



Comprehensive two-dimensional gas chromatography for the analysis of synthetic and crude-derived jet fuels

Rina van der Westhuizen^{a,c}, Mariam Ajam^a, Piet De Coning^a, Jan Beens^b, André de Villiers^c, Pat Sandra^{c,*}

^a Analytical Solutions Department, Sasol Technology R&D, Sasolburg, South Africa

^b Free University, Department of Analytical Chemistry, de Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

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

ARTICLE INFO

Article history:

Received 17 February 2011

Received in revised form 3 May 2011

Accepted 6 May 2011

Available online 13 May 2011

Keywords:

Comprehensive gas chromatography (GC × GC)

Flame ionization detection

Time-of-flight mass spectrometry (TOF-MS)

Synthetic and crude-derived jet fuels

Fuel stability

ABSTRACT

Fully synthetic jet fuel (FSJF) produced via Fischer–Tropsch (FT) technology was recently approved by the international aviation fuel authorities. To receive approval, comparison of FSJF and crude-derived fuel and blends on their qualitative and quantitative hydrocarbon composition was of utmost importance. This was performed by comprehensive two-dimensional gas chromatography (GC × GC) in the reversed phase mode. The hydrocarbon composition of synthetic and crude-derived jet fuels is very similar and all compounds detected in the synthetic product are also present in crude-derived fuels. Quantitatively, the synthetic fuel consists of a higher degree of aliphatic branching with less than half the aromatic content of the crude-derived fuel. GC × GC analyses also indicated the presence of trace levels of heteroatomic impurities in the crude-derived product that were absent in the synthetic product. While clay-treatment removed some of the impurities and improved the fuel stability, the crude-derived product still contained traces of cyclic and aromatic S-containing compounds afterwards. Lower level of aromatics and the absence of sulphur are some of the factors that contribute to the better fuel stability and environmental properties of the synthetic fuel. GC × GC was further applied for the analysis of products during Jet Fuel Thermal Oxidation Testing (JFTOT), which measures deposit formation of a fuel under simulated engine conditions. JFTOT showed the synthetic fuel to be much more stable than the crude-derived fuel.

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1. Introduction

The increased interest in the production of synthetic fuels via Fischer–Tropsch (FT) technology as an alternative to crude-derived fuels is driven mostly by unstable crude oil prices, the need for energy security, greater strategic flexibility and the need for cleaner (green) transportation fuels. Sasol (the South African Coal, Oil and Gas Corporation), the world's leading producer of synthetic fuels, has been blending a synthetic component known as Synthetic Paraffinic Kerosene (SPK) with a crude-derived, straight run Merox (mercaptan oxidation) kerosene stream to produce a semi-synthetic jet fuel (SSJF) since 1999. Approved SSJF blends may contain a maximum of 50% synthetic product blended with kerosene from conventional crude-derived sources. The ASTM standard specification D7566 [1] that was approved in September 2009, implied that kerosene, produced by either coal-to-liquid (CTL) or gas-to-liquid (GTL) processes and meeting the specification, can be used to blend SSJF for commercial use in the USA.

Sasol's fully synthetic jet fuel (FSJF) has been approved for commercial use in April 2008, as published in the British Ministry of Defense Standard (DEF STAN 91-91) [2]. ASTM International has also been working closely with the British Ministry of Defense and the writing of Sasol's FSJF into ASTM D1655, as a specific approval, was completed in June 2009 [3]. Sasol's FSJF meets all commercial Jet A-1 specifications as stipulated by the reference method DEF STAN 91-91 [2].

In modern aircraft, the aviation turbine fuel is increasingly used as the primary coolant, thereby increasing the thermal stress that the jet fuel is exposed to. Thermal stability demands on jet fuel are anticipated to become even more stringent as military aircraft approach extreme speeds of Mach 2–4. At such high speeds, jet fuels are expected to withstand temperatures up to 500 °C for short residence times [4]. Considerable improvement in jet fuel thermal stability is therefore required to ensure optimum performance for next generation jet engines.

Fuel stability relates to the resistance of the fuel to changes in physical and/or chemical properties which could hinder the aircraft performance or operation. Two types of instability are distinguished: storage stability refers to the effect of long-term ambient-temperature storage conditions on fuel properties,

* Corresponding author.

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

whereas thermal and oxidative instability refers to the effect of short-term high-temperature stress conditions on the fuel properties. The long-term storage stability involves oxidation leading to hydroperoxide intermediates, oxygenates and eventually gums. Peroxides cause significant deterioration of nitrile rubber, neoprene and Buna-N O-rings in jet engine fuel pumps, which could result in the leakage of fuel [5]. Thermal and oxidative stability, on the other hand, involves the formation of insoluble deposits which could result in reduced heat transfer efficiency, plugged fuel nozzles and filters, restricted fuel flow and degraded valve performance. These factors could eventually lead to engine malfunction and catastrophic engine failure. Jet fuel used in modern aircraft fuel systems is required to be free of water, dirt and other foreign contaminants and is sent through multi-stage filtration systems to ensure a good quality fuel. Clay treatment is used to remove polar species from jet fuel [6] that may cause deposit formation and contribute to thermal oxidative instability [7].

Accurate analysis methods for these fuels are essential. Because of limited international experience with the use of synthetic fuels, test requirements were identified specifically for these fuels and blends. The DEF STAN 91-91 standard stipulates various tests to ensure suitability of the fuel, e.g. the analysis of aromatics by fluorescent indicator absorption (FIA) [8] and high performance liquid chromatography (HPLC) [9], total sulphur and mercaptans by X-ray fluorescence [10] and potentiometry [11,12], naphthalene content by ultraviolet spectroscopy [13] and fatty acid methyl ester (FAME) content by gas chromatography–mass spectrometry (GC–MS) (Method IP PM-DY/09) [14] or GC × GC [15]. FAMEs originate from contamination by biodiesel that is transported in the same pipelines as aviation fuels.

Detailed information on the content of individual chemical species is mandatory in predicting fuel performance, stability, emissions, etc. Method ASTM D2425 is based on MS and is commonly used for hydrocarbon type analysis of middle distillates [16]. According to this method mass fragments and molecular ions of a hydrocarbon family are summed and used to calculate concentrations from coefficient matrices depending on carbon number. An HPLC separation (ASTM D2549) is performed prior to MS analysis to obtain separation of different chemical families of identical mass [17]. A method without HPLC pre-separation was proposed by Bernabei et al. [18] for the determination of total and polycyclic aromatics in jet fuels.

The most accurate way to obtain detailed compositional information for highly complex petrochemical mixtures is, however, by means of comprehensive two-dimensional gas chromatography [19–26]. GC × GC offers high peak capacity, structured separations and high sensitivity. GC × GC in the reversed mode i.e. a polar × non-polar column combination, was used for the qualitative and quantitative analysis of individual hydrocarbon and heteroatomic compounds that might affect fuel properties in FSJF and Merox kerosene. Structure elucidation was performed by time-of-flight mass spectrometry (TOF-MS) and quantitation by flame ionization detection (FID). GC × GC was further applied for the analysis of products during Jet Fuel Thermal Oxidation Testing (JFTOT), which measures deposit formation of a fuel under simulated engine conditions.

2. Experimental

2.1. Samples

The Merox process is a licensed refinery process that converts mercaptans to disulphides. Merox is a straight run kerosene stream

originating from the crude oil distillation (CDU) column. After the Merox unit, the kerosene was passed through an Attapulugus clay filter to remove colour bodies, impurities and surfactant type molecules. The Sasol Secunda refinery utilizes a high temperature Fischer–Tropsch (HTFT) process with an iron-based catalyst to produce a hydrocarbon product. Synthetic Paraffinic Kerosene (SPK) was produced in the CTL (coal-to-liquid) facility by catalytic polymerization of the C₃ and C₄ olefins in the synthetic crude product. Samples were kept refrigerated at all times to prevent loss of volatile material and ensure sample integrity. Samples were injected neat and GC-vials were recapped after each injection.

2.2. Chromatographic conditions

A Pegasus 4D GC × GC system (Leco Co., St. Joseph, MI, USA) equipped with FID and TOF-MS was used. Conditions for the reversed GC × GC mode were as follows. The primary column was a 60 m StabilWax capillary column (0.25 mm i.d and 0.25 μm d_f). The secondary column was a 2 m Rxi-5 ms column (0.1 mm i.d. and 0.1 μm d_f). Both columns were supplied by Restek (Bellefonte, PA, USA). The primary oven was programmed from 40 °C (0.2 min) at 2 °C/min to 240 °C. The second oven followed the first oven program with a 10 °C offset. A dual jet thermal modulation system was used with an 8 s modulation period. Helium carrier gas was used at a constant flow of 1.2 mL/min. Conditions for the normal GC × GC mode were as follows. The primary column was a 60 m Rxi-5 ms capillary column (0.25 mm i.d and 0.25 μm d_f). The secondary column was a 2 m Rtx-wax (0.1 mm i.d. and 0.1 μm d_f); both from Restek (Bellefonte, PA, USA). The primary oven was programmed from 40 °C (0.2 min) at 2 °C/min to 240 °C. The second oven followed the first oven program with a 10 °C offset. The modulation period was 4 s. Helium carrier gas was used at a constant flow of 1.2 mL/min. 0.1 μL was injected using an Agilent Technologies 7683 auto injector. The split ratio was 400:1 for normal injections and 20:1 for hetero-atom analysis. Data collection for the TOF-MS and FID was at 100 spectra/s and 100 Hz, respectively.

2.3. Analytical procedure

GC × GC-FID was used for quantification using the standard addition method. Three standards were used for hydrocarbon analysis to compensate for differences in response factors between different chemical classes. Standards of iso-octane (anhydrous, ≥99.8%, Sigma–Aldrich, Midrand, South Africa), xylene (standard for GC, ≥99.5%, Fluka, Midrand, South Africa) and decalin (cis + trans, ≥98.0%, Fluka) were weighed (see masses in Table 1) and diluted to 50 mL with *n*-hexane (BDH, HiPerSolv, 97%, VWR International, Arlington Heights, IL, USA). Solutions were prepared by diluting 1 mL of the standard solution and 10 mL jet fuel to 50 mL hexane.

Three-point standard addition procedures were done using iso-octane, cis/trans-decalins and a mixture of *m*, *p* and *o*-xylenes for the quantification of non-cyclic aliphatic hydrocarbons, cyclic aliphatic and aromatic species, respectively. The peak areas for the standards (the isomers *m*-, *o*-, *p*-xylene and cis/trans-decalin were grouped together) were determined using the classifications in the ChromaTOF-GC software (Leco, V4.21). Standard addition calibration curves were used to determine the concentration of each of the three standard compounds in the sample. Sample compounds were labeled as non-cyclic aliphatic, cyclic aliphatic or aromatic and this elucidation determined which standard to use for quantification (for example the concentrations of aromatic compounds were calculated by comparing the peak areas and concentration of the xylenes with the peak areas of the sample peaks). It was assumed that compounds of the same class have the same FID response factors. The eight standard mixtures as well as the sam-

Table 1
Solutions used for quantification by standard addition.

Sol.	Iso-octane	Xylene	Decalin	Volume sample	Total volume (hexane added)	Iso-octane	Xylene	Decalin
	Mass weighed (g)	Mass weighed (g)	Mass weighed (g)	(mL)	(mL)	Concentration ($\mu\text{g/mL}$)	Concentration ($\mu\text{g/mL}$)	Concentration ($\mu\text{g/mL}$)
1	0.0166	0.0133	0.0694	10.00	50.00	6.6	5.3	27.8
2	0.0238	0.0190	0.1591	10.00	50.00	9.5	7.6	63.6
3	0.0738	0.0590	0.3095	10.00	50.00	29.5	23.6	123.8
4	0.1692	0.1352	0.4973	10.00	50.00	67.7	54.1	198.9
5	0.3291	0.2629	1.4166	10.00	50.00	131.6	105.2	566.6
6	0.5289	0.4226	2.9432	10.00	50.00	211.6	169.0	1177.3
7	1.5066	1.2037	10.4420	10.00	50.00	602.6	481.5	4176.8
8	3.1303	2.5009	14.3585	10.00	50.00	1252.1	1000.4	5743.4

ples were each analyzed five times to obtain repeatability data. Recoveries were determined by summing the concentrations for all the peaks in a sample and averaging for the five repeated analyses.

Hetero-atomic species, present at low $\mu\text{g/mL}$ levels in the Merox kerosene, could not be observed in the FID-trace because of the detector's lack of response. Analysis of these compounds was therefore performed by GC \times GC-TOF-MS. To increase on detectability, the split ratio was decreased to 20:1 for these analyses. This led to overloading of the hydrocarbons, but the hetero-atomic species could be identified using extracted ion chromatography. Poor repeatability resulting from column overloading necessitated the use of internal standards for semi-quantification of hetero-atomic species. Thiophene (Sigma-Aldrich) and o-cresol (Sigma-Aldrich), spiked at 5 $\mu\text{g/mL}$ each, were used as internal standards for sulphur compounds and oxygenated compounds, respectively. Semi-quantification was done by adding the peak areas of the compounds and comparing with that of the internal standards assuming a similar detector response.

2.4. Stability tests

Thermal stability tests were performed by evaluating the break point temperatures of fresh fuels using the JFTOT procedure according to ASTM D3241 [27]. JFTOT was measured at 10 °C intervals from 260 to 360 °C until the break point temperature of the fuel was reached. Test fuels were also clay treated before stability analysis to remove polar species, water and colour bodies. Dry Attapulugus clay (500 g) was loaded into a glass vessel and 5 L test fuel was subsequently loaded and allowed to pass through the clay at a rate of 100 mL/h. JFTOT and GC \times GC analyses were performed on the fresh and clay-treated jet fuels.

3. Results and discussion

3.1. GC \times GC optimization

GC \times GC analysis of fuels is commonly performed in the normal GC \times GC mode i.e. a non-polar column in the first dimension and a polar column in the second dimension [19]. The reversed mode i.e. a

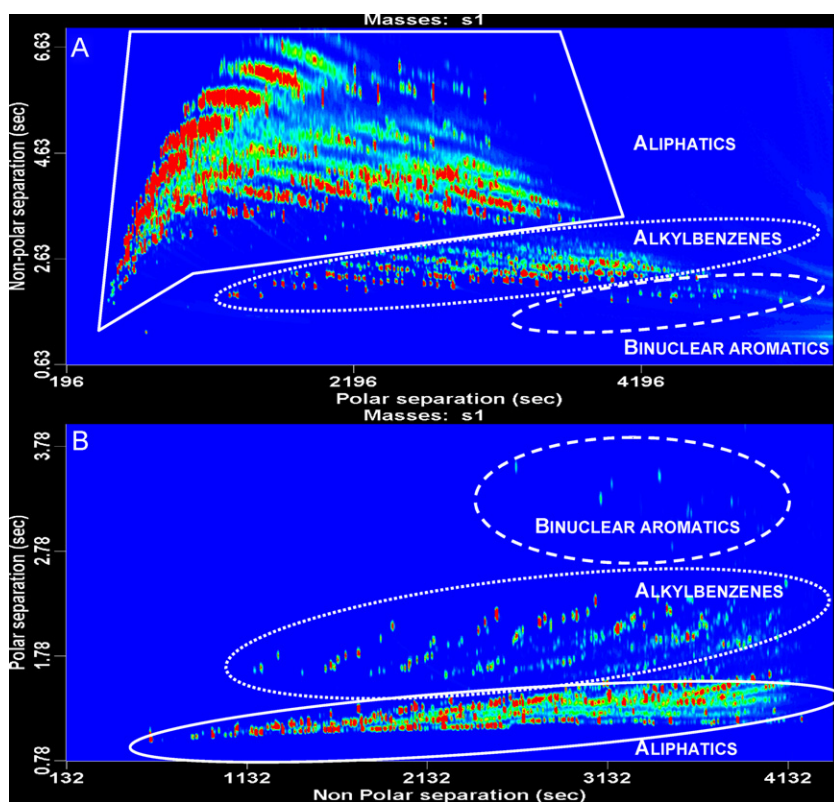


Fig. 1. GC \times GC separation of FSJF with the polar \times non-polar column configuration (A) and the non-polar \times polar column configuration (B). For experimental details, refer to Section 2.

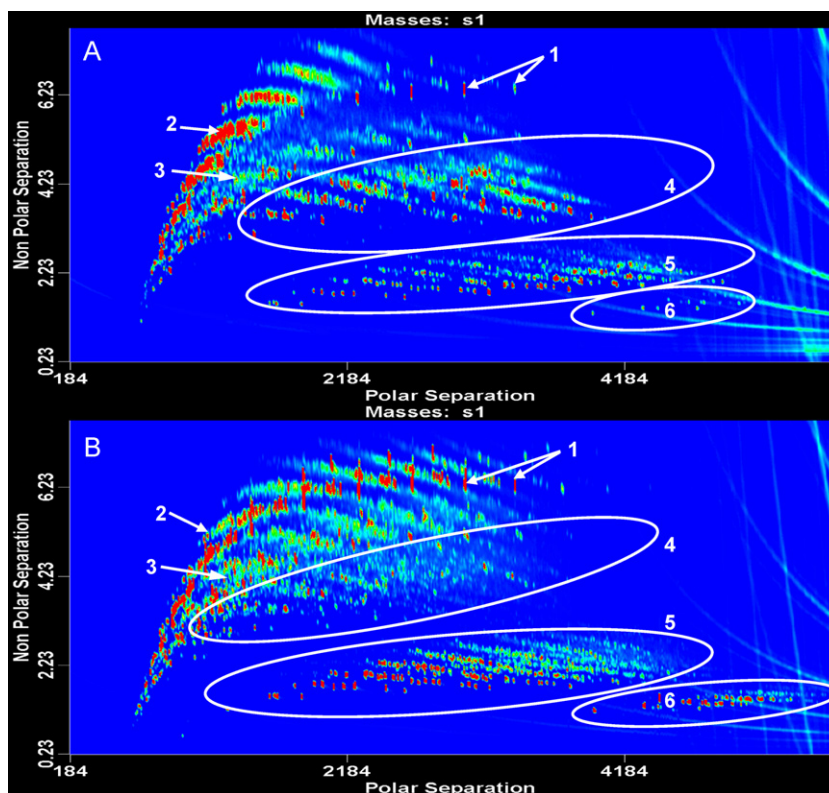


Fig. 2. GC \times GC analysis of (A) FSJF and (B) crude-derived jet fuel using a polar \times non-polar column combination. Numbering: (1) *n*-paraffins, (2) branched paraffins, (3) monocyclic aliphatics, (4) bi- and polycyclic aliphatics, (5) mononuclear aromatics and 6. binuclear aromatics.

polar \times non-polar column combination is considered 'less orthogonal' [28] but has shown to be advantageous to extend the separation space for the characterization of the aromatic fraction in petroleum middle-distillates [29], to provide improved resolution of FAMES from hydrocarbons in biodiesels [30] and for the characterization of Fischer–Tropsch fuels [31–33]. Contour plots comparing the class separations for an FSJF by reversed and normal mode GC \times GC are shown in Fig. 1A and B, respectively.

The improved separation space for the aliphatic compounds is obvious, while a similar separation space is noted for the alkylbenzenes and a worse one for the binuclear aromatics. The selected column combination provides excellent separation of individual components as well as of the different aliphatic classes and between aliphatics and hetero-atom compounds for both synthetic and crude-derived jet fuels. All of these factors are especially advantageous for the analysis of FT fuels that are relatively high in aliphatic content, low in aromatics and do not contain significant amounts of hetero-atomic species.

TOF-MS is the preferred detector for GC \times GC because this detector provides structural information. In addition, the high data acquisition rate prevents spectral skewing and deconvolution software can locate and identify closely eluting analytes based on unique ions. However, in petrochemical products that consist of thousands of compounds, determining the TOF-MS response factor for every compound for quantitative analysis is unrealistic. Moreover, another disadvantage of TOF-MS is that the data files are very large and as a result, data processing can be very time-consuming, which is especially problematic in routine applications. In contrast, use of FID significantly reduces data processing time. TOF-MS was therefore used initially to identify the hydrocarbon peaks, and subsequently FID was used for quantification of the identified compounds. On the other hand, FID failed to detect hetero-atomic species in the fuels at trace levels. TOF-MS in the ion-extraction

mode was used for elucidation of the hetero-atom containing compounds but accurate quantification was hampered by the very low levels (sub- $\mu\text{g}/\text{mL}$) of the individual compounds and the large differences in mass spectral intensity of the compounds of the same class (see further). Calibration details used for the quantification of the hydrocarbons in the FSJF samples by FID are summarized in Table 2. Small changes in the calibration graphs have a relatively large effect on quantitative results and therefore it was found that sufficient calibration data points were required to decrease the standard deviation.

The hydrocarbon compounds were classified using the classification software available in ChromaTOF software. Eight compound classes (*n*-alkanes, branched alkanes, monocyclic-, bicyclic- and polycyclic alkanes, alkylbenzenes, cyclic alkylbenzenes and naphthalenes) were identified in FSJF and Mercox kerosene, with each of these classes ranging in carbon numbers from C_6 to C_{20} . Boundaries of the classes in the contour plots are elucidated via the TOF-MS data through ion extraction of the molecular masses of the compound classes. These boundaries are then matched with the FID separation. As an example, for the C_{12} alkane classes, m/z 170 is selected for the *n*- and branched dodecanes. *n*- C_{12} is completely separated from the pre-eluting branched C_{12} alkanes and both solute groups can be quantified. In a similar way, m/z 168 is selected for the monocyclic C_{12} alkanes, m/z 166 for the bicyclic C_{12} alkanes, m/z 164 for the tricyclic C_{12} alkanes, etc. The alkylbenzenes and binuclear aromatics can easily be distinguished from the contour plots. The quantitative data are summarized in Table 3.

3.2. Chemical composition of fully synthetic and crude-derived jet fuels

A comparison of the FSJF and Mercox kerosene was performed to investigate whether the synthetic fuel contains

Table 2
Summary of calibration results.

Standard	Slope	y-Intercept	Sample concentration ($\mu\text{g/mL}$)	Linear range ($\mu\text{g/mL}$)	R^2	% RSD ($n=5$)
Iso-octane	284.97	14446.89	50.70	50.7–1302.8	0.9999	2.35
Xylene	409.81	517175.20	1261.99	1261.99–2262.37	0.9946	1.68
Decalin	320.37	1228019.09	3833.17	3833.17–9576.55	0.9990	0.90

components not present in crude-derived products that may potentially affect fuel properties and/or pose an environmental threat.

For the hydrocarbons, a high degree of similarity in terms of chemical content is observed between both fuels. All hydrocarbons present in the synthetic fuel are also observed in the crude-derived product, although present at different ratios (Fig. 2 and Table 3). The synthetic product is characterized by more aliphatic compounds with a higher degree of branching and relatively higher amounts of bi- and polycyclic aliphatics. Moreover, the FSJF contains significantly less aromatic species, especially naphthalenes and their derivatives. This difference in hydrocarbon composition of the FSJF is expected to affect jet fuel characteristics like cold flow properties, while the absence of any “new molecules” ensures that the fuel is suitable for use in commercial aircraft. Moreover, the lower aromatic content ensures a cleaner-burning fuel with less soot and smoke pollution.

Hetero-atomic species were observed in the crude-derived kerosene even after clay-treatment. These species are absent in the FT fuel. The total amounts of these compounds were at low $\mu\text{g/mL}$ (ppm) levels and individual compounds could only be observed

by decreasing the split ratio to 20:1 and using extracted ion chromatograms.

Acidic pollution, arising from the emission of sulphur and nitrogen oxides, has been implicated in acidification of water resources, damage to trees and buildings and also in some respiratory diseases. Typical sulphur components that are found in crude-derived fuels are mercaptans, sulphides, disulphides, and thiophene derivatives [34,35]. The Merox process is a sweetening process that converts sulphur species and mercaptans (thiols) to disulphides in the presence of oxygen under alkaline conditions (NaOH). The mercaptans, unlike the disulphides, are undesirable species because they are corrosive and have an offensive odor. In this chemical sweetening process, the total sulphur content of the fuel remains unchanged. Most of the sulphur species can be removed easily [36,37], although the heterocyclic thiophene derivatives are less reactive and more difficult to remove.

In the clay-treated Merox kerosene, the presence of more than 50 sulphur-containing compounds was noted. It was not possible to obtain standards for each of these. The internal standard, thiophene, was therefore used for semi-quantification of S-compounds and above all for comparison with the S-compounds in the FT

Table 3
Quantitative data for FSJF and Merox kerosene obtained by GC \times GC-FID.

Carbon number	n-Paraffins (mass%)	Branched paraffins (mass%)	Monocyclic paraffins (mass%)	Bicyclic paraffins (mass%)	Polycyclic paraffins (mass%)	Alkyl benzenes (mass%)	Cyclic alkyl benzenes (mass%)	Naphthalenes and other binuclear aromatics (mass%)	Total (mass%)
<i>Fully synthetic jet fuel</i>									
C ₅	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C ₆	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C ₇	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.01
C ₈	0.00	0.90	0.34	0.00	0.00	0.12	0.00	0.00	1.36
C ₉	0.14	7.52	2.36	0.49	0.01	0.55	0.00	0.00	11.07
C ₁₀	0.34	11.00	3.14	3.70	0.01	0.59	1.09	0.02	19.89
C ₁₁	0.36	11.86	2.45	4.65	0.02	0.41	1.86	0.08	21.69
C ₁₂	0.56	5.96	2.38	4.85	0.51	0.38	2.12	0.14	16.90
C ₁₃	0.65	3.35	1.47	4.02	2.32	0.33	1.96	0.10	14.20
C ₁₄	0.59	1.63	1.05	1.92	3.82	0.24	1.21	0.00	10.46
C ₁₅	0.07	0.49	0.52	0.69	1.62	0.11	0.27	0.00	3.77
C ₁₆	0.00	0.05	0.10	0.08	0.38	0.00	0.00	0.00	0.61
C ₁₇	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C ₁₈	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C ₁₉	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C ₂₀	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	2.71	42.77	13.84	20.39	8.68	2.73	8.48	0.35	99.95
<i>Merox kerosene</i>									
C ₅	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.01
C ₆	0.01	0.01	0.18	0.00	0.00	0.01	0.00	0.00	0.20
C ₇	0.11	0.08	0.52	0.00	0.00	0.11	0.00	0.00	0.83
C ₈	0.40	0.33	3.56	0.04	0.00	0.97	0.00	0.00	5.30
C ₉	2.18	1.55	4.04	0.52	0.00	4.43	0.00	0.00	12.72
C ₁₀	3.64	5.67	3.55	0.52	0.00	3.44	0.52	0.22	17.57
C ₁₁	3.65	5.42	2.95	1.75	0.11	1.97	1.12	0.86	17.82
C ₁₂	3.16	4.87	2.50	1.45	0.16	1.27	1.22	1.37	16.00
C ₁₃	2.74	4.25	1.70	1.39	0.06	0.78	1.18	0.99	13.08
C ₁₄	2.12	3.50	1.02	0.76	0.20	0.63	0.73	0.19	9.15
C ₁₅	1.27	2.46	0.28	0.29	0.00	0.37	0.23	0.03	4.93
C ₁₆	0.35	1.39	0.02	0.01	0.00	0.08	0.00	0.00	1.85
C ₁₇	0.06	0.32	0.00	0.00	0.00	0.00	0.00	0.00	0.38
C ₁₈	0.01	0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.08
C ₁₉	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.03
C ₂₀	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	19.69	29.94	20.34	6.73	0.53	14.05	5.01	3.66	99.95

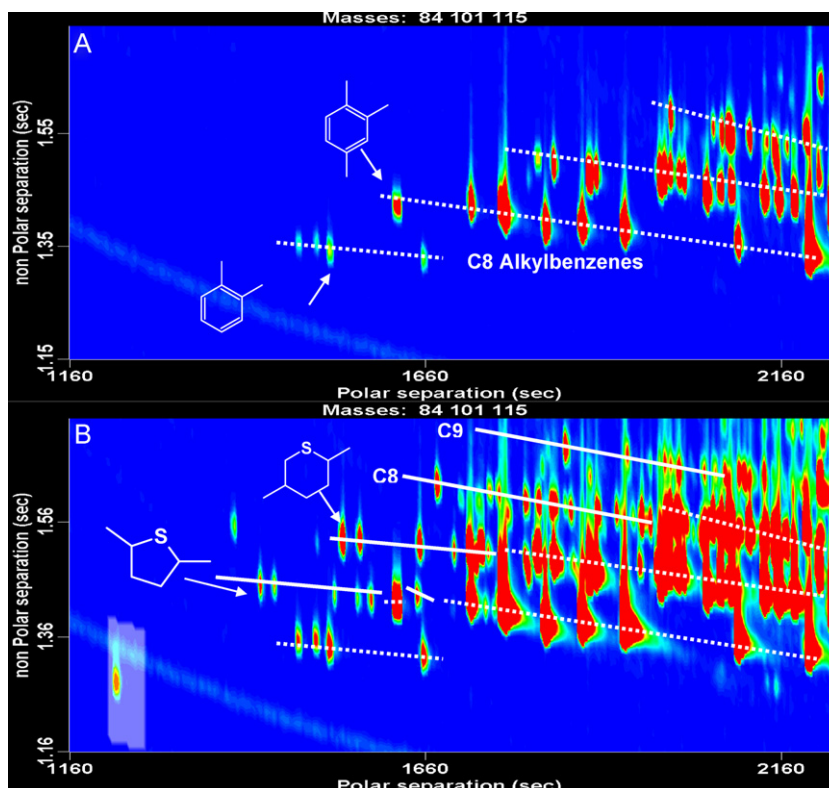


Fig. 3. Extracted ion contour plots of m/z 84 (thiophene), 101 (thiophanes) and 115 (thianes) in (A) FSJF and (B) crude-derive jet fuels.

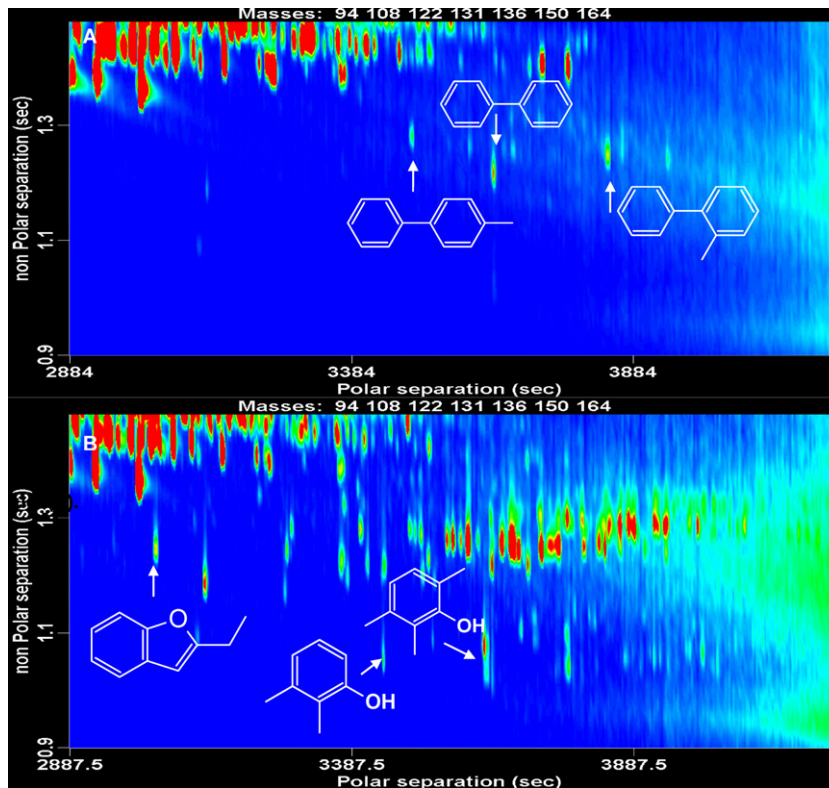


Fig. 4. Extracted ion contour plots of m/z 94, 108, 122, 131, 136, 150 and 164 showing the presence of oxygenates in the crude-derived fuel (B) and their absence in the synthetic fuel (A).

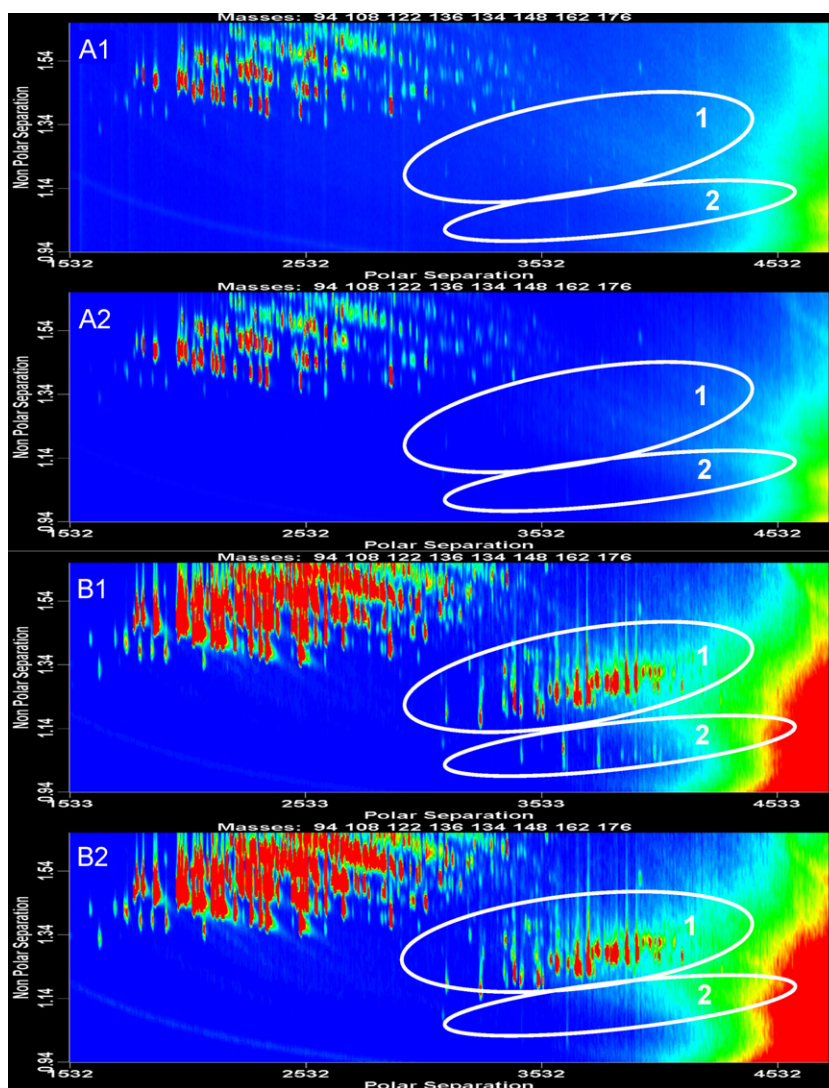


Fig. 5. Comparison of extracted ion GC \times GC plots of FSJF (A1) before and (A2) after clay treatment, and Merox kerosene (B1) before and (B2) after clay treatment. Numbering: (1) benzothiophenes, (2) phenols.

fuel. Assuming that the TOF-MS detector has the same response for all sulphur compounds as for the internal standard, a total of 0.13% S-compounds was measured in the clay-treated Merox kerosene. The main sulphur-containing classes were the thiophenes, hydro-thiophenes, thianes, thiophanes, benzothiophenes and hydro benzothiophenes.

As an illustration, the ion extracted plots at m/z 84, 101 and 115, typical for thiophene thiane and thiolane derivatives for FSJF and Merox kerosene, without addition of the thiophene as internal standard, are presented in Fig. 3. Thiophene is not present in the samples and can thus be used as internal standard. Notwithstanding the overloading of the plots with the alkylbenzenes (dotted lines) that contains similar ions in their spectra, the thiolanes (C_6) and thianes (C_7) together with C_8 and C_9 homologues can be observed in the crude-derived fuel and not in the FT fuel. The high degree of peak co-elution, in this case thianes–thiolanes and the alkylbenzenes, makes correct quantification very difficult. The use of a sulphur-selective detector, the sulphur chemiluminescence detector (SCD), is currently being investigated for accurate quantification of sulphur species in crude-derived fuels after several treatments e.g. the Merox process and clay-treatment.

Nitrogen-containing species, especially with a basic character, also have a negative environmental impact. Moreover, these compounds cause deactivation of the acidic catalysts used in catalytic conversion. Typical nitrogen compounds found in crude-derived fuels are the neutral indoles, carbazoles and tetrahydrocarbazoles as well as basic nitrogen compounds like anilines, quinolines, acridines, cinnolines and aminoindanes [38]. None of these compounds could be observed in the clay-treated crude-derived or synthetic jet fuels by selective ion extraction.

Hydrotreated fuels tend to form significant quantities of peroxides during storage. Phenolic antioxidants are generally added to jet fuel in the range of 17–24 $\mu\text{g}/\text{mL}$ to prevent peroxide formation. Antioxidants are naturally found in crude-derived fuels but are removed from synthetic fuels during severe hydro-processing. The clay-treated crude-derived fuel still contained trace levels ($\approx 30 \mu\text{g}/\text{mL}$) of phenols and other benzene alcohols as well as benzofurans and indanones. By decreasing the split ratio to 20:1 and using extracted ions of m/z 94, 108, 122, 131, 136, 150 and 164, which are typical for phenols and other aromatic oxygenates (e.g. m/z 131 for ethylbenzofuran), the presence of these oxygenates in the Merox kerosene and their absence in FSJF could be observed (Fig. 4).

The last class of compounds that is of interest to investigate in jet fuels is the olefins. While crude-derived fuels contain negligible amounts of olefins, FT fuels are hydrotreated to remove olefinic material that might cause fuel instability and gum formation. For fuels with negligible amounts of olefins, the presented GC \times GC method can be used directly. If olefins are expected (as indicated by the bromine number [39] or FIA analysis [6]), fractionation using silver ion chromatography prior to the GC \times GC separation is required [32,40]. These fractionation methods use a silver modified column for fractionation of unsaturates from saturates. The fractions can then be analyzed separately by GC \times GC and the results consolidated. Data on olefins in jet fuels will be presented elsewhere.

We have to note that synthetic fuels exhibit borderline lubricity compared to crude-derived fuels and that corrosion inhibitor/lubricity additives (LIA) are required to improve fuel lubricity. The DEF-STAN 91-91 [2] standard provides a list of the type and concentration of LIA's allowed in jet fuels.

3.3. Fuel stability

Current Jet A-1 specification requires the fuel to pass the JFTOT procedure at a test temperature of 260 °C. JFTOT is used as a qualitative pass/fail rating instrument for thermal oxidative stability at this temperature. The JFTOT procedure measures the deposit formation tendencies of jet fuel in the presence of oxygen and a metal surface. The degree of fuel degradation due to thermal oxidation is determined by the amount of deposit formation, rated using a tube deposit ratio (TDR) on a scale from 0 (no deposit) to 4 (heavy deposit). The “break point temperature” can be evaluated by operating the JFTOT apparatus at the highest temperatures at which a fuel still passes the specification rating criteria. The thermal stability of the fuels studied here was investigated according to ASTM D3241 [27].

FSJF exhibited excellent thermal oxidative stability characteristics with a JFTOT break point temperature above 360 °C, while the crude oil-derived Merox kerosene which had been clay-treated once, exhibited a JFTOT break point temperature at 280 °C. This observation points to the presence of problematic species causing jet fuel instability. After a second clay treatment, the JFTOT break point temperatures of the Merox kerosene improved to 290 °C, confirming that clay treatment has a positive effect on the JFTOT break point temperatures.

GC \times GC-TOF-MS extracted ion contour plots for ions *m/z* 94, 108, 122 and 136 (phenols) and 134, 147, 161, 176 (benzothiophenes) of FSJF and crude-derived fuel before and after clay-treatment (Fig. 5), show the removal of trace levels of phenols from the crude-derived fuel, while the benzothiophene content remains unchanged. No benzothiophenes or phenols were observed in the FSJF. Benzothiophenes and other components with cyclic sulphur structures could be responsible for the lower JFTOT break temperatures of the crude-derived fuel.

4. Conclusions

A GC \times GC method utilizing a polar \times non-polar column combination which demonstrated excellent separation for the various compound classes in jet fuel was developed. The increase in available separation space for aliphatic compounds was especially advantageous for the analysis of synthetic fuels because of their relatively high aliphatic to aromatic ratio. The degree of peak co-elution that was observed for some of the sulphur-containing species and alkylbenzenes did not significantly affect the analysis of aromatics but prevented accurate quantification of the sulphur species.

A detailed comparison of FSJF with crude-derived Merox kerosene showed that the fuels have very similar hydrocarbon compositions, although compounds were present at different ratios. Significantly, this implies that synthetic fuels do not introduce “new” molecules into aircraft's fuel systems that might negatively affect the fuel's properties. The presence of hetero-atomic species in the Merox kerosene and their absence in the FSJF were confirmed. The effect of clay treatment on JFTOT break point temperatures for the test fuels was investigated and the hetero-atomic content of the fuels was compared before and after clay treatment.

The proposed method proved to be suitable for quantification of the hydrocarbon compound classes in both synthetic and crude-derived jet fuels and to provide valuable information regarding the hetero-atomic species that affect fuel stability.

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