ANALYSIS OF HYDROCARBON TYPES IN SUSTAINABLE AVIATION FUEL

WHITE PAPER
BUREAU VERITAS

CONTENTS

APPLICATION OF GC X GC-MS/FID/SCD AND ASTM D2425 TO THE ANALYSIS OF HYDROCARBON TYPES IN SUSTAINABLE AVIATION FUEL

By Felix Anyakudo, Jimmy Matheussen, Appa-Rao Tottempudia

PREFACE

The first quarter of 2021 was one of the most significant milestones concerning the accelerated progress towards achieving global CO2 reduction. In recent months, major airlines have reported that they are trialing the use of Sustainable Aviation Fuel (SAF) on commercial flights. This development is significantly helping the aviation industry accelerate the use of SAF.

Supporting the decarbonization of the aviation industry, Bureau Veritas - through its state-of-art global laboratory network - has drafted a study based on analysis carried out by its highly versatile oil & gas laboratory in Antwerp. A comparative analysis was undertaken to evaluate the tests currently available on the market and how they can be optimized to produce the highest quality SAF. The primary intention of the study was to provide independent guidance for private and governmental companies as they develop SAF programs.

ABSTRACT

The road map set by European's aviation sector to achieve zero CO2 emission by 2050 has led to significant growth in the production of SAF which is mostly used to power aircraft. ASTM D7566 specification for aviation turbine fuel containing synthesized hydrocarbon prescribes limits for aromatics and cycloparaffins content. ASTM D2425 is the official method for hydrocarbon composition in SAF but the use of this method is still a focal point of controversy because it was based on petroleum middle distillates with high aromatic content. In order to ensure good operational conditions of aircraft, accurate compositional analysis of SAF becomes very important. In this work, detailed hydrocarbon analysis of SAF using comprehensive two dimensional gas chromatography (GC x GC) coupled to MS (mass spectrometer), FID (flame ionization detector) and SCD (sulphur chemiluminescence detector) was evaluated and compared to group hydrocarbon type analysis using D2425 methodology. MS channel was used for identification, FID channel was used for quantitation while the SCD was used for sulphur speciation. Results obtained from both methods were comparable to each other. At the Bureau Veritas Antwerp laboratory, the use of these methods are continuously explored on a routine basis to accurately determine the composition of hydrocarbon types in SAF in order to ensure that samples analyzed are fit for purpose.

KEY WORDS:

Sustainable Aviation Fuel (SAF),
ASTM D2425, GC x GC, alkane profile

1. INTRODUCTION

Sustainable Aviation Fuels are mostly used to power aircraft. SAF are developed from Synthetic Paraffinic Kerosene (SPK) produced from biomass through various production processes, they can be and blended into a conventional petroleum product. The pathways leading to the production of SAF fuel has been reviewed by some authors [1, 2]. SPK has approximately the same composition as that of fossil aviation fuel but with superior fuel properties such as cetane number, lower cloud point and lower emissions. The road map set by the aviation industry to achieve zero emission by 2050 and lower dependence of fossil fuel has been the major driving force in SAF production. Companies such as Neste, Honeywell, Repsol and others have set up refineries to produce SAF in order to meet the growing demand. Major airlines have also responded to these initiatives by investing in SAF.

ASTM D7566 specification for aviation fuel containing SPK determined a limit for maximum aromatic (0.5 %m) and cycloparaffin (15 %m) content using ASTM D2425 as the official test method. The precision data of this method was based on petroleum distillates with higher aromatic content, in this regard errors cannot be completely eliminated when this method is applied to SAF which contains mainly paraffins with little or no aromatic content. Three techniques ASTM D2549, D1319 and D6379 were recommended for the fractionation of samples into saturates and aromatics in the recently updated 2019 version of D2425 which might lead to inconsistency in results due to errors associated with different fractionation procedures. In light of this development, Bureau Veritas Antwerp collaborated with Neste and carried out a comparative study of the three analytical protocols [4] where significant bias was observed in results between participating laboratories.

GC x GC has been reported as a powerful tool for detailed hydrocarbon type analysis of SAF and middle distillates [4]. UOP 990 is the official method for the analysis of organic distillates using two dimensional GC x GC equipped with two stage thermal flow modulator. In D2425 components are grouped into

paraffins, non-condensed cycloparaffins, condensed dicycloparaffins, alkylbenzenes, indans or tetralins, indenes, naphthalenes, acenaphthylenes and tricyclic aromatics while in reality SAF might contain up to 1000+ components within these groups which makes complete identification very challenging and difficult.

The aim of this work at Bureau Veritas Antwerp is to carry out comparative component analysis of SAF using GC x GC-MS/FID/SCD (Mass spectrometry/flame ionization detector/sulphur chemiluminescence detector) and ASTM D2425. Results obtained from these different techniques will be compared to each other.

2. ANALYSIS

2.1 GC X GC-MS/FID/SCD

This technique was carried out using Agilent 5977B GC-MS system, HP –PONA 50 m x 0.2mm ID x 0.5µm was used in the first column connected to the second column VF 17ms 10 m x 0.10 mm x 0.20 µm via a split union. The thermal modulator serves as an interphase between both columns. Initial oven temperature was kept at 40°C and ramped at the rate of 1.5°C/min to 350°C, a modulation time of 8000 ms was used throughout the analysis, the MS, FID and SCD data were collected simultaneously. GC x GC image software from JSB (version: 2.6b0) was used to process data. Quantitation of hydrocarbon types was carried out using FID, MS was primarily used for identification while sulphur speciation was carried out using SCD from Agilent.

2.2 ASTM D2425

Samples were separated into saturate and aromatic fractions by liquid chromatography using test method ASTM D2549. 10 gram samples were charged on top of chromatographic column packed with activated bauxite and silica gel. N-pentane was used to elute the non-aromatics while diethyl ether, chloroform and ethyl alcohol was used to elute the aromatic fractions. The lower boiling sample procedure using Kuderna – Danish apparatus was applied for sample evaporation.

The fractionated sample (0.2 µL volume) was analyzed using Thermo DSQ II GC-MS system (Procedure B D2425) equipped with CTC auto-sampler from Analytics AG, Switzerland (Combi PAL-xt). Rxi-5MS, 30 m, 0.25 mm ID, 0.5 µm film thickness column was used to separate target analytes. The initial oven temperature was kept at 50°C for 2 min and increased at the rate of 12 °C/min to 245°C and held for 10 min, helium was used as a carrier gas at a constant flow of 1.0 mL/min. An inlet temperature of 250°C was used at a split flow of 100 mL/min. The transfer line and the ion source temperature were kept at 250°C. MS ionization voltage was set at 70eV with a scan range from 45 to 250 amu. Xcalibur software was used to process acquired data.

3. RESULTS

3.1 HYDROCARBON TYPES BY GC X GC-MS/FID/SCD

Most of the SAF sample analyzed consists mainly of n-paraffins and ISO paraffins. The 3D chromatogram of the FID is shown in Fig. 1. The X-axis represents the retention time from the first column (Column I), the y axis represents the retention time from the second column (Column II) while the 3rd axis represents the FID signal intensity. Prior to analysis, a synthetic mixture containing n-paraffin, iso-paraffin, cyclo-paraffin and aromatics were analyzed and results found were in line with expected concentration. The synthetic mix was also used to adjust the previously established FID template used for quantitation. The MS channel was primarily used for identification. Results are shown in table 1. The presence of sulphur compounds were not detected in any of the SAF sample investigated.

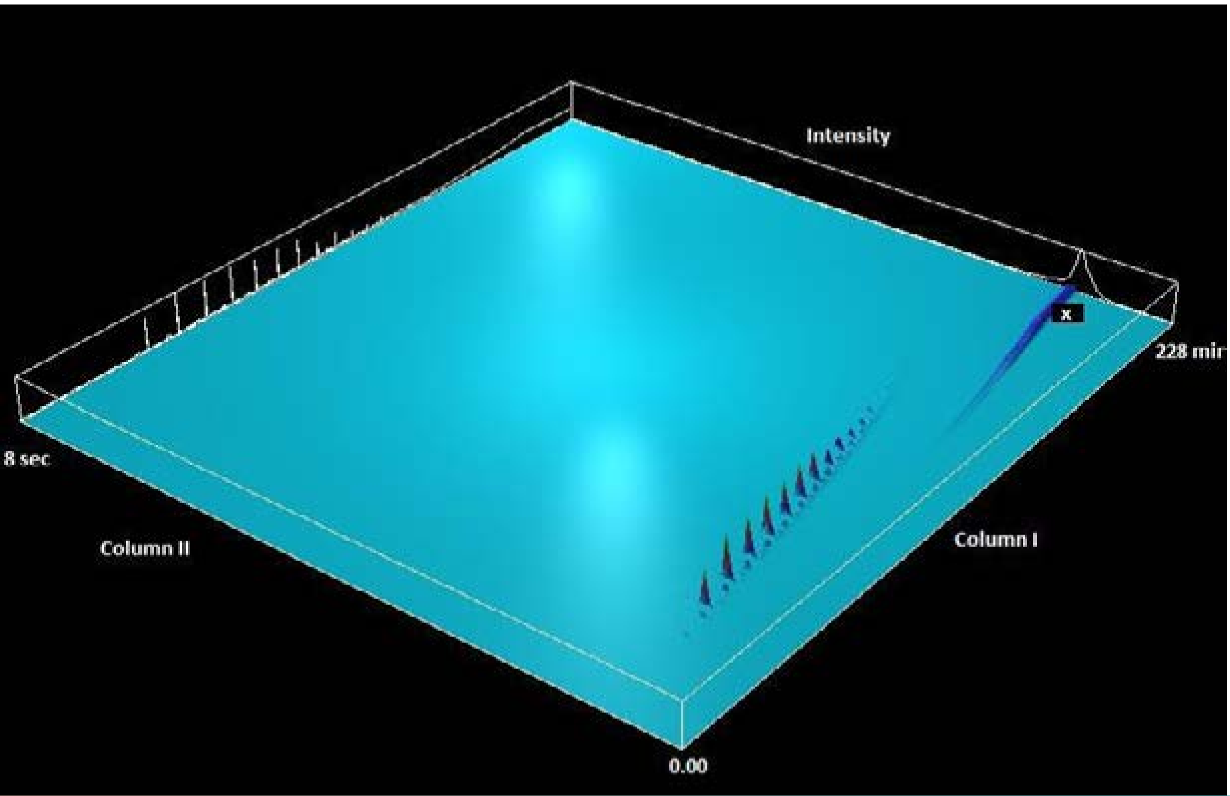

Fig. 1. Chromatogram of SAF sample marked Sx: peak x = column bleed.

Table 1. GC x GC chromatogram of SAF sample marked Sx: C-nr= Carbon number, n-Par = Normal parraffins, i-par = iso paraffins, Cp+ Ol= Cycloparaffins +olefins, Mo-Ar = Mono aromatics, Di-Ar = Di aromatics, Sum C-nr = Sum of hydrocarbon per carbon number

GC x GC (%m)						
C-nr	**n-Par**	**i-Par**	**Cp + Ol**	**Mo-Ar**	**Di-Ar**	**Sum C-nr**
7	0.01	0	0	0	0	0.01
8	0.1	0.08	0	0	0	0.18
9	0.2	0.65	0.01	0	0	0.87
10	0.16	0.9	0.03	0.02	0	1.11
11	0.13	0.91	0.03	0.01	0	1.08
12	0.12	1.03	0.02	0	0	1.17
13	0.12	1.2	0.05	0	0	1.37
14	0.23	1.98	0.1	0.04	0	2.35
15	0.59	7.81	0.11	0.02	0	8.53
16	1.45	23.4	0.04	0.17	0	25.07
17	3.53	17.1	0.01	0.04	0	20.68
18	0.99	34.29	0.1	0	0	35.38
19	0	0.44	0	0	0	0.44
20	0	0.52	0	0	0	0.52
21	0	0.1	0	0	0	0.1
22	0	0.25	0	0	0	0.25
23	0	0.3	0	0	0	0.3
24	0	0.13	0	0	0	0.13
25	0	0.15	0.02	0	0	0.17
26	0	0.09	0.01	0	0	0.1
27	0	0.22	0	0	0	0.22
28	0	0	0	0	0	0
29	0	0	0	0	0	0
30	0	0	0	0	0	0
Total	**7.6**	**91.6**	**0.5**	**0.3**	**0**	**100**

3.2 HYDROCARBON TYPES BY GC-MS D2425

The aromatic and the saturate fraction were analyzed independently as described in the method. The GC-MS chromatogram of the saturate fraction is displayed in Fig. 2. Summation of the mass fragments of both fractions were used to determine the concentration of the hydrocarbon types as shown in table 2.

Fig. 2. GC-MS chromatogram of typical SAF sample marked Sx.

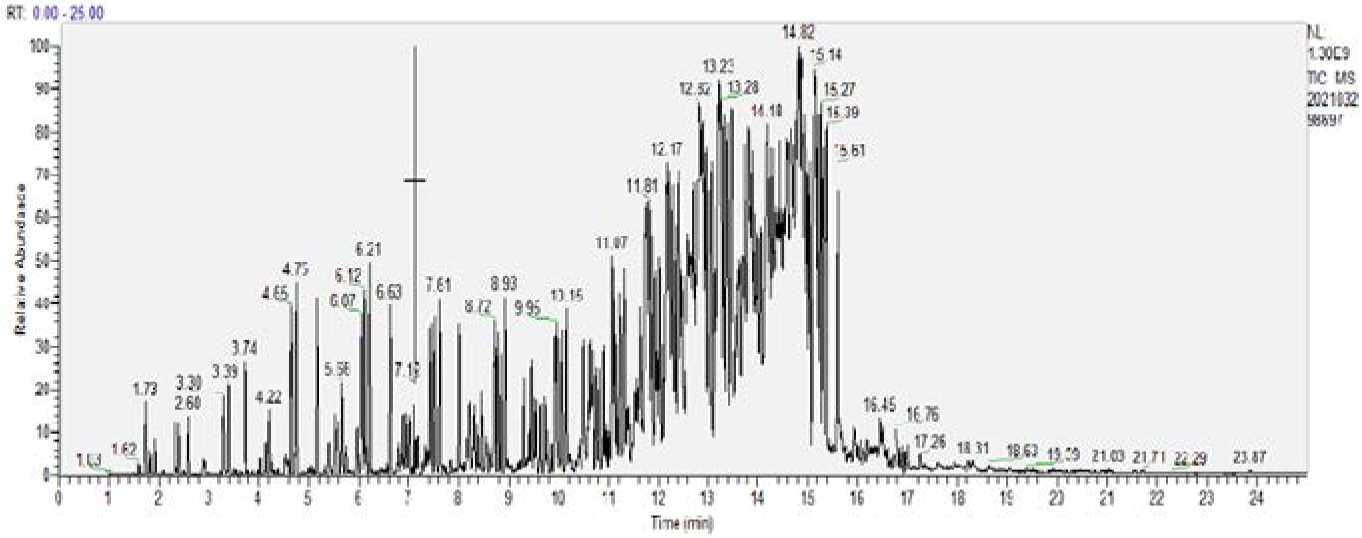

Table 2. D2425 results of the sample marked Sx.

D2425	
Test parameter	**Results (%m)**
Paraffins	95.3
Monocycloparaffins	2.2
Dicycloparaffins	2.1
Tricycloparaffins	0.1
Benzenes	0.3
Indans/Tetralins	0
CnH2n-10	0
Naphthalene	0
Naphthalenes	0
CnH2n-14	0
CnH2n-16	0
CnH2n-18	0
Total aromatics	0.3
Paraffins	95.3
Cycloparrafins	4.4

4. CONCLUSION

GC x GC-MS/FID/SCD was applied to the analysis of hydrocarbon types and sulphur speciation in SAF. Results of aromatic content obtained by GC x GC is mostly in line with D2425 but significant deviation was observed for paraffins and cycloparaffins. The reason for this deviation is still under investigation at Bureau Veritas' Antwerp facility although both results can be considered comparable on the basis of D2425 reproducibility. Sulphur species were not detected in SAF samples investigated but the SCD channel can be used to monitor and quantify any sulphur compound that might find its way into SAF either through feedstock or during logistic operation.

Sample fractionation according to D2425 is laborious and time consuming as compared to GC x GC that involves direct injection. However, GC x GC-MS/FID/SCD methodology becomes an obvious choice when detailed composition and sulphur speciation is needed and can be recommended as an alternative for hydrocarbon composition in ASTM D7566 specification for aviation fuel containing SPK.

AUTHOR CONTRIBUTIONS

Felix Anyakudo, PhD.: Conceptualization, Writing, Analysis, Investigation, Visualization, Review, validation & Supervision, Jimmy Matheussen: Investigation, Data analysis, Sample analysis & Validation, Appa-Rao Tottempudi: Investigation, Data analysis & Sample analysis

ACKNOWLEDGEMENT

This work was carried out at Bureau Veritas Antwerp laboratory. The authors acknowledges the contributions of Andy De Ridder, Gunter Verhestraeten and Vivian Takahashi for their initiatives and support toward the completion of this work.

5. REFERENCES

[1] C. Gutiérrez-Antonio, F.I.Gómez-CastrobJ, A.de Lira-Flores, S. Hernández, A review on the production processes of renewable jet fuel, Renewable and Sustainable Energy Reviews, 79 (2017) 709-729

[2] NicolaeScarlat, Jean-FrançoisDallemand, FabioMonforti-FerrarioManjola, BanjaVincenzoMotola, Renewable and Sustainable Energy Reviews, Volume 51, (2015) 969-985

[3] K. Elias Ikonen, Katherine E. Wehde, Felix Anyakudo, Hilkka I Kenttämaa, Comparison of three different analytical protocols for 2019 updated D2425 method for renewable jet fuel product certification analysis, Journal of Chromatography A, 1634 (2020) 461667

[4] R. C. Striebich, L. M. Shafer, R. K. Adams, Z. J. West, M. J. DeWitt, and S. Zabarnick, Hydrocarbon Group-Type Analysis of Petroleum-Derived and Synthetic Fuels using two- dimensional gas chromatography, Energy fuels, 28 (2014) 5696-5706.

6. GREEN LINE SOLUTIONS AND SERVICES

By 2030 the Agenda for Sustainable Development will come into force within the European Union (EU). The agenda is a commitment to eradicate poverty and achieve sustainable development, it demands the promotion of renewable energy within the electricity, heating & cooling, and transport sector industry. In light of this, the shift in aviation towards sustainable fuel production is a key player in this journey.

Bureau Veritas has, at the core of its strategy, the green line of services and solutions, aimed at supporting initiatives linked to sustainability. Client Relations & Marketing Director for Bureau Veritas, Gunter Verhestraeten states, *“Companies that own advanced technology should share best practices and support others to shorten the path, thereby helping the industry to achieve the objectives defined by the European Union.”*

CONTACT US

contactus@bureauveritas.com

Bureau Veritas
Romeynsweel 14
B-2030 Antwerp
Belgium

Tel: + 32 3 546 0888

https://commodities.bureauveritas.com/

https://www.bureauveritas.be/

BUREAU VERITAS

Shaping a World of Trust