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

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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 hetero-atomic 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.

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,

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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 PMDY/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 Attapulgus 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 C_3 and C_4 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 duel 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-