SUSTAINABLE AVIATION FUELS AND THEIR DETERMINATION IN BLENDS WITH (FOSSIL) JET FUELS

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Sustainable Aviation Fuel (SAF) is one of the most significant challenges in the decarbonization of aviation, not only due to its complex production process but also because of the difficulties in detecting it when blended with conventional jet fuel (Jet A-1). The most common method for detecting biofuels involves radioanalytical techniques. However, these methods are often complex in terms of sample preparation, instrumentation, analysis time, and overall cost. Therefore, exploring alternative methods for identifying SAF approaches that are faster, more cost-effective, and offer an acceptable level of measurement uncertainty is essential. This article focuses on SAF from multiple perspectives: detection challenges, alternative detection methods, relevant legislation, and standardization efforts. It also provides an overview of the current state of this rapidly evolving sector.

Key words: Jet A-1, SAF, determination

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1. Introduction

Aviation fuel is a hydrocarbon-based fuel used to power the majority of civil and military airplanes and helicopters. These aircraft are typically equipped with gas turbine engines, which are characterized by the fact that the intake, compression, combustion, and expansion processes all occur simultaneously in different parts of the engine [1]. The most common and widely used types of aviation fuel are JET-A1 and JET-A. They primarily differ in their regional application. JET-A is mainly used for US domestic flights within the United States, while JET-A1 is intended for transatlantic and other long-distance routes and for the use in other parts of the world. In fact, the only difference between their physicochemical properties is their freezing point: JET-A1 has a maximum freezing point of -47°C, whereas JET-A has a maximum of -40°C [2].

According to data from the International Energy Agency, the global consumption of aviation kerosene (jet fuel) in 2023 reached approximately 330 million tons (Mt) [3]. In the same year, carbon dioxide emissions from flights departing airports within the EU27 (European Union Member States) and EFTA (European Free Trade Association) regions were estimated at around 133 Mt CO_2eq [4]. According to the European Commission, aviation contributes roughly 4% to the European Union's total carbon footprint and about 14% of emissions within the transport sector, making it the second-largest source of emissions in this category after road transportation [5]. For this reason, the aviation fuel sector is a prime candidate for decarbonization in efforts to reduce the overall carbon footprint.

Currently, the only viable method for decarbonizing air transport is the use of SAF (Sustainable Aviation Fuel), a more sustainable alternative to conventional fossil jet fuel. SAFs are hydrocarbon-based fuels that can be produced synthetically from captured CO_2 and green hydrogen (produced via electrolysis of water), or from waste-type biomass or recycled carbon sources [5]. These SAFs are usually used as a sustainable blending component of standard jet fuels.

The European Union has introduced mandatory SAF blending targets, with requirements set to increase over time [6]. This policy shift brings a growing need for reliable methods to verify SAF content in aviation fuel. One such method involves tracing biogenic carbon (^{14}C), which is present in SAF but absent in fossil jet fuel. This is due to the fact that SAF contains carbon originally sourced from the atmosphere, specifically in the form of the isotope ^{14}C [7]. This isotope is formed in the upper atmosphere through interactions between cosmic radiation (neutrons) and nitrogen atoms, and subsequently enters the SAF supply chain via biomass feedstocks or direct atmospheric CO_2 capture [8]. It is necessary to add that even such sophisticated methods cannot detect and quantify SAFs based on recycled carbon fuel (RCF).

However, analytical methods based on ^{14}C detection are capital-intensive and require complex sample preparation prior to analysis. Consequently, there is ongoing research into alternative approaches for SAF quantification in jet fuel that aims to reduce analytical costs and simplify the detection process. Moreover, there is a chance to detect and quantify even RCF-type SAFs.

2. Legislation on jet fuel and SAF

2.1. EU legislation

To understand the legislation governing the use of SAF, it is first essential to clarify the underlying motivation for its deployment. The widespread adoption of SAF stems from international climate commitments, most notably from the Paris Agreement, signed in 2016. Under this accord, the majority of the world's nations producing approximately 98% of global greenhouse gas emissions

pledged to limit the increase in global average temperature to well below 2 °C, and ideally to no more than 1.5 °C above pre-industrial levels [9]. As a regional response to the Paris Agreement, the European Green Deal was launched in 2019, establishing a long-term political vision to make Europe the first climate neutral continent by 2050 [10]. This overarching objective is supported by a series of intermediate goals and legislative frameworks. One such milestone is the "Fit for 55" package, which sets the binding target of reducing greenhouse gas emissions by 55% by 2030 relative to 1990 levels. These strategic goals have been translated into specific legislative instruments aimed at enforcing the green transition in sectors such as industry and transport. A key example in the aviation sector is the RefuelEU Aviation Directive, which mandates the increasing use of sustainable aviation fuels [6]. Figure 1 illustrates the projected evolution of total SAF usage and specifically the use of synthetic aviation fuels over time.

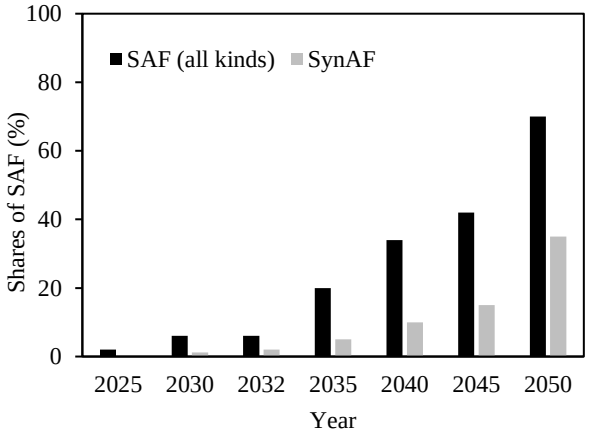

Fig. 1 Minimum required Share of SAF (Sustainable Aviation Fuel) and SynAF (Synthetic Aviation Fuel) according to the ReFuelEU Aviation Regulation

2.2. Technical standards

Jet fuel quality is based on several standards, which vary depending on the region of origin. To simplify the relationships and binding nature of these standards, it is helpful to highlight three of the most important aviation organizations. The first is the International Civil Aviation Organization (ICAO), a specialized agency of the United Nations (UN), which encompasses 193 member states worldwide [11]. In addition to ICAO, there are also regional organizations that implement their quality standards. One such organization is the Federal Aviation Administration (FAA), which operates primarily within the United States [12]. In regions under FAA jurisdiction, the quality of Jet A-1 aviation fuel is governed by ASTM D1655 a standard that defines the minimum chemical and physical requirements, as well as the permitted types of additives used in jet fuel [13]. Another key organization is the European Union Aviation Safety Agency (EASA), which oversees aviation safety across Europe and EU member states [14]. Within EASA-regulated territories, Jet A-1 fuel can be used in compliance with either ASTM D1655 or DefStan 91-091 [15,16]. However, the differences in parameter limits between these two standards are minimal.

The only standard that specifically defines various types of Sustainable Aviation Fuel (SAF), is ASTM D7566 [17]. This standard outlines seven different types of SAFs, along with their maximum allowable blending ratios with conventional fossil jet fuel. An overview of these types and their blending limits is provided in Table 1.

Tab. 1 SAFs and their blending limits overview described by ASTM D7566 (BL – blending limit)

Abbreviation	Description	Blending limit (%)
FT-SPK	Fischer-Tropsch hydroprocessed Synthetic Paraffinic Kerosene	50
HEFA-SPK	Hydroprocessed Esters and Fatty Acids	50
HFS-SIP	Synthetic Iso-paraffins from Hydroprocessed Fermented Sugars	10
FT-SKA	Fischer-Tropsch (FT) Synthetic Kerosene with Aromatics	50
ATJ-SPK	Alcohol To Jet	50
CHJ	Catalytic Hydrothermolysis Jet	50
HC-HEFA	Hydroprocessed Hydrocarbons, Esters and Fatty Acids (different from HEFA-SPK)	10

Despite the permitted blending limits, the final mixture of conventional jet fuel and SAF must first and foremost meet the quality requirements defined by ASTM D1655 [17].

3. SAF analysis

3.1. Jet fuel and SAF group-type analysis

Jet fuel is primarily composed of hydrocarbon molecules containing between 8 and 16 carbon atoms per molecule. The main molecular groups found in jet fuel include: *n*-paraffins, iso-paraffins, cycloparaffins, alkylbenzenes, cycloaromatics, and aromatics [18]. In contrast, the composition of Sustainable Aviation Fuels (SAF) is generally simpler. An example comparing the composition of HEFA, HFS-SIP, and conventional fossil jet fuel is shown in Figure 2 and comparison of selected parameters for JETA-1 and HEFA-SPK is shown in Table 2.

In addition to the SAF types presented in Table 1, there are studies describing the production of synthetic SAF through the reaction of CO_2 with H_2 using catalysts

such as Fe-Mn-K [20]. This process primarily yields a mixture of *n*-paraffins as the product.

As illustrated in Figure 2 and supported by studies on SynAF production, there are notable differences in hydrocarbon group distributions between SAF and fossil-based jet fuel. Compared to these SAFs, conventional jet fuel exhibits a greater diversity of molecular types.

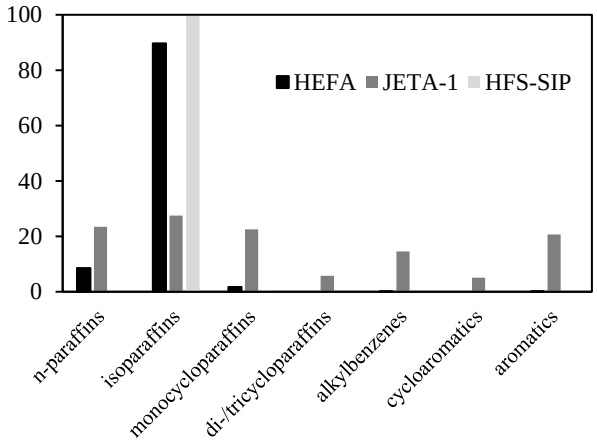

Fig.2 Comparison of the composition of conventional fossil jet fuel, SIP and HEFA.

Tab. 2 Comparison of selected parameters for JET-A1 and HEFA-SPK fuels [19]

Fuel	JET-A1	HEFA-SPK
Density (15 °C)	<840	762
Smoke Point (mm)	19	5.6
Kinematic Viscosity (mm^2/s)	<8	5.7
Calorific value (MJ/kg)	42.8	43.8
Freeze point (°C)	<-47	-
Flashpoint (°C)	>38	>38

Due to decarbonization requirements mandating the blending of SAF with conventional jet fuel, it is essential to be able to accurately determine the SAF content within the fuel mixture.

3.2. Radioanalytical methods

Determining the SAF content in jet fuel is not a simple task, primarily because both, conventional jet fuel and various types of SAF, are composed of hydrocarbons that have identical chemical nature. There is no clear or distinctive chemical marker that can be used for detection, as is the case, for example, in determining the presence of FAME (Fatty Acid Methyl Esters) in diesel fuel using infrared spectroscopy, where the carbonyl vibration around 1745 cm^{-1} serves as a reliable FAME indicator [21]. At present, the only standardized method for detecting biogenic content in fossil-based fuels is through radiocarbon (^{14}C) analysis. The presence of Carbon-14 is characteristic for fuels derived from biomass and for fuels made from CO_2 captured from the atmosphere. It is formed through interactions between cosmic radiation and atmospheric nitrogen (^{14}N), and enters biomass via photosynthesis, eventually making its way into bio-based fuels, or directly into fuels in the case of PtL (Power-to-Liquid) synthesis [22].

According to standards such as EN 16640 and ASTM D6866-22, three main analytical methods are used for ^{14}C detection and quantification: Accelerator Mass Spectrometry (AMS), Liquid Scintillation Counting (LSC), and the less commonly applied Beta counting (BC) [23,24]. However, these general standards are designed for a broad range of sample matrices, prompting the development of a specific German standard, DIN 51637, which is based on the LSC method and tailored for analyzing diesel and biofuel blends (FAME or HVO – Hydrotreated Vegetable Oil) [25].

The LSC method relies on the interaction of β particles, emitted during ^{14}C decay, with a scintillator present in a scintillation cocktail. The resulting collisions generate photons that can be detected. The method is relatively accurate (with uncertainties as low as 0.5% biogenic carbon in some studies), but it is time-intensive, often requiring several hours. Furthermore, it is sensitive to the color of the matrix, which can interfere with photon detection. The ASTM D6866 standard employs the so-called indirect LSC technique, which requires the sample to be converted into benzene. This involves gasification of the sample followed by chemical synthesis of benzene. The conversion to benzene eliminates the color interference that would otherwise reduce the detection sensitivity. The scintillation cocktail used for such analyses typically consists of two main components: a solvent and a scintillating compound. One example of a scintillator commonly used is octylphenol polyethoxyethanol [22,26-28].

AMS, on the other hand, is a highly precise form of mass spectrometry capable of distinguishing between individual isotopes that might otherwise cause interferences in identification. Its typical uncertainty is also around 0.5% of the ^{14}C content. However, a significant disadvantage of AMS is the lengthy sample preparation process, which takes several hours, mainly due to the need to oxidize the sample into CO_2 and then reduce it to graphite form for analysis. In the AMS method, the sample is directly converted into gaseous CO_2 or solid graphite, which is subsequently transformed into CO_2 for analysis. The AMS system includes a source of negatively charged ions, which plays a crucial role in the process. This component is particularly important because the isotope ^{14}N, a potential source of interference, does not form stable negative ions, thereby allowing for effective discrimination between ^{14}C and ^{14}N during measurement [22,29].

3.3. Alternative ways of analysis

In addition to the considerable time requirements associated with the radioanalytical methods described in

the previous section, the financial cost of such analyses is also a significant factor. For this reason, alternative methods have been developed for determining the content of SAF in mixtures with conventional jet fuel. One such approach involves the use of mid-infrared (MIR) spectroscopy in transmission mode to quantify the content of HEFA (Hydroprocessed Esters and Fatty Acids) in jet fuel, followed by the development of a predictive model based on the spectral data. In this case, the predictive model was built using the Partial Least Squares (PLS) regression method. The resulting Root Mean Square Error of Prediction (RMSEP) for the most robust model was approximately 0.7 wt.% [30]. Infrared spectroscopy-based methods have also been applied to analogous fuel pairs such as HVO and diesel. In addition to mid-infrared (MIR) spectroscopy, near-infrared (NIR) spectroscopy has been utilized as well. The reported RMSEP (Root Mean Square Error of Prediction) values were in the low single-digit volume percent range. However, the final performance strongly depends on the calibration and validation strategy employed, as these directly influence the robustness and practical applicability of the resulting predictive models [31-34].

Another promising, though not necessarily the simplest alternative, is the use of a technique known as Saturated-Absorption Cavity Ring-Down Spectroscopy for the monitoring of molecular absorption of radiation, thereby enabling the quantification of the target compound. This high-sensitivity laser-based technique measures the decay rate of light trapped in an optical cavity and exploits isotope-selective absorption features [35]. The advantages of this method include faster analysis compared to LSC and the possibility of deploying a portable solution, which is a distinct benefit over AMS, all while maintaining a measurement uncertainty of around 1% [36].

4. Conclusion

With the projected increase in SAF consumption, it will become essential to monitor the content of SAF in jet fuel quickly, affordably, and with sufficient accuracy. While the basic reference radioanalytical methods offer high precision, they are also time-consuming and expensive. Moreover, these methods cannot detect and quantify SAF based on recycled carbon fuel.

A few studies have investigated the determination of SAF content in jet fuel, but these either involve highly complex instrumentation or focus solely on quantifying HEFA (Hydroprocessed Esters and Fatty Acids) content.

The following experimental work will focus on analyzing another type of SAF using a simpler and faster instrumental approach, Attenuated Total Reflectance Infrared Spectroscopy (ATR-IR) combined with the development of predictive models based on Partial Least Squares (PLS) regression.

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