



Fractionation by liquid chromatography combined with comprehensive two-dimensional gas chromatography–mass spectrometry for analysis of cyclics in oligomerisation products of Fischer–Tropsch derived light alkenes

Rina van der Westhuizen^a, Hein Potgieter^a, Nico Prinsloo^a, André de Villiers^b, Pat Sandra^{b,*}

^a Sasol Technology R&D, PO Box 1183, Sasolburg 1947, South Africa

^b Stellenbosch University, Department of Chemistry and Polymer Science, Private Bag X1, Matieland 7602, South Africa

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ABSTRACT

In oligomerisation products of High Temperature Fischer–Tropsch (HTFT) derived light alkenes using a solid phosphoric acid (SPA) catalyst, the presence of cyclics was presumed although their occurrence could not be explained by the generally accepted oligomerisation mechanism. Notwithstanding the use of GC×GC–TOFMS, the cyclic alkanes could not be differentiated from the alkenes. On the one hand, compounds co-eluted in GC×GC and, on the other hand, MS cannot distinguish between these classes because of identical molecular masses and very similar mass fragmentation patterns. An LC pre-fractionation procedure utilising a silver-modified column was developed to separate the saturates from the unsaturates. Using this approach we were able, for the first time, to confirm the presence of cyclics, probably resulting from secondary reactions, in HTFT oligomerisation products. The occurrence of cyclics can be an indication of the beginning of carbonaceous deposit formation that could eventually lead to catalyst deactivation.

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1. Introduction

Synthetic crude oil derived during High Temperature Fischer–Tropsch (HTFT) synthesis is rich in highly valuable alkenes and oxygenates, unlike conventional crude oil, which only contains these compounds at trace levels. During refining, some of these alkenes and oxygenates are extracted or converted to higher value fuels and chemicals. The rest of the synthetic crude is refined to transportation fuels.

In order to address the increasing demand for jet fuel and diesel, the gaseous alkenes ($\approx C_3$ – C_5) are oligomerized with a solid phosphoric acid (SPA) catalyst to produce higher molecular weight oligomers. The oligomerisation products are then hydrogenated and distilled into gasoline, kerosene and diesel cuts. The oligomerisation of C_3 – C_5 alkenes over SPA to produce heavier alkenes has been practised commercially in crude-oil refineries since the 1930s [1]. The oligomerisation process is not only of value in fuel production e.g. kerosene and high octane gasoline, but also for the production of chemical starting materials like alcohols, acids, esters and detergents. Alkene oligomerisation is especially suited for tuning the gasoline/kerosene/diesel ratio according to market requirements during High Temperature Fischer–Tropsch (HTFT) refining because of the abundance of C_3 – C_5 alkenes in the primary

FT product [2]. Another advantage is the conversion of short chain hydrocarbons (that have relatively good octane numbers but whose presence in gasoline is limited by the vapour pressure specification of the fuel) to molecules with higher molecular mass and excellent fuel properties. Moreover, the catalyst SPA is relatively inexpensive and the spent catalyst can be used as fertilizer, which makes the process environmentally friendly and cost effective [3,4].

Little is known regarding the exact composition of the complex mixture produced by SPA catalysts. Bekker and Prinsloo [5] identified the principal alkenes in the C_8 fractions of four butene oligomerisation experiments performed with liquid phosphoric acid and SPA catalysts by gas chromatography–mass spectrometry (GC–MS). 38 out of 93 possible butene dimeric (C_8) isomers were identified, despite a large degree of peak overlap in the one-dimensional GC analysis. Co-elution, combined with a lack of alkene reference materials, hampered further identification of oligomeric products. In addition, different isomers frequently yielded similar mass spectra and, as a result, the authors had to rely on Kovats retention index data, which were often found to be contradictory and difficult to reproduce.

The number of isomers increases exponentially with each additional carbon number (for example for C_{12} products the number of isomers is 3226). Considering that the peak capacity for a conventional 30 m high resolution capillary GC column is ca. 500–600 [6], it is clear that separation of all of these compounds by one-dimensional GC is impossible. Comprehensive multidimensional GC (GC×GC) provides a powerful method for the separation of

* Corresponding author.

E-mail address: pat.sandra@richrom.com (P. Sandra).

complex mixtures and is therefore extensively applied for petrochemical analysis [7–10]. In combination with time-of-flight mass spectrometry (TOFMS), providing data acquisition rates of up to 500 spectra per second, closely-eluting peaks can be deconvoluted by differentiating between unique fragments in the mass spectra [11–16].

Preliminary GC×GC-TOFMS experiments with hydrogenated fuels indicated the possible presence of 3 to 10% cyclic alkanes. A clear differentiation of cyclic alkane and alkene classes could, however, not be achieved by GC×GC. The presence of low levels of alkenic hydrocarbons was confirmed by bromine number analysis [17] (note that the residual alkene content for HTFT-derived fuels is limited to a bromine number of 10 g Br₂/100 g by the South African Department of Minerals and Energy (DME)).

Components with cyclic structures are commonly detected in both crude-derived and conventional FT fuels. The presence of cyclics in oligomerized products, on the other hand, cannot be explained by the accepted oligomerisation reaction mechanism. No previous reports on the presence of cyclics in these products can be found.

As the chemical and physical properties of fuels and their blends can directly be correlated to their chemical composition, it is of utmost importance to confirm the presence of cyclics in the oligomerisation products. For example, cyclics increase the density and viscosity of a fuel and affect distillation profiles. Other properties like cetane numbers, combustion quality, seal swell, cold flow properties, etc. are also affected. Moreover, the cyclics could be aromatic precursors that are formed in secondary reactions similar to what is observed for the reaction with mordenite and skeletal isomerisation [18], or could be part of a carbonaceous deposit formation [19] that is responsible for catalyst deactivation.

Identifying complex cyclic alkane profiles in the presence of alkenes by one-dimensional GC-MS is impossible due to the fact that these compounds have identical molecular masses and similar fragmentation patterns as the corresponding alkenes, as well as similar GC retention times. For these same reasons, even GC×GC-TOFMS is unable to unambiguously differentiate between these classes. A way of improving the separation is to apply a fractionation step prior to GC×GC analysis [20–22].

The goal of this work was therefore to evaluate and optimize a fractionation method that would separate the cyclic alkanes from the alkenes. It is known that silver ions interact with double bonds of olefinic compounds by complexation [23]. In light of this, an LC fractionation procedure was developed using a silver-ion modified column to separate the oligomerisation product (hydrogenated) into saturated and unsaturated fractions [23,24]. Each of these fractions was analyzed by GC×GC-TOFMS to distinguish between non-cyclic and cyclic alkanes in the saturated fraction, and the non-cyclic and cyclic alkenes in the unsaturated fraction. GC×GC-FID was then used to quantify the cyclics and olefins in gasoline, kerosene and diesel HTFT fuels.

2. Experimental

2.1. Oligomerisation reactions

Alkene oligomerisation was performed using a SPA catalyst similar to the patented UOP SPA catalyst described in Refs. [1,25] and consisting of phosphoric acid supported on silica [26]. The feed was obtained from three FT condensate streams which were fractionated in a feed debutaniser column. The C₃ and C₄ overheads fraction (distilled between 130 °C and 160 °C) was used as feed for the oligomerisation unit. Feed water content was adjusted to control the SPA catalyst hydration level. Oligomerisation of the light olefins occurred via condensation reactions to form dimers,

trimers, tetramers and their mixtures. The oligomer mixture was subsequently hydrogenated to a bromine number of 4.0 g Br₂/100 g, resulting in almost complete saturation of the alkenes.

The final product was distilled at atmospheric pressure into three cuts namely gasoline (<150 °C), kerosene (150–170 °C) and diesel (>170 °C). Standard mixtures containing 1-octene (Sigma-Aldrich, Johannesburg, SA, Fluka ≥99.5) and n-dodecane (Sigma-Aldrich, Fluka, ≥99.8%) were used as internal standards for alkenes and cyclic alkanes, respectively. The standards were selected because no linear 1-alkene or n-alkane products were found in the oligomerisation products (based on retention times and mass spectral information) for both the unhydrogenated and hydrogenated products. The standards were added to the samples before fractionation. Quantification was performed from GC×GC-FID data using the Classifications function in the Leco ChromaTOF software (Version 4.21).

The final hydrogenated oligomerisation product as well as the distillation cuts, were analyzed neat and after LC fractionation using both GC×GC-TOFMS and GC×GC-FID. The final product was also brominated to confirm the LC fractionation.

It may be difficult to correlate the bromine number of a compound directly with the degree of unsaturation (e.g. a product can undergo extensive hydrogenation but still give a bromine number). By using products with different bromine numbers, the decreasing amount of alkenes could be monitored by GC×GC. Therefore, to further aid with the identification, two oligomerisation products were hydrogenated to bromine numbers of 0.7 (low alkene sample) and 30 g Br₂/100 g (high alkene sample), respectively. These samples were subjected to the same analyses.

2.2. Bromination

The standard test method ISO 3839 for the determination of unsaturates in petroleum [17] was used for determination of bromine number. Following the initial analysis of the brominated product (Fig. 5 below), brominated products were removed by elution through a silica gel column prior to GC×GC analysis to prevent contamination of columns and syringes. Silica gel, 60–100 mesh and activated overnight at 250 °C (Sigma-Aldrich) was slurry-packed with n-hexane in a 1 m × 15 mm ID glass column. 1 g of sample was applied to 40 g of silica gel. The non-brominated solutes were eluted with 100 mL hexane (Chromasolv, Sigma-Aldrich). Brominated compounds were retained on the column and visible as a yellow band.

2.3. LC fractionation

Optimization of the LC fractionation was performed using a standard mixture consisting of 1% (v/v) of each of the components listed in Table 1 in n-hexane.

A Dionex Ultimate 3000 HPLC system, equipped with autosampler, degasser, dual gradient pumping system and column compartment was used for the fractionation (Dionex, Sunnyvale, USA). Detection was performed by a corona charged aerosol detector (CAD) supplied by ESA Biosciences (Chelmsford, USA), operated with a total nitrogen gas flow of 4 L/min and a temperature of 30 °C. A sulphonic silica-based strong cation-exchange column (Nucleosil 100-5 SA, 25 cm L × 4.6 mm ID, 5 μm d_p from Macherey-Nagel, Düren, Germany) was used. The column was loaded with silver-ions according to the procedure described by Sandra et al. [24]. The injection volume was 15 μL and an analysis temperature of 30 °C was used throughout. During the first 6 min 100% n-hexane (Chromasolv, Sigma-Aldrich) was used to elute the saturated hydrocarbons. At 6 min the mobile phase was changed to 100% acetone (Chromasolv, Sigma-Aldrich) to elute the unsaturated hydrocarbons. A flow rate of 1 mL/min was applied and the

Table 1
Composition of the standard mixture used for optimization of the LC fractionation procedure.

Nr.	
	<i>Alkanes</i>
1	n-Nonane
2	3,3-Dimethyloctane
3	3-Methylnonane
4	Dodecane
	<i>Cyclo-alkanes</i>
5	1-Methyl-2-propylcyclohexane,
6	1,2,4-Trimethylcyclohexane (c&t)
	<i>Alkenes</i>
7	3-Dodecene
8	2-Methyl-3-heptene
9	2,5-Dimethyl-2-hexene
	<i>Cyclic alkenes</i>
10	1,2,3-Trimethylcyclopentene
11	4-Methylcyclohexene
	<i>Dienes</i>
12	2,4-Dimethyl-1,3-pentadiene
13	1,3-Cyclooctadiene
	<i>Aromatics</i>
14	4-tert-Butyltoluene
15	Indane
16	1,2,3-Trimethylbenzene

column was conditioned with n-hexane for 15 min before the next injection. After the retention times were determined by CAD, the detector was disconnected and the eluent was collected manually. The n-hexane fraction was collected between 2.5 and 4 min and the acetone fraction between 10 and 10.75 min corresponding to 1.5 mL and 0.75 mL volumes, respectively.

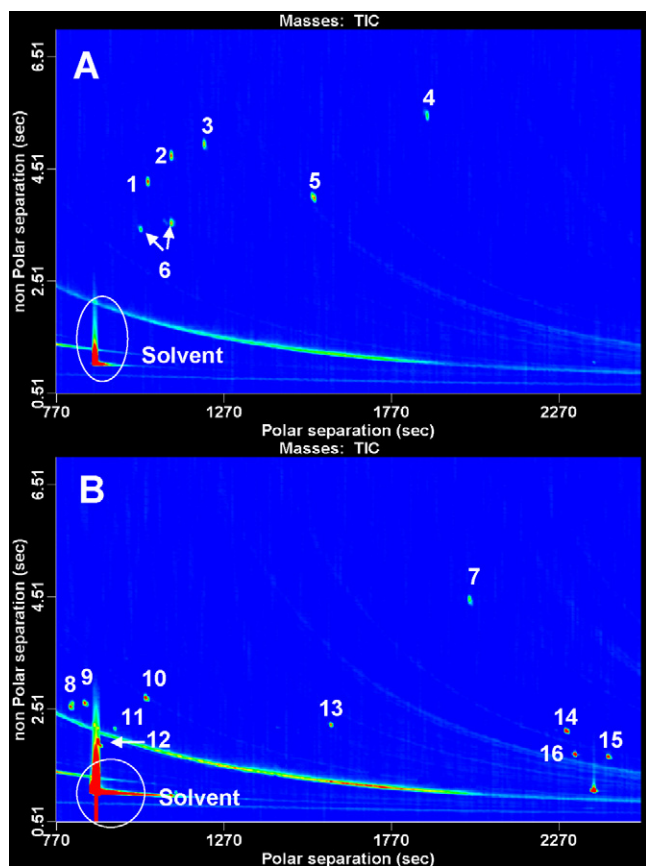


Fig. 1. Contour plots obtained for the GC \times GC-TOFMS analysis of the n-hexane (A) and acetone (B) LC fractions of the standard mixture showing the separation of alkanes and cyclic alkanes from the alkenes, cyclic alkenes and aromatics in the standard mixture. Peak numbers correspond to Table 1.

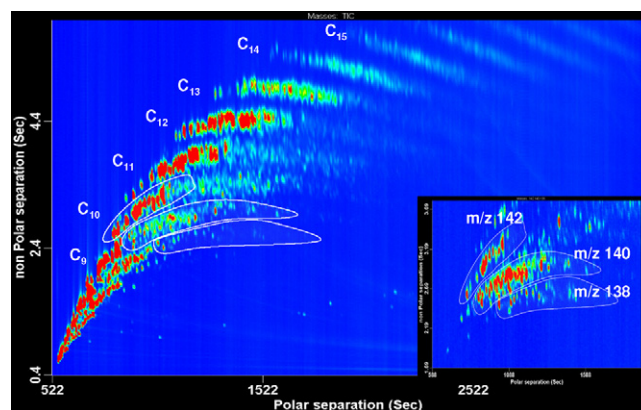


Fig. 2. GC \times GC-TOFMS contour plot for the analysis of the total oligomerised product after hydrogenation and prior to LC fractionation (bromine number 4 g Br₂/100 g). Extracted ion plots for m/z 142, 140 and 138 (insert) show the C₁₀ non-cyclic alkanes, cyclic alkanes and/or alkenes and the cyclic alkenes/dienes/bicyclic alkanes.

2.4. GC \times GC-TOFMS and FID analyses

The GC \times GC instrument was a Pegasus 4D from Leco Corporation (St. Joseph, USA) equipped with a 7683B auto injector system (Agilent Technologies, Little Falls, USA). FID was used for quantification purposes due to the wide linear range and universal detection of hydrocarbons. In all other cases, TOFMS was used. The reversed phase column set described in Ref. [27] was used: in the first dimension a 60 m \times 0.25 mm ID, 0.25 μ m d_f DB Wax column (J&W Scientific, Folsom, USA) and in the second dimension a

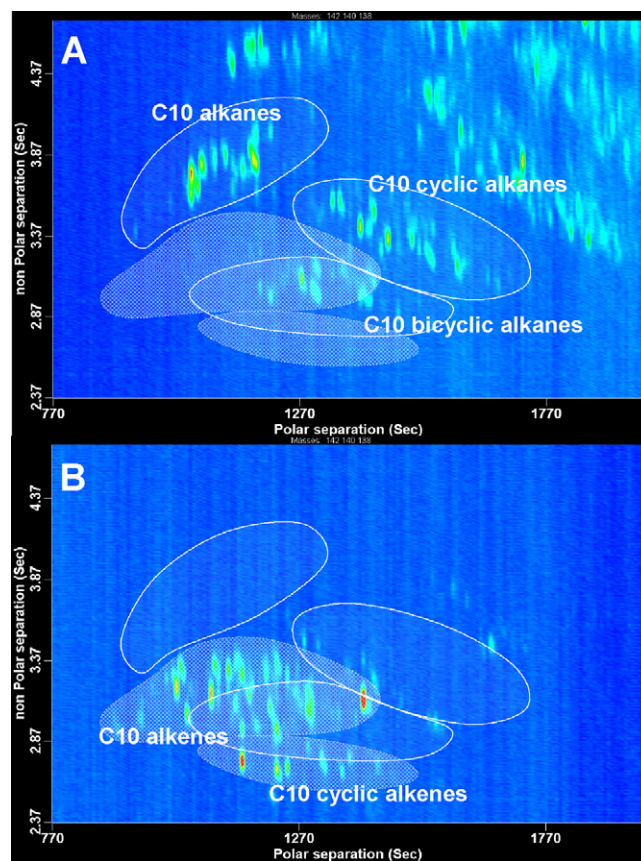


Fig. 3. Extracted ion GC \times GC-TOFMS contour plots of m/z 142, 140 and 138 of the LC fractions of the oligomerisation product (bromine number 4 g Br₂/100 g). (A) The n-hexane fraction shows the presence of C₁₀ non-cyclic, cyclic and bicyclic alkanes, (B) the acetone fraction shows the presence of C₁₀ alkenes and cyclic alkenes.

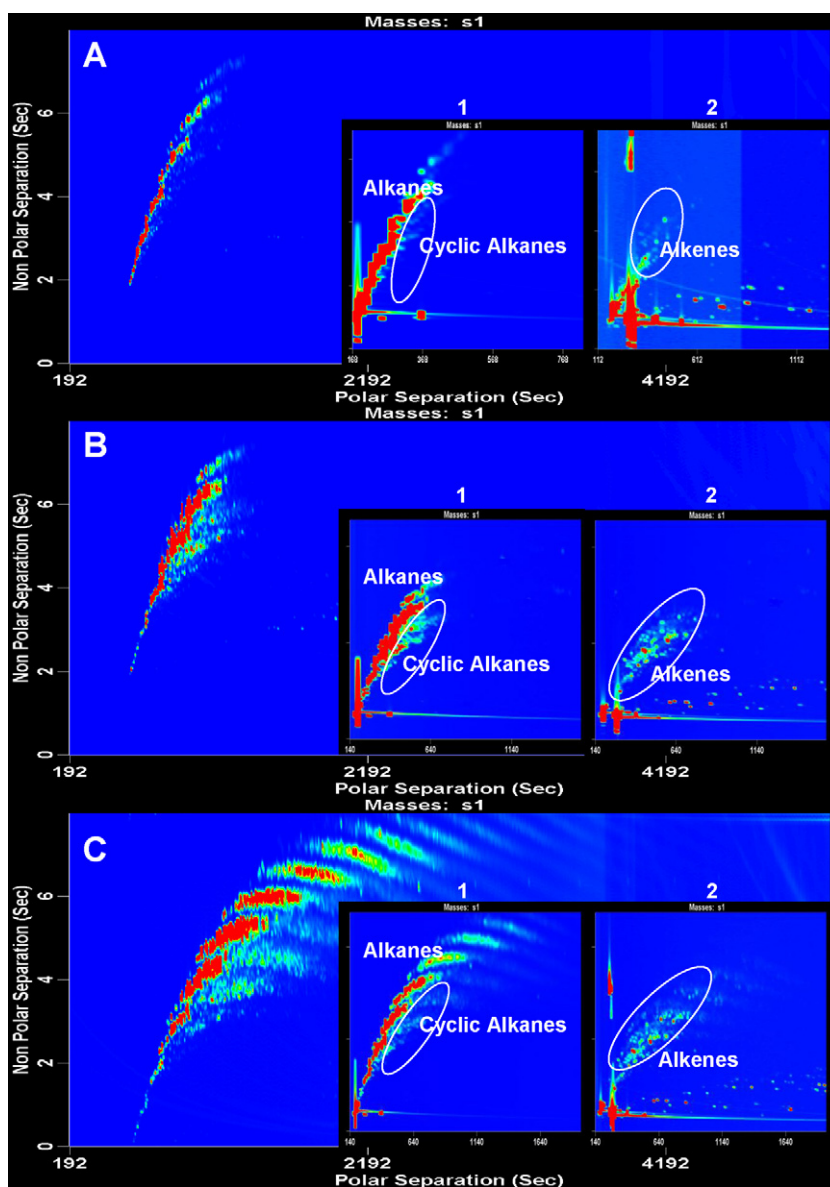


Fig. 4. GC \times GC-TOFMS TIC contour plots for (A) gasoline, (B) kerosene and (C) diesel distillation samples. Inserts show the fractionation of the alkanes and cyclic alkanes (1) and alkenes and cyclic alkenes (2) for each of the samples.

2 m \times 0.1 mm ID, 0.1 μ m df RTX-5 column (Restek, Bellefonte, USA). 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 0.05 μ L were used for the analysis of the fuels while for the LC fractions the split ratio was 20:1 and the injection 1 μ L to compensate for the dilution. The first oven was programmed from 40 $^{\circ}$ C (0.2 min) to 240 $^{\circ}$ C at 2 $^{\circ}$ C/min. The second oven and modulator followed the first temperature program but started at 50 $^{\circ}$ C and 70 $^{\circ}$ C, respectively. TOFMS and FID data were collected at 100 spectra/s and 100 Hz, respectively.

3. Results and Discussion

3.1. Optimization of the LC fractionation procedure

Using a silver-modified column, the saturated hydrocarbons were not retained and passed through with n-hexane. After 6 min the mobile phase was changed to acetone and all retained unsaturated compounds were eluted as a single peak. The GC \times GC contour plots (Fig. 1) obtained for the analysis of the n-hexane and acetone fractions of the standard mixture con-

firm that the LC fractionation procedure successfully separated the non-cyclic and cyclic saturated hydrocarbons (n-nonane, 3,3-dimethyloctane, 3-methylnonane, n-dodecane, 1-methyl-2-propylcyclohexane and 1,2,4-trimethylcyclohexane) from the unsaturated non-cyclic and cyclic hydrocarbons and from the aromatics (3-dodecene, 2-methyl-3-heptene, 2,5-dimethyl-2-hexene, 1,2,3-trimethylcyclopentene, 4-methylcyclohexene, 2,4-dimethyl-1,3-pentadiene, 1,3-cyclooctadiene, 4-tert-butyltoluene, indane and 1,2,3-trimethylbenzene).

3.2. LC fractionation combined with GC \times GC-TOFMS analysis of the final oligomerisation product

The oligomerisation products of a selected fuel ranged in carbon numbers from C₃ to around C₁₈ (Fig. 2).

The hydrogenated product contained mainly alkanes but the bromine number was 4 g Br₂/100 g indicating the presence of low levels of remaining alkenes. This is confirmed by the mass spectral data as several components had molecular masses – 2 units lower than expected for saturated hydrocarbons e.g. *m/z* 142 for C₁₀

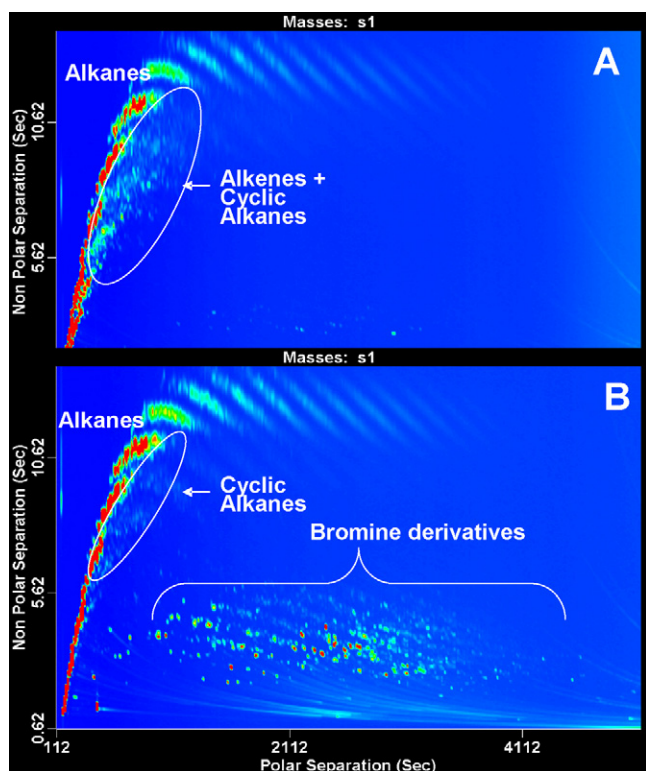


Fig. 5. GC \times GC-TOFMS contour plots indicating the oligomerisation product (A) before (bromine number 4 g Br₂/100 g) and (B) after bromine derivatisation.

alkanes. However, m/z 140 corresponds to C₁₀ alkenes or C₁₀ cyclic alkanes. In addition, some of the components had molecular masses – 4 units lower than expected for saturated hydrocarbons i.e. for the C₁₀ domain m/z 138 which can correspond to cyclic alkenes, dienes or bicyclic alkanes. Based on ion extraction, these m/z values form 3 separate bands in the GC \times GC plot (see insert). Trace levels (≈ 0.2 mass %) of aromatic compounds were also observed (data not shown).

The complexity could be drastically reduced by fractionation with silver-ion chromatography. Fig. 3 shows the C₁₀ part of the GC \times GC-TOFMS contour plots at m/z 142, 140 and 138 for the hexane fraction (A) and for the acetone fraction (B). In the hexane fraction only the non-cyclic, cyclic and bicyclic alkanes are detected while in the acetone fraction the alkenes and cyclic alkenes are recovered. As dienes are unstable and would have been hydrogenated before the mono-alkenes and cyclic alkenes, it was assumed that no dienes remained in the product.

Note that the elution areas for the cyclic alkanes and alkenes overlap in the contour plot, making their differentiation, even with TOFMS without pre-fractionation, very difficult. Similar trends were observed for the other carbon numbers and in the different distillates.

The GC \times GC contour plots of the gasoline, kerosene and diesel distillation cuts as well their respective LC fractions (Fig. 4) confirm that the LC fractionation procedure is equally successful for each of these samples (note that the peaks visible at low 2D retention times in the inserts are from the HPLC solvents used).

As an alternative to the LC fractionation procedure, the bromination reaction can lead to similar results. Fig. 5 illustrates the contour plots obtained for the analysis of the oligomerisation product before (A) and after bromination (B). The alkenes reacted with the bromine to form high molecular mass bromine derivatives while the alkanes and cyclic alkanes were not affected. Disadvantages of this approach are that MS interpretation of the brominated alkene

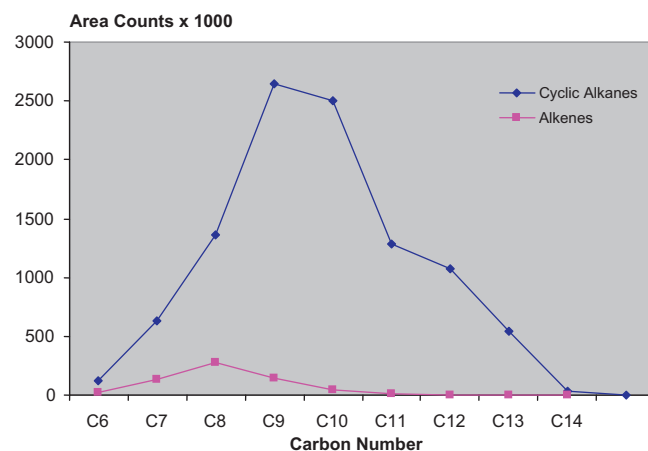


Fig. 6. Graphic illustration of the distribution of alkenes and cyclic alkanes for the oligomerisation product with a bromine number of 0.7 mg Br₂/100 g.

spectra is difficult, but above all that injection of the brominated sample contaminates the autosampler and the column. Fractionation by chromatography on silica gel could overcome this problem as the brominated species are retained (Section 2.2) but the procedure is more time-consuming and samples have to be enriched increasing the risks of contamination.

Literature reports on reactions similar to SPA oligomerisation provide possible explanations for the presence of cyclics in the SPA product. Tabak et al. [18] reported a kinetic and modelling study of *n*-butene oligomerisation over H-mordenite. The authors proposed a simplified kinetic mechanism for the mordenite reaction and suggested that the newly formed molecules undergo secondary reactions like isomerisation, cracking, aromatization, etc. It is possible that the cyclics from the SPA oligomerized product are formed during similar secondary reactions, for example as aromatic precursors. In another study, Van Donk et al. [19] described the effects of carbonaceous deposit formation on the deactivation of zeolites used for butene skeletal isomerisation. Skeletal isomerisation over microporous material is generally performed at high temperatures (≈ 350 °C), where aliphatic coke is initially formed and subsequently slowly transformed to aromatics. Carbonaceous deposit formation was also observed on SPA catalysts used for skeletal isomerisation [28]. Although the temperatures used during SPA oligomerisation are not as high (140–230 °C) as for skeletal isomerisation, the presence of cyclics could be an indication of the initial stages of carbonaceous deposit formation that will lead to the formation of aromatics and eventually to catalyst deactivation.

3.3. Determination of the cyclic/alkene distribution in oligomerisation products

GC \times GC-TOFMS plots of the oligomerisation products with bromine numbers 30 and 0.7 g Br₂/100 g were compared using the described methodologies and the following conclusions could be drawn. For the product with the lower bromine number, where the alkene/cyclics fraction contained mostly cyclics and very few alkenes, the highest concentration was distributed in the C₉–C₁₀ carbon number range. On the other hand, for the product with the higher bromine number, containing more alkenes than cyclics, the highest concentration was distributed in the C₃–C₇ region. Using GC \times GC-FID, the cyclic and alkene distributions for the oligomerisation products could be quantified. Fig. 6 shows the data for the oligomerisation product with bromine number 0.7 g Br₂/100 g.

The cyclic alkane and alkene content in the distillation fractions of gasoline, kerosene and diesel of the 0.7 g Br₂/100 g product obtained by GC \times GC-FID are summarised in Table 2.

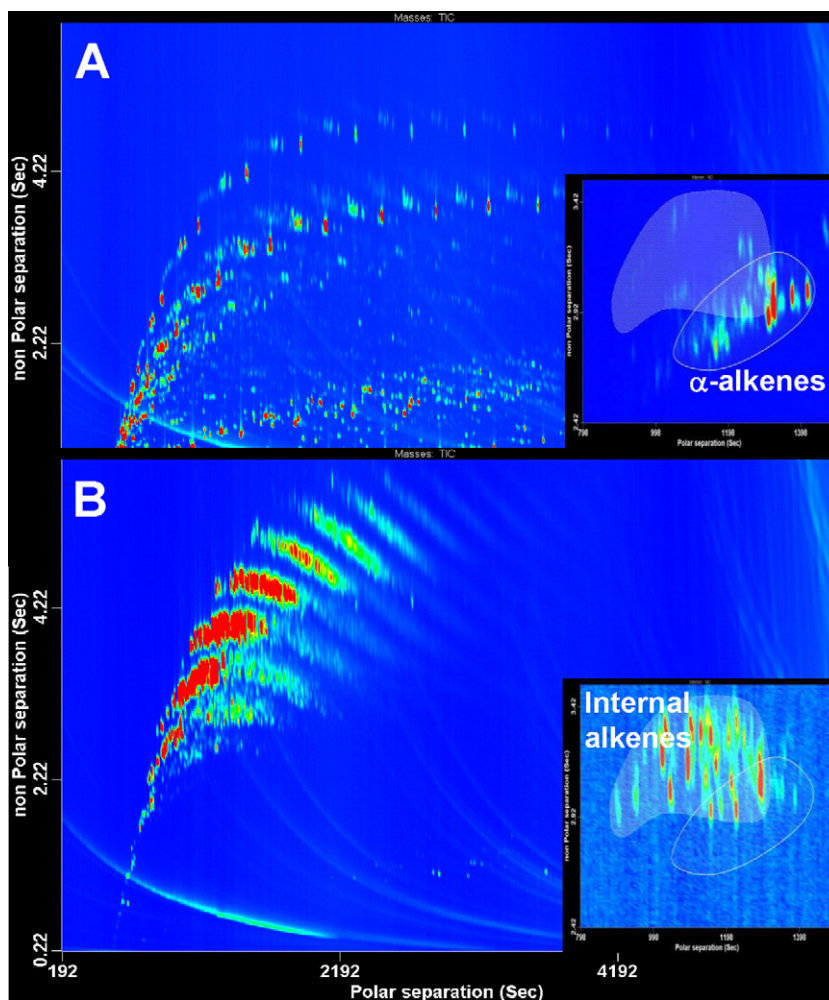


Fig. 7. A comparison of the GC×GC plots for a highly alkenic HTFT condensate (A) and an oligomerised product (B). Insets show selected ion contour plots (m/z 140) for the acetone fractions of these samples, demonstrating the difference in elution positions of α -alkenes and internal alkenes.

The total amount of cyclics in this product is ca. 2.5%. As they are mainly distributed over the C_9 – C_{10} carbon numbers, they will have the highest concentration in the kerosene (2.38%) and diesel (3.64%) cuts. The boiling points of C_9 – C_{10} cyclic alkanes are in the region of 150–170 °C (for example isopropylcyclohexane 154.5 °C, isobutylcyclohexane 169 °C). The gasoline fraction showed the highest fraction alkene concentration (refer Fig. 4). Slight variations in distillation conditions could shift the majority of the cyclics to either the kerosene or the diesel cut.

3.4. Comparison of the alkene composition in oligomerisation products versus in conventional FT products.

Alkenes in the oligomerised product contain mostly internal double bonds. This is contrary to what is observed in the HTFT syn-

thetic crude, that are known to contain predominantly α -alkenes [27,29]. Fig. 7 compares the GC×GC-TOFMS profiles for a standard HTFT (A) and the oligomerisation product with a bromine number of 30 g $Br_2/100$ g (B). The inserts of the figure show the selected ion plots at m/z 140 for the fractionated acetone fractions. The HTFT condensate contains high levels of C_{10} α -alkenes, identified by mass spectra and retention times (m/z 140). The C_{10} alkene peaks in the oligomerised product elute in a region adjacent to that of the α -alkenes. Similarly, a comparison of the m/z 138 extracted ion contour plots show a shift of the elution window for cyclic alkenes with internal double bonds on the side chain relative to those with α -double bonds (results not shown). The same trend was observed for the product with bromine number of 4.0 mg $Br_2/100$ g, thereby eliminating the possibility that the linear α -alkene was hydrogenated preferentially. No dienes were expected in either of

Table 2
Quantitative results obtained by GC×GC-FID for the cyclic alkanes and alkenes in the LC fractions of the hydrogenated oligomerisation product (0.7 g $Br_2/100$ g) and its distillation cuts.

	Distillation temperatures (°C)	Distillation mass balance		Cyclic alkanes	Alkenes
		g	Mass %	Total mass %	Total mass %
Oligomerisation product		2.956		2.52	0.69
Gasoline cut	<150	1.538	52.03	0.17	1.90
Kerosene cut	150–170	0.412	13.94	2.38	0.34
Diesel cut	>170	0.879	29.74	3.64	0.29
			95.70		

these two samples because the second double bond of the diene would be hydrogenated before the mono-alkenes or cyclic alkenes. Neither was any n-alkanes observed in the hydrogenated products.

4. Conclusions

The analysis of cyclic alkanes and internal alkenes in SPA catalyzed oligomerisation products of FT derived alkenes is problematic as co-elution of peaks occurs, even when using GC×GC. Mass spectrometry is also not of much help because of similar molecular masses and very similar mass fragmentation patterns for these component classes.

An LC fractionation procedure utilising a silver-modified column was developed to separate saturated and unsaturated components in oligomerised products. Combined with GC×GC-TOFMS, the separation of alkanes and alkenes into non-cyclic, mono-cyclic and bicyclic component classes could be obtained. This allowed us to confirm that cyclics are present in SPA catalyzed oligomerisation products of FT derived alkenes. The developed procedure could be applied to (i) determine the concentration of alkanes, cyclic alkanes and alkenes in oligomerised products and (ii) to tune the distillation conditions to shift the cyclic alkanes either in the kerosene or diesel cuts. The study made also clear that contrary to standard HTFT condensates, SPA catalyzed oligomerisation products of FT derived alkenes contain internal alkenes and nearly no α -alkenes.

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