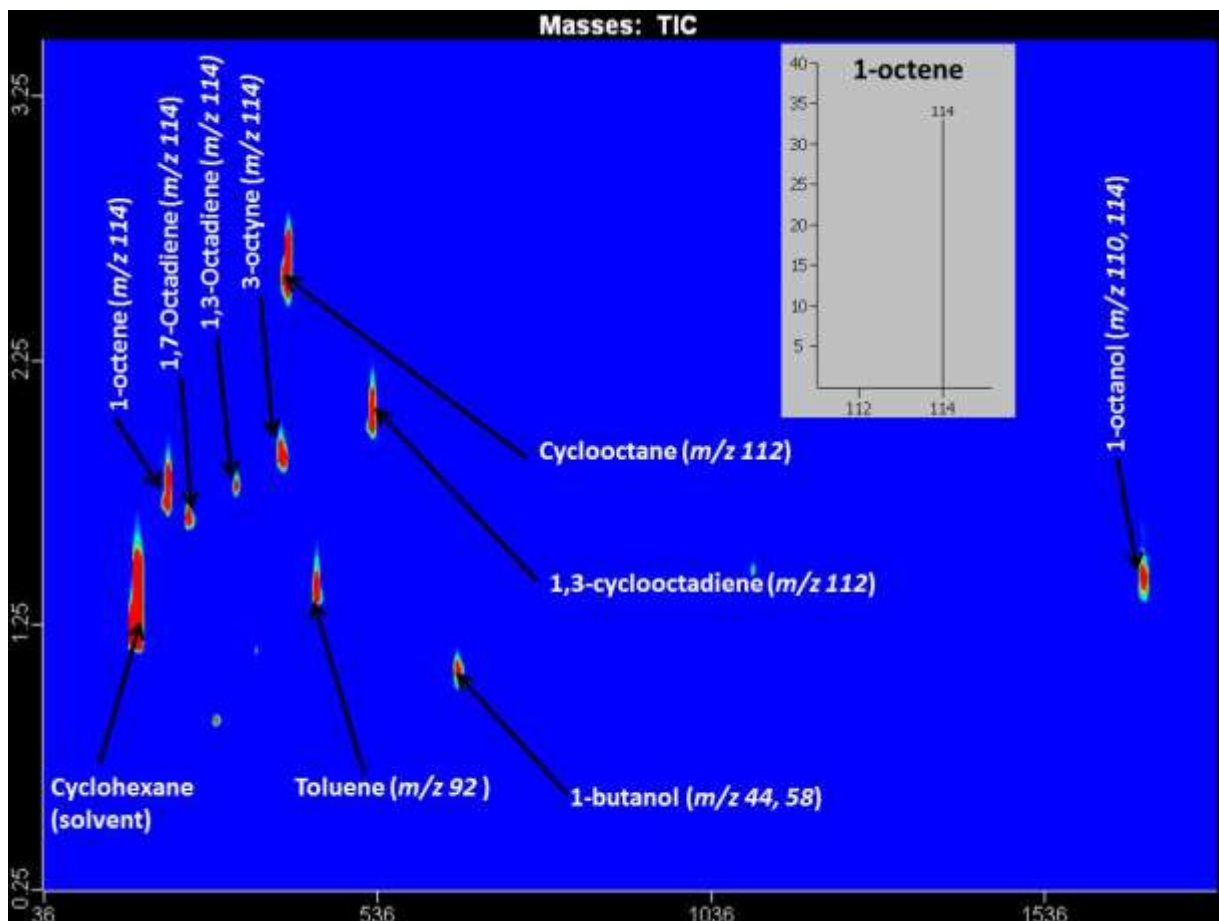
Figure 6 GC × GC-hydrogenation-TOFMS chromatogram utilising the 0.18 mm capillary reactor coated only two times in combination with a 0.10 mm 2nd dimension column.

The mass spectra of all the alkenes show that complete hydrogenation was achieved using the 0.18 mm column containing 72 µg platinum. The molecular ion region of the 1-octene mass spectrum also shows that all the 1-octene was hydrogenated to octane with no 1-octene remaining after hydrogenation. The successful hydrogenation confirms that the incomplete hydrogenation observed with the 0.10 and 0.15 mm reactors is as a result of the reactor diameter (contact time) and that a sufficient amount of platinum for complete hydrogenation was present in all the reactors. These results show that the linear flow rates achieved through the capillary reactors with reactor diameters smaller than 0.18 mm are too high for complete hydrogenation within a reactor with limited length (210 mm) installed in the TOF-MS transfer line.

Only slight peak tailing was observed in the second dimension with the use of the 0.18 mm capillary reactor. This was also observed by other authors [19-21, 23] and is credited to the adsorption of the compounds on the surface of the catalyst. This peak

tailing did not significantly influence the GC×GC separation and was considered acceptable.

3.3 <u>Optimization of transfer line temperature</u>

As mentioned in the previous section, the rate of hydrogenation is influenced by the temperature, pressure, residence time and catalyst loading. The reaction temperature can be optimised by controlling the temperature of the transfer line. Normally the TOF-MS transfer line is operated at 250 °C with no capillary reactor installed. In order to optimise the hydrogenation reaction temperature, the 0.15 mm reactor was installed in the TOF-MS transfer line since only partial hydrogenation was obtained with this reactor and molecular masses of both unhydrogenated and hydrogenated species were observed. The ratio of the un-, partially and fully hydrogenated molecular masses was determined at various temperatures from 150 – 340 °C. Table 2 shows the calculated ratios for 1-octene at various TOF-MS transfer line temperatures.

Table 2. Calculated ratios of the un- and fully hydrogenated molecular masses for 1-Octene.

Temp.	Molecular Mass Ratio
	1-Octene 112:114 *(m/z)*
150	1 : 0.95
200	1 : 0.42
250	1 : 0.31
300	1 : 0.27
340	1 : 0.23

It is observed in Table 2 that the degree of hydrogenation decreases with increasing temperature. Henneberg *et al.* [19] also reported a lower degree of hydrogenation at higher temperatures and ascribed it to the lower residence times of the molecules on the metal. Another possible reason for the observed decrease in the degree of hydrogenation with increasing temperature is the possibility that the hydrogenation reaction has reached equilibrium. Hydrogenation is a strongly exothermic reaction and an increase in temperature will shift the reaction equilibrium towards reactants, according to the Le Chatelier principle. The free energy was calculated for the hydrogenation of 1-octene and 1,3-octadiene at the investigated temperatures (Table

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2) at pressures of 50, 100 and 500 kPa to determine if the reaction is at equilibrium conditions. It was determined that the hydrogenation reaction is not at equilibrium at 340 °C. This is also shown in the equilibrium conversion of the dehydrogenation of C2-C15 alkenes described in Ullmann's Encyclopaedia of Industrial Chemistry [25]. The decreased hydrogenation observed at 340 °C is therefore due to lower residence times of the molecules within the column (higher volume flow rates for the same mass flow, hence higher linear flow rates and lower residence times). In order to support the findings, the influence of temperature on the degree of hydrogenation achieved with the 0.18 mm reactor was also investigated. Complete hydrogenation was obtained at all the investigated temperatures and no unreacted reagent was observed at 340 °C. This also shows that the hydrogenation reaction is not at equilibrium conditions at these temperatures.

Because the degree of hydrogenation achieved with the 0.18 mm capillary reactor was not influenced by the transfer line temperature, the transfer line temperature was kept at 250°C for both the GC×GC separation with and without post column hydrogenation.

3.4 Application to petrochemical sample

The potential of the developed technique was demonstrated by applying it to a complex petrochemical sample. The sample contains low concentrations of compounds with different degrees of unsaturation attributed to a combination of rings and double bonds. GC×GC-TOF analysis of the sample revealed the presence of both these features and it is of great importance to distinguish between them since they will behave differently in downstream processing units. Diolefins are gum precursors [26] and may deactivate certain catalysts whilst the same behaviour is not true for cyclic olefins and/or bicyclic components. The accurate identification of these compounds is therefore very important for the control and optimization of conversion processes. Figure 7 shows the C9 region of the GC×GC-TOF chromatogram of the petrochemical sample. The mass spectra of five selected C9 compounds are also included in the chromatogram.
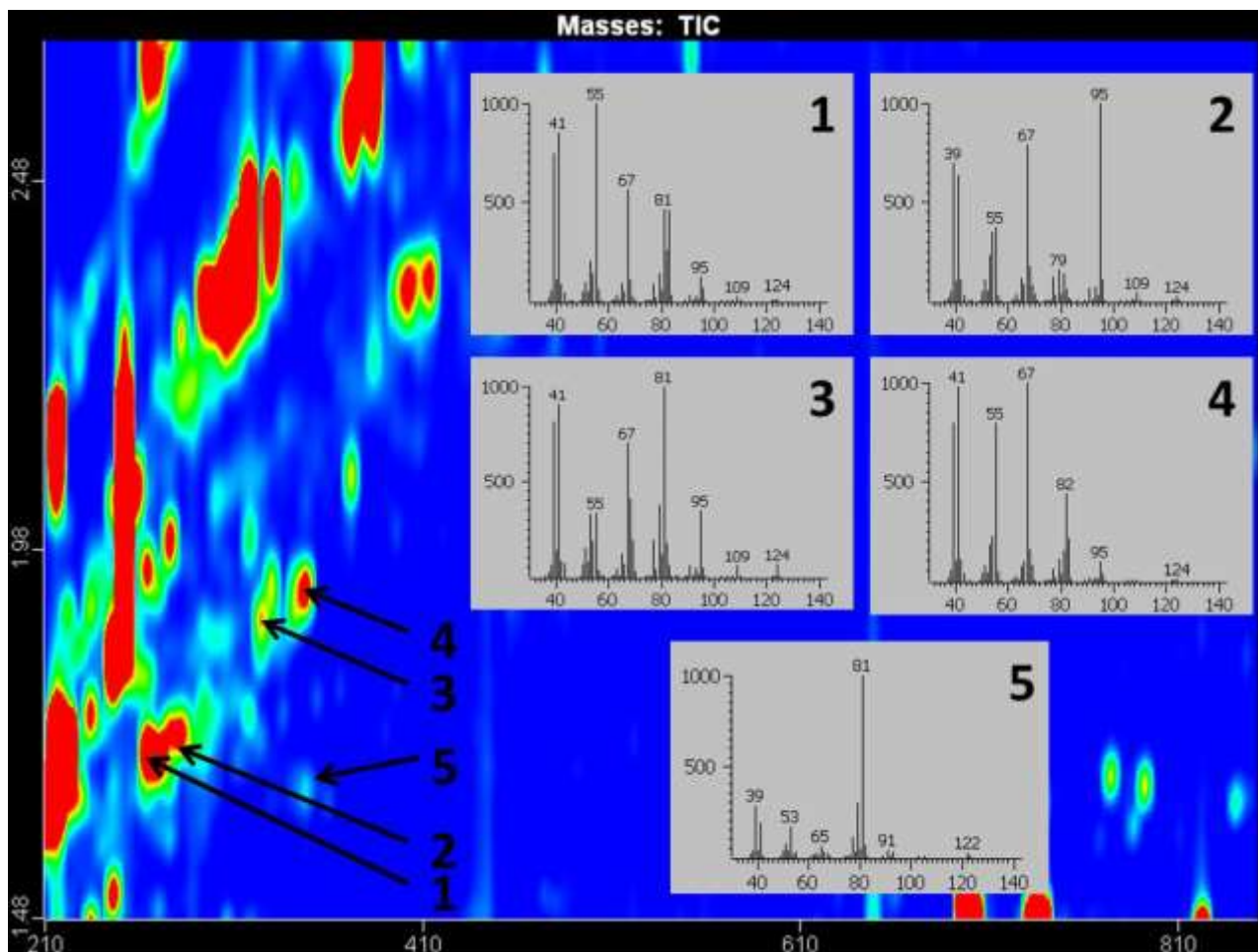
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Figure 7 GC × GC-TOFMS chromatogram of the HT-FT light oil sample without the capillary reactor.

Compounds 1 – 4 have molecular masses of *m/z* 124 which corresponds to C9 compounds with two double bond equivalents whilst compound 5 has a molecular mass of *m/z* 122 that corresponds to a C9 compound with three double bond equivalents. For all the compounds library matches can be obtained for more than one component class. The sample was therefore analysed by means of GC×GC-TOF with capillary hydrogenation (Figure 8).
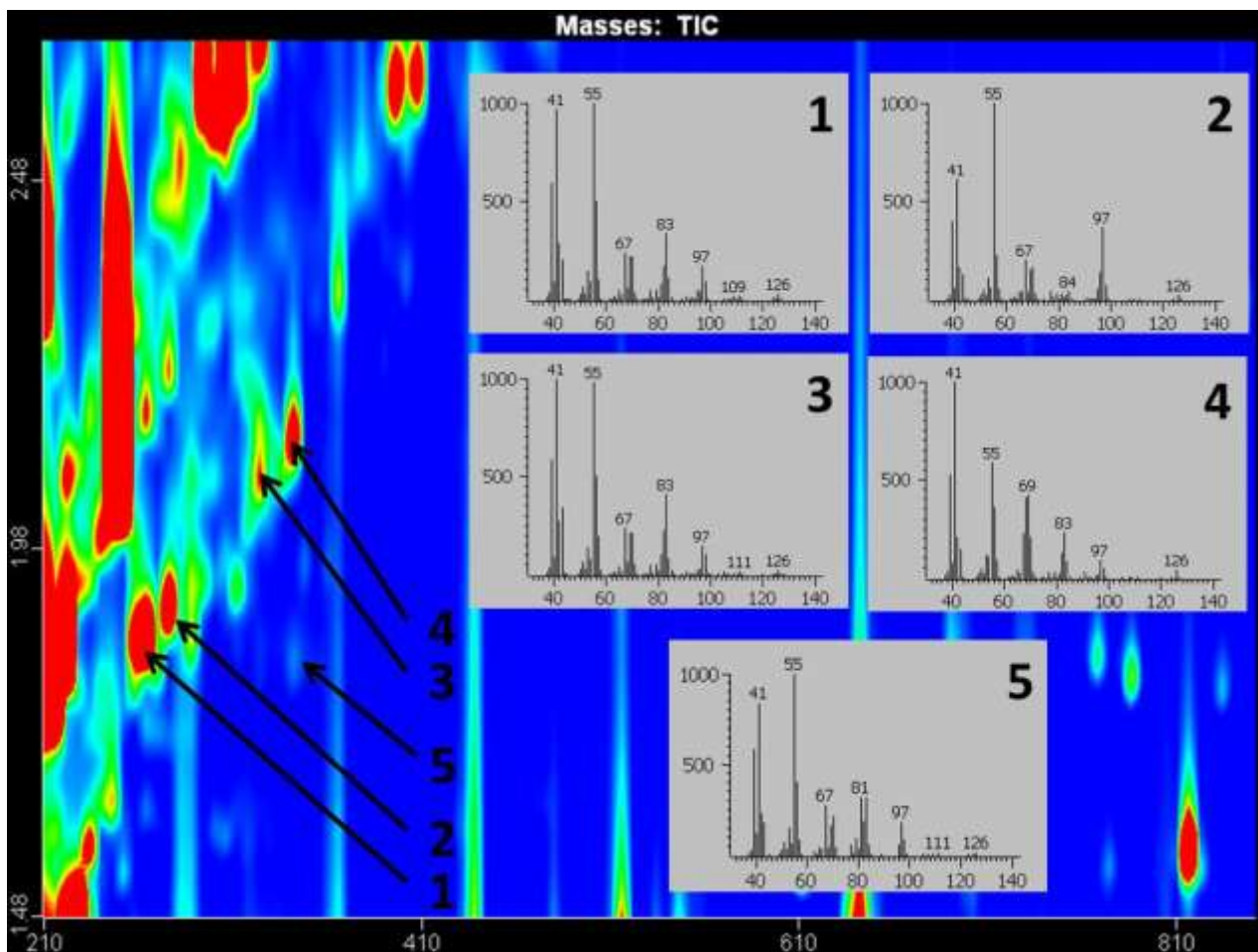
Figure 8 GC × GC-hydrogenation-TOFMS chromatogram of the HT-FT light oil sample.

Almost identical separation was observed in the initial GC×GC-TOF analysis and during hydrogenation GC×GC-TOF analysis and the compounds of interest are easily recognized in Figure 8. Compounds 1 - 4 all have a molecular mass of m/z 126 (C9 cyclic alkane) after hydrogenation. This confirms that compounds 1 - 4 are C9 cyclic olefins before hydrogenation. After hydrogenation, compound 5 also has a molecular mass of m/z 126 (C9 cyclic alkane) which confirms that compound 5 is a C9 cyclic diene before hydrogenation. Compounds 1, 3 and 5 have identical mass spectra after hydrogenation, indicating that they have a similar cyclic backbone.

These results clearly demonstrate the ability of this method to determine the backbone of cyclic/olefinic structures in complex petrochemical samples which enables differentiation between classes like dienes and cyclic olefins.

4   CONCLUSIONS

A two dimensional gas chromatographic method with post column hydrogenation, by which the analytes undergo hydrogenation after the second dimension separation, was developed. Installing a capillary reactor in the TOF-MS transfer line enables complete hydrogenation of alkene double bonds at convenient transfer line temperatures without instrument modifications. The catalytic hydrogenation step is fast enough to prevent distortion of the narrow second dimension peaks. The number of rings and alkene double bonds in the compound structure can be determined from two GCxGCMS injections and comparison of the mass spectra from identical chromatographic peaks with and without hydrogenation. The influence of capillary reactor diameter and temperature on the degree of hydrogenation was also extensively investigated to achieve complete hydrogenation of olefinic compounds. The developed method makes it possible, for the first time, to identify the level of unsaturation in hydrocarbon molecules (eg. dienes and cyclic olefins) in complex petrochemical streams previously separated by GC×GC without post column hydrogenation.

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